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MINISTERUL GEOLOGIEI
INSTITUTUL DE GEOLOGIE ȘI GEOFIZICĂ

ANUARUL INSTITUTULUI de GEOLOGIE ȘI GEOFIZICĂ

VOL. LXII

lucrările congresului al XII-lea al asociației geologice carpato-balcanice



138754

MINERALOGIE-
GEOCHIMIE ȘI ZĂCĂMINTE-
SEDIMENTOLOGIE

BUCUREȘTI
1983

Institutul Geologic al României

Les auteurs assument la responsabilité
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MINISTERUL GEOLOGIEI
INSTITUTUL DE GEOLOGIE ȘI GEOFIZICĂ

MINISTÈRE DE LA GÉOLOGIE
INSTITUT DE GÉOLOGIE ET DE GÉOPHYSIQUE

ANUARUL INSTITUTULUI DE GEOLOGIE ȘI GEOFIZICĂ

ANNUAIRE DE L'INSTITUT DE GÉOLOGIE ET DE GÉOPHYSIQUE

VOL. TOME LXII

lucrările congresului al XII-lea al asociației geologice carpato-balcanice

travaux du XII-ème congrès de l'association géologique carpatho-balkanique





MINERALOGIE-GEOCHIMIE ȘI ZĂCĂMINTE – SEDIMENTOLOGIE

MINÉRALOGIE-GÉOCHIMIE ET GISEMENTS – SÉDIMENTOLOGIE

BUCUREȘTI
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MINÉRALOGIE — GÉOCHIMIE — GISEMENTS

MINERALOGY — GEOCHEMISTRY — ORE DEPOSITS

МИНЕРАЛОГИЯ—ГЕОХИМИЯ—МЕСТОРОЖДЕНИЯ

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CARACTÈRES CRISTALLOGRAPHIQUES, OPTIQUES ET CHIMICO-STRUCTURAUX DE L'ADULAIRE CANTONNÉ DANS LES FILONS ALPINS DE ROUMANIE ; CONTRIBUTIONS AU „PROBLÈME DE L'ADULAIRE" [1]

PAR

EMIL CONSTANTINESCU [2], GAVRIL SĂBĂU [3]

Le terme d'adulaire a été introduit par Pini en 1873 qui, tenant compte de l'examen des cristaux prélevés du St.-Gothard (Alpes — Suisse), l'a considéré une variété de feldspath potassique monoclinique (orthose) dont les traits saillants sont le habitus caractéristique et la genèse associée aux filons alpins.

Les mesurages cristallographiques effectués jusqu'à présent (Hintze, 1897 ; Goldschmidt, 1916 ; Niggli, 1923 ; Ramdohr, 1948) n'ont guère mis en évidence des écarts de la symétrie monoclinique. Les recherches effectuées au microscope (Alling, 1923 ; Barth, 1928 ; Kohler, 1948) ont cependant établi l'existence de l'adulaire à optique triclinique et la présence des macles qui suivent la loi de l'albite-péricline et de l'akline-B, propres à la symétrie triclinique. D'autres données optiques obtenues ultérieurement par Chaisson (1950), Ansilewski (1958) et Nowakovski (1959) indiquent une large variation en ce qui concerne la position de l'indicatrice et l'angle formé par les axes optiques dans différents adulaire. Les recherches röntgénographiques (Laves, 1950, 1952 ; Smidt, 1972) et les études par absorbtion en infra-rouge (Hafner, Laves, 1957) révèlent qu'aux adulaires à optiques tricliniques correspondent aussi des constantes du réseau triclinique. En conséquence on a considéré l'adulaire (Bambauer, Laves, 1960) un état intermédiaire métastable entre la sanidine (à distribution Al/Si désordonnée) et le microcline (à distribution Al/Si ordonnée).

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[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

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En Roumanie, l'adulaire a été déterminé, au microscope, pour la première fois, par G i u ş c ă (1960) qui l'a décrit comme un feldspath potassique de néoformation, résulté de l'altération hydrothermale des volcanites néogènes des Monts Gutîi. Plus tard on l'a identifié dans différents gisements des Carpathes Orientales, du Banat, de la Dobrogea et des Monts Apuseni associé aux minéralisations aurifères, de Cu-W ou de Cu-Mo, fait qui a conduit à la considérer comme un indicateur métallogénique.

Les affleurements d'adulaire des Monts Parîng, qui sont les premières occurences de filons alpins signalées dans les Carpathes de Roumanie [4], ont offert un grand nombre de cristaux bien développés et examinés au point de vue minéralogique d'une manière complexe. Les données obtenues dénotent la modification des caractères optiques et structuraux dans le cadre de différents cristaux d'adulaire voire dans le cadre d'un même cristal, fait mis sur le compte de la variation des conditions génétiques.

Occurence et paragenèse

L'adulaire examinée a été identifiée dans plusieurs filons du massif de Parîng dont les plus représentatifs affleurent dans la vallée du Gruniu (Maleia) à une distance de 9,3 km E de Petroşani, dans une carrière localisée dans le versant gauche de la vallée. La roche-hôte est constituée de schistes séricito-quartzitiques à chlorite, épidote, actinote revenant à la série de Drăgşani, série dont la migmatisation est mise sur le compte des granites syncinématiques de Parîng (U n g u r e a n u, 1974) [5]. Les filons alpins se développent le long des fissures discordantes orientées approximativement N-S ; ils ont une longueur de 1-3 m et largeur de 2 à 50 cm.

La paragenèse est constituée de : quartz, qui apparaît sous forme de gros cristaux (jusqu'à 20 cm) incolores, blancs, fumés ou verts avec des faces en forme de prismes ou de pyramides ditrigonaux bien développées ; chlorite (ripidolite) en agrégats compacts de couleur verte ; actinote disposée sous forme de fines aiguilles englobées dans le quartz et l'adulaire ; épidote en cristaux jaune-brun gros de 2-4 mm ; sphène et apatite.

Morphologie des cristaux d'adulaire

On a effectué des analyses sur 97 cristaux. Ceux dont l'habitus est court-prismatique sont gros de 1-4 cm. Les faces (110), ($\bar{1}10$), (001), ($\bar{2}01$) sont bien représentées. Parfois on observe un plus large développement de la face ($\bar{2}01$) au détriment de la face (001) (fig. 1).

Dans les cassures orientées perpendiculairement à l'axe C on observe une variation des couleurs à caractère zoné, notamment : la partie centrale sombre ou gris foncé, plus transparente, est entourée de bandes blanc-laiteux, parallèles aux faces en forme de prisme.

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La face (110) montre deux directions de clivage : très bon suivant (001) et bon suivant (010).

On observe souvent l'intercroissance régulière des cristaux suivant les faces (001) — loi Manebach et (021) — loi Baveno. On rencontre

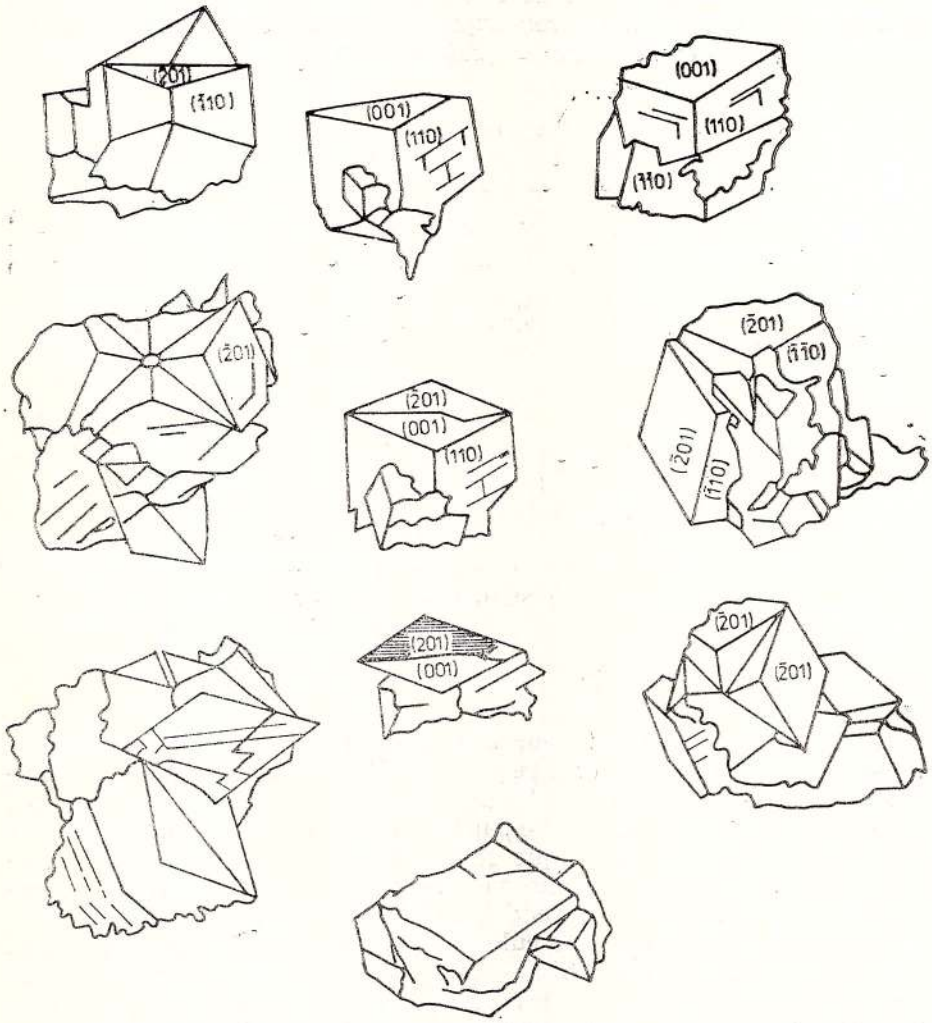


Fig. 1. — Morphologie des cristaux d'adulaire de Gruniu-Monts Parîng, Carpathes Méridionales.

aussi des macles complexes à trois ou quatre individus (Baveno + Manebach). Outre ces macles caractéristiques des feldspaths à symétrie monoclinique il y a aussi des cristaux qui laissent voir des stries sur la face (201) pouvant suggérér des plans de macle suivant la loi du péricline (001) ou acline B (100) macles caractéristiques aux feldspaths à symétrie triclinique.

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Chimisme

L'analyse chimique illustrée dans le tableau 1 met en évidence le fait que par rapport à d'autres analyses chimiques effectuées sur des cristaux d'adulaire provenant de différentes occurences, celle-ci montre une teneur réduite en Na. On remarque également la teneur réduit en Ca par rapport aux analyses no 4 (Taiwan, Chine) et no 3 (Dauphiné,

TABLEAU 1

Analyses chimiques

Oxydes %	1	2	3	4	5
SiO_2	64,20	64,00	64,87	64,45	62,3
Al_2O_3	19,26	19,25	18,51	18,97	19,6
Fe_2O_3	0,11	—	0,23	0,07	—
FeO	0,09	—	—	0,25	—
MgO	0,05	—	—	0,03	—
CaO	0,12	0,15	0,23	0,53	0,01
BaO	1,42	0,41	0,92	—	2,6
Na_2O	0,70	1,86	1,99	0,95	1,05
K_2O	13,04	14,01	13,08	14,98	14,2
H_2O^+	0,63	0,50	—	0,11	0,08
H_2O^-	0,07	0,50	0,07	0,06	—

1, Maleia, Paring; 2, St. Gotthard, Suisse (B e l i a n k i n, 1915); 3, Dauphiné, France (Z a n i e w s k a, 1937); 4, Taiwan (H u a n g, 1953) (— fide D e e r et al.); 5, Cavradischlucht, Alpes (W e i b e l 1957).

France) et par contre une teneur élevée en Ba par rapport aux mêmes analyses. Selon V e i b e l et M e y e r (1957), qui ont examiné le chimisme de l'adulaire de Cavradischlucht-Alpes (analyse 5) et qui ont suivi systématiquement la participation du Ba dans la composition de l'adulaire, il n'est pas exclu que la teneur plus élevée en Ca de certaines analyses de l'adulaire ne vienne pas des déterminations incorrectes de la teneur en Ba qui tend à se concentrer dans ce minéral.

La formule structurale calculée en prenant comme base 32(O) est : $K_{3,092}$ $Na_{0,245}$ $Ba_{0,100}$ $Ca_{0,022}$ $Si_{11,901}$ Al $_{4,427}$ O_{32} et la participation des termes extrêmes du groupe des feldspaths en mole% est : Fk 89% Ab 7% Cs 3%, An 1%. Les teneurs réduites en Na et Ca dénotent que l'absence d'homogénéite optique et structurale est due exclusivement des variations structurales.

Caractères structuraux

Données röntgénographiques. L'analyse par diffraction en RX a été effectuée par la méthode du diffractomètre [6]. Les valeurs dα/n et I/100 consignées dans le tableau 2 sont similaires à celles obtenues

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TABLEAU 2

Valeurs d/n et I/I_0 calculées à partir du diffractogramme exécuté sur l'adulaire de Maleia

	Adulaire Maleia		Adulaire Tirol (selon Gruner 1936)	
	dα/n	I/100	dα/n	I/10
1	3,93	10	3,94	1
2	3,766	15	3,77	4
3	3,45	10	3,48	2
4	3,29	20	3,313	10
5	3,229	100	3,227	8
6	2,985	35	2,995	4
7	2,889	10	2,901	2
8	2,760	10	2,763	2
9	2,55	25	2,56	6
10	2,319	10	2,319	1
11	2,154	10	2,165	4
12	2,119	10	2,119	2
13	2,049	10	2,050	1
14	1,887	45	1,881	1
15	1,795	35	1,792	8
16	1,615	10	1,622	2
17	1,449	15	1,447	2
18	1,406	10	1,402	2
19	1,382	10	1,381	2

pour d'autres cristaux d'adulaire provenant des différentes occurences de filons alpins.

Le détail du secteur $2\theta : 22\text{-}25°$ du diffractogramme réalisé et reproduit dans la figure 2 révèle, par la manière dont se présente le

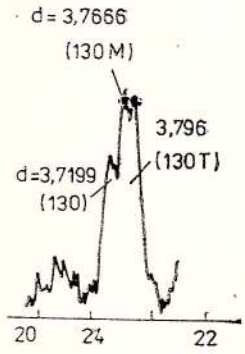


Fig. 2. — Détail du secteur 2Ø : 22—25° du diffractogramme obtenu pour les cristaux d'adulaire de Gruniu.

peak correspondant aux réflexes 130, l'absence d'homogénéité dans le cristal analysé, fait qui indique tant une symétrie monoclinique qu'une symétrie triclinique, mises en évidence par sa bifurcation. Le calcul de la triclinicité a donné la valeur $\Delta = 0,8$.

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Spectroscopie d'absorbtion en infrarouge. Le spectre d'absorbtion en IR [7] reproduit dans la figure 3 présente les bandes d'absorbtion

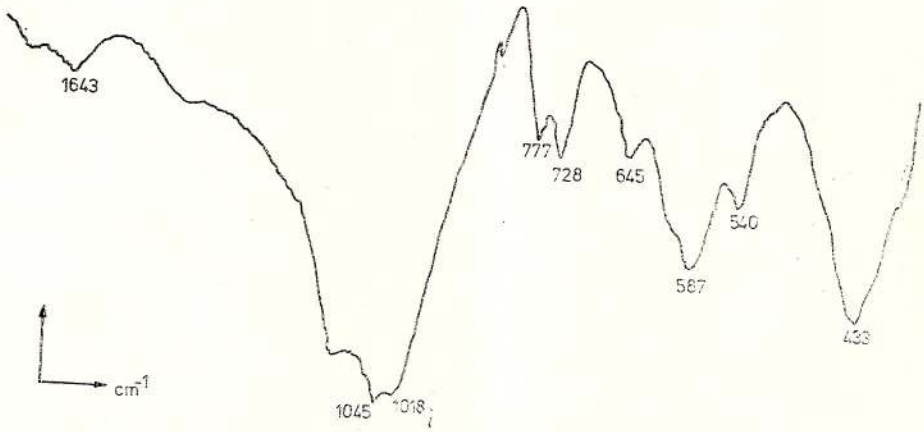


Fig. 3. — Spectre d'absorbtion en IR d'adulaire de Gruniu.

caractéristiques aux liaisons d'allongement : Si-O (1142-1·100 cm^{-1}) ; Si(Al)-O (1044-1010 cm^{-1}) ; Si-Al-Si (742-728^{-1}) ; Si(Al)-O (1044-1010) cm^{-1} ; Si-Al-Si (742-728^{-1}) et les bandes de déformation caractéristiques au : Si-O-Si de 439 cm^{-1}.

Les valeurs de ces bandes se maintiennent entre les limites des valeurs connues pour l'adulaire de différentes occurences compilées par Gadsden (1975) et elles sont caractéristiques à certains états de transition entre les termes tricliniques et ceux monocliniques.

Dans le microcline la valeur minimum de transition de 645 cm^{-1} se déplace vers la valeur 650 cm^{-1} au fur et à mesure qui l'indice de triclinicité (Δ) augmente. Dans la sanidine ce minimum apparaît à 639 cm^{-1} et à mesure qu'un arrangement ordonné intervient il se déplace vers 650 cm^{-1}.

La position des bandes d'absorbtion des domaines 18,3-18,7 μm et 15,4-15,8 μm qui a été illustrée sur le diagramme Hafner Laves dénote un état d'ordre intermédiaire.

Caractères microscopiques

Au microscope, les observations ont été effectuées sur 27 coupes minces, dont quelques-unes à orientation quelconque et d'autres orientées [parallèlement aux faces (110), (001), (201) ou perpendiculairement à l'axe Z].

Les mesurages exécutés à l'aide de la platine universelle ont montré l'absence d'homogénéité optique mise en évidence par la variation de l'angle $2V\alpha$ comprise entre 67-83° et de l'angle d'extinction $c\wedge\gamma$ comprise entre 12-17° dans différentes zones du cristal. On a identifié même des zones à caractère uniaxe. On a pu distinguer des structures zonées caractérisées par la présence de lamelles minces,

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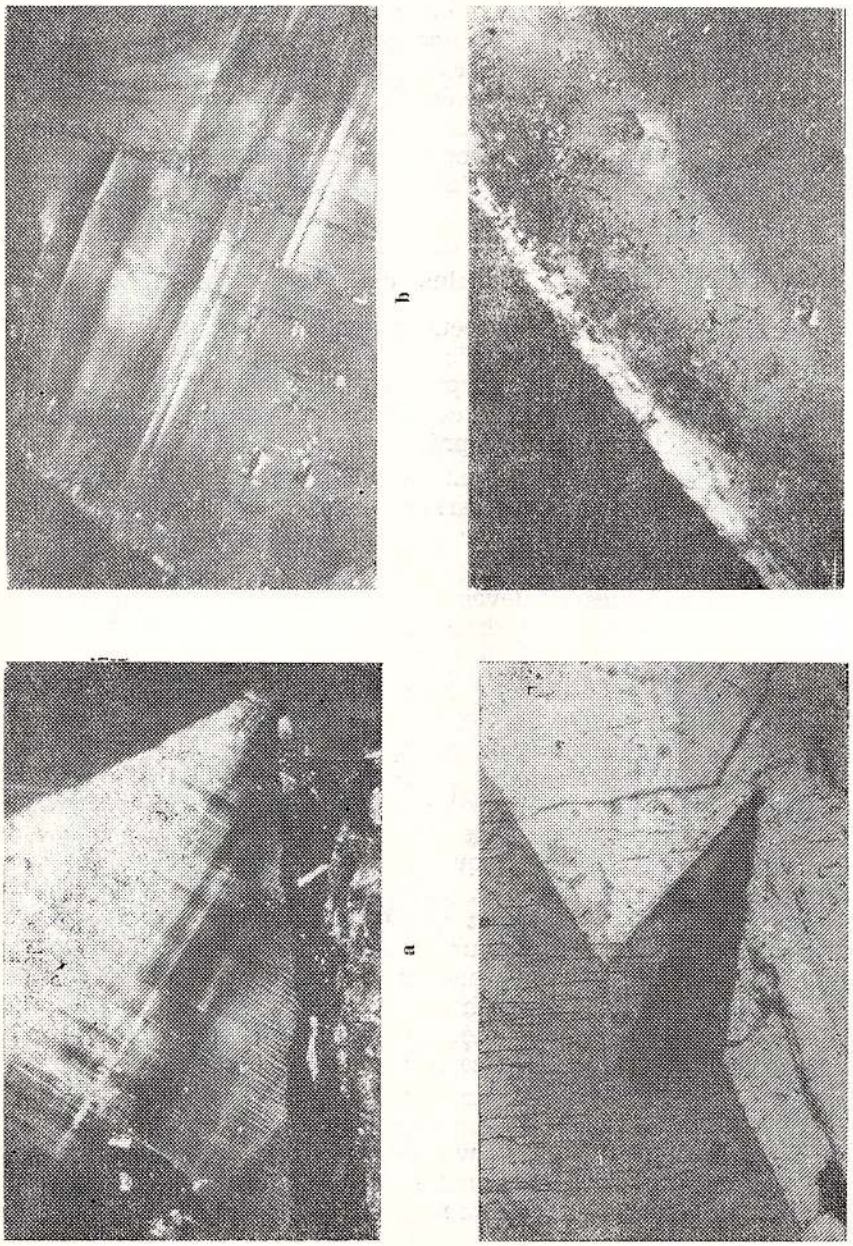


Fig. 4. — Images microscopiques d'adulaire de Gruniu.

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parallèles aux faces de prisme (110), qui délimitent une zone centrale plus développée (fig. 4). En ce cas, les zones centrales présentent des valeurs proches de la symétrie monoclinique et les zones marginales des valeurs caractéristiques du microcline intermédiaire. La zone de raccordement des lamelles, comprise dans l'angle aigu des faces de prisme, présente des valeurs caractéristiques d'un arrangement ordonné plus marqué par rapport à la zone comprise dans l'angle obtus des faces de prisme. Des valeurs propres à la symétrie monoclinique et des macles de type albite + péricline ont été également saisies dans les voisinage de certaines fissures ou de certaines inclusions.

Conclusions

En tenant compte de ses aspects marphologiques, de son chimisme, de sa structure et de ses propriétés optiques, l'adulaire de Maleia-Parîng présente les caractères typiques de l'adulaire de type „filon alpin" bien connu dans différentes occurences de la chaîne alpino-carpathique, mais inconnu jusqu'à présent dans les Carpathes roumaines.

Par son statut, même de phase métastable, l'adulaire présente dans chaque occurence outre les caractères typiques une série de traits particuliers qui peuvent contribuer à mettre en évidence quelques-uns de ses aspects minéralogénétiques.

L'un des problèmes soulevés a été le suivant : les zones tricliniques ont-elles pu être engendrées au cours de la cristallisation du cristal (possible plutôt pendant la phase finale de la cristallisation) ou représentent-elles le résultat d'une transformation ultérieure, respectivement d'une triclinisation du feldspath monoclinique ?

D'une part, l'occurence et la paragenèse excluent la possibilité de cristallisation à des températures supérieures à 400°C (les déterminations géothermométriques effectuées sur les inclusions fluides des cristaux de quartz associés dénotent des températures de tout au plus 180°). Il y a donc des conditions inadéquates pour la formation d'une phase monoclinique stable. D'autre part la vitesse à laquelle se déroule le processus de cristallisation permet plutôt la formation d'une structure partiellement désordonnée que d'une structure bien ordonnée, conduisant donc à l'apparition d'un stade monoclinique métastable dans le domaine de stabilité du feldspath K triclinique. Cette possibilité est parfaitement d'accord avec la symétrie monoclinique des cristaux isolés et avec la symétrie des macles saisies de type Manebach et Baveno. Aussi considérons-nous que les stries de la face (201) ne représentent pas les plans des macles de type albite spécifiques au système triclinique, comme les considérait N o w a k o w s k i (1959), mais les limites de certaines zones avec de différents degrés d'ordre Si/Al orientées parallèlement à la face (100) comme l'ont suggéré B a m b a u e r et L a v e s (1960).

Les observations microscopiques effectuées sur l'adulaire de Maleia-Parîng ont mis en évidence la tendance de changement de la symétrie monoclinique, avec le temps, en symétrie triclinique. Les domaines avec un degré élevé d'ordre — mis en évidence par les

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valeurs des angles $2V\alpha$ et c/γ et par les macles de type péricline + albite — se disposent, comme il a été déjà indiqué, dans les zones marginales, parallèles aux faces (110), autour des inclusions ou dans le voisinage des fissures.

Ces éléments nous permettent d'associer la cinétique des transformations aux propriétés particulières du réseau cristallin du voisinage immédiat de certaines surfaces.

En ce sens nous admettons deux possibilités :

1. Dans le voisinage des surfaces le cristal monoclinique a un surplus d'énergie libre (dû à la tension superficielle) qui augmente la force motrice de l'inversion polymorphe. À l'appui de ce mécanisme vient aussi le degré d'ordre plus élevé existant dans les zones comprises dans les angles aigus, formées par les faces de prisme (110) par rapport aux zones comprises dans les angles obtus formées par les mêmes faces de prisme (110) ;

2. Sur les surfaces internes du cristal (dans le voisinage des inclusions et des fissures) ou externes a existé un fluide aqueux adsorbé qui a rempli un rôle catalitique, efficace pour la transformation du stade monoclinique métastable en une phase ordonnée, triclinique.

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[5] Thèse de doctorat, Université de Bucarest (non-publiée).

[6] Diffractomètre Phillips radiation CuKα filtre Ni étalon interne sylvine.

[7] Spectrophotomètre Zeiss UR 20 pastille KBr 0,20%.

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BLASTIC PLAGIOCLASES IN THE PIATRA ȘURLIGATĂ ANDESITE — APUSENI MOUNTAINS [1]

BY

RADU CONSTANTINESCU [2], LIVIU ANTON [2]

Geological and Petrographic Background. The post-Pannonian andesite pillar (Ianovici et al., 1969) crosses the crystalline schists 7.5 km SSW of Baia de Arieș (Apuseni Mountains). Two rock varieties can be distinguished within this body : a prevailing one bearing quartz and hornblende phenocrysts and another one bearing hornblende and biotite phenocrysts, in the northern, marginal part — samples 31 of Table. The crystallized andesitic groundmass often resembles a plagioclasite. The andesite fluidal structure is given by the orientation of the elongated amphibole prisms, the subsequently crystallized feldspathic component having its own glomeroporphyric massive texture and structure.

On the whole the porphyritic character of the rock is due to the existence of the agglomeration of plagioclase megacrystals (16.3%) which are comparatively huge, reaching 25 mm in size (Pl., Fig. 1), and of blastic nature.

Augustithis (1964) calls tecoblastesis the process of the appearance of the "crystalloblastic structural features" in basalts, that is the "assimilation and digestion of the pre-existent crystalline phase by plagioclase". We took over this term, using it for defining the plagioclase blastesis in the hot, consolidated volcanic rock (andesite in this case).

The tecoblastic plagioclase. The *exterior cover* (Pl., Figs. 1, 2) of the tecoblastic aggregates generally shows very reduced thicknesses, of the order of the dimensions of the groundmass crystals and appears as a homogeneous, clear, crystallized, independent plagioclasic material. In the direction of the maximal growth rate this exterior cover emits protuberances (Pl., Fig. 3) which fuse through the ends and include parts of the andesitic rock, assimilating them ; in the direction of the

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minimal growth rate the exterior aspect of this border is idiomorphous, partly rectilinear and generally "in steps" (imbricated). The exterior cover appears as a reaction front bordering the megacrystals in most cases, interposing between their following exterior mat zone and the andesitic matrix, therefore between the tecoblastic material and its alien bodies (Pl., Fig. 2). Feldspathic bands also occur in the groundmass, showing the same composition and aspect as the borders and not covering a coherent structure, as well as plagioclase amoeboidal irregular isles of the same nature, which develop skeletally, including and digesting other mineralogical elements. The small matrix plagioclase crystals external zones get formed also blastically, as overgrowths on a restructuring material. When a macrotecoblast contacts the groundmass plagioclase crystals the exterior part of the latter fuses with the exterior clear cover of the megacrystal, being reoriented, while their isotropic reddish core — disaggregated hornblende — remains as inclusion in the advancing cover of the macrotecoblast (Pl., Fig. 2).

The composition variation within the cover is concentric-zoned (Pl., Fig. 2. — detail), with flowing transitions between zones, the extinction taking place rather undulatory from the exterior towards the interior. The zoning follows the exterior outline of the border; when two protuberances of the border touch their heads, then their zones of the same chemism join and adopt the shape of the new outline (Pl., Fig. 2). The zoning avoids the reaction plagioclasic aureole round the inclusions (Pl., Fig. 2).

Behind the clear cover the tecoblasts show a *mat friable and porous zone* of variable thickness; this material may constitute the whole filling of the exterior cover, but usually it has one or several nuclei of clear, well crystallized plagioclase to which it gradually passes; the boundary between the mat zone and the clear border is fringed by the partially assimilated inclusions, but it is generally much more regular than the boundary with the core. The mat material may appear also devoid of border, showing various, sometimes skeletal shapes, but it appears generally as zones within which the matrix structure disappears, the aspect becoming pulverulent, translucent in crossed nicols and preserving the depreciated outlines of the disaggregated minerals. The mat zone within tecoblasts shows a typical texture. At the exterior it is cryptocrystalline, probably partly vitreous, fine-fibrous, vaguely optically oriented, so that the extinction is never complete; the colour of the domain is often reddish — like that of the nuclei of the matrix microcrystals — due to the hematite and limonite; the opacite strengthens the mat character of the material. The boundary between the mat zone and the clear border is the agglomeration place of the neoformation magnetite. Round the inclusions of andesitic matrix or other minerals caught in the mat zone there forms a clear, reaction plagioclasic aureole, which continues by filaments within the host mass (Pl., Fig. 4). The structure of the mat zone gradually changes towards the clear nuclei of the tecoblast: the material becomes obviously "fibrous" (Pl., Fig. 5), its optical orientation ever clearer and more unitary, its extinction ever surer; opacite gradually disappears,

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the transparency of the material grows, its mat character blurs; the included and opacitized hornblende is biotitized (Pl., Fig. 2), the frequency of the biotite associated with magnetite increases to the amphibole detriment; the dimensions of the fibres in the mat zone greatly increase. The two domains practically interpenetrate — the mat zone dissolves in the nuclei (Pl., Fig. 5); in an advanced transformation stage, the perfectly crystallized material of the nucleus preserves tiny plagioclase crystals or drops of refringence and extinction differing from those of the host mass and isotropic domains geometrically delimited; the massif clear nuclei replaced the skeletal plagioclase of the mat zone.

The germs of the *clear central plagioclase* occur rhythmically in the mat material, transversally elongated on the direction [100] (Pl., Fig. 3), that of the maximal growth rate of the crystals; from them the growth of nuclei in several domains towards the exterior starts; the concentric zoning between two germs takes place finely (Pl., Fig. 2), with recurrences and inversions of low amplitude, the general tendency of the anorthite content being to decrease; when reached, the germ of the exterior domain is corroded, the final ensemble being a clear central tecoblastic area, falsely recurrently zoned; the advance of the clarifying front often leaves behind it islands and half islands of mat material or rows of various inclusions zonally disposed. Neosomatic magnetite inclusions agglomerate at the boundary between the mat domain and the clear nucleus. The "patchy" zoning occurs as a result of the isolation of a part of the andesitic groundmass or of an unstructured mat material behind a clear border that advances metasomatically; the isolated material, uncrossed by a blastic structuring front, has the aspect of a motley agglomeration of plagioclasic domains of varied refringence, cimented by a clear feldspathic "matrix" showing the same composition as the borders (Pl., Fig. 3); the agglomeration includes many vacuoles — the water of the decomposed melanocrate minerals — and opacite $\pm$ biotite randomly disposed.

Between several *fusioned megacrysts* the exterior clear border is eliminated and the mat zone is rapidly assimilated; the glomeroporphyric aggregate gets a unique shell, consisting of a clear cover and a mat exterior zone common to all the fused crystals, with clear joined nuclei, intercorroded, twinned by joining, with common cover growths, reoriented, coherent with the new crust.

The *twins* clearly prevailing in tecoblasts are those of parallel and complex hemitropy (Pl., Fig. 7). The twins often extend from the border to the clear central zone of the megacrystals, but usually they are not evident in the exterior mat domain, masked for the lack of the structure of the domain and the dilution of the feldspathic crystalline phase; the fibres of the mat domain are symmetrically oriented with respect to the twin plane, being the components of a unique skeletal crystal. The number of the twin individuals gradually decreases from the border to the nucleus, becoming ever thinner in steps.

Analytical data (Tab.) indicate that the growth of the megablasts is accompanied by: the total elimination of TiO_2, FeO and P_2O_5; the

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increase of the Al_2O_3 amount by 5-6%; the gradual elimination of MgO, K_2O and Fe_2O_3, partially retained in the mat domain and transformed in biotite-opacitic melanosome in the clear central domain; (the increase of the Fe^{3+}/Fe^{2+} ratio); the steady growth of the CaO amount; the relative accumulation of Na_2O only in the clear central part of the megacrystals.

The exclusive consideration of the *M* (octahedral) cations proportion within feldspars allows some remarks: K_2O decreases from the rock to the mat domain and from the latter to the clear tecoblastic nuclei; a cationic polarization takes place within megacrystals — CaO concentrates in the mat domain, Na_2O in the clear domain, the tecoblastesis implying a rectilinear change of their ratio (Pl., Fig. 6); the final product of this process — the clear central domain — contains a CaO amount similar to that of the rocks, but it is much richer in Na_2O.

The greatest *anorthite amount* is found in the mat domain of the tecoblasts — 62-80% An, on the average of 70% An (67-70% An — after the refraction index of glass; 72.97% An — calculated from analytical data); the plagioclase of the andesitic groundmass shows contents round 50% An (51.13% An — calculated from analytical data); the clear border of tecoblasts shows a similar composition, slightly more basic towards the mat domain — 50-60% An (Pl., Figs. 2, 7); the weight centre of the compositions of the clear nuclei is situated at about 45% An on the curves from the stereograms and 45-50% An on the curves of the refraction indices (the mean of 30 determinations by the refractometer: on crystalline oriented fragments — 46.47% An; on pearls — 47.57%. The values calculated from the data of chemical analyses are of 39.85-44.82% An). Within a glomerular tecoblastic agglomerate the composition of the macrocrystalline elements is almost identical, only the orientation differing from one granule to another.

The *structural investigation* of tecoblasts led to some rather contradictory results:

— according to the determinations by the Fedorov five axes universal stage, the optics of crystals would be intermediary, between the high temperature structural type and the low temperature structural type; the consideration of the extinctions on definite crystallographic planes, related to the anorthite content determined by the Fedorov stage leads to the same conclusion;

— the projection of $2V\gamma$ versus % An shows rather a tendency towards the high temperature structure, especially for the mat domain (Pl., Fig. 8);

— the results of investigation by X ray diffraction invariably shows a structural state of low type, both for the clear central domain and for the mat domain of the tecoblasts; the Beta function (Smith, 1974) has the value of 0.9 for 50% An — the clear domain, and of 0.85 for 70% An — the mat domain; the structural indicator (131) (Bambauer et al., 1967) shows the value of 1.75 for 50% An — clear plagioclase and 2 for 70% An — mat plagioclase; for checking, the ratio of the values of the indicators (131) and ($\bar{2}41$) (idem) is of

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TABLE

Chemical analyses (down detailed)

No.	Sample number	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O+	Total
1	27	59.95	0.96	17.50	2.81	1.70	0.09	2.58	7.30	3.32	1.52	0.20	1.41	99.49
2	28	59.70	0.86	17.50	2.87	1.92	0.11	3.70	5.40	3.32	1.64	0.20	2.02	99.37*
3	29	59.90	0.92	17.85	2.51	2.44	0.12	2.82	6.30	3.32	1.58	0.20	1.12	99.23*
4	30	59.90	0.86	17.00	2.34	2,09	0.11	3.52	6.45	3.24	1.70	0.19	1.75	99.24*
5	30_A			17.30		4.73**	0.11	3.70	5.78	3.50	1.67			
6	7/30			18.86		2.33**	0.062	1.78	6.14	3.62	1.68			
7	30_R	58.11	0.64	17.98	3.11	1.50	0.23	3.96	6.11	3.29	1.71	0.22	2.63	99.49
8	30_S	57.85	0.40	17.70	2.93	2.02	0.09	3.08	7.27	3.39	1.70	0.21	3.60	100.24
9	31	61.95	1.14	16.80	3.89	1.27	0.14	1.40	5.90	3.24	1.75	0.31	1.40	99.28*
10	31_A			17.30		5.64**	0.14	1.60	5.11	3.33	1.82			
11	31_S	57.11	0.38	18.61	4.14	1.42	0.15	2.43	9.72	3.39	1.01	0.19	1.74	100.29
12	12	56.72	0.33	20.10	4.51	2.35	0.28	1.80	6.19	4.37	1.32	0.17	2.18	100.42
13	3	59.85	0.98	18.00	2.41	2.37	0.11	4.00	6.30	3.04	1.76	0.23	1.51	100.56
14	11									2.94	1.54	0.31		
15	5	59.94	0.68	18.60	2.24	1.53	0.10	3.16	6.00	3.13	1.63	0.12	2.07	99.25
16	1	59.48	—	24.60	1.16	—	0.05	0.97	7.85	2.82	1.40	—	0.89	99.22
17	7_M			23.10		1.13**	0.041	1.23	7.02	2.96	1.45			
18	9/4									3.80	1.49			
19	7_A			23.90		0.92**	0.055	0.81	7.50	4.49	1.02			
20	4	57.90	—	24.40	0.76	—	0.25	0.62	7.95	5.20	0.78	—	1.52	99.38
21	8			24.75		0.60**	0.041	0.40	7.47	5.02	0.72			
22	9			25.90		0.49**	0.037	0.34	7.67	5.62	0.49			
23	2	61.20	0.28	23.40	0.24	—	0.02	0.21	7.32	6.40	0.32	—	0.89	100.28
24	8/3									7.04	1.11			
25	10/4									6.46	0.29			
26	6	57.65	—	26.72	0.30	—	—	—	8.88	6.41	0.60	—	—	100.55
27	7_G			25.90		0.12**	0.022	0.13	7.62		0.24			

* without FeS (0.09—0.15); ** FeO + Fe_2O_3 as Fe_2O_3.

Analysed-by atomic absorbtion : nos. 1—4, 9, 13, 15—16, 20, 23 (analyst : A. Medeșan), 5—6, 10, 17, 19, 21—22 (analyst : M. David); — gravimetrically : nos. 7, 26 (analyst : A. Medeșan), 8, 11 (analyst T. Murariu); nos. 12 — from Ianovici et al, 1969 (probably gravimetrically); by flame photometry : nos. 14, 18, 24—25 (analyst A. Medeșan).

Nos. : 1—12 — rock samples; 13—14 — rock 30 without tecoblasts (extracted); 15 — leucocrate fraction + tecoblasts from rock 30; 16—18 — mat domain of tecoblasts; 19—21 —mat + clear domains; 22 — whole tecoblasts; 23—27 — clear central domains of tecoblasts (Plate, Fig. 6).

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1.75 : 0.5 for the clear plagioclase, which plots the projection point at 50% An on the low temperature curve. Although the mat domain has the special previously mentioned physiographic-chemical characteristics, its diffraction spectrum indicates the presence of a single crystalline phase — the plagioclase feldspar.

The data presented so far provide enough **arguments in favour of the novel tecoblastesis phenomenon:** the plagioclase megacrystals are subsequent to the fluidal texture, marked by hornblende; the tecoblastic aggregates are gigantic and are not deformed; they are idiomorphic; the tecoblasts include rock fragments, untransformed or in various assimilation stages; the presence of the skeletal-spongy texture containing andesitic matrix portions; the existence of the clear external border, tentacular in the direction of the maximal growth rate of the crystals; the obvious assimilation by the border of the andesitic matrix, whose melanocrate fraction furnishes — after decomposition — the opacitic material behind the border; the zoning of the border, parallel to its tentacular contour; the appearance of the blastic border, as boundary of some domains of andesitic, plagioclasic, eventually isotropized matrix; the evidence of the border differentiated advance, retired in front of the inclusions from the tecoblast; the existence of the mat-fibrous domain behind the generating border, as a domain of purification and reorganization of the andesitic matrix crossed by the border; the elimination of the mat domain between the individuals of a glomerule in expansion and its appearance, together with the external border, as a common cover of the whole aggregate, from whose external surface the entering angles tend to disappear; the bounding of the inclusions of matrix or melanocrate minerals from the mat domain by the clear reaction plaglioclasic border of the same type as the border separating the mat domain from the andesitic groundmass; the appearance of the "clarifying germs", disposed parallel from place to place in the direction of the maximum growth rate of the tecoblast and parallel to the concentrical — subsequent — zoning of the clear central domain and to the external border; the growth of the dimensions of the "fibres" of the mat domain towards the clear central domain; the skeletal character of the mat domain, very obvious at the boundary of the connection with the nucleus; the mat relicts, in various assimilation stages, disposed concentrically-zonally in the clear nuclei and often accompanied by opacitic restites; the elimination of the non-assimilable material, partly at the boundary between the external border and the mat domain, partly at the boundary between the clear central nucleus and the mat domain; the "patchy" zoning of the nucleus or of some zones — included and transformed andesitic matrix — surrounded by the mat domain and border; the zoning of nuclei, differentiately corroding the external mat domain that interrupts it; the twins inherited by the clear nuclei from the mat domain become thinner in angular steps, proving the genesis in a solid environment (Starkey, Brown, 1964); the frequency of the pericline twin, characteristic for granites and metamorphics (Barth, 1969); the lack

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of the albite and albite-Carlsbad twins which are not characteristic for the crystallization in a solid environment (idem); the intermediate chemism of the mat domain, between that of the clear nuclei and that of the rock on the whole, pointing to a transformation by stages; the global chemism of tecoblasts identical to that of the matrix plagioclase; the X ray diffraction spectrum pointing to the presence of a single plagioclasic crystalline phase in the mat domain; the rather high temperature structure of the first formed mat domain (hence not an alteration!); the low temperature structure of the central clear nucleus.

Tecoblastesis develops as follows: *1.* — after the crystallization of hornblende which extracts iron, magnesium and partially the calcium of the andesitic melt, the formation of the plagioclasic matrix An_{50} takes place; its formation meant also the volcanic consolidation. The nucleation of the matrix plagioclase often takes place on the pre-existent hornblende; *2.* — the physical conditions and the particular chemism of plagioclase determines its maximal structural lability (Barth, 1969); *3.* — this fact leads to the remobilization in a solid environment of a feldspathic phase — An_{50} — which takes the form of skeletal crystals or of the clear plagioclasic fronts from the matrix — the first clear borders — representing now the monocrystalline feldspar mass of the largest dimensions and therefore the most stable; *4.* — by the separation of the neosomatic plagioclase An_{50} the pre-existent matrix crystalline structure is destroyed in the separation volume and the isotropisation of the feldspathic material takes place. Within the large-sized skeletal monocrystals An_{50} the orientation of the restitic phase after the host takes place; simultaneously hornblende is decomposed into a ferro-magnesian opacite and an isotropic cryptocrystalline phase that comprises the rest of the amphibolic material; *5.* — the plagioclasic neosome An_{50} begins to advance, assimilating the surrounding rock; the advance is enabled by the plagioclase assimilation from the andesitic matrix, which seems to be re-oriented quasi-instantaneously and anyway always totally — the protuberances and the tentacles of the clear border (cover) occur; the border inlets mark the slower assimilation of the concomitantly decomposed non-feldspathic material. The mobile border is zoned, the advance front being constantly of An_{50}, more acid than the inner zones — therefore the segregation of the feldspathic material is permanent; *6.* — a reoriented feldspathic material remains behind the border — the "fibres" of the plagioclasic phase — different from An_{50}, to which there add a feldspathizable material, resulted from the hornblende disaggregation, opacite, hematite and a mobile phase of the An_{50} composition; *7.* — the process of feldspathic segregation continues in the mat domain behind the border. The An_{50} phase is again the first to crystallize, producing the germs rhythmically disposed transversally on the direction [100]. The rate of segregation in this domain is higher than that of the border advance which feeds the domain, due to the finess of the mat material — therefore the larger reaction surface, to the more adequate chemism

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after the elimination of FeO and MgO in inert opacite and to the beginning of organization. *8.* — a polarization of the compositions in the mat domain takes place : a more and more acid feldspathic material migrates towards the clear An_{50} germs, which will bring about the fine concentric zoning with slight recurrences. At the periphery, behind the border, the anorthite and non-feldspathic restite contents increase, being zonally disposed — the opacitic non-feldspathic restite prevails at the exterior, while inwards there forms a microcrystalline phase of the An_{70} composition. *9.* — the expansion of the clear initial germs of An_{50} take place by the deposition of some more and more acid beds, which at one time "bathe" the An_{70} crystals. The uniformisation of the composition in this junction domain is made either by the overgrowth of a more acid plagioclase on the An_{70} crystals or by their corrosion and dissolving to a greater or less extent or — most probably — by the conjunction of the two processes. Through this mechanism the clear central domain enters şkeletally-tentacularly the mat domain, the corrosion proceeding inwards outwards. The feldspathic undigestible material is preserved in the clear nuclei as isotropic accidents, tiny crystals variously oriented — structural resisters — and as irregular zones of another composition — chemical resisters ; the non-feldspathic material agglomerates in isotropic domains or changes into biotite and magnetite. The elimination of the structural tensions from the clear domain manifests by the gradual elimination of twins ; *9 a.* — a variant of the tecoblastesis process in that of the "patchy" zoning in which the "cement" of the "patches" — the mobilizate — is also of the An_{50} composition.

In conclusion, tecoblastesis is a process of diffusion within the solidus, at a rate marked by the distances between the first formed clear germs in the mat domain. The process is enabled by an adequate temperature — probably 150-200°C below solidus (Lofgren, 1972) and by an extremely adaptable structure. It is not accidental that the process operates especially with the An_{70}, An_{50}, An_{33} compositions — those of the main structural discontinuities (Megaw, 1960 ; Barth, 1969 ; Smith, 1974). As a matter of fact the possibility of the existence of a formation mechanism as above described is supported also by the results of the experiments performed by O'Neill and Taylor (1967).

The plagioclase tecoblastesis phenomenon is widespread and obvious especially in the volcanic and subvolcanic rocks of diorite-granodiorite composition, from the Apuseni Mountains, the East Carpathians and Dobrogea too.

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Fig. 2 - Drawing after thin section: glomerular tecoblast; structure (graphic scale). Crossed nicols

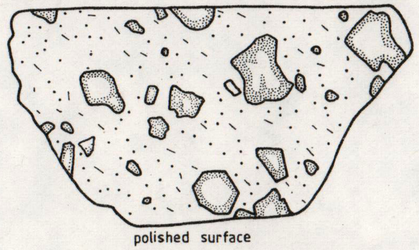


Fig. 1 - Glazed surface in the Surligata andesite (Scale 1:1)

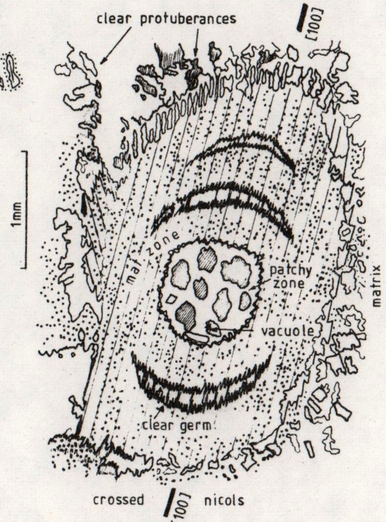


Fig. 3

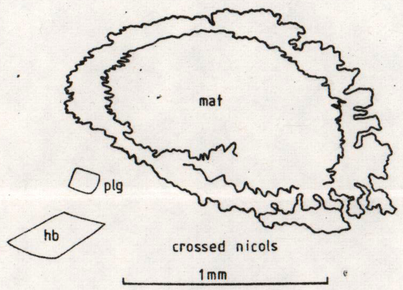


Fig. 4

Figs. 3-4 - Forming tecoblasts: advancing clear border surrounding the mat domain (with clear „rhythms" Fig. 3 - the germs of the future nucleus) „patchi zoning" Crossed nicols.

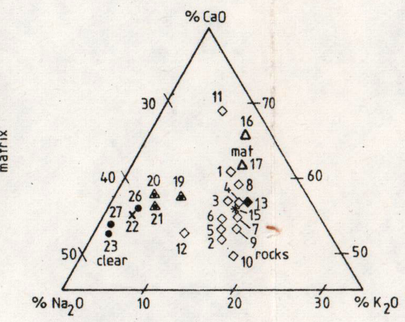


Fig. 6 - Tecoblastic differentiation

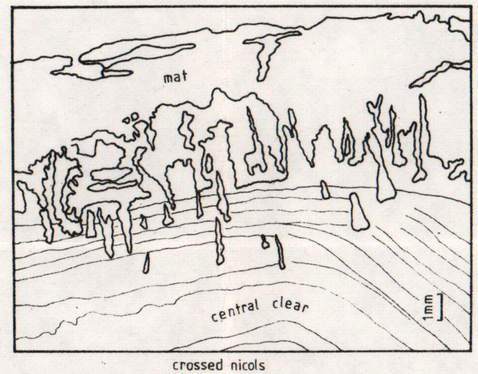
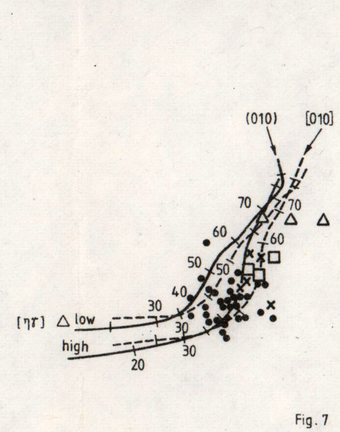


Fig. 5 - Digestion of the external mat domain by the clear tecoblastic nucleus - detail.



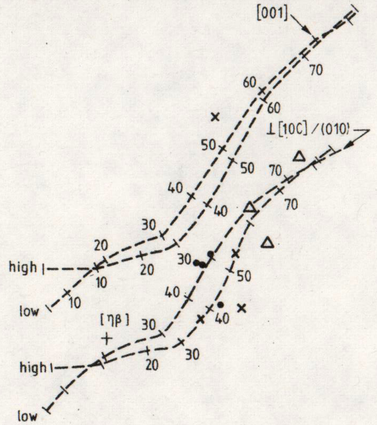


Fig. 7

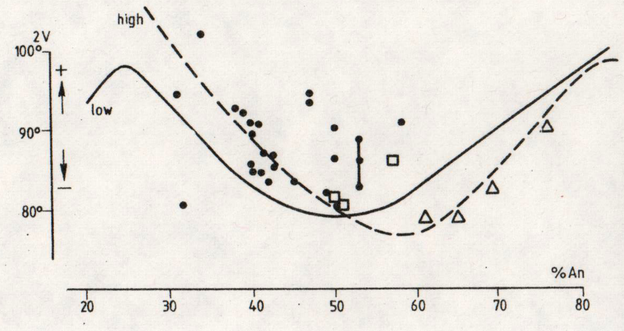


Fig. 8

Figs. 7-8 Structural state and composition of the various tecoblastic domains deduced from optical constants.

COMMON KEY FOR Fig. 1-8

- Mat zone
- Ancient mat zone
- Clear central zone
- Mat + clear composition
- Clear border
- Matrix plagioclase or small tecoblasts as a whole
- Leucocrate fraction of rock + tecoblasts from sample 30
- Rock samples
- Rock 30 without tecoblasts

Imprim. Atel. Inst. Geol. Geof.

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ZEOLITIC VOLCANIC TUFFS OF ROMANIA [1]

BY

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Introduction

Zeolitic volcanic tuffs of Romania were first mentioned by Lucca (1939).

Neacșu (1969) identified zeolites in the Hădăreni tuff of Ocna Mureș, carrying out the first quantitative determinations, while Pop (1973) pointed out the high percentage of zeolites in the Perșani Mountains.

Popescu et al. (1975) evidence the presence of clinoptilolite in the dacitic tuffs of Bocșa, Mirșid, Cășeiu and Apahida and, subsequently (Popescu, Asvadurov, 1978), also in other zones of Transylvania.

Caraman, in his thesis for a doctor's degree (1976) points out the economic importance of the zeolitic volcanic tuffs in the northern part of the Transylvanian Depression.

Bedelean et al. (1978) noted the presence of laumontite, and Istrate (1980 a, 1980 b) that of mordenite, also within some tuffs of Transylvania.

New data on the zeolitization degree and the possibility of turning to account the tuffs appear in the papers of Hibomvschi et al. (1978), Mocanu et al. (1979) and Cosma (1977, 1980, 1981).

Extension of Volcanic Tuffs in the Geological Formations of Romania

The subsequent Alpine volcanism, marked by three paroxysmal phases and showing a preponderantly explosive evolution, generated great amounts of volcanic ashes that gave rise to the volcanic tuffs by sedimentation and diagenesis.

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September 8—13, 1981, Bucharest, Romania.

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The volcanic tuffs are well developed within the Miocene and Pliocene formations, being identified in the following geological units: the Moldavian Platform, the East Carpathians (the Perşani compartment, the Tarcău Unit, the Carpathian Foredeep), the South Carpathians (the Getic Depression and the Strei Depression) as well as in the Transylvanyan, Sylvanian and Sighet intermontane depressions.

The tuffs at the base of the Badenian are the most important both as regards their extension and the presence of zeolites; they are known as the "Dej tuff horizon" in the Transylvanian Depression, the "Perşani tuff" in the Perşani Mountains or the "globigerina tuff horizon" in the Carpathian Foredeep, the Getic and the Sighet Depressions. The thickness of this horizon varies from one zone to another, ranging between 2-200 m, the tuff beds being 0.1-40 m thick.

Except for the Borşa-Iclod and Ghiriş tuffs in the Transylvanian Depression, the post-Badenian volcanic tuffs show a reduced extension, small thicknesses and low zeolitic contents.

The Presence of Zeolites in the Volcanic Tuffs of Romania

The cinerites of Romania can be differentiated depending on the zeolite content (Tab. 1) as follows:

TABLE 1

Mineralogical Composition of Volcanic Tuffs of Romania

Geological unit	Sample number	Mineralogical components							
		Quartz	Feldspars	Biotite	Muscovite	Calcite	Volcanic mass	Zeolites	
								microscope	Roentgen
Perşani Compartment	138	1–6	0–10	0–2	0–1	0–5	84–99	30–82	43–87
Tarcău Unit	23	0–3	0–8	0–1	0–1	0–15	79–100	0–63	0–95
Carpathian Foredeep	29	0–2	0–20	0–2	0–2	0–40	57–98	0–56	0–60
Getic Depression	25	0–2	0–3	0–3	0–2	1–50	55–99	0	0
Strei Depression	17	0–2	0–1	0–1	0–1	0–6	93–100	0	0
Transylvanian Depression	237	0–7	0–20	0–1	0–1	0–16	72–100	5–84	23–90
Sylvanian Depression	18	0–20	0–15	0–1	0–1	0–45	55–100	0–69	0–70
Sighet Depression	21	1–10	1–6	0–1	0–1	0–4	79–99	29–80	45–80

— zeolitic tuffs with high zeolite contents (40-90%) in the Perşani Mountains, the Transylvanian and Sighet Depressions;

— tuffs showing variable zeolite contents (0-95%) in the Tarcău Unit, the Carpathian Foredeep and the Sylvanian Depression;

— tuffs devoid of zeolites, in the Getic Depression.

Microscopic analyses demonstrate that the zeolitization of the volcanic glass is more intense for the coarse tuffs than for the finer ones.

Clinoptilolite, present in most of the analysed samples, represents the typomorphous zeolite of the volcanic tuffs of Romania.

X ray analyses allowed the identification of other zeolitic minerals, such as:

— mordenite, at Codor and Orman, in the Transylvanian Depression (Cluj district);

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— analcime, in the Carpathian Foredeep, at Nereju (Vrancea district).

In the Perșani Mountains the zones rich in zeolites (50-80%) show a lenticular development ranging between 0.5-5 m in thickness.

The zeolite content of the samples provided by the drillings carried out in the Aluniș and Orman zones (the Transylvanian Depression) does not greatly vary with depth.

The comparative study of the cinerites in the Transylvanian Depression points out the modification in the course of time of the character of the pyroclastic material from acid to basic, concomitantly with the decrease of the zeolite content, as shown in the following table :

Tuff name	Age	Character of the pyroclastic material	Maximum zeolite content
Dej tuff	Badenian	rhyodacitic	87
Borșa-Iclod tuff	Badenian-Buglovian boundary	dacitic	72
Ghiriș tuff	Buglovian-Volhynian boundary	andesitic	53

The Pliocene andesitic tuffs from the Moldavian Platform are devoid of zeolites.

Zeolitization of Volcanic Tuffs

The following zeolites have been identified in tuffs : heulandite, clinoptilolite (dominant), mordenite, laumontite, desmin, phillipsite, analcime, chabasite and erionite. Clinoptilolite is the most frequent zeolite in the tuffs of Romania as well as in the cinerites of Bulgaria (Kirov, 1976) or Hungary (Nemecz, 1976).

Zeolites form by the reaction between volcanic glass and the interstitial water (Sheppard, Gude, 1973) ; this phenomenon is controlled by the following factors :

— petrographic composition, permeability and age of the host rock ;

— temperature, pressure and water chemism.

Collela et al. (1976) consider hydration as an initial stage of the zeolitization of volcanic glass. Water pH is also an important factor in the reactions generating zeolites (Hay, 1976). At a pH of 9.5 important amounts of zeolites can be generated in the course of several years.

The formation of zeolites is favoured by the existence of an "open hydrogeological system" (Höller, Wirsching, 1976), allowing the enrichment in Na^+ and K^+ of the rock.

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The tuffs have been zeolitized during several million years after deposition (Read, Eisbacher, 1974) under temperature and pressure conditions up to 65°C and respectively 4 kb.

Possibilities of Turning to Account the Volcanic Tuffs of Romania

The high percentages of zeolites within tuffs lend them the property of natural exchanger of cations, which leads to new possibilities of using these rocks.

Technological researches in the laboratory or pilot as well as industrial researches for establishing the fields of utilization of the volcanic tuffs were accomplished by the Institute of Research and Mining Projection for non-metalliferous substances in Cluj-Napoca in cooperation with numerous productive and research units in Romania in the period 1976—1979 (Fodor et al., 1979). These studies were made on the tuffs from the Transylvanian and Sylvanian Depressions, especially on those in the Pîglișa (Cluj district) and Mirșid (Sălaj district) areas.

So far 28 possibilities of turning to account the tuffs have been identified in the following fields : chemical industry, building materials, fine glass and ceramics, paper, abrasives, transports and agrozootechny. The tuffs devoid of zeolites can be utilized in the industry of building materials and transports.

Taking into account the necessity of a valuable turning to account of the tuffs throughout the country, fields of utilization for each geological unit (Tab. 2) are proposed on the basis of the quantitative para-

TABLE 2

Possibilities of Turning to Account the Volcanic Tuffs of Romania

Geological unit	Fields of utilization							
	Industry of building materials			Industry of glass and ceramics	Industry of abrasives	Chemical industry	Transports (road beds)	Agrozootechny
	Natural stone	Light concretes	Trass cements					
Perșani Compartment	×	×	×	×		×	×	×
Tarcău Unit		×	×			×	×	×
Carpathian Foredeep		×	×		×		×	
Getic Depression		×	×		×		×	
Transylvanian Depression	0	×	0		0	0	×	0
Sylvanian Depression		×	×	0		0	×	×
Sighet Depression			×	×	×	×		×

0 fields of utilization indentified by technological studies;

x fields of utilization identified on the basis of qualitative parameters.

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Zones of Economic Prospect for the Zeolitic Volcanic Tuffs of Romania.

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meters and of the deposit conditions. These proposals are to be confirmed by the subsequent technological researches in order to identify new fields of utilization.

Zones of Economic Prospect for the Volcanic Tuffs of Romania

Taking into account the thickness of the useful rocks and of the overlying rocks, the possibilities of exploitation and the characteristic features of the volcanic tuffs — especially the zeolite content — 17 zones of prospect have been identified, being located in 6 geological units belonging to 8 districts of Romania (Fig.).

The numerous zones of prospect and the possibilities of turning to account of the volcanic tuffs of Romania lend them a remarkable economic importance.

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QUESTIONS

I. Kostov: 1. Is there any zoning in the distribution of clinoptilolite and the other zeolites, especially analcime, laumontite and mordenite ?

2. Is there any connection between zeolitization and tectonics and particularly between distribution of mordenite and fault systems ?

3. Could you tell something more specific about the genesis of zeolitic beds ?

Answers: 1. In the drillings of the Perșani Mountains it was noticed that the zones rich in clinoptilolite (over 50%) show a lenticular shape and thicknesses of 3-5 m. In the drillings of Aluniș and Orman in the Transylvanian Depression no zoning was observed in the distribution of zeolites.

2. Our researches did not reveal any connection between the zeolitization process and the tectonization degree of the volcanic tuffs.

3. As we have already shown, the researches carried out in the United States, Canada, Bulgaria, the U.S.S.R. and in other countries as well as our studies led to the conclusion that zeolites formed by the transformation of volcanic glass during diagenesis.

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L'ÉTUDE DES GRENATS DU MASSIF SYÉNITIQUE DE DITRĂU (ROUMANIE) [1]

PAR

GYULA JAKAB [2], SILVIA MÎNZATU [3]

Dans la bordure sud-est du massif syénitique de Ditrău, au contact avec les schistes épimétamorphiques de la série de Tulgheș, dans le secteur Aurora, apparaissent des syénites altérées, parfois à pseudomorphoses de liebnérite d'après la néphéline, contenant des grenats almandins-spessartiniques.

Dans la zone située entre les sources des ruisseaux Aurora et Csanod de même que dans la vallée Csanod, les microsyénites à biotite qui affleurent, contiennent des grenats andraditiques.

Les grenats almandins-spessartiniques

L'étude des grenats témoigne de la multitude des conditions génétiques, ainsi qu'une grande variété chimique. On admet généralement que les grenats pyralspitiques ont la genèse liée au métamorphisme régional, mais ils ont été signalés aussi dans les auréoles de métamorphisme thermal (H a r k e r, 1960 ; H s u, 1968).

Les syénites du prémier cas présentent dans la zone d'endocontact une couleur variable, partant du blanc sale jusqu'au gris et rose-pâle. La granulation n'est pas uniforme et on remarque fréquemment des schliers de cornéennes plus au moins digérées. De tels aspects ont été mentionnés pour la première fois dans la région, par I a n o v i c i (1932) et plus tard par C o d a r c e a et al. (1958) au nord du massif Ditrău.

Dans la proximité des schliers apparaissent parfois des grenats almandins-spessartiniques. Leur présence a été signalée en 1977, dans les travaux miniers récents du secteur Aurora, par G î n s a c (1977), et puis en 1978, A n a s t a s i u et C o n s t a n t i n e s c u, signalent les grenats pyralspitiques dans le ruisseau Pîrîul Turcului au nord du massif et dans le ruisseau Pîrîul Cetății, au sud.

Le contact sinueux entre les schliers et la syénite du secteur Aurora, est marqué par une zone fine, millimétrique, à caractère exclusivement feldspathique, suivie par une zone de concentration de bio-

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[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

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tite avec une disposition linéaire, en suggérant un front détâché de schliers biotitiques, qui a leur tour ont été injectées lit-par-lit du matériel syénitique. Vers l'intérieur de la masse syénitique se retrouvent les lamelles biotitiques, ayant le même caractère que celles des schliers.

Les grenats à teinte rouge foncé commencent à apparaître tout près des schliers, leurs dimensions variant entre 3 et 10 mm diamètre. On remarque que la syénite entourant les grenats, est dépourvue de biotite, mais enrichie par feldspath, avec une vague disposition radiale.

L'étude microscopique des lamelles minces met en évidence un grenat moins unitaire, fissuré, fragmenté, rempli de la biotite verte, de la chlorite et très rarement de la calcite.

Parfois, la pyrite idiomorphe est déposée au centre du grenat. Sa présence, de même que celle de la chlorite à caractère secondaire, nous indique une activité hydrothermale ultérieure, manifestée aussi par une minéralisation polymétallique.

Dans la pluspart des cas, les grenats sont entourés d'une croûte de biotite verte, plus largement cristallisée, présentant une structure décussate. C'est la chloritisation de cette biotite qui efface la structure décussate et modifie le contour du grenat. Dans des degrés de substitution avancés, au lieu du grenat s'installe un agrégat biotito-chloritique qui conserve parfois comme reliquats, des petits fragments de grenat frais, vitreux.

Dans certains lieux, le grenat est remplacé par un agrégat opacifié à l'intérieur, avec des aiguilles d'ilménite (sagénite). Des feuillets de biotite occupent les interstices du réseau sagénitique, mais la zone périphérique est une vraie couronne, représentée par une biotite de couleur brune intense avec un pléocroïsme faible.

L'analyse par diffraction X, indique la structure d'un type intermédiaire de grenat entre almandin et spessartine : $a° = 11{,}576$ Å[4] et $a° = 11{,}560$ Å[5] et d'autres, $a° = 11{,}520$ Å[4] et $a° = 11{,}541$ Å[4]. Ces valeurs sont très proches de celles données par Skinner (11,526 Å), Fleischer (11,518 Å) et Stokwell (11,516 Å) pour almandin pur et pour almandin à une petite tenneur en spessartine.

Il y a probablement aussi des grenats avec une composition spessartinique propre, mais les diffractogrammes ne l'ont pas surpris. Cette supposition est basée sur la présence de différents aspects d'altération des grenats du sécteur Aurora. Le fait que les uns sont remplacés par biotite + chlorite et les autres par un agrégat opacifié-ferrugineux, nous suggère l'argument pour l'existence d'une variation chimique entre les limites almandin et spessartine, avec la prédominance du type plus proche du spessartine dans le premier cas d'altération, ou plus proche de l'almandin dans le second.

L'investigation chimique met en évidence une grande ressemblance avec l'almandin-spessartine des cavités des rhyolites provennant d'Utah (Miyashiro, 1955 fide Deer et al., 1965). L'existence du composant $Fe_3^{2+}Mn_2^{3+}(SiO_4)_3$ ressort du calcul normatif du notre grenat, ce composant étant prédominant quantitativement. Le fait que le rayon de l'ion Mn^{3+} est un peu plus grand que le rayon du Al^{3+} explique

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aussi les dimensions plus grandes des paramètres de la cellule élémentaire du grenat d'Aurora par rapport aux données de la littérature (tab. 1).

TABLEAU 1

Oxydes	Almandin-Spessartine (Aurora) [1]	Almandin-Spessartine (Utah) [2]
SiO_2	35,12	36,38
TiO_2	0,20	0,27
Al_2O_3	9,70	19,42
Fe_2O_3	1,00	1,08
FeO	23,08	22,23
CaO	3,13	0,56
MgO	4,10	0,82
MnO	22,00	18,42
Na_2O	0,10	—
K_2O	0,60	—
H_2O^+	0,44	—
H_2O^-	0,40	0,10
CO_2	0,11	—

[1] analyste Sabliovschi, IGG-Iasi.
[2] analyste Miyashiro (1955) fide Deer et al., 1965.

Ainsi, pour définir ce type de grenat, nous allons utiliser dorénavant la dénomination de „grenat d'Aurora". La présence du CaO en corrélation avec une petite quantité de CO_2 est justifiée par l'existence, éventuellement, des impuretés de calcite pelliculaire.

Le rapport Mn/Fe est proche de 1/1. Le même rapport d'égalité a été indiqué par l'analyse non-dispersive RX de fluorescence [6] ce qui suggère une manière différente de genèse par rapport à celui précisé par Goldschmidt (1921) pour l'almandin-spessartine des roches métamorphiques où le rapport Mn/Fe est de 2/3. Hsu (1968) mentionne pour les grenats des cornéennes la relation $Mn > Fe \geqslant Mg$. Dans le cas du grenat d'Aurora, cette relation a un aspect différent, $Mn = Fe \geqslant Mg$.

La composition normative pour l'almandin-spessartine de l'Aurora est la suivante :

Pyrope — $Mg_3Al_2(SiO_4)_3 = 13,75$
Almandin — $Fe_3Al_2(SiO_4)_3 = 16,19$
Spessartine — $Mn_3Al_2(SiO_4)_3 = 23,75$
Andradite — $Ca_3Fe_2(SiO_4)_3 = 3,18$
Grossulaire — $Ca_3Al_2(SiO_4)_3 = 5,46$
Grenat d'Aurora — $Fe_3Mn_2(SiO_4)_3 = 37,73$.

Tenant compte de la composition chimique et normative, ainsi que de la relation Mn-Fe-Mg, l'origine du grenat analysé peut être considerée différente. Un aspect caractéristique du grenat d'Aurora,

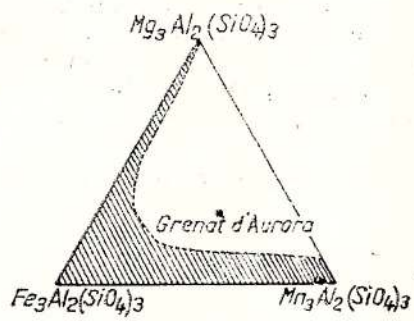
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est le pourcentage relativement élevé en MnO. Les analyses des grenats métamorphiques des séries de Rarău et de Rebra (Carpathes Orientales) ainsi que des Carpathes Méridionales (K a s p e r, 1973), indiquent un pourcentage maximum de 4,03% MnO, tandis que pour nos grenats, la teneur en MnO est de 22,0%. Seulement dans les grenats formés dans les gisements manganifères des Carpathes Orientales, ces valeurs sont dépassées. P o p a (1974) a trouvé dans les grenats de Dealul Rusului, deux valeurs du MnO, 29,29% et 33,34%.

Il faut mentionner que dans la série de Tulgheș appartenant au faciès des schistes verts, les grenats sont liés au niveau manganifère. Leur présence est due moins au degré de métamorphisme que notamment à la réserve du Mn dans les roches, qui leur favorise l'apparition. Dans cette idée, l'apparition des grenats dans les syénites du contact avec les cornéennes de la zone d'Aurora, peut être due au chimisme modifié de la roche par l'assimilation de certains schistes à teneur élevée de manganèse. De tels schistes manganifères sont connus dans l'horizon Tg_2 de la série de Tulgheș, horizon percé et probablement assimilé partiellement par le magma syénitique.

L'apparition en excès du manganèse à l'éxtremité orientale, ainsi que dans d'autres zones du massif alcalin de Ditrău, est confirmé aussi par le fond très élevé de cet élément de certaines roches et minéraux. Même dans la zone centrale du massif Ditrău (à Dealul Magaș), dans une enclave constituée de schistes quartzo-graphitiques manganifères, on a signalé des grenats (N. G a r b a ș e v s k i, information verbale).

L'affinité du grenat pour le manganèse étant si grande, toute la quantité présente dans la roche qui l'entoure, sera prise dans le grenat. L'analyse du feldspath de la proximité des grenats dans la syénite d'Aurora, confirme cette hypothèse par des valeurs très diminuées, de 45 ppm Mn. Nous supposons donc, basés sur les relations de terrain et les observations macro et microscopiques, de même que sur le chimisme, que le grenat d'Aurora est né dans le processus d'assimila-



Le diagramme triangulaire du champ de miscibilité des grenats pyralspitiques.

tion de certains schistes, partiellement manganifères, par le magma syénitique.

Les conditions totalement particulières qui ont conduit à la formation du grenat en discussion, sont suggérées encore par le diagramme de miscibilité des grenats pyralspitiques, où le grenat d'Aurora est projeté justement dans la zone de lacune de miscibilité (fig.).

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Les analyses spectrographiques [7] ainsi que celles par activation à neutrons [8] pour les éléments mineurs et les lanthanides (la moyenne de 3 analyses), indiquent l'accumulation de ceux-ci dans les grenats :

Ag	As	Co	Ga	Cu	Mn	Mo	Ni	Pb	Sn	V	Zn	In	Ba	Sr	Sc
0,1	20	1	15	85	>	14	20	30	33	140	1600	12	175	175	10

En faisant une comparaison entre ces valeurs et la moyenne de 26 almandins provenant des formations cristallines des Carpathes Orientales et Méridionales (K a s p e r, 1973), on observe que dans le grenat d'Aurora, les valeurs sont plus grandes en Ga,2 fois ; Cu,2-3 fois ; Ni,4 fois ; Pb,5-6 fois ; V,2,5 fois ; Ba,3,5 fois et Sr,35 fois. L'incorporation de ces éléments pendant la cristallisation du grenat indique une température très élevée de formation.

En ce qui concerne les éléments Cr, Co et Sc, ils sont déficitaires en comparaison avec les grenats métamorphiques. Si la moyenne du Sc, de 26 grenats métamorphiques (K a s p e r, 1973) est de 212 ppm, dans le grenat d'Aurora il est seulement de 18,2 ppm, à cause de la carence du Sc même dans le matériel d'origine. De toute façon la carence du Sc qui se manifeste aussi dans les feldspaths aux environs des grenats montre que l'affinité du grenat d'Aurora pour Sc a déterminé sa concentration en entier dans le grenat. Ainsi nous sommes en concordance avec E n g e l et E n g e l (1960) qui relie la présence du Sc au Mn.

À leur tour, Y, Zr et les lanthanides se trouvent dans le grenat d'Aurora à des valeurs assez élevées : Y = 355 ppm ; Zr = 500 ppm, ne permettant pas sa répartition à un type correspondant. La valeur d'Y est ainsi normale pour la spessartine ; R a n k a m a et S a h a m a (1950), donnent pour un tel type, 79-790 ppm Y, valeur qui est beaucoup inférieure à la valeur de la moyenne, de 1 073 ppm Y, donnée par M a k r î g h i n a et al. (1980) pour les grenats métamorphiques.

Dans le tableau 2, on donne pour comparaison, les valeurs des lanthanides de différents grenats et du feldspath qui entoure le grenat d'Aurora.

TABLEAU 2

Type \ TR_2O_3%	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu
1	23,05	40,63	4,04	2,96	0,16	1,1	0,45	25,47	2,15
2	2,34	3,81	60,60	0,90	0,30	1,0	11,71	16,70	2,64
3	2,16	6,94	4,01	3,40	0,30	2,0	27,00	47,50	6,64
4	7,30	28,10	28,90	11,20	1,60	1,40	9,90	9,90	1,70
5	34,30	37,10	11,90	10,30	0,20	0,20	3,50	2,20	0,30

1 = grenat d'Aurora — le massif Ditrău.
2 = almandin des schistes mésométamorphiques de la série de Rarău.
3 = almandin — spessartine, moyenne d'après M i n e e v (1968).
4 = andradite impur de la zone Csanod — le massif Ditrău.
5 = feldspath de la proximité du grenat d'Aurora.

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Le comportement des lanthanides du grenat d'Aurora est différent par rapport à celui des lanthanides des grenats métamorphiques de la série de Rarău ou de ceux notés dans la littérature (M i n e e v, 1968). La prédominance de TR dans les grenats du massif Ditrău reflète une association originaire, liée, dans notre cas, au magma syénitique (R a n k a m a et S a h a m a, 1950).

Les relations mutuelles d'abordance entre les lanthanides se présente ainsi :

$$1 = Ca > Yb > La \geqslant Nd > Sm > Lu > Tb > Dy > Eu$$

$$2 = Nd \geqslant Yb > Dy > Ce > Lu \geqslant La > Tb > Sm > Eu$$

$$3 = Yb > Dy \geqslant Ce \geqslant Lu > Nd > Sm > La \geqslant Tb > Eu$$

Ces relations nous indiquent la différence nette entre les trois grenats et dans chaque cas, une origine particulière. La teneur totale des lanthanides dans le grenat d'Aurora est beaucoup plus grande que dans les grenats métamorphiques de la série de Rarău, respectivement de 1 467,93 ppm TR, par raport à 341,5 ppm TR, fait explicable par l'abondance des lanthanides dans les roches syénitiques du massif Ditrău, dans lequel ils apparaissent.

Les grenats andraditiques

Les grenats andraditiques ont été reconnus aussi pour la prémière fois, dans les affleurements des roches microsyénitiques de la vallée Aurora, par l'un des auteurs (J a k a b, 1977).

Les dimensions des grenats sont presque constantes (0,5 mm ∅) et ils ont l'aspect de tâches noires avec un vague contour cristallographique, entourés par une masse plus richement feldspathique et en même temps plus appauvrie en minéraux mélanocrates que le reste de la roche (de même que dans le cas du grenat d'Aurora).

On ne remarque aucun aspect de contamination avec du matériel étranger schisteux ou calcaire, ces roches aux grenats andraditiques étant relativement homogènes.

L'étude microscopique met en évidence un aspect tout particulier du grenat. Celui-ci a une structure poïkilitique-spongieuse, avec une zone périphérique fortement entrecroisée de prismes plus larges de feldspath potassique intermédiaire entre orthose et microcline. Son aspect est nébuleux. Vers le centre, le feldspath devient de plus en plus fin et rare, de telle sorte qu'on peut observer l'andradite frais, finement fissuré, ayant une couleur variant de brun puissant au rouge. Les inclusions sont sous-millimètriques, noires, opaques, probablement magnétite (à titane ?). Tout près des fissures, l'andradite présente une faible anisotropie et des pellicules noires aussi magnétiques, des pellicules de chlorite et de calcite.

Les processus avancés d'altération ont conduit à une substitution totale avec un agrégat d'opacite à caractère ferrugineux.

À cause des caractères microscopiques signalés ci-dessus, une analyse chimique aurait été hasardée. Pourtant, sur une fraction fine au

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plus haut degré de pureté, on a executé une analyse RX qui indique l'andradite avec $a^\circ = 12{,}048$ Å[4], comparable aux valeurs données pour andradite : 12,059 Å (ASTM) et 12,048 Å (Skinner, 1956). Les observations se réfèrent à l'aspect extrêmement net et symétrique des réflexes, ce qui suggère un degré supérieur de rangement du réseau cristallin et probablement une origine différente par comparaison à l'almandin-spessartine d'Aurora [4].

L'investigation chimique pour TiO_2 a donné une teneur de 1,15% qui ne justifie pas suffisamment son appartenence à un type shorlomitique, mais pourrait représenter un mélanite. La teneur en TiO_2 est supérieure à celle du grenat d'Aurora (0,20% TiO_2).

Aussi la valeur de Zr est beaucoup plus supérieure (1 300 ppm), à celles pour l'almandin-spessartine d'Aurora (355 ppm), en constituant un argument de plus pour l'origine magmatique d'andradite.

Nous rappelons ainsi les valeurs des lanthanides, tout particulièrement celles de Ce (tab. 2). Quoique, d'habitude, les grenats magmatiques contiennent des lanthanides lourds, l'accumulation préférentielle des terres cériques dans l'andradite du massif Ditrău, est due au caractère nettement cérique des roches du massif en ensemble.

En conclusion, nous pouvons affirmer que les grenats étudies pour la première fois dans le massif alcalin de Ditrău, sont représentés par deux types à composition et genèse différentes.

L'almandin-spessartine de la zone Aurora est une variété dont le composant prédominant est $Fe_3Mn_2(SiO_4)_3$ et auquel on a attribué la dénomination de „grenat d'Aurora". Ce grenat a été formé dans la zone d'endocontact du massif syénitique de Ditrău, où les syénites à néphéline ont un caractère hybride, résulté de l'assimilation de certains schistes cristallins de la série de Tulgheș parmi lesquels, probablement, des schistes manganifères aussi. Les arguments d'ordre physique et chimique viennent à l'appui de leur origine métasomatique.

L'andradite a pourtant une origine magmatique primaire et représente le minéral accessoire dans les faciès micro et mélasyénitiques.

Les deux types de grenats ont subi des altérations intenses en manières différentes selon leur nature chimique. Ces transformations les attribuent aux mêmes phénomènes qui ont provoqué la transformation de la néphéline liebnérite et en partie la rougeur des feldspaths.

[4] Analyste T. Urcan, IGPSMS, București.
[5] Analyste F. Popescu, IGG, București.
[6] Analyste G. Grabari, IGG, București.
[7] Analyste O. Kalman, IPEG, Miercurea Ciuc.
[8] Analisées à IFIN, București.

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STRUKTURUNTERSUCHUNG DER OPALVARIETÄTEN DES KARPATENBECKENS [1]

VON

JÓZSEF TAKÁCS [2]

Obwohl der Opal seit langem gut bekannt und in der letzten Zeit auch mittels moderner Technik untersucht worden ist, gibt es immer noch kein Übereinstimmen über die innere Struktur dieses Minerals. Deswegen ist eine komplexe Untersuchung der Struktur des Opals berechtigt, um so mehr, als das Karpatenbecken reich and Opalvorkommen ist. Diese enthalten verschiedene Opalabarten, die unterschiedlicher Herkunft sind. Die vorliegenden Resultate werden grösstenteils anhand der aus den Eperjes-Tokajer Bergen stammenden Proben dargestellt. Die angewandten Methoden sind : Röntgendiffraktometrie, Polarisationsmikroskopie und Elektronenmikroskopie.

Mikrostruktur

Die Mikrostruktur der unterschiedlichen Opalvarietäten haben wir mit dem Röntgendiffraktometer Phillips Müller Mikro 111 und mit dem Elektronenmikroskop Jeol Jem 100 U untersucht. Die Variabilität der Ordnungs- bzw. Kristallisationsgrades ist aus der Abb. 1 zu sehen. Der diffuse Reflex bei etwa 4,1 Å des ersten Diffraktogrammes ist charakteristisch für röntgenamorphes SiO_2. Die Erhöhung des Kristallisationsgrades ist durch den bei 2,5 Å erscheinenden Reflex und die Aufspaltung des obengenannten Reflexes (4,3 und 4,1 Å) angedeutet. Weitere Erhöhung des Kristallisationsgrades wiederspiegelt sich in der grösseren Intensität, in der Abnahme der Halbwertsbreite und in der Erscheinung einiger flachen Reflexe bei kleinen d-Werten. Die Intensität dieser letzten folgt, sogar bei den bestkristallisierten aus Telkibánya stammenden Opalvarietäten die Erhöhung der anderen drei Reflexen nicht. Auf Grund der Diffraktogramme kann man einen allmählichen Übergang vom amorphen Zustand bis zu der gut kristallisierten Varietät feststellen.

[1] Vorgetragen am 12. Kongress der Karpato-Balkanischen Geologischen Assoziation, 8—13 September, 1981, Bukarest, Rumänien.

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Man sollte darauf aufmerksam gemacht werden, dass eine Seite eines bisher überdeckten Reflexes infolge der Abnahme der Halbwertsbreite der Reflexen bei 4,3 und 4,1 Å sichtbar wird, auf derer Deutung wir noch zurückkommen.

Auf Grund der großen Intensitäten der 4,1 und 4,3 Å — Reflexe werden die kristallinen Opalabarten in der internationalen Fachliteratur

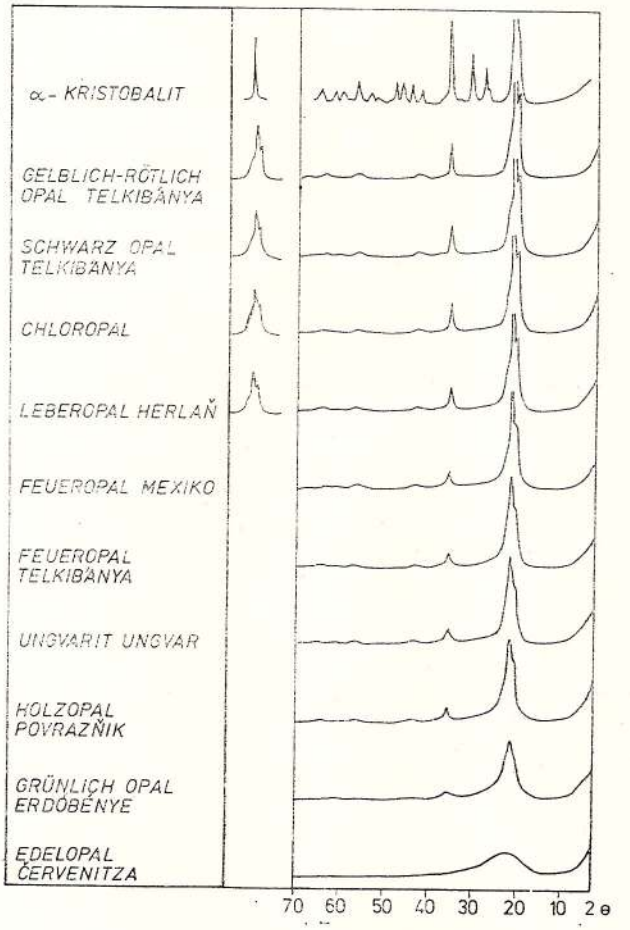


Abb. 1. — Röntgendiffraktogrammen verschiedener Opalvarietäten und des Tief-Kristobalits.

(seit der Arbeit F l ö r k e-s 1955), als eine Gemeinschaft von eindimensionell fehlgeordnetem Kristobalit und Tridimit gedeutet. Diese Deutung ist jetzt allgemein angenommen. Darauf weist die von J o n e s und S e g n i t in 1971 eingeführte Benennung „Opal-CT", d.h. „Opal Kristobalit-Tridimit-Type", während die amorphen Varietäten die Benennung „Opal-A" erhielten.

Jedoch lassen sich Einwände gegenüber dieser Identifizierung mit Kristobalit + Tridimit erheben. Im Vergleich mit den Opal-Aufnahmen weisen die der ASTM-Kartei entnommenen d-Werte und Intensitäten

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des Kristobalits und Tridimits kleine, aber nicht vernachlässigen Abweichungen auf. Es wurde auch das Diffraktogramm eines Kristobalits untersucht, der aus Silikagel durch Heizung an 1 200°C hergestellt wurde. Man kann folgendes feststellen :

— Der Hauptreflex (intensität 100) des Tief-Kristobalits befindet sich bei 4,05 Å, dergenige des Hoch-Kristobalits bei 4,15 Å, während der entsprechende reflex des Opals zwischen diesen beiden Werten anzutreffen ist.

— Der Reflex bei 4,3 Å stimmt mit dem Hauptreflex des Tief Tridimits nicht überein.

— Selbst bei dem bestkristallisierten Opal fehlen die charakteristischen Kristobalit reflexe bei 3,13, 2,84 Å sowie der bei 2,96 Å bekannte Reflex des Tridimits, um nur die wichtigsten Unterschiede zu erwähnen.

Eben deswegen wurden die Bezeichnungen „anomale, abnormale Kristobalite" eingeführt. Diese leere Bezeichnung führt aber um keinen Schritt näher zur reelen Erkenntnis der Struktur.

Das Opal Elektronendiffraktionsbild zeigt (Abb. 2), dass die Zonenachsen der 4,3 und 2,5 Å Intervalle identisch sind, während des Inter-

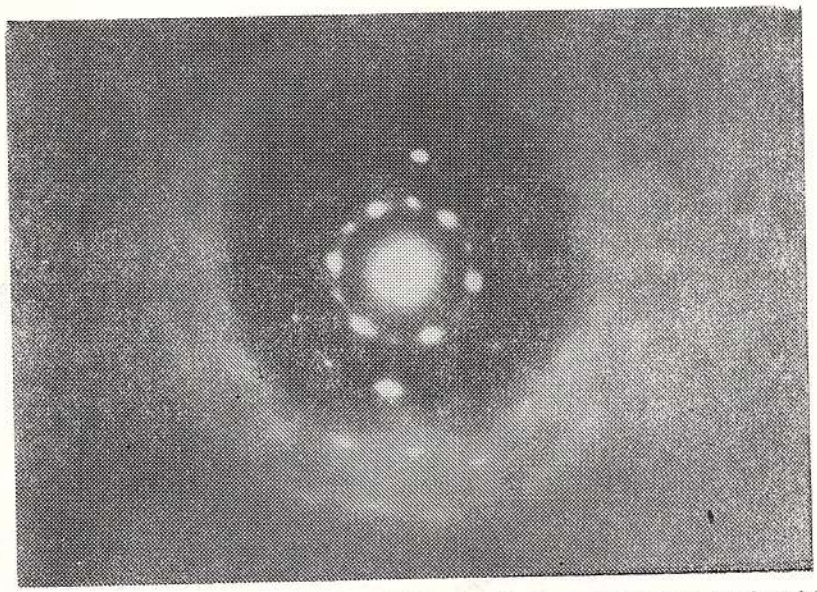


Abb. 2. — Elektronendiffraktionsbild des Opals aufgenomen senkrecht zu den Tetraederebenen.

vall von 4,1 Å in dieser Orientation gar nicht erscheint. Mit Inbetrachtnahme der zusammengehörenden Intensitätsmaxima ergibt sich aus dem Diffraktionsbild ein reguläres hexagonales Modell (Abb. 3).

Der Grund der Identifizierung mit dem Kristobalit und Tridimit besteht darin, dass diese auch von solchen Ebenen aufgebaut sind, die bei 4,05 bzw 4,07 Å auftreten, mit dem Unterschied, dass die Sequenz

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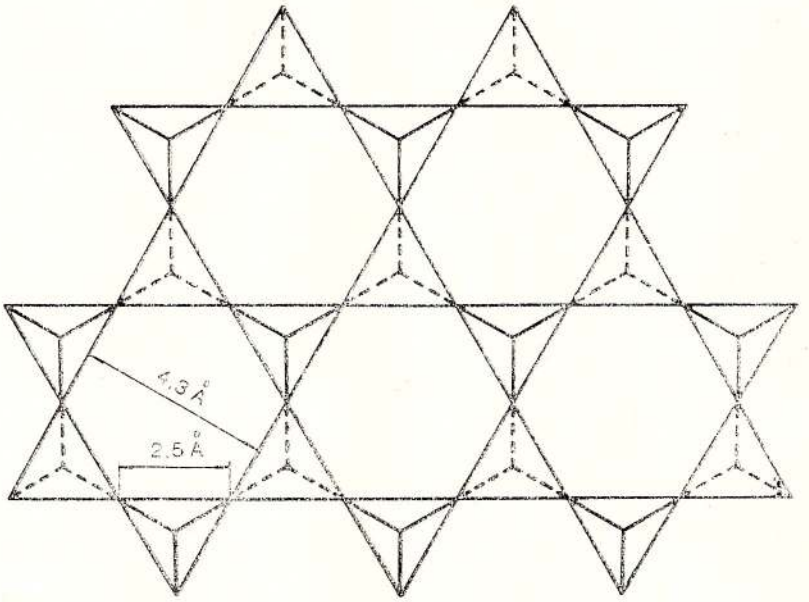


Abb. 3. — Modell der Opalstruktur senkrecht zu den Tetraederebenen.

ABCABC im ersten Fall, im zweiten Fall dagegen ABAB ist. Eine derartige reguläre Aufeinanderfolge gibt es im Falle des Opals überhaupt nicht. Die Struktur des Opals besteht aus einer irregulären Wechselfolge der erwähnten Ebenen.

Die nächsten Diffraktionsbilder (Abb. 4) zeigen eine im Vergleich zum vorangehenden viel beschränkte Kristallinität auf. Das Ausfallen

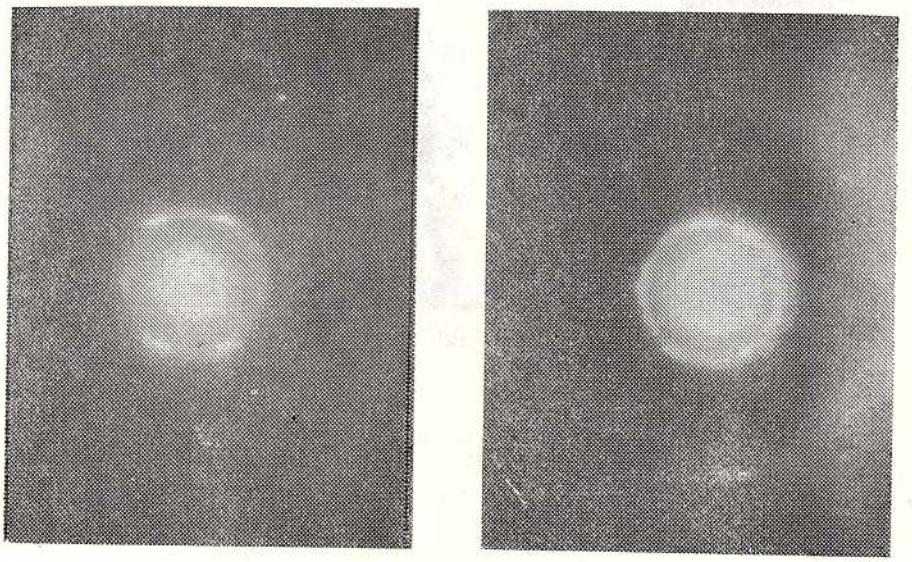


Abb. 4. — Elektronendiffraktionsbilder der Opale.

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der kleinen d-Werte und die Gestaltung der Reflexe weisen darauf hin, dass die Dimensionen der gut geordneten kristallinen Domänen abnehmen und zueinander unorientiert sind.

Die durch Elektronendiffraktion bewiesene Abnahme der Domänengrösse bietet eine Erklärung auch für den an den Röntgendiffraktogrammen erkennbaren allmählichen Übergang vom amorphen zum kristallinen Zustand. Nämlich haben wir in allen Fällen mit der oben vorgeführten, für das Opal charakteristischen tetraedrischen Anordnung zu tun, die bei den weniger kristallisierten auf kürzeren Distanzen, bei den gut kristallisierten auf längeren Distanzen verwirklicht wird. Die Distanz ist jedoch auch im letzteren Fall sehr gering, höchstens XOO Å.

Aus diesem Anlass möchten wir zum Abb. 1 zurückkommen, wo sich die 4,1 und 4,3 Å — Reflexe über einen diffusen Reflex überlappt. Diese Erscheinung wird als eine amorphe Phase gedeutet welche die kristalline Phase begleitet. Ohne weiteres kann sie aber auch mittels der kleinen Domänengrösse erklärt werden.

Die geringe Domänengrösse wird auch dadurch bestätigt, dass sich die gut kristallisierten Opale unter dem Polarisationsmikroskop meistenfalls als optisch isotrop erweisen. Schlecht kristallisierte Opale sedimentärer Herkunft können sich in einigen Bänden als optisch anisotrop verhalten. Unserer Meinung nach hängt diese optische Doppelbrechung des Opals nicht nur von der Kristallinität, sondern — vielleicht sogar vor allem — von der Orientation der einzelnen kristallinen Domänen ab. Da die Orientation wiederum von den Entstehungsbedingungen abhängig ist, ermöglicht die Rückschlüsse, ob man mit sedimentärem oder vulkanogenem Opal zu tun hat.

Sekundäre Struktur

Das Material des Opals bildet neben der Mikrostruktur auch eine sog. sekundäre Struktur, die aus morphologischen Elementen von 0,05—10 μm Grösse besteht und je nach der gegebenen Varietät verschiedene Formen aufweisen. Die sekundäre struktur wurde mit dem Elektronenmikroskop an mit HF geätzten Brechungsflächen, bzw. Karbon-Repliken studiert.

Die Untersuchungen wurden einerseits auf die Morphologie des Opalmaterials, andererseits auf die in ihnen anweisbaren lokalen Elemente gerichtet.

In der Morphologie des Opalmaterials betrifft die augenfälligste Veränderung die relative Lage der einzelnen Elemente. Die in dieser Hinsicht zu beobachtende Ordnungsbildung ist mit derjenigen der Tetraederebenen, aus denen die um mehrere Grössenordnungen feinere Mikrostruktur besteht nicht zu verwechseln.

In der sekundären Struktur der farbigen Opalvarietäten von Erdőbénye und Monok konnten keine symmetrischen Anordnungen festgestellt werden.

Im Milchopal von Monok (Abb. 5), der aus perlenschnurartig angeordneten Kügelchen besteht bilden die Fasern radiale Gruppierungen (im Bild um einen Punkt und um eine Linie).

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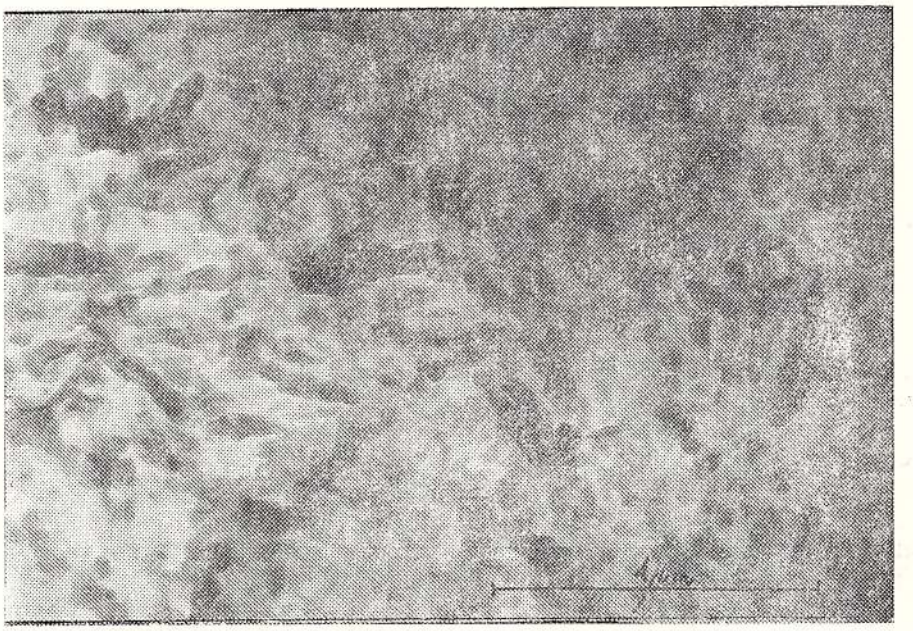


Abb. 5. — Lokale Ordnungen der sekundären Struktur im Milchopal von Monok.



Abb. 6. — Morphologie der geätzten Brechungsflächen des grünlich gefärbten Opals von Telkibánya.

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Diese Erscheinung ist noch ausgeprägter bei dem grünlich gefärbten Opal von Telkibánya (Abb. 6). Bei stärkerer Vergrösserung sieht man, dass die einzelnen Aggregate aus innen nicht-orientierten, aussen dagegen orientierten radialen Fasern bestehen (Abb. 7).

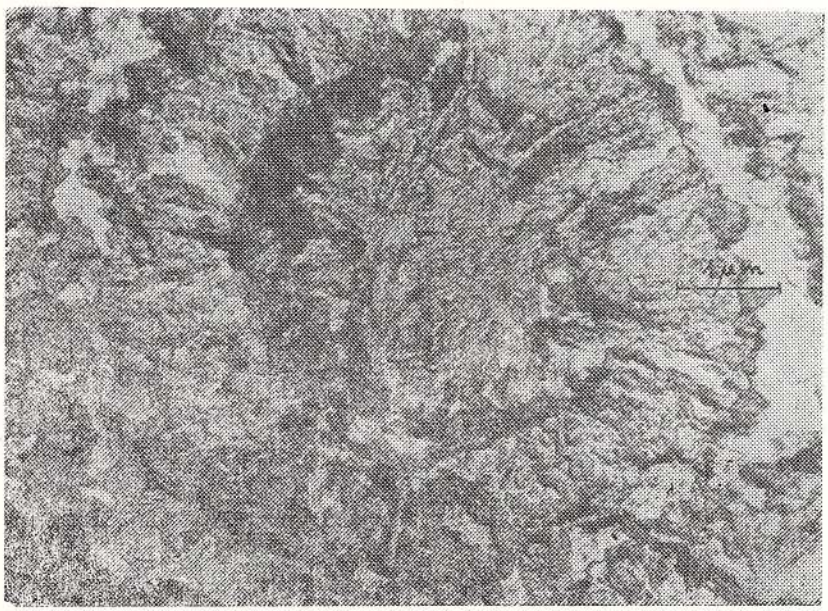


Abb. 7. — Zwei Teile mit verschiedener Orientierung im morphologischen Element des grünlich gefärbten Opals von Telkibánya.

Das, in einem Feueropal gefundenes Körnchen (Abb. 8), in welchem hexagonale Wachtumslinien einer Kristallstruktur zu erkennen sind (Abb. 9), kann wahrscheinlich als Produkt eines durch Temperatureinfluss bedingten Anordnungsvorganges betrachtet werden.

Eine andere Möglichkeit der Anordnung zeigen der Milchopal und der Edelopal. Im Milchopal (Abb. 10) befinden sich sphärische unorientierte Elemente ungefähr gleicher Grösse. Die gleichgearteten, in die Grössenordnung der Lichtwellenlänge fallenden morphologischen Elemente des Edelopals (Abb. 11) bilden eine im Raum sich periodisch wiederholende dreidimensionelle Gitterstruktur. Auch in Ungarn kommt Edelopal vor und wurde aus Telkibánya 1979 angekündet.

Die zwei eigentümlichen Lichterscheinungen — die Opaleszenz und die Opalisierung — die für den Opal so charakteristisch sind, lassen sich von der sekundären Struktur ableiten (S a n d e r s, 1968).

D ó d o n y und T a k á c s (manuskript eingereiht im Oktober 1980) haben gezeigt, dass die Gestalt des Edelopals von Červenica (Abb. 12) sowie die Anordnung-Symmetrie von denen des australischen Edelopals abweichen. Auf diesem Grunde wurden die Unterschiede im Farbenspiel gedeutet. Auf Grund unserer Untersuchungen, ist die Struktur des Edelopals von Telkibánya der des australischen Edelopals ähnlich.

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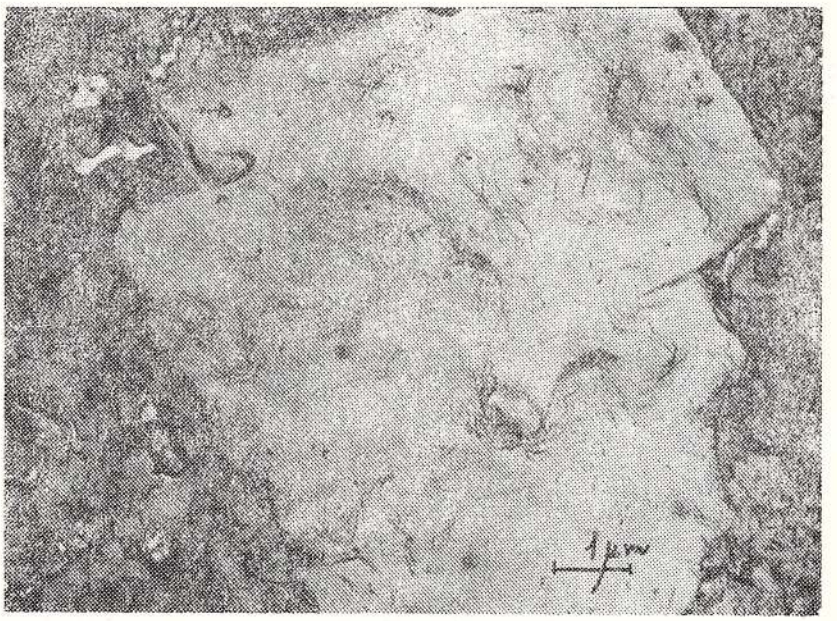


Abb. 8. — Kristallines Körnchen im Feueropal von Telkibánya.



Abb. 9. — Wachstumslinie des kristallinen Körnchens im Feueropal von Telkibánya.

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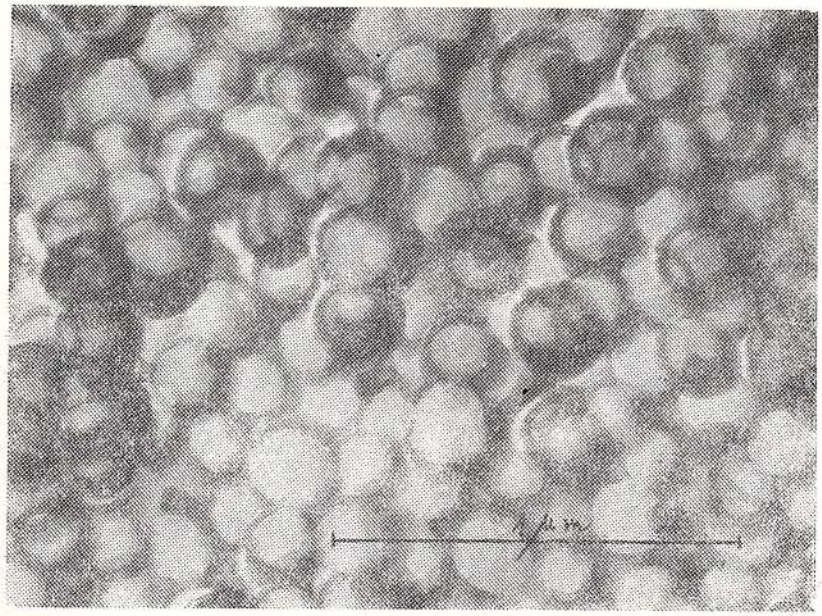


Abb. 10. — Morphologie der geätzten Brechungsflächen des Milchopals von Červenica.

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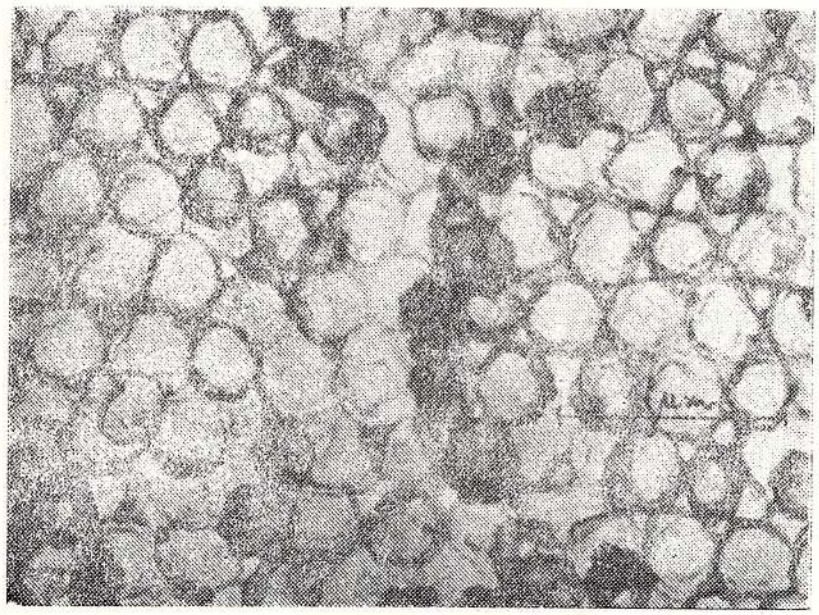


Abb. 11. — Morphologie der geätzten Brechungsflächen des Edelopals von Australien.

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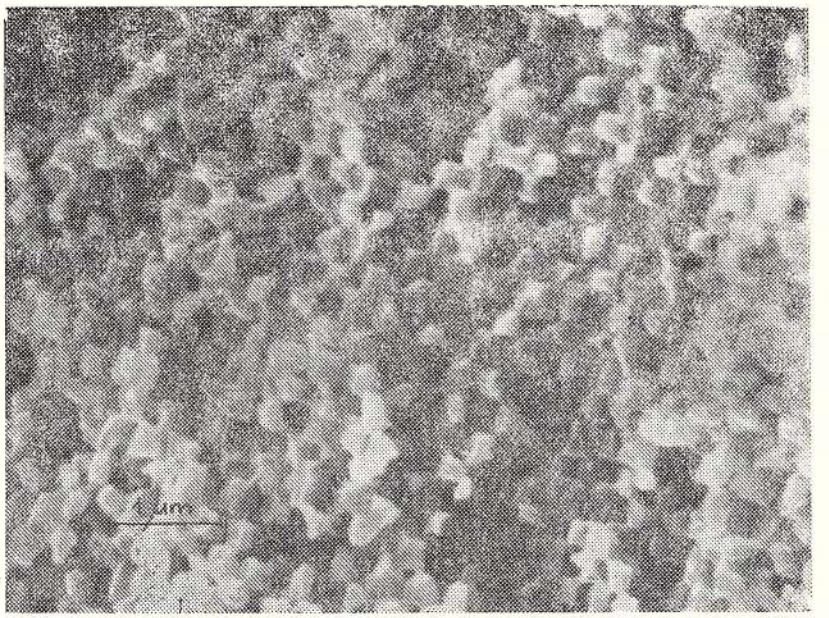


Abb. 12. — Morphologie der geätzten Brechungsflächen des Edelopals von Červenica (SEM-sche Aufnahme).

Wenn man die Anordnung der morphologischen Elemente mit der Kristallinität der Mikrostruktur vergleicht, kann kein Zusammenhang festgestellt werden. Zum Beispiel sind der eben erwähnte ungeordnete Milchopal und der gut geordnete Edelopal von Červenica röntgenamorph.

Lokale Elemente

Um die Genesis aufzuklären, erwiesen sich — unserer Meinung nach — die lokalen Elemente (fremde Phasen) die in der sekundären Struktur vorzufinden sind, besonders geeignet.

In einem Opal von Erdőbénye wurde ein Bruchstück eines Diatoms, entdeckt (Abb. 13). Das stimmt mit dem Süsswasser- bis Brackwasserablagerungscharakter der Schichtfolge von Erdőbény überein. Ein küstennahes Milieu wird angedeutet durch die Anwesenheit von Phytolitharia (mündliche Mitteilung von Frau Dr. M. Hajós) (Abb. 14). Die zerstreut vorkommenden, konzentrisch-sphärischen Hämatitaggregate (Abb. 15) erklären die bräunlich-rote Färbung dieser Varietät.

Ausserdem charakterisieren den Opal sedimentärer Herkunft die unter dem Polarisationsmikroskop gut zu beobachtenden Bänden, die mit der ehemaligen Schichtung parallel angeordnet sind, sowie die dazu senkrecht angeordneten Fasern.

Das Material der von postvulkanischer Heissquellentätigkeit erzeugten Höhlenausfüllung in Monok enthielt eingewachsene Kristo-

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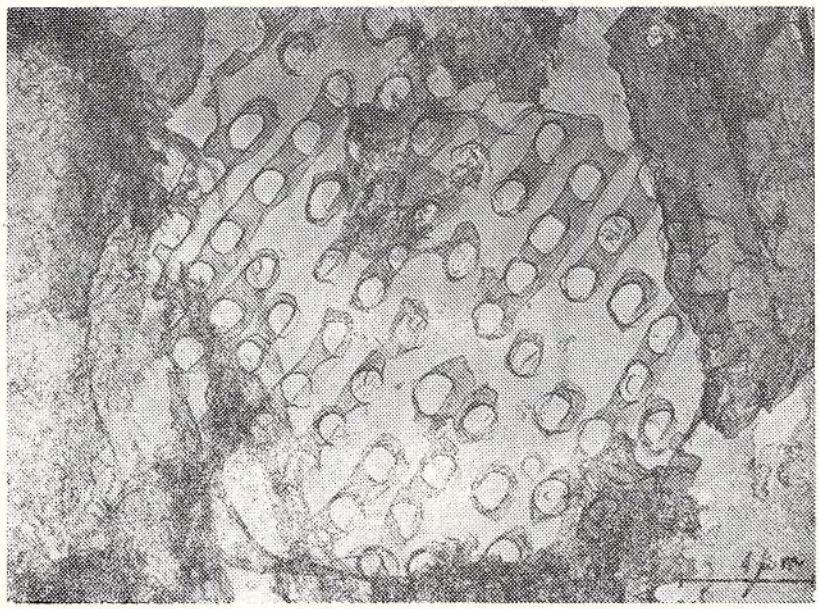


Abb. 13. — Bruchstück eines Diatoms in grünlichen Opal von Erdőbénye.

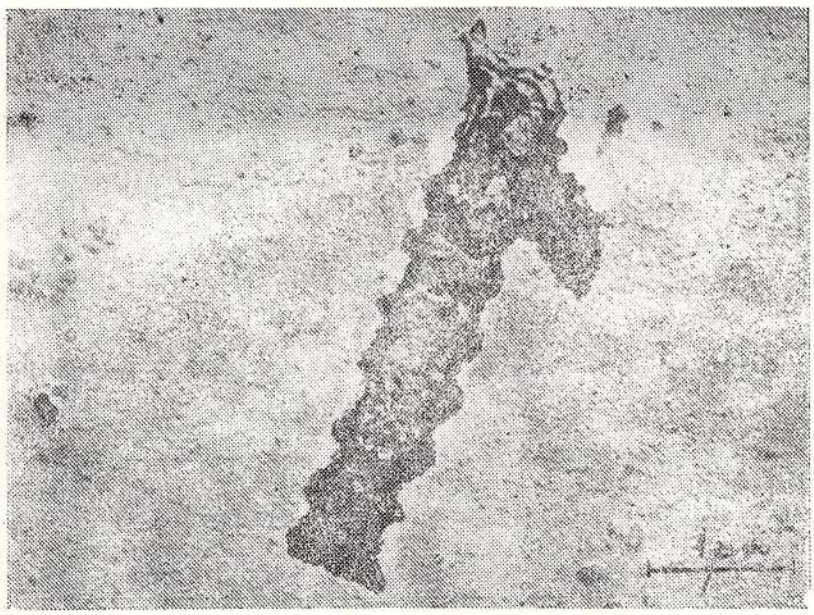


Abb. 14. — Phytoliharia im Opal von Erdőbénye.

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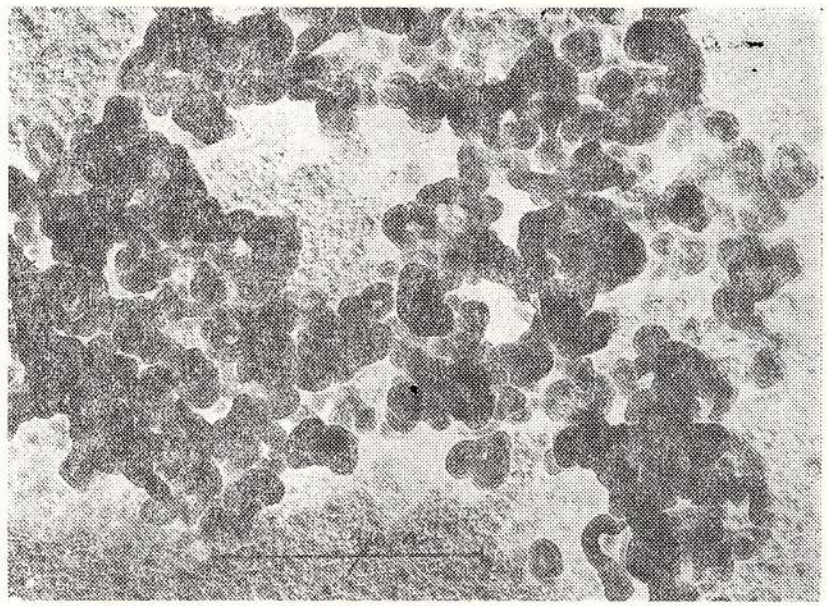


Abb. 15. — Hämatitaggregate im bräunlich-roten Opal von Erdőbénye.

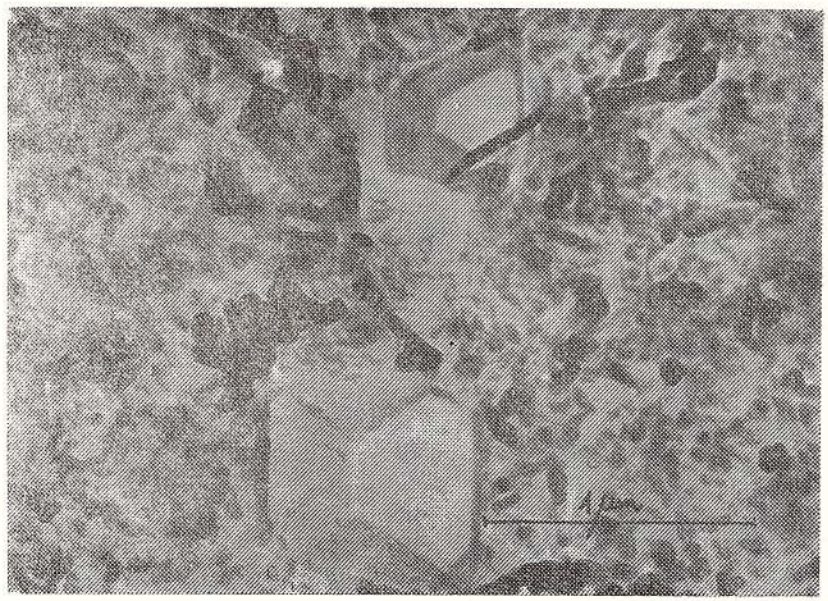


Abb. 16. — Eingewachsene Kristobalitkristalle im Opal von Monok.

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balitkristalle (Abb. 16). In den aus Opal bestehenden Gangausfüllungen kommen öfters Glimmerfragmente und besonders Hämatitaggregate vor, die das Material in Opakrot verfärben. Die hier zu findenden Opalvarietäten weisen viele gemeinsame Züge mit denen von Herlań auf.

Die transparenten Varietäten von Telkibánya, die unter subvulkanischen Bedingungen entstanden sind, werden als die best kristallisierten betrachtet. In diesen konnten wir keine fremde, verunreinigende Phase finden.

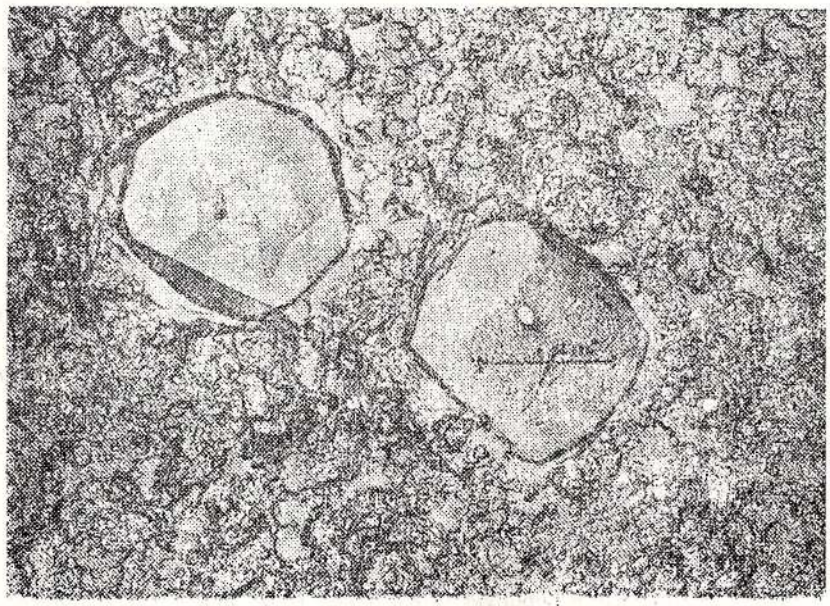


Abb. 17. — Eingewachsene Tridimitkristalle im Glasopal von Červenica.

Die Milch- und Edelopale, die Aushöhlungen und Spalten im Vorkommen von Červenica ausfüllen, enthalten öfters — dem Monoker Opal ähnlich — eingewachsene Kristobalitkristalle. In dem vollkommen durchsichtigen Glasopal (bläulich gefärbt) kommen dagegen Tridimitkristalle vor (Abb. 17), die aber in anderen Vorkommen nicht wiederzufinden waren. Das Material der Opale von Červenica ist dabei Röntgenamorph.

Zusammenfassung

Zum Schluss könnten wir die Ergebnisse der Strukturuntersuchung des Opals wie folgt zusammengefasst werden :

— Die Mikrostruktur des Opals besteht aus von hexagonal zusammengefügten Tetraedern gebildeten Ebenen. In der Reihenfolge der Schichten kann keine Regelmässigkeit erkannt werden. Demzufolge

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kann diese Struktur nicht als eine Gemeinschaft von Kristobalit und Tridimit gedeutet werden.

— Die kristalline Ordnung des Opals besteht aus nebeneinander angeordneten Domänen von geringer Grösse.

— Der Übergang von den amorphen bis zu den gut kristallisierten Varietäten ist allmählich und kann als Änderung der Dimension der kristallinen Ordnung gedeutet werden.

— In der Grössenordnung von 0,05 bis 10 μm entsteht eine sekundäre Struktur. Je nach der Varietät und dem Vorkommen weisen die morphologischen Elemente und ihre Anordnung beträchtliche Unterschiede auf.

— Die lokalen Elemente des Opals sind gute Anzeiger der Entstehungsbedingungen. Dementsprechend ermöglicht ihre Untersuchung eine Verfeinerung des genetischen Bildes.

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THE GEOCHEMISTRY AND GENESIS OF THE VARISCAN GRANITES OF THE WEST CARPATHIANS [1]

BY

D. HOVORKA [2], J. SPIŠIAK [3]

Introduction

The plutonic rocks of the granite clan form the backbone of the core mountains and the Veporide zones of Slovenské rudohorie Mts. In the course of the last decades only a few works have attempted to clarify the genesis of the massifs (Kamenický, 1968, in Maheľ, Buday, 1968; Hovorka, 1980, in print). Within the individual bodies several essential petrographic types have been distinguished. On the basis of space relationship and mineral composition, Hovorka (in print) distinguished and presented the basic geochemical characteristics and genetic conclusions concerning 4 granitoid types of the West Carpathians Variscan "level" namely :

I — medium-grained biotite (locally with accessory to minor portion of amphibole granodiorites) tonalites (Vysoké Tatry Mts. type and its equivalents) ;

II — two-mica, frequently porphyric granodiorites ;

III — leucocratic facies of granodiorite massifs (leucogranodiorites with local facies of albite, and/or alaskite granites) ;

IV — porphyric granodiorites/granites with pink K-feldspars ("Prašivá" type and its equivalents).

The main characteristics of granites

No definite evidences for distinguishing several phases of magmatic activity within the Variscan orogen, have as yet existed. The present radiologic data suggesting the intrusions to have existed for 220-380 m.y., may also as well reflect the varied grade of alpine metamorphic recrystallization, and/or the alpine overheating. Field obser-

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vations indicating gradual transitions of the main type (type I) into the marginal ones (porphyric, and at the same time, more leucocratic) can be noticed.

I. Medium-grained biotite granodiorites/tonalites (locally with accessory to minor portion of amphiboles) are considered to be the most widespread type. They are designated according to localities (Vysoké Tatry Mts type, Smrekovica type, Sihla type and other types). In the case the whole plutonic massifs are preserved, that type always

TABLE 1

Chemical Composition of West Carpathian Variscan Main Type Granitoides

	I		II		III		IV	
	$\bar{x}$ (%)	s	$\bar{x}$ (%)	s	$\bar{x}$ (%)	s	$\bar{x}$ (%)	s
SiO_2	67,34	2.66	71.33	1,78	73.37	2,13	70,32	2,23
TiO_2	0,53	0,27	0,29	0.16	0,19	0,21	0,36	0,19
Al_2O_3	15,78	1,39	14,59	1.39	14,14	1,49	14,79	1,13
Fe_2O_3	1,47	0,89	1.31	0,73	0,99	0,58	1.47	0,87
FeO	2,10	0.86	1,27	0,56	0,67	0,46	1,43	0,68
MnO	0,08	0,08	0,06	0,06	0,05	0,05	0,06	0,06
MgO	1,58	0,66	1,00	0,65	0,79	0,81	1,15	0,72
CaO	3,12	0,87	1,88	0,82	1,47	0,91	2,13	0,77
Na_2O	4,01	0,89	3,65	0,71	3,69	1,36	3,61	0,65
K_2O	2,47	1,15	3,52	1,22	3,52	1,27	3,55	0,84
P_2O_5	0,26	0,11	0,16	0,08	0,14	0,09	0,15	0,08
n =	171		86		65		100	
trace elements (g) g^{-6} :								
B	13		14		20		21	
Ba	1033		533		673		780	
Co	9		3		3		3	
Cr	17		11		8		17	
Cu	7		5		6		7	
Ni	8		4		3		5	
Sc	9		5		3		4	
Sn	5		5		5		5	
Sr	664		231		208		428	
V	69		13		12		37	
Y	22		16		8		10	
Zr	182		104		73		111	
Pb	18		18		—		—	
n =	77		67		8		14	

$\bar{x}$ — arithmetic mean; s — standard deviation.

Given oxide contents of main elements according to D. Hovorka's paper (in print). Trace elements from B. Cambel, J. Medveď (1981, tab. 7, p. 18) — adapted. Value in the I. type corresponds to weighted arithmetic mean of quartz diorite and granodiorite groups. Group II corresponds to granites; trace elements of group III are equal to leucogranites; group IV shows values given for "autometamorphic" granites.

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appears to be the central part of the massif. In the marginal-trend the bodies pass into the next types. For biotite granodiorites/tonalites the following two features are typical : the homogeneity of both granularity and mineral composition in certain mountains and the transition into hybrid facies towards the marginal parts of the other massifs.

II. Two-mica, frequently porphyric granodiorites form the marginal fringes of e.g. the massif of Slovenské rudohorie Mts in its southern part. As a matter of fact, the whole Bratislava Massif of Malé Karpaty Mts is of the same character.

III. A typical development of leucocratic differentiates of granodiorite massifs can be seen in the NW marginal zone of the Tatry massif. In some mountains the presence of garnets coexisting with other silicate minerals of the rock is observed (Malá Magura Mts). The rock types of this group are fine-up to coarse-grained.

IV. Porphyric granodiorites/granites with pink K-feldspars (Prašivá type) are known to occur in several core mountains. In contrast to older conceptions of kalium metasomatosis as the most important process in the origin of these types, new ideas have appeared in recent years claiming their late-magmatic development (H o v o r k a, 1979, in H o v o r k a, 1980).

Discussion

The "complete" development (locally preserved) of the granite series Variscan massifs of the core mountains and Slovenské rudohorie Mts indicates their isolated development in the past. This concept and arguments supporting the theory proposed recently (H o v o r k a, 1980) are consistent with the fact that magmas of granite massifs in pre-Variscan formed continental crust did not from the continuous "layer". On the contrary, they originated by means of anatectic processes in places of elevated heat flow. Granite melts *s.l.* penetrated (protruded) into higher levels of the continental crust after the culmination of the Variscan orogenic cycle (late-kinematic to post-kinematic massifs) in places of tectonic predisposition of pre-Variscan substratum.

For the Variscan granite massifs and their tectonic-metamorphic derivatives the constant presence of tourmaline, as the main boron concentrator, is typical and it is of regional extent. Regionally widespread tourmaline and consequently, the role of boron as the most important volatile of granite melts, enable to consider the Variscan massifs of the West Carpathians as belonging to the "boron province" of the anatectic crustal massifs (H o v o r k a, 1980).

Within the distinguished granite groups of the West Carpathian Variscan (types I-IV), REE contents tend to decrease depending on the increasing acidity (SiO_2) of the rocks (Tab. 1, 2). Since the boundaries between the distinguished types do not appear as the strong ones, the differences between REE contents are not great, yet they can be dis-

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TABLE 2

Rare Earth Elements in the West Carpathian Variscan Granites

Type	No	La	Ce	Nd	Sm	Eu	Gd	Tb	Tm	Yb	Lu	REE	Eu/Eu *	La/Yb
I	HG— 3	25	68	33	5,00	1,50	5,50	0,60	0,10	0,75	0,10	139,55	0,87	33
	HG— 5	33	83	46	6,00	1,80	7,00	0,65	0,20	1,45	0,14	179,24	0,85	23
	HG— 9	51	120	62	8,90	1,80	—	2,20	—	3,00	0,30	249,2	0,53	17
	HG—15	38	83	45	6,10	1,26	10,00	0,67	0,34	2,10	0,26	186,73	0,63	18
II	HG—16	30	67	33	4,10	1,11	10,00	0,27	0,07	0,88	0,12	146,55	0,87	34
	HG— 8	38	94	44	7,60	1,28	3,30	0,60	0,20	0,95	0,10	190,03	0,56	40
III	HG— 6	25	59	33	5,70	0,75	4,00	0,84	0,56	1,14	0,12	130,11	0,46	22
	HG— 7	13	29	18	2,70	0,78	3,20	0,22	0,09	0,49	0,05	67,53	0,81	27
IV	HG— 4	29	73	38	7,00	1,30	—	1,20	—	1,00	—	150,50	0,53	29
	HG—10	28	65	19	4,20	1,11	4,00	0,61	0,15	0,94	0,11	123,12	0,82	30
	HG—11	20	47	23	3,80	0,90	—	0,24	0,13	0,95	0,09	96,11	0,77	21
	HG—14	32	77	36	6,40	0,89	5,00	0,71	0,18	1,47	0,17	159,82	0,47	22

Eu/Eu = Observed Eu-value divided by value from linear interpolation between Sm and Gd.

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tinguished. The normalized pattern of REE contents in the West Carpathians Variscan magmatites of the granite clan (Fig. 1) is identical with that of the granite clan magmatites of calc-alkaline type (E m m e r m a n et al., 1975 ; P r i c e, T a y l o r, 1977 and others). Marked LREE enrichment and at the same time, relatively weak HREE enrichment can be noticed in the mentioned types. For all distinguished types negative Eu anomaly is characteristic. Considering the petrographic investigation and analyses of the main oxide contents, taking into account REE contents in basic silicate and accessory minerals reported

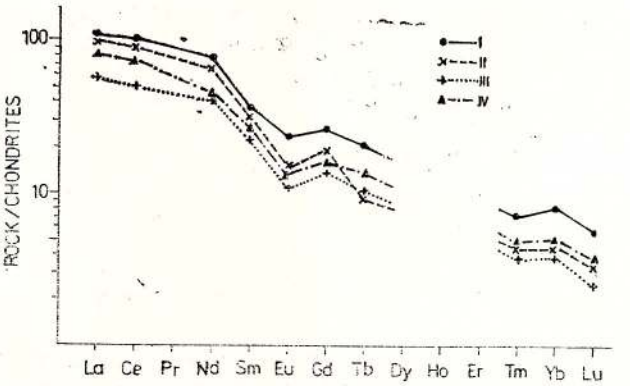


Fig. 1. — Chondrite normalized pattern of Variscan Western Carpathians granites. I-IV = main rock types characterized in the text.

elsewhere, as well as regarding the distribution character of REE, the genesis of the West Carpathian Variscan granites may be the consequence of the following processes :

a) partial melting of metamorphic supercrustal series in the anatexis zone. The melt outcome was relatively high in relation to the whole rock body ;

b) the consequence of basic rock anatexy, mainly of garnet amphibolites, eclogites and other similar types.

Although the first model concerning the origin of granite melts was regarded as the decisive process in the origin of crustal melts, yet, marked negative Eu anomaly in most of the granite rocks developed in the continental type crust, makes the mentioned model as whole, a complicated one. The given model could have taken place only in fraction crystallization of feldspars (which carry the substantial part of Eu and in the separation (from on-developing) melt. The presence of such processes is confirmed by the occurrence of at least 2 generations of certain accessory minerals typical for metapsammites and basic metavolcanics. At the same time, relicts of metamorphites with high portions mainly of biotite to glimmerite nests, and/or the presence of 2 biotite generations provide the evidence for the anatectic melts to have originated mostly from gneiss type rocks. On the other hand, in the case of the Variscan massif of the West Carpathians granites, there does not exist any facies which could correspond to facies isolated in the depth and consolidated there, consisting mostly of feldspars, and/or there do not occur xenoliths of anchimonomineral feldspar rocks,

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as in the case of the Mesozoic plutonites from Nigeria (B o w d e n et al., 1979).

Viewing the mentioned observations and present data on REE contents and distribution in granitoids of the West Carpathians Variscan, their genesis may be the following : the melt originated by the partial anatexy of the sedimentary-volcanic complex, in which, apart from the prevailing metasediments of clastic-clay type, a substantial portion was occupied by metavolcanics of tholeiitic type. The presence of the latter ones in the zone of anatexy is confirmed by occurrences of anatectically variously intensively transformed metabasites of meladiorite to hornblendite types, which occur in only partly homogenized (mostly marginal) parts of the granite massifs.

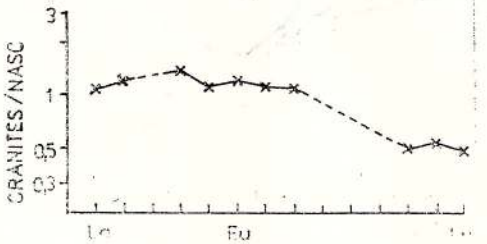


Fig. 2. — NASC normalized Variscan Western Carpathians granitoid main rock type (type I of the text).

Figure 2 shows the comparison of REE distribution in the Variscan granites of the West Carpathians with NASC (North American Shale — H a s k i n et al., 1968). The normalized REE distribution pattern in NASC is presented as the prototype of REE distribution pattern in developed continental type crust. The flat pattern with LREE values around 1 is the result of the mentioned comparison. In the case of HREE declining trend of normalized pattern can be noticed, which indicates the HREE depletion of the rocks under consideration in comparison with NASC contents. A normalized pattern like that confirms also the original material to have melted partially (e.g. P r i d e, M u e c k e, 1980), while refractory accessories (garnet, apatite, and/or pyroxenes which show high HREE concentrations) remained as restites in the anatexy zone. The REE normalized pattern in the basic (I) and Prašivá (IV) types are parallel (Fig. 1). Negative Eu anomaly is a feature characteristic of both types. Alkaline metals migrating in the autometasomatic or hydrothermal alteration of granitoids are accompanied by REE (B o w d e n et al., 1979). When applying this observation to the genesis of IV type West Carpathians granites, it is quite clear that these types have not originated by processes of extensive alkaline (mostly potassium) metasomatosis, since in such case the normalized pattern of REE distribution in the IVth type would have been considerable higher than in the Ist type. The association of Eu^{2+} with alkaline metals in case of potassium metasomatosis would surely result in stronger Eu anomaly during the origin of these rocks.

Conclusions

The Variscan granitoids of the West Carpathians from the province of anatectic massifs originated within the continental crust. In

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pre-Variscan developed continental crust the anatectic processes took place only in zones of elevated heat flow — the newly formed melts did not form the continuous "layer". The processes of fraction melting and fraction crystallization caused the origin of poorly differentiated rock suites. Biotite is the main dark mineral.

If the massifs are completely preserved, the following rock filling can be generalized : the central part is built by medium-grained biotite granodiorites/tonalites. Towards the margins (laterally and vertically) they pass into two-mica, frequently porphyric granodiorites. The marginal zone is formed by porphyric types with pink K-feldspars (Prašivá type), or by leucocratic granodiorites/granites. The chondrite normalized pattern of REE contents suggests the granite melt to have originated from metamorphosed supercrustal sequences of metaclastic type and from metapelites with traces of basic metavolcanics of tholeiitic type. It can be said that the negative Eu anomaly is characteristic of distinguished basic petrographic types. HREE depletion in comparison with NASC indicates the existence of partial anatexy, whilst in the zone of anatexy there concentrated minerals with high HREE contents. The normalized REE pattern does not enable us to assume wide-ranging alkaline-metasomatic processes to have taken part in the origin of porphyric type Variscan granitoids.

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TiO_2 DISTRIBUTION IN VOLCANIC ROCKS OF THE EAST CARPATHIANS (ȚIBLEȘ-BÎRGĂU SUBVOLCANIC ZONE AND CĂLIMANI-PERȘANI VOLCANIC ZONE) [1]

BY

SERGIU PELTZ [2], MARGARETA PELTZ [2]

Introduction

In modern petrological studies TiO_2 is used as a superior discriminant of other oxides constituting the eruptive rocks, as petrochemical indicator being comparable with SiO_2. Nowadays, TiO_2, besides other oxides, is considered a criterion for the chemical classification of the volcanic rocks (Rittmann, Pichler, 1972; Pichler, Stengelin, 1977). More and more researchers use the synthetical parameter $\tau = Al_2O_3 - Na_2O/TiO_2$ (Gottini, 1968) correlated with Rittmann serial index $\sigma = (K_2O + Na_2O)^2/SiO_2$-43 in order to test the bimodal character of the volcanism, to define the parental magmas. These fundamental implications — petrochemical and petrogenetical — of the TiO_2 utilization are due to the TiO_2 geochemical peculiarities, its behaviour during the magmatic processes. It is known that titanium, strong lithophile cation belonging to the iron group, had a low mobility. Titanium separates from the magma in the early crystallization stage and concentrates in ferromagnesian silicates. Titanium presence in certain percentages in the eruptive rocks is closely connected with their genesis. Subsequent processes do not modify sensitively the Ti values in the magmatic rock because Ti is an element with a high field strength.

In the last decade the concerns on the geochemistry of the Neogene volcanics in the East Carpathians have been intensified. An important bulk of data have been accumulated, which refer equally to the major and the trace elements. During investigations carried out for the recovery in the petrologic studies of the data, our attention

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has been called to the TiO_2 utilization for the chemical characterization of different petrotypes, their classification and for the petrogenetic clearings up. Some of the results obtained will be presented further on. They have in view a large and significant eruptive area in the East Carpathians, lying between the Ţibleş Massif, in the north, and the Perşani Mts, in the south. This zone comprises all the products of the calc-alkali series rhyolite-dacite-andesite-basaltic andesite (andesites prevail), generated during the Pannonian-Pliocene by subduction processes and accumulated in various facies (mostly volcanic, subvolcanic subordinately). The products of the intraplate Quaternary basaltic volcanism in the southernmost part of the zone are added too.

Almost 200 chemical analyses have been used, published by P e l t z et al., 1972 a, 1972 b, 1973. Their distribution on geographic units is, as follows : a) 155, Călimani-Gurghiu-Harghita volcanic zone ; b) 40, Ţibleş-Bîrgău subvolcanic zones ; c) 6, Perşani volcanic zone.

Geological and Petrological Setting

Over the territory of Romania, within the East Carpathians area, the magmatites generated by subduction processes have displayed predominantly volcanic forms, and in other regions exclusively subvolcanic forms. The region where the subvolcanic bodies are located is to be found between two zones within which a prevailing extrusive volcanic activity has taken place, namely in the Oaş-Gutîi Zone, in the north-western part, and in the Călimani-Gurghiu-Harghita Zone, in the southern part. It deals not only with a geographical situation but also with the coincidence related to subvolcanic peculiar manifestation form of the volcanic activity determined by a structural regime proper to this region. Considering the geographical position of the subvolcanic bodies as the main criterion the latter may be grouped, as follows : a) Toroiaga, b) Ţibleş-Hudin, c) Rodna-North Bîrgău, d) South Bîrgău. The eruption has been assigned to the Pannonian.

Within the calc-alkali magmatites, pyroxene-hornblende andesites and diorites are prevailing. Generally an agreement between the petrographical-mineralogical diagnosis of acid rocks and their chemical characters may be observed.

Under the peculiar geotectonical conditions of the northern area of the Central-East Carpathians, it may be admitted that the magmas generated by subduction processes had accumulated in several magmatic chambers, and at various depth in the earth's crust. It is most likely that the former have been supplied by a main basin, the host of an andesitic magma.

The Călimani-Harghita volcanic area represents a maximum development region of the young volcanism inside the Carpathian Orogen, extending over a surface of about 6,400 sq.km. Over the whole territory the andesitic volcanism was prevailingly displayed. Varied forms of manifestation, namely effusive, explosive and subordinately intru-

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sive, are recognized. Two components may be distinguished in the structure of the edifice, each one consisting of products of volcanism from one stage under special lithogenetic conditions: the volcano-sedimentary character of the lower compartment and the strato-volcanic one of the upper compartment.

Pyroxene andesites and pyroxene-hornblende andesites display a regional extension. The dacites crop out in the east of the Călimani Mts and the basaltic andesites in the south of this region. In the south of the Harghita Mts hornblende-biotite $\pm$ quartz andesites are widespread. Generally, in agreement with the normative composition the rocks proved to be more acidic than it is evidenced by the mineralogical diagnosis.

Volcanism has developed within some apparata displaying predominantly a mixed activity. Volcanoes and eruptive bodies are located along the tectono-volcanic alignments trending NW-SE (the predominant ones), N-SE, N-S, E-SW.

The volcanic activity started in the Pannonian D/E and continued during the Pontian and the Pliocene (Rădulescu et al., 1973 a).

The most important basalt eruptions occurred in the terminal part of the eruptive chain in the inner part of the East Carpathians, even the western area of the Perșani Mts. The volcanics are located between Racoșu de Jos and Comana, being more developed in the Racoș-Bogata-Hoghiz area. Generally, the Quaternary basaltic volcanism in this region had a mixed character, mostly effusive; the most important apparata occur at Racoș, Mateiaș, Bogata. The volcanic apparata mark a tectono-magmatic alignment with a SW-NE trend.

According to Rădulescu, Săndulescu (1980), Rădulescu (in Rădulescu et al., 1981) the basaltic volcanism in the Perșani area belongs to an intraplate magmatic activity centre. This activity has been favoured by a crustal fracture generated after the Alpine consolidation (Rădulescu, 1969).

On the basis of the paleontological, paleomagnetic and radiometric data obtained in the last years the Upper Pliocene-Middle Pleistocene age (Mihăilă, Peltz, 1977) of the Perșani basaltic volcanism has been specified.

The petrographical, petrochemical and geochemical study (Peltz et al., 1972 b) made us assign the Perșani basalts to the olivine basalts with virtual nepheline. The upper mantle represents the source of the alkali olivine basalt magma ascendent nondifferentiated and noncontamined towards the surface (Peltz et al., 1972 b).

TiO_2 Abundances

The studies of compared petrology point out that as a discriminant TiO_2 is superior to any other oxides and similar to SiO_2. Indeed, the examination of the way in which the different types of eruptive rocks in the East Carpathians are distributed indicates that for each petrotype and each volcanic unit the variation domains and

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the average values are different. We start from the fact that the TiO_2 values increase without deviations from rhyolites to basalts. Thus, TiO_2, like SiO_2, behaves as a good indicator for the magmatic differentiation.

Figure 1 shows the variation of the TiO_2 and SiO_2 values for a total of 181 samples on classes of frequency. It is observed that TiO_2 is grouped mostly in classes 0.30-1.20, the highest frequency having

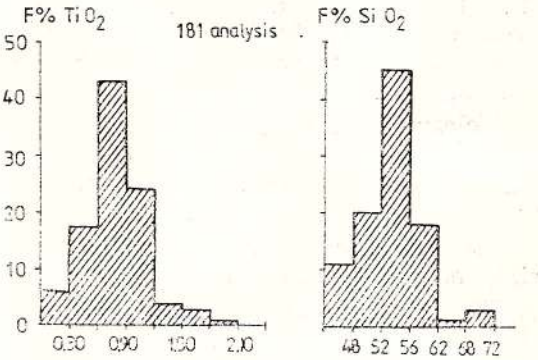


Fig. 1. — TiO_2 and SiO_2 frequency diagram.

the values of the class 0.60-0.90 to 43%. As regards SiO_2, the values range between 48 and 62%. In the Perșani basalts the average value of TiO_2% (Fig. 2) is higher as compared to the value given by D a l y (1.36), but it is lower as compared to the values presented by H. d e l a R o c h e et al., 1980 (1.79). The average values of the Călimani-Harghita andesites (0.74) and Ţibleș-Birgău (0.60) are also lower.

Similar observations result in case of the comparison of the average values of dacites and rhyolites (Fig. 2).

TiO_2% average values are different at the Călimani-Harghita andesites (0.74) as compared to the Ţibleș-Birgău ones (0.60). At the same time, in case of the Călimani-Harghita area, the Gurghiu andesites indicate the highest values (0.82).

TiO_2, like SiO_2, varies systematically from one geographic unit to another as well as from one petrotype to another (Fig. 2). There have been observed : a) differences between the basaltic rocks (Perșani basalts and Călimani basaltic andesites) ; b) differences between some types of andesites from the same volcanic zone (low K-low Si andesite, low-Si andesite, low-K andesite) or from different zones (high-K andesite, low-K andesite) ; c) differences between dacites ; d) similarities between the Ţibleș-Bîrgău andesites and the Călimani-Harghita andesites.

At a regional scale there is observed the geographical differentiation of the TiO_2 values in correlation with the tectonic setting of eruption. Thus, TiO_2 increases from the Ţibleș-Bîrgău eruptive unit southwards in the Călimani-Harghita Unit. In the latter unit the Gur-

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ghiu andesites are richer than the Harghita ones. It is due to the participation in the Harghita volcanic area of the more acid andesites with hornblende, biotite ± quartz.

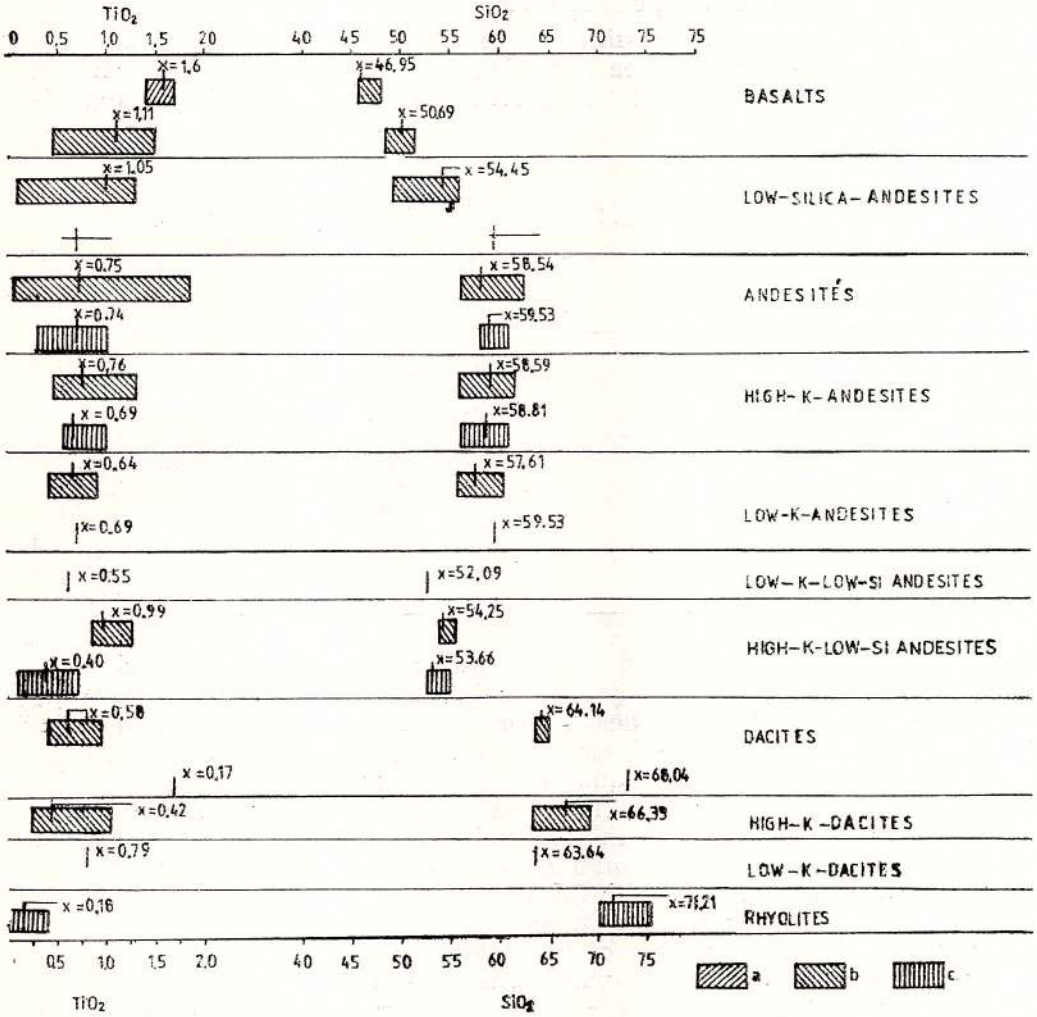


Fig. 2. — Variation domains and average values of SiO_2 and TiO_2. a, Perșani ; b, Călimani ; c, Țibleș-Bîrgău.

TiO_2 and the Chemical Classification of the Volcanic Rocks

In the last years, within the IUGS Subcommission on Systematics in Petrology, several proposals have been made with a view to improving the classification of the volcanic rocks. Some of them bring contributions to the separation of the volcanic rocks occurring most frequently in the fields in the QAP diagram (S t r e c k e i s e n, 1967).

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In this context one has in view the utilization of TiO_2 for the chemical classification, its values being included in the parameters $\tau = Al_2O_3 - Na_2O/TiO_2$ (Gottini, 1968) and $\tau' = Al_2O_3 - Na_2O/TiO_2 + P_2O_5$ (Pichler, Stengelin, 1972).

Table shows the classification of the volcanic rocks in the Călimani-Gurghiu-Harghita area according to Rittmann and Pichler, 59 representative cases of this region have been chosen for exempli-

TABLE

Classification of volcanic rocks from Călimani-Gurghiu-Harghita Mts according to Rittmann and Pichler (1972). Exemplification on 59 analysis

Field	Colour Index		Petrotype
3b	0—20		Rhyodacite (n = 1)
5	10—30		Plagidacite (n = 3)
8	10—35	A. $\sigma < 4$ and $\tau > 9$	Latite (n = 1); Leucolatite (n = 1)
9'	15—38		Quartz latiandesite (n = 8); Leucoquartz latiandesite (n = 6)
9	15—38	B. $\sigma > 4$ and $\tau \geqslant 9$	Latiandesite (n = 3)
9'	15—38		Quartz mugearite (n = 1)
10	20—38		Andesite (n = 3); Leucoquartzandesite (n = 16); Quartzandesite (n = 16).
10'	20—38		

fications. Among petrotypes predominate: a) pyroxene andesites and pyroxene-hornblende andesites according to their mode; b) andesites, low-Si andesites, low-K andesites according to SiO_2-K_2O (Peccerillo, Taylor, 1976). On the basis of the relationship between τ, σ, C.I., quartz andesites and leucoquartz andesites predominate; most of the studied rocks are projected in fields 9' and 10'. Thus, the more acid character of the andesites in the study region is pointed out and the necessity to take into account for the classification of the τ, σ complex parameters in correlation with C.I. is proved.

The τ-σ diagram was utilized by Rittmann and Pichler (1972) for the classification of the volcanic rocks. In Figure 3 one can observe the different fields where the calc-alkaline, tholeiitic and basaltic series with increasing τ figures are arranged. In this way the rocks of the calc-alkaline series in the Călimani-Harghita and Țibleș-Bîrgău areas are well-separated from the Perșani basalts. In detail, field A evidences the arrangement of the various types of calc-alkaline associations with increasing τ figures.

The problem of a correct classification of the volcanic rocks in fields 10 and 9 led Pichler and Stengelin to the utilization of the τ' parameter (τ Gottini modified).

As concerns the rocks from the Călimani-Gurghiu-Harghita volcanic chain the values of τ' are comprised between 8.5-26.5 and correspond to: basaltic andesites, andesites, low-Si andesites, low-K andesites, high-K andesites, high-K-low-Si andesites.

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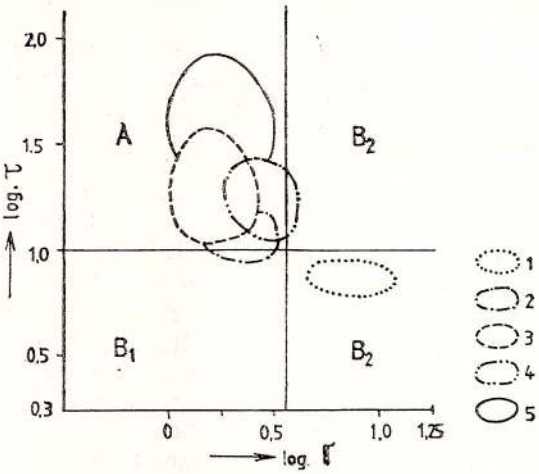
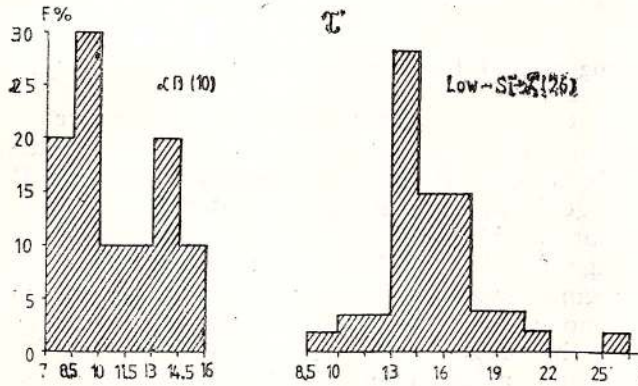
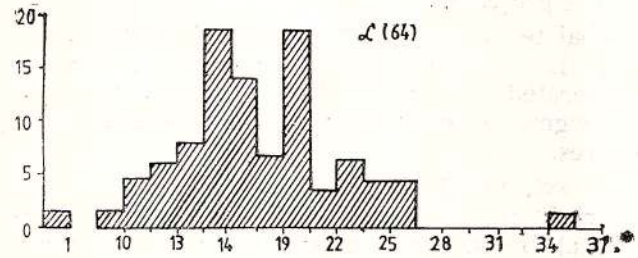


Fig. 3. — Log τ-log σ diagram (acc. Rittmann and Pichler, 1972). A, calc-alkaline field; B1, tholeiitic field; B2, alkaline field. 1, basalts, Perșani; 2, basaltic andesites, Călimani; 3, andesites, low-K andesites, low-Si andesites, low-K-low-Si andesites; 4, high-K andesites, high-K-low-Si-andesites; 5, rhyolites, dacites, high-K dacites.





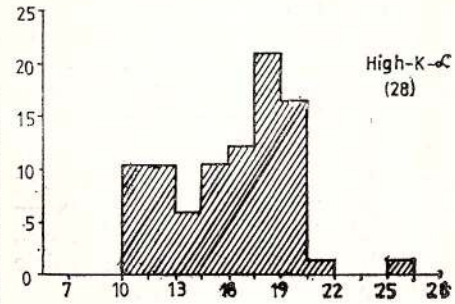


Fig. 4. — τ' frequency diagram.

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The statistical evaluation of our data file for τ' (see Fig. 4) shows that, generally, the values are situated between 5.5 and 10 for the basalts in the Perşani Mts. The andesites present values predominantly comprised in the interval 8.5-26.5. Most of the analysed rocks are situated in the value limits of 10 to 26.5, with maximal intervals between 14.5 and 20.5. The high potassium andesites present τ' values situated, for most of them, between 10 and 22. Only the samples from the subvolcanic area present a higher value than 25; most of them show values ranging between 17.5-21.5.

On the basis of the τ' values one can obtain a clear separation between the Perşani basalts and the Călimani-Gurghiu-Harghita basaltic andesites, as well as between andesites and low-Si andesites. At the same time the different τ' values (Fig. 4) in case of the same petrotypes in the Ţibleş-Bîrgău and Călimani-Harghita areas point out the appurtenance to consanguine magmas, but spatially independent, with a different evolution of the differentiation processes.

Petrogenetical Implications

Log τ-log σ diagram (Gottini, 1968) was used by numerous authors for its petrogenetical implications. Rittmann (1969) considered that the diagram "is surely the most instructive one" as it separates very well the orogenic magmas from the cratonic ones, and, at the same time, points out the bimodality of the volcanism. On the basis of the log τ-log σ diagram, Gottini demonstrated that one can differentiate the simatic magmas originating in the upper mantle, which erupt in the consolidated zone, from the magmas coming from the sialic crust, which erupt in the orogenic zones. In field B of the diagram, the calc-alkaline orogenic magmas are situated, and in field C the crustal simatic magmas are projected.

In the view of the global tectonic concept, developed subsequently to the mentioned diagram, one can admit that the orogenic magmas represent the magmas generated by subduction processes, and the simatic magmas represent magmas coming from the mantle and transported on transcrustal fractures.

In the geotectonic context, within which the Neozoic volcanism in the East Carpathians started and developed, different parental magmas have been generated: a) by subduction processes; b) by intraplate processes. This situation is clearly illustrated in Figure 5. All andesites (the basaltic andesites inclusively), dacites and rhyolites in the Ţibleş-Harghita volcanic zone are situated in field B; the Perşani basalts occupy field C. The independent character of the two magmas is also controlled by τ-SiO_2 diagram (Fig. 6). The Perşani basalt field is located at the values $\tau < 9$; the Ţibleş-Bîrgău and Călimani-Harghita magmatite fields occupy the area of the $\tau > 9$ values. It is also interesting to point out that the lower part of the two mentioned fields — mostly andesitic — occurs in the "Chilean Andesite Formation" field. It was considered by Pichler, Zeil (1969) as characteristic andesitic formation, generated by the partial melting of the lower crust.

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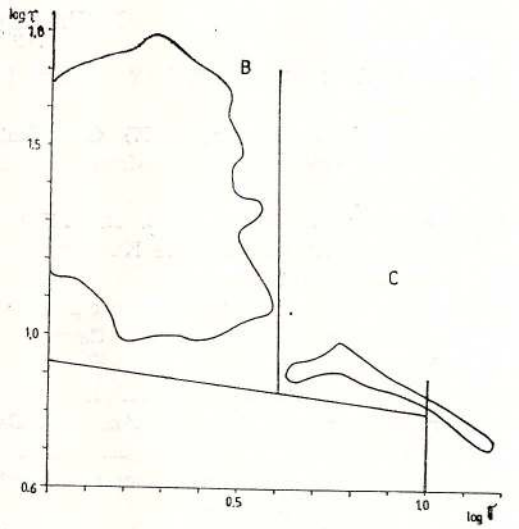


Fig. 5. — Log τ-log σ diagram of the East Carpathian volcanics. B, subduction volcanics of the Ţibleş-Harghita Zone; C, intraplate volcanics of the Perşani Mts.

Log τ-log σ and τ-SiO_2 diagrams are still interesting and useful in the modern petrological concepts based on the plate-tectonics models. In case of the Ţibleş-Perşani eruptive zone, the petrological observations resulting from the previous studies (P e l t z et al., 1972 a, b), concerning the frequency of the parental magmas with different composition and independent in time and space, are confirmed.

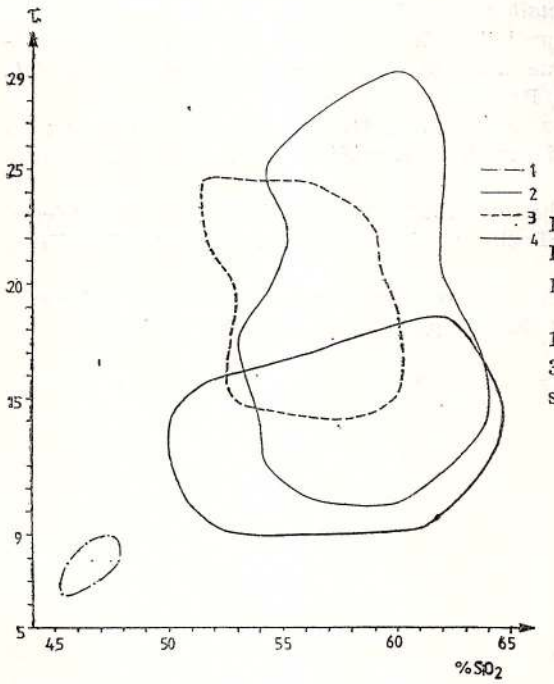


Fig. 6. — τ-values vs SiO_2 of the East Carpathian volcanics in comparison to the volcanics of the Chilean Andesite Formation.
1, Perşani; 2, Călimani-Harghita; 3, Ţibleş-Bîrgău; 4, Chilean Andesite Formation (acc. P i c h l e r, Z e i l, 1969).

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REGIONAL DISTRIBUTION OF THORIUM IN THE NORTHERN HIGHLAND OF HUNGARY AS SHOWN BY AERIAL GAMMASPECTROMETRY [1]

BY

BÉLA WÉBER [2]

Regional airborne (radiometric and magnetic) surveys in Hungary were made in two periods (1956, 1965—1968) and carried out by Mecsec Ore Enterprise, using Soviet techniques and helps. The territory covered by airborne surveys is shown in Figure 1.

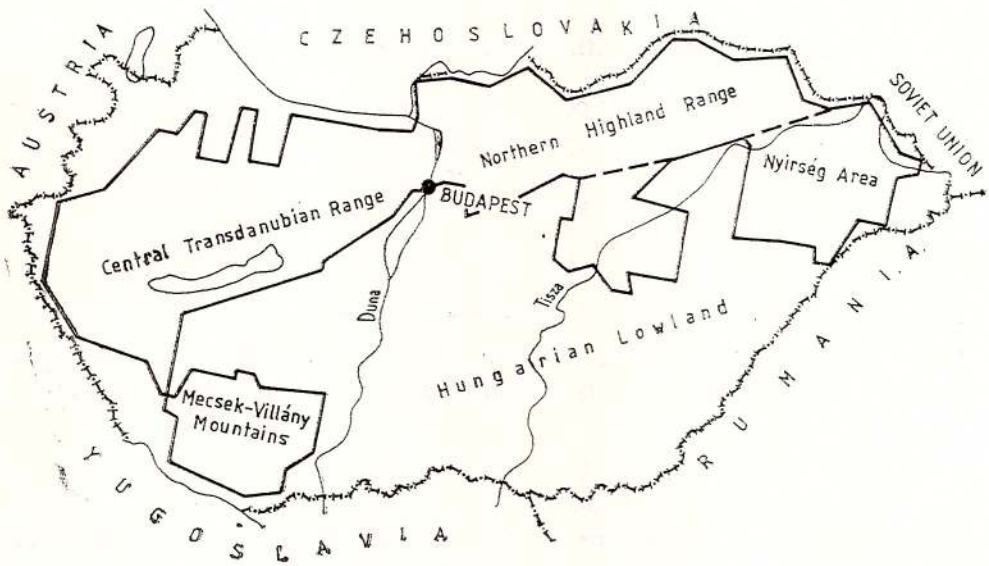


Fig. 1. — The investigated areas by aero-geophysical measurements in Hungary.

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September 8—13, 1981, Bucharest, Romania.

[2] Mecsek Ore Enterprise, Pécs, 7633, Hungary.

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Papers discussing some geological results of airborne measurements in Hungary have been published since 1970. Mainly potassium distribution was dealt with, having got data for a more complete knowledge of the volcanic areas in the Northern Highland Range of Hungary (Wéber, Géresi, 1970; Wéber, Nagy, Géresi, 1972; Wéber, Géresi, 1972; Wéber, 1974). The interpretation and published data about the distribution of U and Th till now refer to the formation, facies and sequences only in the Northern Highland Range (Wéber, 1975). In what follows the author avails himself of the opportunity to focus on the geological information included in the regional distribution of the Th without requirement of any completion.

Attentively following the development of airborne techniques since 1968 dealing with the discussed surveys we can consider them old fashioned today. But these measurements are suitable for geological interpretations with generalized purposes and well known restrictions. That has been proved not only by our experiences of checking and identifying numerous points in the fields, but by external publications too (e.g. Singh, 1975). Therefore more investigations and explanations of the information content of aerial gammaspectrometric data at our disposal are absolutely necessary for the economic activity.

The content of lithofacies and geological sequences

There is also a significant coherence between the regional interpretation and the Th content of different lithofacies and sequences. In this respect the aerial gammaspectrometric data of the Northern Highland Range are shown in Figure 2 and Figure 3.

Particular data on the frequency distributions and the arithmetic means on Figure 2 were calculated by using the Th isoconcentration contour maps and the same scale geological maps as well as by surface measurements. So frequency data on the Y axis reflect the real surface ratios of the X axis intervals and the arithmetical means are weighted by surface.

Likewise, the data on Figure 3 are also weighted means.

The frequency curve on Figure 5 is built upon the data of outcropping areas of 3 008 km^2 inside the total territory of 10 000 km^2. This curve shows longnormal distribution. The weighted means of the Th content is $10.8 \cdot 10^{-4}$ %. Maximum likelihood computed upon the density function : M/X/ = $9.4 \cdot 10^{-4}$ %. Standard deviation : D/X/ = 3.4. Covariance : V/X/ 36.2%. Lower limit of the positive anomalies : C = $25 \cdot 10^{-4}$ % Th, probability : p = 0.9985.

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Regional distribution of Th

The geological sketch map of the surveyed territory can be seen on Figure 4 ; the same scale isoconcentration map is shown in Figure 5. Comparing the maps it is clear that the Th-distributions in differenciated on the whole territory (including the volcanic and sedimentary areas).

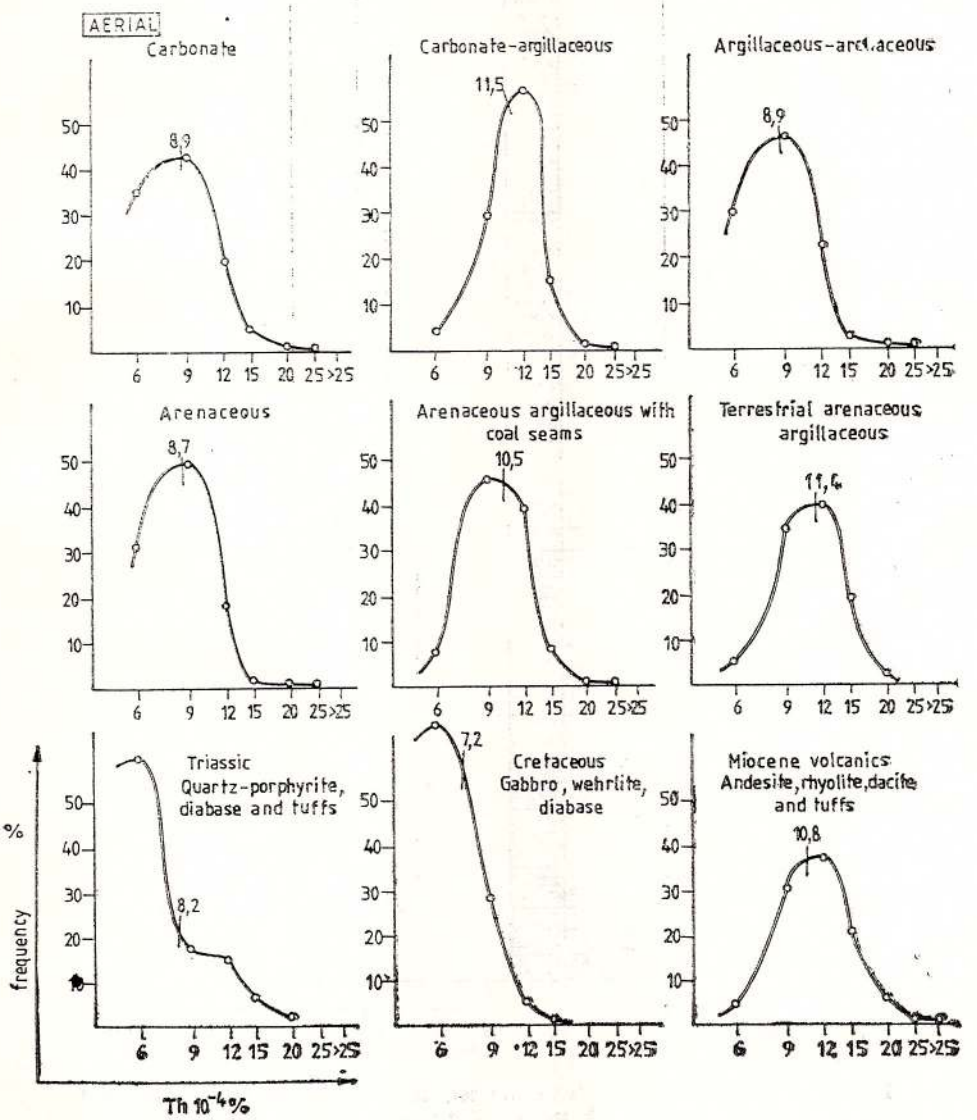


Fig. 2. — Frequency curves of Th data, measured on different facies of rocks in the territory of Northern Highland Range of Hungary (W é b e r, 1970).

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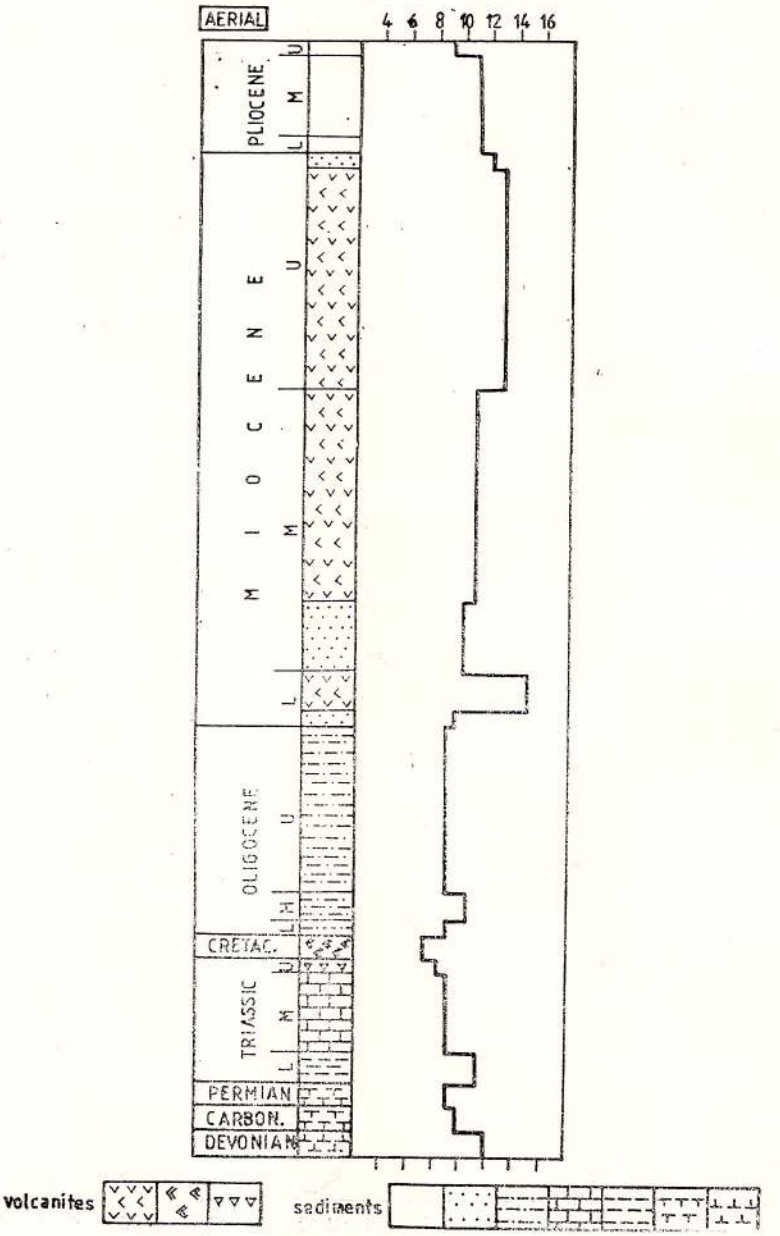


Fig. 3. — Distribution of Th in the sequence of the Northern Highland Range of Hungary (W é b e r, 1975).
(The thickness of formations in column is approximately proportionate to its extension at the surface).

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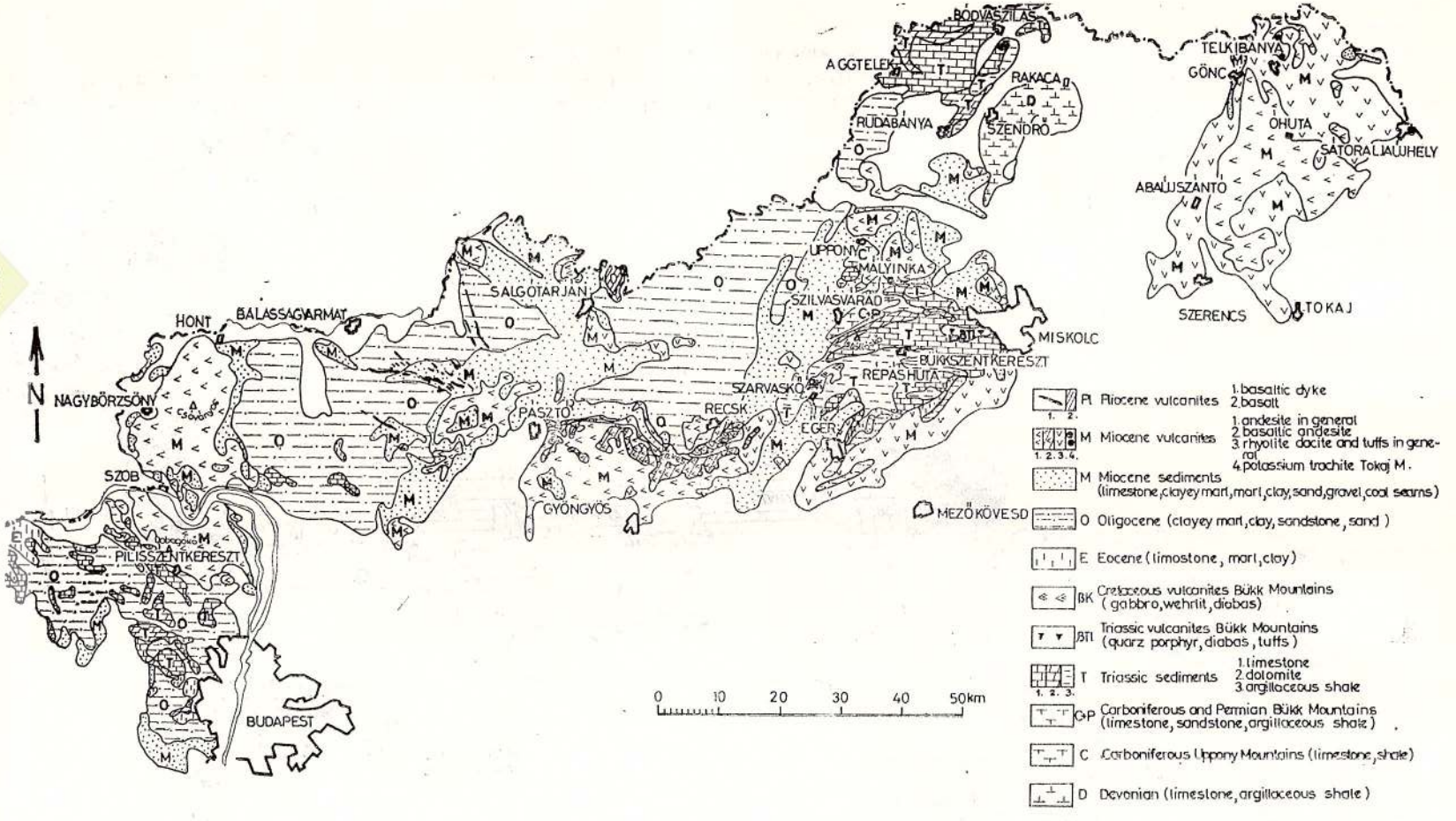


Fig. 4. — Geological sketch map of the Northern Highland Range of Hungary. (Based on the maps, 1 : 200 000, constructed and edited by the Hungarian Geological Institute, 1962—1966).

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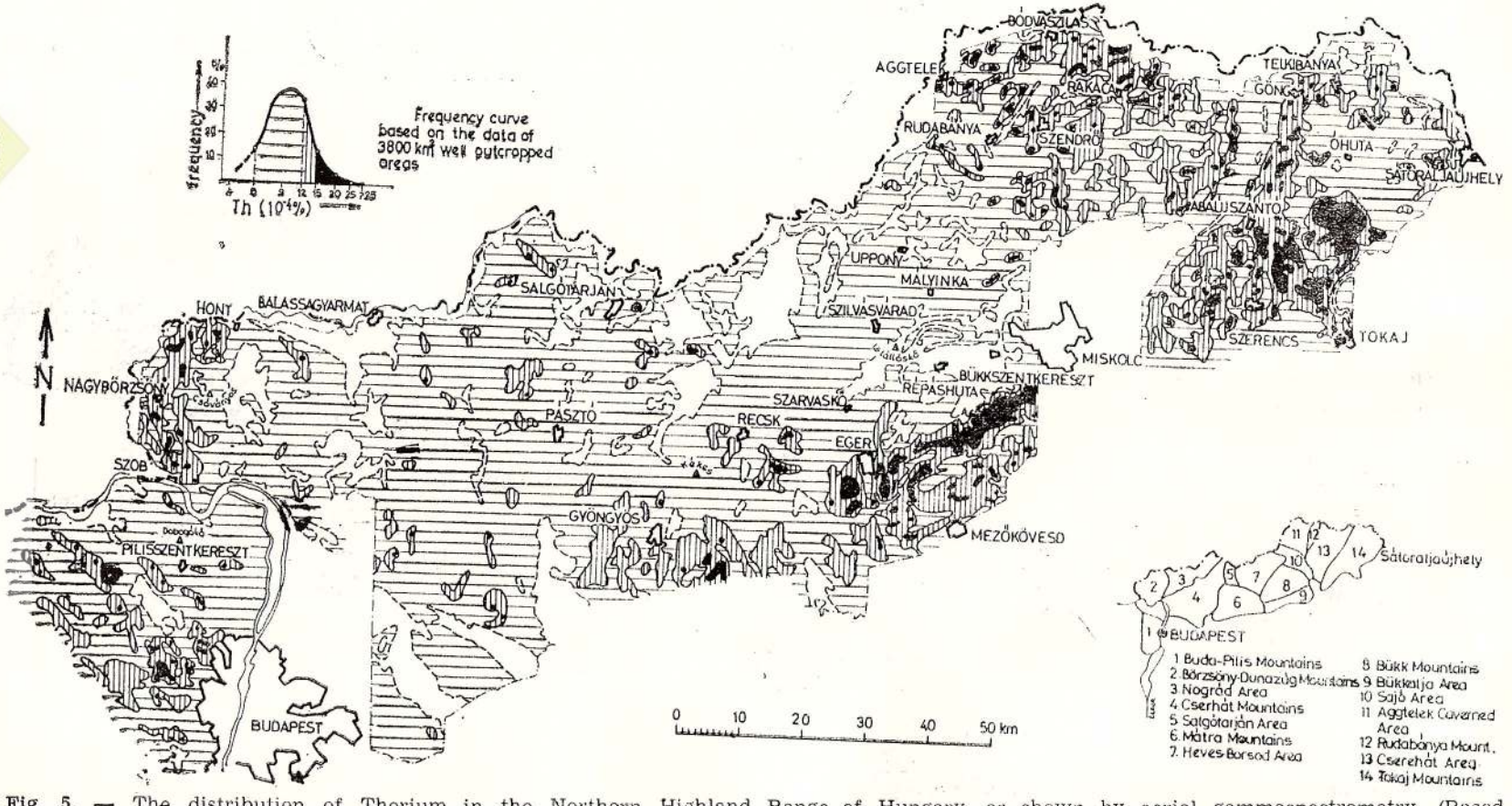


Fig. 5. — The distribution of Thorium in the Northern Highland Range of Hungary, as shown by aerial gammaspectrometry. (Based on particular maps constructed by Tyihomirov and Géresi (1966—1967) modified by Wéber (1976). The measurements were carried out by the Mecsek ore Enterprises.

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Volcanic areas

It is well known that the volcanic complexes play an important role in the geology of the Northern Highland Range of Hungary. They are made up of Triassic, Cretaceous and Miocene volcanites and exhibit a very large scale of chemism (ultramafic-mafic-intermediary-acidic). Average Th contents measured above the volcanic rocks-corresponding to the geochemical properties of Th-change in correlation with the chemism of rocks. Data calculated from airborne surveys are shown on Figure 6.

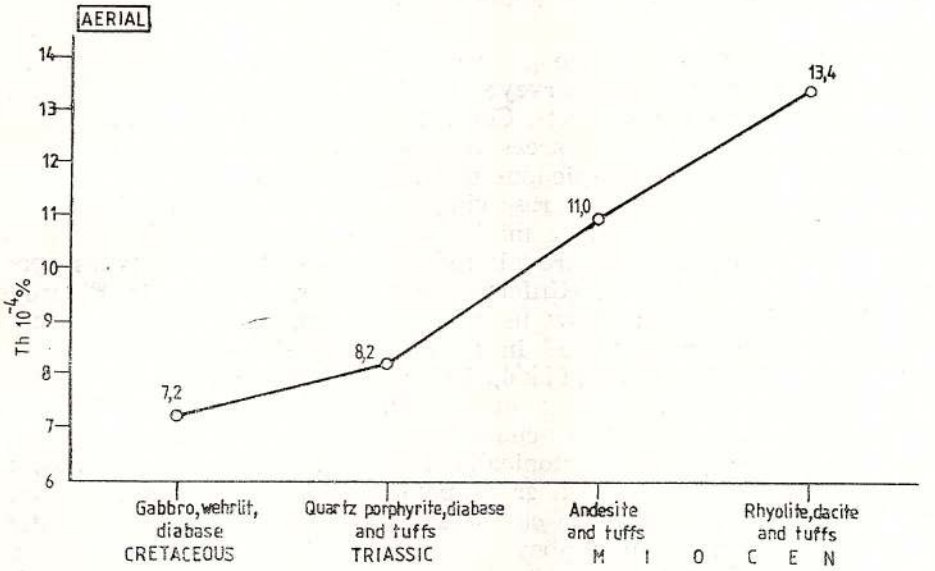


Fig. 6. — The distribution of Th in the different facies of volcanics in the Northern Highland Range of Hungary (W é b e r, 1975).

The surveyed occurrences of Mesozoic volcanites are situated in the Bükk Mts.

The Triassic Óhuta Diabase and Bagolyhegy Quartzporphyry (paleorhyolite) with outlined contours on the surface (β T1) can be found near the western edge of the city of Miskolc at the village of Bükkszentkereszt and are represented by a maximum value of $20 \cdot 10^{-4}$ % Th content on the Th map (Fig. 5). The second maximum of the frequency curve of Figure 2 referring to Triassic volcanites represents "lithological anomalies". On the same area there is no close connection between the Th and K anomalies. The mafics (diabase, gabbro, wherlite) near the village of Szarvaskö which are assigned to the Cretaceous (β K) at present — belong to areas with low Th content like the carbonate rocks of the Bükk Mts.

The frequency curves of the Triassic and Cretaceous volcanites in Figure 2 can be written by the Poisson distribution. By testing the

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homogeneity of the Th contents of the above mentioned groups (having different rock chemism also) they have been found to be statistically equal to each other, with probability of 0.9995. Because the data are loaded with errors having the same properties, this statistical state must be caused by geological-geochemical factors. The structural geological importance of the answer to this question (genetical and age problems) can be considered evident with respect to the Th distribution. At the same time data of the Th distribution aim at directing the attention to the possibility of detailed radiogeochemical investigations.

In the Northern Highland Range Cenozoic volcanism is mainly represented by calc-alkaline andesites, rhyolites and dacites of Miocene age.

At the surface we have got relatively low Th contents especially in the western part of the surveyed territory built up by andesitic volcanites (Börzsöny-Dunazúg Mts, Central part of the Cserhát Mts, Mátra Mts) but for the andesitic areas of the Tokaj Mts. Inside the listed mountains there is no conspicuous differentiated distribution in general. As regards a more detailed resolving it must be recognized that the Th contents decrease or have minimum values in those places (zones) where the orthovolcanites are altered to hypo-meta rock types (propylite-potassium trachyte). (Unfortunately the map's scale in Figure 4 and Figure 5 does not allow us to observe it). Such rocks and processes are known and studied in detail in Börzsöny-Dunazúg-, Mátra- and Tokaj Mts (Pantó, Mikó, 1964; Kubovics, Pantó, 1970; Fux Széky, 1970; Varga et al., 1975; Gyarmati, 1977). One of the essential geochemical characters of the above mentioned processes, that take place in tectonically performed zones, is the potassium surplus (result of low to high grade potassium metasomatism), indicated by airborne surveys too. The character of the Th-K ratio in the potassium rich zones determined above is shown in Figure 7. This connection evidences that knowing the Th distribution is one of the possibilities to determine the origin of the potassium enrichment or anomalies, detected by aerial gammaspectrometry (for example they are in connection with hypo-metamagmatic alterations or with orthorocks rich in potassium only). The problem is important for instance in ore prospecting because in the Carpathian volcanic area there is an intimate connection between occurrences of the mentioned altered rock types and the ore bearing processes.

So, on the maps shown in Figure 4 and Figure 5 an example is given of a minimum area of Th concentration above the sulphide-precious metallic ore bearing potassium trachyte at Telkibánya, in the Tokaj Mts. The identification of this area together with data of a geological study (Fux Széky, 1970) called for further researches.

Rhyolites, dacites and their tuffs ranging from the southern foreland of the Bükk Mts to the Tokaj Mts are distinctly separated from the surroundings because of their Th anomaly. Even the small rhyolite — cone of Kis-hegy (in the Mátra Mts, 4 km north of the town of Gyöngyös) can be noticed on the Th concentration contour map. Top of average Th concentrations ($> 16.10^{-4}$ %) characterize the volcanites

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in the southern foreland of the Bükk Mts (the so called "Bükkalja volcanites") between the cities of Miskolc and Eger. We should say that the orthite crystal-fragments could be enriched through the influence of the alluvial fan of a small stream (by N y á r i, in 1971).

According to the Th distribution, the Tokaj Mts can be divided in two parts.

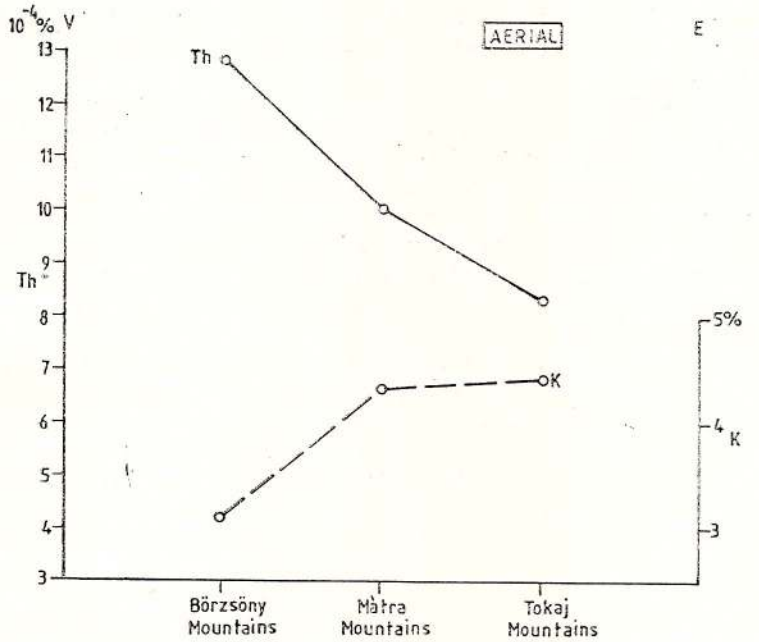


Fig. 7. — Distribution of Th in the zones of potassium mobilization of the Miocene volcanic areas in the Northern Highland Range of Hungary (W é b e r, 1974).

The SW part has an increased Th content in general. In addition, the trend lines of the Th anomalies are in accordance with part of the volcanic tectonic lines established by detailed geologic mapping (G y a r m a t i, 1979). So directions of the Gönc-Abaújszántó-Szerencs line and the Tokaj-Abaújszántó line are reflected by the regional Th distribution. The most extended Th anomaly (between the villages of Óhuta and Tokaj) with continuously high concentrations represents the so called "lithological anomaly" and belongs to the fluidal rhyolite of the Szokolya hill. In spite of the fact that in the northern part of the Tokaj Mts (NE of the Gönc-Sárospatak direction) rhyolites and dacites are predominant as well, the Th map reflects a smaller Th content than on the SW part. The reason may be, among others, the extended potassium mobilization, which is more characteristic in this part of the Tokaj Mts. It is concerned with a few data : the presence of potassium trachyte at Telkibánya : westwards of the city of Sátoraljaújhely there is the Rudabányácska-Vágáshuta-Károlyfalva potassium anomaly

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with occurrences of potassium trachyte, like at Telikibánya ; the rhyolite tuffs are adularised (Vargáné, 1961) and there are relatively many areas with increased content of potassium ($K > 3\%$), according to the airborne survey (Wéber, Géresi, 1972).

Sedimentary areas

Sediments that take part in the sequence of the Northern Highland Range are of Cenozoic (Neogene and Paleogene), Mesozoic and Paleozoic ages (Fig. 4).

Holocene-Pleistocene accumulations having an effect on the Th distribution are noticed in the south foreland of the Mátra Mts and south of the Bükkalja volcanites, and in the Cserehát area (among Gönc-Abaújszántó-Szendrö-Rakaca). On the first mentioned forelands there is a dispersion area of 85 km length and 8—10 km width (among Gyöngös-Mezökövesd-Miskolc) which refers to erosion processes from the mountains to the south, indicated by eroded volcanic matters. In the Cserehát area the Th distribution may be related to the upermost layers of the Pannonian.

Miocene and Oligocene clastic sediments differ from each other not only in age, but in their Th content too. Comparing the maps (Fig. 4, Fig. 5) it is discernible that while average Th content changes $6\text{-}12.10^{-4}$ % on Miocene areas, the more characteristic values for the Oligocene are $> 6.10^{-4}$ %. There are exceptions too : in the Miocene of the right bank area of the Sajó River (east of the village of Uppony) and with lower Th content in the Oligocene surroundings of the Mesozoic blocks on the left side of the Danube River, east of the Börzsöny Mts.

It seems that the total geological structure of the Börzsöny area is reflected by the Th distribution in the following way. In the east the sedimentary bedrock of the stratovolcanic complex (Rupelian-Lower Badenian) shows a lower Th content than the average of the Oligocene, in the west the covering sediments show higher Th concentrations than the average of the Miocene. Also there is an areal correlation between the Th and K sharply outlined in arch shape by the Th map referring to rocks more acidic than andesites. That is why the volcanic materials (e.g. tuffites, tuffaceous marls) existing in the covering sediments may be acidic in origin, according to the Th and K distribution.

Triassic, mainly carbonate rocks can be found at the surface in the Buda-Pilis and Cserhát Mts, in the left side blocks of the Danube, in the Bükk Mts, in the Aggtelek Caverned Area and its eastern edge in the Rudabánya Mts. Among them, carbonate rocks of the Bükk Mts are recognized as the lowest average Th concentration plot of arch — opened in the SW direction — bordering the Kisgyör sericite-slate Formation which consists of Triassic clayey, fine detrital layers with volcanogene intercalations showing higher Th content. This significant view is one of the remarkable experiences in the interpretation of Th distributions registered by aerial gammaspectrometry. Similarly, the carbonate rock belt with a sharp structural contour in the Rudabánya Mts was distinguished from their surroundings. In the neighbouring Aggte-

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lek Caverned Area -- in spite of the carbonate rocks — the Th map shows higher average Th contents. The reason may be the residual red clay which formed on the surface of carbonate rocks and covered it because of low flow down coefficient, in general. Within the Aggtelek Caverned Area there is a remarkable belt of higher Th content ($> 12.10^{-4}$ %). It begins north of the Rudabánya-Aggtelek line and meets the Rudabánya Mts, joining at the border of the country. According to this interpretation it is connected with a tectonical line.

The airborne surveys had good results in the Buda-Pilis Mts too. West of Budapest such an anomalous area has been known where the accumulation of Th on the present surface of Triassic dolomite and limestone should be regarded as having an ascendant origin as a result of hydrothermal processes, according to field investigations. It is proved first of all by the presence of a mineral named cheralite ~ [$2CaTh(PO_4)_2$] which was determined after magnetic separation by the Petrological Geochemical Institute of Sciences L. Eötvös und the direction of prof. I. Kubovics (1980). Applied equipments for that purpose were the LAMA-10 type Laser spectrograph and the MAR-2 type electron probe micro analyser. In addition the base sample contained some niobium. Another evidence of the connection with the depth was given by a mafic-ultramafic rock type (biotitite) (Wéber, 1962) drilled in an anomalous area.

The above mentioned "biotitite" consists of pyroxene, apatite, garnet and pseudomorphosis after olivine. The chemical composition of one of the samples given by Hoffmann (1980) is :

SiO_2	39.23%	CaO	15.15%
TiO_2	1.74	Na_2O	0.9
Al_2O_3	6.6	K_2O	1.5
Fe_2O_3	7.29	P_2O_5	1.46
FeO	1.09	loss on ignition	14.38
MnO	0.05	CO_2	8.0
MgO	10.20	$-H_2O$	0.71

Above the Permian, Carboniferous and Devonian areas of the Northern Highland Range (such as the northern part of the Bükk Mts, in the Uppony Mts, between the villages of Mályinka and Uppony, in the Szendró Mts, between the villages of Szendró and Rakaca), consisting of clastic-clavey and carbonate layers, there were no interesting Th anomalies worthy of detailed interpretation at present.

A bit higher Th contents were measured above the Szendró Mts (Devonian) which together with the increased K content-measured in the field by a portable gammaspectrometer — refers to the presence of a volcanogenic substance in the slightly metamorphosed slate.

Summarizing the experiences about the geological interpretation of the Th distribution, measured by the aerial gammaspectrometry

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method in the Northern Highland Range of Hungary it has been found that :

— the geological and petrological relationships are reflected by the Th distribution under the given morphological and climatic circumstances.

— the Th distribution is relatively sensitive to structural connections which may be manifested in positive (e.g. volcano-tectonic lines) or in negative (e.g. potassium zones, potassium trachyte) anomalies including important information for the knowledge of structural or ore-bearing processes in both cases.

— there is an interesting connection between Th and K ; it might be non functional but should be considered an acceptable experience in the investigation of the Carpathian Neogene volcanism.

— referring to sedimentary areas it must be emphasized that knowing and checking the distribution of Th is one of the ways to make an evaluation of an area, for instance the Buda-Pilis Mts, that had been qualified as having few perspectives for ore prospecting in general. After the example of the Buda-Pilis Mts it was established that the knowledge of the distribution of Th is particularly important for the geological search/research in Hungary, and presumably in other countries of the Carpatho-Balkan Belt too.

Conclusions and motions

The differences in the Th distribution in connection with geologic relations of surface, the extension of the airborne survey under similar physical conditions on the whole territory allows the presented Th map to be qualified as regional geochemical. These maps are equivalent geological documentations, among others characterizing the geological aspects of the region. Inside the above mentioned drawing of those maps would be seasonable out of consideration, e.g. the plate tectonical revision of structural development. Of course the Th map is not panacea but our knowledge may be more complete, if we make use of it, in respect of geochemistry. Therefore well arranged and coordinated airborne geochemical and correlation maps (1 : 2 000 000 ?) should be worked out and edited as they are of common interest. The above mentioned maps may be considered economical to be produced because in all likelihood aerial gammaspectrometric (and simultaneously aerial magnetic) measurements have been performed in some of the Carpatho-Balkan countries.

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CONTRIBUTION À LA CONNAISSANCE DES ASPECTS PARAGÉNÉTIQUES DE LA MINÉRALISATION ASSOCIÉE AU MASSIF ALCALIN DE DITRĂU [1]

PAR

EMIL CONSTANTINESCU [2], NICOLAE ANASTASIU [2], NICOLAE POP [3], NAZAR GARBAŞEVSCHI [4]

Le massif alcalin de Ditrău, décrit pour la première fois par Herbich en 1972, est bien connu au point de vue pétrographique, pétrochimique et structural. Sur sa pétrogenèse nous renseignent les amples études effectuées par Ianovici (1933, 1938), Codarcea et al. (1954), Streckeisen (1954, 1960) et complétées par celles plus récentes qui nous viennent d'Anastasiu et Constantinescu (1974, 1978, 1980), de Jakab (1975) et de Zincenco, Vlad (1978).

Dans le cadre des études pétrographiques, les observations sur les minéralisations associées ont été sporadiques, limitées tout spécialement à l'identification isolée de quelques minéraux. Les premières informations sur la minéralisation nous viennent de Ianovici (1933, 1938) qui décrit les affleurements de blende, galène, pyrite, chalcopyrite et goethite localisés dans la vallée de la Jolotca et de Panto (1942) qui décrit pyrite, chalcopyrite, blende.

D'autres minéraux ont été identifiés par Koch (1886) — orthite, Zepharovich (1859) — pyrochlore, Stanciu (1955) — baddeleyte ; Codarcea et al. (1958) — rhönite, xénotime, molybdénite ; Jakab, Garbasevschi (1975) — arsenopyrite.

Les recherches effectuées en terrain, les observations microscopiques détaillées et les analyses complexes (RX, DTA, IR, microsonde électronique, spectrographie laser) effectuées au laboratoire ont conduit

[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

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à l'identification de quelques minéraux nouveaux et à préciser le chimisme, la structure et les propriétés optiques d'autres minéraux. Elles ont également mis en évidence les rapports réciproques entre ces minéraux autant que leur position au cours de l'évolution pétrographique et métallogénique du massif.

1. Cadre géologique

Selon Anastasiu et Constantinescu (1980) le pluton alcalin de Ditrău, qui présente un contour quasicirculaire, constitue une intrusion complexe développée au cours de plusieurs stades, dont la position est en discordance avec la masse des schistes cristallophylliens qui reviennent aux séries de Rebra et Tulgheș.

Sa structure géologique et sa pétrographie sont compliquées. On y distingue deux compartiments structuraux : l'un septentrional „Jolotca-Putna" et l'autre central-méridional „Valea Mare-Güducz-Belcina" constitués de roches calco-alcalines (mafites, diorites, monzonites, syénites, granites) et respectivement alcalines (essexites, monzonites foïdiques, syénites foïdiques). Les deux compartiments sont traversés par tout un cortège de roches filoniennes (lamprophyres, aplites, syénitoïdes).

2. Mode de présentation de la minéralisation

En fonction du cadre géologique et pétrographique on peut séparer deux types distincts au point de vue chimique et minéralogique autant qu'en ce qui concerne la forme de gisement correspondant à la zone septentrionale et respectivement centrale-méridionale du massif.

Dans la zone septentrionale les minéralisations, localisées dans le complexe des mafites et des ultramafites qui remplissent exclusivement le rôle de roche hôte de la minéralisation, constituent de manière prédominante des filons qui sont soit simples soit sous forme de systèmes de filons quasiparallèles, groupes le long des alignements dont l'orientation générale est E-W/N. Localement peuvent apparaître des zones d'imprégnations, des nids ou de fins réseaux de filonets. Dans l'espace les zones minéralisées s'associent aux roches filoniennes (lamprophyres, albitites, carbonatites).

Dans la zone centrale-méridionale la minéralisation apparaît sous forme d'imprégnations, parfois largement dispersées, et en moindre mesure sous forme de nids ou de bandes courtes épaisses de l'ordre des millimètres. Elle est cantonnée dans des roches leucocrates. Les plus importantes concentrations se disposent de manière discontinue le long des auréoles de contact et sont contrôlées au point de vue pétrographique et minéralogique par le complexe des syénites alcali-feldspathiques et par le complexe des roches quartzo-feldspathiques situées à la périphérie du massif.

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3. Description des principaux minéraux

Les minéraux constituants de la minéralisation (tab.) reviennent aux classes des oxydes, des sulfures, des carbonates, des phosphates et, de manière tout à fait subordonnée, des silicates et des éléments natifs. Au point de vue quantitatif prédominent les minéraux comportant des T.R. (phosphates, oxydes), des bisulfures de molybdène et de fer, des oxydes de titane.

TABLEAU

Les mineraux constituants de la mineralisation associée au massif alcalin de Ditrău *

Sulfures	*Oxydes*	*Carbonates*
arsénopyrite	**anatase**	ankérite
bismuthine	baddeleyite	azurite
blende	**brookite**	bastnäsite
chalcopyrite	corindon	malachite
chalcopyrrhotite	goethite	parisite
covelline	lépidocrocite	sidérite
cubanite	hausmanite	
galène	hématite	
josseïte	ilménite	*Phosphates*
mackinawite	**ilménite pyrophanitique**	apatite
marcasite	ilménorutile	monasite
molybdénite	magnétite	xénotime
pyrite	molybdite	
pyrrhotine	niobite (columbite)	*Silicates*
vallériite	picotite	mélanocérite
tétradymite	pyrochlore	mélinophane
	pyrolusite	orthite (allanite)
Elémenis natifs	**pseudobrookite**	thorite
argent, or, cuivre	psilomélane	zircon
	rutile	
Halogènures	tapiolite	
fluorite	thorianite	
	titanomagnétite	

* les caractères aldins marquent les minéraux mentionnés pour la prémière fois.

Molybdénite. Elle apparaît sous forme de filonets, de pellicules fines le long des microfissures ou sous forme d'imprégnations très fines dans la masse des roches. Les cristaux, de dimensions variées, sont prédominants, gros de 0,04-0,06 mm. Leur aspect est lamellaire, souvent incurvé, tordu à la suite des efforts mécaniques. Les analyses par diffraction en RX (principales lignes : 6,06 ; 2,26 ; 2,038 ; 1,53) ont indiqué la prédominance du polytype hexagonal 2H et de manière subordonnée la présence du polytype trigonal 3R marqué par l'accroissement de la valeur de l'axe „b" et la diminution de la dureté. Les valeurs R% (tab.) sont un peu inférieures aux valeurs étalon (U y t e n b o g a a r d t, B u r k e, 1971). La molybdénite constitue des associations caractéristiques avec les carbonates, les oxydes et les sulfures. Elle apparaît fréquemment le long des fissures de blende, galène, au contact ilmé-

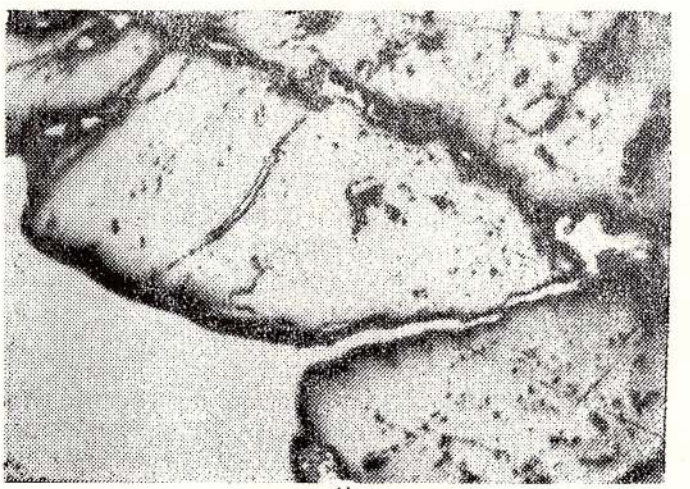
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nite-quartz, moule les cristaux de pyrite et de blende (fig. 1 a) ou constitue des agrégats radiaires à carbonates, étant, évidemment, déposée ultérieurement par rapport aux minéraux mentionnés.

Bismuthine. Elle apparaît sous forme de plages dans la galène ou constituant des intercroissances avec celle-ci. Sa dureté au polissage



1a



1b

Fig. 1. — Images microscopiques de la minéralisation de Ditrău — zone Jalotca.
1 a : mo, molybdénite ; bl, blende, grés foncé, carbonates.
1 b : il, ilménite ; gn, galène.

est sensiblement égale à celle de la galène, sa couleur est plus jaune et sa biréflection et anisotropie sont fortes.

Josseïte. Elle apparaît sous forme de cristaux prismatiques-aciculaires, englobés dans la galène (fig. 2 a) ou la bismuthine. Au contact

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avec la galène elle est jaune, sa dureté au polissage est moindre, son pouvoir de réflexion plus élevé ; la biréflexion et l'anisotropie sont faibles, mais visibles. Au contact avec la bismuthine elle gagne une teinte bleuâtre.

Blende. Elle apparaît sous forme de filonets épais de 2-3 mm, de

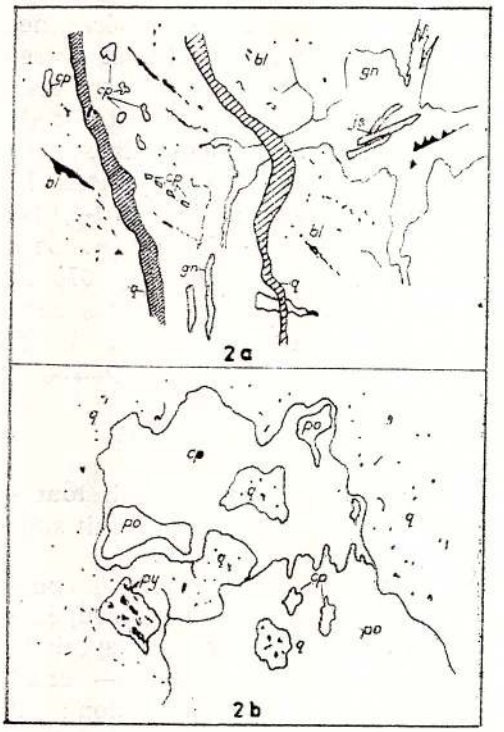


Fig. 2. — Relations spatiales entre les minéraux constituants de la minéralisation.
2 a : cp, chalcopyrite ; gn, galène ; bl, blende ; js, josseïte ; q, quartz.
2 b : py, pyrite ; cp, chalcopyrite ; po, pyrrhotite ; q, quartz.

nids généralement dans les zones marginales des filons et de plages centimétriques ou de petites granules allotriomorphes dans la gangue. La valeur du paramètre réticulaire „a" calculée à partir des analyses RX est égale à 5 Å correspondant à une teneur de 7% FeS. La microdureté Vnh = 192 kgf/mm^2 et le pouvoir de réflection R%. Elle est associée aux minéraux de bismuth et comporte des inclusions de chalcopyrite, de cubanite et de pyrrhotite. Elle constitue des intercroissances d'aspect mirmékitoïde avec la galène et les carbonates.

Chalcopyrite. Elle apparaît sous forme de plages isolées, d'inclusions dans la blende ou de pellicules intergranulaires associées aux agrégats de pyrite. En compagnie de la calcite elle s'y insinue sous forme de filonets discontinus le long des discontinuités mécaniques de la monazite, du rutile, de l'ilménite et de la pyrite ou des plans de clivage de la galène.

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Pyrrhotite. Elle apparaît sous forme d'inclusions xénomorphes dans la pyrite ou d'ovoïdes dans la magnétite. Elle peut renfermer de petites granules de pyrite. Elle est marcassitisée le long des fissures.

Monasite. C'est le plus important minéral quant à la fréquence et la teneur en T.R. Elle se présente sous forme de cristaux tabulaires constituant des agrégats microgranulaires ou radiaires épais de 0,01-0,10 mm et longs, généralement, de 1-2 mm. À l'oeil nu elle est de couleur brun-rougeâtre et présente l'éclat de la cire. Au microscope on observe, à la limite d'entre les cristaux et le long des fissures, des accumulations d'hydrogoethite et de lépidocrocite qui lui impriment la couleur. Le pléocroïsme faible ; la biréfringence élevée $2V\alpha = 15°\text{-}16°$. Les valeurs $R^0/_0$ sont réduites. Les principales lignes de diffraction déterminées sont : 5,18-4,79-4,18-3,50-3,30-3,09-2,99-2,87-2,60-2,44-2,19-2,14-1,97-1,90-1,87-1,75-1,69 Å. Le spectre d'absorbtion en IR présente des bandes d'absorbtion à 1 070 cm^{-1}, 625 cm^{-1}, 585 cm^{-1}, 475 cm^{-1}. Elle constitue des associations caractéristiques avec les carbonates qui apparaissent souvent le long des fissures, avec le rutile, la pyrite, la galène, la chalcopyrite, l'apatite, l'orthite et la zéophilite (fig. 3, 4). On saisi la transformation de la monazite en orthite, tout spécialement au contact avec la zéophilite.

Xénotime. Elle apparaît tout spécialement dans la zone de SE du massif et de manière tout à fait subordonnée dans la zone septentrionale.

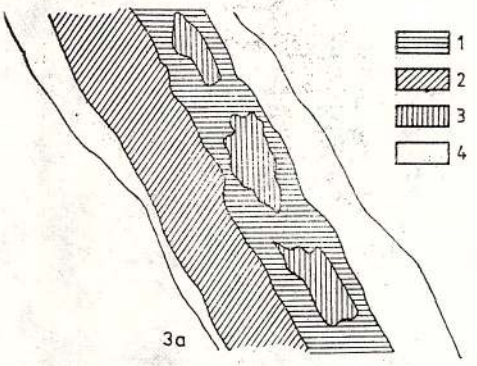
Orthite. À l'oeil nu elle apparaît sous forme de cristaux prismatiques de couleur noire, groupés en agrégats radiaires. Les cristaux présentent des macles polysynthétiques et une structure zonée. Pléocroïsme intense : incolore — brun-rougeâtre — rouge intense. Biaxe négatif. Lignes de diffraction : 8,007-5,06-4,68-3,51-3,01-2,89-2,69-2,60-1,62. Il y a des échantillons où les analyses par diffraction RX et thermodifférencielles révèlent la présence de l'orthite métamictique. Elle constitue des associations communes avec la calcite, la monazite, la pyrite, le rutile, et la zéophilite.

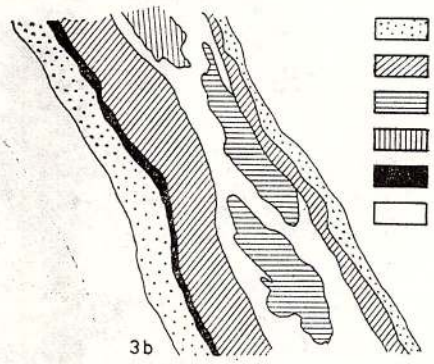
4. Structures et textures de la minéralisation

Les structures les plus fréquentes (fig. 3) sont celles granulaires dont les dimensions des grains des minéraux sont supérieures à 1-2 mm, excepté la molybdénite dont les grains sont de 0,05 mm. On y rencontre fréquemment les structures de substitution : ilménite-rutile ; josseïte-bismuthine ; monasite-orthite ; sphène-ilménite. Apparaissent également des structures d'exsolutions : ilménite-hématite ; blende-chalcopyrite. Les textures sont massives et compactes au cas de la pyrite et d'aspect radiaire ou en nids au cas de la monazite. On y rencontre aussi des

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textures d'imprégnation et des textures microbrécheuses, milonitiques (fig. 3 c), tout spécialement dans le cas de la pyrite qui dans les zones marginales des filons est cataclasée et cimentée par des minéraux plus récents, plastiques. On remarque également des intercroissances épitaxiales : molybdénite-chlorite, molybdénite-biotite ; bismuthine-josseite.





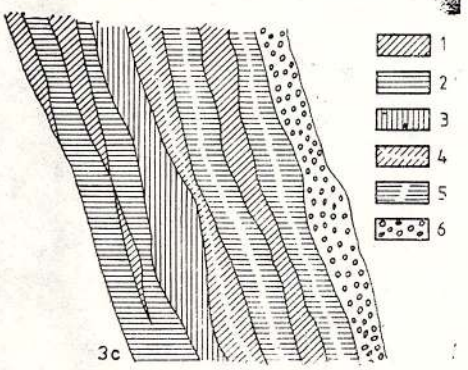


Fig. 3. — Structures et textures de la minéralisation de Ditrău — secteur Jalotca.
3 a : 1, monasite ; 2, pyrite ; 3, ilménite ; 4, carbonates. 3 b : 1, quartz ; 2, pyrite ; 3, monasite ; 4, ilménite et chalcopyrite ; 5, molybdénite ; 6, carbonates. 3 c : 1, pyrite ; 2, monasite et orthite ; 3, orthite ; 4, pyrite, ilménite et galène ; 5, nids de monasite et orthite en carbonates ; 6, zone milonitique avec de la monasite cataclasée.

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5. Associations caractéristiques

Tenant compte des relations spatiales d'entre les minéraux constituants de la minéralisation (fig. 4) autant que des relations d'entre ces minéraux et la gangue on peut séparer une série d'associations carac-

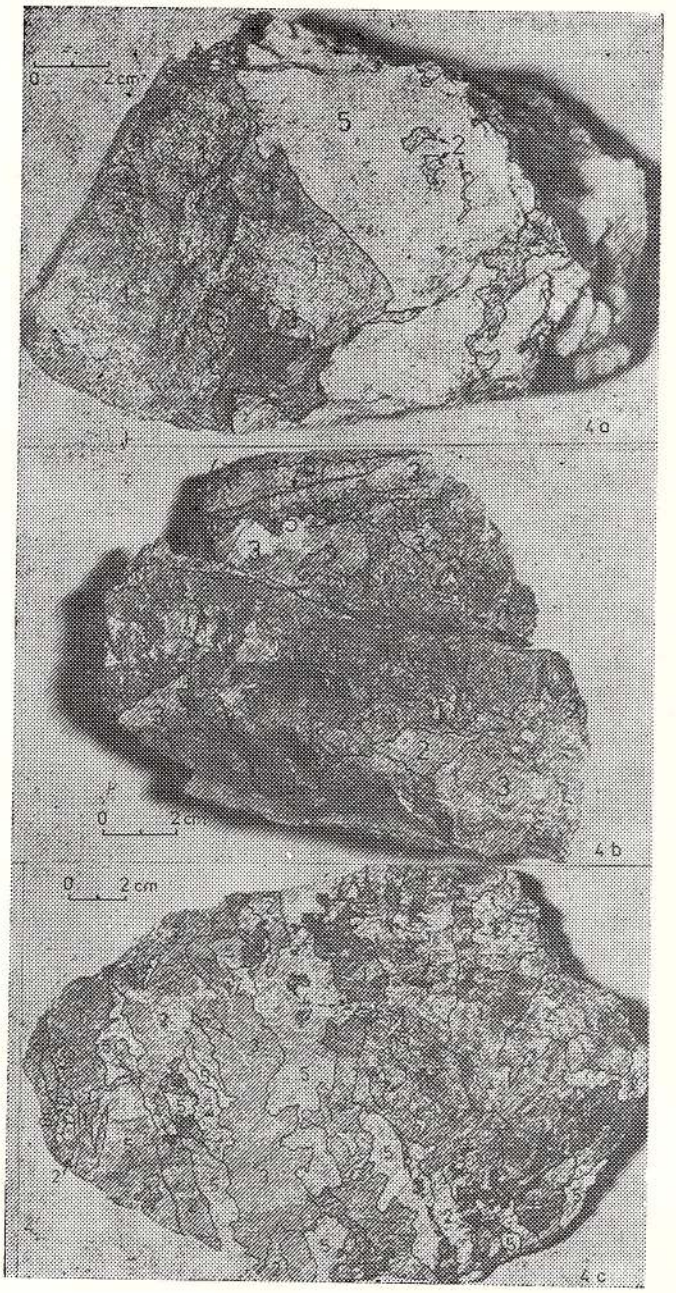


Fig 4. — Associations caractéristiques des minéraux dans la minéralisation associée au massif alcalin de Ditrău — secteur Jalotca.
4 a, 4 b : 1, ilménite ; 2, pyrite ; 3, monasite ; 4, orthite ; 5, carbonates ; 6, chlorites. 4 c : 1, ilménite ; 2, pyrite ; 3, carbonates ; 4, chlorites ; 5, blende ; 6, molybdénite.

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téristiques de minéraux qui constituent des paragenèses distinctes : (1) sphène-apatite-magnétite-titanomagnétite-ilménite-rutile-zircon ; (2) monasite-rutile-pyrite-carbonates$_1$ ± (albite) ; (3) xénotime-rutile-anatase-pyrite-calcite-sidérite ; (4) monasite-bastnäsite-parisite ; (5) rutile-ilménite (± ilménorutile-ilménite pyrophanitique ± hématite ± magnétite)-carbonates$_1$; (6) monasite-orthite (± orthite métamictique)-zéophyllite-carbonates$_1$; (7) carbonates$_2$-quartz-zéophyllite-chlorite (polytype IIb)-lépidolite-hydromicas (polytype 1M) ; (8) pyrite-blende-pyrrhotine-chalcopyrite (± chalcopyrrhotite ± mackinawite ± cubanite)-galène (± bismuthine ± josseïte ± tetradymite) ± or-carbonates$_3$ (dolomite-calcite ± manganocalcite-sidérite) ; (9) molybdénite (polytype 2H)-carbonates$_4$-chlorite ; (10) goethite-lépidocrocite-covelline-cuivre natif-malachite-azurite.

6. Considérations minéralogénétiques

La minéralisation associée au massif alcalin de Ditrău est le résultat d'une série de processus complexes et d'une longue évolution dans le temps au cours de laquelle on peut distinguer plusieurs stades de développements, notamment :

— le stade magmatique, pendant lequel ont cristallisé les minéraux de la paragenèse 1) : sphène-apatite-magnétite-titanomagnétite-ilménite-rutile-zircon. Ces minéraux constituent la fraction des minéraux accessoires des roches du complexe syénitique et du complexe dioritique-hornblenditique. Ils sont intimement associés (maintes fois sous forme d'inclusions ou d'exsolutions) aux minéraux essentiels des roches : feldspaths, feldspathoïdes, amphiboles, pyroxènes, micas. Ils sont présents en un taux assez élevé pouvant dépasser 10% du volume de la roche, tout spécialement dans le cas de mafites du secteur septentrional ;

— le stade pneumatolytique pendant lequel se sont formées les paragenèses 2-6 constituées de minéraux des T.R. (phosphates, carbonates, oxydes, silicates) et d'oxydes de Ti, Fe, Th, Nb. Ces minéraux s'associent tout spécialement des carbonates et de l'albite. Au cours de ce stade on constate une spécialisation métallogénique entre le compartiment septentrional caractérisé par la présence de quelques T.R. à poids atomique faible — cérium (paragenèse à monazite) et le compartiment central-méridional à T.R. à poids atomique lourd — yttrium (paragenèse à xénotime) associés au Th ;

— le stade hydrothermal pendant lequel s'accumulent les paragenèses 8-9 constituées de sulfures dont le poids atomique le plus élevé revient à la molybdénite. La transition du stade pneumatolytique (carbonatique-albitique) à celui hydrothermal est marquée par l'association (7) constituée de phyllosilicates-carbonates-quartz qui empiètent aussi sur le domaine hydrothermal. La présence du bismuth et des inclusions polyphasées d'exsolutions dans la blende (chalcopyrite-pyrrhotite-mackinawite-cubanite) dénote une température de formation élevée (méso-hypothermale) et un refroidissement rapide avec la conservation des phases métastables (cubanite, chalcopyrrhotite).

Localement, aux associations susmentionnées se superposent la paragenèse (10) : goethite-hydrogoethite-lépidocrocite-covelline-cuivre natif-azurite-malachite ± molybdite, à caractère supergène.

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Les caractères minéralogiques de la minéralisation formée pendant les principaux stades (pneumatolytique et hydrothermal) dénotent sa formation en séquences. Celles-ci sont mises en évidence par la présence de plusieurs générations de minéraux (carbonates, orthite, pyrite, magnétite) et par l'existence des discontinuités marquées par les étapes de bréchification. Le caractère prédominant thioïdique ou oxydique de la minéralisation pendant certaines périodes révèle la modification en temps des rapports de la fugacité du O_2 et S.

La minéralisation des T.R. : Nb-Ti(± Th) peut être considérée comme affiliée, au point de vue génétique, aux roches alcalines, les observations minéralogiques et géochimiques mettant en évidence une voie géochimique commune des T.R. avec le Ca et du Nb avec le Ti. La complexité minéralogique et quelques incompatibilités minéralogiques par rapport aux paragenèses décrites dans d'autres massifs alcalins connus (Vlasov, 1968 ; Sorensen, 1974) pourraient être expliquées par le caractère partiellement agpaïtique que, sur un fond prédominant miaskitique, a présenté pendant quelques moments la paragenèse des roches alcalines de Ditrău (Anastasiu, Constantinescu, 1978, 1981). Ainsi le Nb et le Ta qui dans la zone méridionale apparaissent sous forme d'éléments majeurs dans le pyrochlore, bastnäsite, niobite (columbite) associés aux roches alcalines miaskitiques dénotent, dans la zone septentrionale, le caractère d'une différenciation agpaïtique, apparaissant comme des substitutions izomorphes du Ti dans l'ilménite et l'ilménorutile. En ce qui concerne la minéralisation de Mo, selon toute vraisemblance, elle n'est pas associée au point de vue génétique aux roches foïdiques ou ultrabasiques. Sa localisation dans le complexe des roches mafitiques de la zone septentrionale suggère le rôle „d'écran" ou de „milieu catalytique" qu'elle remplit pour la précipitation des solutions hydrothermales pendant un moment ultérieur à la formation de la minéralisation des T.R.-Nb-Ti.

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FLUID INCLUSION STUDIES ON THE Pb-Zn-Cu ORE DEPOSIT AT GYÖNGYÖSOROSZI, NORTH HUNGARY (I. OUTCROPS) [1]

BY

ISTVÁN GATTER [2]

Introduction

Ore-geological application of the gaseous-liquid ("fluid") inclusion studies was frequent in the late sixties ; the establishment of cryoscopic technics as well as the adoption of some other methods (mass spectrometry, gas chromatography, etc.) provided fundamental data for ore geology. Especially the conditions of the formation of the stratiform sulphide and porphyry copper deposits have been successfully elucidated by means of inclusion studies.

The examinations are double-aimed : I. contribution to the basic theoretical data on the conditions of the formation of polymetallic deposits, and on the basis of the theoretical results of comparative studies between the Carpathian Basin and other similar deposits ; II. detailed mapping proceeding in the area could be more effective taking into consideration the results obtained.

Ore-geological setting of the area

Outcrops existing in a Miocene, so-called middle ("variable") andesite pyroclastic series have already been known for approximately 300 years in West Mátra at Gyöngyösoroszi (Fig. 1). Sztrokay (1939), Rozlozsnik (1942), Vidacs (1961), Koch (1966), Siklóssy (1977) described the vein-like hydrothermal Pb-Zn-Cu deposit. The ore bearing mineralization is of polyascendent nature. Sulfide minerals are

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September 8—13, 1981, Bucharest, Romania.

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accompanied mainly by quartz-chalcedony, subordinately barite-calcite. Rock alterations (propylisation, silicification, siallitization) can be studied in the environment of the dykes.



Fig. 1. — Location of the examined area.

Fluid inclusion studies

Microscopic observations

Microscopic observations of doubly-polished sections made from samples of the outcrops can be summarized as follows : Three optically distinct varieties of quartz-chalcedony can be separated.

I. *Chalcedony* — needle-like-radial aggregates, aggregate polarization is characteristic. Gaseous-liquid inclusions between the fibres are subordinate or even absent. Samples are unsuited for further examinations.

II. *Chalcedony-quartz "transition" phase* — larger, xenomorph fields accumulate to fine-fibrous aggregates continuously turning into quartz-strips of wave extinction, turbid, rich in small inclusions and indistinct outlines.

III. *Quartz* — aggregates of idiomorph-xenomorph granules only seldom with optical anomalies. Most of them contain fluid inclusions.

Biphase inclusions in the granules can be found sporadically, along growth zones, on the former healing fractures showing varied forms. They are 5-150/u by size, contain 10-30 volume per cent gaseous phase at room temperature. In places some single-phase gaseous inclusions of the same age as the above mentioned can be recognized, often negative crystal shaped ones. Biphase inclusions could be gradually transformed into single-phase ones by phase-proportion transition in consequence of boiling. That is why the interpretation of the data needs intense caution.

10-20 volume per cent bitumen as dark drops besides the gaseous phase can be identified in some secondary sheet-inclusions existing along the fractures. The presence of hydrocarbons has also been proved by gas chromatography.

Daughter minerals in the inclusions provide important data concerning composition of ore forming fluids. Some solid components examined : opaque granules (small), calcite, barite, needle-like not identified crystallites.

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Phase Transition Studies

Phase changes in fluid inclusions (homogenization, cryoscopic phenomena, etc.) have been measured on Chaixmeca microscope-stage from —180 to 600 °C (Poty et al., 1978).

Homogenization Measurements

Biphase fluid inclusions with low salinities formed in an open system homogenize at a temperature (T_H) approximately identical with the minimal mineralization temperature in the hydrothermal range, as proved by artificial crystal-growing experiments (Khetchikov, 1973).

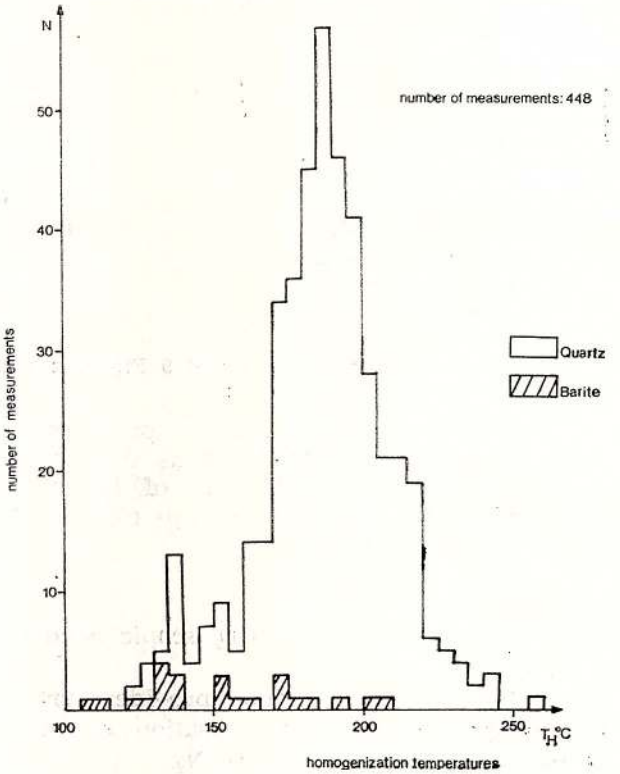


Fig. 2. — Histogram of homogenization temperatures (T_H) of fluid inclusions.

All homogenizations occurred into the liquid phase when measured primary and pseudosecondary inclusions 4 types of T_H diagrams were obtained :

I. Sharp maximum between 180-200 °C (Pelyhes, István, Katalin, etc. dykes)

II. Wide maximums between 170-240 °C (Hidegkut, Aranybánya-bérc, etc. dykes)

III. Wide maximums between 160-210 °C (Kistölgyesbérc, Béla, etc. dykes)

IV. Maximum at 140 °C (Hársashegy dyke)

The identification of dykes becomes easier due to the fact that the samples from different parts of a dyke show similar T_H diagram.

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The summarized T_H diagram can be seen in Figure 2, with a two-peak profile (135-155 °C, 180—220 °C), showing that barite was formed at a lower temperature than quartz. The present surface predominantly indicates a paleothermic level of 180-220 °C.

1. Károly
2. Aranybányabérc N.
3. Aranybányabérc I-II.
4. Péter-Pál
5. Malombérc
6. Béke
7. Arany-Péter
8. Kiskut
9. Jávoroskut
10. Hikkszél
11. Hidegkut I-II.
12. Nagytölgyesbérc
13. Bányabérci I-II.
14. Mátraszentimre
15. Gubolaház
16. Bagolyirtás
17. Pelyhes
18. Béla
19. Katalin
20. Kistölgyesbérc
21. Hársashegy
22. Vőröskő
23. Szákacsurgó
24. no. 1600
25. Keresztesbérc
26. István
27. Asztagkő (geyser quartzite with barite)

Fig. 3. — Appendix for 4 and 9 Figures : (name of ore-bearing veins)

Data on homogenization projected into the area examined (Fig. 3.4) show that the nucleus in the central part of higher temperature is followed by zones of lower temperature with a local temperature rise, farther outcrops can be fitted in this system (Hársashegy, Asztagkő).

Cryoscopic Studies

The cryoscopic method provides further valuable information on the composition and concentration of the ore forming fluids. The samples were frozen by cooled N_2.

Because of overcooling, biphase inclusions solidified deeply below the freezing-point to fine-grained, slightly transparent aggregates (T_0). T_0 was measured on the average —40 — —50°C.

The first melting point (T_1) observed slowly warming up the system by the room temperature, that is the eutectic point is characteristic of the composition (Borishenko, 1977). Two main solution systems can be distinguished in Figure 5 :

I. Alkaline sulfate-carbonate system (—1 — —6°C) ;

II/a) NaCl containing system (—19 — — 22°C) ;

II/b) NaCl + (Mg-Ca chlorides) containing system (—24 — —55°C).

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According to the diagram barite has been crystallized from the Ca-Mg system. This observation is in accordance with the data of literature (Ucsamejsvili, Hitarov, 1965).

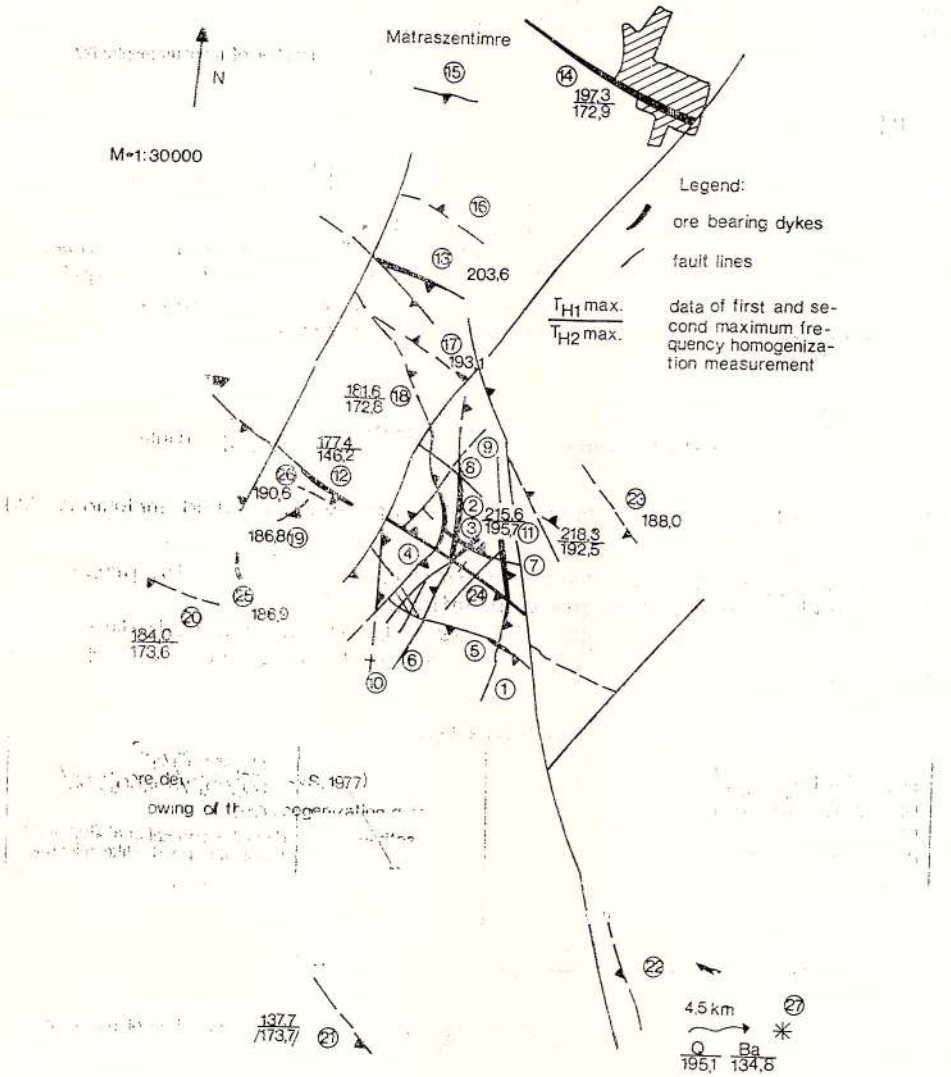


Fig. 4. — Sketch map of Gyöngyösoroszi ore deposits (Skilóssy, 1977) showing the homogenization data of fluid inclusions of quartzes and barites.

The genetic scheme of the inclusion can be brought into connection with the solution systems as well as the different formations examined (Fig. 6). The chemical composition of the vein-like quartz forming fluids is different from that of the apophyses, grown-up crystals. Daughter minerals are also sharply distinct in the two main types

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of the solution systems. This way of separating the genetically different quartz-containing formations becomes possible.

1—2 volumes per cent carbon dioxide condensate is sometimes observed at freezing. It forms a thin reaction rim at the solid-gaseous phase surface, then its contour turns pale.

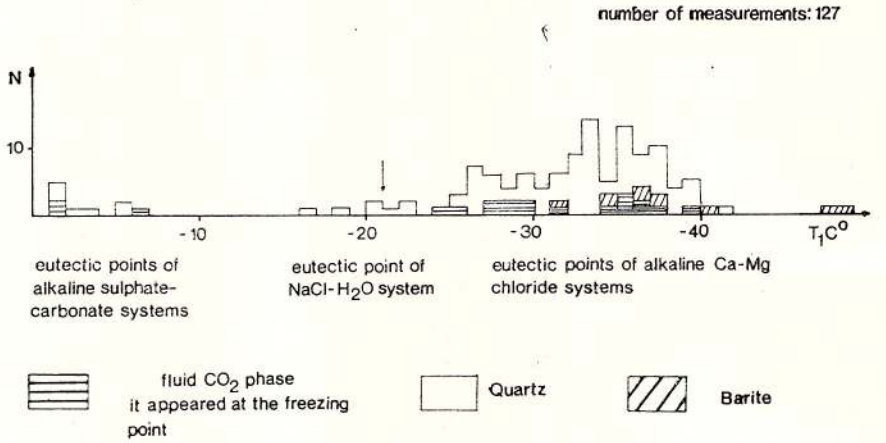


Fig. 5. — Histogram of first melting point temperatures of fluid inclusions (T_1).

Both types of solutions are accompained with CO_2. Its presence is also proved by crushing stage examinations.

The final melting point (T_2) depends on the concentration. Concentration expressed in equiv. wt.-per cent NaCl can be calculated

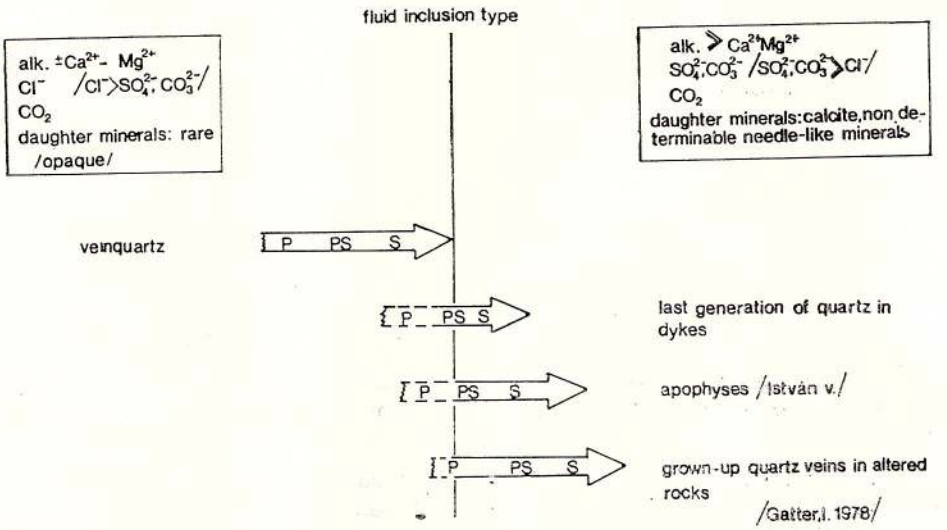


Fig. 6. — Changing of the composition of fluid inclusions on the basis of the freezing data.

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from T_2 (P o t t e r et al., 1978), or read in NaCl-H_2O diagram (R o e d d e r, 1963). Maximum in T_2 diagram (Fig. 7) can be observed at —3.5 — —5°C. Concerning diagram "C" salinity of the inclusions comes about 5-9 equiv. wt.-per cent NaCl. Barite works show considerable deviations; as a consequence of boiling extraordinarily altering concentrations have been left. Maximum, observed at a low concentration, is exhibited by inclusions of low eutectic point fixing deviated conditions (Solution type I).

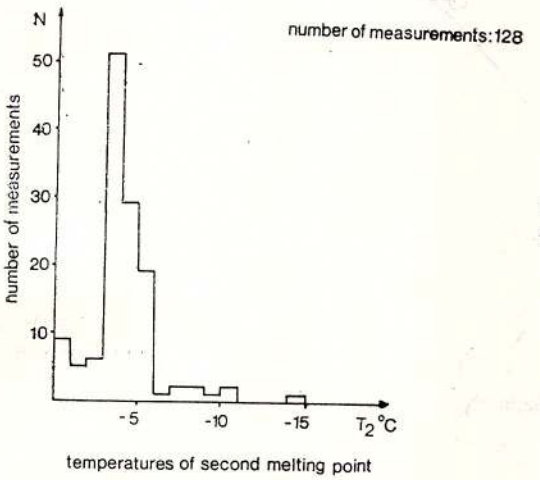


Fig. 7. — Histogram of second melting point temperatures of fluid inclusions (T_2).

Freezing negative crystal shaped gaseous inclusions — besides freezing phenomena of vapour, condensation of some gas (0.1 volume per cent) at —100 — —120°C can be observed, the homogenization point of which was measured at —84 — —86°C.

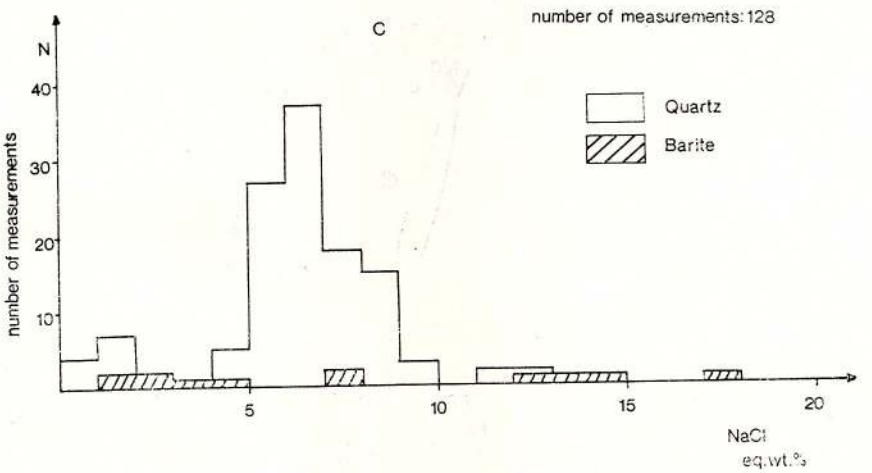


Fig. 8. — Histogram of salinity of fluid inclusions (C).

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Concerning the Zagoruchenko, Zhuralev diagram (1970) this condensate consists of methane (in: Mullis, 1979), density of which is ≈ 0.075 g/cm³.

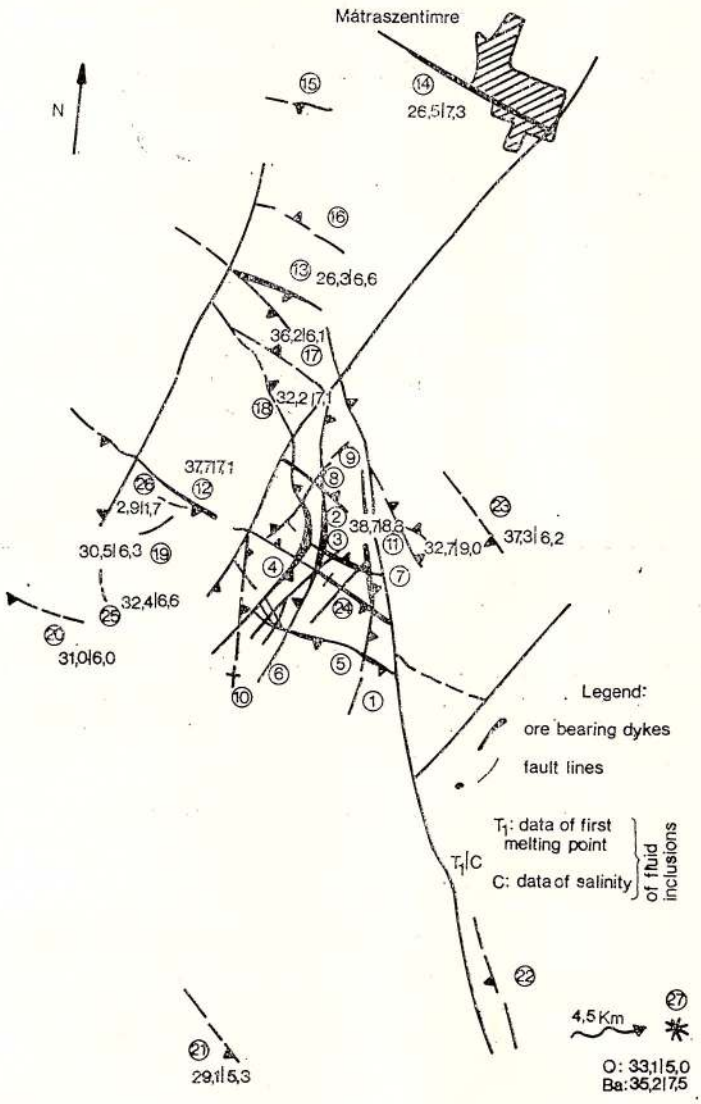


Fig. 9. — Sketch map of Gyöngyösoroszi ore deposits (Siklóssy, 1977) showing the freezing data of fluid inclusions of quartzes and barites.

Bitumen drops observed in some inclusions stiffened at the same time as the fluid phase, with slight contraction. Its melting phenomena can be studied between —9.4 — +7.7°C. CO_2-hydrate of indistinct contour is seldom present in barite samples to +2.4°C.

The cryoscopic data, put down on the sketch map (Fig. 8, 9) show a zonal order similar to the T_H data. The highest average concentration

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and the lowest euthectic point correspond to the central part. Only apophyses of the István dyke have data quite different from the other results.

The densities of the ore forming fluids can be estimated from the cryoscopic-homogenization data according to Haas (1971), Copeland et al. (1953), Urusova (1975), etc.

The samples examined have density of 0.88—0.98 g/cm^3. The deepest level where vapour-bubble formation possibly occurred, can be established in a boiled, hydrothermal system according to Haas (1971). The depth of formation (which corresponds to the possible maximum denudation) as well as the vapour pressure of the system can be established concerning T_H and C data. The boiled systems are proved with the maximum denudation of 90—260 m, and the vapour pressure of 10-25 bar.

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ON THE MINERALOGY AND GEOCHEMISTRY OF SOME STRATIFORM SULPHIDE DEPOSITS IN THE SPIŠSKO-GEMERSKÉ RUDOHORIE MOUNTAINS [1]

BY

JÁN HURNÝ [2]

The stratiform sulphide ore deposits and occurrences are found in the Gelnica Series situated in the eastern part of the Spišsko-gemerské rudohorie Mts. This ore deposit type has been most intensively explored in the Smolnik area (I l a v s k ý, 1956, 1964) being the only exploited one in the whole Spišsko-gemerské rudohorie Mts region, while further

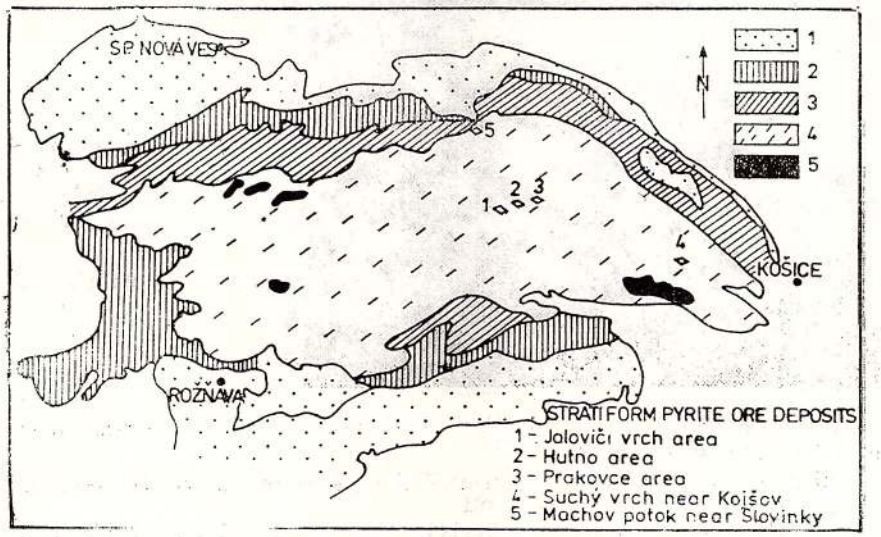


Fig. 1. — Schematic map of the Spišsko-Gemerské Rudohorie Mts. 1, Mesozoic; 2, Carboniferous, Permian; 3, Rakovec Series; 4, Gelnica Series; 5, granites.

occurrences in the Mnišek n/ Hnilcom-Prakovce area as well as near Kojšov and close to Slovinky have been investigated for orientation only (Fig. 1).

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September 8—13, 1981, Bucharest, Romania.

[2] Czechoslovakia.

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The criteria of the localization of these deposits were recently studied in detail by Grecula (1972) and Grecula et al. (1975), who consider the geological-lithological criterium as the most important for the explanation of the lithostratigraphic evolution, temporal position of volcanism in the frame of this evolution and of the tectonic pattern

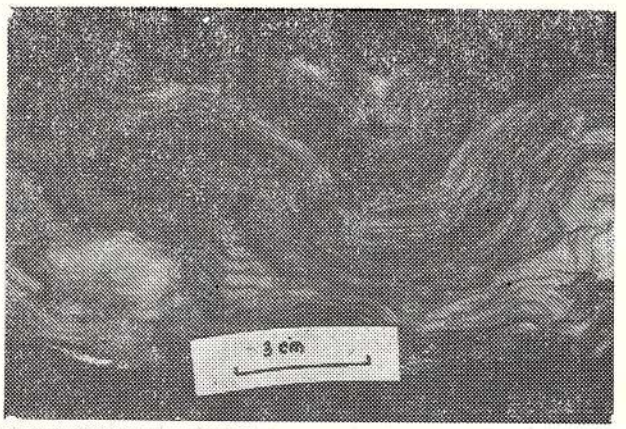


Fig. 2. — Bedded-folded and banded structures of pyrite-sphalerite-galena-chalcopyrite association in chlorite quartzite. Mníšek n/Hnilcom, photo K. Hegenbart.

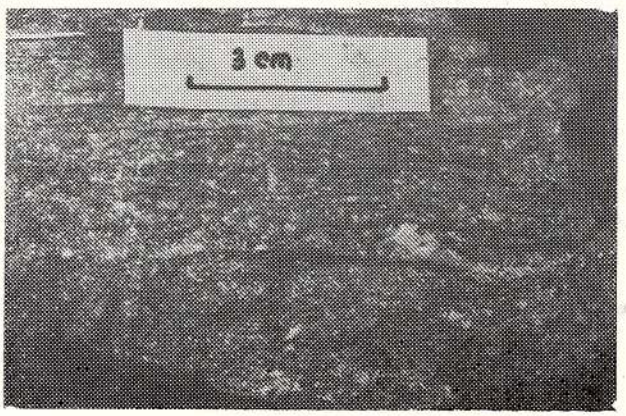


Fig. 3. — Gradation structures with mineral association change in vertical direction, in the frame of ore rhythm. Mníšek n/Hnilcom, photo K. Hegenbart.

as well. According to Grecula two producing ore bearing horizons are distinguishable there :

a) the lower horizon overlying the graphitic phyllite beds, at the base of the volcanogene beds, and

b) the upper horizon underlying the acid volcanic rocks (porphyroids) in the middle of the volcanogene beds.

The ore occurrences of Jaloviči vrch, Hutná dolina, Suchý vrch near Kojšov and Machov potok close to Slovinky, as well as the upper part of the Prakovce occurrence are situated in the upper ore-bearing horizon. They have all proved to be (directly and indirectly) related to basic volcanism horizons.

On the basis of their compositions, the stratiform sulphide deposits may be referred to pyrite-polymetallic (Mníšek nad Hnilcom, Hutno, Prakovce and Kojšov) and pyrite-chalcopyrite (Prakovce, Slovinky) formations. The mineralization is characterized by bedded, banded and

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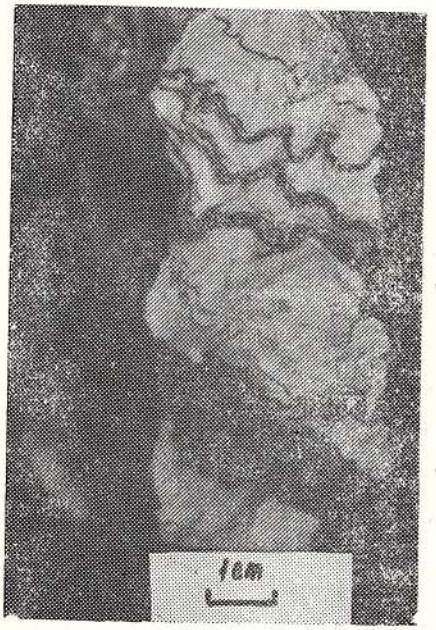


Fig. 4. — Bedded-folded structures with ore laminae (pyrite-sphalerite-chalcopyrite association) and rock intercalation (albite-chlorite quartzite) alternation. Mníšek n/Hnilcom, photo K. Hegenbart.

disseminated structures (Figs. 2, 3, 4, 5). Pyrite is considered as the predominant ore mineral being accompanied by sphalerite, chalcopyrite and galena. In terms of the different quantitative ratios of these minerals present in ore laminae, the following associations have been distinguished : pyrite, pyrite-chalcopyrite-sphalerite, pyrite-sphalerite-

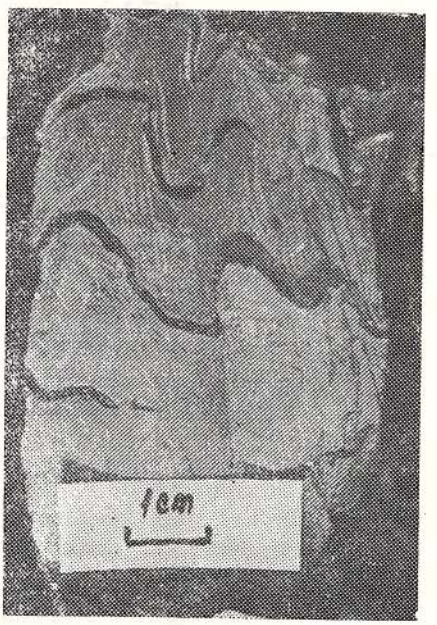


Fig. 5. — Bedded-folded structures composed of pyrite-sphalerite-chalcopyrite association and of chlorite-sericite phyllite. Mníšek n/Hnilcom, photo K. Hegenbart.

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chalcopyrite-galena, pyrite-sphalerite-galena-chalcopyrite, pyrite-sphalerite, pyrite-chalcopyrite and pyrite-arsenopyrite. The laminae/and band-like mineralization is characterized by a relatively stable composition in horizontal direction. In vertical direction (towards schistosity), it is rather variable. In the rocks of keratophyre composition, a stockwork-impregnation type mineralization has been noticed representing sub-volcanic mineralization. Some minerals are related to quartz metamorphic veins, which are, with regard to metamorphic differentiation, more abundant in mineral varieties representing, however, only a negligible part of the mineralization from the quantitative point of view.

The ore bearing rocks are of tuff-quartzite nature characterized by rhythmic alternation of centimetric laminae of quartz-psammite and diabase-pyroclastic composition (mainly chlorite, sericite, quartz, less albite, carbonates, accessory zircon, rutile, tourmaline and apatite). In some cases, rocks of keratophyre composition have been also observed having orthophyre texture and formed by fine-grained albite mass with a small amount of quartz. In the Slovinky area, their composition corresponds to that of porphyroids.

Description of Minerals

The minerals described below have been stated on the basis of microscopic study, chemical composition, identification and microprobe analyses as well (Tab.).

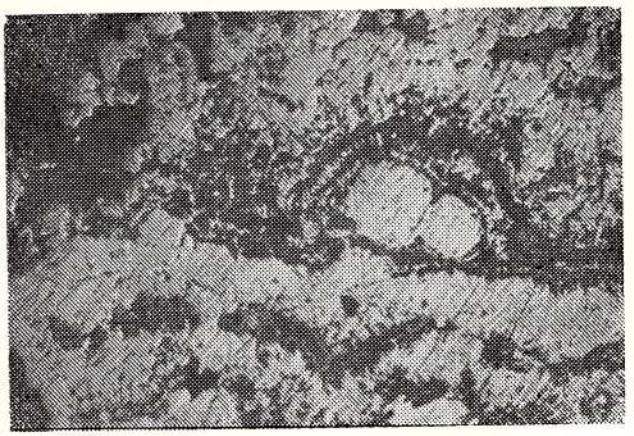


Fig. 6. — Pyrite globules in the middle of crustal and botryoidal aggregates. Mníšek n/ Hnilcom, polished section, nicols parallel, ×250, photo author.

Pyrite is the most common and widespread mineral in all the occurrences studied. It is present in massive accumulations, laminae, bands and aggregates or is disseminated in ore-bearing rocks. Pyrite forms hexahedrons, in rare cases pentagonal dodecahedrons or irregular grains often of colloform nature. On the basis of morphological dif-

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TABLE

Mineral composition of the stratiform ore deposits of pyrite-polymetallic formation

	Mníšek n/Hnilcom	Hutno	Prakovce	Kojšov	Slovinsky
Pyrite	+++	+++	+++	+++	+++
Chalcopyrite	++	++	++	++	+++
Sphalerite	++	++	++	++	+
Galena	++	++	++	++	
Arsenopyrite	+	+	+	+	+
Marcasite	+	+	+	+	+
Tetrahedrite	+	+	+	+	
Pyrrhotite	+	+			+
Cubanite	+	+			
Ullmanite	+				
Glaucodote	+				
Bournonite	+	+	+	+	
Boulangerite	+				
Jamesonite				+	
Cosalite	+				
Bi-mineral (?)	+				+ [2]
Dyscrasite	+				
Native gold	+				
Cobaltite (?)	+ [1]				+ [2]
Quartz	+++	+++	+++	+++	+++
Sericite	+++	++	+++	+++	++
Albite	+++	+++	+++	+++	++
Chlorite	+++	++	+++	+++	+++
Tourmaline	+	+			
Siderite	+	+	+	+	+
Fe-dolomite-ankerite	+	+	+		+
Rutile	+	+	+	+	+
Apatite	+				
Barite	+				

ferences, globules and globular aggregates (Figs. 6, 7, 8) as well as spherulites, colloform aggregates, atoll aggregates, idiomorphic, idioblastic, glomeroblastic, xenoblastic and poikiloblastic grains (Figs. 9, 10) or cataclased (Fig. 11) and some other irregular ones may be distinguished there. Skeleton growth, zonal growth and sulphide accumulation in pressure shadows is also observed (Fig. 12).

Chalcopyrite is the second most widespread sulphide mineral. It forms allotriomorphically limited granular aggregates, veinlets and accumulations and is closely associated with sphalerite being always younger in comparison with this. Chalcopyrite is referred to mobile sulphides, that is why it has been more conspicuously affected by metamorphic agents. It is present in ore-bearing rocks, in veinlets to be

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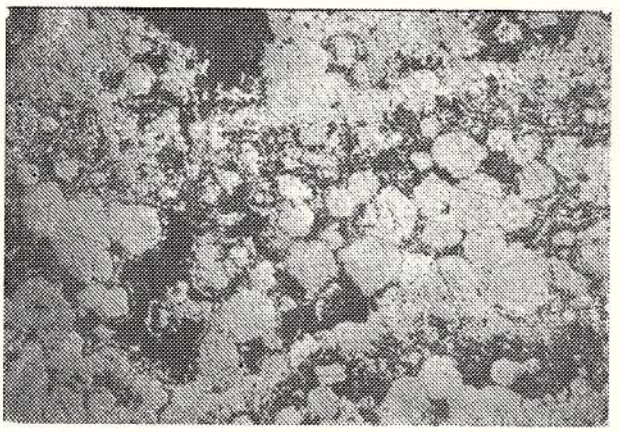


Fig. 7. — Colloform textures of pyrite formed by globules, globular and crustal aggregates. Mníšek n/ Hnilcom, polished section, nicols parallel, ×160, photo author.

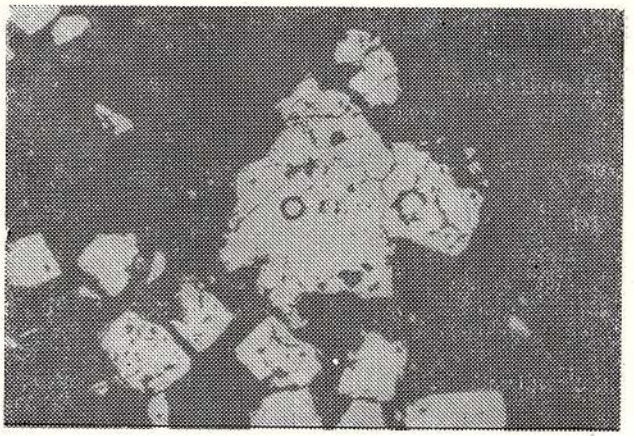


Fig. 8. — Pyrite globules in pyrite metacrystals. Hutno, polished section, nicols parallel, ×20, photo author.

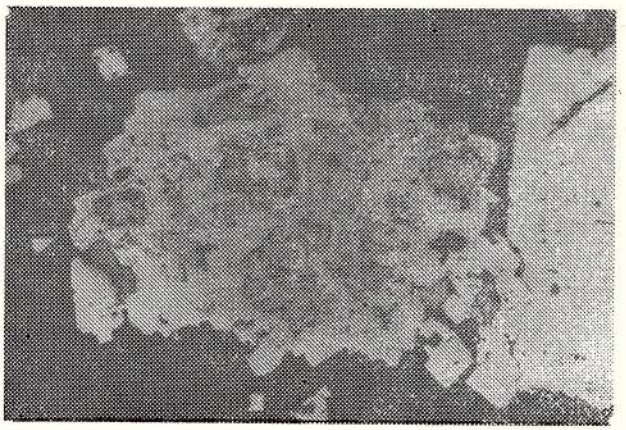


Fig. 9. — Texture of "idioblastic net" type, where chalcopyrite is enclosed by pyrite porphyroblast. Hutno, polished section, nicols parallel, ×50, photo author.

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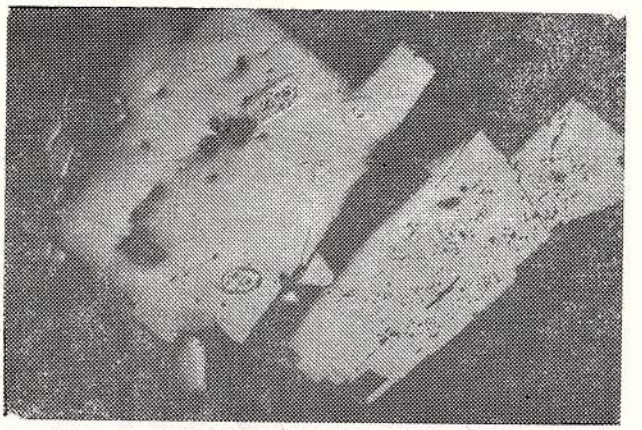


Fig. 10. — Poikiloblastic texture formed by pyrite II, porphyroblast enclosing pyrite I. Mníšek n/Hnilcom, polished section, nicols parallel, ×160, photo author.

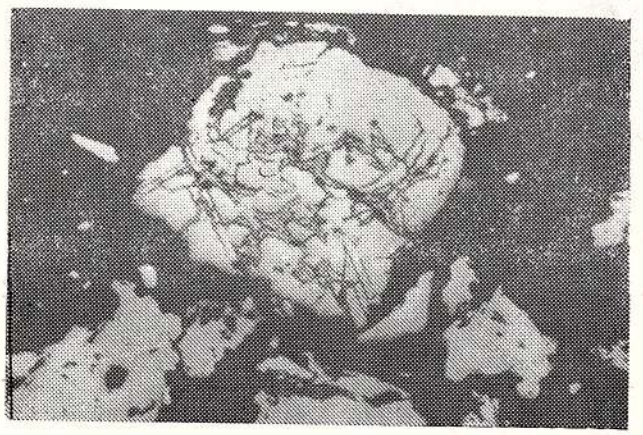


Fig. 11. — Cataclased pyrite grain filled with chalcopyrite. Prakovce, polished section, nicols parallel, ×50, photo author.

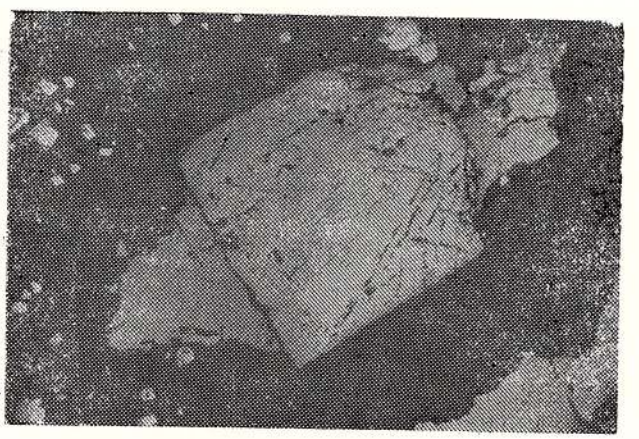


Fig. 12. — Pressure shadows of chalcopyrite around a pyrite grain. Prakovce, polished section, nicols parallel, ×20, photo author.

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found on the Alpine cleavage planes and in the metamorphic quartz veins as well. In rare cases, it forms emulsion-like textures passing somewhere, however, into corrosive ones (Fig. 13).

Sphalerite is closely associated with chalcopyrite and is considered as a rather widespread mineral; only near Slovinky it is rare. It is

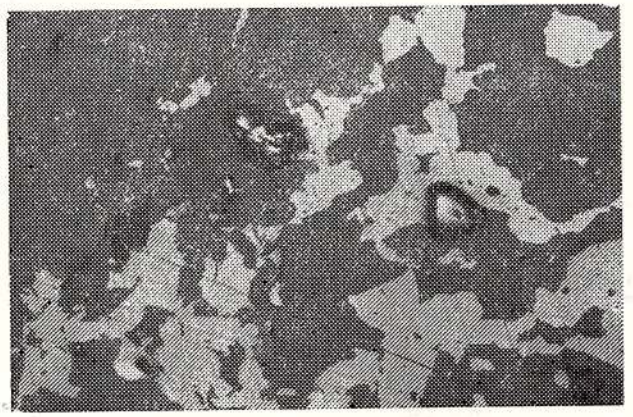


Fig. 13. — Sphalerite-chalcopyrite intergrowth with pyrite inclusions. Mníšek n/ Hnilcom, polished section, nicols parallel, ×200, photo author.

present mainly in the ore-bearing rocks, in the ore veins in small amounts only. It forms irregularly limited grains and aggregates and is often replaced by chalcopyrite, galena and tetrahedrite. Sphalerite is of dark brown to brown colour (Fe content of 4.60 % to 5.70 %) and comprises minute inclusions of chalcopyrite.

Galena is present as an accompanying mineral mainly in the ore-bearing rocks. Large accumulations (up to 5 cm) have been observed in the metamorphic quartz veins. The grain shape is irregular, sometimes it forms rims and veinlets.

Arsenopyrite is present as disseminated or as small bands in the rock. It is idiomorphically limited and surrounded by sulphides being often cataclased. Selective corrosion of the grains is a common feature there.

Marcasite is relatively rare being present in the places of colloform texture occurence only. Originally more widespread, it has been altered into pyrite probably due to metamorphic processes.

Tetrahedrite does not form conspicuous concentrations in the mineralization, but it may be seen also macroscopically. It is present as rims and intergrowths with chalcopyrite containing dyscrasite segregates. According to its chemical composition, it is a ferro-zincous tetrahedrite.

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Pyrrhotite is very rare and may be observed only microscopically (grain size 10-200 μm) in association with chalcopyrite, pyrite and sphalerite. It is present both in ore-bearing rocks and in metamorphic quartz veins. In addition to it, some characteristic textures of "porous" pyrite with marcasite have been noticed with parallel grain arrangement representing pseudomorphs of pyrrhotite.

Cubanite has been observed in the chalcopyrite inclusions found in sphalerite. It may occur in ore-bearing rocks and metamorphic quartz veins as well. Cubanite forms lamellae or irregular grains of 5 to 10 μm (variable length and thickness) in chalcopyrite not passing beyond the chalcopyrite grain boundary.

Ullmanite is present in metamorphic quartz veins in the Mníšek area being associated with chalcopyrite, sphalerite and galena. It forms isolated grains (1-3 mm), irregular limitations or aggregates.

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Glaucodote is associated with pyrite in the Mníšek Lense area. Its grain size varies between 5 and 20 μm and has oval limitation.

Bournonite is referred to rare minerals of this mineralization type and except for the Slovinky area, it has been noticed in all the subject occurrences. It forms independent grains up to 0.5 mm large, rims or irregular aggregates on the tetrahedrite periphery usually replacing this. Bournonite may be frequently observed at the contact of galena with tetrahedrite.

Boulangerite has been somewhere observed in metamorphic quartz veins, at the contact of quartz with tetrahedrite. It forms fine needles (1 mm long and 0.1 mm thick) either in quartz or is rimming tetrahedrite, in rare cases also penetrating into this.

Jamesonite has been noticed as a very rare mineral in the occurrence situated near Kojšov. It forms needles (up to 50 μm) in quartz being surrounded and in some places also replaced by chalcopyrite.

Cosalite is associated with chalcopyrite and pyrite occurring in minute metamorphic quartz veins near Mníšek in the form of needles up to 2 mm long. It may be seen also microscopically.

Dyscrasite has been found as separate grains (up to 20 μm) in metamorphic quartz veins at the contact of tetrahedrite with chalcopyrite. This mineral is considered as the result of chalcopyrite and tetrahedrite interreaction having been formed by Ag and Sb segregation.

Native gold is present in some tetrahedrite grains where it forms minor yellow inclusions (grain size up to 5 μm) of very high reflection.

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Quartz, sericite, albite and chlorite have been found as main gangue minerals ; less tourmaline, siderite, ankerite, rutile, apatite and barite are present there.

Geochemistry of Minerals

Observation of minor and rare elements was an integral and very significant part of the subject study. These are present in the mineralization either as admixtures in sulphides or as separate mineral inclusions. By using quantitative and qualitative analyses, the following elements have been found : Au, Ag, Bi, As, Sb, Ni, Co, Cd, In, Ga, Tl and Se. Gold has been noticed as separate grains of native gold and as admixture in pyrite (0.18-2.40 g/t), arsenopyrite (6.3 g/t) and tetrahedrite (n. 10^{-3} %). Silver is present as a special mineral — dyscrasite, but galena (0.200-0.052%) and tetrahedrite (0.003-2.115%) are also considered to be important Ag concentrators, less chalcopyrite (1.1-830 g/t) and sphalerite (0.0032-0.011 %). Bi is a stable ore accompanying element being present as cosalite, but important concentrations are also found in galena (0.007-0.050%) and tetrahedrite (0.01%) Cd concentrations are related to sphalerite (1 000-2 000 g/t), while indium is associated with chalcopyrite, sphalerite and pyrite as well (0.01-0.001%). Interesting gallium concentrations are present in sphalerite (0.021-0.027 %). An element associated with pyrite (4-65 g/t) is thallium typical for pyrite deposits. The highest amounts of selenium being typical for this mineralization, too, have been noticed in galena (411 g/t), then in pyrite (2-97 g/t), sphalerite (23 g/t), chalcopyrite (46-48 g/t) and arsenopyrite (21 g/t).

It has been found that zoning reflected the changes taking place in the mineralization. The most remarkable changes have been noticed across the ore body, in vertical direction. In the lower barren zone, pyrite and barite predominate, the latter passing towards the hanging-wall into a pyrite and pyrite-chalcopyrite zone. The pyrite-sphalerite-galena (± chalcopyrite) zone is best developed in the uppermost part of this sequence. Towards the periphery, the central pyrite zone with galena, sphalerite and chalcopyrite is passing in horizontal direction into pyrite-chalcopyrite and pyrite-barite zone.

In vertical direction, very important changes of mineral associations have been observed in the frame of ore rhythm, being manifested by bedding gradation. In the lower part of this rhythm, pyrite-arsenopyrite association is developed passing upwards into pyrite-chalcopyrite, pyrite-chalcopyrite-sphalerite and sphalerite-galena-pyrite associations. There is a direct vertical zoning involved of regressive order (Rundkvist, Neženskij, 1975) typical of conformable layers.

From the above mentioned data it follows that the subject deposits are the results of the action of paleovolcanic gas-hydrothermal activity connected with the volcanism of Caledonian or Caledonian-Early Hercynian geosyncline respectively. The predominant part of minerals originated in sedimentary-hydrothermal stage (exhalation-sedimentary and hydrothermal-metasomatic facies). In the course of the meta-

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morphic stage, the material accumulated in such a way has been reworked and the structural reconstruction of mineralization took place. The final stage of mineralization is the hydrothermal-remobilization stage characterized by conformable and cross quartz vein, and secretion lense formation as well.

QUESTIONS

T. Todorov: Have you any data about the concentration of gold in pyrite and other minerals, and about the concentration of silver and mercury in tetrahedrite ?

Answer: a) Au in pyrite-0.18-2.40 g/t ; in arsenopyrite-6.3 g/t, in tetrahedrite-0.001 g/t. b) Hg has not been found in tetrahedrite. Ag in tetrahedrite-2.115-0.003 %. In tetrahedrite there are also Fe and Zn.

G. Udubaşa: Did you observe any geochemical differences between the first and the second pyrite generations ?

Answer: Pyrite of the first and of the second generations was mentioned in a study of ore textures and structures.

S. Strashimirov: What kind of sulfosalts have you found in these ores and what is their position in the ore forming process ?

Answer: Jamesonite, cosalite, bournonite and boulangerite have been found in these ores.

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BEITRÄGE ZUR KENNTNIS DER GOLDVERTEILUNG IN DER POLYMETALLAGERSTÄTTE VON BAIA DE ARIEŞ [1]

VON

CONSTANTIN LAZĂR [2], ŞERBAN ANASTASE [2]

Einleitung

Im Gebiet von Baia de Arieş sind die kristallinen Schiefer und Kalke der präkambrischen Baia de Arieş-Serie von neogenen andesitischen Gesteinen durchgedrungen (Taf., Abb. 1).

In der von Ambrului und Lacului Tälern begrenzten Zone treten zahlreiche aus andesitischen Gesteinen der Kalkalkalireihe bestehenden subvulkanische und vulkanische Körper auf. Die an biotitführenden Quarz-Amphibolandesite-Mikrodioritporphyre gebundenen polymetallischen Erze liegen in der Nähe der bekannten Goldlagerstätte von Baia de Arieş.

Die polymetallische Vererzung, die vorwiegend einen Pb-Zn-Charakter aufweist, kommt am meisten in aus Explosionsbrekzien bestehenden Körpern vor.

In der polymetallischen Lagerstätte sind folgende Erzmineralien bestimmt worden: Hämatit, Magnetit, Pyrit, Zinkblende, Kupferkies, Bleiglanz, Fahlerze, Alabandin, Pb-Sulfosalze, Antimonglanz und Gold. Diese sind gewöhnlich von Quarz, Karbonaten (Calcit, Dolomit, Ankerit, Manganocalcit, Kutnahorit, Rhodochrosit etc.) und Sericit (Illit) begleitet.

Die Bildung von Skarnmineralien und Eisenoxyden, die bei hohen Temperaturen stattgefunden hat, stellte den Beginn der Vererzung dar. Die Sulfide, die die Hauptparagenesis der Erzlagerstätte bilden, sind während der hydrothermalen Etappe enstanden (Lazăr, Udubaşa, 1965; Lazăr, 1966; Udubaşa, Lazăr, 1968).

Die Bestimmung der Goldgehalte im Nebengestein, im Erz und in den Hauptmineralien aus der polymetallischen Lagerstätte erfolgte nach Neutronenaktivierung-Analysenverfahren. Die vorliegende Arbeit

[1] Vorgetragen am 12. Kongress der Karpato-Balkanischen Geologischen Assoziation, 8—13 September, 1981, Bukarest, Rumänien.

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hat mehr den Charakter vorläufiger Mitteilung, wenn wir die relativ geringe Anzahl der erhaltenen Analysendaten gegenüber der Vielfältigkeit der gestellten Probleme betrachten. In dieser Arbeit wird zum erstenmal über die Goldverteilung in einer Polymetallagerstätte aus Rumänien berichtet.

Die Bestimmungen sind unter folgenden technischen Bedingungen durchgeführt worden : Die Menge des Ausgangsmaterials war verschieden : 100-3000 g (Gesteinsproben und Erzproben) und 1-25 g (Einzelmineralproben). Es wurden auch einige Grossproben (je 25-50 kg) sowie Aufbereitungsproben verwendet. Die analysierten Proben wogen 0,5 g (Gesteins-und Erzproben) bzw. 20-30 mg (Minerale). Das Radionuklid ^{198}Au mit der Halbwertszeit 64,8 Std. und γ-Strahlen 0,412 MeV (Anastase, Cercasov, 1969) wurde durch Aktivierung mit thermischen Neutronen im Reaktor des IFIN-Bucureşti erzeugt. Es folgte danach eine radiochemische Trennung mittels DOWEX-2 Ionenaustauschers. Die radiometrische Messungen erfolgten unter Verwendung einer für Gamma-Spektrometrie anwendbare Anlage (Typ DIDAC-800, Intertechnique). Innere Standards. Die Empfindlichkeit ist 10^{-10} g ; die Genauigkeit der Messungen beträgt ca. $\pm$ 5%.

Insgesamt wurden auf diese Weise 67 Proben analysiert.

Ausser der durch mikroskopische Untersuchung (im Auflicht und Durchlicht) erhaltenen Angaben sind zur Ergänzung der vorliegenden Arbeit auch die Ergebnisse anderer Analysen (nasschemische, atomabsorbtionsspektrometrische und röntgenographische Analyse, Emissionsspektralanalyse usw) benutzt worden (ca. 800 Analysendaten). Wir möchten an dieser Stelle allen denen Dank sagen, die zur Durchführung dieser Arbeit beigetragen haben.

Die Goldverteilung

A) *In Nebengesteinen*

Die in der Lagerstätte auftretenden kristallinen Schiefer weisen höhere Au-Gehalte als andere vergleichbare Schiefer auf (Tab.). Diese Zunahme des Au-Wertes kann möglicherweise auf die hydrothermale Umwandlung der Schiefer zurückgeführt werden. Die wichtigsten Mineralneubildungen sind : Sericit, Quarz und Pyrit. Die hydrothermale Herkunft der Au-Anreicherung stützt sich auf die Bemerkung, dass die goldreichere Schiefer-Probe auch grössere Cu-, Pb-, Zn- und Mn-Werte zeigt. Die Zunahme des Au-Mittelwertes mit stärkerer Hydrothermal-Metamorphose und Pyritisierung hatten schon vorher Nozhkin et al. (1971, vide Schtscherbakow, 1974) an grobklastischen Gesteinen des Jenisseymassivs erkannt.

Die analysierten kristallinen Kalke, die hydrothermal weniger intensiv umgewandelt sind, weisen gewöhnliche Goldgehalte auf (Tab.). Ausser metasomatischen Karbonaten kommen selten auch Sulfide, Quarz, Serizit, Chlorite u.a. vor. Die Zunahme der Metasome ist von einer geringen Au-Anreicherung begleitet.

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TABELLE

Au — Gehalte in Gesteins- Erz-und Mineralarten

Probe	Fundort	Goldgehalt (ppm) Streubereich	$\bar{x}$	N	Au/Ag	Bemerkungen
Quarz-Glimmerschiefer Kristalline Schiefer	Baia de Arieș (PL)	0,0207–0,2611	0,1402 0,0057	2 11	0,176	Hydrothermal umgew. Gesteine, Py, (NA) Schtscherbakow, 1974 (NA)
Kristalline Kalke	Baia de Arieș (PL)	0,0041–0,0075	0,0061	3		Hydrothermal umgew. Gesteine, Py, (NA)
Marmor	Altai (NO-Teil) (UdSSR)	0,0002–0,0003	0,0003	4		Schtscherbakow, 1974 (SA)
Andesite	Baia de Arieș (PL)	0,0513–0,1655	0,1018	4	0,039	Hydrothermal umgew. Gesteine, Py, (NA)
Quarzandesit	Baia de Arieș (GL)	Sp – 0,7				Cochet, 1957
Quarzandesit	Barza-Carpen. (Metaliferi Geb. Rumänien)	0,0015–0,0047	0,0027	3		Propylitisierte Andesite (NA). Udubaşa et al., 1976 unveröff
Verkittungsmaterial der Explosionsbreccie Andesitische Breccie	Baia de Arieș (PL)	0,0554–0,3208	0,1680	4	0,059	Hydrothermal umgew. Gesteine, Py, (NA)
	Zebrac-Mermezeu (Călimani Geb. Rumänien)		0,080			Peltz et al., 1981 (NA)
Polymetallisches Erz	Baia de Arieș (PL)	0,0454–2,2405	0,5485	15	0,004	Einzelproben (NA)
Polymetallisches Erz	Baia de Arieș (PL)	0,2–1,0	0,6167	6	0,24	Aufbereitungsproben (CA)
Pyrit	Baia de Arieș (PL)	0,7778–4,4450	2,6810	8	0,04	Reinheitsgrad mikroskopisch und spektrographisch geprüft, (NA)
Pyrit	Brad (Metaliferi Geb., Rumänien)		0,1			Ramdohr, 1960
Hydrot. subvulk. Pyrit	ČSSR	0,008–0,340	0,136	6		Cambel et al., 1980 (AA)
Zinkblende	Baia de Arieș (PL)	0,0149–0,2210	0,0707	9	0,002	Reinheitsgrad u.d.M. und spektrographisch geprüft (NA)
Zinkblende	Bulgarien	0,0012–4,0863		64		Mintschewa-Stefanowa, Stefanow, 1972 (NA)
Bleiglanz	Baia de Arieș (PL)	0,2192–69,0276	8,3375	10	0,006	Reinheitsgrad u.d.M. und spektrographisch geprüft (NA)
Bleiglanz	Baia de Arieș (PL)	2,5–82		6		,, (SA)
Bleiglanz	Carleton Place, Ont. (Canada)		0,015			Rein. Boyle, 1979
Calcit	Baia de Arieș (PL)	0,0421–0,0696	0,0558	2		Mn-führender Calcit ohne Sulfide (NA)
Calcit			0,00045	1		Schtscherbakow, 1974

Erläuterungen: PL = Polymetallagerstätte; GL = Goldlagerstätte; $\bar{x}$ = arithmetisches Mittel; N = Probenzahl; Py = Pyrit vorhanden; AA = Atomabsorbtionsspektrometrische Analyse; CA = Chemische Analyse (Dokimasie); NA = Neutronenaktivierungs-analyse; SA = Emissions-Spektralanalyse.

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Die wenigen Analysen zeigen, dass die untersuchten Andesite Au-Gehalte enthalten, die höher als diejenigen der vergleichbaren Andesite sind (Tab.). Der auf Grund einer kleinen Probenzahl errechnete Durchschnittswert (0,10 ppm Au) weist auf einen Konzentrazionskoeffizient von ca. 20 mal in bezug auf den Mittelwert der diorit-andesitischen Gesteine hin. Diese erhebliche Anreicherung kann auf die intensive hydrothermale Umwandlung der analysierten Andesite zurückgeführt werden. Die Hauptneubildungen sind : Sericit, Quarz, Karbonate, Chlorite und Sulfide (überwiegend Pyrit). Die Au-Anreicherung in den hydrothermal umgewandelten Gesteinen ist aus der Literatur bekannt (Petrowskaja, 1973 ; Schtscherbakow, 1974).

Bemerkenswert ist eine positive Korrelation Au-S in Andesiten (Taf., Abb. 2). Das stimmt mit der früheren Beobachtung überein, dass starke Au-Anreicherungen nur jene hydrothermal umgewandelten Gesteine zeigen, die zugleich eine Sulfidisierung aufweisen (Schtscherbakow, 1974). Diese Behauptung konnte auch durch die positive Korrelation der Au-Fe Werte in den untersuchten Andesiten gestützt werden (Taf., Abb. 2, 3). Wenn wir die niedrigen Cu-, Pb-, Zn- und As-Werte in Betracht nehmen, ergibt sich daraus, dass der Pyrit in den veränderten Andesiten der Hauptgoldträger sein muss. Der maximale Au-Gehalt wurde in einem stark umgewandelten und pyritisierten Andesit gefunden. Seine chemische Zusammensetzung deutet auf eine Schwefelzufuhr und einen erhöhten Eisengehalt hin.

Die mit dem Magnetscheider gewonnene Probe zeigte einen grösseren Au-Gehalt im Vergleich zum Ausgangsmaterial (weniger veränderter Andesit). Auf diesem Grund kann angenommen werden, dass das Gold zum Teil an Magnetit gebunden ist, wie früher Schtscherbakow (1974) für unveränderte magmatische Gesteine gezeigt hat.

Das Gold weist in den analysierten Andesiten eine positive Korrelation mit den Erzelementen (Pb, Zn, Cu) auf, gegenüber einer negative Korrelation mit dem Silber (Taf., Abb. 4). Die Proben mit erhöhtem Au-Gehalt zeigen auch höhere Co-Werte (Taf., Abb. 4).

Das Verkittungsmaterial der Explosionsbrekzie enthält eine den Andesiten vergleichbare Goldmenge (Tab.). Das Trümmergestein ist intensiv hydrothermal umgewandelt ; die charakteristischen Neubildungen sind : Karbonate, Quarz, Sericit und Pyrit. Gegenüber den Andesiten weisen die untersuchten Breccien eine negative Au-Fe und Au-S Korrelation auf (Taf., Abb. 5).

B) *In Erzen*

Das Gold wurde in 15 Erzproben mit unterschiedlichen Pb- und Zn-Gehalten bestimmt. Die Analysenergebnisse zeigen eine erhebliche mit Literaturangaben vergleichbare Streuung der Au-Werte (Tab.). Über einen kleineren Streubereich verteilen sich die mittels chemischer Analyse (Dokimasie) der 6 Aufbereitungsproben erhaltenen Au-Werte. Ihr Durchschnittsgehalt unterscheidet sich nicht sehr wesentlich von jenem berechneten aufgrund der durch NA-Verfahren erzielten Ergebnisse der Stückproben. Diese Mittelwerte sind jedoch niedriger als

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jene einiger Polymetall-Goldlagerstätten, die einen Übergangscharakter erkennen lassen. Das Au/Ag-Verhältnis ist aber in jedem Falle niedriger als 1. Das arithmetische Mittel (0,5485 ppm Au) stimmt mit dem Maximum der Häufigkeitsverteilung der Goldgehalte im polymetallischen Erz von Baia de Arieș nicht überein (Taf., Abb. 6).

Die Au-Gehalte lassen im Bereich der Lagerstätte eine Teufenabhängigkeit erkennen. Hierbei zeigt sich, dass in den oberen abgebauten Sohlen der Lagerstätte, wo das Pb/Zn-Verhältnis grösser war (U d u-b a ș a, L a z ă r, 1968), auch das Gold angereichert wurde (Taf., Abb. 7).

Im polymetallischen Erz zeigt das Gold eine am deutlichsten ausgeprägte, wenn auch nicht statistisch gesicherte, positive Korrelation mit den S- und Fe-Werten, was darauf hinweist, dass das Gold in Sulfiden und vor allem im Pyrit enthalten ist (Taf., Abb. 8). Die Goldzunahme geht, in den meisten Erz-Proben, parallel zu jenem von Pb und Zn (Taf., Abb. 9). Das weist darauf hin, dass ausser Pyrit auch der Bleiglanz und die Zinkblende als Goldträger zu betrachten sind. Die negative Korrelation des Au-Mn Paares macht es weniger wahrscheinlich Alabandin als Goldträger im polymetallischen Erz anzusehen. Links oben im Feld des Korrelationsdiagramms sind Pb- und Zn-arme Erze ($Pb + Zn < 1\%$), welche fast nur Pyrit enthalten, dargestellt. Das Pyriterz und das Pb-Zn-Erz sind auch im Au-Ag Variationsdiagramm zu erkennen (Taf., Abb. 10). Beide Erzarten weisen eine positive Korrelation auf. Die oben erwähnten Erztypen sind auch im Au-As- und Au-Cu-Diagramm gut erkennbar (Taf., Abb. 10). Es ist nicht auszuschliessen, dass zumindest ein Teil des Goldes im polymetallischen Erz an Sulfosalzen gebunden ist, wie das Dreieckdiagramm Au-As-S hinweist (Taf., Abb. 11).

C) *In Sulfiden*

Zur Untersuchung der Goldverteilung in den erzbildenden Sulfiden und der Beziehungen zwischen Gold und Spurenelementen der Sulfide sind die Hauptsulfidminerale analysiert worden.

P y r i t is der Hauptträger von Gold, das als gemeinsame Mikrokomponente der Sulfide betrachtet worden ist (B o y l e, 1979).

Die untersuchten Pyrite erschienen unter dem Erzmikroskop frei vom „sichtbaren" Gold. Zuweilen sind kleine Einschlüsse von Hämatit $\pm$ Magnetit vorhanden. Spärlich kommen auch sehr feine, am Rand der Pyritkörner gelegene, Sulfideinschlüsse (Kupferkies, Zinkblende, Bleiglanz) vor.

Das Gold konnte in allen analysierten Pyritproben nachgewiesen werden. Die Gehalte schwanken in einem relativ engen Streubereich (Tab.). Die Streuung der Werte ist kleiner als jene, die in der Literatur für hydrothermale Pyrite angegeben ist (S c h t s c h e r b a k o w, 1974).

Die Goldgehalte des Pyrits sind mehrgipflig verteilt (Taf., Abb. 12). Die errechneten Au/Ag-Werte bestätigen die Feststellung, dass die Menge des Silbers in den meisten hydrothermalen Sulfiden den Goldgehalt übertrifft (G o l d s c h m i d t, P e t e r s, 1932-vide R a n k a m a, S a h a m a, 1970).

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Der Pyrit weist mit abnehmender Teufe eine geringe Au-Anreicherung auf.

Au und Cu zeigen keine wechselseitige Abhängigkeit, während die Au-As und Au-Ti Paare eine negative Korrelation zeigen (Taf., Abb. 13). Eine positive Korrelation gibt es zwischen dem Goldgehalt und den Co/Ni-Werten (Taf., Abb. 14), die grösser für die bei höheren Temperaturen gebildeten Pyrite sein sollen (Hawley, 1952-vide Fleischer, 1955).

Auf Grund der bereits oben angegebenen Daten, dürfen wir deshalb annehmen, dass das Gold in den von uns untersuchten Pyriten, auch wie in anderen Pyriten (Ramdohr, Strunz, 1967; Petrowskaja, 1973; Boyle, 1979), submikroskopisch fein verteilt sein kann.

Die Zinkblende kann Gold als mechanische Verwachsung enthalten (Palache et al., 1963; Ramdohr, Strunz, 1967 u.a.).

Die analysierten Zinkblende-Proben weisen unter dem Auflichtmikroskop feine Entmischungskörperchen von Kupferkies auf. Stellenweise sind feine Bleiglanz- und seltener auch Pyriteinschlüsse vorhanden. Das Gold konnte u.d.M. nicht beobachtet werden.

Die untersuchten Zinkblenden sind goldarm. Gewöhnlicherweise sind Au-Gehalte bestimmt worden, die niedriger sind als die von anderen Autoren zitierten (Tab.). Die Goldgehalte liegen in einem breiteren Streubereich als beim Pyrit. Häufiger kommen die kleinen Werte vor (Taf., Abb. 15).

Eine Tendenz zur Au-Anreicherung lässt sich in den aus den oberen Teufen stammenden Zinkblenden feststellen.

In Zinkblenden zeigt das Gold eine schwache Korrelation mit den Fe- und In-Gehalten. Der Au-Gehalt einerseits und die Cd- und Mn-Gehalte andererseits zeigen keine wechselseitigen Beziehungen. Die Cd-Gehalte bleiben nahezu konstant (Taf., Abb. 16).

Das Vorhandensein von Gold im Bleiglanz wurde etwas seltener erwähnt (Palache et al., 1963; Karapetian, Atabekian, 1969; Lehmann, Pietzner, 1970; Petrowskaja, 1973).

Gediegenes Gold konnte u.d.M. in den analysierten Bleiglanzproben nicht nachgewiesen werden. Diese sind oft einschlussfrei von Erzmineralien. Zuweilen kommen feinste Kupferkieseinschlüsse und kleine Pyrit- und Zinkblendeeinschlüsse vor. Pb-Sulfosalze treten spärlich in den Randteilen der Bleiglanzkristalle auf.

Das Gold konnte auch in allen untersuchten Bleiglanzproben nachgewiesen werden und weist höhere Werte auf, als diejenigen, die im Schriftum zu finden sind (Tab.). Wenn wir die Streubreite der Goldgehalte in den untersuchten Sulfiden vergleichen, können wir gleich feststellen, dass die Streuung im Bleiglanz grösser ist. Das arithmetische Mittel (8,34 ppm) entspricht etwa dem Hauptmaximum der Häufigkeitsverteilung der Au-Gehalte im Bleiglanz (Taf., Abb. 17).

Im Gegensatz zu den durch NA-Verfahren gefundenen Au-Werte sind die in gleichen Bleiglanzproben spektralanalytisch bestimmten Au-Gehalte um ca. 20% höher.

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Das Goldgehalt im Bleiglanz nimmt mit der Teufe ab.

Während die Bi-Gehalte mit den Au-Gehalten zunehmen, bleiben dagegen die Ag- und Sb-Mengen relativ konstant (Taf., Abb. 18). Daraus erklärt sich die Goldanreicherung besonders im wismuthaltigen Bleiglanz, den F l e i s c h e r (1955) als eine relativ hochthermale Bildung ansah.

Da im Bleiglanz enthaltenes Gold erzmikroskopisch nicht bestimmbar ist, wurde eine Prüfung mit der Elektronen-Mikrosonde [3] unternommen. Die erhaltenen Scanning-Bilder lassen eine gleichmässige räumliche Goldverteilung im Bleiglanz erkennen, die ähnlich denen des Pb und Ag ist (Abb.).

D) *In Gangmineralen*

Es wurde das Vorhandensein von Gold in Karbonaten untersucht. Die für analysierte Manganokalziten gefundenen Au-Werte sind höher als diejenigen, die für Calcit bekannt sind (Tab.).

Schlussfolgerungen

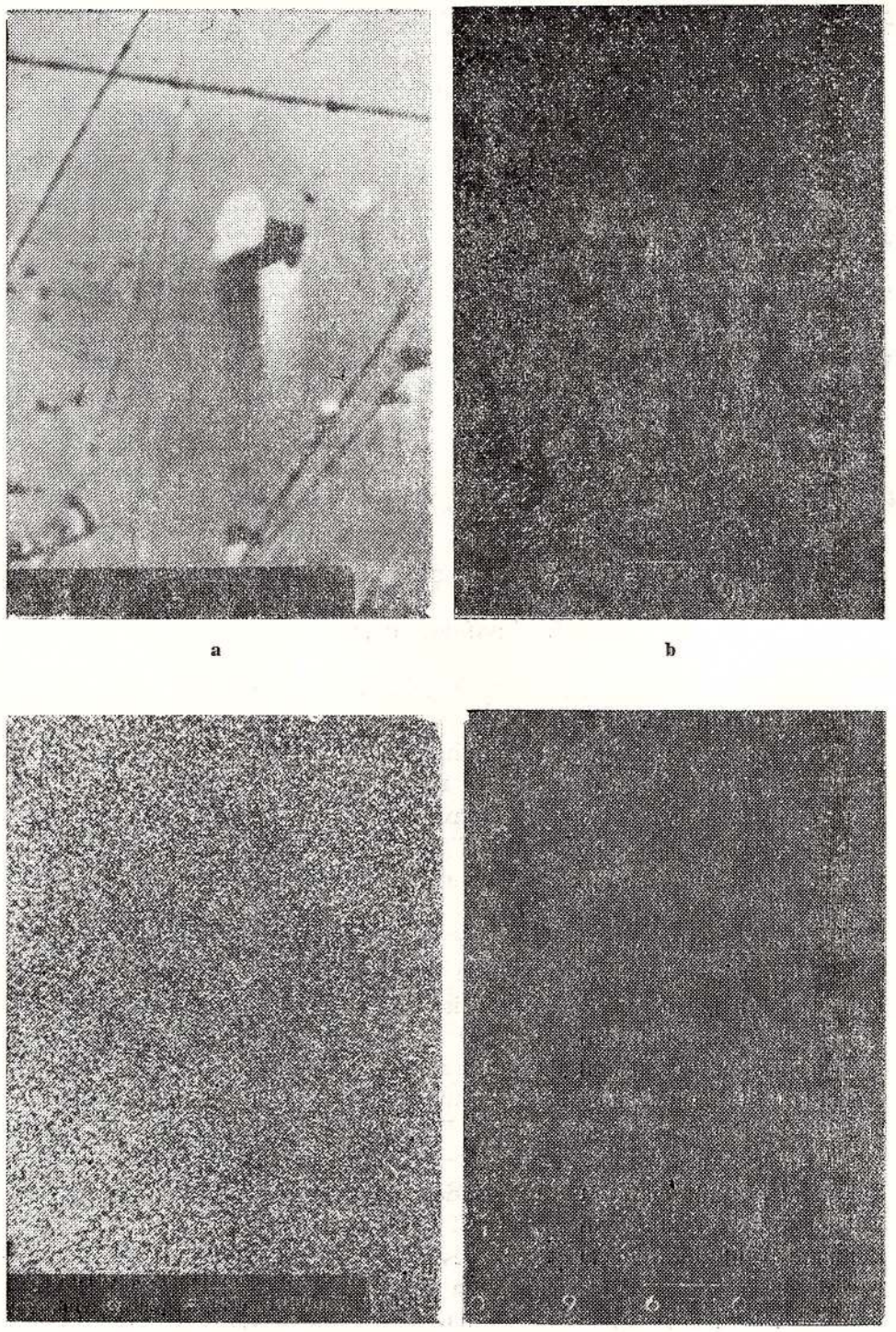
Aus den oben mitgeteilten Ergebnissen lassen sich die folgenden Feststellungen ableiten.

Als Folge der unterworfenen hydrothermalen Umwandlungen und Sulfidimprägnationen (überwiegend mit Pyrit) weisen die untersuchten Gesteine, im Vergleich zu den unveränderten Gesteinstypen, höhere Au-Gehalte auf. Das deutet darauf hin, dass in den umgebenden Formationen der Erzkörper eine primäre Dispersionsaureole gebildet worden ist.

Man könnte annehmen, dass während der Differentiation der hydrothermalen Lösungen auch eine Au-Anreicherung stattgefunden hat.

Wenn es überhaupt gestattet ist, mit wenigen Gold-Analysen von den Hauptsulfiden der Lagerstätte die Entwicklung der Goldkonzentration in den Erzlösungen gleichzeitig mit der Altersfolge der Erzmineralien, bzw. mit abnehmender Temperatur, zu verfolgen, dann lässt sich folgendes Bild rekonstruieren. Die parallel mit der Vererzung verlaufene Goldabscheidung erreichte zwei Maxima (Taf., Abb. 19). Nach den bisher gewonnenen Daten findet die erste vermutete Konzentrationszunahme von Au bei hohen Temperaturen statt, wenn der Pyrit sich auszubilden begann, da in diesem Fall ein goldreicher Pyrit entstanden ist. Die Goldkonzentration in den hydrothermalen Lösungen nimmt danach ab, wie der Au-Gehalt der hochtemperierten Zinkblende hinweist. Die Goldkonzentration ist anscheinend gegen das Ende der Zinkblendebildung wieder angestiegen und erreicht ein zweites Maxi-

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a b

c d

Scanning-Bilder für $Pb_{L\alpha}$ (b), $Ag_{L\alpha}$ (c) und $Au_{L\alpha}$ (d) im Bleiglanz (a). Vergr. 1000×.

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mum zum Beginn der Bleiglanzabscheidung. Der kleine Au-Gehalt der Gangminerale könnte die Folge der Lösungsverdünnung sein.

Der Goldgehalt ist im Pyrit und Bleiglanz höher und in Zinkblende niedriger als er in den entsprechenden Sulfiden zu sein pflegt.

Bei den oben genannten Mineralen handelt es sich um ein Gold, das mit grösster Wahrscheinlichkeit als submikroskopisch disperse Phase vorhanden ist, weil es unter dem Erzmikroskop (bei 1000—1500 facher Vergr.) nicht erkennbar ist. In diesem Zusammenhang bemerkenswert ist die Tatsache, dass dieses Gold im Bleiglanz eine statistische homogene Verteilung aufweist, so wie die Elektronenmikrosonde-Analyse andeutet.

Das an Sulfiden gebundene Gold entspricht möglicherweise entweder einer adsorbierten Phase, die gleichmässig auf den Wachstumsflächen des Wirtminerals verteilt ist, oder einer festen Lösung. Infolgedessen weist das Gold einen syngenetischen Charakter in Bezug auf den „Träger" hin.

Die Anwesenheit von Gold fast ausschliesslich als hochdisperse Phase wurde wahrscheinlich von der sehr höhe Aktivität des Schwefels in den Erzlösungen bedingt. Schtscherbakow (1974) bemerkte, dass die zunehmende Sulfidmenge in den Goldlagerstätten von Kusnezkij Alatau und Gornyi Altai (UdSSR) das Abnehmen des Verhältnisses „sichtbares" Gold/submikroskopisches Gold bewirkte.

Die hier beschriebene Goldabscheidung in der Polymetallagerstätte von Baia de Arieş steht auch in Einklang mit der von Karasik (1963) geäusserte Bemerkung, dass die Elementen, die als Zusatzkomponenten in den Mineralen abscheiden, können in den späteren Entwicklungsetappen der Vererzung selbstständige Minerale bilden ; umso mehr als in der Nähe dieser Pb-Zn-Lagerstätte auch später gebildete Golderze vorhanden sind.

Die Mittelwerte der Au-Gehalte in den analysierten Mineralen und Gesteinen aus der Polymetallagerstätte von Baia de Arieş sind höher als der Au-Durchschnittswert in der Erdkruste, was darauf hinweist, dass eine Goldanreicherung im Bereich der Lagerstätte durch magmatische und postmagmatische Prozesse stattgefunden hat.

Der Ursprung dieses Goldes liegt möglicherweise ausserhalb der Polymetallagerstätte. Das Gold könnte von den Erzlösungen sowohl aus dem Stammagma als auch durch Auslaugung der durchgedrungenen Gesteinnen herbeigebracht werden.

---

[3] Bauart JXA-50 A ; 25 KV Elektronenbeschleunigung. Analytiker : N. Farbaş, ISIM, Timişoara.

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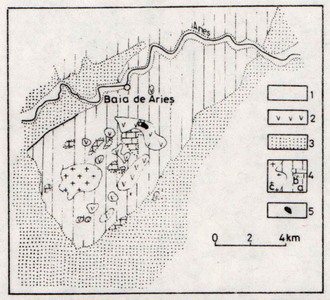


Abb.1 Geologische Karte des Baia de Aries Gebietes (Nach der geolog. Karte Rumäniens 1:200 000 Blatt Turda z.T eigene Angaben)
1 Quartär; 2 Andesite; 3 Kreide; 4 Kristalline Schiefer (a) und Kalke (b), Granite (c); 5 Polymetallagerstätte

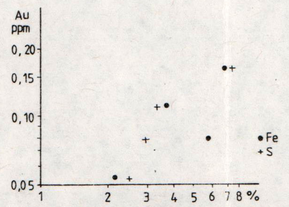


Abb. 2 Variationsdiagramm der Au-und Fe-bzw. S-Werte in Andesiten

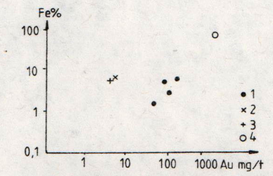


Abb.3 Korrelation zwischen Fe und Au in Andesiten von Baia de Arieş (1), in Andesiten (2), in Dioriten (3) und in Meteoriten (4), 2-4 nach Dalys und Schtscherbakows Angaben

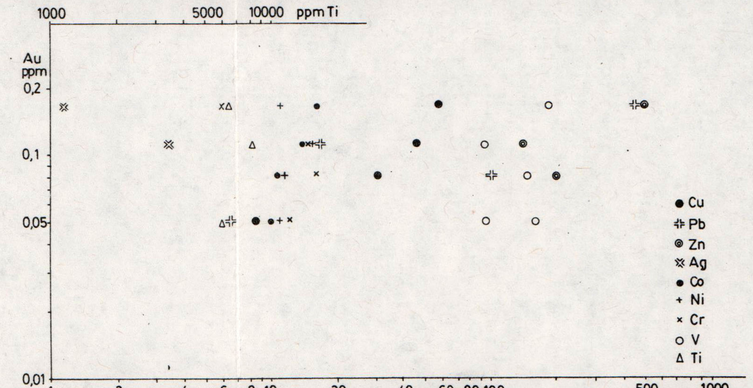


Abb.4 Diagramm der Variation zwischen Au-Gehalt und den Cu-, Pb-, Zn-, Ag-, Co-, Ni-, Cr-, V- und Ti-Gehalten in Andesiten

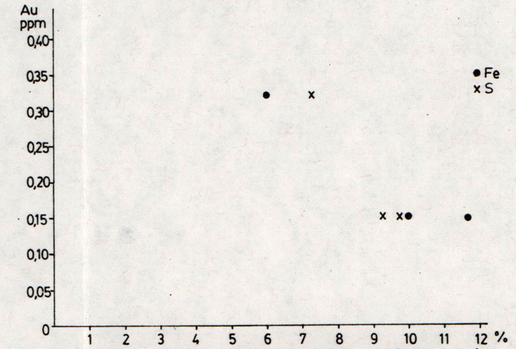


Abb.5 Die Veränderung der Au-Werte mit Fe- und S-Gehalten in Explosionsbreccien

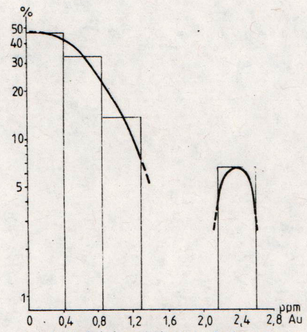


Abb. 6 Häufigkeitsverteilung der Goldgehalte im polymetallischen Erz.

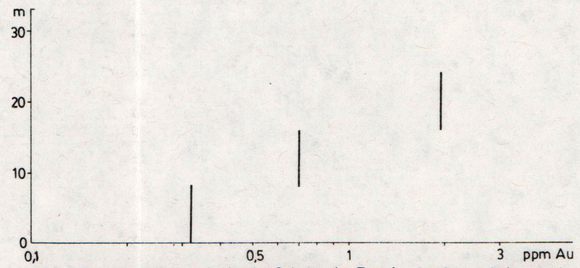


Abb. 7 Teufenabhängigkeit der Au-Gehalte der Erze in der Grube Baia de Arieş

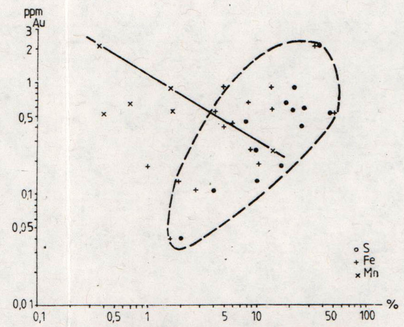


Abb.8 Abhängigkeit der Au-Werte vor S-, Fe- und Mn-Gehalten im polymetallischen Erz

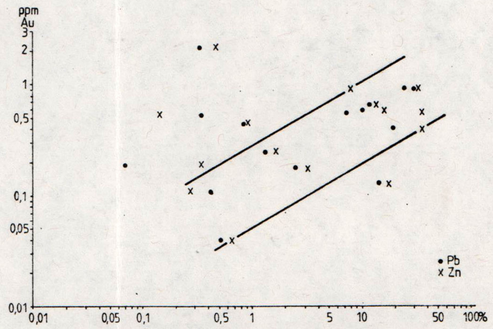


Abb. 9 Korrelationsdiagramm Au-Pb und Au-Zn im Erz

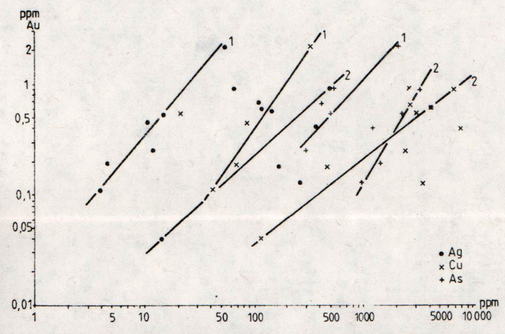


Abb. 10 Zusammenhang zwischen Gold und Ag-, Cu- und As-Gehalten der Erze

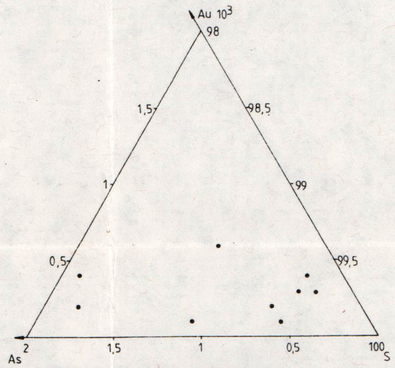


Abb.11 Au-As-S-Dreieckdiagramm für Erze

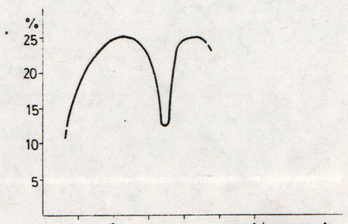


Abb.12 Häufigkeitsverteilung der Au-Gehalte im Pyrit

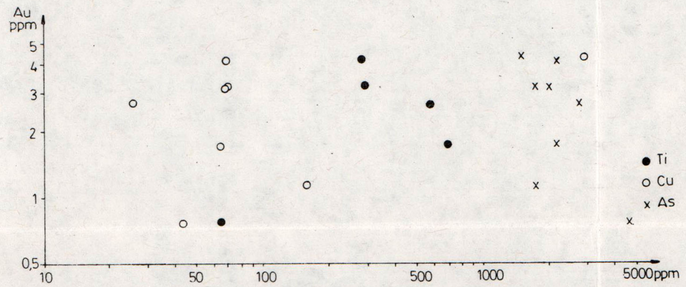


Abb.13 Korrelationsdiagramm zwischen den Au-Werten und As-, Cu-, und Ti-Gehalten im Pyrit

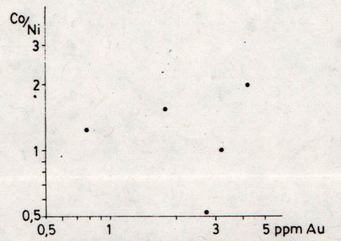


Abb. 14 Korrelation zwischen dem Co/Ni-Verhältnis und Au-Gehalt im Pyrit.

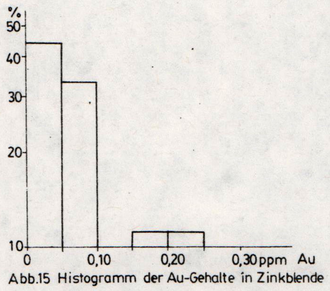


Abb.15 Histogramm der Au-Gehalte in Zinkblende

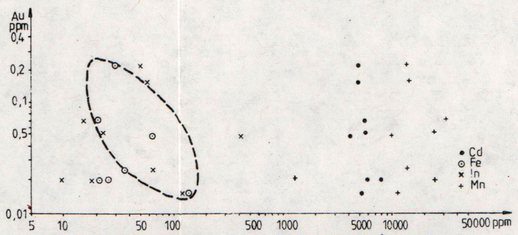


Abb 16. Zusammenhang zwischen Au und Cd, Fe, In und Mn in Zinkblende

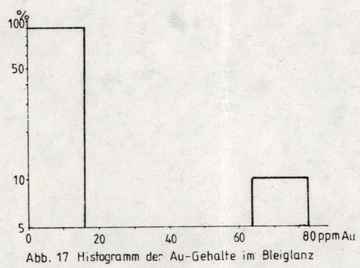


Abb. 17 Histogramm der Au-Gehalte im Bleiglanz

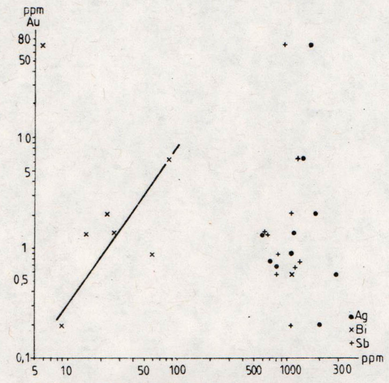


Abb. 18 Variationsdiagramm der Au- und Ag-, Bi- und Sb-Werte im Bleiglanz

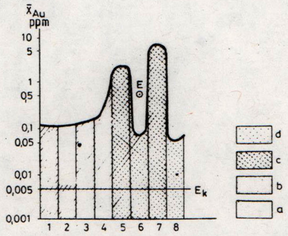


Abb 19 Schematische Darstellung von Goldkonzentration in den Erzlösungen
1 Kristalline Schiefer., 2 Kristalline Kalke, 3 Andesite. 4 Explosionsbreccie. 5 Pyrit. 6 Zinkblende. 7 Bleiglanz, 8 Karbonate, a Unveränderte Gesteine, b Hydrothermal umgewandelte Gesteine, c Erze, d Gangart; E Mittelgoldgehalt des polymetallischen Erzes von Baia de Aries, Ek. Clarkewert

Imprim. Atel. Inst. Geol., Geof.

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DATA ON THE TEMPERATURES OF HYDROTHERMAL AND EPIGENETIC TRANSFORMATIONS [1]

BY

VASILE MANILICI [2], AURELIA DUMITRESCU [2], VIOREL MACALEȚ [2]

The improvement of the dilatometric method for determining the formation temperature of minerals (Bolgiu, Manilici, 1976) enabled the direct determination of the hydrothermal or other type of transformation. This method has been used for establishing the temperature of the hydrothermal transformations in the Baia Mare region, being correlated with the crystallization temperature of the mineralization (Manilici et al., 1978, 1981), for establishing the formation temperature of barytines from Romania (1980) as well as for determining the epigenesis temperature of limestones from the Piatra Craiului and Bucegi synclines (Manilici et al., 1982).

Since through the investigation of the processes of hydrothermal metamorphism in the Baia Mare region (Manilici et al., 1971; Stanciu, 1972) it has been demonstrated that the hydrothermal transformations may be previous, synchronous or subsequent to the Sarmatian, Pannonian and Pontian mineralizations, the temperatures of hydrothermal transformations were followed separately in the three stages of each metallogenetic cycle.

A) *Temperatures of Hydrothermal Transformations Previous to the Metallogenetic Processes*

Hydrothermal transformations in the Baia Mare region take place within a wide temperature range. The quartzites in the region were investigated, their temperature being also established (Manilici et al., 1981). The silicification processes generating them took place between 449 and 110°C. The highest values are recorded for the Sarmatian quartzites of Piatra Handalului (418-405°C), for the Pontian ones of Piatra Malnașului in the Cavnic mining field (449-428°C) and of Piatra Vărateculuí (400-392°C), while the lowest values were recorded for

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September 8—13, 1981, Bucharest, Romania.

[2] Polytechnical Institute, Bucharest.

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the Pontian quartzites of Pietrele Onciului at Jereapăn (110°C). Locally, as in the case of Piatra Handalului, the silicification process was achieved practically throughout this temperature range (418-137°C), 2-3 distinct quartz generations being observed under the microscope.

A good correlation between the microscopic and paleogeothermometric data is noticed in all the examined cases.

Quartzites consisting of homogeneous quartz present a single formation interval, while those made up of two or three quartz types, exhibiting various granulometric and microscopic characteristics, show 2-3 distinct temperature ranges. In the latter case there are 2-3 quartz generations corresponding to 2-3 silicification temperature ranges.

The researches carried out show that each quartzite outcrop formed within a specific temperature range.

The opal depositions making up the filling of the fissures crossing the Sarmatian andesites of Seini in the Cicărlău zone formed between 416-247°C, while those constituting the filling of the Pannonian quartz andesites of Piscuiatu, from Băiţa, formed between 416-222°C. Three temperature ranges were recorded in a quartzite sample with opal veinlets at Tarna Mare : 260-250°C, 183-170°C and 95-80°C. If we accept that the first two temperature ranges correspond to quartzite, it follows that the last one corresponds to opal. One can conclude that the deposition of opal in the region took place at a temperature between 416-80°C.

High temperatures are also recorded for the propylitized rocks. In a propylitized andesite sample on the Nistru Valley the epidote-chlorite-sericite paragenesis formed between 358-342°C, while in another propylitized andesite sample on the Cicărlău Valley four temperature ranges were recorded : 464-431°C, 394-379°C, 342-327°C and 162-152°C. The respective rock comprises the following neoformation minerals : biotite, epidote, zoisite, quartz, monoclinic adular and sericite. We think that the interval between 463-431°C might represent the formation temperature of biotite, the one between 394-379°C that of epidote and zoisite, the one between 342-327°C, based on the previous data (M a n i l i c i et al., 1978), might correspond to the formation temperature of quartz and monoclinic adular, while the interval between 165-152°C to the chlorite formation temperature.

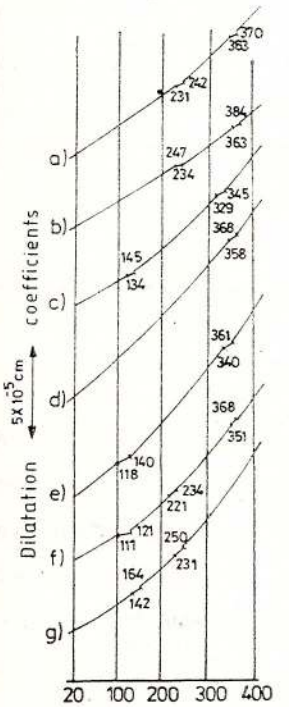
In the case of other propylitized andesites at Brad, in the Apuseni Mountains, the chlorite-epidote-quartz neoformation paragenesis formed within two intervals : 370-363°C and 242-231°C (Fig., a). The same intervals are also found in the epidote concentrations within which this mineral reaches about 70 % of the rock mass (Fig., b). In this case, too, the upper limit of this range seems to represent the formation temperature of epidote and the lower one that of chlorite and quartz.

In the case of the silicified and tourmalinized andesites with fluorine of Mădăraş, in the Harghita Mountains, which were investigated by T ă n ă s e s c u (1978), the transformation process took place between 368-329°C (Fig., c, d, e), as did the simple silicification (Fig., f). Chloritization of these samples took place between 234-221°C (Fig., f), sericitization between 250-231°C (Fig., g) and argillization between

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164-111°C (Fig., e, f, g). The last transformation may be synchronous with the deposition of the cinnabar mineralization at Sîntimbru.

It is evident that the silicification and propylitization processes take place partly at the level of the pneumatolytic phase, at which both



Temperatures of propylitization processes of the Brad andesites in the Apuseni Mountains (a, b) and temperatures of tourmalinization, fluorization, silicification and argillization processes of the Mădăraș andesites in the Harghita Mountains (c-g).

tourmalinization and respectively fluorization of volcanics also take place.

Sericitization (Manilici et al., 1978, 1981) takes place between 265-123°C, chloritization between 250-70°C, while argillization takes place between 170-100°C.

B) *Temperatures of Hydrothermal Transformations Synchronous with the Mineralizations*

In order to follow the temperature of hydrothermal transformations at the contact of metallic veins geothermometric determinations were carried out through the dilatometric method both on ore samples and the host rocks. Sampling covered the whole width of the vein, especially in the zones with banded structure. The samples on the vein walls were collected from the same points, from the foot wall and hanging wall, up to 10—15 m of the vein, depending on the nature of the transformation.

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So far such investigations have been carried out in the Baia Mare region, in the Sarmatian mining fields at Ilba and Nistru, in the Pannonian ones at Tyuzoșa and Săsar-Valea Roșie as well as in the Pontian ones at Jereapăn and Țibleș. Some of the results obtained are presented in the following Table :

TABLE

Crystallization Temperatures of the Vein Minerals and Hydrothermal Transformations Temperatures in the Vein Walls Determined by the Dilatometric Method

No	Paragenesis	Sample location	Temperature °C	
			Dilatometric method	Decrepitometric method
	Ilba deposit			
1	pyrite, blende, quartz	Firizan vein, hanging wall	363, 331	—
2	pyrite, quartz	Firizan vein, centre	127—105	—
3	silicified andesite, impregnated with pyrite	Firizan vein, 2 m in the hanging wall	340—310	315
4	pyrite, chalcopyrite, quartz, chlorite	Nepomuc vein, hanging wall	340—331 284—273	— —
5	pyrite, chalcopyrite, quartz, hydromicas	Nepomuc vein, median zone	342—331 147—137	— —
6	blende, pyrite, chalcopyrite, quartz, calcite	Nepomuc vein, centre	294—276	—
7	silicified and chloritized andesite, impregnated with pyrite	Nepomuc vein, foot wall	315—242	305
	Tyuzoșa deposit			
8	pyrite, quartz	Lens 1, foot wall	347—337	310
9	pyrite, blende, galena, quartz	Lens 1, median zone	237—229	240
10	silicified, adularized and pyritized andesite	Lens 1, hanging wall	276—265	250
	Valea Roșie Deposit			
11	pyrite, quartz, sericite	Vein 3, hanging wall	351—344 171—160	350
12	silicified, adularized, sericitized and pyritized andesite	Vein 3, hanging wall	352—334 159—150	345

One can notice that the hydrothermal transformation of the rocks at the contact with the veins takes place at the crystallization temperatures of the ore belonging to several generations, which indicates that the respective transformations are connected with the emplacement of the mineralization. The beginning of pyrite decrepitation impregnating the host rock coincides in most cases with the crystallization

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temperature of the first generation ; this fact shows that pyritization of the host rock took place especially at the beginning of the mineralizing process. Towards the end of this process the sericitization of the surrounding rock is achieved between 270-150°C, and its argillization between 150-100°C.

C) *Temperatures of Hydrothermal Transformations Subsequent to the Mineralizations*

This category of transformations includes the kaolinization process, which takes place at about 100 and 76°C. As kaolinite is often found in the centre of the vein, being formed at about 100°C, it follows that kaolinization is partly achieved in the final phase of the mineralization process.

Also to this category belong the alunitization process in the Călimani Mts, between 100-60°C, and partly the zeolitization and benthonization processes in the Băița-Nistru zone (Manilici et al., 1978).

The introduction of the dilatometric method enabled the determination of the formation temperatures of the barytine and celestine fine-grained aggregates to which the omogenization method cannot be applied. According to the published data (Manilici et al., 1980) the barytines on the Romanian territory crystallized between 318-180°C, while witherite, associated with barytine in the Ostra deposit, crystallized between 250-245°C. All the three methods could be applied to the transparent barytine crystals at Baia Sprie, the dilatometric method indicating 263-251°C, decrepitation being achieved at 260°C, while the omogenization method indicating about 294°C. In all the analysed cases, the beginning of decrepitation, which represents the real crystallization temperature of barytine, coincides with the interval determined by the dilatometric method.

The barytization process of the Ostra gneisses took place between 298-275°C.

The use of the dilatometric method for determining the epigenesis temperature of the sedimentary rocks provided interesting results in the case of the limestones in the Bucegi and Piatra Craiului synclines. The temperatures thus obtained range between 63-167°C, which, considering a rise in temperature of 1°C to a depth of 33 m, corresponds to a burial of 2.079 m at Piatra Caselor and Dragoslavele and 5.566 m at Zărnești. The values obtained appear to be high, compared to the stratigraphic data in the region, which pleads for an ascendant thermal flux during the burial period in both synclines. Nevertheless, they correspond very well to the tectonic data, pointing out the uplifted compartments, such as that at Dragoslavele, as well as the sunk ones at Zărnești. The calcite filling the veins crossing the limestones crystallized at temperatures between 385-316°C, which are higher than those of the transformations of limestones.

No relevant data were obtained by the use of the dilatometric method for determining the transformation temperature of the clay-marly rocks, as the clay minerals with a low dilatation coefficient,

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determining a slight inclination of the curve, make difficult the separation of the levels, respectively of the inflexions indicating the temperature of the transformations.

Conclusions

The use of the dilatometric method in the paleogeothermometric investigations in Romania enabled the determination of the crystallization temperatures of hydrothermal minerals in the filling of the metalliferous veins, the temperatures of the hydrothermal and partly pneumatolytic processes as well as the temperatures of the epigenetic processes. Dilatometric data could be checked by the omogenization method in the case of the clear macrogranular aggregates, to which this method could be applied. They could be also checked by the decrepitometric method, in which case only the beginning of decrepitation is achieved at the level of the temperature determined by the dilatometric method or near it. Dilatometric data could not be checked by the decrepitation method in the case of the sericitized, chloritized, argillized or kaolinized rocks as these do not decrepitate. The checking of the dilatometric data by the other two methods shows that the formation temperature of a mineral aggregate can be determined only by the dilatometric method when the omogenization and decrepitometric methods cannot be applied.

Negative results were also obtained by applying the dilatometric method. The microscopic study of some samples shows that the negative results obtained in determining the temperature of hydrothermal transformations are due to either the lack of neoformation minerals or their reduced amount. A large amount of secondary minerals always provides obvious results. Negative results were also recorded for some hydrothermal minerals in the vein fillings, quartz, sulphides etc., which are as a rule fine-grained. In these cases the microscopic study of the respective samples indicates the lack of the biphasic inclusions, probably due to the crystallization conditions. Negative results were also obtained for the strongly oxidized ore samples on the dumping places. In this case the lack of some disturbances on the dilatometric curve is very probably due to the fact that during advanced oxidation there form submicroscopic fissures allowing the yielding of the content of fluidal substances from the aggregate mass.

We point out that if a sample that has provided good results is reheated by the dilatometer it no longer provides good results, the respective curves showing no disturbance. This means that during heating of the sample by the first experiment, the high pressure developed within each inclusion above the crystallization temperature determines, according to Nackman (1921), Scott (1948) and Kennedy (1950) — from Pomârleanu (1971), a fine fissuring of the sample which favours the loss of fluidal substances from the respective inclusions.

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DISCUSSIONS

R. Cădere: A paper of present interest which relates directly with the thermometry works in the hydrocarbon wells.

It would be interesting to use this investigation method in the prospection works.

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FLUID INCLUSIONS AND THEIR SIGNIFICANCE IN THE THERMOBAROGEOCHEMISTRY AND GENESIS OF PEGMATITES IN ROMANIA [1]

BY

VASILE POMÂRLEANU [2], ELEONORA-ANA POMÂRLEANU [2]

Introduction

Pegmatites, compared to other genetic types of ore deposits are characterized by a very large variety of inclusions which show up the complex conditions of their formation. In the last two decades in our country fluid inclusions have also been noted in some pegmatite minerals (P o m â r l e a n u et al., 1967, 1968, 1969, 1971, 1973, 1975, 1979, 1981).

The purpose of this paper is to present a synthesis regarding the study of fluid inclusions in the quartz, muscovite, plagioclases, apatite, spodumene, beryl, garnets and tourmaline of the main pegmatite areas in Romania and to discuss some of the data concerning the temperature, pressure and composition of the solutions from which these minerals have been formed. On the basis of these results and of field observations regarding structural relations between pegmatite bodies and host rocks we have come to the conclusion that the majority of concordant pegmatites have resulted by a tectonic-hydrothermal process.

Location and mineralogical composition of pegmatites

Within the Romanian Carpathians there are many pegmatitic fields the most important of which are : the pegmatites of the Rodna Mts (Rebra Valley), of the Preluca Mts (Răzoare-Copalnic), of Gilău-Muntele Mare (areas : Someşul Cald-Iara Valley and Geamăna-Măzăratu) and the pegmatites of the South Carpathians (areas : Semenic-

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Muntele Mic ; Cerna-Godeanu-Mehedinți ; Sebeș-Cibin-Lotru and Almaj Mts).

The pegmatites of the crystalline schists have an epigenetic character. They have gradational to abrupt contacts.

The pegmatites of the Carpathian Mts are characterized by a simple mineralogical composition (alkaline feldspars, quartz and muscovite). Subordinately they consist of biotite, garnets, tourmaline, apatite, beryl, spodumene, kyanite and metallic minerals (magnetite, molybdenite, pyrite, etc.). The beryl, spodumene and tourmaline crystals are usually inclined up to a perpendicular position towards the contact of the pegmatite bodies with the host rocks.

Fluid inclusions

According to the genetic relations with the host crystal, fluid inclusions can be primary, pseudosecondary and secondary.

According to their distribution in crystals, primary fluid inclusions can be zonal (oriented according to the growing zones of the crystals or after their crystallographic elements) and non-zonal (non-uniformly distributed or isolated in the crystals).

Pseudosecondary fluid inclusions have resulted along "the healed" microfissures of the inner zones of the crystals, which are not connected with the outer zones of the crystals.

Secondary fluid inclusions were formed as a result of healing microfissures which penetrated the whole crystal or whole mineral granules.

Examined at room temperature, according to the relations of the fluid or crystalline phases which they contain, fluid inclusions can be monophase (liquid or gas only) ; two phase (aqueous solution and liquid CO_2 + gas CO_2 + crystal, or aqueous solution + vapours + many crystalline phases).

Along with the above inclusions, in beryl two or three-phase tabular inclusions which have final crystalline phases have been noticed.

Geothermometrical data

Based on the study of fluid inclusions the temperature of the formation of the pegmatite minerals has been determined by homogenization and decrepitation methods. The temperature ranged from 175° to 500°C.

Geobarometrical data

To estimate the pressure at the time of the formation of the host mineral, on the basis of fluid inclusions, several methods are known. In this paper the method given by N a c k e n (1921) and developed by K a l y u z h n y and K o l t u n (1953) has been applied. This method relies on the hypothesis that in a mineral, along with two-phase fluid inclusions (aqueous solution + vapours), CO_2 inclusions would exist, too. Both are formed simultaneously and in the same thermodynamical

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conditions. Such inclusions have been identified in the quartz which substitutes the feldspars and in the quartz of the core of pegmatites.

If the P-T diagrams for CO_2 and H_2O with specific isochores are superposed in the same plane, the formation pressure and temperatures will be determined by the intersection of the isochore corresponding

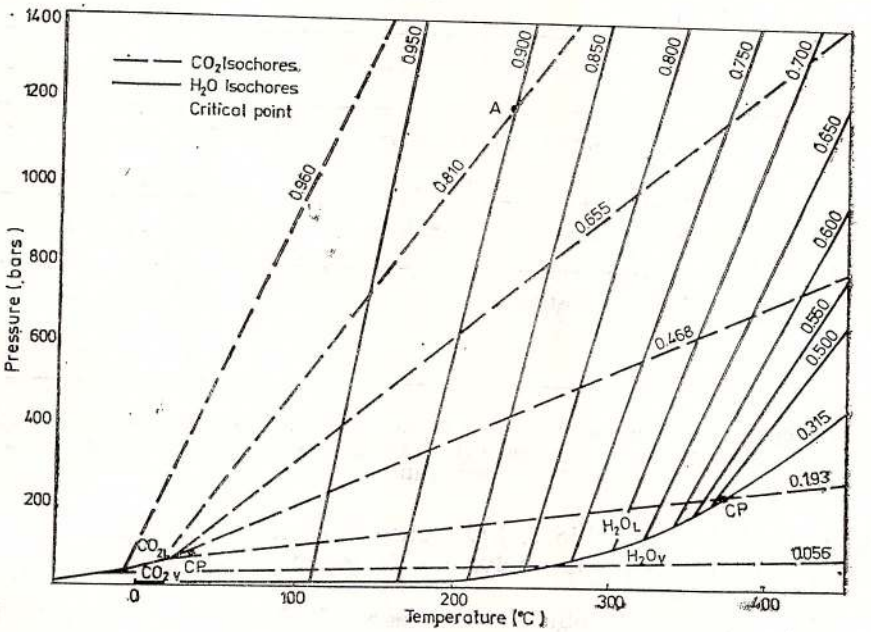


Fig. 1. — Combined P-T diagrams for CO_2 and H_2O with specific isochores (after Nacken, 1921, Kalyuzhnji and Koltun, 1953, and recently completed by Roedder and Bodnar, 1980).

to the CO_2 inclusion with the one corresponding to the H_2O inclusion (Fig. 1.). "Thus a CO_2 inclusion homogenizing in the liquid phase at 11°C and a H_2O inclusion homogenizing in the liquid phase at 167°C would both have been trapped at 237°C and 1180 bars" (Roedder, Bodnar, 1980).

As it can be seen from Table 1 the formation temperature and pressure of the last quartz generation, determined according to the above diagram, ranges between 230° and 360°C and between 925 and 1 500 bars.

Composition of the fluid inclusions

The quantitative chemical data refer to the CO_2, H_2O determination and the salinity of solutions.

To determine carbon dioxide and water in fluid inclusions the gas chromatography method has been used. The results for each mineral

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TABLE 1 *

Temperature and pressure formation in the quartz of pegmatites

Location	Sample number	Assemblage	Type of inclusions	D	$T_H CO_2$	$T_H H_2O$	T°C	P bars
Rodna (Rebra Valley)	1406	Q substitutes F	pseudosecondary	10	20	280	360	1150
Preluca	1688	Q substitutes F	primary	16	17	180	230	1180
			secondary	20	15	240	330	990
Gilău (Rișca Valley)	1601	Q core	primary	35	11	220	280	1500
Semenic (Secaș Valley)	1701	Q substitutes F	primary	18	20	170	240	1410

* Homogenization temperature of : CO_2 inclusions H_H CO_2 and of aqueous inclusions H_H H_2O ; Temperature (T°C) and pressures (P) of formation of quartz crystals from pegmatites ; Q — quartz and F — feldspars ; D — determination number

sample are listed in Table 2. CO_2 concentration versus H_2O one, as the main compounds in fluid inclusions is given in CO_2/H_2O that varies from 0.055 to 0.719.

The salinity of solutions between 35-55 weight per cent NaCl has been obtained from the dissolution temperature of the halite crys-

TABLE 2

Carbon dioxide content versus water content in fluid inclusions of pegmatite minerals

Mineral	District, Location	Sample number	Molar ratio CO_2/H_2O
Quartz	Gilău — Muntele Mare (Vința Valley)	1611	0.578
		1631	0.196
		1646	0.073
Apatite	Preluca (Răzoare)	2007	0.055
Tourmaline	Semenic — Muntele Mic	2003	0.094
	Preluca (Răzoare)	1313	0194.
Spodumene Beryl Kyanite	Sebeș — Cibin	2002	0.242
		2006	0.719
		D	0.117

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tals (250°-450°C) trapped in fluid inclusions. The salinity has been determined from the diagram of the H_2O-NaCl system (Sourirajan, Kennedy, 1962).

Source and emplacement of pegmatites

There are many theories regarding the source and the way of emplacement of pegmatites, from of which the magmatic and the metamorphic ones are the most important.

Recently the idea has been promoted that the granitoids with their whole scale of products (migmatites, granites, aplites, etc.) could be the result of an unitary anatexis process which acted in many steps followed by a magmatic differentiation (residual magma) and by metamorphic differentiation when the fusion was partial (Mârza, 1980). According to this conception it has been shown that the pegmatites in our country were formed in the anatexis process followed by migmatic solutions (Savu, 1977) or by metamorphic differentiation (Mârza, 1980). In both cases it appears that the main source of potassium feldspars was the quartz and muscovite of the host crystalline schists.

The model proposed by Gresens (1967) corresponds with those points of view regarding the explanation of the pegmatite genesis. The author shows that the pegmatite bodies rich in muscovite were formed within low pressure zones by the reaction Q + Ms + (Na^+, K^+) → Perthite + H^+, and residual intergranular fluids, in the final stage, reacting with earlier formed feldspar, from the above reaction, to yield muscovite as a late component. The proposed model of the formation of pegmatites by a tectonic-hydrothermal process depends on two basic conditions : 1, the presence of an alkali chloride intergranular fluid phase that could be in equilibrium with the solid phase (minerals) in the host rock ; 2, the deformation produces low pressure zones in the host rock.

The results obtained from the study of fluid inclusions and structural relationships between pegmatites and country rocks would appear to solve two of the main genetic problems of the pegmatites of the crystalline schists. The first problem refers to the fact whether there are arguments that could satisfy the two basic conditions mentioned above. The second one refers to the fact whether the model proposed by Gresens is in agreement with the theory regarding the explanation of the pegmatite genesis by an anatexis process followed either by migmatic solutions or by metamorphic differentiation.

Microscopic observations both in pegmatite minerals and in crystalline schist minerals have evidenced the existence of many fluid inclusions, with different contents in volatile components and in alkaline salts. The presence of these inclusions shows the existence of intergranular fluid rich in alkaline salts, which is in equilibrium with the minerals of the country rocks.

The second condition was also met with, as, simultaneously with the emplacement of concordant pegmatite bodies, under the action of

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dilation mechanisms on the host rocks, low pressure zones have been created. Certain pegmatite bodies at the end of the metamorphic phase have been emplaced when the rocks were still plastic. In this case, under the influence of dilation the host rocks have been subjected to plastic deformations (Preluca, Semenic). When the pegmatites are em-

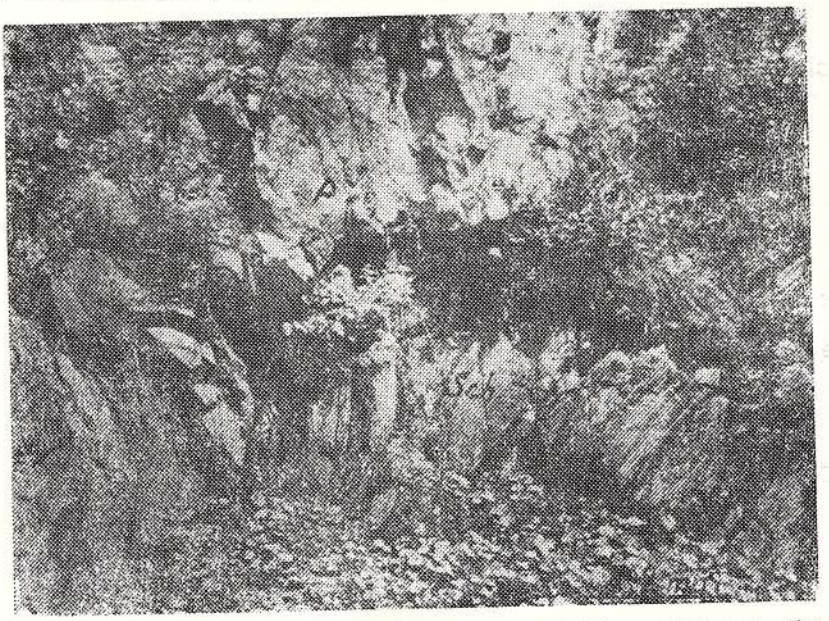


Fig. 2. — Brittle deformation in the crystalline schists at the contact with pegmatite body (Rodna Mountains, Rebra Valley). P — pegmatite and Sch — host rock.

placed after the metamorphic phase, the wall rock was subject to brittle deformations (Rodna and Preluca, Fig. 2).

Regarding the second problem, the structural characters and mineralogical-chemical composition of both pegmatites and crystalline schists show that the emplacement of pegmatites after the model described by Gresens does not in contradiction with the idea of the pegmatite formation by migmatitic solutions and metamorphic differentiation but also they complete each other by the fact that both mechanisms are based on a common process, that of lateral secretion.

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МОРФОЛОГИЯ САМОРОДНОГО ЗОЛОТА — ИНДИКАТОР УСЛОВИЙ РУДООБРАЗОВАНИЯ [1]

В. Н. КВАСНИЦА [2]

Самородное золото характеризуется богатством форм выделений, для него на примере многих рудопроявлений и месторождений установлена тенденция определенного изменения форм выделений в зависимости от глубинности рудообразования — ,,усложнение гранных форм индивидов золота и увеличение роли дендритных и дендритоидных выделений по мере перехода от глубинных месторождений к малоглубинным, а в пределах месторождений — от ранних продуктивных ассоциаций к поздним'' (Петровская, 1980).

В данной работе сопоставлены особенности кристаллических форм самородного золота из рудопроявлений Украинских Карпат, Закарпатья и Добруджи, золотая минерализация которых связана с определенными минеральными комплексами, сформировавшимися на разных глубинах и в неодинаковых по составу и возрасту образованиях (табл.).

Рудопроявление 1 расположено среди древних метаморфических образований северо-западного окончания Мармарошского массива. Вмещающими породами являются разновозрастные образования рифея — нижнего палеозоя (белопотокская гнейсово-сланцевая и деловецкая карбонатно-сланцевая свиты). Золотая минерализация сосредоточена в кварцевых и кварц-карбонатных телах (жилы, линзы, пластовые залежи), залегающих согласно со сланцеватостью серицит-хлорит-кварцевых, мусковит-серицит-хлорит-кварцевых и субграфит-серицит-кварцевых сланцев.

Оруденение отнесено к метаморфогенно-гидротермальному типу, предполагают его связь с региональным метаморфизмом зеленосланцевой фации (Матковский, Ясинская, 1979). Выделяют два минеральных типа оруденения, с которыми связана золотая минерализация: золото-кварцевый и золото-кварцкарбонатный. Они различаются ассоциациями рудных минералов: для золото-кварцевого характерны пирит, арсенопирит, гетит, лепидокрокит и гематит: для золото-кварц-карбонатного — галенит, сфалерит, пирротин, халькопирит, пирит, марказит

[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13 , Бухарест Румыния.

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ТАБЛИЦА

Типоморфные особенности самородного золота из рудопроявлений, сформированных на разных глубинах

Геологическое положение золоторудной минерализации	Рудная формация	Ассоциирующие с золотом минералы	Морфология золота, простые формы кристаллов	Проба золота. Элементы-примеси, характер распределения серебра
Зелено-сланцевые толщи кристаллического фундамента Украинских Карпат.	Малосульфидная больших-средних глубин	Кварц, доломит, пирит, арсенопирит, гетит, лепидокрокит, гематит, галенит, сфалерит, пирротин, халькопирит и др.	Ксеноморфные выделения, редко кристаллы. Габитусная форма: [111] Второстепенные и редкие формы: [100], [110]	840—975 Ag до 16%, Cu до 0,1%, Fe до 0,02%. Распределение Ag относительно равномерное [3].
Метасоматически преобразованные и вулканогенно-осадочные породы миоцена внутреннего Закарпатского прогиба.	Малых убин	Кварц, барит, каолинит, диккит, гидрослюда, алунит, окислы и гидроокислы железа, реликтовые сульфиды и др.	Кристаллы, их простые и сложные двойники, дендритные образования. Характерно искажение облика кристаллов. Ксеноморфные выделения редкие. Габитусные формы: [111], [100], реже [311] Второстепенные формы: [100] [111], [311], [210], [110]	650—780. Ag до 35%, Cu Fe и Te до 0,1% [3]. Неравномерное и зональное распределение Ag, часто увеличение содержания Ag в центральных частях кристаллов.
Осадочно-вулканогенные углеродсодержащие толщи Добруджинского поднятия.	Малых глубин?	Кальцит, кварц, пирит, пирротин, сфалерит, галенит и др.	Кристаллы, реже ксеноморфные выделения. Среди кристаллов сложные двойники и искаженые формы. Габитусные формы: [111], [100] Второстепенные формы: [100], [110].	770—840. Ag до 25%, Hg до 0,6%, Ti до 0,3%, Ag и Mn до 0,1%. Распределение Ag неравномерное.

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и др. Содержание сульфидов очень низкое, в телах резко преобладают кварц и доломит. Оруденение отнесено к малосульфидной формации больших глубин.

Золото высокопробное (840—975) и представлено преимущественно ксеноморфными выделениями, в кварцевых жилах встречаются многогранники золота и их сростки. Кристаллы несовершенные, с округлыми ребрами и вершинами. Их габитус октаэдрический, редко кубический, иногда октаэдры осложнены неполногранным ромбододекаэдром. Наблюдается уплощение октаэдров вдоль тройной оси симметрии; встречаются октаэдры, удлиненные вдоль L_4 и кубооктаэдры, уплощенные по L_4. Нередки случаи нарастания на относительно крупные пластинки золота более мелких округленных его кристаллов. Размер кристаллов до 0,3 мм.

Рудопроявление 2 приурочено к горстовому поднятию донеогенового фундамента в юго-западной части Закарпатского прогиба. Оно связано с постмагматическими процессами неогенового липарито-андезитового вулканизма. Золотая минерализация развита на различных стратиграфических горизонтах эффузивно-осадочных отложений миоцена и представлена разнообразными минеральными типами:золото-колчеданно-полиметаллическим, золото-полиметаллическим, золото-кварц-гематитовым, золото-кварц-адуляровым, золото-кварц-бариат-каолинит-гидрослюдистым (Матковский, Ясинская, 1979). Оруденение сосредоточено преимущественно среди гидротермально измененных липаритовых туфов жерловых и околожерловых фаций. Это типичное близповерхностное (формация малых глубин) вулканогенно-гидротермальное оруденение.

Ограненное кристаллическое золото этого рудопроявления обнаружено главным образом в кварц-баритовых жилах и в зонах с прожилково-вкрапленной минерализацией, которые сформировались в пределах деятельности более ранних гидротермальных процессов (на площади развития кварц-адуляровых метасоматических тел по липаритовым туфам, жильных и вкрапленных полиметаллических руд), связанных с миоценовой андезитовой формацией (Лазаренко, Лазаренко, Малыгина, 1973). Минеральный состав жил: кварц, барит, каолинит, гидроокислы и окислы железа и др. Этот тип руд характеризуется обилием хорошо ограненных кристаллов золота, их сростков, дендритов и дендритоидов. Основная масса кристаллов представлена кубооктаэдрами с различной степенью развития этих простых форм. Большинству кубооктаэдров свойственно искажение облика: уплощение кристаллов вдоль одной из осей симметрии третьего порядка до образования пластинок и, реже, удлинение кристаллов вдоль двойной оси симметрии. В огранке индивидов, слагающих разнообразные дендриты, в основном принимают участие комбинации куба и октаэдра. Индивиды дендритов обычно удлинены вдоль двойной оси симметрии. Ветки дендритов нарастают на ствол под углами, близкими к 45, 55 и 90°. Размеры кристаллов равны 0,2—0,8 мм, а дендритных образований — 2—7 мм при толщине 0,1—1,5 мм. Пробность золота 650—780.

Значительный процент видимого золота составляют сложные двойниковые сростки кристаллов — пятерники кубооктаэдров (класс m3m),

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с двойникованием пар кубооктаэдров по шпинелевому закону 6′/m′mm′/. Внешняя ложная симметрия таких образований близка к $L_5 6P5L_2$.Двойниковые простые формы являются комбинацией ложных форм пятигранной призмы и дипирамиды. При измерении двойниковых сростков на гониометре ГД-1 установлено, что угол между нормалями к каждой грани ,,призмы'' и примыкающими к ней гранями ,,дипирамиды'' равен 54°44;, отвечающий полярной координате октаэдра. Углы между нормалями для каждой пары смежных граней ,,призмы'' (,,дипирамиды'') сдвойникованных индивидов колеблются в пределах 70—72°, часто близкие к 72°.

Таким образом, ,,призма'' сложена гранями куба пяти кубооктаэдров, а ,,дипирамида'' — гранями октаэдра этих же пяти комбинационных многогранников. Двойниковое строение таких образований подтверждается рентгеновскими исследованиями. Лауэграмма пятерника, снятая при прохождении рентгеновских лучей вдоль мнимой оси пятого порядка, отображает его сложную симметрию и двойниковое строение. С мнимой осью пятого порядка совпадает одна из двойных осей симметрии каждого индивида, в этой же L_5 пересекаются все двойниковые плоскости (111) (плоскости срастания).

При идеальном срастании угол поворота сдвойникованных индивидов должен составлять 70°32′. Пять кристаллов, образующих такой циклический сросток, заполняют пространство, оставляя только щель в 7°20' между двумя индивидами, которые не сдвойникованы между собой. Угол 7°20' зарастает в процессе формирования пятерника и лишь иногда проявляется внешне в виде притупления ребра между смежными гранями ,,призмы''. Лауэграмма пятерника, снятая в направлении проходящих лучей вдоль L_4 (перпендикулярно грани ,,призмы'') одного из индивидов сростка, также подчеркивает его двойниковое строение. Симметрия расположения пятен этой лауэграммы понижена до L_2 2P, тогда как симметрия лауэграммы монокристалла вдоль L_4 отвечает L_4 4P. Сильный астеризм пятен лауэграммы как монокристаллов, так и двойниковых сростков указывает на их мозаичное сложение. Если учесть рентгеновские и гониометрические исследования, то истинная суммарная симметрия двойниковых образований понизится до L_2 2P и P. Но так как угол поворота индивидов 70°32' не всегда строго выдерживается и колеблется от 70° до 72°, то это создает для таких сростков внешнюю ложную симметрию $L_5 6P5L_2$. Очевидно, такое явление обусловлено мозаичным строением индивидов, образующих двойник.

При травлении в Cr_2O_3 + HCl плоскости среза пятерников, перпендикулярной мнимой оси L_5 , вскрывается их зональное строение: богатая серебром внутренняя часть и более высокопробная узкая оторочка. Зональность пятерников также четко выступает на концентрационных кривых Au и Ag, записанных на рентгеновском микроанализаторе JxA—5.В этой же плоскости среза пятерников установлено увеличение содержания Au по направлению к внешним частям сростков, их центральные части обогащены серебром. Такое же изменение концентрации Au и Ag свойственно и монокристаллам золота.

Из-за сильного развития граней куба на пятерниках отсутствуют входящие углы и поэтому не наблюдается характерного для двойников значительного преобладания по величине над монокристаллами. Раз-

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меры пятерников и монокристаллов сопоставимы. Величина пятерников вдоль L_5 колеблется от 0,4 до 1 мм при толщине 0,2—0,5 мм. Поверхность граней простых форм пятерников и монокристаллов шероховатая, куб обладает более сильным блеском. Грани [100] имеют несколько вытянутые прямоугольные очертания, а грани [111] — в виде правильных треугольников.

Ранее (Воларович, Николаев, Хамидулин, 1966) обнаружены подобные нашим двойниковым сросткам образования в гидротермально измененных породах мезо-кайнозойских вулканических формаций Приамурья (в андезитах и трахилипаритах Белой Горы). Здесь наблюдались комбинации шести- и пятигранных ,,призм'' с ,,дипирамидами'', а также таблитчатые формы — уплощенные монокристаллы, ограненные кубом и октаэдром. Как и в нашем случае, рудопроявления Белой Горы приурочены к гидротермально измененным породам жерловых и околожерловых фаций. Своеобразный циклический сросток золота по шпинелевому закону из близповерхностного месторождения Бэица в Румынии, также связанного с молодыми вулканогенными породами андезитовой формации (Лазаренко, Лазаренко, Малыгина, 1973) , еще в 1831 г. описан Г. Розе. Этот двойниковый сросток отличается преобладанием октаэдра на слагающих его кубооктаэдрах и четко выраженными входящими углами.

Циклическое двойникование кристаллов по шпинелевому закону свойственно многим минералам, их искусственно выращенным аналогам и другим веществам, кристаллизующимся в кубической сингонии (алмаз, золото, шпинель, кубический карбид кремния, арсенид галлия, полупроводниковые германий и кремний). Возникновению сложных двойников роста способствует большое перенасыщение растворов, повышенная степень предварительной ассоциации атомов в растворах и быстрая кристаллизация. Очевидно, подобные условия периодически возникали при формировании золотого оруденения данного рудопроявления. Не исключено, что существенную роль в образовании дендритов и двойников, роста золота сыграла его кристаллизация из аллюмокремниевых гелей, характерные признаки которой зафиксированы в виде типичных коллоидных текстур минеральных агрегатов, трещин и полостей дегидратации.

Рудопроявление 3 находится среди палеозойских углеродсодержащих осадочно-вулканогенных пород в районе Добруджинского поднятия. Палеозойская толща (породы карбона, девона, кембрий — ордовика) сложена известняками, аргиллитами, песчаниками, конгломератами и эффузивами. Породы сильно трещиноваты, развиты зоны интенсивного дробления, брекчирования и катаклаза.

Золотая минерализация сосредоточена в кварц-кальцитовых прожилках известняков девонского возраста. Известняки в различной степени доломитизированы, в них также проявлены процессы амфиболизации, окварцевания и пиритизации. Среди рудных минералов (пирит, пирротин, сфалерит, галенит и др.) резко преобладает пирит.

Золото представлено комковидными зернами, пластинками и многогранниками. Размер золотин 0,05—0,7 мм. Габитусными формами крис-

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таллов являются октаэдр и куб. Встречены сильно уплощенные по L_3 октаэдры, кубооктаэдры с различным развитием относительных площадей граней форм [111] и [100] и их закономерные сростки-пятерники по шпинелевому закону. Кристаллы золота из данного проявления по своей форме аналогичны многогранникам золота из близповерхностных месторождений. Проба золота 770—840.

Сопоставление форм выделений самородного золота из изученных рудопроявлений показывает, что их различие, как и во многих месторождениях мира (Петровская, 1973, 1980), зависит от глубины рудообразования. Морфологические особенности закарпатского золота — это характерные признаки золота, образовавшегося в близповерхностной вулканической обстановке (Моисеенко, 1974; Новиков, 1968; Петровская 1973, 1980; Щербаков, 1966). Наряду с дендритными образованиями, сложностью и совершенством форм кристаллов, искажением их облика, низкой пробой и зональностью, сложные двойники золота выступают типоморфным признаком близповерхностных условий рудообразования.

Самородное золото из терригенно-карбонатной толщи Добруджи по своим основным типоморфным особенностям (морфологии кристаллов, пробности и характеру распределения серебра в золотинах) наиболее близко к закарпатскому золоту неогенового возраста.

Высокопробное древнее карпатское золото несет признаки условий более глубинного рудообразования (незначительное развитие хорошо ограненных кристаллов, меньшее разнообразие форм, несовершенство огранки, более изометричный облик индивидов и др.).

Таким образом, на примере изученного самородного золота рудопроявлений Украинских Карпат, Закарпатья и Добруджи подтверждено, что форма выделений самородного золота и его кристалломорфологические особенности (наряду с пробой, элементами-примесями, характером неоднородности золотин и др.) являются чувствительным индикатором условий рудообразования и служат показателем формационной принадлежности рудных образований.

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ГЕОХИМИЧЕСКИЕ КРИТЕРИИ ПОТЕНЦИАЛЬНОЙ РУДОНОСНОСТИ ЛЕЙКОГРАНИТОВ[1]

ЕЛЕН АЛЕКСИЕВ ИВАНОВ[2]

В настоящем этапе изучения гранитов прежде всего возникают вопросы о способе их образования и их потенциальной металлоносности. Классические петрографические и петрохимические методы, основывающиеся на данных силикатного анализа, не дают удовлетворительной информации по этим вопросам. Более показательными в этом отношении являются редкие и рассеянные элементы, которые зависят как от состава исходной магмы, так и от условий гранитообразования.

I. Петрологические сведения об исследованных лейкогранитах

Двуслюдяные герцинские граниты из Центрального французского массива выбраны в качестве эталона для сравнения, т.к. они хорошо изучены в генетическом и металлогеническом отношении (La Roch et al., 1980). В эту группу входят: кислые двуслюдяные граниты, претерпевшие эволюцию в более поздние стадии своего развития. Де ля Рош и др. (La Roch et al., 1980) доказывают два вида эволюции:

— поздняя трансформация *in situ* — кремниево-калиевая (микроклинизация) или кремниево-натриевая (альбитизация). Явления грейзенизации ограничены или отсутствуют. Пример: массив Квестемберг.

— позднее внедрение геохимически эволюировавшей магмы, обычно с подчеркнуто натриевым характером и сильно развитой грейзенизацией. Примеры: массивы Монтебра и Эшасьер.

Следовательно, могут быть разграничены 2 типа альбитизированных лейкогранитов (альбит — кварц — мусковит): автометасоматических, названных некоторыми авторами ,,апограниты'' и магменные дифференциаты.

Поздние кремниево-щелочные граниты связаны с двумя группами плутонизма: синкинематическим анатексисом (Брам-Сен-Сильвестр, Сен-Матьо, Милеваш), более щелочным и более алюминиево-калиевым (Au-

[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13, Бухарест Румыния.

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bert, 1969) и посттектоническим, глубинного происхождения (Гере, Марш-Оксиденталь, Марш-Орьенталь) (Gautheer, 1975), с типично кремниевым характером.

Принимается коровое происхождение французских герцинских лейкогранитов, аргументированное начальными изотопными отношениями Sr, а также и геохимией Rb и Cs. Магма образована в результате частичного расплавления (под давлением) или палингенеза, главным образом, в одном циалическом цоколе.

С металлогенной точки зрения для французских лейкогранитов характерны индикации и более значимая минерализация Sn, W, Li, Be, U, Au (Renard, 1977; Gautheer, 1975; La Roch et al., 1980).

Лейкограниты из Руанды включены в качестве характерного примера гранитного магматизма, с которым связаны промышленного типа минерализации олова, вольфрама и урана. Многочисленные гранитные массивы внедрены в докембрийские метаморфиты Рузизиенской и Бурундиенской формаций. По возрасту они также принимаются докембрийскими. Единственное радиоизотопное определение калиево-аргоновым методом биотита из гранита Гитарамы дало абсолютный возраст 555—560 МА.

В петрографическом отношении группа охватывает следующие фации:

— Лейкомезократные биотитовые граниты, состоящие из 30—40 % кварца, 20—35% плагиоклаза (10—20% An), 20—40% микроклина, 8—15% биотита. Акцессорные минералы: апатит, циркон, турмалин, реже титанит (Кабана) и монацит (Рузомо).

— Лейкограниты, в которых биотит частично замещен мусковитом. Например, гранит из массива Лутциро состоит из 30—40% кварца, 20—30% плагиоклаза, 30% микроклина и 5—10% мусковита и биотита. Акцессорные минералы: апатит и циркон.

— Двуслюдяные граниты с доминирующим мусковитом или чисто мусковитовые. Эта пегматоидная, альбитизированная и мусковитизированная фация имеет наибольшее распространение.

В каждом отдельном массиве можно проследить вторичную минералогическую эволюцию, характеризующуюся перекристаллизацией, развитием глобулярного кварца, микроклина, пертитового альбита, мусковита и иногда присутствием турмалина. В химическом отношении эта вторичная эволюция выражается в слабом увеличении содержания SiO_2 и понижении содержания TiO_2.

С образованием оболее поздних ,,посттектонических'' субщелочных гранитов связано формирование пегматитовых полей и жил — носителей касситеритовой, вольфрамовой, урановой и др. минерализаций в Руанде.

Лейкограниты Болгарии принадлежат к трем формационным группам:

1. *Габбро-монцосиенит-гранитовая формация из Средногорской структурной зоны*

Названная группа состоит из гипабиссальных плутонов, внедренных во время позднего этапа среднеальпийского тектономагматического периода. Распространение плутонов контролируется глубинными разломами. Ранние интрузивные фазы образованы габбро и габбро-диори-

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тами. Промежуточные фазы имеют средний состав — диориты, монцодиориты, монцониты. К наиболее поздним фазам относятся биотитовые граниты, граносиениты и плагиограниты.

Плагиогранит состоит в основном из плагиоклаза (54%), кварца (37%), биотита (8%) и амфибола (0,5%). Акцессорных минералов очень мало: магнетит и апатит (Каменов, 1969). Биотитовый гранит содержит 35—50% плагиоклаза, 15—31% калиевого полевого шпата, 19—30% кварца и 4—8% биотита. Акцессорные минералы — апатит цирон, ортит, магнетит, титанит (Колчева, 1970; Каменов, 1969).

Лейкограносиениты характеризуются высоким содержанием SiO_2 и щелочных элементов. Они мелкозернистые, полностью лейкократовые, состоящие главным образом, из калиевого полевого шпата (80—85%) и подчиненного количества кварца, плагиоклаза и биотита.

2. *Габбро-плагиогранитовая формация из Стара Планина и Краиштидов*

Формация представлена контрастными членами габбро и лейкогранитов. Она развита в линеаментно-геосинклинальной зоне раннего этапа инверсной геосинклинальной стадии герцинского орогенеза, в пространственной связи со спилит-диабазовой формацией (Димитрова и др., 1975).

Лейкограниты Стакевского и Клисурского массивов в западной части Стара Планина характеризуются сланцеватостью, параллельной структурой и аплитоидной текстурой. Они состоят из 30—31% плагиоклаза, (15—20%An), 30% калиевого полевого шпата, 33—34% кварца и 5% биотита. Акцессорные минералы (~ 1%) представлены магнетитом, ортитом, апатитом, цирконом и гранатом (Димитрова, Арнаудова, 1977).

Струмские диориты из Краиштидов принимаются Димитровой как широкое площадное раскрытие эндоконтактной зоны, в которой гранитный магматизм подвергается чувствительному влиянию состава основных вмещающих пород. Этот же автор выдвигает точку зрения о формировании этих пород, как процесс магматического замещения, согласно теории Коржинского. По минеральному составу плагиогранитная фация аналогична лейкогранитам Западной части Стара Планина (Димитрова, 1967).

3. *Группа так называемых „южноболгарских гранитов" батолитового типа*

Граниты развиты в 3-х структурных зонах: Средногорской, Рило-Родопской и Краиштидной, где образуют ряд больших тел батолитового типа. Это следующие массивы: Центральное Средногорье, Сакар, Рило-Родопский, Пирин и Осоговский. Везде они залегают среди высококристаллинных пород. По возрасту принимаются за палеозойские, но согласно более новым геохронологическим данным, они сформированы в продолжении длительного интервала времени: от 330 до 40 млн. лет (Алексиев и др., 1980).

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Для южноболгарского гранитоидного магматизма характерны: слабый размах дифференциации, ограниченная фациальная изменчивость, однородность состава и богатство пегматитовых жил и тел.

Лейкограниты состоят из плагиоклаза (28—35%), калиевого полевого шпата (18—25%), кварца (30—40%), биотита (4—5%) и мусковита (до 8%). Они значительно беднее акцессорыми минералами в сравнении с биотитовыми гранитами, но в качественном отношении более разнообразны. Характерная для южноболгарских гранитов ассоциация — ортит, титанит, апатит, — в лейкогранитах обогащена редкоземельными минералами монацитом и ксенотитом, а в отдельных случаях встречаются и тантало-ниобаты, ортит и уранинит. Часто наблюдается совместное присутствие в незначительных количествах минералов-антагонистов: ортита и монацита, титанита и монацита (Алексиев и др., 1980).

Обильные пегматитовые дифференциаты южноболгарских гранитов являются носителями характерной редкометальной минерализации: бериллиевой, тантало-ниобиевой, ураново-редкоземельной.

В некоторых более мелких плутонических телах Родопского массива, образованных на меньшей глубине, наблюдаются вторичные изменения грейзенового типа (Каменов и др., 1974).

II. Геохимическая специализация лейкогранитов из Франции и Руанды

Как видно из рисунка 1, две гранитные группы характеризуются одной исключительной специализацией, сходной со специализацией „редкометальных лейкогранитов плюмазитового типа", по классификации Таусона. (Таусон, 1977). Они похожи на граниты из Рудных гор (Чехия, ГДР), Карловского массива (Чехия), Восточного Забайкалья, Восточного Монгольского массива и др.

Это наиболее поздние дифференциаты крупных глубинных палингенных магм, насыщенных летучими компонентами. Они имеют сильно повышенные концентрации Li, Rb, Cs, Sn, Nb, F, U, т.е. летучих компонентов и элементов, образующих с ними устройчивые комплексы.

Главную роль в формировании отмеченной исключительной геохимической специализации редкометальных плюмазитовых лейкогранитов играл процесс эманационной дифференциации. Другая характерная черта этих гранитов — ограниченная роль инертных в процессе эманационной дифференциации элементов, как Sr, Ba, Zr, Th, Mo, вследствие чего значения отношений Zr/Hf, Th/U, Ba/Rb сильно занижены.

Фации с кремниево-щелочно-натриевой тенденцией являются более благоприятными для концентрации Li, Cs, Sn, в то время как фации с кремниево-щелочно-калиевой тенденцией более благоприятны для концентрирования Rb и U.

Редкометальные плюмазитовые лейкограниты отличаются от „редкометальных гранитов щелочного ряда", по классификации Таусона, которые также являются палингенными более богатым содержанием F, Li, Rb, Sn, Ta, низкими концентрациями Sr, Ba, Zr, TR, и значительно более низкими значениями отношений Ba/Rb и Nb/Ta. В Руандийских лейкогранитах раскрывается еще одна характеристика плюмазитового

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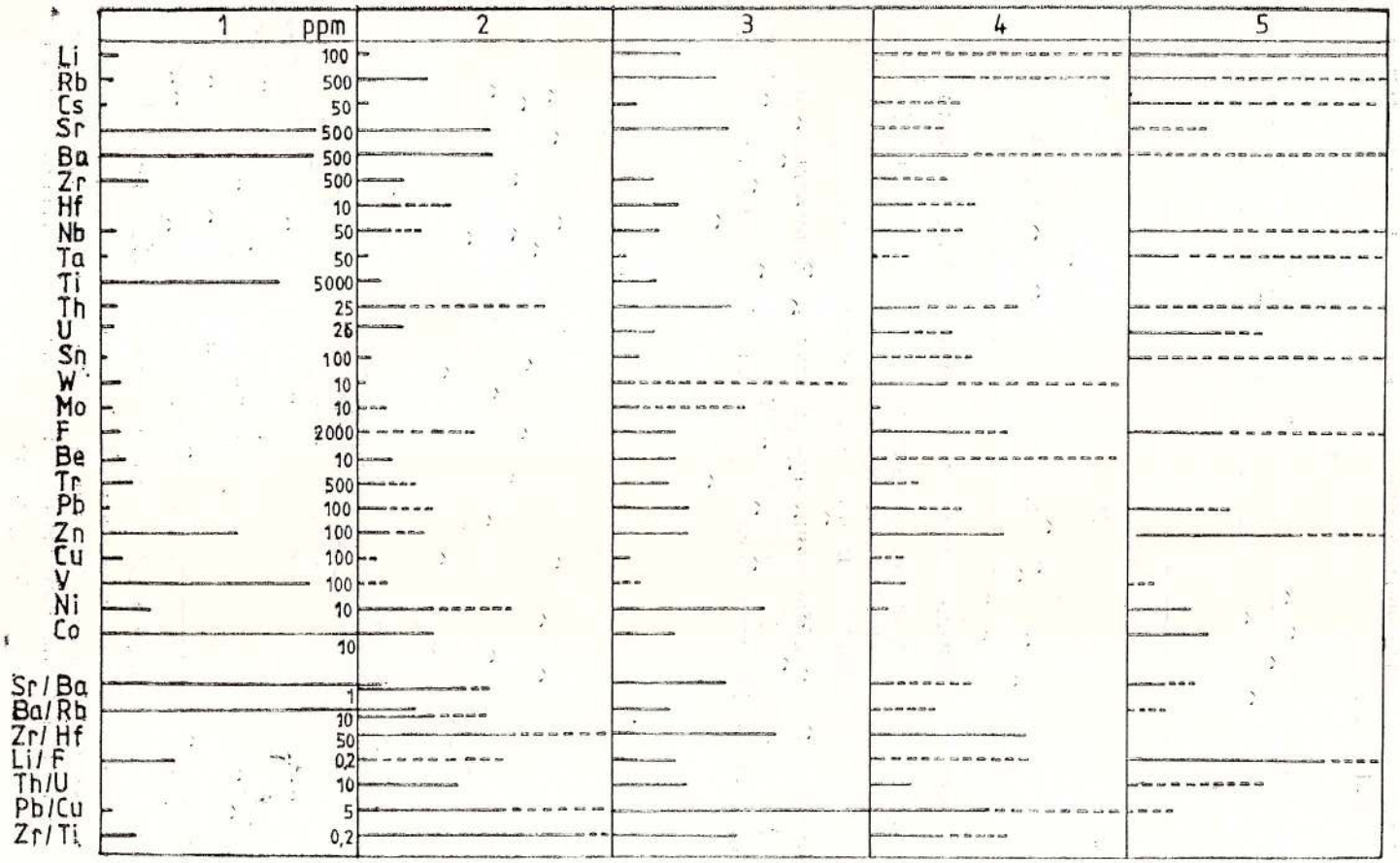


Рис. 1. — Редкие и рассеянные элементы в лейкогранитах.

1, плагиогранит из габбро-монцонит-гранитовой формации (Франция) 2, лейкограниты из габбро-плагиогранитовой формации (Болгария); 3, лейкограниты из „Южноболгарских гранитов" (Болгария); 4, лейкограниты из Руанды; 5, лейкограниты из Франции.

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типа — значительно повышенные концентрации Ti, Sn, Ta и Nb в биотите и мусковите (табл. 1).

ТАБЛИЦА 1

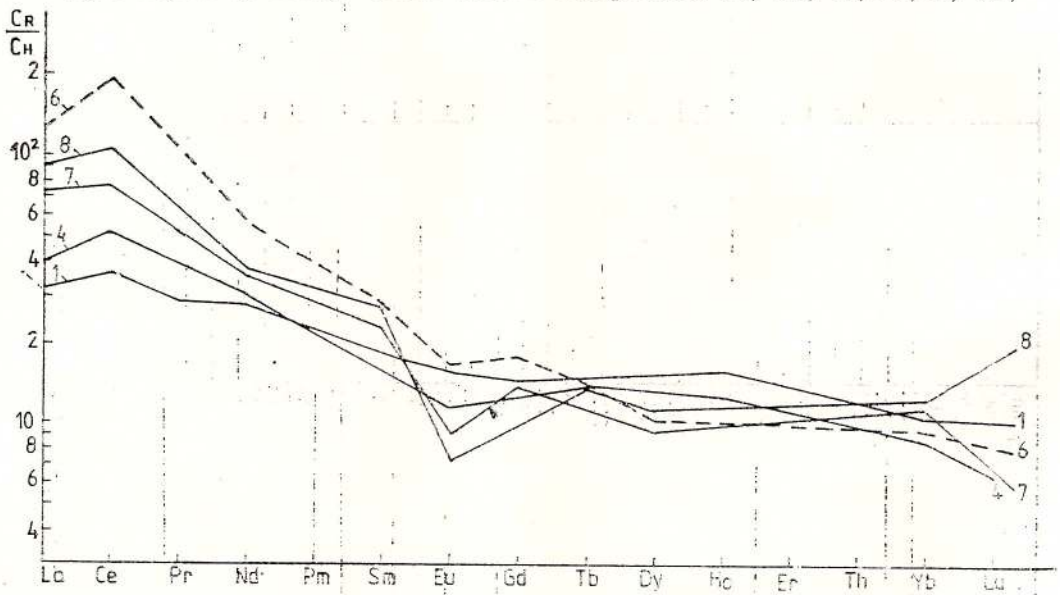
Слюды из Руандийских лейкогранитов: редкие элементы

Минералы	Массив	Элементы (г/т)				
		Sn	Ta	Nb	Ti	Li
биотит	Кабана	10	92	158	15000	1400
мусковит		250	49	112	670	1150
биотит	Гитарама	6	20	111	15000	170
мусковит		30	41	48	1723	31

III. Редкие и рассеянные элементы в лейкогранитах Болгарии

Данные, графически представленные на рисунке 1, показывают, что вариация редких и рассеянных элементов хорошо подчеркивает различие между тремя гранитоидными формациями в Болгарии.

Плагиограниты габбро-монцонит-гранитовой формации предлагают одну исключительную, нехарактерную для гранитов геохимическую характеристику: очень низкое содержание Li, Rb, Cs, Zr, F, Sn,



Фис. 2. — Распределение РЗЭ, нормализированное по хондритам.

1, плагиогранит из габбро-монцонит-гранитовой формации; 4, лейкогранит из габбро-плагиогранитовой формации; 6, биотитовые граниты южноболгарского типа; 7, лейкограниты южноболгарского типа; 8, измененные лейкограниты южноболгарского типа.

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Be, Pb, и TR, повышенные содержания Ti, Cr, V, Zn, Co, содержания Sr>Ba, Ni⩽Co, Pb<Cu; почти хондритовый тип нормированной по отношению к хондритам кривой TR, с отсутствием дефицита Eu′, (рис. 2). Те же геохимические характеристики наблюдаются в плагиогранитах массива Троодос (Кипр), Маинского комплекса (Западные Саяны) и серии Витилеву (Фиджи) — все они объединены Таусоном (Таусон, 1977) в генетическую группу „плагиогранитов толеитового ряда".

С редкими и рассеянными элементами делается вклад в аргументацию (подтверждения) гипотезы мантиевого происхождения гранитоидов габбро-монцонит-гранитовой формации. Исходные магмы были значительно бедны F, H_2O и другими летучими компонентами, с высокотемпературной эвтектикой, отсутствием условий для эманационной дифференциации и, следовательно, не являются перспективными для промышленной минерализации по отношению к Sn, W, Li, Be, (U).

Характерно для **южноболгарского типа гранитов** более высокое содержание Li, Rb, Cs, Nb, Ta, F, Sn, Be, Pb, TR; содержание Sr < Ba, Ni⩾Co; относительный излишек более легких лантаноидов и дефицит Eu′ (рис. 2). Отмеченные тенденции свидетельствуют о коровом происхождении магматизма. Таусон объединяет граниты из различных районов с подобным составом (Сусамирский батолит, Восточные Саяны, Рудные горы, Восточная Монголия и др.) в одну геохимическую группу, названную „палингенные граниты кальциево-щелочного ряда".

Слабая вариация как в макрохимизме, так и в распределении редких и рассеянных элементов (Sr/Ba ; Nb/Ta ; Zr/Hf ; Th/U ; Pb/Cu ; TR, Eú) в биотитовых гранитах и одной части лейкогранитов подтверждает генетическое единство южноболгарских гранитов. Одновременно с этим, между тремя гранитными фациями существуют различия, которые показательны для внутренней эволюции гранитов.

Хорошо отмечена тенденция во внутренней эволюции южноболгарских гранитов, связанная с метасоматическими изменениями. В наиболее общих линиях метасоматическая эволюция сопровождается увеличением пропорции Rb, Zr, Ba, Hf, Nb, Ta, Pb, Th с сильной вариацией и геохимическими аномалиями Sn, W, Mo, Li, U, чрезвычайно низкими значениями отношений Sr/Ba, Th/U, Ni/Co, и Pb/Cu. Хондрит-нормированная кривая TR позволяет увидеть доминирующую роль более тяжелых лантаноидов и большой дефицит Eú (рис. 2, кривая 5).

Вариация элементов-следов в метасоматически измененных лейкогранитах в зависимости от степени и характера щелочности показана в таблице 2.

Как видно из таблицы, низкая щелочность измененных лейкогранитов оказывает неблагоприятное влияние на концентрирование редких элементов, за исключением U и Mo. Элементы Li, Cs, и Zr имеют повышенное сродство к кремниево-щелочно-натриевым фациям, а элементы Rb, U, Sn — к кремниево-щелочно-калиевым фациям.

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ТАБЛИЦА 2

Содержание элементов-следов в Барутино-Буйновском плутоне

Обр. №	Щелочность		Li	Rb	Cs	Sr	Ba	Ba/Rb	Zr	U	Sn	Nb	Ta	TR	Eú	Mo
	K + Na	K/Na														
1	5.5	0.9	87	160	4.9	368	586	3.7	147	2.8	4.8	15	1.7	168	0.70	—1
2	6.1	0.5	38	272	16	193	793	2.9	181	7.0	1—10	18	4.5	118	0.47	2
3	5.7	7.5	31	301	4	55	253	0.8	110	12	46	12	3.0	161	0.25	1—6
4	0.4	0.5	10	20	5	48	210	11	32	12	сл.	сл.	1.2	110	0.66	40

I. биотитовые граниты: 2. натриево-щелочная фация; 3. калиево-щелочная фация; 4. кальциево-щелочная фация.

Лейкограниты габбро-плагиогранитовой формации из западной части Стара Планина и Краиштидов с пониженными содержаниями Li, Cs, Zr, TR, F, Be, Ni, Pb (рис. 1) и толеитоподобной хондрит-нормированной кривой распределения TR со слабым дефицитом Eu′ (рис. 2) приближаются к ,,плагиогранитам толеитовой серии'' по Таусону. Аналогия более отчетлива для лейкогранитов из Краиштидов. Можно отметить также, что лейкограниты из западной части Стара Планина как по распределению элементов-следов, также и по химической типологии не представляют нормальное развитие биотитовых гранитов в районе (Св. Николски, Белоградчийски, Петрохански и др.).

По другим признакам — сравнительно повышенным концентрациям Rb, Sr, Ba, Nb, Sn, Ni>Co те же плагиограниты приближаются к группе ,,палингенных гранитов кальциево-щелочного ряда'', по Таусону. Вероятно, лейкограниты этой формации имеют ,,смешанное'' происхождение в результате гибридизации или контаминации между дифференцированной мантийной магмой и коровым материалом.

Дискуссия

Рудопродуктивность гранитных интрузий обычно связана с двуслюдяной и лейкократовой фациями. Последние образуются или как более поздние фазы кристаллизационно-эманационной дифференциации богатых летучими компонентами магм, или в результате позднего щелочно-метасоматического изменения гранитов, потенциально богатых редкими элементами. Таков случай с плюмазитовым типом лейкогранитов из Франции и Руанды, которые являются перспективными на олово, вольфрам, уран, редкие земли и др. редкие элементы.

Лейкограниты Болгарии по распределению редких и рассеянных элементов не принадлежат к генетическим гранитным типам, для которых характерна редкометальная минерализация. Лейкограниты толеитового ряда, к которым относятся верхнемеловые плагиограниты Средногорья, образованы из ,,сухих магм'', имеют низкое содержание летучих компонентов и являются наименее перспективными в отношении потенциальной рудоносности. Палингенные граниты кальциево-щелочного ряда, к которым относятся южноболгарские лейкограниты, при известных

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условиях (внедрение более поздних недегазированных дифференциатов в более верхние зоны земной коры) могут быть источником редкометальной минерализации при аметасоматических процессах. Такие проявления существуют в Барутино-Буйновском плутоне Родопского массива.

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ЗАМЕЧАНИЕ

Ч. Димофте: Мы можем подчеркнуть интересное сходство состава малых элементов (Sr, Ba, V, Ti, Co) лейкогранитов Болгарии и очковых и гранитовых гнейсов Средних Карпат Румынии.

Также интересно подчеркнуть генетические процессы перетерпленные гранитами НРБ (ассимиляции) и гнейсами СРР (мигматизация, метасоматизм).

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РУДООБРАЗОВАТЕЛЬНЫЕ ПРОЦЕССЫ ЗИДАРОВСКОГО РУДНОГО ПОЛЯ (ВОСТОЧНОЕ СРЕДНОГОРИЕ)[1]

В. В. КОВАЧЕВ[2]

Для решения проблем, связанных с изучением рудных месторождений, в последние годы широко применяется моделирование рудообразовательных процессов на основе конкретных, эмпирически определеных начальных условий (P, T, C и др.). Модели дают возможность получить предварительную геолого-экономическую оценку месторождений, притом еще в начальных периодах их исследований.

Зидаровское рудное поле находится в самой восточной (Причерноморской) части Банато-Средногорской металлогенической зоны. Проведенные геологические исследования показывают, что Бургасский рудный район, в котором находится Зидаровское рудное поле, сложен преимущественно породами верхнемелового возраста—осадочными, вулканогенно-осадочными, типично вулканогенными и интрузивными (Богданов и др., 1970; Василиев, Станушева-Василева, 1970; Димитрова и др., 1975; Иванов, 1965; Станишева, 1968, 1971, 1972). Самое широкое распространение имеют магматические породы слагающие вулкано-интрузивный комплекс, который включает в себя андезито-базальтовую, трахиандезит-трахибазальтовую, калиево-щелочную-базальтоидную, габбро-диорит-гранодиоритовую и габбро-монцонит-сиенитовую формации. В Зидаровском рудном поле (Рис. 1) установлены только андезито-базальтовая, трахиандезит-трахибазальтовая и габбро-монцонит-сиенитовая формации. Последние являются результатом действия Зидаровского палеовулкана — центрального типа (Рашков и др., 1978; Popov et al., 1979). Месторождения, слагающие Зидаровское рудное поле, характеризуются наличием медной до полиметаллической минерализаций, а рудные тела имеют форму жил, местами в виде рудных столбов.

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[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13, Бухарест, Румыния.

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Рис. 1. — Геологическая карта Зидаровского рудного поля (по /14,21/).
1, Четвертичные отложения; 2, Плиоцен; 3, Породы Росенского вулкана; 4, Габбро-монцонит-сиенитовая формация; 5, Дайки (трахиандезит-трахибазальтовая формация); 6, Трахиандезит-трахибазальтовая формация: а) жерловые и субвулканические тела; б) лавы и пирокластиты; 7, Андезито-базальтовая формация (сиенодиориты); 8, Андезито-базальтовая формация (пирокластиты и лавы); 9, Олистостромная толща; 10-Турон; 11, Разломы; 12, Рудные жилы; 13, Геологическая граница.

Минералогия и зональность руд Зидаровского рудного поля

В результате минералогических исследований (Ковачев, 1965; 1979) при помощи современных методов и аппаратуры, в том числе оригинальных (Ковачев, Страшимиров, 1979; Ковачев и др., 1980) выявлены 49 минералов, сгруппированных в 6 минеральных ассоциациях и 14 минеральных парагенезисов (схема). В некоторых из этих минералов обнаружены включения, различающиеся по морфологии, заполнению и генезису. Установленная температура, гомогенизация, солевая концентрация и агрегатное состояние вакуолей, вместе с минеральным составом и общее геохимическое развитие минералообразования, дают возможность для моделирования процессов рудообразования. В результате аналогичных исследований (Ковачев, Страшимиров, 1979) установлено, что минералы как и рудные парагенезисы сформировались в довольно широким температурном диапазоне (<650°C — —100°C), при низкой солевой концентрации рудообразующих флюидов (>10 % NaCl) и низким давлением во время гидротермального синтеза. Разные температуры, при которых формировались минералы, показы-

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вают, что они имеют зональное распространение, вызванное морфологией палеотемпературного поля. В действительности, минералогические исследования доказывают, что имеет место концентрическая минералогическая зональность, с одним температурным центром — афлоримент Зидаровского интрузива (Рис. 2).

Минералы, слагающие самый высокотемпературный ряд-магнезиоферрит-хлорапатитовой ассоциации, встречаются преимущественно в глубоких частях Зидаровского интрузива и ассоциируют с габбро-монцонитовой наставкой. Эпидот-хлорит-пиритовая минеральная ассоциация имеет большое площадное распространение и локализована она, чаще всего, в лавовых и пирокластических материалах. Только калиевые полевые шпаты встречаются в монцосиенитовой наставке интрузива. Все остальные промышленные минеральные ассоциации (халькопирит-висмутинитовая и халькопирит-сфалерит-галенитовая) образуют три концентрические зоны вокруг афлоримента Зидаровского интрузива (Рис.2).

Внутренняя зона состоит из минералов халькопирит-висмутинитовой ассоциации. Существуют данные, что на глубине жильный тип оруденения переходит в прожилково-вкрапленный тип. В том же направлении уменьшается количество висмутина за счет остальных сульфосолей висмута и теллура. Вторая зона смешанная. Она составлена минералами халь-

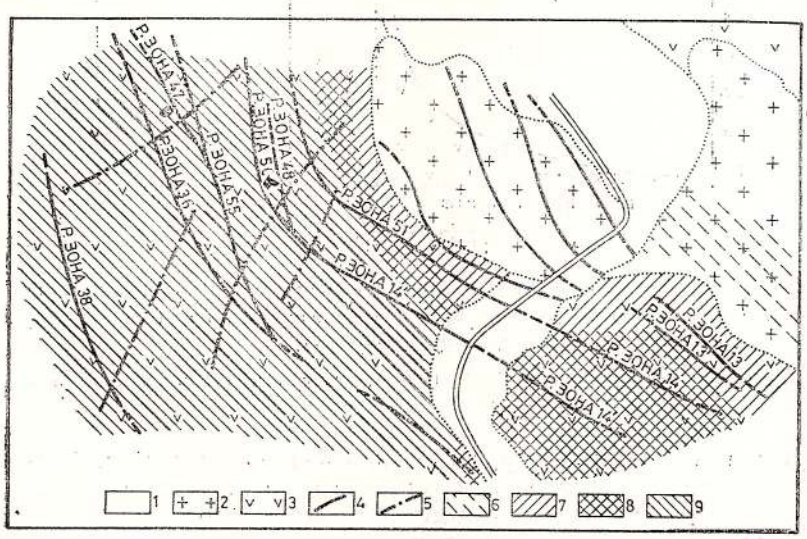


Рис. 2. Схема горизонтальной минеральной зональности месторождения Зидарово.

1, Четвертичные отложения; 2, Зидаровский интрузив; 3, Трахиандезит-трахибазальтовая толща; 4, Рудные зоны (радиальные); 5, Рудные зоны (концентрические); 6, Зона распространения магнезиоферрит-хлорапатитовой ассоциации; 7, Зона распространения халькопирит-висмутинитовой ассоциации; 8, Зона смешения между халькопирит-висмутинитовой и халькопирит-сфалерит-галенитовой ассоциациями; 9, Зона распространения халькопирит-сфалерит-галенитовой ассоциации.

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копирит-висмутинитовой и халькопирит-сфалерит-галенитовой ассоциации. Внешняя зона характеризуется минералами халькопирит-сфалерит-галенитовой ассоциации. Она прослеживается на глубине свыше 500 м. В каждой из этих промышленных ассоциаций существует горизонтальная зональность, выражающаяся в постепенном переходе между отдельными минералами. Например, халькопирит вблизи Зидаровского интрузива не содержит включений. При удалении от интрузивного тела появляются „сфалеритовые звездочки", дальше идет сфалерит с халькопиритовой эмульсией, переходящий в чистый клеофан. Подобные переходы обнаружены и в кварце.

Построенная зависимость между палеотемпературой и расстоянием до центра афлоримента интрузивного тела в месторождении Зидарово, характеризуется тремя зонами, имеющими разный температурный градиент пространственно совпадающие с описанными выше тремя кон-

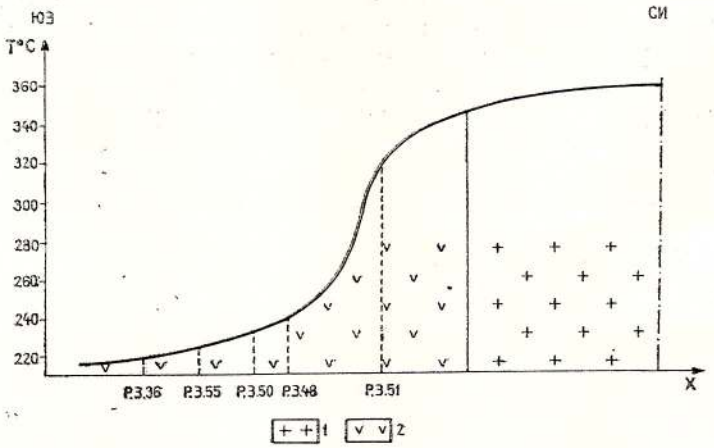


Рис. 3. — Изменение температуры образования кварца (кварц-халькопиритового и борнит-сфалеритового парагенезисов) в зависимости от расстояния до интрузива.

1, Зидаровский интрузив; 2, Трахиандезит-трахибазальтовая толща.

центрическими зонами минералогической зональности (Рис. 3). В результате температурного воздействия Зидаровского интрузива, температурный профиль имеет пологую форму при высоких абсолютных значениях температур. Зона с наиболее высоким температурным градиентом ограничивается фронтом термического поля, созданным во время формирования основных промышленных ассоциаций. Сравнительно большие, чем обычные значения температурного фона и небольшой температурный градиент в ЮЗ части температурного профиля, объясняется высоким палеотемпературным фоном. Это предположение подтверждается проведенными расчетами по методике Гогеля (Г о г е л ь, 1978), при которых доказывается наличие палеотемпературного фона 200°С во время промышленного рудообразования. Он вызван активной дорудной вулканической деятельностью.

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Если пренебречь анизотропией среды и принять температурный интервал промышленного рудообразования 360°С—200°С (Ковачев, Страшимиров, 1979) то путем экстраполяции можно определить, что размах оруденения в горизонтальном направлении доходит до 2200 м от центра интрузива. Экстраполяция изотерм на глубине позволяет определить возможный вертикальный размах оруденения мощностью около 1300 м. При интерпретации значений размаха оруденения в горизонтальном и вертикальном направлении, необходимо иметь ввиду возможное влияние апофизов интрузива, которые не установлены на поверхности и, следовательно, неприняты во внимание при расчетах. Однако, наличие локальных температурных максимумов в пределах Зидаровского рудного поля (Ковачев, Страшимиров, 1979) подтверждает вероятное наличие таких дайкообразных тел.

Описанные особенности минеральной и температурной зональности гидротермального оруденения Зидаровского рудного поля определяют ее моноасцендентный характер. Наиболее важными доказательствами в этом отношение являются следующие:

1. Общее геохимическое развитие рудообразовательного процесса от силикатов через окислы и сульфиды до карбонатов и сульфатов, как и факт, что в целостном процессе гидротермального минералообразования участвуют одни и те же главные элементы (Fe, Cu, Bi, Pb, Zn, Au, Ag).

2. Постепенный переход одного парагенезиса в другой и наблюдаемая эволюция кварца, халькопирита и сфалерита в двух главных промышлених ассоциациях.

3. Наличие смешанной зоны между халькопирит-висмутинитовой и халькопирит-сфалерит-галенитовой минеральными ассоциациями, что объясняется миграцией оптимальных для рудообразования физико-химических условий.

4. Отсутствие температурных ,,скачков'' между отдельными парагенезисами и ассоциациями и постепенное уменьшение палеотемператур по мере удаления от интрузива.

Последовательность минералообразования и модель рудообразующих процессов

Основываясь на характерных особенностях руд Зидаровского рудного поля, рудообразующий процесс определен как непрерывно-прерывистый. Притом основной причиной прерывистого характера являются региональные тектонические процессы, сопровождаемые магматическими проявлениями. Непрерывный характер обусловен постепенным эволюционным развитием минерализационных процессов во время спокойных периодов, вызванным изменением температуры, давления, концентрации и наличия катализаторов.

На основе проведенных минералогических исследований Зидаровского рудного поля установлены три этапа минералообразования: интраплутонический, гидротермальный и гипергенный (схема). Они дают представление о прерывистом характере процесса и выделяются благодаря интенсивным тектоническим подвижкам, иногда—проявлениям магматизма.

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Первый этап содержит один парагенезис-магнезиоферрит-хлорапатитовый. Последовательность образования минералов в этом парагенезисе связана с эволюционными процессами остывания интрузивного тела. Характерной для этого этапа является прямая генетическая связь между парагенезисом и габроидной наставкой Зидаровского интрузива, установленная на основе пространственного расположения минералов, их структурных, текстурных и температурных особенностей. Эти характерные признаки, наряду с фактом, что после рудообразования формируется следующая, монцонит-сиенитовая наставка интрузива, определяют оруденение как интраплутоническое (Дымкин, 1970). Факты, установленные при исследовании включений в минералах этого этапа дают основание предположить минералообразование в надкритическом состоянии флюида в замкнутой системе, при низкой концентрации и активности серы. Встречающиеся в хлорапатите газовые и газово-жидкие включения предполагают, что в конце этапа происходило вскипание рудообразующих флюидов, т.е. разгерметизация систем и внедрение последующей монцонит-сиенитовой наставки.

Гидротермальный этап начался после втвердения монцонит-сиенитовой наставки интрузива и является результатом гидротермальных процессов связанных с остыванием этой же наставки. Эпидот-хлорит-пиритовая ассоциация отражает развитие предрудных гидротермальных изменений вмещающих пород. Последовательность минералообразования и исследование газово-жидких включений показывает, что в самом начале формировались минералы в условиях кипения (гранат, кварц и др.), а затем выделились минералы, продукты нормального кристаллизационного процесса. Эта особенность дает возможность применяя метод Хааса (Haas, 1971) определить размер эрозионного среза, который для объекта изучения достигает 900 м.

Халькопирит-висмутинитовая, халькопирит-сфалерит-галенитовая и карбонат-цеолитовая ассоциации являются типичными гидротермальными продуктами. Первые минералы, слагающие эти ассоциации, образовались в редукционных условиях (мушкетовитизация гематита). Растворы были ненасыщенные, а гидротермальная система — относительно открытая. Последовательность минералообразования обусловлена различием во времени достижения температурного фронта до данной точки пространства, как и изменением физико-химических условий рудообразования, связанного с проявлением локальных тектонических движений (схема).

В геохимическом отношении минералообразование начинается с выделения окислов, проходит через формирование сульфидов и оканчивается образованием карбонатов и сульфатов.

Несмотря на то, что генетическая связь между гидротермальными оруденениями и монцонит-сиенитовой интрузивной наставкой менее представительна, она может считаться доказанной с большой достоверностью благодаря следующим сбстоятельствам:

1. Существование палеотемпературной и минеральной зональности около афлоримента Зидаровского интрузива.

2. Пространственная связь между монцосиенитовой наставкой и оруденением и небольшая разница во времени образования интрузива и первого промышленного парагенезиса (1000 лет), рассчитана по методу Гогеля (Гогель, 1978; Ковачев, 1981)

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3. Последовательность развития интрузивообразования и рудообразовательных процессов.

Существенное значение для выяснения генезиса и пространственного положения оруденения в Зидаровском рудном поле имеют вопросы, обусловившие активную магматическую и рудообразующую деятельность. На основе ряда геологических и геофизических исследований (Долапчиева, Христова, 1978; Йосифов и др., 1978; Тумбев

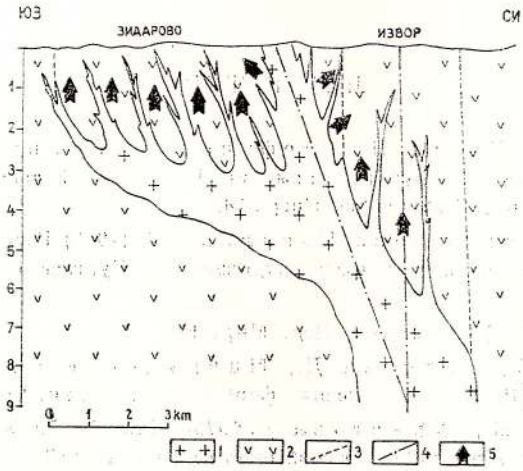


Рис. 4. — Схематическая пространственно-генетическая модель Зидаровского интрузива.

1, Зидаровский интрузив; 2, Трахиандезит-трахибазальтовая толща; 3, Проекционные контуры гравитационных и магнитных аномалий; 4, Оси Зидаровского интрузива и гравиметричной аномалии; 5, Направление тепловых потоков.

и др., 1976) и геометрических построений можно построить вероятную пространственно-генетическую модель, выясняющую эти вопросы (Рис. 4).

Анализ этой модели приходит к следующим наиболее важным выводам:

1. Видимая часть Зидаровского интрузива представляет собой дайкообразную апофизу, расположенную в северо-восточном конце большого и сложно устроенного интрузивного тела, с апикальной частью на глубине около 4,5 км, маркированного магнитным максимумом. В свою очередь, это тело связано с еще более глубокой магматической камерой, о наличии которой можно судить по гравитационному максимуму в окрестностях поселка Извор. Созданная модель подтверждает высказанное ранее мнение о подкоровом источнике магмы (Станишева, 1971).

2. Установленное направление температурных и гидротермальных потоков около Зидаровского интрузива дает возможность прогнозировать перспективы для поиска рудных тел в ЮВ части рудного поля, где обнаружена магнитная аномалия. В СВ направлении промышленные рудные тела можно ожидать либо вблизи интрузива, либо на глубине.

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С целью комплексного использования полезных компонентов оруденения в Зидаровском рудном поле обособлены следующие типы руд: железо-фосфорные, медные, висмутово-теллуровые и медно-свинцово-цинково-золотые. Второй и четвертый тип руд имеет доказанное промышленное содержание, а для остальных пока еще не установленно промышленное значение.

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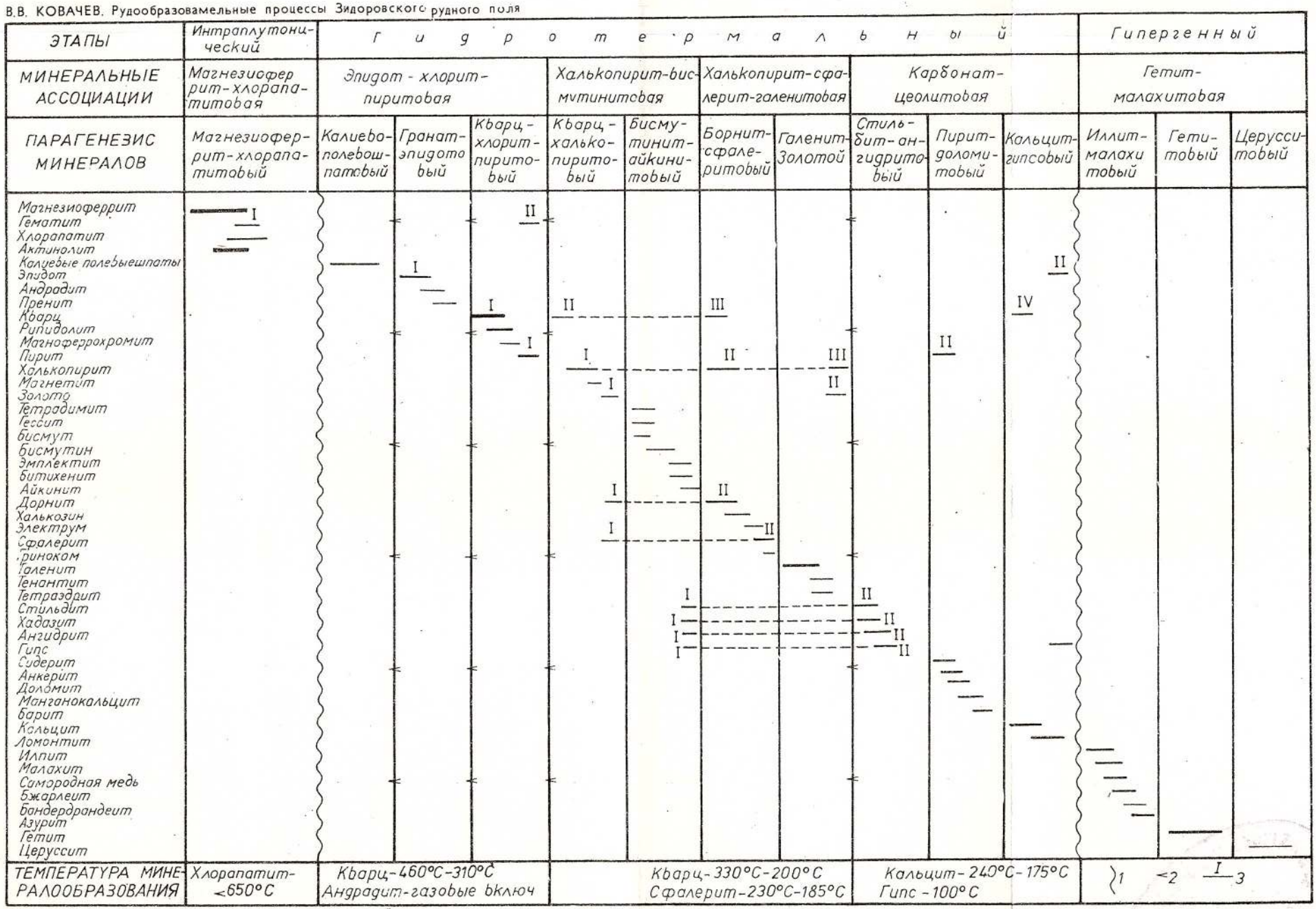
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Imprim. Atel. Inst. Geol., Geof.

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ГЕОХИМИЧЕСКИЕ ОСОБЕННОСТИ РУДООБРАЗОВАТЕЛЬНОГО ПРОЦЕССА МОЛИБДЕН-МЕДНОГО МЕСТОРОЖДЕНИЯ „МЕДЕТ" (НРБ)[1]

СТР. СТРАШИМИРОВ [2]

Месторождение „Медет" (Центральная часть Средногорской металлогенической зоны, НРБ) приурочено к породам интрузивного тела, обозначаемым как Медетский плутон (У ш е в и др., 1962). По своему составу и структурным особенностям Медетский плутон относится к интрузивам верхнемелового-ларамийского возраста, с которыми в ряде случаев парагенетически ассоциируются месторождения меди в Средногорской металлогенической зоне.

Медетский плутон сформировался при последовательном образовании кварц-монцодиоритов и гранодиоритов, расположенных в пересеченной зоне систем разломов с направлениями ССЗ и ВСВ. Рамка плутона сложена из метаморфических пород (преимущественно гнейсы) и гранитов палеозойского возраста. К палеозою, по наиболее новым исследованиям (З а г о р ч е в и др., 1973) относится и раскрывающееся в направлении ВЮВ тело из кварц-габродиоритов, выделяемое некоторыми авторами как первая наставка плутона (У ш е в и др., 1962; А н г е л к о в, 1974). Консолидация апикальных частей плутона была последована образованием аплит-микропегматитовых и кварц-полевошпатовых жил, предшествующих по времени рудообразовательную деятельность.

Оруденение в месторождении находится под формой прожилок и вкрапленников сульфидных минералов, распространенных в кварц-монцодиоритах по близости до их контакта с гранодиоритами. Основными рудными минералами для месторождения являются халькопирит и пирит, а второстепенное распространение имеют молибденит, гематит, сфалерит и галенит. Во время настоящих исследований был установлен и ряд редких по своему распространению минералов, таких как сульванит, колусит, карролит, гессит, самородное золото и др., которые дают ценную информацию о геохимической характеристике рудообразовательных растворов в различных периодах их развития. Из нерудных минералов более широкое

[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13, Бухарест, Румыния.

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распространение в месторождении имеют кварц, полевые шпаты, хлорит, биотит, кальцит, как и некоторые виды цеолитов.

Взаимоотношения минералов в месторождении показывают, что здесь можно выделить шесть минеральных парагенетических ассоциаций. Последовательность их образования следующая; магнетит-гематитовая, пирит-молибденит-халькопиритовая, кварц-молибденитовая, кварц-пиритовая, кварц-сфалерит-галенитовая и кальцит-цеолитовая. Среди них промышленное значение для месторождений имеют пирит-молибденит-халькопиритовая и кварц-молибденитовая, в то время как остальные представлены в ограниченом объеме. Первые две из вышеуказанных ассоциаций представлены под формой прожилков и вкрапленников, а остальные распространены преимущественно в виде жил.

Во время настоящего исследования наряду с минерально-парагенетическим анализом использованы и методики имеющие своей целью выяснить форму и распределение элементов примесей в рудах. Большая часть минералов в месторождении исследованы на основе последовательного приложения спектрального, лазеро-спектрального и рентгено-спектрального анализа. Условия, при которых были проведены анализы указаны в соответствующих таблицах 1, 2 и 3.

Начало рудообразования в месторождении ,,Медет'' характеризуется преобладанием минералов железоокисного типа минерализации. Преобладающее распространение в магнетит-гематитовой ассоциации имеют минералы магнетит и гематит, а наличие ильменита и рутила указывает на содержание титана в начальных фазах рудообразовательного процесса. Рентгено-спектральные анализы минералов этой ассоциации фиксируют широкую гамму элементов примесей, которые дают дополнительную информацию насчет геохимической обстановки на этом этапе. Характерные примеси в магнетите и гематите это Ti, Cr, Mn, V. Проведенные исследования для выявления распространения указанных элементов в анализированных минеральных индивидах показывают, что они распределены равномерно, что предполагает их возможное участие под формой изоморфных примесей. В результате сравнения анализов магнетита и гематита, можно заметить, что последный выделяется как ,,более чистый'' в геохимическом отношении (табл. 2 и 3). Особенность гематита включать меньше элементов примесей, когда ассоциирует с магнетитом, отмечена в ряде исследований (Hegemann, Albrecht, 1954; Kisvarsanyi et al., 1967). Возможное объяснение этой закономерности можно искать на основе различий в строении кристаллической решетки обоих минералов, сбуславливающих меньшее количество позиций для замещения в структуре гематита, чем магнетита, Наблюдаемая мушкетовитизация в ассоциации, с другой стороны косвенное указание на присутствие определенных флюктуаций в окислительно-восстановительном потенциале среды, в которой протекает минералоотложение.

Минералотермометрические исследования кварца из рассматриваемой ассоциации определяют сравнительно высокую температуру (около 400°C) и относительно наивысшую концентрацию солей флюидов (около 12% NaCl эквивалент) в минералообразующей среде (Страшимиров, 1979, 1981). Установленные CO_2 и угольная кислота в включениях маркируют сравнительно кислотный характер растворов в начале рудообразовательной деятельности.

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ТАБЛИЦА 1

Результаты лазерного спектрального анализа минералов

минеральная ассоциация	минерал	содержания элементов в весовых процентах								
		V	Cr	Mn	Ti	Co	Ni	Ag	Bi	Cd
магнетит-гематитовая	магнетит	0,05—0,1	0,05	0	0,1 — 0,3	—	—	—	—	—
	гематит	0,5	0,05	0,1	0,1—0,5	—	—	—	—	—
	андрадит	—	0,05	1	0,1—0,5	—	—	—	—	—
пирит-молибденит-халькопиритовая	пирит	—	—	—	—	0,01	0,01	0,001	—	—
	халькопирит	—	—	—	—	0,01	следы	—	—	—
	магнетит	—	0,005	0,1	—	—	—	—	—	—
	гематит	—	—	—	0,01—0,03	—	—	—	—	—
	сфалерит	—	—	0,1—0,3	—	—	—	—	—	0,1—0,3
	галенит	—	—	0,1	—	—	—	0,1	0,01	—
кварц-сфалерит-галенитовая	пирит	—	—	—	—	0,001	—	следы	—	—
	халькопирит	—	—	—	—	следы	—	—	—	—
	сфалерит	—	—	0,1	—	—	—	—	—	0,3
	галенит	—	—	—	—	—	—	1	1	—

Условия анализа: апарат LMA-1, спектрограф Q-24, разрядное напряжение 2,3—3,5 kV

Анализировал: н.с. Л. Петкова, ЦНИЛ „Геохимия", ВМГИ, София.

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ТАБЛИЦА 2

Результаты рентгеноспектрального анализа минералов

минеральная ассоциация	минерал	содержания элементов в весовых процентах							
		Cu	Fe	Co	Ni	Ag	Bi	Cd	Se
пирит-молибденит-халькопиритовая	пирит	1,2	45,6	0,1	0,05	0,05	—	—	—
	кобальт-пирит	1,2	29,8—44,6	1,5—17,8	0,4	0,05—0,1	—	—	—
	никель-пирит	1,0	38,2	2,2	5,3	0,1	—	—	—
	халькопирит	34,3	30,1	0,3	0,4	0,1	—	—	—
	карролит	15,8—16,4	1,6—2,1	37,5—38,9	2,0—3,2	0,0—0,05	—	—	—
	борнит	63,7	10,7	—	—	0,05	—	—	—
	самор. золото	—	—	—	—	8,4—19,3	—	—	—
	сфалерит	0,7	2,4	—	—	—	—	0,4	—
	галенит	—	—	—	—	0,1—0,4	0,11	—	0,47—0,79
кварц-сфалерит-галенитовая	халькопирит	34,9	30,8	—	—	0,1	—	—	—
	сфалерит	0,1	0,3	—	—	—	—	0,3	—
	галенит	—	—	—	—	0,4—0,7	0,17	—	0,17—0,21

ТАБЛИЦА 3

минеральная ассоциация	минерал	содержания окисей в весовых процентах							
		SiO_2	Al_2O_3	TiO_2	Cr_2O_3	Fe_2O_3	FeO	MnO	CaO
магнетит-гематитовая	магнетит	35,5	0,35	0,05	—	6,4	90,65	0,15	—
	гематит	—	0,1	0,2	—	9,95	89,3	0,05	—
	андрадит	35,5	0,1	—	—	3,2	28,8	0,65	32,5
пирит-мол.-халькопирит.	магнетит	—	0,1	—	—	6,9	92,5	0,05	—
	гематит	—	—	—	—	10,0	90,0	—	—

Условия анализа: апарат „Микроскан — 9", ускоряющее напряжение 20 и 25 kV,
Анализировали: д-р К. Кийфт и В. Люстенауер (Институт геологии, Свободный университет, Амстердам)

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Переход от окисного к сульфидному минералообразованию в месторождении вероятно осуществляется резко, на что указывает ограниченное распространение низкосернистых минералов в промышленной сульфидной ассоциации. Массовое образование минералов этой ассоциации вызывается усиленной активностью серы и доминирующим присутствием меди и железа в растворах. В отношении железа можно предполагать и его частичное взаимствование из вмещающих пород, в то время как в ряде случаев халькопирит и пирит развиты по темноцветным минералам в кварц- монцодиоритах. Выделенный в ассоциации молибден сравнительно ограниченный по объему, что является особенностью в геохимическом развитии рудообразовательного процесса в месторождении в сравнении с классической моделью меднопорфировых месторождений, при которых основной объем молибденовой минерализации по времени предшествует образование медных сульфидов (П а в л о в а, 1978).

Специфической особенностью в геохимической характеристике пирит-молибденит-халькопиритовой ассоциации является широкая гамма элементов примесей. Многие из них, как золото, селен, телур и др. часто встречаются в медно-порфировых месторождениях и в этом смысле их можно рассматривать как типоморфные для этого типа (П о п о в, 1978).

В ходе настоящих исследований было установлено, что некоторые из элементов примесей в месторождении „Медет" распространены под формой самостоятельных минералов субмикроскопических размеров, другие — преимущественно под формой изоморфных примесий, для третьих характерны и обе формы.

Так например под формой самостоятельного минерала находится золото, элемент, который в более ранних исследованиях относили к изоморфным примесям в пирите. Исследования шлифов пирита и халькопирита, в которых в результате спектрального анализа регистрировано золото, показывают, что в этих минералах всегда присутствуют субмикроскопические включения самородного золота.

К элементам примесям, которые обнаружены в месторождении под формой самостоятельных минералов и изоморфных примесей, относится элемент кобальт. Основной объем этого элемента выделяется в пирит-молибденит-халькопиритовой ассоциации под формой изоморфной примеси в пирите. Следует указать на факт, что кобальт-содержащий пирит формирует хорошо выраженные прожилки и индивиды в халькопирите. Это подтверждает предположение о более позднем выделении элемента из гидротермальных растворов по отношению к образованию основного объема сульфидной минерализации. Содержания кобальта в этой разновидности пирита варьируют от 1,2 до 17,5 весовых процента, что само собой редкий случай в меднопорфировых месторождениях. В ходе настоящих исследований в месторождении был обнаружен и собственный кобальтовый минерал — карролит, который под формой субмикроскопических индивидов ассоциирует с включениями кобальт-содержащего пирита в халькопирите. Несмотря на то, что между двумя минералами не наблюдаются прямые взаимоотношения, более вероятно предположить, что карролит образуется после достижения максимальной степени насыщения кобальта в пиритовой структуре.

Подобно поведение никеля, который, хотя и в меньших количествах (до 5,3 весовых процента) обнаружен в никельпирите из рассматри-

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ваемой ассоциации. Полученные предварительные данные насчет наличия ваесита в ассоциации показывают, что никель тоже вероятно находился в количестве, достаточном для формирования собственных минералов.

К элементам примесям, обнаруженным до сих пор единственно под формой изоморфных примесей, можно отнести селен, регистрированный в результате рентгено-спектральных анализов галенита в месторождении.

Широкий спектр элементов примесей пирит-молибденит-халькопиритовой ассоциации иллюстрирует хорошо разнообразный состав гидротермальных флюидов, из которых она образована. Включения сульванита, колусита, гессита указывают на участие таких элементов как ванадий, олово, мышяк, теллур, серебро в составе растворов.

Специфической особенностью в геохимическом развитии рудообразовательного процесса в месторождении является формирование второй железоокисной минерализации, представленной магнетитом и гематитом образованные в рамках пирит-молибденит-халькопиритовой ассоциации. Их отличительная черта — более ограниченное содержание элементов примесей в сравнении с магнетитом и гематитом одноименной ассоциации. Образование окисей железа во время формирования промышленного сульфидного оруденения фиксирует изменения в окислительном потенциале среды.

В конце образования пирит-молибденит-халькопиритовой ассоциации растворы выделяют незначительные количества свинца и цинка, которые под формой галенита и сфалерита, обнаруживаются спорадически в халькопирите этой ассоциации. Как характерные элементы-примеси установлены селен, серебро, висмут (в галените) и кадмий (в сфалерите). До сих пор, проведенные исследования о распространении селена в меднопорфировых месторождениях предполагают его участие в качестве изоморфной примеси в пирите и халькопирите (П о п о в, 1977). Рентгено-спектральные анализы минералов в месторождении ,,Медет'' показывают, что здесь этот элемент находится в более значительных концентрациях единствено в галените. Не исключено, что регистрированный спектральным анализом селен в пирите и халькопирите, обязан присутствию галенита в анализированных пробах.

Телур, один из специфических элементов примесей в меднопорфировых месторождениях, чье распространение предполагается также под формой изоморфной примеси в пирите и халькопирите, в месторождении ,,Медет'' был обнаружен под формой собственных минералов — гессит и тетрадимит (?). Первый из них встречается в качестве субмикроскопических включений в пирите, а второй — в халькопирите промышленной ассоциации. Специфический элемент, характеризующий геохимическую обстановку к концу формирования пирит-молибденит-халкопиритовой ассоциации — это серебро. Проведенные рентгеноспектральные анализы включений самородного золото показывают, что содержание серебра увеличивается от центра к периферии индивидов. Кроме того серебро обнаружено под формой изоморфной примеси в галените, а также и в пирите, халькопирите и карролите. Были установлены и три отдельных минерала, в которых содержание серебра достигает 30-40 весовых процентов, но из-за маленьких размеров индивидов их точный анализ до сих пор невозможен.

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Минералотермометрические исследования кварца пирит-молибденит-халькопиритовой ассоциации определяют температурный диапазон формирования от 380 до 320°С и соленость гидротермальных флюидов 12-5 NaCl эквивалент (Страшимиров, 1979, 1981).

Преобладающий сульфидный характер минералообразовательных процессов сохраняется и во время формирования следующих трех из минеральных парагенетических ассоциаций в месторождении. Несмотря на то, что температурный переход к их образованию плавный, условия, в которых протекает рудообразование очевидно меняются, на что указывает смена штокверкового типа минерализации преобладающим жильным.

Характерный элемент, который выделяется из растворов в начале этого периода это молибден. Можно отметить, что соотношение Cu: Mo в месторождении сохраняется в границах 30: 1 до 60: 1, типичных для меднопорфировых месторождений, но отчетливая коррелятивная связь между этими двумя элементами в месторождении не установлена (Уше в и др., 1962). Типичный элемент примесь в молибдените кварц-молибденитовой ассоциации — ений, один из типоморфных элементов примесей в медно-молибденовых порфировых месторождениях.

Геохимическая последовательность, характерная для пирит-молибденит-халькопиритовой ассоциации повторяется в общих чертах и при формировании кварц пиритовой и кварц-сфалерит-галенитовой ассоциации в месторождении. По объему, однако, минералы этих ассоциаций уступают предыдущим. Это показывает, что основные количества рудообразующих элементов в гидротермальных растворах уже отделились от системы. Формирование самостоятельной кварц-сфалерит-галенитовой ассоциации к концу рудообразовательной деятельности — типичная особенность геохимического развития минералообразовательных процессов медно-порфировых месторождений (Мовсесян, Исаенко, 1978). Образование сульфидов цинка и свинца в этой ассоциации указывает на относительно высокую активность серы, а подчиненное участие пирита и халькопирита отражает заниженое содержание меди и железа в растворах. Характерные элементы примеси в галените этой ассоциации снова серебро, висмут и селен, но в то время как содержание серебра и висмута относительно увеличивается, селена же имеет тенденцию к уменьшению.

Конец гидротермальной деятельности в месторождении отмечается образованием кальцитовых жил и цеолитов, которые концентрируют оставшиеся свободными в системе кальций, алюминий и кремний. Последовавшее незначительное по своему размаху супергенное изменение приводит к частичному перераспределению элементов в верхних частях месторождении. За счет первичных медных сульфидов образуются окиси и сульфаты, а окиси и сульфиды железа переходят в гидроокислы.

Рассмотреную выше последовательность в геохимическом развитии эндогенного рудообразовательного процесса в месторождении „Медет" можно условно выразить следующим образом:

Fe(Cr, Ti, Mn)—Fe (Mo) Cu (Co, Ni, Au, Te) (Zn, Pb, Bi, Se, Ag)—
—Mo(Re)—Fe (Cu)—Zn (Cd) Pb (Bi, Se, Ag)

Эта последовательность в значительной мере приближается к характерному в медно-порфировых месторождениях геохимическому развитию

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рудообразовательных процессов (Павлова, 1978). Специфическими особенностями в месторождении „Медет" выделяются более позднее образование основного объема молибденита в отношении промышленного количества сульфидов меди, как и формирование второй железоокисной минерализации в рамках основного сульфидного оруденения.

В отношении пространственного распределения элементов в месторождении можно отметить, что здесь прослеживаются только некоторые из наиболее важных тенденций, характеризирующие геохимическую зональность в медно-порфировых месторождениях, обобщенных в модели Lowell Guilbert, 1970. В месторождении „Медет" более отчетливо выражен латеральный тип зональности выражаемой в концентрации основного объема меди и молибдена в центральных частях месторождения и в некотором увеличении свинца и цинка в периферийных частях. В вертикальном отношении заметные изменения в доступном для наблюдения интервале не установлены.

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ВОПРОСЫ

Я. Гурхый: Вопрос содержания Se в галените — равномерно или неравномерно?

Ответ: Микрозондовыми анализами установлено равномерное содержание Se в галените.

Н. Щербак: I. Какое место занимает в зональности молибденовая минерализация?

2. В каком минерале и в каком количестве находится кобальт?

Ответы: I. Молибденовая минерализация занимает центральную часть месторождения.

2. Кобальт находится главным образом в кобальт-пирите в концентрации варьирующей от 1,2 до 17 весовых %. Установлен также и собственный кобальтовый минерал, карролит.

Т. Тодоров: Каковы взаимоотношения между кобальт-пиритом и карролитом на месторождении?

Ответ: Эти два минерала образовались одновременно и в конце формировали пирит-молибденит-халькопиритовую ассоциацию. Можно предполагать раннее образование Co-пирита и когда Co достигает максимальной степени насыщения. Взаимоотношения между Co-пиритом и карролитом до сих пор не установлены.

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ТИПЫ СУРЬМЯНОЙ МИНЕРАЛИЗАЦИИ БОЛГАРИИ И ИХ ХАРАКТЕРНЫЕ ОСОБЕННОСТИ[1]

Т. А. ТОДОРОВ[2], В. П. ФЕДОРЧУК[3]

Введение

Территория Болгарии является составной частью глобального Средиземноморского сурьмяно-ртутного пояса (Металлогения ртути, 1976). Как на западном (Югославия, Италия) и северозападном (Карпаты — Румыния, Словакия, СССР), так и на юго-восточном (Турция) и северовосточном (Крым, Кавказ — СССР) продолжении основных региональных структур страны располагаются рудные зоны с промышленными месторождениями сурьмы и ртути (Федорчук, 1964; Твалчрелидзе 1972; Церцвадзе, 1972; Металлогения ртути, 1976; Бергер, 1978; Janković, 1965; Arsenic, Mercury, ..., 1970; Gümüs, 1971, Ilavský, 1980; Kubat, 1978; е. а. В связи с этим особенное внимание заслуживает вопрос о характерных особенностях различных типов месторождений и рудопроявлений сурьмяной минерализации и их место в комплексе остальных типов рудной минерализации.

На территории Болгарии установленно два месторождения и ряд рудопроявлений сурьмяной минерализации. По составу руд их можно разделить на собственно сурьмяные и сурьмусодержащие.

Группа собственно сурьмяных месторождений и рудопроявлений

Группа собственно сурьмяных месторождений и рудопроявлений включает в себя два типа минерализации сурьмы — это тип собственно сурьмяных монометальных (моноантимонитовых) месторождений и рудопроявлений и тип собственно сурьмяных комплексных рудопроявлений.

I.1. *Проявления собственно сурьмяной моноантимонитовой минерализации*

Собственно сурьмяные моноантимонитовые месторождения и рудопроявления имеют преобладающее распространение в Болгарии. Они уста-

[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13, Бухарест, Румыния.

[2] Болгария.

[3] СССР.

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новлены в пределах западных и южных частей страны и локализуются в бортовых частях палеогеновых и неогеновых депрессий (зоны автономной активизации) Родопского массива или в палеозойских и более древних ядрах Беласицкой горст-антиклинали и Осоговского антиклинория Сербско-Македонского (Дарданского) массива, Берковского и Свогенского антиклинория Старапланинской зоны и Ихтиманского антиклинория Среднегорской зоны. Минерализация этого типа представлена двумя месторождениями (Рибново и Черничево) и несколькими рудопроявлениями, из которых только некоторые заслуживают внимание с промышленной точки зрения (Сеславци, Еленов дол, Осиково, Скребатно и др).

Проявления собственно сурьмяной моноантимонитовой минерализации Болгарии относятся к двум ведущим для мировой практики структурно-морфогенетическим типам монометальных сурьмяных месторождений — джаспероидный тип и тип согласных межформационных залежей кварц-джаспероидных брекчий под экранирующими структурами и жильный тип и тип секущих кварцантимонитовых жил в менее или более метаморфизованных толщах палеозоя и докембрия или в герцинских интрузивах. Сравнительная характеристика всех представителей этих двух типов показывает следующее:

Проявления джаспероидного типа собственно сурьмяной минерализации Болгарии установлены на югозападе страны (Рис.). Это одно

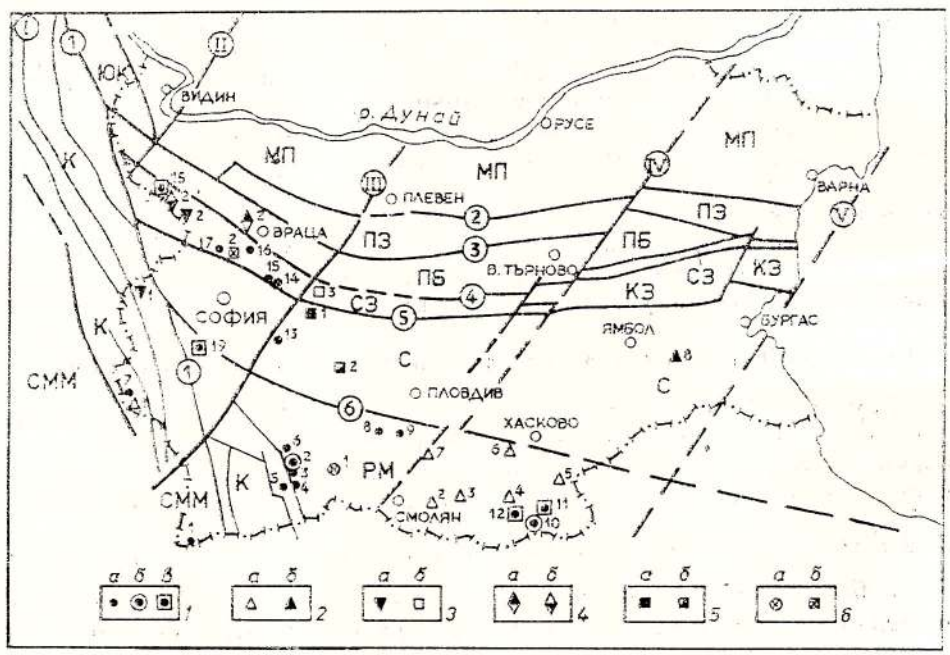


Схема распределения проявлений сурьмяной минерализации на территории Болгарии (Геотектоническая основа по Б о н ч е в у, 1974).

А — Собственно сурьмяные моноантимонитовые и комплексные месторождения и рудопроявления:

1, проявления собственно сурьмяной минерализации: а) рудопроявления моноанти-

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месторождение (Рибново) и четыре рудопроявления (Осиково, Скребатно, Гостун, Господинци?), образующие, так называемое, Рибновское рудное поле. Пластообразные метасоматические залежи этих проявлений сформированы в кровле пологопадающих мраморных горизонтов, непосредственно под залегающими на них гнейсами, сланцами и амфиболитами протерозойского комплекса. Они представляют хорошо выдержанные пологие (10—30°) зоны кварц- джаспероидных брекчий, образующиеся за счет замещения кремнеземом отдельных пластов карбонатных пород, чаще всего под сланцевым экраном.

Проявления собственно сурьмяной минерализации джаспероидного типа располагаются недалеко от так называемого Рибновского разлома, но локализуются они в пологих межформационных нарушениях на контакте „кристаллических сланцев и мрамора". В зонах этих нарушений антимонитовое оруденение обычно имеет неравномерное распределение в телах хорошо выраженных кварц-джаспероидных брекчий и приурочено к небольшим секущим кругопадающим тектоническим нарушениям и в участках мелких (до нескольких десятков м) изгибов мраморных горизонтов. Минерализация обычно встречается в одном ярусе, но в рудопроявлении Осиково наблюдается и многоярусное размещение оруденения. Приведенные данные указывают на четкий структурный и литолого-стратиграфический контроль минерализации в Рибновском рудном поле.

монитовых руд (1 — Иванник; 3 — Кремница; 4 — Скребатно; 5 — Господинци; 6 — Гостун; 7 — Равно рид; 8 — Пещера; 9 — Жребичко; 13 — Аканджиево; 14 — Готен; 15 — Сеславци; 16 — Еленов дол; 17 — Искрец); б) месторождения моноантимонитовых руд (2 — Рибново; 10 — Черничево); в) рудопроявления комплексных антимонитсульфоантимонитовых и антимонит-сульфидных руд (11 — Тинтява; 12 — Друмче; 18 — Стайна чука; 19 — Дрен).

Б — Сурьмусодержащие месторождения и рудопроявления:

2, свинцово-цинковые и полиметаллические (а) и золото-полиметаллические (б) месторождения (1 — Осоговского района; 2 — Маданского района; 3 — Давидковского района; 4 — Звездел-Галенитского района; 5 — Маджаровского района; 6 — Спахиевского района; 7 — Лыкинского района; 8 — месторождение Бакаджик); 3, кварц-золоторудные (а) и медно-порфировые (б) месторождения (1 — Злата; 2 — Говежда; 3 — Елаците); 4 медно-свинцово-цинковые (полиметаллические) стратиформные (а) и серебро-свинцовые (б) месторождения (1 — Врачанского района; 2 — Чипровци); 5, золото-медноколчеданные (а) и колчеданные и медно-колчеданные (б) месторождения (1 — Челопеч; 2 — Панагюрского района); 6, грейзеновые висмут-молибденитовые (а) и баритовые (б) месторождения и рудопроявления (1 — Буйново; 2— — района Зверино-Елисейна).

Обозначения на карте: I — Главные глубинные разломы в Краништидной структурной зоне; II — Олтенский криптоскрытый пояс; III — Етрополъская разломная система; IV — Твердицкая разломная система; V — Восточно-Фракийская линия; 1 — Княжевац-Пиротская дислокация; 2 — Предбалканский разлом; 3 — Брестнишко-Преславская флексура; 4 — Старопланинская лобовая линия; 5 — Забалканский глубинный разлом; 6 — Родопский глубинный разлом; МП — Мизийская платформа; ПЗ — Преходная зона; ПБ — Предбалканская зона; СЗ — Старопланинская зона; КЗ — Котелская зона; С — Среднегорская зона; РМ — Родопский массив; СММ — Сербско-Македонский массив; К — Краништиды; ЮК — Южные Карпаты.

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Главными минералами монометальных проявлений сурьмяной минерализации джаспероидного типа являются кварц и антимонит, при этом кварц слагает основную часть рудной зоны, а антимонит встречается в виде небольших вкрапленников и прожилок (мелкокристаллический антимонит) и реже как гнезд и пятен (крупнокристаллический антимонит) в кварце и гидротермальноизмененных кристаллических сланцах. Установлены кроме того и некоторые другие более или менее редко встречающиеся минералы (пирит, арсенопирит, марказит, бертьерит, реальгар, сфалерит, галенит и др.), а также и их зональное распределение. Последнее выражается в резком преобладании антимонита (при подчиненом участии сфалерита и галенита) в северных частях рудного поля (месторождение Рибново) и обратные соотношения этих минералов (минерализации) на юге рудного поля (рудопроявление Кремница). Образование минералов произошло в течение трех стадий минерализации: основная сульфидно-кварцевая, вторая-антимонит-кварцевая и третья-кальцит-реальгар-кварцевая стадии. Судя по минеральным парагенезисам, взаимоотношениям сурьмяной минерализации с свинцово-цинковой, типоморфизму некоторых минералов и особенностям геологического строения района рудного поля можно считать, что сурьмяное оруденение джаспероидного типа сформировалось на небольшой глубине хорошо отсепарированными средне-низкотемпературными гидротермальными растворами.

Второй тип собственно сурьмяной минерализации — кварц-антимонитовый жильный имеет более широкое распространение на территории Болгарии. К этому типу относится тоже одно месторождение (Черничево), но рудопроявления в данном случае больше по количеству и по размерам (Сеславци, Еленов дол, Искрец, Готен, Аканджиево, Жребичко, Пещера, Иванник, Равнио рид). Они встречаются в бортовых частях зон автономной активизации Родопского массива или в древних ядрах ряда антиклинальных структур и представлены одной или несколькими жилами заполнения и линейными зонами дробления в метаморфизованных докембрийских и палеозойских сланцах и гнейсах и в герцинских гранитоидах. Кварц-антимонитовые жилы преимущественно заполняют крутые и разветвляющиеся тектонические нарушения обычно сравнительно небольших размеров. Только часть из этих разломов однако является заполненной кварцем с прожилками, вкрапленниками и гнездами мелко- и крупнокристаллического антимонита. Вместе с отмеченными двумя минералами в месторождениях и рудопроявлениях установлены ещё пирит как главный минерал, арсенопирит, марказит, реальгар, сфалерит, галенит и ряд других редких и второстепенных минералов. Для некоторых рудопроявлений Старопланинской зоны характерным тоже является кобальтин. Кроме того, более широкое распространение в сравнении с остальными рудопроявлениями имеет здесь сфалерит.

Минералообразование в кварц-антимонитовых жильных месторождениях и рудопроявлениях, как и в проявлениях кварц-джаспероидного типа, происходило в течение трех стадий минерализации (основная сульфидно-кварцевая антимонит-кварцевая и карбонат-реальгар-кварцевая), на небольшой глубине и из хорошо отсепарированных средне-низкотемпературных гидротермальных растворов. Для герцинских рудопроявлений Старопланинской зоны сразу после образования минералов

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сульфидно-кварцевой стадии, намечается кроме того проявление еще одной стадии минерализации — сфалерит-кварцевой, во время которой отлагался сфалерит с халькопиритом и кварцем.

1.2. *Проявления комплексной сурьмяной минерализации*

К этому типу сурьмяной минерализации относятся несколько рудопроявлений с невыясненным пока промышленным значением. Сюда входят киноварь-антимонит-сульфоантимонитовое рудопроявление Стайна чука (восточный участок известного сурьмусодержащего серебро-свинцового месторождения Чипровици), киноварь-сульфидно-антимонитовое рудопроявление Дрен, антимонит-сульфидное рудопроявление Тинтява и антимонитсульфоантимонитовое рудопроявление Друмче. Два последних рудопроявления находятся в Восточных Родопах недалеко от собственно сурьмяного месторождения Черничево и тоже локализованы в бортовых частях Восточнородопского палеогенового прогиба (зона автономной активизации). Другие два рудопроявления — Стайна чука и Дрен располагаются в ядрах соответственно Берковского антиклинория (Старопланинская зона) и Белчинской моноантиклинали (Краиштидная зона). Во всех рудопроявлениях кварц-антимонитовая (с киноварью) и сульфоантимонитовая минерализации накладываются на проявленное раннее полиметалльное оруденение и в общем имеют подчиненное значение. Минералы сурьмы здесь представлены тетраэдритом (фрайбергитом), антимонитом, булажеритом, пираргиритом и миаргиритом. Эти минералы в основном отложены на заключительной стадии образования рассматриваемых рудопроявлений.

Близкое расположение монометальных и комплексных сурьмяных месторожденний и рудопроявлений на территории Восточных Родоп позволяет нам сделать вывод о хорошо выраженном зональном распределении свинцово-цинкового и сурьмяного оруденения в этий частях Родопского массива. Зональность здесь проявляется в более широком развитии полиметаллической минерализации на севере Тинтявско-Чернического рудного поля и постепенном понижении ее интенсивности на юге, в районе антимонитового месторождения Черничево. И наоборот, антимонитовая минерализация характеризуется подчиненным развитием на севере, в районе полиметаллического рудопроявления Тинтява. Характерно кроме того вертикальное распространение обоих типов минерализации, выражающееся в том, что антимонитовая минерализация уменьшается в глубину, где появляется полиметалльная минерализация. Проявленные горизонтальная и вертикальная минеральные зональности указывают на развитие единого минерализационного процесса в Тинтявско-Черническом рудном поле. При этом раньше образовалось полиметаллическое оруденение, а сразу после того и накладывающаяся на него собственно сурьмяная минерализация.

1.3. *Возраст сурьмяной минерализации*

Первые сведения о присутствии сурьмяной минерализации в Болгарии в районе месторождении Рибново приводит Б о н ч е в (1923), связывая ее генетически с раскрывающимися недалеко от месторождения риолитами олигоцена. Позднее однако было установлено, что эти рио-

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литы рассекаются свинцово-цинковой минерализацией, в сравнении с которой сурьмяное оруденение относительно моложе и в то же время узко связано (накладывается на нее, зональное распределение обеих минерализаций). Наблюдалась также гидротермальная карбонатизация олигоценовых брекчеконгломератов. Эти данные, вместе с закономерным региональным размещением сурьмяной минерализации в бортовых частях палеогеновых депрессий (по Щеглову, 1968, зоны автономной активизации), позволяют нам связать все месторождения и рудопроявления сурьмы Родопского массива с его альпийской (терциерной) активизацией и рассматривать их вместе с проявлениями флюоритовой минерализации как заключительной стадии широко проявленной гидротермальной деятельности, в результате которой образовались как известно, многочисленные свинцово-цинковые и полиметаллические месторождения Родоп. Определить однако, точный возраст формирования проявлений сурьмяной минерализации Болгарии пока трудно. Преобладает мнение о верхнеолигоценмиоценовом возрасте оруденения (Костов, 1963; Щеглов, 1968; Димитров и Маврудчиев, 1970; и др.), но для сурьмы-мышьяковой минерализации Лойана и Алшар (Македония) Антонович (Antnović, 1962) приводит сведения о их миоцен-плиоценском возрасте. Очень вероятно, что образование преобладающей части рассматриваемой минерализации произошло раньше среднего миоцена. В Болгарии точных данных об этом не имеется, но если сослаться на сведения Симича (1957) о присутствии рудных кусков кварц-антимонитового оруденения месторождения Буяновац (Югославия) в среднемиоценовых отложениях, то мы наверное должны согласиться с этим выводом. Аналогичные верхнеолигоцен-среднемиоценовый возраст имеют по-видимому и рудопроявления Иванник и Равнио рид, находящиеся на самом югозападе и западе страны, в пределах Сербско-Македонского (Дарданского) массива. В соответствии с общей металлогенической характеристикой всей Средногорской зоны, альпийский, хотя и более древний возраст (ларамийский), предполагается и для кварц-антимонитового рудопроявления Аканджиево.

Кроме проявления альпийской сурьмяной минерализации, на территории Болгарии установлены и сурьмяные (монометалльные и комплексные) рудопроявления с герцинским возрастом. Эти проявления находятся в пределах Старопланинской (Сеславци, Готен, Искрец, Еленов дол и Стайна чука) и Краиштидной (Дрен) структурно-металлогенических зон. Кварц-антимонитовые жилы этих рудопроявлений залегают в более или менее метаморфизованных толщах палеозоя или в интрузивных породах герцинского возраста. Некоторые из них показывают узкую связь с серебро-свинцовой минерализацией и являются звеном в общей зональности рудного поля и месторождения (например место рудопроявления Стайна чука в зональной схеме сурьмусодержащего месторождения Чипровци, по Dimitrov, 1964). В последнее время получены изотопные данные, которые указывают на герцинский возраст (модельной возраст около 300 млн. л.) серебро-свинцового оруденения в месторождении Чипровци (Amov et al., 1981). Этот возраст характерен и для его восточного участка, где проявлен комплексный киноварь-антимонит-сульфоантимонитовый тип сурьмяной минерализации (рудопроявление Стайна чука). Для остальных герцинских рудопроявлений подобных сведений не име-

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ется, но их общая геологическая позиция и преобладающая роль варисского металлогенезиса Старопланинской и Краиштидной зон позволяют нам отнести их к тому же этапу минералообразования. Следовательно, считать что вся сурьмяная минерализация Болгарии образовалась во время альпийской металлогенической эпохи неправомерно. Это потверждается также данными для югославских монометалльных и комплексных сурьмяных месторождений, которые раньше принимались как альпийские (J a n k o v i ć, 1965), а сейчас уже установленно, что они формировались в двух этапах — герцинский (варисский) и альпийский (Б е р г е р, 1978; K u b a t, 1978).

II. Группа сурьмусодержащих месторождений

К сурьмусодержащим месторождениям нами отнесены месторождения всех остальных металлов, в рудах которых отмечено проявление собственно сурьмяных минералов (прежде всего сульфоантимониты меди, свинца и серебра и реже самородная ртуть, надорит и нагиагит) и/или повышенных содержаний сурьмы в ее главных минерало-носителях и и концентраторах (галениты, теннантиты). Выделены следующие типы: I — свинцово-цинковые и полиметаллические месторождения (жильные и метасоматические) Родопского и Сербско-Македонского массивов (Маданский, Лыкинский, Давидковский, Маджаровский, Спахиевский и Звездел-Галенитский районы и район Осогово); II — медно-свинцово-цинковые (полиметаллические) месторождения стратиформного типа Балканидной структурно-металлогенической зоны (Седмочисленици и другие месторождения Врачанского района, а также полиметаллическая минерализация месторождения Кремиковци); III — серебро-свинцовое месторождение Чипровци; IV — золото-полиметаллическое месторождение Бакаджик в Средногорской зоне; V — колчеданные, медно-колчеданные и золото-медно-колчеданные месторождения Средногорской зоны (Панагюрский и Челопечский районы); VI — кварц-золоторудные месторождения Говежда и Злата соответственно Балканидной и Краиштидной структурно-металлогенических зон; VII — медно-порфировое месторождение Елаците в Балканидной зоне; VIII — висмут-молибденовое рудопроявление грейзенового типа Буйново в Родопском массиве и IX — баритовые месторождения района Зверино-Елисейна Балканидной зоны (рисунок). Во всех этих месторождениях сурьма является сопутствующим элементом. Она присутствует в рудах как в виду своих собственных минералов (без антимонита), так и как изоморфная примесь в некоторых других минералах. Отметим, что часть из выделенных типов сурьмусодержащих месторождений может иметь промышленное значение для извлечения сурьмы — это типы I, II, III и IV.

Выводы

В заключение можно сделать следующие более общие выводы:

1. На территории Болгарии, целиком находящейся в пределах глобального Средиземноморского сурьмяно-ртутного пояса, до сих пор установлен ряд месторождений и рудопроявлений сурьмяной минерализации. В соответствии с их составом их можно разделить на

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собственно сурьмяные (моноантимонитовые и комплексные) и сурьмусодержащие;

2. В группе собственно сурьмяных месторождений и рудопроявлений представители моноантимонитового типа имеют преобладающее распространение. Они относятся к двум ведущим для мировой практики структурно-морфогенетическим типам: джаспероидный и жильный. Менее интересными с промышленной точки зрения являются комплексные представители этой группы;

3. Собственно сурьмяная моноантимонитовая и комплексная минерализация накладываются на свинцово-цинковую и полиметаллическую, при этом намечается хорошо выраженное зональное распределение обоих типов минерализации в горизонтальном и вертикалном направлениях. Полученные данные приводят к выводу о проявьении собственно сурьмяной минерализации (вместе с флюоритовой и ртутной) на заключительных стадиях интенсивно проявленных гидротермальных процессов, в связи с которыми образовались многочисленные свинцово-цинковые и полиметаллические месторождения страны.

4. В региональном плане устанавливается приуроченость собственно сурьмяных месторождений и рудопроявлений преимущественно к бортовым частям палеогеновых депрессий Родопского массива (зоны автономной активизации) или к древним ядрам ряда антиклинальных структур Сербско-Македонского массива, Старопланинской, Среднегорской и Краиштидной зон. Возраст месторождений принимается как варисский для проявлений Старопланинской и Краиштидной зон или альпийский (верхний олигоцен-средний миоцен) для проявлений Родопского и Сербско-Македонского массивов. Альпийским (ларамийским) является наверняка и возраст рудопроявления Аканджиево в Среднегорской зоне.

5. Сурьмусодержащие месторождения имеют широкое распространение в Болгарии. К ним относятся ряд свинцово-цинковых, полиметаллических, серебро-свинцовых, золото-полиметаллических, колчеданных и медно- и золото-медно колчеданных, кварц-золоторудных, медно-порфировых, баритовых и висмут-молибденовых месторождений и рудопроявлений страны. В этих месторождениях сурьма присутствует в рудах за счет своих собственных минералов (прежде всего сульфоантимониды меди, свинца и серебра и реже самородная сурьма, надорит и нагиагит) или в виду изоморфных замещений в таких минералах как галенит и теннантит. В этой группе сурьмяной минерализации выделены девять типов месторождений, но промышленное значение для извлечения сурьмы как попутный компонент имеет только часть из них.

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ВОПРОСЫ

Н. П. Щербак: Каков возраст сурьмяных месторождений Болгарии?

2. Есть ли в Болгарии древние стратиформные сурьмяные месторождения?

Ответы 1. В Болгарии до сих пор установлены только альпийские и варийские месторождения сурьмы.

2. У нас пока не известны более древние чем варийские месторождения. Не установлена тоже и стратиформная минерализация сурьмы варийского возраста, хотя и этот тип в последнее время является очень интересным с генетической и практической точки зрения.

Г. Удубаша: 1. Если в кварц-антимонитовых месторождениях жильного типа существует какая-нибудь зональность?

2. Где установлен кермезит?

Ответы: 1. Да, зональность намечается. Она выражается в преобладающем распространении свинцово-цинковой минерализации в глубину, а сурьмяной — в верхних горизонтах. Установлены и горизонтальная зональность в распеределении обеих минерализаций.

2. Да, кермезит установлен в месторождениях Рыбново и Черничево.

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MINERALOGISCHE UNTERSUCHUNG DER TONHALTIGEN SEDIMENTE IM VILLÁNYER-GEBIRGE [1]

VON

G. BIDLÓ [2]

Das Villányer-Gebirge befindet sich im südlichen Teil Ungarns. Seine Lage im Alpen-Karpaten System wird in Abb. 1[3] gezeigt. Die geologische Untersuchung des Gebirges wurde schon Mitte des vorigen Jahrhunderts begonnen (P e t e r s, 1862). Vor einigen Jahren sind meh-

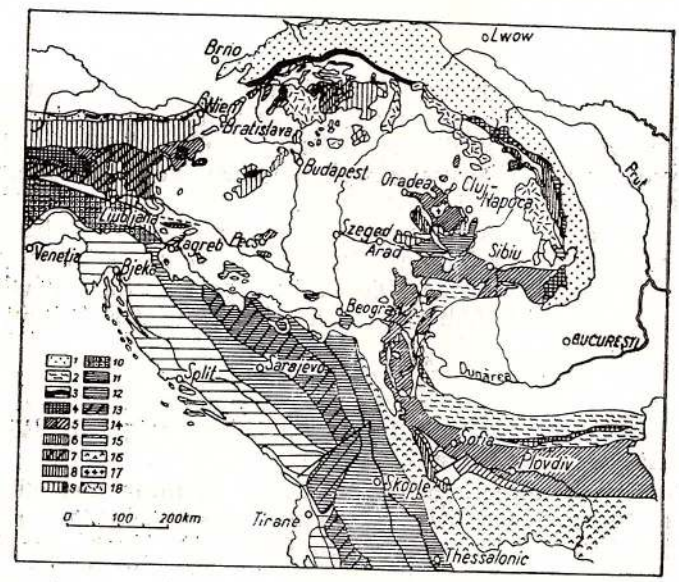


Abb. 1

[1] Vorgetragen am 12. Kongress der Karpato-Balkanischen Geologischen Assoziation, 8—13 September, 1981, Bukarest, Rumänien.

[2] Ungarn.

[3] Die Erläuterungen der Abbildungen wurden von Verfasser nicht eingerlicht (red. note).

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rere Monographien über den geologischen Aufbau des Gebirges erschienen (Fülop 1966; Janossy 1979; Kassai 1976; Kretzoi 1956; 1962; Nagy E., Nagy I. 1976). Die Grundmonographien enthalten nur sehr wenige Angaben über die mineralogische Zusammensetzung der Tonsedimente, deshalb war es nötig diese Lücke auszufüllen.

Die Tonsedimente — überwiegend „Rotetone" — bedecken den nördlichen Teil des Gebirges und besitzen eine mächtige Dichte. Einige Ausfüllungen der Dolinen kann man auf der ganzen Oberfläche des Gebirges auffinden (Abb. 2).



Abb. 2

Der Tonmineralgehalt der Tonsedimenten kann thermoanalytisch gut characterisiert werden, denn die röntgendiffractometrische Analyse im Falle schlecht Krystallisierter Bestandteile bleibt erfolglos; die Thermoanalysen mittels Derivatographen geben, auch bei kleinen Mengen, gute DTA-Kurven (Todor 1972).

Die Tonsedimente stammen aus verschiedenen Zeitaltern; die ältesten befinden sich im Villány-Kalkberg in einem Aufschluss, zwischen Trias-und Jura-Schichten. Die derivatographische Aufnahme zeigt einen kleinen Tongehalt (Abb. 3), der aber für das Villány-Gebirge characteristisch ist.

Im „Rose" Steinbruch neben Siclós finden wir in den roten Doggerkalkschichten kleine Menge von Tonmineralen (Abb. 4). Die DTA weist auf „Limonit" und Kalcit, daneben zeigt die Röntgenaufnahme auch Hämatit und Quarz.

Das Bauxitvorkommen in Nagyharsány stammt aus der Kreidezeit (Fülöp 1966) und wird von roten Tonsedimenten begleitet die gut krystallisierten Kaolinit enthalten (Abb. 5). Nach der Röntgenaufnahme handelt es sich um ein Kaolinit T, mit 7.13 Å Basisreflexion. Wegen der breiten Reflexion kann man die Anwesenheit von Dickit nicht ausschliesen, wie Neacşu (1968) im Pădurea Craiului Gebirge annimmt.

Die Sedimente von Csarnöta, aus denen die „Csarnotánum Fauna" stammt (Kretzoi 1954, 1956, 1962; Jánossy 1979), zeigen eine typische DTA-Kurve mit Wasserabgabe in zwei Stufen, Gitterzerfall bei 580°C und einer endotherm-exothermen Unwandlung im Bereich von

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900°C. Die Röntgenaufnahme zeigt eine schwache Reflexion bei 7.13 Å und eine grössere bei 4458 Å.

In der DTA Kurve der Probe aus dem klassischen Vorkommen von „Villányien" fehlt die endotherm-exotherme Umwandlung.

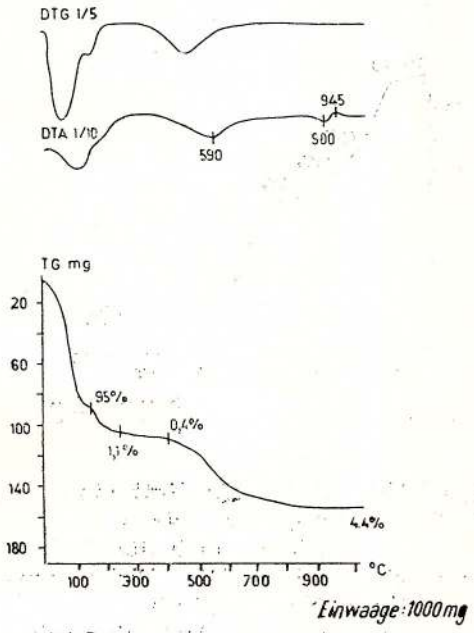


Abb. 3

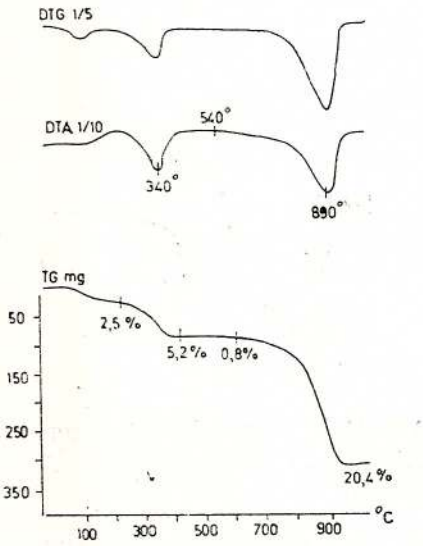


Abb. 4

Bei „Zuhánya" neben Siklós, findet man den typischen Vertreter der in Villányergebirge vorkommenden „Rotetone". Auf der DTA

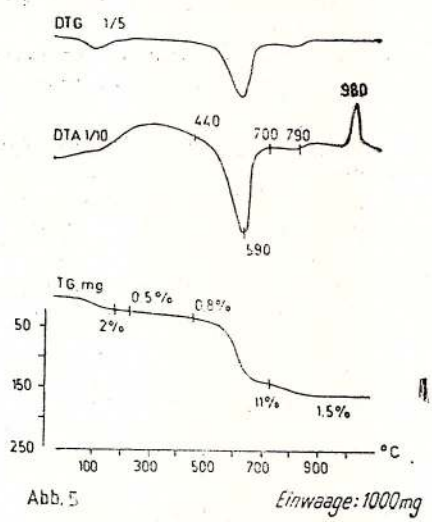


Abb. 5

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Kurve (Abb. 6) kann man die zweistufige Wasserabgabe gut beobachten. Der dem Gitterzerfall entsprechende endotherme Peak befindet sich bei 570°C; der entsprechende Gewichtsverlust beträgt 7.6%. Das weist eindeutig daraufhin, dass es sich in den Proben um zweischichtige Tonminerale (TO) handelt. Die endotherm-exotherme Inversion liegt bei

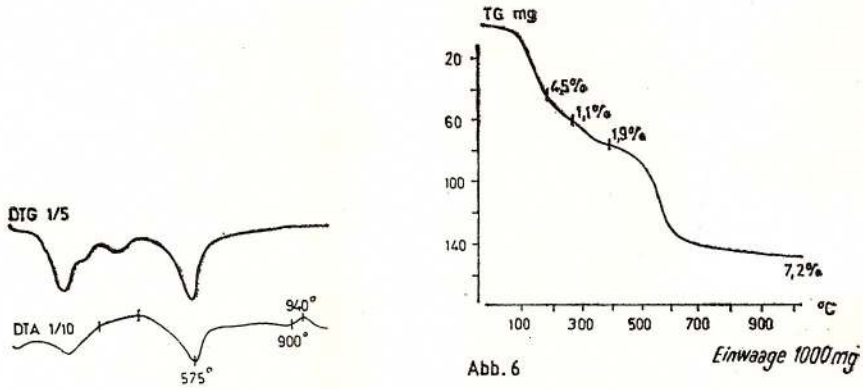


Abb. 6

900-940°C. Auf der Röntgenaufnahme (Abb. 7) ist die Reflexion bei 7.13 Å ganz klein, aber die jenige bei 4458 Å viel grösser. Die Aufnahme hat einer Grundschwärtzung von 50% und man kann auch die Reflexe von Quartz und $2M_1$-Muscovit bemerkt werden. Die Elektronendiffraktion-Aufnahme entspricht einen degradierte Kaolinit.

Auf der nördlichen Seite des Gebirges sind zwei Aufschlüsse bekannt. Beim Vókany erscheinen Tonsedimente mit typischer DTA-Kurve. Die Wasserabgabe verläuft in zwei Stufen; die Probe enthält 1,8% organisches Material. Eine endotherm-exotherme Inversion erscheint bei 895-925°C. Die Röntgenaufahme zeigt auch die Reflexionen von „Low albite" und Pyrophillit.

Bei Kistótfallu können wir das gleiche Material finden (Abb. 8).

Südlich von Villányer-Gebirge auf der Kalkberg von Beremend befindet sich ein Steinbruch in welchem viele Höhlen mit Tonausfüllung aufgeschlossen wurden. Eine Probe aus diesen Ausfüllungen enthält neben Kaolinit auch Gibbsit (Abb. 9) hydrothermaler Herkunft (V a d a s z 1949; B á r d o s s y 1977). Das genauere Alter der erwähnten Proben kann nicht festgestellt werden, da die Tonlagerstätten im Kalkstein direkt vom Holozän bedeckt sind und keine Tierreste enthalten. Auf Grund der ähnlichen mineralogischen Zusammensetzung wird angenommen, dass diese Ablagerungen mit denen von Csarnóta (=Csarnotánum) gleichaltrig sind.

Ganz jung ist die sich im Lössaufschluss von Palkonya befindende rote Tonschicht. Die derivatographische Aufnahme ist den anderen Aufnahmen ähnlich (Abb. 10). Die Röntgenaufnahme weist jedoch eine ganz andere mineralogische Zusammensetzung, mit viel Muskovit, hin.

Die Proben wurden auch nasschemisch analysiert. Die Tonminералen sind jedoch mit vielen fremden Bestandteilen zusammen-

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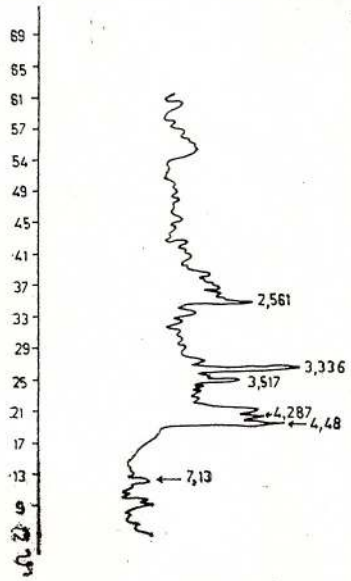


Abb. 7

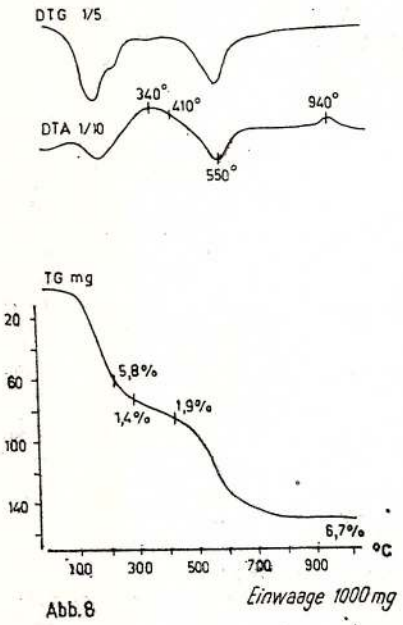


Abb. 8

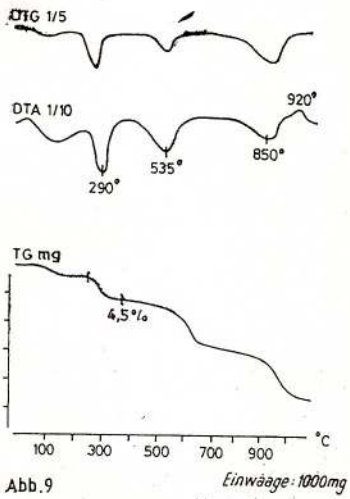


Abb. 9

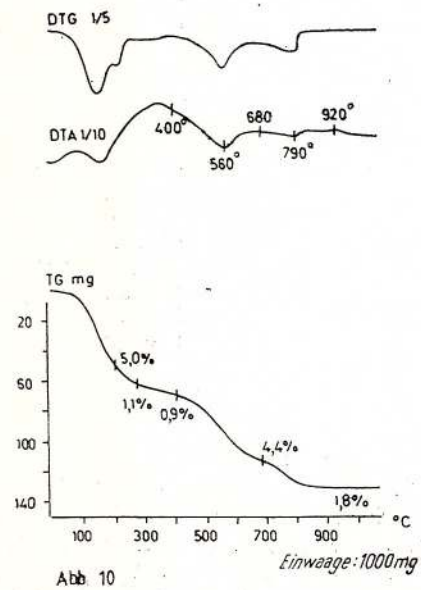


Abb. 10

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geschwämt, so dass man keine weitführende Folgerung ableiten kann. Als Beispiel möchte ich die chemische Zusammensetzung der ältesten Probe (von Villány) und der Probe von Zuhánya vorführen.

TABELLE 1

Chemische Analyse der „Rotetone" aus Willány

	Zuhánya	Villány
SiO_2	38.34 %	50.24 %
Al_2O_3	32.76 %	22.93 %
Fe_2O_3	8.58 %	7.95 %
CaO	1.54 %	1.38 %
MgO	1.47 %	2.14 %
Gluhverlust	7.60 %	4.40 %
H_2O^+	1.20 %	1.10 %
H_2O^-	5.90 %	9.50 %
organisch	1.80 %	0.40 %
Summe	99.16 %	100.02 %

Analytiker: G. Bidlo

Der Tongehalt der Proben wurde durch Sedimentationsanalyse bestimmt (Abb. 11). Den höchsten Gehalt an feinsten Körnern ergab die Probe aus Vokany, die Proben von Kistótfalu und Zuhánya enthalten gröbere Körner in grösseren Mengen.

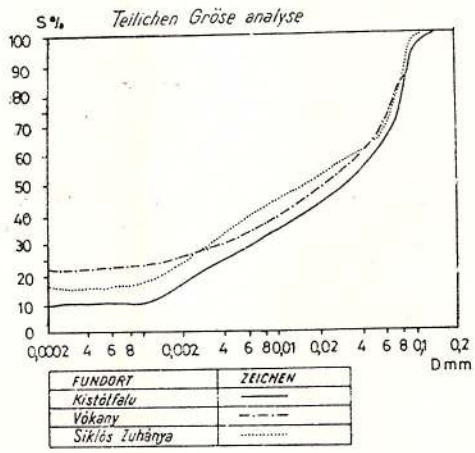


Abb 11

Schon die ersten Untersuchungen stellen die Frage über die Herkunft der grossen Menge von Tonsedimenten. Dies ist um so interessanter, als Tonsedimente mit ähnlichen Tonmineralen im ungarischen Mittelgebirge (Bükk, Pilis und Bakony) nicht zu finden sind. Am Rand der Grossen-Tiefene beim Dunaujváros und neben Gödölö war ich aber in der Lage, die Anwesenheit ähnlicher Sedimente zu bestätigen

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Betreffs der Genese der untersuchten kann angenommen werden dass es sich um sekundäre Tonablagerungen handelt. Als primäre Lagerstätten können Tonmineral-Bildungen in vulkanischen Tuffen des Jura angesehen werden. Durch Pleistozäne Denudation und sekundäre ablagerung wurden die heutigen Tonsedimente gebildet.

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CARBONATE EXOTICS OF THE INNER CARPATHIAN FLYSCH IN POLAND [1]

BY

JÓZEF CHOWANIEC, JAN GOLONKA [2]

Introduction

The exotic rocks represent the parent formations for flysch series. They might have come from the margin of the flysch geosyncline as well as from the intrageosynclinal island arches which separated individual flysch basins (so called cordilleras). Examinations of exotic rocks were first made by Hohenegger (1881), the first complex description of the crystalline and sedimentary exotics has been done by Novak (1927). There are many publications on the exotics of the Polish Carpathians, concerning the area of the Outer Carpathians, but the detailed description of the exotics of the Inner Carpathians in Poland is still missing. There are only some short mentions in the publications of Kuźniar (1908, 1910), Sokolowski (1950), Golab (1952, 1954) and Passendorfer (1958) as well as the work of Grzybek and Halicki (1958) concerned with the localization and geological situation of the submarine slumpings (deposits containing exotics) without the petrographical analysis of exotic rocks. Recently some detailed analysis has been published of the exotic rocks of the flysch of the Slovakian Inner Carpathians (Samuel, Borza, Kohler, 1972, Marschalko, Mišik, Kamenicky, 1976).

The present authors focused on the subject of carbonate exotics, crystalline exotics being the subject of separate studies (Chowaniec, Golonka, 1980, Chowaniec, Wieser, 1981). The localities of exotics are distributed in the Polish part of the Paleogene Inner Carpathian flysch (so called Podhale Flysch). It is the area of Podhale and the Polish Spisz (Fig. 1). The authors have used some of the localities

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September, 8—13, 1981, Bucharest, Romania.

[2] Poland.

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included in the work of Grzybek and Halicki (1958). Several localities have been recently found by the present authors (Kacwin, Niedzica, Chocholow). The authors are indebted to A. Kulka for the study of nummulites as well as for his help in field examinations.

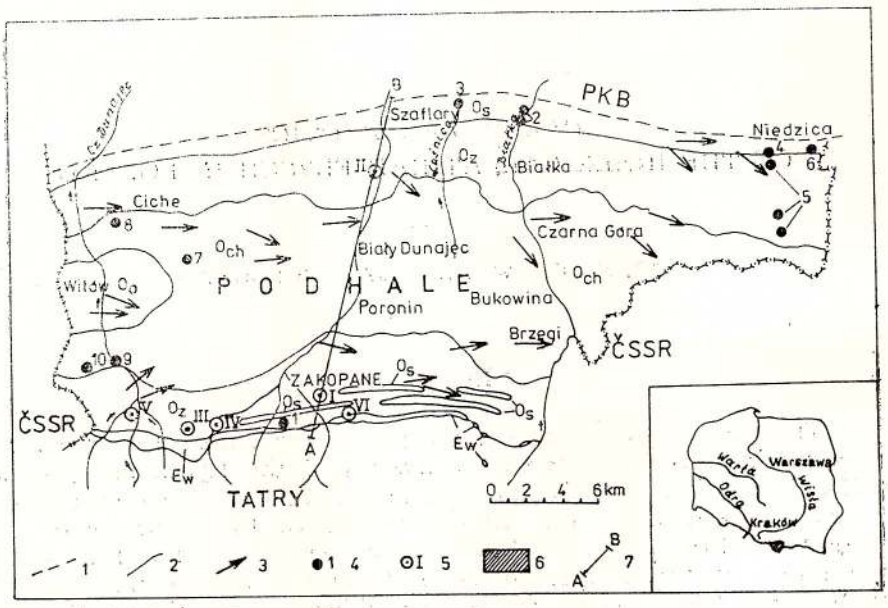


Fig. 1. — Localities of exotics in the Inner Carpathian Flysch in Poland (according to Golab, Sokolowski, Watycha, completed by the present authors : 1, Contact of the Podhale Flysch with the Pieniny Klippen Belt ; 2, Geological boundaries ; Oo-Ostrzysz Beds, Och-Chocholow Beds, Oz-Zakopane Beds, Os-Szaflary member, Ew-Carbonate Eocene, PKB-Pieniny Klippen Belt ; 3, Directions of the current structures according to Radomski (1958) ; 4, Localities of the studied exotics : 1, Bialy Stream at Zakopane, 2, Trybsz, 3, Szaflary, 4, Niedzica, 5, Kacwin, 6, Zloby, 7, Ciche, 8, Zagron Stream, 9, Kojsowka, 10, Mägura Stream ; 5, Boreholes which reached the Pre-Paleogene bottom of the Podhale Trough : I-Zakopane, IG-1, II, Bańska IG-1, III, Hruby Regiel IG-1, IV-Hruby Regiel-3, V-Siwa Woda IG-1, VI-Jaszczurówka ; 6, the analyzed area ; 7, geological section.

Character of the Flysch Deposits Containing Exotics

The flysch deposits of the Polish Inner Carpathians fill the trough in the basement of which there ocurr the Mesozoic deposits of the High-Tatric and Sub-Tatric series and probably crystalline rocks as well. To the north the through is limited by a vertical dislocation from the Pieniny Klippen Belt. The contacts with the High- and Sub-Tatric basement is sedimentary and only locally tectonic.

Directly on the Mesozoic there lie transgressive deposits (conglomerates) passing upwards into carbonate deposits. The series are

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of Middle-Upper Eocene age (B i e d a, 1959, 1963). The Eocene carbonate series pass gradually into flysch series, in which the Zakopane Beds and the Chocholow Beds may be distinguished.

The Zakopane Beds form a predominantly shaly complex. It consists of dark grey, sometimes black argillaceous marly shales (interbedded with thin-bedded, rare medium-bedded steel-grey fine-grained limy sandstones. In the lower part of the complex there occur thin layers of dolomite. There is also an occurrence of bunches of thick-bedded, medium and coarse-grained sandstones and conglomerates. In the northern part of the trough these sandstones reach the thickness of up to 1000 m and they may be distinguished as a separate member in the Zakopane Beds. It is a Szaflary Member (Szaflary Beds according to W a t y c h a, 1959). Southward that member pinches out, it occurs only locally (so called Koziniec Sandstone according to G o l a b, 1959), its maximum thickness being of some score meters. The total thickness of the Zakopane Beds is 2—2.5 km. Its age is stated as Lower Oligocene (B l a i c h e r, 1973, C h o w a n i e c, 1976). Exotics occur as pebbles in conglomerates and are rare in breccias in the Zakopane Beds. The conglomerate layers arrive at the thickness of a few cm to 2.5 m. They occur in the shaly part of the Zakopane Beds as well as in the Szaflary Member. In the northern part breccias of sharp-edged material are mixed with conglomerates. In the layers of coarse-grained and conglomeratic sandstones there occur also some fine exotics.

Directly on the Zakopane Beds there lie the Chocholow Beds. They are sandy in the western part and sandy-shaly in the eastern part (G o l a b, 1959, W a t y c h a, 1959) The sandstones of these beds are medium and thick-bedded, muscovitic, limy, medium and coarse-grained, frequently irregularly-grained. They are interbedded with dark-grey, sometimes greeny-grey shales. G o l a b had distinguished locally a bunch of thick-bedded sandstones, the so called Ostrzysz Beds, which, according to the present authors represent the sandstone member of the uppermost part of the Chocholow Beds. The thickness of the Chocholow Beds is about 1000—1500 m, they are of Oligocene age according to their geological position. The exotics in the Chocholow Beds were investigated in the western part of the trough. They occur most frequently in the submarine slumpings. The dominant lithologic types of slumpings are grey arenaceous shales with loose gravels (gravelstones) and conglomerates whose thickness ranges from some score cm to a dozen m or so. In these slumpings there occur exotics whose size is up to a few meters. They locally form a deposit of olistostrome type. The deposits of the Podhale Flysch make a wide synclinal structure with the axis of the W-E direction (Fig. 2). The gradient of the beds is high in the north and decreases towards the

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central part. Locally in the northern part of the trough there are some beds with a vertical and/or upturned arrangement. There occur some transverse and longitudinal faults in the trough, but the authors have

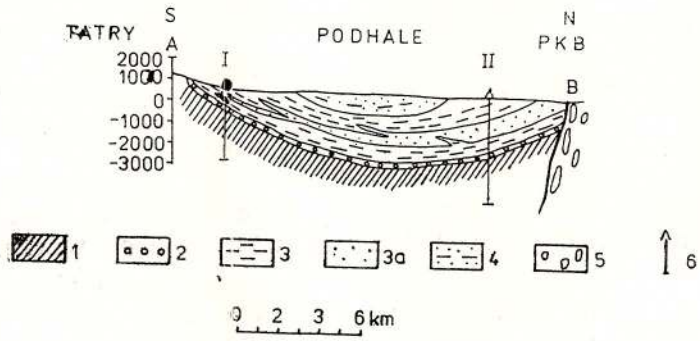


Fig. 2. — Geological cross-section A-B through the Flysch Trough of Podhale: 1, Pre-Paleogene bottom of the Podhale Trough-Mesozoic; 2, Transgressive and Carbonate Eocene deposits-Ew; 3, Zakopane Beds-Oz-Oligocene; 3a, Szaflary member — Os — Oligocene; 4, Chocholow Beds-Och-Oligocene; 5, Pieniny Klippen Belt-Mesozoic-Paleogene; 6, Bore-holes of the Geological Institute: I-Zakopane IG-1, II-Bańska IG-1.

not observed any deformations of overlap or thrust type. In the region near the Klippen Belt and the Tatras there locally occur some structures of fold type.

Character of the Localities Containing Exotics

Within the Zakopane Beds the authors have studied localities with exotics in the southern (Bialy Stream) as well as in the northern (Trybsz, Szaflary, Niedzica, Kacwin, Zloby) part of the Podhale Trough. The locality of the Bialy Stream is situated in the urban area of Zakopane. The exotics occur in the layer of 1—10 cm thick. This layer is situated about 10 m from the floor of the Zakopane Beds. It is a conglomerate built up of pebbles of a few mm to 2—3 cm size. Among the pebbles there are some Triassic dolomites and limestones and Eocene limestones. The localities in Trybsz are situated on the bank of the Bialka River about 0.5 km from the contact line of the Podhale Flysch and the Pieniny Klippen Belt. The lower locality is near the bridge on the Bialka River, the upper one about 150 m higher.

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The exotics were found in breccias. Among the scraps Triassic, Jurassic and Eocene limetsones and Triassic dolomites have been distinguished. At Niedzica and Kacwin there are a few localities. The oldest one is the locality at Niedzica situated at the confluence of the Niedziczanka and the Kacwin Stream, about 50 m from the contact with the Pieniny Klippen Belt. In the layer of the conglomeratic sandstone occur Triassic dolomites and Rhaetico-Liassic, Jurassic, Neocomian and Eocene limestones. In the Kacwin area there are three layers of conglomerates within the flysch of the Zakopane Beds situated 100 m, 800 m and 1200 m from the locality of Niedzica. The central locality is described as a nature monument (Chowaniec, Golonka, 1981). In Kacwin there occur Triassic dolomites, Triassic, Jurassic, Neocomian and Eocene limestones. In the locality of Zloby there is a single layer of conglomerates containing Eocene limestones.

In the western part of the area, within the Chocholow Beds, some localities have been studied (Ciche, Zagrón Stream, Kojsówka, Măgura Stream). In Ciche there is an olistolith of the Eocene limestone. 2 × 1.5 m in size, described as a nature monument (Chowaniec, Golonka, 1981) as well as some pebbles of the Triassic dolomites and Jurassic, Tithonian-Neocomian and Eocene limestones. In the Zagrón Stream there occur conglomerates containing some pebbles of the Triassic dolomites and the Triassic and Eocene limestones. In Kojsówka there is a sandy conglomerate of the submarine slumping containing pebbles of the Triassic dolomites as well as Triassic, Jurassic, Neocomian and Eocene limestones. In the Măgura Stream near Witów there is an argillaceous gravelstone (submarine slumpings) which is exposed within the range of about 100 m. It contains many pebbles whose size is up to a dozen cm or so and are of very diverse composition. There occur crystalline rocks, Triassic dolomites as well as various types of Triassic, Jurassic, Neocomian and Eocene limestones. The localities of exotics are situated in the lower part of the Chocholow Beds, the average distance from the floor of the beds being 200—300 m, only in Ciche about 1000 m.

Character of the Exotics

All the localities have a similar composition of carbonate exotics. The most frequent components are fine, medium- and coarse-grained dolomites enclosing sometimes relict structures (Dasycladaceae) or structures of a loferite type. The dolomites are probably of Triassic age, like some frequent dolomitic sandstones, limestones and pelletal-lump limestones containing interclasts, microoncolites, algae (Dasycladaceae as well as incertae sedis — *Girvanella Tubiphytes, Microtubus)* and foraminifers *(Glomospira densa* Pantič). The algal limestones with *Rothpletzella munthei* (Rothpletz), *Girvanella minuta* Wethered, *Parachaetetes* sp., the limestones with coproliths, the oolites and the ostracods are probably of Rhaetico-Liassic age. To the Jurassic limestones, the pelagic limestones with *Bositra* sp. and *Protoglobigerina* may be assigned, to the Tithonian-Neocomian rocks, the tintinnid limestones with *Calpionella alpina* Lorenz, *Crassicollaria*

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div. sp., *Tintinnopsella carpathica* (Murgeanu et Filipescu), *Calpionellites* div. sp., to the Neocomian rocks, the Biancone type with *Nannoconus* div. sp., Urgonian limestones with algae (*Clypeina* div. sp., *Pianella* div. sp., *Arabicodium* sp.), as well as the limestones with radiolarians and sponge spicules. The radiolarites and Radiolaria limestones are probably of Jurassic or Cretaceous age. Among the Paleogene (Eocene) rocks micritic limestones, micritic sandy dolomites and organodetric or organogenic sometimes sandy limestones containing Bryozoa, red algae (*Lithothamnium* div. sp., *Lithophyllum* div. sp., *Lithoporella* sp., *Archaeolithothamnium* div. sp.) and large foraminifers (among others according to A. Kulka, *Dyscociclina* div. sp., *Grzybowskia* sp., *Nummulites perforatus* de Montf., *N. incrassatus* de la Harpe, *N. puschii* d'Archiac, *N. millecaput* Boub.) have been identified. There frequently occur limestones that have been observed in all the localities.

The microfacies of the Mesozoic exotics of the Podhale Flysch are similar to those which have been observed in the High-Tatric and Sub-Tatric deposits of the Inner Carpathians. The Paleogene exotics probably originate from the so- called Carbonate Eocene (Nummulites perforatus zone). The values of the flatness (according to Cailleux, 1945) are 2.33-5.6 for dolomites, 2.73-5.17 for limestones, 2.6-4.94 for crystalline rocks. The flatness (different from the average), the shape and roundness of the pebbles indicate that they have been carried from the distance of some score km, a differentiation of the sea bottom, as well as the possible repeated redeposition.

Conclusions

1. The exotics occur within some different lithostratigraphical members of the Podhale Flysch. The transport of the exotic material was done intermittently, sometimes vehemently, during the whole period of the flysch deposition.

2. The carbonate material represents different members of the Triassic, Jurassic, Lower Cretaceous and Eocene, the Triassic dolomites and the Eocene limestones being most frequent. The Mesozoic exotics show analogies with the deposits of the High-Tatric and Sub-Tatric series as well as of the Pieniny Klippen Belt. The Eocene exotics are analogous to the Carbonate Eocene rocks.

3. The exotics of the Polish Podhale are also similar to the exotics of the Slovakian Inner Carpathian Paleogene Flysch, as well as of the Paleogene of the Pieniny Klippen Belt and of the boundary zone of the Măgura series.

4. The exotic material was carried most frequently from a zone between the Podhale Trough and the Pieniny Klippen Belt (Neopienian and Šambron cordilleras, see Fig. 3), as well as from the south (Tatra Mts.). It was also redeposited from the Paleogene mantle covering the Mesozoic Tatric series and the cordilleras of the Pieniny area.

5. The redeposition of Eocene rocks, especially Eocene olistoliths evidences the existence of some distinct vertical movements in the Oligocene during the whole period of flysch deposition.

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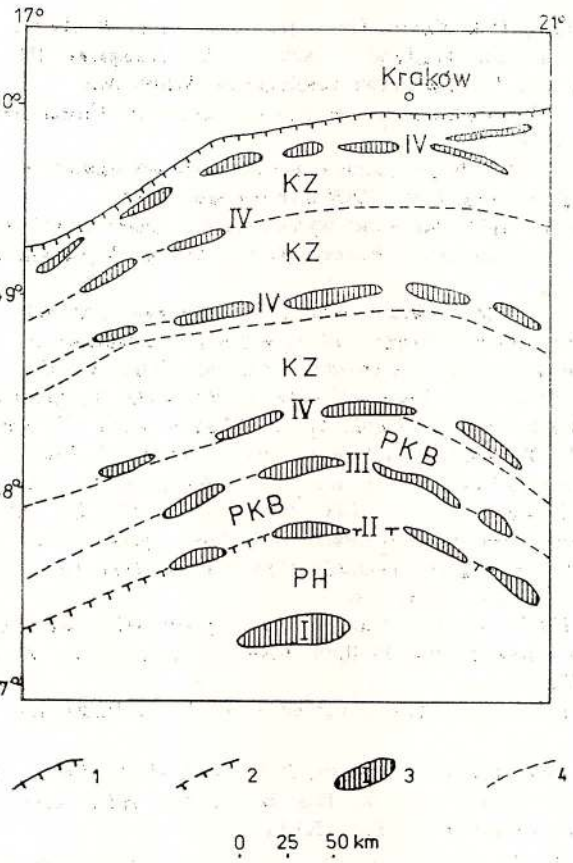


Fig. 3. — The source areas of exotics of the flysch of the Polish West Carpathians: 1, The northern border of the Outer Carpathian Flysch Belt; 2, Boundary between the Inner and Outer Carpathians; 3, The source area of the exotics (cordilleras): I-The Tatras (fragment of the microcontinent) of the Inner Carpathians, II-Šambron cordillera, III-Neopieninian cordillera, IV-Cordilleras of the Outer Carpathians; 4, Boundaries of the flysch basins; PH-basin of the Podhale Flysch, PKB-basins of the Pieniny Klippen Belt, OK-basins of the Outer Carpathians.

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ÉTUDE MINÉRALO-PÉTROGRAPHIQUE ET GÉOCHIMIQUE DE QUELQUES ROCHES SÉDIMENTAIRES D'ÂGE CRÉTACÉ SUPÉRIEUR ET PALÉOGÈNE DE LA ZONE DU FLYSCH SZOLNOK-MARAMUREŞ [1]

PAR

ENDRE DUDICH [2], GEORGE BOMBIŢĂ [3]

Introduction

En Hongrie, les formations en question sont couvertes par une série de sédiments néogènes et quaternaires, dont l'épaisseur varie entre 800 et 2 000 mètres. Par contre, elles affleurent au large dans la région des Monts Lăpuş (NE de la Transylvanie, Roumanie) et dans celle de Maramureş (au nord et au sud de la frontière entre la Roumanie et l'Union Soviétique, R.S.S. d'Ukraine).

Le „flysch hongrois" a été étudié et discuté par de nombreux paléontologues et géologues hongrois (Majzon, Körössy, Juhász, Sidó, Szepesházy, Szalay, Szentgyörgyi et Szots, voir la bibliographie), mais la majorité des données obtenues n'ont été jamais publiées. Elles se trouvent sous forme de rapports internes dans les Archives du Trust Hongrois du Pétrol et du Gaz. Il s'agit des études micropaléontologiques qui permettent le classement et la subdivision biostratigraphique de ces formations, des descriptions de lames minces, données de teneurs en carbonate, sur la granulométrie et sur la porosité. C'est tout, en ce qui concerne la pétrographie et la géochimie.

En 1979 le Laboratoire de Recherches Géochimiques de l'Académie Hongroise des Sciences (MTA, GKL), sollicité par le Trust Hongrois du Pétrole et du Gaz (OKGT), a entrepris une étude complexe sur 32 échantillons prélevés de 15 forages situés entre Tiszapüspöki et Nyirlugos, tout le long et à travers le secteur hongrois de la zone du flysch cachée au-dessous de la Grande Plaine Hongroise (description à l'œil nu et sous microscope — lames minces et surfaces polies — analyses chimiques, analyses de géochimie organique, dosage demi-

[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 Septembre 1981, Bucarest, Roumanie.

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quantitatif des éléments de trace par spectrographie d'émission, ATD, ATG, diffractométrie des rayons X).

On a examiné, de la même manière, 5 échantillons prélevés du forage Han-1 (village de Hanušovce, en Slovaquie orientale, grâce à

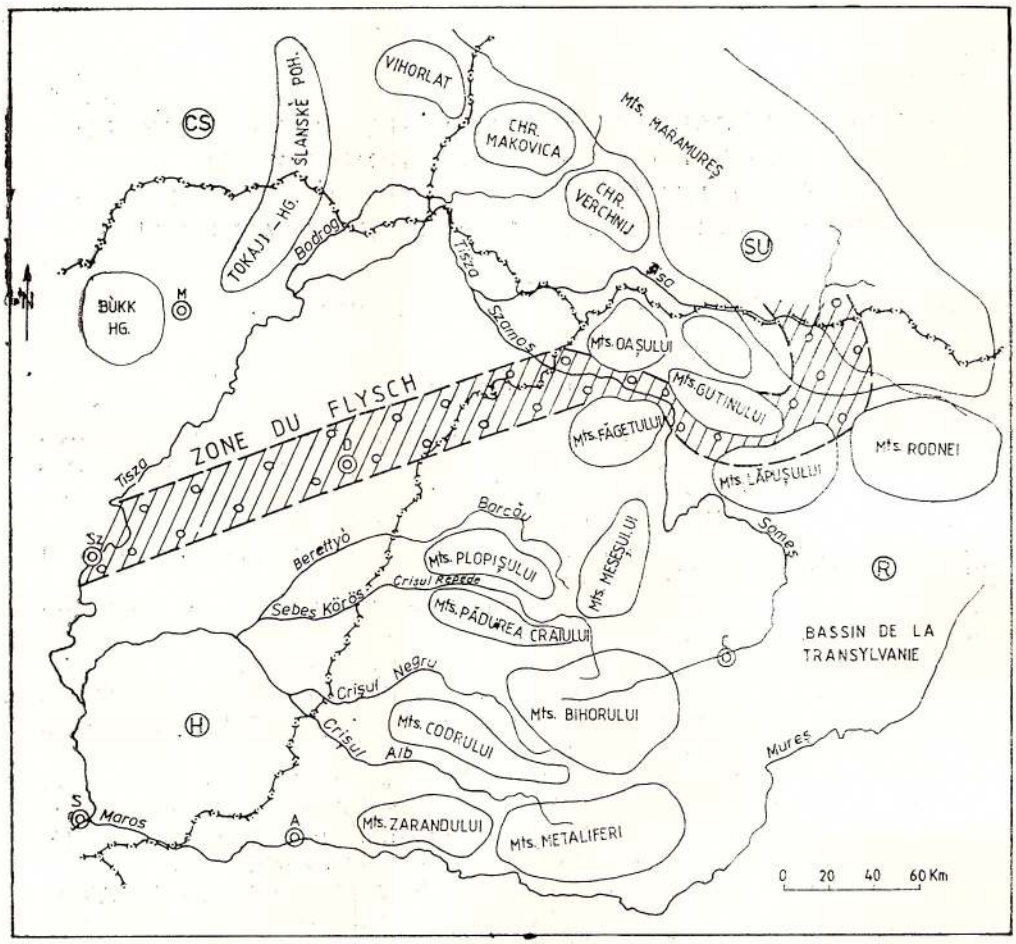


Fig. — Localisation approximative du Flysch Szolnok-Maramureș.

l'amabilité de l'Institut Géologique de l'Académie Slovaque des Sciences) et 3 échantillons prélevés par E. Dudich en Ukraine transcarpatique, à l'occasion d'une excursion du 11ème Congrès de l'AGCB, en 1977 (Kiev-Lvov). En 1980, dans le cadre de l'accord bilatéral de coopération entre l'Académie Hongroise des Sciences et l'Académie Roumaine, Dudich et Bombiță ont effectué un échantillonnage dans les Monts Lăpuș (région de Poiana Botizii). Huit échantillons choisis ont été soumis à la même étude complexe dans le Laboratoire de Recherches Géochimiques de l'Académie Hongroie des Sciences (les analyses chi-

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miques ont été réalisées à l'Institut Géologique de Hongrie, MÁFI (voir le tableau 1).

TABLEAU 1

Liste des échantillons

A) Hongrie

Entre les villages Tiszaüspöki et Nyirlugos, 15 forages. Profondeurs entre 1175 et 2350 m :
Crétacé supérieur, 10 échantillons de marne argileuse jusqu'au grès carbonaté (en partie dolomitiques) ;
Paléocène-Éocène inférieur, 6 échantillons : marne argileuse — siltite (carbonatée-dolomitique) ;
Éocène moyen, 9 échantillons : marne argileuse dolomitique jusqu'au grès carbonaté ;
Éocène supérieur, 3 échantillons : marne argileuse, grès carbonaté, calcaire sableux ;
Oligocène, 3 échantillons : argile, marne argileuse, marne (silteuse et dolomitique).

B) Roumanie

Monts Lăpuş, Poiana Botizii :
Crétacé supérieur, 1 échantillon : marne silteuse ;
Paléocène-Éocène inférieur, 3 échantillons : argile silteuse, grès argileux carbonaté ;
Éocène moyen, 1 échantillon : grès argileux ;
Vallée de Bloaja, Vima Mică et Preluca Izei (la dernière en Maramureş) ;
Oligocène, 3 échantillons : siltite carbonneuse, argile bitumineuse, marne bitumineuse.

C) RSSU, Ucraine transcarptique

Crétacé supérieur (Dolina), 1 échantillon : siltite ;
Éocène supérieur (Sol' et Soysa), 2 échantillons : siltite, grès.

D) Slovaquie

Forage de Hanusovce-1, un intervalle de 795 à 2314 m :
Crétacé supérieur, 5 échantillons : siltite dolomitique, grès carbonaté et dolomitique.

Discussions

Les résultats essentiels des examens faits sur un totale de 48 échantillons sont présentés dans les tableaux 2, 3 et 4.

Caractérisation des formations de Hongrie

Étant donné que les roches sédimentaires grossièrement détritiques (conglomérats, etc.) ont été évitées en révisant les carottes de forage, tout ce qui suit se rapportant aux roches sableuses, silteuses et argileuses (psammites et pélites) plus ou moins carbonatées.

Crétacé supérieur (Cr_3). Sediments psammitiques et pélitiques, relativement matures (beaucoup de quartz, peu de feldspaths), variablement carbonatés. État d'oxydation bien variable (de réducteur au forte-

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Quelques constituants principaux

Age Nombre d'éch.	Slovaquie Han—1 Cr_3 5	NE de la Grande Plaine Hongroise Cr_3 10	 $P_C - E_1$ 6	 E_2 9	 E_3 3
Quartz, %	17—34	10—63	15—42	30—47	30—59
Plagioclase, %	6—12	0—11	7—26	7—29	2—12
Orthose, %	0—2	0—12	0—tr.	0—10	—
Q/Fs	1,7—3,2	<17	0,6—6,0	<5,8	2,5—15
Hydromicas, %	10—24	7—29	17—35	0—25	6—12
Chlorites, %	5—10	0—28	0—20	0—3	1—12
Kaolinite, %	—	0—5	0—11	0—13	—
10—14 Å	0—4	0—7	0—9	0—22	0—1
Phyllosilicates, %	15—33	13—57	26—52	15—53	9—24
Pyrite, %	0—tr.	0—<1	0—1	0—2	tr—1
Calcite, %	3—31	6—67	0—17	0—23	5—60
Dol. + ank.	10—21	0—18	4—19	0—18	0—3
Index de Kübler	0,32—0,41	0,25—0,66	0,41—0,69	0,27—1,07	0,29—0,58
Index, <2 μ	0,39—0,41	0,36—1,06	0,74—1,09	0,47—1,16	0,36—0,81
TiO_2 %	<0,1—0,3	0,2—0,5	0,6—0,7	0,1—0,6	—
Fe_2O_3 %	0,7—1,3	0,1—1,6	0,9—1,3	0,5—3,2	0,8
K_2O %	1,2—2,5	1,1—3,6	1,8—2,8	1,0—3,9	0,8—1,3
Na_2O %	0,9—1,0	0,1—1,1	0,9—3,2	0,3—1,9	0,1—1,1
K_2O/Na_2O	1,1—3,6	1,0—38,3	0,8—2,6	0,8—10,2	1,1—15,4

ment oxydant). Ils renferment des bitumes pour la plupart autochtones, de nature huminitique ou mixte. On constate une transition graduelle de l'Ouest vers l'Est des formations néritiques épicontinentales à la zone „du flysch".

Paléocène-Éocène inférieur ($Pc-E_1$). Sédiments pélitiques, souvent assez dolomitiques, immatures (avec beaucoup de plagioclases) et kaolinitiques (en partie). Les teneurs en Ti et d'autres microéléments sont élevées. État d'oxydation fortement réducteur, la concentration du C org. dépasse souvent le 0,4% (limite inférieure pour les roches-mères d'hydrocarbures). Les substances organiques se trouvent, d'après leur degré de bituminisation et reflectivité de vitrinite (R_0), dans l'étape principale de la génération du pétrole. Les bitumes sont en général huminitiques, la plupart en est soluble en chloroforme. La partie nord de la zone est caractérisée par de hautes teneurs en manganèse. On a pu constaté de „graded bedding" aux rythmes fins.

Éocène moyen (E_2). Les différences entre la partie occidentale et celle orientale s'accentuent, mais en sens invers, par rapport au Crétacé

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BLEAU 2

et paramètres minéralogiques et chimiques

	Ukraine transcarp.	Monts Lăpuş/Roumanie, Transylvanie NE				Ukraine transcarp.
O 3	Cr_3 1	Cr_3 1	$P_c - E_1$ 3	E_3 1	O 3	E_3 2
15—28	32	15	28—41	31	15—33	34—59
0—16	11	3	12—22	18	9—21	8—16
—	—	—	0—2	tr?	—	0—6
<1,75	2,9	5	1,3—2,5	2,0	1,0—4,3	2,1—4,2
15—22	24	17	8—21	19	12—22	16—18
7—23	29	2	2—18	8	11—12	3—16
0—4	—	—	0—2	tr.	0—8	0—tr.
5—6	—	10	0—6	—	0—3	—
31—44	53	29	10—21	27	21—41	19—50
<1—1	—	—	<1	8	6—16	0—tr.
5—38	4	51	1—32	9	0—50	tr—8
6—13	—	—	8	1	0—10	—
0,35—0,72	0,33	n.a.	0,25—0,31	0,23	0,42—0,45	0,34—0,40
0,37—1,86	0,52	n.a.	0,54—3,18	n.a.	1,16	0,54—0,62
0,2—0,4	0,5	0,4	0,5—1,0	0,9	0,5—1,2	0—0,3
0—1,8	7,3	2,8	1,1—4,4	2,1	0,2—19	0,7—1,3
2,0—2,5	2,4	2,0	1,0—3,2	3,3	1,8—3,7	1,8—2,8
0,4—1,3	1,1	0,2	0,6—1,2	1,3	0,6—1,0	1,2—1,4
1,5—5,2	2,2	10,3	0,9—4,0	2,4	3,0—3,5	1,5—1,6

supérieur. Cette fois on trouve du flysch à l'ouest et des sédiments de passage de type épicontinental à l'est.

Ouest : sédiments pauvrement assortis, peu arrondis, aux rythmes fins, à ciment dolomitique-sidéritique. Les hydromicas sont accompagnés par des chlorites et kaolinites. Le faciès géochimique est réducteur, avec une abondance relative de microéléments. La substance organique, en quantité considérable, est prépondérent huminitique, allochtone. L'espèce *Nummulites striatus* Brug. a été identifiée dans la microfaune.

Est : sédiments pélitiques très peu stratifiés, mieux assortis et aux grains assez et bien arrondis. Les minéraux argileux d'origine allochtone (terrigène) sont fortement dégradés : il y a plus de chlorite. On trouve de l'orthose associée aux plagioclases. Le ciment est moins dolomitique, mais on a découvert la présence du gypse et de la barytine dans quelques échantillons. Faciès géochimique légérement oxydant, pauvre en microéléments (à l'exception du B). Peu de substance organique ; le rapport S_{KL}/S_{BA} est assez bas. Ces sédiments rappellent le Lutétien épicontinental du Bassin de la Transylvanie (secteur NE). Ils reposent parfois en position transgressive sur le socle cristallin paléozoïque. Parmi de nombreux fossiles, ils renferment *Nummulites perforatus* (Montf.).

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Géochimie organique

Age Nombre d'éch.	Slovaquie Cr_3 5	NE de la Grande Plaine Hongroise Cr_3 10	 $Pc-E_1$ 6	 E_2 9	 E_3 3
C_{org}, roche % totale	0,23—0,39	0,04—0,69	0,28—0,78	0,13—0,52	0,08—0,23
C_{org}, roche % originale	0,29—1,01	0,07—1,01	0,58—10,0	0,17—1,21	0,18—0,54
S_{Kl} % 1000	6—8	3—27	20—29	8—29	10—18
S_{BA} % 1000	5—14	2—16	5—24	4—38	2—9
S_{Kl}/S_{BA}	0,5—1,4	0,7—3,3	1,2—4,6	0,7—4,0	1,1—6,5
Kl	1,7—3,4	1,9—18,6	3,7—9,9	3,9—12,0	4,3—22,0
BA	1,6—4,3	1,3—26,3	1,6—8,4	1,9—9,4	2,4—4,9
% Parafiniques	n.a.	12—63	21—66	8—53	70
% Aromatiques	n.a.	12—34	8—21	15—26	9
% Résineuses	n.a.	16—41	20—25	23—41	17
% Asphaltène	n.a.	9—14	6,33	9—26	4
E 1470 / E 1710	1,2—1,7	1,1—2,7	1,1—4,1	1,1—3,4	1,7—5,4
E 1470 / E 1610	1,0—3,3	1,1—29,7	1,1—8,5	1,0—6,0	2,6—20,0
E 720 / E 750	0,4—1,0	0,3—1,9	0,3—1,5	0,4—1,4	0,5—2,8
E 1470 / E 1740	1,3—1,7	0,8—2,7	1,3—3,8	1,1—4,0	1,5—2,4
$\bar{R}_0$ max min	1,04—1,39	0,66—1,68	0,76—1,39	0,66—1,74	[1,41]
$\bar{R}_0$ moyen	1,21	1,12	0,90	0,88	

Éocène supérieur (E_3). Sédiments riches en sable quartzeux (mature), très carbonatés (marnes et marnocalcaires sableux). Le faciès géochimique est expressément oxydant, riche en strontium, mais pauvre en d'autres microéléments. Il n'y a que très peu de substance organique (prédominent les bitumes solubles en chloroforme), en partie allochtone. Il s'agit de formations nettement épicontinentales, par endroits en position transgressive, de mer peu profonde. Dans le microbiofaciès les bryozoaires et les algues *(Lithothamnium)* sont associés à *Nummulites fabianii* Prever.

Oligocène inférieur et moyen (O_{1-2}). Connus seulement dans la partie est, ces sédiments se développent en continuité de ceux de

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BLEAU 3

et reflectivité de vitrinite

	Ukraine transcarp.	Monts Lăpuș (Transylvanie NE)				Ukraine transcarp.
O 3	Cr_3 1	Cr_3 1	$Pc-E_1$ 3	E_2 1	O 3	E_3 2
0,10—0,54	0,46	0,03	0,04—0,10	0,45	0,65—5,10	0,17—0,20
0,61—0,99	0,69	0,10	0,08—0,14	0,63	0,74—5,22	0,32—0,38
30—64	10	3	2—5	8	85—930	8—13
5—24	3	14	9—18	17	23—118	4—6
1,2—8,2	3,3	0,2	0,1—0,6	0,5	0,7—7,0	2,0—2,2
7,0—22,2	2,2	9,7	4,8—11,5	1,8	4,1—24,5	3,9—7,7
2,7—5,6	4,6	45,2	14,4—45,0	3,8	3,5—20,4	2,0—3,5
8—58	n.a.	n.a.	n.a	n.a.	11—19	n.a.
10—34	n.a.	n.a.	n.a.	n.a.	21—25	n.a.
19—44	n.a.	n.a.	n.a.	n.a.	43—60	n.a.
13—26	n.a.	n.a.	n.a.	n.a.	5—17	n.a.
1,1—3,5	1,3	1,0	0,7—1,1	1,0	1,4—5,0	1,1—1,7
1,3—4,5	4,9	2,2	1,5—3,4	1,0	1,3—11,9	2,4—3,8
0,4—1,1	1,3	1,5	1,4—4,1	0,4	0,4—2,8	1,2—1,7
1,4—3,5	0,9	0,6	0,6—0,7	0,9	2,2—11,9	0,7—1,0
0,62—0,97					0,66—1,03	1,05—1,97
0,74	[2,39]	n.a.	1,29	0,86	0,84	1,50

l'Éocène supérieur. Il s'agit des roches pélitiques-carbonatées (marnes argileuses etc.) dont le minéral prédominant est la chlorite (et non plus les hydromicas). L'enrichissement en dolomie et pyrite est caractéristique. Le faciès géochimique est trés réducteur, très riche en micro-éléments (surtout les hautes teneurs en manganèse sont frappantes). La substance organique est abondante, malgré la perte considérable par oxydation. Les bitumes de toutes sortes sont présentes, le rapport S_{K1}/S_{BA} est encore plus élevé que dans l'Éocène supérieur (tableaux 5 et 6).

Comparaison régionale. À partir du Crétacé supérieur jusqu'à l'Éocène inférieur, on observe la ressemblance très prononcée des for-

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TABLEAU 4

Microéléments

	Slovaquie Han—1	NE de la Grande Plaine Hongroise					Ukraine transcarpathique	Monts Lăpuș (Transylvanie NE)				Ukraine transcarp.
Age	Cr_3	Cr_3	$Pc—E_{16}$	E_2	E_3	O	Cr_3	Cr_3	$Pc—E_1$	E_2	O	E_3
Nombre d'éch.	5	10	6	9	3	3	1	1	3	1	3	2
ppm B	105—110	75—110	90—110	70—125	105—115	95—130	110	117	48—123	128	93—180	85—100
Co	23—51	15—60	48—72	19—58	14—25	42—75	26	77	6—35	25	5—68	18—30
Cr	75—230	27—150	78—195	68—275	60—76	105—275	65	187	223—290	253	100—273	65—70
Ga	41—110	37—125	62—90	30—95	27—44	34—120	21	47	10—53	23	16—52	12—17
Mn	165—540	430—1120	300—1330	45—1200	405—705	855—1300	300	245	220—580	580	230—570	540—880
Ni	17—51	18—62	23—37	21—42	15—24	29—87	30	121	27—97	57	41—147	15—27
Pb	16—105	15—115	35—71	15—60	21—34	80—132	29	92	19—68	57	30—82	9—40
Ti	2000—2700	400—3150	2050—3300	1500—2700	1000—1280	1275—2800	1550	1325	3470—5100	5700	1500—5200	1450—1725
V	50—330	22—225	100—195	32—140	31—44	130—180	93	198	38—230	152	95—313	32—53
Zn	35—410	20—260	88—305	60—115	0—115	95—160	140	213	77—198	157	70—270	30—84

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TABLEAU 5

Répartition caractéristique de quelques paramètres

	Co	GA	Mn	Pb	V	Zn (ppm)
Psammites	29	49	586	27	57	69
Pélites	74	71	718	55	134	130

Teneur en carbonates	0—20	20—40	40—60	60 moyen
Sr	861	1388	1825	1950
V	82	112	158	61

NE de la Grande Plaine Hongroise	C_{org} %	S_{KI}/S_{BA}	β KI	R_0 % moyen
O	0,38	4,0	13,6	0,74
E_3	0,13	4,0	14,0	?
E_2	0,29	1,6	7,0	0,88
$Pc-E_1$	0,44	2,5	5,9	0,90
K_3	0,26	1,8	8,2	1,12

Monts Lăpuş

O	0,65—5,10	0,7—7,0	4,1—24,5	0,84 (min-max)
E_2	0,45	0,5	1,8	0,86
$Pc-E_1$	0,04—0,10	0,1—0,6	4,8—11,5	1,29
K_3	0,03	0,2	9,7	

mations de diverses régions étudiées. C'est le forage de Han-1, dont les échantillons diffèrent notablement des autres. Ce fait est facile à interpréter en termes paléogéographiques (pas de contact direct). De l'autre côté, on peut déduire un milieu de sédimentation plus éloigné de la côte et de mer plus profonde (de caractère bathyal et même abyssal) pour les formations de Hongrie, tandis que celles des Monts Lăpuş révèlent une proximité à la région épicontinentale, en accord avec les recherches antérieures roumaines.

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TABLEAU 6

Les valeurs particulièrement élevées dans les régions etudiées

Crétacé supérieur Hongrie	Quartz, feldspath potassique, kaolinite, Q/Fp, C_{org}, Mn, Ti
Roumanie	Fe_2O_3, S_{kl} S_{BA}, Ni
Carpathes ukrainiennes	Fe_2O_3, C_{org}
Paléocène-Éoc. inf. Hongrie	Hydromicas, kaolinite, total de phyllosilicates, total des carbonates, Na_2O, C_{org}, fraction parafinique, Co, Ga, Mn
Roumanie	Index de Kübler, TiO_2, Fe_2O_3 β_{BA}, Cr, Ni
Éocène moyen Hongrie	Feldspath potassique, Q/Fp, kaolinite, 10—14 Å structure mixte, dolomie, C_{org}, Ga, Mn
Roumanie	Chlorite, pyrite, $S_{kl} < S_{BA}$, β_{kl}, Ti, V
Éocène supérieur Hongrie	Total des carbonates, $S_{kl} < S_{BA}$, Ga, Mn
Carpathes ukrainiennes	Feldspath potassique, vermiculite, Fe_2O_3, K_2O, $S_{kl} > > S_{BA}$, Ti
Oligocène Hongrie	$S_{kl} > S_{BA}$, fraction parafinique, Ga, Mn, Pb
Roumanie	Plagioclases, Q/Fp, pyrite, $S_{kl} > S_{BA}$, fraction résineuse, Ni, Ti, V, Zn

En ce qui concerne la matière organique, il y a de remarquables différences. Dans la Transylvanie, paraît-il, la teneur en bitumes solubles en chloroforme (S_{Kl}, parafiniques) est subordonnée à celle des bitumes solubles en benzène et alcool, donc ce sont les substances organiques qui prédominent. D'ailleurs les teneurs en matière organique totale, caractérisée par la valeur C_{org}, sont beaucoup plus réduites dans les échantillons de Transylvanie. Pour la matière organique contenue dans ce type de roche, on y trouve des substances huminitiques ainsi que sapropéliques, autochtones et allochtones, disposées d'une façon assez irrégulière. La maturité, ou le degré de diagenèse signalé par les valeurs R_0, reflète une parfaite succession croissante avec l'âge géologique dans tous les deux régions, avec un certain avance pour la Transylvanie.

Dans l'Éocène moyen de faciès marginal du Maramureș et même de Hongrie on trouve des sédiments de mer peu profonde, de type épicontinental, par endroits directement transgressif, à côté des roches représentant la suite à continuité sédimentaire du domaine du flysch ; ces dernières aux teneurs assez élevées en C_{org} pour être considérées comme des roches-mère à potentiel d'hydrocarbures, semblables aux roches plus âgées traitées plus haut.

Dans le secteur hongrois de la zone, l'Éocène supérieur est de type franchement épicontinental. Il diffère donc considérablement

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des „marnes à Globigérines" de Maramureş central (la fosse), non étudiées au laboratoire, et de l'Ukraine transcarpatique où ces marnes (formation de type flysch) se continuent. L'Éocène supérieur du secteur hongrois ressemble plutôt à l'Éocène supérieur du bassin de la Transylvanie.

Pour ce qui est l'Oligocène, le faciès des échantillons hongrois est proche de celui des sédiments bitumineux transylvains de Ileanda, tout en révélant un caractère plus pélagique et moins bitumineux. La matière organique est caractérisée par la prépondérence des substances résineuses. Dans toutes les deux régions, l'Oligocène diffère donc essentiellement de l'Oligocène de type Krosno (flysch) des Carpathes ukrainiennes.

Conclusions

Il est évident que les données présentées plus haut (d'ailleurs entièrement nouvelles pour la connaissance des formations étudiées) ne permettent qu'une première approximation de comparaison régionale. Il serait souhaitable d'augmenter considérablement le nombre des échantillons analysés et évalués. Aussi, il nous semble nécessaire de coopérer avec les collègues de l'Ukraine, qui ont publié quelques ana-

TABLEAU 7

Données sur les formations du Crétacé supérieur et du Paléogène des Carpathes ukrainiennes
(d'après Gabinet et al.)

Age	Total de carbonates %	C_{org} %	S_{KI} 1000 %	S_{BA} 1000 %
Crétacé supérieur	6,5—66,1	0,02—0,93	3—48	5—46
Paléogène	0—67,2	0—2,74	3—770	1—104

On a fait 788 dosages de la teneur en carbonates et en C_{org}, 282 analyses de géochimie organique, etc.

Réflectivité de vitrinitée ($\bar{R}_0$ %) :
Oligocène 0,55—0,62
Crétacé supérieur 0,87—1,01

lyses (tableau 7) qui à présent ne sont pas directement comparables avec les notres (il s'agit de problèmes de subdivision tectonofaciale, stratigraphique, et de méthodologie d'analyse et d'interprétation).

Remerciements

Les auteurs tiennent à exprimer leur gratitude sincère au Département de Géologie de l'OKGT (Trust Hongrois du Pétrole et du Gaz) pour l'initiative, pour le support matériel et pour l'intérêt scientifique accordé au sujet ; aux dirigeants compétents des deux Académies des sciences pour l'assistance et support organisatoires ; et surtout aux spécialistes du MTA GKL (Laboratoire de Recherches Géochimiques de

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l'Académie Hongroise des Sciences) et du MÁFI (Institut Géologique de Hongrie) pour leur travail d'équipe bien complexe mais toujours très collégial et bien harmonisé.

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CONTRIBUTIONS TO THE PETROLOGY AND GEOCHEMISTRY OF THE VILLÁNY (SOUTH HUNGARY) AND APUSENI (ROMANIA) BAUXITES-COMPARISON [1]

BY

ENDRE DUDICH [2], ANDREA MINDSZENTY [3]

Introduction

The correlation of the Villány and Apuseni bauxites — both sandwiched between Late Jurassic and Early Cretaceous limestones — is an idea of tradition, suggested by V a d á s z (1951) and subsequently supported also by Romanian authors such as I a n o v i c i et al. (1976). Since the petrology and geochemistry details of the Villány deposit are far less known than those of the Apuseni occurrences, all these suggestions had to be based on stratigraphic considerations rather than on direct petrographic or geochemical evidence. In order to reveal the possibility of some direct correlation we decided to investigate two sets of samples — one from the Apuseni and the other from the Villány Mts — by the same standard methods, thus providing the correct data required for an acceptable comparison.

Sampling and Material Testing

Being almost completely worked out, the Villány deposit turned out to be unsuitable for representative sampling, thus the original idea of producing petrological and geochemical data strictly comparable with those available from the well-studied Romanian deposits had to be abandoned. Instead we decided to take two sets of random samples, each representing the various petrographic type of occurrences. The Apuseni samples were collected by D u d i c h in 1980 at Roşia, Albioara and J o f i in the Pădurea Craiului area and at Padiş Sub Boţig in the Bihor Mts, while the Villány ones were taken by D u d i c h and P a n t ó in 1979.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September, 8—13, 1981, Bucharest, Romania.

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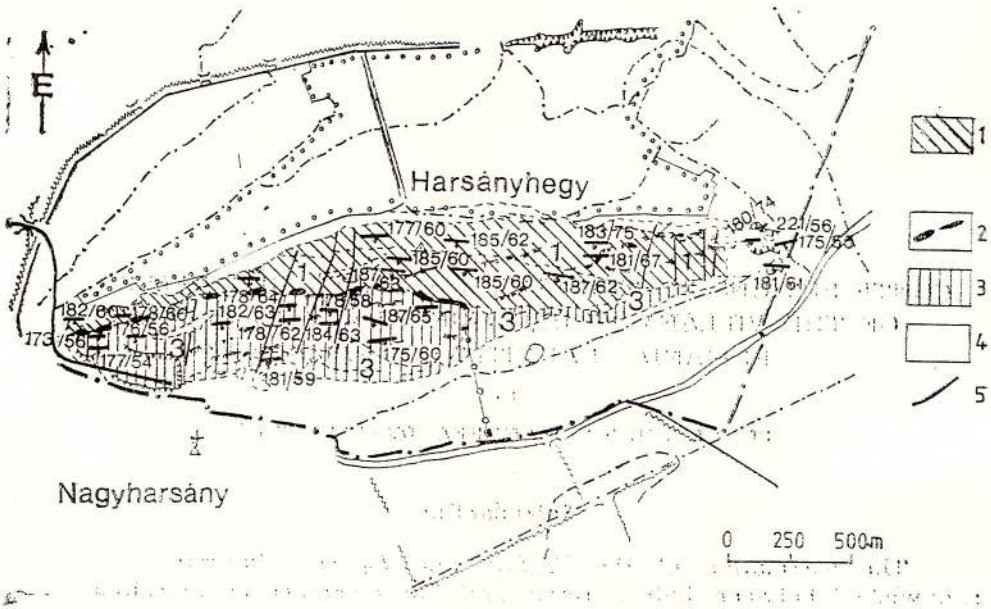


Fig. 1.— Geological sketch map of the Nagyharsány Hill (Villány Mts., South Hungary) (according to J. Fülöp, 1966) : 1, Upper Jurassic Limestone (Tithonian) ; 2, bauxite ; 3, Lower Cretaceous Limestone ; 4, Pleistocene (Loess) ; 5, Fault line.

All samples were analysed for their chemical and mineral constituents (trace elements included), Al_2O_3, SiO_2, Fe_2O_3, TiO_2, L.O.I. and trace elements were assayed in the Laboratories of the Hungarian Bauxite Prospecting Co. Balatonalmádi, X-ray diffraction analyses were carried out at the Hungarian Geological Institute in Budapest. The results are summarized in Tables Nos. 1, 2 and 3 together with the average trace element figures of some typical Transdanubian Central Mts bauxites (after Dudich, 1972).

Geochemistry

As far as the distribution of trace elements is concerned, it can be seen from the tables that except for Mn and possibly Cr there is no convincing difference between the investigated samples. The figures of Mn are of an order of magnitude higher at Nagyharsány (Villány) than in the Apuseni, thus exhibiting a remarkable resemblance to the occurrences of the Transdanubian Central Mts Ga and to a lesser extent also Ni seem also to be somewhat enriched in Nagyharsány when compared to the Apuseni, but this enrichment is far less apparent, indeed.

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TABLE No 1

Chemical composition of the Villany and the Apuseni samples

No. of sample	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	L.O.I.	Ca O	MgO	ΣS	Module
				Nagyharsány/Villány					
Nh— 3	47,4	16,2	9,0	2,5	15,6				2,9
Nh— 4	53,0	19,9	4,5	2,8	13,4				2,7
Nh— 5	46,2	30,3	4,1	2,3	13,5				1,5
Nh— 6	60,9	4,8	13,9	3,2	14,0				12,7
Nh— 7	60,4	4,0	16,4	3,0	14,3				15,1
Nh— 9	45,1	29,4	4,5	2,3	13,3				1,5
Nh—10	53,8	4,2	24,6	3,0	13,9				12,8
				Pădurea Craului/Apuseni					
EB—21	24,9	3,4	10,0	1,2	29,0	30,2	0,6		7,3
EB—22	53,6	3,1	29,2	2,5	10,7				17,3
EB—23	58,7	2,3	22,3	3,1	13,2				25,5
EB—24	59,2	8,3	15,5	2,7	11,9			0,04	7,1
				Bihor/Apuseni					
EB—30	59,9	3,1	21,5	2,4	11,7				19,3
EB—31	56,1	7,2	20,6	2,4	11,9				7,8
EB—32	53,8	3,0	25,4	2,4	12,5				17,9
EB—33	58,7	6,9	16,8	2,4	13,2				8,5
EB—34	54,1	3,5	26,2	2,3	11,2				15,4
EB—35	53,6	6,4	25,3	2,2	11,8				8,4
EB—36	57,6	6,8	18,5	2,3	12,6				8,5

On the contrary, the Cr, V and Zr contents seem to be higher in the Apuseni bauxites than in the Villány ones, but the difference remains within the same order of magnitude.

When compared with the Transdanubian Central Mts. occurrences, however, Hagyharsány should be considered as anomalous from the point of view of its remarkably higher Zr content. In other words from this point of view the Nagyharsány bauxites seem to be more closely related to those of the Apuseni Mts than to the Transdanubian Central Mts bauxites.

As to the V content, the Nagyharsány bauxites turned out to be unique, being remarkably poorer in V than both the Apuseni and the Transdanubian Central Mts deposits.

Mineralogy

As to mineralogy, differences and similarities are apparent and clear-out (see Table 2). All the Apuseni samples are predominantly diasporic while the Nagyharsány deposit is characterized by boehmite as the main alumina mineral. Unlike the Transdanubian Central Mts occurrences there is no primary gibbsite in any of them but they characteristically contain a certain amount of chlorite — unusual in the Transdanubian Central Mts deposits. In terms of bauxite genesis this

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TABLE No. 2

Mineralogical composition of the Villany and Apuseni samples (in percentages)

No. of sample	mont-morill-onite	illite	kao-linite	chlo-rite	dias-pore	boeh-mite	ana-tase	rutile	hae-matite	goe-thite	calcite
Nagyharsány/Villany											
Nh— 3	—	—		27*	9	53	2	<1	3**	—	5
Nh— 4	—	4		29	2	58	2	1	4	—	—
Nh— 5	—	2		58	5	29	1	1	4	—	—
Nh— 6	—	5	5	—	3	74	4	1	8	—	—
Nh— 7	—	3	—	—	6	76	3	<1	9	—	3
Nh— 9	—	3		60	3	29	2	<1	3	—	—
Nh—10	—	6	2	—	5	54	3	1	25		3
Pădurea Craiului/Apuseni											
EB—21			4		31	<1?	<1	<1	9		55
EB—22			5		63		2		30		
EB—23			4		84		1		11		
EB—24				⩾22	76		1	<1	?		
Bihor/Apuseni											
EB—30	5	7	2		75		2		9		
EB—31			5		74		1	<1	19		
EB—32			5		82		<2		5	7	
EB—36		6***		⩽11	71		1	<1	7	3	

* figures written between the columns of "kaolinite" and "chlorite" stand for undistinguishable kaolinite-and-chlorite.

** figures written between the columns "haematite" and "goethite" stand for undistinguishable haematite-and-goethite.

*** figures written between the columns of "illite" and "montmorillonite" represent undistinguishable phases as above.

Note: Chlorite is definitely of the chamosite-type in the Apuseni samples.

means that both the Apuseni and the Villány samples can be considered as belonging to the so-called diaspore-boehmite-chloride facies (Valeton, Combes and others) known to be the representative of quasi-reducing (i.e. low Eh) conditions.

Petrology

Lithological similarities and dissimilarities were expected to be fundamental evidence on correlation. They turned out to be rather difficult to unfold, however. Karst bauxites being essentially transitions between fine-grained clastics and chemical sediments, their petrological characteristics are the joint result of weathering, transportation, deposition, diagenesis and epigenesis, and all these elementary processes are controlled by local environmental factors rather than by regional

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TABLE No. 3

	Ga	Be	Zr	V	Mn	Cr	Ni	Cu	Mo	Pb	Sn
Karst bauxites /average/ /Schroll-Sauer/	53	10	570	220	760	690			17		
Transdanubia * /after Dudich 1972/	40 5,3-180	8 0,7-36	413 70-1800	644 56-1600	1326 0-34000	299 14-800	160 47-692				
Nagyharsány ** /Dudich-Mindszenty/	92 28-179	9 6-13	690 503-1014	360 202-684	1032 189-2082	260 136-370	194 127-314	32 12-69	<7 <7-16	77 27-139	12 8-24
Pădurea Craiului /Dudich-Mindszenty/	40 20-52	7 5-9	710 459-874	532 297-526	495 158-934	328 205-404	162 98-252	24 13-41	<7 4	74 41-105	<8 <8-13
Bihar /Dudich-Mindszenty/	64 43-123	7 6-9	755 681-814	645 392-1512	154 <126-265	433 335-595	122 44-275	24 11-46	<7	87 38-176	18 13-27
Pădurea Craiului Papiu V. 1967		5-115	823 580-1080	352 238-522	<165-1000	429 172-680	145 92-213				
Apuseni *** /average/	55 20-123	7 5-9	739 459-874	604 297-1512	278 126-934	394 205-595	136 44-275	24 11-46	<7	82 38-176	13 <8-27
Vinogradov /1962/ Sediments /average/	30	3	200	130	670	100	95	57	2	20	10

Fig. 2. — Trace elements in the Apuseni and Nagyharsány bauxites.

* The Transdanubian Central Mts figures are the arithmetic means of the Nyirád, Halimba-Szóc, Fenyófő, Iszkaszentgyörgy and Gánt occurrences as given by Dudich in 1972.

** The Nagyharsány figures represent the average of 12 random samples, 7 of which were taken in 1979 and analysed as part of the present study in 1981 while the additional five were taken in 1968 by the geologists of the Bauxite Prospecting Co. in the adits of the abandoned mine, and were analysed in the same year by the laboratories of the company. As to calculations, at first the arithmetic means were produced within each group of samples, and then the weighted averages of the two groups gave the final figures.

*** The Apuseni average is the arithmetic mean of the 1981 analyses of our 11 random samples (4 from Pădurea Craiului and 7 from the Bihor Mts).

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ones. Thus petrographic properties in this particular case are characteristic of the microfacies rather than of the overall geology or tectonic setting of the depositional environment in question.

All samples proved to be essentially the same ooidic-pisoidic, diagenetic, clastic type with the ooids, pisoids and bauxitic interclasts embedded in a more-or-less homogeneous, partly deferrificated matrix. Since deferrification is — in principle — a process of local facies control, it cannot be taken as a decisive factor in most of the samples. (Deferrification processes of the Romanian bauxites have been studied in much detail by P a p i u et al.).

Another textural feature, at first suggesting some overall differences between the two sets of samples had been the degree of segregation of the alumina from the iron oxide within the ooids and pisoids. It turned out to be markedly higher in almost all the Apuseni samples than in the Villány ones. Being again a locally controlled and moreover a grade-dependent phenomenon, it could not be taken, however, for anything but a proof of excellent drainage conditions during late diagenesis — a quite normal environmental factor in the formation of numerous high-grade bauxites.

Of all the structural and textural features it was the overall degree of crystallinity and postlithification fracturings (including the nature of crack filling minerals) which seemed to offer some more-or-less reliable basis of comparison. Both the matrix and the ooids and pisoids of the Apuseni samples turned out to be very well crystallized, consisting of 15 to 30 micrometer size grains on the average but having also irregular groups of diaspore crystals as large as 300 to 400 micrometers with the individuals being of 60 to 100 micrometer diameter as segregation products either within the ooids or simply in the pores of the groundmass. Chlorite occurs in these samples primarily as little 8 to 10 times 3 to 5 micrometer size oriented flakes within the ooids (see Photo No. 3) and secondly as large 120 to 180 micrometer size elongated platy crystals arranged perpendicularly to the walls of microfractures and associated with idiomorphous or hypidiomorphous grains of 80 $\times$ 10 micrometer size diaspore and with isometric or short prismatic crystals of 25 to 50 micrometer size anatase (a phenomenon described earlier and assigned to hydrothermal processes by B á r d o s s y 1977).

The overgrowth of the diaspore crystals beyond the boundaries of diagenic structural elements is quite common in most samples and is interpreted as a sign of intense recrystallization of the material.

The degree of crystallinity of the Nagyharsány samples is remarkably lower than that of the Apuseni ones. Diaspore is visible under the normal petrographic microscope in the middle of a few of the ooids of the investigated samples (see Photos Nos. 8, 10) and its grain size never exceeds 15 micrometers. What is more, the grain size of boehmite — the major alumina-mineral of the Nagyharsány bauxite — is less than the scope of our microscopes. Thus the Nagy-

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harsány samples can be considered as essentially "non-crystalline" (i.e. of the sub-microscopic size) in the petrological sense.

As to postlithification fracturing it is the Nagyharsány samples that bear the imprints of an apparently intense tectonic strain which obviously affects a rock already rigid enough to respond by homogeneous deformation. Microfractures of straight and smooth walls with or without displacement, equally criss-crossing both the ooids and the matrix and generally filled by secondary (probably descendant) haematite or limonite are frequent in almost all the investigated samples. On the contrary, fracturing in the Apuseni samples is much less frequent and most fractures are clearly of diagenetic origin (e.g. shrinkage-cracks within the ooids). Even the obviously secondary-maybe hydrothermal — chlorite-diaspore-anatase veins fill fractures the walls of which are irregular, suggesting some late diagenetic origin (fracturing of a low-rigidity material) or else a rather equivocal stress of the shear type as it was in the case of the Nagyharsány samples.

Discussions

When trying to interpret all the above data with the possibilities of correlation of the two occurrences in mind we are faced by the problem of an apparent contradiction between the geochemistry, mineralogy and petrology of the investigated samples.

In terms of mineralogy the Villány and Apuseni bauxites are quite closely related, or at least both belong to the same low-Eh facies resembling certain North Vietnamese bauxites called "paralic" by Komlössy (1976) and considered to have been accumulated in a near shore essentially lagoonal environment — a hypothesis which seems to be supported by the fact that the cover succession does not contain any definitely uliginal (i.e. swampy) formations (which are generally indicative of the normal ingression succession usual in most Transdanubian Central Mts deposits).

Petrologically, however, they are quite unlike — one of them being highly crystalline and the other essentially amorphous in the optical sense. Whether the higher degree of crystallinity is a direct effect of prelithification tectonism is another question and it cannot be decided at the level of our present knowledge. Maybe that is simply the consequence of mineralogy (the tendency diaspore has to occur in the form of well grown crystals and the generally submicroscopic grain size of boehmite are widely known although yet uninterrupted phenomena).

Microtectonics again is something hard to interpret, especially when one tries to be in accordance with the petrological observations. If only fracturing (i.e. homogeneous postlithification deformation) is taken into account, the Nagyharsány seem to be much more tectonized than the Apuseni occurrences. This complies with the difference in their tectonic situation, the Nagyharsány deposit being imbricated, while the Pădurea Craiului deposits are of subhorizontal position.

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The Apuseni samples, although apparently less fractured, are, however, not completely free from fractures either. Their secondary anatase-chlorite-diaspore veins undoubtedly suggest the possibility of some tectonic remobilization of their constituents.

As to trace element geochemistry, no correlation can be made on the basis of the available data. By their Mn content the Villány bauxites are obviously related to the Transdanubian Central Mts occurrences rather than to the Apuseni ones, while the interpretation of the other trace elements is far from being unambiguous. Conclusions as to differences in source areas would be premature.

In what follows we shall try and give the tentative explanation of the above apparent contradictions together with some comments on the methods used.

1. Being locally controlled, the distribution of the investigated trace elements in a restricted number of bauxite samples seems to be unsuitable for the correlation of deposits so wide apart.

2. The petrological features of bauxites are indicative primarily of the elementary processes of formation controlled by the microfacies rather than by the overall paleoenvironment.

3. The use of mineral make-up as a facies indicator has been confirmed by our investigations.

4. By their mineralogy the Villány and the Apuseni bauxites may be considered as two members of one and the same "paralic" zone of bauxitic sedimentation, although their origin cannot be proved by mineralogy alone. It should be noted, however, that stratigraphic evidence is a strong support to the assumption, which complies more with the megatectonic setting of the two bauxite occurrences studied.

5. Microtectonic and petrological evidences suggest that the post diagenetic history of the two was different. We are not of the opinion that tectonism may have affected the Apuseni bauxites prior to the complete lithification while the most intense tectonic phase (of imbrication) to which the Villány bauxites were subject has taken place quite obviously long after the lithification.

The authors wish to thank dr. C. V. Papiu for his valuable advice, the competent Romanian authorities for the permission of sampling in the Apuseni Mts, dr. Gh. Mantea for his kind assistance in the sampling, the Bauxite Prospecting Co. for the chemical analyses and for the preparation of the thin sections, dr. L. Farkas for the X-ray diffraction work and dr. I. Vörös for his kind permission to use the photomicroscope of ALUTERV to prepare the photomicrographs for the present paper.

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(Supplement No. 1)

LIST OF SAMPLES

No of sample	Locality	Petrology
Nh—3	Nagyharsány villány Mts South Hungary	argillaceous bauxite, yellow with a greenish tint, hard, compact with carbonatic and/or Mn-rich coating on the surface of joints. Consists of ooids and bauxite pebbles embedded into the greenish groundmass.
Nh—4	,,	bauxite, brick-red with white and brown or russet roundgrains, the rim of which is always pale. Hard, compact.
Nh—5	,,	argillaceous bauxite, pale russet with white, yellowish, red and bluish ooids and roundgrains, bauxite pebbles and concretions. There are pores in the matrix, coated by a dark yellowish-brown goethitic material and filled by some white or pink clayey or aluminous material.
Nh—6	,,	bauxite, light yellow with a brownish tint, contains 0.1 to 0.8mm size black or red iron-rich roundgrains and irregular patches. Thoroughly fractured with a densenetwork of fine lithoclases. Joint-surfaces are coated by haematite and/or clay. Hard, compact.
Nh— 7	,,	bauxite, light yellow, hard, compact, with white, red, green and bluish-green ooids, roundgrains and angular fragments probably also of bauxitic composition. Most ooids are surrounded by a pale rim. The whole material is penetrated by fine lithoclases.
Nh— 9	,,	argillaceous bauxite, pale pink with lighter or darker ooids and 3 to 4 mm size bauxite pebbles. Contains pores and irregular pale patches of decoloration. Medium-hard, when thin easy to crumble by hand.
Nh—10	,,	bauxite, yellow with a brownish tint, containing large — several centimeters — irregular, red and black iron-rich patches, somewhat less frequently also decoloration structures. There are mm-size iron-rich round-grains and yellowish ooids in it. Hard, compact. It is penetrated by a dense network of fine lithoclases, part of which exhibit thin carbonatic coating on their surface.
EB—21	Pădurea Craiului/Apuseni (Romania)	bauxite, very hard, pink with large red 1 to 2 cm, irregular iron-rich patches, 0.2 to 3.0 mm ooids, roundgrains and subangular bauxitic intraclasts. Large 4 mm to 1.5 cm diameter fragments of the wall rock and carbonatic pore-filling is common.

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LIST OF SAMPLES (Continued) Supplement No. 1

No. of sample	Locality	Petrology
EB—22	,,	bauxite, russet, very hard, compact; consists of dark red or brown spastoids, ooids, roundgrains and bauxitic intraclasts embedded into a russet bauxitic matrix. Slightly porous, with the pores either empty or partly filled by dark iron-rich, or white, aluminous? material.
EB—23	,,	bauxite, very hard, compact, slightly porous, brown whith a yellow tint and 1 to 2 cm black haematite-rich patches. Ooids and yellow goethitic pore-space fillings are common.
EB—24	,,	bauxite, light grey with dark grey or brownish ooids, roundgrains and angular to subangular bauxitic intraclasts. Very hard, compact.
EB—30	Bihor Mts/Apuseni (Romania)	bauxite, pink with small 0.X mm diameter white or pink ooids, irregular 1 to 6 mm patches of red to violet haematite. Slightly porous, hard, compact
EB—31	,,	bauxite, hard, compact, dark-red with dark-brown ooids and occasional black iron-rich patches.
EB—32	,,	bauxite, hard, brittle, porous, pale red with a tint of violet and/or yellow. Dark-brown ooids, pisoids and spastoids are frequent with their central part being occasionally white or pink.
EB—33	,,	bauxite, hard, compact, with an argillaceous lustre on the surface. Pale brick-red with a brownish or yellowish tint. Contains ooids and roundgrains the inner part of which is definitely green and is surrounded by a pale yellowish rim.
EB—34	,,	bauxite, hard, compact, greenish-grey, with brown and greenish-brown ooids, roundgrains and angular fragments of probably bauxitic composition. Penetrated by diaspore—chlorite, veins of 0.x to x.0 mm width. Occasionally there is a thin dark haematite-rich crust coating the joint-surfaces.
EB—35	Bihor Mts/Apuseni	bauxite, hard, compact, russet with brown and red ooids, pisoids and bauxitic intraclasts surrounded by a white or yellowish pale rim.
EB—36	,,	bauxite hard, compact, very much like EB—33 but with no green ooids.

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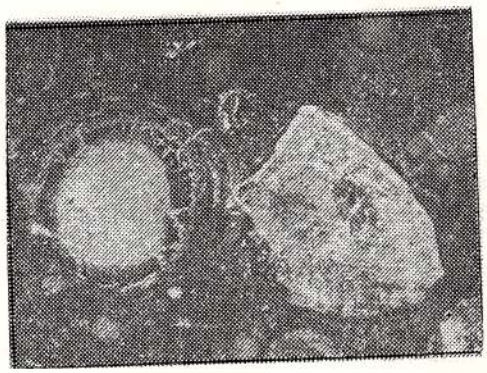


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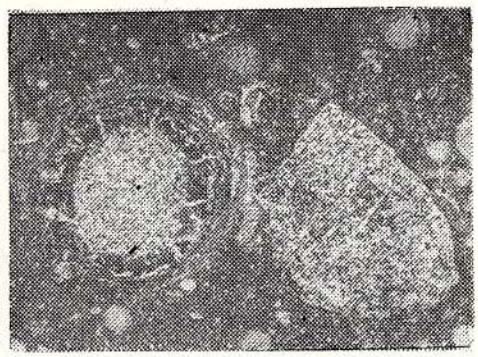


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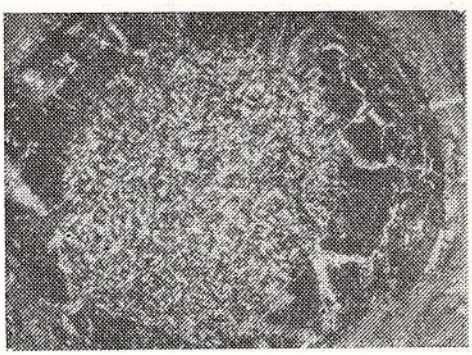


Photo No. 3



Photo No. 4



Photo No. 5



Photo No. 6

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Photomicrographs of the Apuseni Samples

Photo No. 1. — Ooidic-diagenetic-clastic bauxite. Note the central part of the ooid consisting of chlorite (most probably chamosite) and surrounded by a rim of shrinkage-cracks filled by diaspore. Pădurea Craiului/Apuseni, (EB-24).

Photo No. 2. — The same as Photo No. 1 with the polars crossed. Note the almost equally well crystallized nature of matrix, ooids and interclast.

Photo No. 3. — Interior of a chloritic-diasporic ooid consisting of oriented flakes of chamosite. The radial and subradial cracks are filled by diaspore. Detail of Photo No. 2. Crossed polars.

Photo No. 4. — Textural detail with an ooid and an irregular intraclast penetrated by syneresis-cracks. Note the large group of transparent diaspore crystals (white) of segregation origin on the left side of the intraclast. Pădurea Craiului/Apuseni. (EB-24). Crossed polars.

Photo No. 5. — Chlorite-diaspore-anatase vein (chlorite=light grey ; diaspore= white ; anatase=dark grey) filling an irregular crack in ooidic diasporic bauxite. Bihor Mts/Apuseni. (EB-34). Crossed polars.

Photo No. 6. — Idiomorphous prismatic crystals of anatase. Vein filling. Bihor Mts/Apuseni. (EB-34). Crossed polars.

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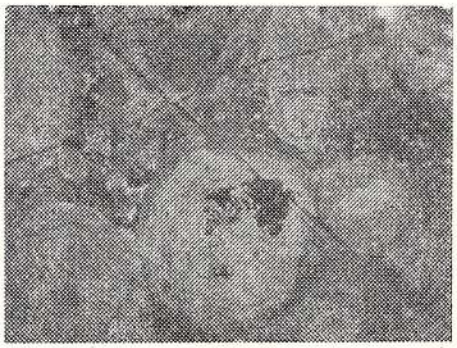


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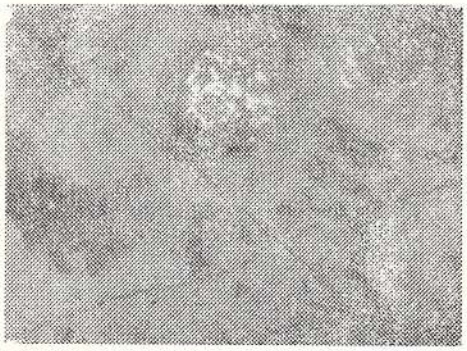


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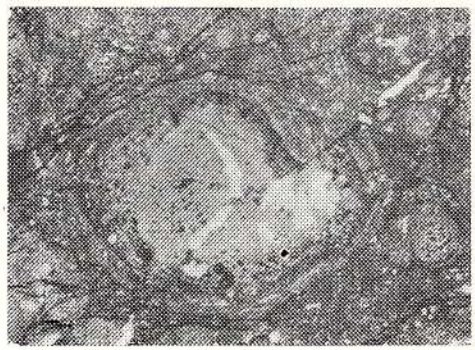


Photo No. 9



Photo No. 10

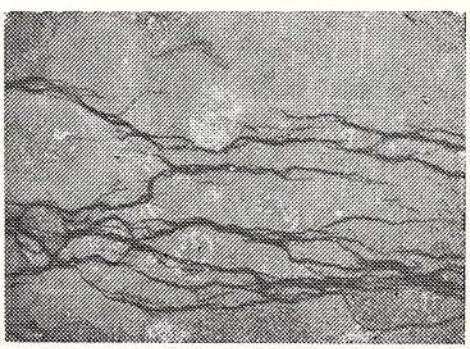


Photo No. 11

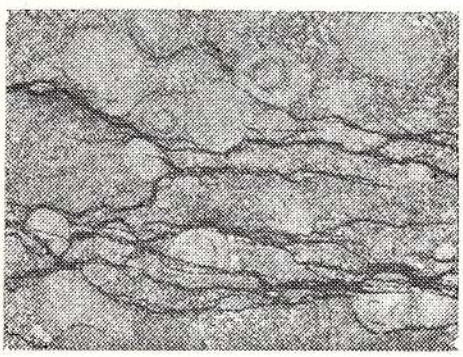


Photo No. 12

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Photomicrographs of the Nagyharsány Samples

Photo No. 7. — Ooidal, kaolinitiferous boehmitic bauxite of the low-segregation type, penetrated by two lithoclases intersecting at an angle of about 50 degrees. Nagyharsány/Villány. (Nh-5).

Photo No. 8. — The same as Photo no. 7. with the polars crossed. Note the overall low degree of crystallinity and the group of small-size diaspore grains in the mid of the large ooid. Crossed polars.

Photo No. 9. — Boehmitic bauxite of ooidic character with lithoclases resulted by postlithification tectonism — in this particular case with slight displacement. Nagyharsány/Villány. (Nh-10).

Photo No. 10. — The same as Photo No. 9. with the polars crossed. The interior of the large ooid in the mid contains well-crystallized diaspore but the matrix is optically amorphous. The lithoclases are filled by haematite.

Photo No. 11. — Ooidic boehmitic bauxite penetrated by a dense network of lithoclases of postlithification origin. Note that the degree of segregation of alumina from ironoxide is rather high in most ooids (ironoxide-rich phase = dark ; alumina-rich phase = light coloured). Nagyharsány/Villány. (Nh-7).

Photo No. 12. — The same as Photo No. 11. with the polars crossed. Note that — independent from segregation — the degree of crystallinity is generally very low ; the diaspore is visible, under the form of small white grains, only in a few of the ooids.

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Photomicrographs of the Nagyharsány Samples

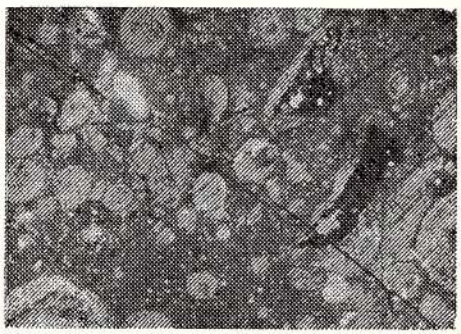


Photo No. 13. — Classical example of lithoclases produced during postlithification tectonism. Nagyharsány/Villány (by courtesy of the Bauxite Prospecting Co. Balatonalmády, Hungary).

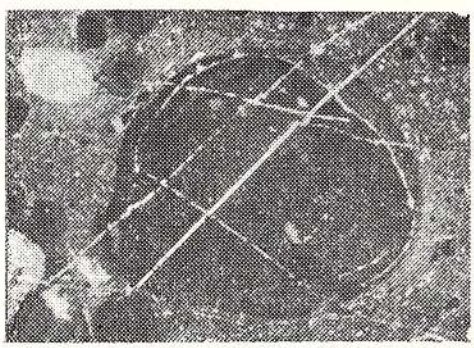


Photo No. 14. — Lithoclases with and without displacement criss-crossing an iron-rich low-segregation type round-grain and continued straight in the matrix. Nagyharsány/Villány. (Nh-4). Crossed polars.

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FACIOLOGICAL ANALYSES OF THE CYCLICAL DACHSTEIN LIMESTONE FORMATION IN THE BAKONY MOUNTAINS [1]

BY

IÁNOS HAAS [2]

Introduction

The classical unit of Alpine geology described for the first time by Peters (1854) from the Alps and first referred to by Hantken (1861) in the Transdanubian Central Range as Dachstein Limestone Formation, plays a significant role in the geological construction of the Transdanubian Central Range, being traceable as far as the Himalayas. Since, a rather large number of specialists have analysed from the stratigraphical or sedimentological viewpoints the sequences of several sections. However, the study and interpretation of these rather thick series could not be regarded as satisfactory in the light of present-day sedimentological knowledge.

Borehole Po-89, sunk in 1979 at Porva (N Bakony Mts), within the scope of National Key Section Program, crossed in a thickness of 410 m the lower — and, on the basis of macro- and microfauna analyses, completely Norian — part of the Dachstein Limestone, then, the section's lowermost part, i.e. the unit representing the transition between the Dachstein Limestone and the Hauptdolomit.

The section was studied mainly to carry out a precise and detailed sedimentological analysis concerning facies reconstruction and identification of revolutionary trends.

The aim of the analyses was to find a suitable system of investigation where emphasis was laid on the coordination of macroscopic and microscopic observations by laboratory measurements (chemical, mineralo-petrographical, paleontological), to make an exact comparison of the results and to guarantee their joint interpretation.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September, 8—13, 1981, Bucharest, Romania.

[2] Hungarian Geological Institute, Budapest XIV, Népstadion ut 14.

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Evaluation of the Investigations General Features of Cyclicity

Regarding the cyclical development of the analysed formation, special attention was paid to the features of cyclicity and regularities during the macroscopic survey and the evaluation of the analyses. The cycles may be well distinguished and separated even with the naked eye ; the basic pattern and the individual basic elements of their development are well known from literature.

The cycles under study are essentially in agreement with those described by Sander (1936), Schwarzacher (1948, 1954) and in even more detail by Fischer (1964) as Lofer cyclothems, within the Dachstein Limestone of the northern Calcareous Alps.

During our macroscopic investigations 138 cycles could be determined and separated into various subtypes within the cycles of substantially similar development (Fig. 1)[3] and the deviations from the ideal cycles described by Fischer (1964) could be shown.

The most significant deviations are the following :

1. In the sequences we studied, the greater part of the cycles was less denuded, thus the regressive cycle elements of algal mat origin (symbol B′) are rather different from those observed by Fischer (1975) in the Alps and are not rare at all, moreover they are predominant. In this case the disconformity and then member „A" appear above the algal mat layer. Thus the complete cycle in the above sequence can be regarded as basic type and written with the aid of the formula d-A B C B′-d (Fig. 1, Type 1).

2. Because of some intra-cycle anomalies of development or some minor internal unconformities, or as a result of erosion, any member can really fail within the cycle, or it may be atypical. Most often member „A" is absent or strongly reduced. The absence of member „C" or its total erosion is unfrequent.

3. In several cases and generally in the upper part of the sequence, there is a cyclical development but between the regressive and transgressive branches there is no rupture or discordance and the unit can be described by the formula d-A-B-C-B' +B-C-B' +B-C-d (Fig. 1, Type 11).

4. Occasionally, some special elements can be observed in the Dachstein Limestone, too. Thus, for example, in member "A" there may be a 2-6 m-thick red silty marl layer (Fig. 1, Type 12) or, even more often, an originally evaporitic, porous dolomite of Sabhka facies between members "A" and "B" can be observed.

The thickness of the cycles varies between 0.3 and 8.5 m.

The regularity described by Schwarzacher (1954) and then by Fischer (1964) that in the cyclic sequence 5 to 8 cycles of upwards decreasing thickness would form megacycles, could not be proved, only some indistinct traces can be observed in the lower part of the formation.

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[3] The figures have not been sent by the author. (n. red.).

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Facies Types of the Cycle Members

On the basis of macroscopic observations and analyses the following types can be differentiated within members A, B and C (Figs. 2 and 3) :

Member "A"

1. Silty (dolo-) marl (often intraclastic)
2. Argillaceous carbonate (limestone, dolomite)
   - 2.1. intraclastic (plastotype)
     - 2.1.1. intraclastite
     - 2.1.2. bioclastic
     - 2.1.3. with few intraclasts and bioclasts
   - 2.2. birdseye type
     - 2.2.1. pelmicrite
     - 2.2.2. intramicrite

Member "B"

1. A transition to member "A"
   - 1.1. silty micrite
   - 1.2. pelmicrite devoid of silt
2. Banded with algal mat
   - 2.1. crinkled
   - 2.2. flat
3. Banded structure (with an indistinct algal mat or without it)
   - 3.1. finely banded pelmicrite
   - 3.2. micrite with obscure sparite bands
4. Birdseye type — drusy
5. A transition to member "C"

Member "C"

1. Ragging algal mat
2. Oncoidal
3. Birdseye type
4. Light grey, microfauna bearing, with Megalodontidae
   - 4.1. biomicrite, biopelmicrite
   - 4.2. pelmicrite
   - 4.3. micrite
   - 4.4. intrapelmicrite
   - 4.5. algal-drusy micrite, pelmicrite

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Environmental Interpretation

Intensive sedimentological research in recent years has contributed to clarify even more precisely the conditions of deposition in warm marine shallow-water carbonate platforms, in the neighbourhood of tidal zones. On the basis of observations concerning the Dachstein Limestone cycles carried out on the Bahama Bank (Ginsburg and Hardie 1975), in the Shark Bay area, Australia (Hagan and Logan 1975; Woods and Brown 1975) and in the Persian Gulf (Shinn 1973; Evamy 1973; Purser and Lorean 1973; Schneider 1975), it could be rather well determined how in the small environmental units of peritidal zones the individual rock types were formed and with what kind of observed present-day sedimentary phenomena the particular lithological features might be identified.

The rocks of member "A" formed in the supratidal zone and perhaps in the uppermost transitional part of the intertidal zone.

The thick red silty dolomarl sediments (A.1.) are extremely terrestrial in character (upper part of the supratidal zone), and during the subsequent transgressions were not submitted to redeposition.

Intraclastic rock types of member "A" (A.2.1.) developed according to present-day analogies, in the lower part of the supratidal zone. Similar yellow and brown intraclastic rocks were described from the Shark Bay.

This part above the supratidal zone is flooded by seawater 10 to 20 times a year during storms. This powerful water movement is responsible for the development of breccias and micritic matrix including mixed marine microfossils and even terrigene elements derived from redeposition of poorly or completely consolidated sediments.

The deposits of birdseye structure (A.2.2.) underwent significant changes during early diagenesis: partly in the arid period with dissolution of carbonates (cavity formation) or subsequent precipitations (radiaxial rim), partly during later water inflow (internal intrasedimentary infill) and finally in the period of a new emergence (coarse sparite infill of freshwater origin).

Member "B" has most frequently shown banded, fenestral structure of wavy outline (B.2.1.) and the ragged algal mat (B.4.) may represent the upper part of the intertidal zone. The flat and finely banded fenestral structure (B.2.2.) relates to the lower part of the intertidal zone. The banded, and non-fenestral types (B.3) may similarly be assigned here. Type B.1. forming a transition to member "A" seems to have been formed at the upper boundary of the intertidal zone, while type B.6., transitional to member C, may have been formed near its lower boundary.

In the studied sections member "C" has predominantly a micritic matrix. Very rarely and atypical are the ooidic rocks or those of winnowed matrix with sparry cement (grainstone) indicative of highly agitated environments of deposition. Thus every microfacies separated as a type was deposited in the shallow, nonagitated, photic waters of a subtidal backreef platform (lagoon). The ragged algal mats (C.1.)

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represent in all probability the outer margin of the subtidal zone. The oncoidic type (C.2.) is similar to that before, but indicating an environment of higher energy. The remaining types were deposited in adjoining and only slightly differing environments.

The infills of birdseye or drusy structure, further on the recrystallization destroying the original texture-patterns, and dolomitization accompanied by recrystallization, are the result of diagenetic alterations.

Dissolution and infilling took place partly during early diagenesis, in the loosely consolidated sediments. These relate always to emergence. Along flat desiccation cracks, or in the wake of gas-bubbles even larger cavities may develop by dissolution, which during the period of emergence are totally or partly filled up by marine water or calcitic sparite precipitated from freshwater of meteoric origin. After a complete lithification the re-dissolution of cavities and their repeated refilling by sparite may frequently be encountered (late cavity infills).

Recrystallization and the dolomitization associated with it in the lower part of the sequence are undoubtedly early diagenetic phenomena which is indicated also by their relation to the cycles. Dolomitization with recrystallization occurred when the loosely consolidated uppermost sediments of the cycle emerged to the surface and because of Ca fixed in $CaSO_4$ precipitated on the sabhka-like surface the Mg^{2+} content of interstitial water was largely enriched. Therefore the dolomitic portion occurs at the base of each cycle, because the penetration of infiltrating interstitial water was stopped by the pelitic basal layer or by the already consolidated layer underneath and thus the interstitial water of high Mg^{2+} content concentrated within a few decimetres above the cycle-base.

The environmental model and the supposed place of generation of the microfacies types can be seen in Figs. 2, 3.

The interpretation of cyclical sedimentation very frequently observable in Upper Triassic sequences of shallow carbonate platform facies, may, in spite of some contradictory theories, not be regarded as definitively settled. The model postulating world-wide eustatic changes in water level, that is, epirogenic emergence-subsidence processes, is very unprobable if we consider the hundreds of cycles included in the several thousand meter thick carbonate complex. It seems to be more reasonable to assume a steady rate of subsidence with somewhat changing rates of accumulation and evaporation. Perhaps in each case there may be climatic factors involved. We need not think of drastic changes, but just an alternation of relatively more arid and more humid periods.

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MOLASSE AND MARGINAL GEOSYNCLINAL FACIES — A DISCUSSION [1]

BY

DAN C. JIPA [2]

As pointed out by various sedimentological investigations, toward the periphery of the geosynclinal basin the flysch deposits are laterally passing into different non-flysch deposits (Dzulyński, Smith, 1964). According to Knill (1959) these two types of deposits are the axial and marginal facies of the geosynclinal trough.

Main Characters of the Marginal Deposits

More than one type of marginal geosynclinal deposits are known. Some marginal deposits are dominantly lutaceous, occasionally with calcareous intercalations. This is the case of the Dîmbovicioara Series, of Neocomian age (Patrulius, 1963, 1969), shallow-water sediments occurring on the border of the geosynclinal trough filled with the synchronous Sinaia Beds flysch deposits.

Frequently the marginal geosynclinal deposits are made up of a thick pile of rudaceous and arenaceous sediments. This type is well represented by the Albian Bucegi-type conglomerates.

Other marginal deposits consist of an alternation of fine-grained, lutaceous sequences and coarser-grained, sandy-conglomeratic sequences. This type of marginal deposits is illustrated by the Paleogene deposits of the Getic Area, synchronous and consanguineous with Şotrile and Pucioasa flysch deposits.

The above-presented examples indicate that the large lithofacial variations are one of the striking features of the marginal geosynclinal deposits. Their lithology and stratonomy entirely depends on the local supply of clastic material, a highly changeable character.

In accordance with their position within the geosynclinal trough the marginal deposits are frequently in direct contact with the source area of the geosynclinal sediments. The paralic depositional areas, including shallow marine as well as continental environments, is

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1961, September 8—13, Bucharest, Romania.

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characteristic of the marginal sediments. The restless sedimentation regime, proper to these environments, generates sedimentary gaps and unconformities within the marginal sequences.

The existence of a synchronous formation — mostly of flysch type — located in the central, deeper water zone of the same geosynclinal trough, represents a basic feature for the identification of the marginal deposits.

Interfingering with the corresponding flysch sediments is not an imperative feature of the marginal deposits. The continental slope may interpose between the two facies. Interfingering appears more frequently between the flysch and base of slope facies.

Mistaking Marginal Deposits for Molasse Deposits

The marginal geosynclinal deposits as well as the molasse deposits are accumulated nearby their source area, marginal to the continent and to the sea. This community of sedimentation environment leads to similar lithofacies. The marginal as well as the molasse formations are not characterized by a certain lithofacies, but rather by their lithologic variety (Vialov, 1963; Dzulynsky, Smith, 1964; Lombard, 1972). As pointed out by van Houten (1974) the molasse formations consist of common sediments accumulating usually in the various paralic environments. Under the circumstances, the unfounded — but still widespread — opinion that there exists a characteristic molasse facies is probably the main factor allowing the coarser-grained marginal geosynclinal deposits to be mistaken for molasse deposits.

Confusion with the marginal deposits is leading straight to the belief that, within the same geosynclinal trough, the molasse deposits may be synchronous and even interfingering with flysch deposits (Contescu, 1964; Săndulescu, 1979).

Due to their sedimentation environment, the marginal deposits reflect even the slightest relief variations of the contributing source areas. As, by definition, the geosyncline is the mobile zone of the earth crust, such morphologic variations are frequent and normal during the existence of the geosyncline system. That is why most of the tectonic phases are leading to the occurrence of marginal geosyncline deposits, even if these phases are not reflected by the axial sedimentation. Mistaking the marginal deposits for molasse deposits induces the conclusion that all tectogenetic phases with morphogenetic effects may produce molasse deposits, not only the paroxysmal phase turning the geosynclinal trough into a mountain chain.

Distinction between Marginal and Molasse Deposits

Marginal sediments as well as the molasse deposits are devoid of distinctive lithologic features. On the contrary, between the two facies there are lithologic similarities. Accordingly, any differentiation between marginal and molasse deposits has to rely exclusively on genetic characters.

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It is well known that the flysch formations are considered characteristic of the development period of the geosyncline. Coexisting in time and within the same trough with flysch sediments, the marginal geosynclinal deposits are also representative for the development stage of the geosyncline.

Unlike flysch and marginal deposits, the molasse formations are essentially postgeosynclinal (as well as tardigeosynclinal, according to Aubouin, 1964). This means that the molasse deposits are a consequence of the mountain chains which rose on the area previously occupied by the geosyncline.

Representing different stages of the same development sequence, the molasse deposits cannot be synchronous with the flysch deposits within the same geosynclinal trough. Consequently, their position in the local geosynclinal evolution appears as the sole differentiation criterion between marginal geosynclinal deposits and the molasse deposits.

The geosynclinal sequence is not immutable, so deviations from it are to be expected. Such cases are to be throughly documented, before being presented as the reasons of some unorthodox field relationships.

The highly claimed orogenic characters of the geosynclinal facies are today beginning to fade out. The flysch facies can survive these changes, because it possesses a characteristic lithofacies. Not being supported by a distinctive lithologic facies, the molasse term is in a much worse situation. The denial of the exclusive connection between the molasse formation and the postgeosynclinal mountain building is inevitably leading to the abolition of the molasse concept or to its confused and detrimental use.

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QUESTIONS

M. Micu: 1. Do you consider Lower Miocene conglomerates as representing a molasse deposit? Their material is clearly coming from the foreland and this feature is in strong contradiction with your opinion concerning the source of molasse.

2. The so-called Milcov Beds (Sarmatian-Pliocene), at least their lower part, were considered, by Macarovici, Motaș, Contescu, as having also a foreland source area. Which is your opinion in this case, because it is very well known that their equivalents have very clearly a Carpathian origin.

Answers: 1. Lower Miocene conglomerates have been laid down during the molassic period, but their pebbles do not come from the erosion of the mountain chain built up within the area previously occupied by the geosyncline. Consequently it would not be called a molasse deposit (Jipa, 1980).

2. According to Macarovici et al. (1967) the Milcov Beds have been laid down by longitudinal (north to south) currents. Our own paleocurrent measurements in the same area pointed out the existence of additional transversal supply of material from west toward east (Jipa, unpublished report). It results that the clastic material of the Milcov Beds is of Carpathian origin, as it should be for a Carpathian molasse.

S. Rântea: 1. In the Himalayas, are the Siwaliks a molasse? It seems to me the flysch formations are missing there.

2. By analogy, may the Villafranchian Cindești Beds be considered a cratonic protomolasse?

Answers: 1. If considered within the Himalayan chain the Siwaliks are a true molasse. The Siwaliks also represent a marginal geosynclinal facies versus the flysch of the Indo-Gangetic abyssal fans. In the latter case, the comparison is made between lithologic entities belonging to different geosynclinal units.

2. Cindești Beds seem to display all characters of molasse deposits.

A. Mindszenty. The author's point of view has been mainly that of the petrologist. There are, however, also other possibilities for differentiation between flysch and molasse. One of them is to distinguish the two on the basis of style of tectonic movements they were affected by. Being confined to the geosynclinal stage of mountain building the style of folding in flysch should be much more of the linear type than it is in the case of molasse — belonging to the orogenic phase already. The question is whether the author has tried to find any accordance between his basically petrological ideas and tectonics?

Answer: The author would be glad to have any additional criteria to distinguish molasse and flysch (including its marginal equivalents). However, the tectonic style (more precisely the style of folding) does not seem to be promising

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from this point of view. First of all it is based on secondary features of these deposits. The style of folding is also a reflection of the lithologic constitution of a deposit, a very variable character of the molasse formations.

DISCUSSIONS

K. Birkenmajer: We should discriminate between active and passive margins in a geosynclinal trough. An example is given from the Upper Senonian of the West Carpathians. At that time the Pieniny Klippen Belt was already folded together with the Central Carpathians and represented an active margin of the flysch geosyncline. The material it supplied to the flysch trough consisted of reworked rocks from the folded Pieniny Klippen Belt and its southern Exotic Massif.

We may trace transition from supralittoral gravel (fresh-water molasse) to shallow-water marine molasse and deep-water Wildflysch fans, finally to axial flysch trough sedimentation. So it was a Senonian molasse formed after closing the inner Carpathian geosyncline simultaneously with flysch deposition in the trough.

Answer: From sedimentological viewpoint the described case of Upper Senonian deposits clearly depicts a marginal geosynclinal facies and its axial flysch equivalent. It is the task of the geologists having first-hand knowledge on the area to argue it. This is or is not a peculiar case when the marginal geosynclinal facies is also a molasse formation.

R. Hesse: Molasse and flysch are no doubt useful terms because they provide a kind of geological short-hand. On the other hand, if we look at modern continental margins and ocean basins we may distinguish between at least 15 different types of flysch basins as far as their tectonic setting is concerned. I would imagine that there are also several different types of molasse basins according to their tectonic setting and that one way of clarifying and better defining the molasse concept would be to include the causes of basin subsidence as a major controlling factor of molasse development.

Answer: Subsidence is indeed a major factor in molase development. But the present knowledge of subsidence causes is rather vague. Molasse definition needs a much better defined and known criterion.

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CONDITION OF DEVELOPMENT OF THE UPPER CRETACEOUS BAUXITE FORMATION AT HALIMBA (TRANSDANUBIAN CENTRAL RANGE) IN THE LIGHT OF COMPUTERIZED ANALYTICAL RESULTS [1]

BY

EMŐKE JOCHA-EDELÉNYI [2]

One of Hungary's most significant mineral raw materials is bauxite, occurring mainly in the Transdanubian Central Range. It is well known the fact that the genetics of karstic bauxites is not completely cleared up yet. The relation of bauxite to the overlying sediments deposited during several transgressions is a question of controversy. Studies on the relation between the bauxite body and its basement and even more the connection with the stratigraphic units deposited in its hanging wall, as well as the detailed study of the chemical and mineralogical composition of the bauxite, will significantly contribute to resolve this problem. The investigations were carried out at Halimba (Bakony Mountains) which is one of the most important Hungarian bauxite deposits. Given the tens of thousands of data available, a computer was used in analysing the chemical and mineralogical composition.

Foot- and Hanging Wall to the Bauxite of Halimba

The footwall consists of Upper Triassic sediments, in the west and southwest exclusively of dolomite of the Hauptdolomit Formation, which has a tectonic contact with the younger Triassic rocks. Otherwise, in the area limestone is predominant, while dolomite is of secondary importance, belonging to the Dachstein Limestone Formation, or to a transitional unit between the Dachstein Limestone and the Hauptdolomit.

Only a few boreholes crossed in greater thickness the footwall. In some of these boreholes it was a striking phenomenon that on the

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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boundary of the two stratigraphic units, in several dekameters thickness, some alternating horizons of red clayey siltstones, bauxitic clays, clayey bauxites lay steeper than the slope of the bedrock and very frequently included abraded Upper Triassic, Jurassic and Middle Cretaceous rock fragments of varying size. These rocks may be regarded as the infill of the karstic fissure-cavity system.

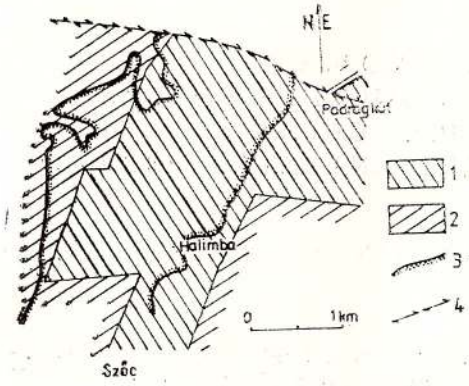
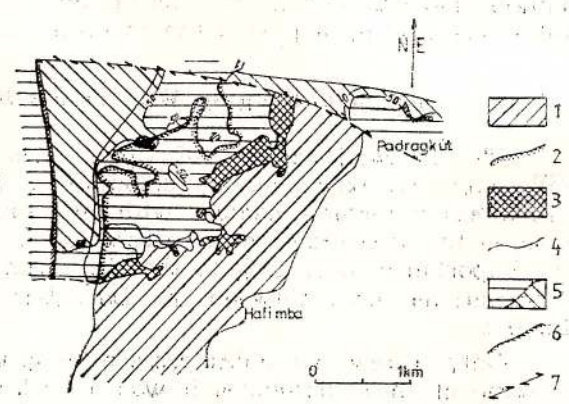


Fig. 1. — Underlying rocks of the Halimba Bauxite Formation : 1, Upper Triassic, Hauptdolomit Formation ; 2, Upper Triassic, Dachsteinkalk Formation and transitional layers ; 3, Upper Cretaceous Extension of the Halimba Bauxite Formation ; 4, Transform Fault.

In the northern part of the area the contours of a nearly 2 km long horizontal slope control the extension of the underlying formations, the bauxite and its hanging wall.

The Halimba Bauxite attains its most significant thickness (about 30 m) on the rough Upper Triassic karstic surface along the tectonic line separating the two units of different Triassic basement, more precisely in the nearly parallel row of dolinas showing the significance of the tectonic control.

Fig. 2. — Overlying rocks of the Halimba Bauxite Formation : 1, Halimba Bauxite Formation ; 2, Extension of the Halimba Bauxite Formation ; 3, Csehbánya Formation ; 4, Extension of the Csehbánya Formation ; 5, Thickness of the Ajka Coal Formation ; 6, Extension of the younger Upper Cretaceous layers ; 7, Transform Fault.



The area concerned lies at the southern margin of the present-day occurrence of Upper Cretaceous sediments. The original Upper Cretaceous bauxite-overlying sediments can be studied — as a consequence of denudation — only in the NW part of the area (Fig. 2).

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In other regions the overlier is formed of Eocene rocks. Above the bauxite of a couple to 30 m thickness, mainly clays, clay marls and marls deposited which at the base were variegated, upwards generally brown, then grey coloured, locally including rock fragments, or pebbles (Csehbánya Formation). To the west the unit is extending slightly more westward than the zero line of the bauxite and in the north it meets the horizontal slip line.

Above the Csehbánya Formation there follows a coal-bearing unit, the Ajka Coal Formation. The maximal thickness (50-100 m) of the formation begins more westward from the western pinching out of bauxite and the Csehbánya Formation in a strip of several hundred metres width, parallel to the above-mentioned deposits. More to the west or to the east from this strip the thickness decreases, as proved by younger Senonian overlying formations. Highly informative of the space and time relation of the bauxite and the Ajka Coal Formation is the fact that some coal bearing layers are locally intercalated within the bauxite.

Chemical and Mineralogical Composition of the Halimba Bauxite

As mentioned above, a very important fact in the explanation of the genetic conditions of the bauxites is the study of the chemical and mineralogical composition. Therefore a map was compiled with the aid of computer on the main components of the bauxite, i.e. Al_2O_3, SiO_2, Fe_2O_3, TiO_2, and on the mean ignition loss. For the characterization of bauxites a map was also prepared on the basis of the widely used $Al_2O_3 : SiO_2$ ratio, the average silica modulus. From the relative quantities of these two main elements the ratio of "fixed" or "free" aluminium associated with Si can be calculated with a good approximation, which gives information on the clay minerals — bauxite ratio in the sample being studied. According to the categories used in industry, six categories were separated on these maps. The rock is named bauxite if more than 78% of the total aluminium in the sample is fixed to bauxite minerals (i.e. the value of the modulus is above four). Clayey bauxite is spoken of in cases when more than 25% free aluminium is contained in the rock (modulus is above 1.14). Bauxitic clay includes less than 25% free aluminium, and in the clay there is no bauxite mineral (the modulus is less than 0.85). Assuming that bauxite develops by gradual desilicification of the alumo-silicates, information can be gained on the extent of bauxitization by considering the ratio of aluminium fixed to siallitic and allitic minerals. Therefore the total thickness of each category is represented on our maps. In other words, information is given on how much per cent of the bauxite complex belongs to the given category in any particular point. In addition, the number of units in which the given categories are vertically present was determined to see if the process of bauxitization

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was continuous or periodical. On this basis four regions could be separated : a middle, a southern, a northwestern and a northeastern one (Fig. 3).

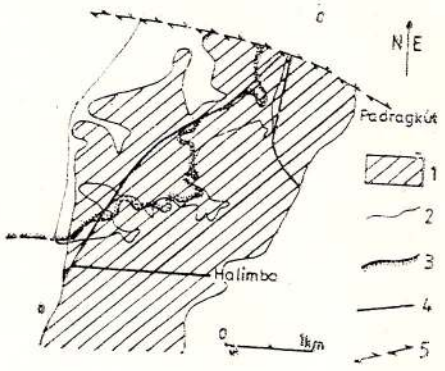


Fig. 3. — Areal units of deposition of the Halimba Bauxite Formation: 1, Halimba Bauxite Formation ; 2, Extension of the Csehbánya Formation ; 3, Extension of the Ajka Coal Formation ; 4, Outlines of the areal units of deposition ; 5, Transform fault.

The characteristics of each region are the following :

— The maximum thickness (30 m) of *bauxite* occurs in the middle region, in the above mentioned row of dolinas of NW-SE direction. These trends continue also to the south but the total thickness is smaller. In the NW the thickness is small, it attains 10 m in a single case. In the NE the thickness is variable.

— The average of the *aluminium oxide* content attains its maximum in the middle region (more than 60%, i.e. 50 to 60%), being somewhat smaller in the south. It varies between 30 and 40, that is, 20 and 30% in the NW and NE.

In the middle region the average of *silica* is minimal (less than 10%, i.e. 10 to 20%). In the south it is a little more. In the NW this value is 10 to 20%, or 20 to 30%, and in NE a little higher, 20 to 30%, or 30 to 40%.

The value of the *ignition loss* is in the middle and southern regions low (10 to 15%). In the NW it is very variable, but higher. In the NE it is similar to that of the middle region.

Obviously the average of the modulus is the highest in the middle and southern regions, well over 10 (i.e. 10 to 4). In the NW the average is very variable. In the NE it is low, it has only sporadically a higher value.

In the middle region a significant part of the bauxite complex is made up of *bauxite rock*, which is usually present in a single unit. In the southern region the development is similar, only the total thickness is smaller and locally there are more units. In the NW bauxitic rocks frequently form a significant part of the bauxite complex, though the whole thickness is not too much and the bauxite occurs in two units. In the NE bauxite beds were found only in a few boreholes.

Clayey bauxite is present over the whole middle region, though its amount in relation to total thickness is insignificant and the number

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of units in which it occurs is variable. Similar is the case in the southern region. In the NW the layers of clayey bauxite frequently constitute a considerable percentage of the total thickness, being usually present only in a single horizon. In the NE only 10 to 20% of the total thickness is clayey bauxite appearing in two or three units.

Bauxitic clay in the middle and southern regions can be met with just sporadically, in a rather low thickness and generally in a single unit. In the NW it is common and frequently making up 10 to 20% of the total thickness, in one or two units. In the NE it is quite common, its ratio to the total thickness is significant, being predominant in two or, locally, in three or four units.

Rocks free of bauxite mineral in the middle and southern regions are rare, their total thickness is minimal and they appear in a single unit. In the NW the total thickness of these rocks is low. It is in the NE that they are most frequent and locally even their thickness is considerable.

Starting from the analysis of each region and using also the results of other studies, we can reconstruct the paleo-environment in which the Halimba Bauxite was formed as follows :

— After Mid-Cretaceous time the area was affected by considerable — though uneven — erosion during the phase of emergence. Karstification started in the exposed carbonate rocks, mainly in the Upper Triassic limestones, which are very liable to this process. As a consequence of epirogenic movements provoking the Upper Cretaceous sedimentation cycle, subsidence commenced during the Santonian. The area in question was situated on the southern margin of the Senonian sedimentary basin with a slight inclination to the NW (Fig. 4). In the deeper parts eroded material from the relatively higher situated areas started to accumulate. It consisted mainly of clayey rocks accumulated in a great amount on the karstic relief. Lateritization of detritus formed on a strip of Paleozoic rocks under suitable climatic conditions on the southern margin of the Transdanubian Central Range structural unit began — as shown by convincing evidence — before the Middle Cretaceous cycle. The transportation of this detritus over the deeper-situated strip of mainly karsted Mesozoic rocks, and its allitization there, continued very probably with interruptions for a long time, and thus it was repeated also at the beginning of the Senonian cycle. After differentiation of the area, these rocks, having suffered desilicification in various proportions, together with other Mesozoic detritus of the surface, would be carried to the deepest parts of the region, including the Halimba area. Naturally, first they filled up those subsurface fissure-cavity systems which were in tight connection with the karstic surface. Such rocks could be studied in the north-eastern region.

— Subsurface bauxitization did not continue owing to the unsuitable conditions as suggested by the intact surfaces of detrital material present in varying amount and grain-size. However, as evidenced by the varied pattern of quality distribution, the material of the infill must have been affected by desilicification to varying degrees. After subsurface cavity systems had been filled in, the material transported to deeper parts of the region was deposited already on the sur-

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face where favourable oxidation conditions provoked further bauxitization, as evidenced by the regular distribution of differently bauxitized rocks. Rocks of highest modulus, i.e. of strongest desilicification, occur in the north-western region, as well as in the thickest strips of the middle and southern regions. In the same region — mainly in the NW — the bounded water content of the rocks is high, too. In the thin complexes of the middle and southern regions bauxite minerals to clay minerals ratio is much lower. According to our opinion, such a marked difference in the rate of leaching and removal of silica within sequences greatly differing in thickness and deposited close to one another can be interpreted by the different lengths of time, during which the material transported by water or remoistened several times as a result of rainfall remained reliable to reactions, i.e. in a wet state in the thicker and the thinner complexes. This is emphasized also by the fact that in the thicker sequences some categories occur in lower number than in the thinner ones. This may be the proof of a longer stable period in the first case, and of several shorter successive periods in the latter one. The high degree of loading in the north-western region may be explained by closeness of the groundwater table to the surface from the very beginning in that area.

With gradual subsidence of the sedimentary basin, the deepest strip got below the groundwater table in the Santonian, when coal formation started. As a result of subsidence, in the western strip of the Halimba bauxite area the prerequisite for bauxite formation would be lost very soon and the material transported here was not desilicified and clayey-detrital rocks were formed. In the higher-situated subareas accumulation and formation of bauxite continued further on. The steady subsidence of the region was interrupted by minor oscillations, as indicated by carbonaceous interlayers within the bauxite complex.

Continued subsidence resulted in that the study area gradually became unsuitable for bauxite formation, in the early Campanian, when lacustrine and freshwater swamps got dominant, followed in turn by the progressive development of a more and more genuine marine environment.

The emergence that followed the late Cretaceous cycle caused heavy erosion of the Senonian formations. The Halimba Bauxite was also significantly denuded in accordance with the north-north-western slope developed in the region. This was the time when in the NE the bauxitic infill of the subsurface cavity system was exposed to the Mesozoic surface. The next bauxitization, associated with the beginning of the Eocene cycle, could not be identified in the study area, only some slight redeposition of material could be observed. The tectonic line across the northern part of the area was formed in post-Eocene, and probably Miocene time.

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THE YOUNGEST OLISTOSTROME IN THE FLYSCH DEPOSITS OF THE SKIBA NAPPE (POLISH CARPATHIANS) [1]

BY

JANUSZ KOTLARCZYK [2]

The role of turbidites in the sedimentation process of the flysch deposits of the Polish Carpathians has already been explained, exhaustingly and variously, in literature (e.g. Ksiazkiewicz, 1958a, 1962; Dzulynsky, Ślaczka, 1959; Radomski, 1958; Dzulynski, 1963; Dzulynski, Smith, 1964; Peszat, 1967; Ślaczka, Unrug, 1976; Krawczyk, 1980). Less attention was paid to the role of traction currents (Dzulynski, Kotlarczyk, 1962) and to the mechanism of fluxoturbidites (e.g. Dzulynski, Ksiazkiewicz, Kuenen, 1959; Unrug, 1963; Kotlarczyk, 1978, 1979) of pebble mudstones, submarine slumps and olistostromes (e.g. Bukowy, 1956; Ksiazkiewicz, 1958b; Kotlarczyk, 1961; Ślaczka, 1961; Dzulynski, Kotlarczyk, 1965; Burzewski, 1966; Bromowicz, 1974; Szymakowska, 1976).

A tentative systematization and classification of submarine mass movements was recently presented for the Przemysl Carpathians (Dzulynski, Kotlarczyk, Ney, 1979). Olistostromes *sensu lato* are fairly abundant in the Skiba Unit of the Polish Carpathians (Fig. 1). They occur here in definite stratigraphic horizons (Fig. 2.). In their maximal development they constitute several percents of the sedimentary sequence, about 5 km thick. The most important olistostromes can be described in the following manner:

a) Makówka Slump Debris (Upper Maastrichtian) (Kotlarczyk, 1978) lenticular lithosomes, up to several hundred meters thick, were found to occur in the upper part of the Ropianka Formation (Inoceramian Beds) showing maximal development in outer parts of the Skiba Basin; lenticular Węgierka Marls that form large olistoliths in the olistostrome in question, and locally occur as independent slide blocks (Burzewski, 1966; Kotlarczyk et al., 1972, Kotlarczyk, 1978).

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September, 8—13, 1981, Bucharest, Romania.

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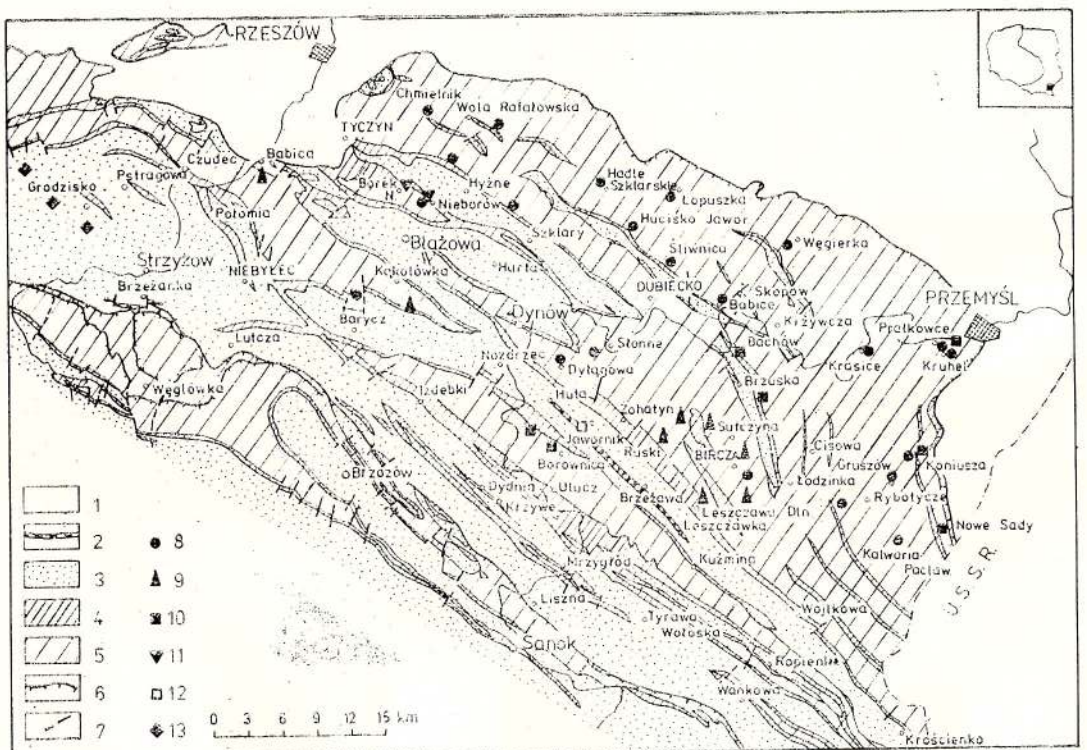


Fig. 1. — Main occurrences of olistostromes in the Skiba Unit of the Polish Carpathians : 1, Miocene and Quaternary deposits of the foreland ; 2. Leszczawka Diatomite Horizon; 3, Krosno Beds ; 4, Menilite Beds ; 5, Beds older than the Menilite Beds ; 6, Lines of major overthrusts ; 7, faults ; 8—13, occurrences of olistostromes : 8, Makówka Slump Debris with Węgierka Marls, 9, Babica Clays, 10, Popiele Beds and their equivalents, 11, Olistostromes in the Menilite Beds, 12, Olistostrome in the Leszczawka Diatomite Horizon, 13, Subsilesian olistostromes on the Skiba Nappe.

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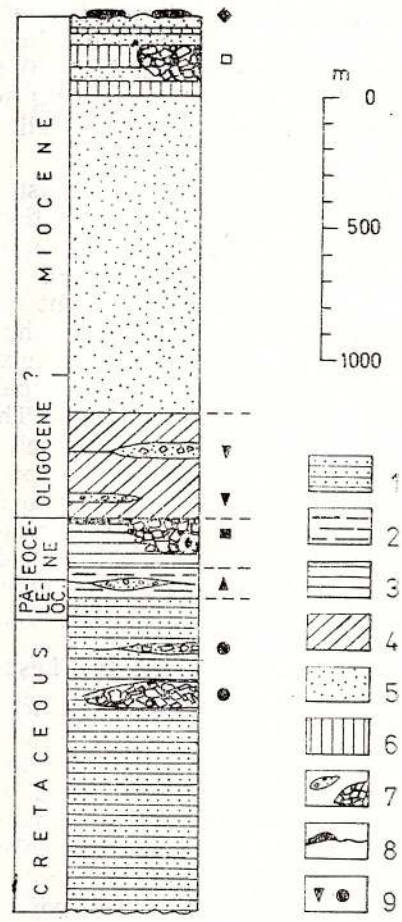


Fig. 2. — Stratigraphic position of the main olistostromes in the Skiba Nappe of the Polish Carpathians : 1, Ropianka Formation ; 2, Variegated Shales ; 3, Hieroglyphic Beds; 4, Menilite Beds ; 5, Krosno Beds ; 6, Leszczawka Diatomite Horizon ; 7, olistostromes in flysch sequence; 8, Subsilesian olistostromes on the Skole Nappe ; 9, main olistostromes (marked as in Fig. 1).

b) Babica Clays (Upper Paleocene) (B u k o w y, 1956)-lense-shaped lithosomes of pebble mudstones, up to several ten meter thick occur in the lower part of the formation of Variegated Shales ; these are strongly desintegrated olistostromes (K s i a z k i e w i c z, 1975), containing abundant exotics.

c) Popiele Beds (Uppermost Eocene-Lowermost Oligocene) (D z u l y n s k i, K o t l a r c z y k, 1965) — enormous, up to 200 m thick olistostrome, striking from the neighbourhood of Przemysl, along the margin of the Ukrainian Carpathians ; in the inner parts of this unit its equivalents are represented by poorly developed olistostromes, destroying the bottom part of the Menilite Beds.

d) Olistostromes lithosomes in the Menilite Beds (Lattorfian Chattian), up to 20 m thick, usually accompanying thick-bedded Kliwa Sandstones, which represent sand flow deposits and occurring in different parts of the Menilite Beds.

e) Olistostrome in the Leszczawka Diatomite Horizon (Upper Burdigalian) up to 150 m thick, described in this paper.

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The last olistostrome is the youngest occurring within the profile of flysch sequence. It should be explained that a still younger olistostrome (younger than Helvetian) found within the Skiba Nappe (Szymakowska, 1976) consisting of rocks belonging to the innermost Subsilesian Nappe, that have slid on the Skiba Nappe, does not occur within the flysch but on it.

The above described olistostromes predominantly contain fragments of rocks of older flysch formations or of flyschoid ones which formed a sedimentary sequence in the outer (perycratonic) part of the Skiba Basin, actually not preserved. Exotic rocks (found only in the first three types) are usually present in small quantities. Their content varies depending on the position of the olistostrome. The filling mass is represented by structureless matrix or sedimentary breccia. The olistostromes of the *a*, *b* and *c* types are very widespread, occurring in definite stratigraphic horizons. They are supposed to be the result of an increased diastrophism which took place at the adjacent platform and, probably, of bottom compensation within the geosynclinal area. The appearance of these olistostromes approximately corresponds to the Laramian and Pyrenean phases. The olistostromes recognized in different horizons of the Menilite Beds *(d)* are the results of the eroding activity of grain flows. The diatomite olistostrome can be related to the initial phase of the Carpathian folding.

Lithology of the Leszczawka Diatomite Horizon

Detailed geological and lithological characteristics of the Leszczawka Diatomite Horizon have been already presented by the author (Kotlarczyk, 1966). It should be mentioned that the horizon in question consists of three members of diatomite shales, showing variable thickness and lithology and separated by complexes of the Krosno Beds (Fig. 2). It was observed that only the lower part of the lower member displays a fairly constant lithology. There locally occurs a horizontal lamination of diatomites and porcellanites. Tuffitic, benthonic and cherty intercalations as well as sandstone beds of the Kliwa type are present. Different varieties of diatomites occurring in the upper part of the horizon show no properties which could indicate quiet sedimentation. There occur exclusively nonlaminated diatomites formed of well mixed clay-siliceous material with diatom frustules and their detritus. The structurelless type of sediment suggests that the material was transported to the deposition place by mud flow. A similar transport mechanism can be reconstructed for the accompanying sandstones of the Kliwa type (i.e. grain flows). These sediments, before final consolidation, were often subjected to mass movements — usually flows. This can be well observed in the cases when the diatomite sediment containing thin arenaceous intercalations was subjected to the flow. The material of these intercalations was disintegrated and chaotically mixed with the diatomite matrix to form fine arenaceous bodies. Their shape suggests the plasticity of the deposit, and their spatial distribution — the flow of the whole mass. Locally the sandstone material is completely ground and quartz grains are mixed with diatomite mud to form arenaceous diatomites.

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A very characteristic feature of the Leszczawka diatomites is their facial variability, rendering difficult the parallelization of complete profiles of these horizons outcropping in exploration trenches situated at distances of several hundred or even several ten meters from each other. The present author tried to explain this variability (Kotlarczyk, 1966) by multi-phase sedimentation. The lenticular lithosome of each variety of diatomites was the result of a separate diatomaceous mud flow, displaying specific lithological properties (clay and frustule content, porosity etc.). Recently, this mechanism of the formation of the diatomite horizon was confirmed by preliminary results of diatom analysis (Kotlarczyk, in press), which allowed to distinguish marine and fresh water diatom assemblages in separate lithosomes of diatomite varieties.

Olistostrome in the Diatomite Horizon

The results of the last years exploitation works in the diatomite deposit near Jawornik Ruski have offered new data for the interpretation of the origin of the diatomite horizon. The olistostrome nature of the middle diatomite member exposed within the area of about 1 ha explained the impossibility of correlating the profiles in not distant exploration trenches. In other exploration exposures, the olistostrome nature of the underlying barren rocks was estimated. As it results from the composition of the olistoliths, both the lower and the middle member of the diatomite, as well as the complex of the Krosno Beds separating them, participated in the mass movements.

The lithosome of the olistostrome, about 150 m thick, shows a complex structure, probably corresponding to two general phases. The lower part, about 80 m thick, consists of large blocks — olistoliths, several meters in diameter, consisting of arenaceous clayey Krosno Beds or of Kliwa Sandstones, siliceous-argillaceous and sometimes diatomaceous shales. Smaller blocks of tuffs, diatomaceous cherts, fragments of porcellanite, characteristic of the diatomite member, occur in subordinate amounts. Locally an arenaceous matrix occurs. This part of the olistostrome is the product of the debris flow which embraced the lower part of the diatomite member and the overlying intercalation of the Krosno Beds.

The upper part of the olistostrome, about 70 m thick, mainly consists of blocks of diatomite rocks, siliceous-clay shales, diatomaceous cherts and sandstones of the Kliwa type, i.e. of the rock assemblage, of the middle diatomite member. Some varieties of diatomites and of siliceous-clay shales are accompanied by concentrations of Fe-Mn concretions. The lack of exotics and of rock fragments from older flysch members is very characteristic. Because of the strong cleavage in all the diatomite varieties, it is difficult to decide if the olistostrome in question consists exclusively of blocks of different diatomite varieties, or some of these varieties, before cleavage processes, formed the matrix of the olistostrome body. Several years of observations, carried out in two levels of exploitation in the quarry indicate that the matrix did not occur in the examined part of the olistostrome.

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In the cross-section of the middle diatomite member, oriented perpendicularly on the sedimentary plane of the olistostrome (Fig. 3), we observe the olistolithic character of the occurrence of the diatomaceous cherts and siliceous-clay shales. In some places it was possible to find also the contours of diatomite blocks, but generally, because of the present state of the exposures and the strong weathering of the diatomites, such observations could not be carried out. Consequently,

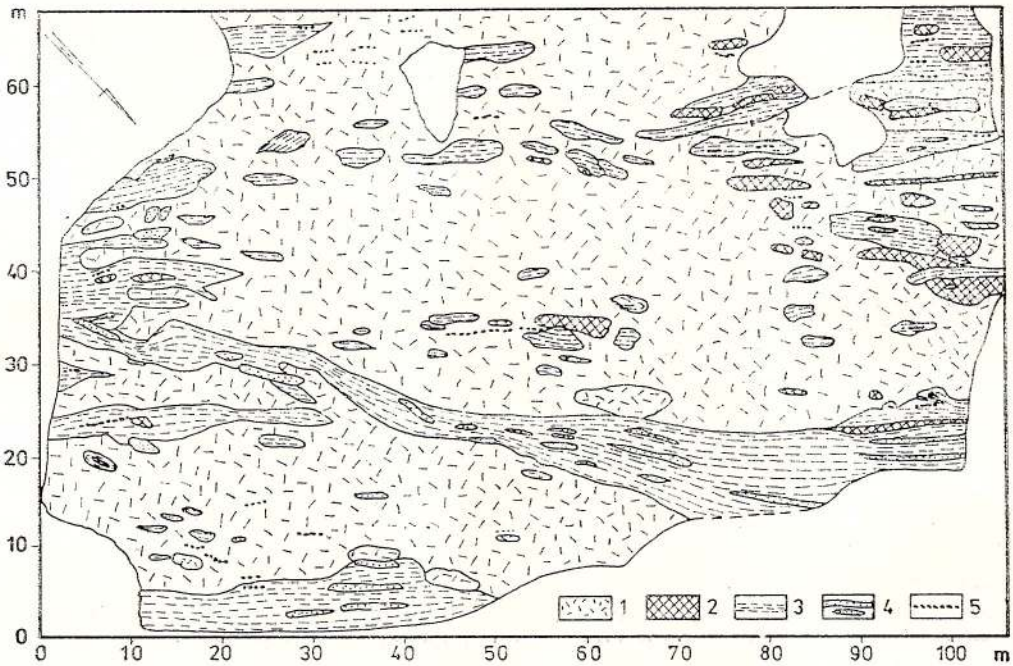


Fig. 3. — Outcrop of the middle member of the Leszczawka Diatomite Horizon in the Jawornik Ruski quarry showing olistostrome structure (bottom of the visible part of olistostrome in the lower part of the figure) : 1, diatomites ; 2, diatomaceous cherts ; 3, argillaceous-siliceous shales ; 4, sandstones of the Kliwa type ; 5, oxidized Fe-Mn concretions.

the lack of data on the contours of these blocks in the figure does not mean that the diatomites form the matrix for shaly or diatomaceous chert olistoliths.

The shapes of the diatomite and diatomaceous chert olistoliths indicate that the mass movement took place after the diagenesis of sediments and even after the formation of diagenetic cherty rocks. This movement has destroyed the already formed diatomite member. Chronologically, it was the third displacement of diatomite matter (1-diatomite mud flow, 2-syndiagenetic flow). It is striking that in the described part of the olistostrome under consideration we note the lack of such elements as blocks of sandstones and shales of the Krosno Beds, tuffs and porcellanite which are so abundant in the lower part

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of the olistostrome. This part of the body was formed when the middle diatomite member was moved and transported to the region of deposition of the earlier olistostrome body. The distance of this transport was not long but, just like the spread of the olistostrome, it cannot be evaluated because of the fragmental preservation of the Leszczawka Diatomite Horizon in the Skiba Unit. This horizon occurs there but in axial parts of some deeper synclines (Fig. 1).

An alternative hypothesis to the above presented two-stage model of the olistostrome genesis consists in accepting a single mass movement which would embrace a complex of sediments from the upper part of the lower diatomite member of the middle member inclusively. This movement resulted in the disintegration of individual rock complexes and in the displacement of the olistoliths relative to each other but not in their getting mixed in the vertical profile. In order to explain this phenomenon, we have to assume a rather small lateral displacement of the olistostrome. The same conclusion results from the distinctly low amount of the matrix.

The olistostrome in Javornik Ruski is covered by a mantle of predominantly shaly Krosno Beds, about 100 m thick, with intercalations of the upper diatomite member. We can, thus, conclude that after its formation, normal flysch sedimentation still proceeded in this part of the basin. As already mentioned, the described olistostrome was formed, most probably, as the result of initial movements folding the bottom of the Carpathian Basin. Contrary to earlier olistostromes, it was not slid on the continental slope but on that of generating geanticline. Consequently this is an intra-basin and synorogen olistostrome. Absolute age data for tuffs of the Leszszawka Diatomite (Wieser, 1979 — 15.6±1.1 m.y. B.P.) suggest that this olistostrome was formed in the same period. Most probably, its origin can be related with the Styrian phase of the Alpine orogenesis.

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LES CALCAIRES Á MINÉRALISATIONS MAGNÉSIENNES DES MASSIFS BIHOR ET PĂDUREA CRAIULUI (MONTS APUSENI DU NORD) [1]

PAR

ALEXANDRU Z. MANEA [2]

Introduction. Les travaux de prospections géologiques faites à la partie NO des Monts Apuseni du Nord, dans les massifs Bihor et Pădurea Craiului ont mis en évidence des concentrations de minéralisations magnésiennes dans les formations carbonatées mésozoïques appartenant du point de vue structurai au système des nappes de Codru. Les minéralisations magnésiennes sont représentées par périclase, brucite, α-sépiolite, hydromagnésite, magnésite et shéridanite. Dans certaines zones, les formations carbonatées à minéralisations magnésiennes sont en contact avec les magmatites larramiennes de type banatitique, cas dans lequel apparaissent des zones de skarne à diopside, vésuvien, olivine, wollastonite, d'épaisseur réduite (0,5-1 m) et en longueurs qui dépassent à peine quelques mètres.

La présence de la brucite dans le massif Bihor a été signalée pour la première fois par R a f a l e t (1963) dans l'association de minéraux de contact générés par les massifs banatitiques de Budureasa et Pietroasa. La brucite a été considérée comme un produit de la hydratation de la périclase qui a été formée à la suite de l'action du métamorphisme thermique sur certains calcaires dolomitiques purs.

En 1975, M a n e a a signalé la possibilité de l'emploi de la périclase et surtout de la brucite comme minerai utile en tant que suppléant industriel de l'oxyde de magnésium. A cause de cet intérêt économique on a entrepris des recherches détaillées des travaux miniers et des forages sur les formations à minéralisations magnésiennes, en obtenant plus de 1700 échantillons qui ont été analysés du point de vue chimique.

L'échantillonnage a été fait à l'aide des sillons de 1—2 m de longueur, menés tant dans les zones d'affleurement, que dans les travaux miniers de surface (fossés et puits).

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[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

[2] Entreprise géologique de prospections pour substances minérales solides. Str. Caransebeș nr. 1, 78344 Bucarest, Roumanie.

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Au but d'encadrer les roches carbonatées dans les types lithologiques établis dans les classifications en usage, tous les échantillons analysés ont été calculés selon les contenus en résidu (SiO_2 + Al_2O_3 + + Fe_2O_3 + ...etc.), $CaCO_3$ et Ca Mg $(CO_3)_2$, en partant des coefficients indiqués par Ruhin (1958). Ayant en vue le contenu en H_2O déterminé à la température de 450°C et donc lié au réseau de la brucite, on a calculé le contenu en $Mg(OH)_2$ qui a été déterminé aussi par A.T.D. A l'aide des calculs rationnaux et de l'analyse thermodifférentielle on a élaboré des diagrammes ternaires ayant dans l'un des coins $Mg(OH)_2$, déduit par ces calculs et par A.T.D., en élaborant en même temps une classification nouvelle des roches à minéralisations magnésiennes, en tenant compte des contenus en $Mg(OH)_2$.

La géologie des formations carbonatées. Les formations carbonatées à minéralisations magnésiennes font partie du système structural des nappes de Codru. Elles ont été séparées en trois zones : 1. — la zone septentrionale, comprise entre Dealul Băinșoara et la vallée du Binșel, où les formations carbonatées ont été attribuées au Norien ; 2. — la zone centrale, comprise entre Valea Plaiului, la localité Ferice et le sommet de Custuri, où la formation carbonatée a été attribuée à l'Ansien, au Norien et au Rhétien-Lias ; 3. — la zone méridionale s'étend entre Dealul Dîncoasa, la vallée du Sebișel, Măgura Guranilor et la vallée de la Galbena. La formation carbonatée à minéralisations magnésiennes a été attribuée ici à l'Anisien.

Etudes pétrographiques et données pétrochimiques. Du point de vue pétrographique, les formations carbonatées à minéralisations magnésiennes sont formées d'une masse de calcite à l'aspect cryptocristallin, parfois faiblement recristallisé (si la formation carbonatée se trouve en contact avec les magmatites banatitiques). La calcite est impure et à contour non-défini, étant intimement associée à la dolomie, celle-ci évidenciée seulement par les réactions de coloration. Elle se présente sous forme d'agglomérations qui entourent les nodules et les nids de brucite. Dans cette masse carbonatée apparaissent des nodules et des nids de brucite, des granoblastes petites de périclase et de quartz qui forment ensemble des microlentilles. On a observé aussi des filonnets de α-sépiolite et hydromagnésite qui intersectent tant les nodules et les nids de brucite, que la masse de calcite. D'habitude, la hydromagnésite et la magnésite apparaissent sous forme de granules cryptocristallines entre les lamelles de α-sépiolite. La périclase apparaît en petites granoblastes à habitus cubique, incolore ou faiblement jaunâtre, isotrope. Au bord des microlentilles à quartz on observe fréquemment des gerbes de brucite ou des fibres disposées autour des granoblastes idiomorphes de périclase, ou des fibres de brucite insinuées sur les fissures des cristaux cataclasés de périclase. Les nodules et les nids de brucite ont des dimensions de 0,02-0,70 mm et parfois même de 1-2 mm, mais on a observé aussi des nids de brucite lamellaire de 5/7 mm. Dans ce cas, les lamelles de brucite présentent aussi un maclage bisynthétique, situation qui n'a pas été signalée jusqu'à présent dans la littérature de spécialité. La α-sépiolite apparaît en masses

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fibreuses, comme remplissage de certaines fissures, tandis que la masse carbonatée est recristallisée au contact avec les fibres de α-sépiolite, qu'elle moule. Parmi les lamelles de α-sépiolite apparaît une masse cryptocristalline de hydromagnésite et de magnésite. Toujours sous forme de filonnets, mais à épaisseurs pelliculaires, apparaît la chlorite magnésienne de type shéridanite.

Les formations carbonatées à minéralisations magnésiennes ont été séparées en types lithologiques qui sont marqués dans les dia-

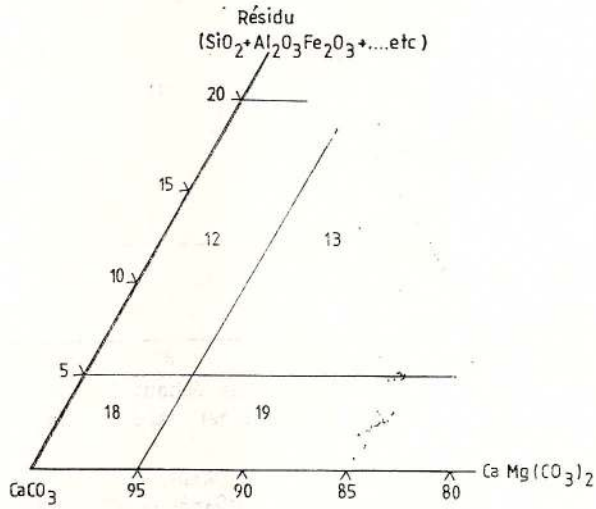


Fig. 1. — Distribution des échantillons collectés de la zone septentrionale (124 échantillons) dans le diagramme Ruhin. 12, Dolomito-marne ; 13, Calcaire argileux ; 18, Calcaire pur ; 19, Calcaire dolomitique.

grammes Ruhin. Ainsi le diagramme de la figure 1 relève l'appartenance de la plupart des échantillons collectés dans la zone septentrionale, au type de calcaires dolomitiques, à l'exception de deux échantillons qui sont projetés dans le champ attribué aux calcaires argileux. Pour les échantillons de la zone centrale, la distribution présentée dans le diagramme de la figure 2 relève une concentration des échantillons dans le champ attribué aux calcaires argileux, avec une distribution linéaire vers le sommet qui représente le résidu.

La plupart des échantillons de la zone méridionale est distribuée dans le champ des calcaires dolomitiques, ceux-ci ayant aussi une distribution linéaire, mais on remarque aussi quelques échantillons dans le domaine du champ des calcaires argileux, comme on peut observer dans le diagramme de la figure 3.

En tenant compte des possibilités technologiques existentes de concentrer la minéralisation magnésienne, la participation de la composante carbonatée et de celle dolomitique, on a élaboré la suivante classification des roches carbonatées à minéralisations magnésiennes du Massif Bihor : 1, brucitites ; 2, marno-calcaires à brucite ; 3, marne dolomitique à brucite ; 4, dolomie-marne à brucite ; 5, calcaires à brucite ; 6, calcaires dolomitiques à brucite ; 7, dolomie à brucite. La représentation ternaire de cette classification présente aux coins les composantes suivantes : $Mg(OH)_2$, obtenu par des calculs rationnaux ;

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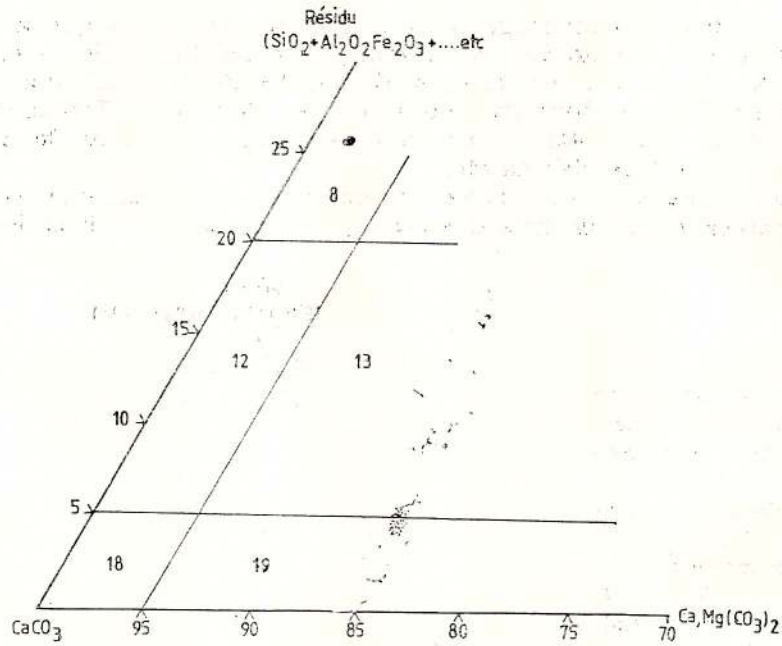


Fig. 2. — Distribution des échantillons collectés de la zone centrale (1139 échantillons) dans le diagramme Ruhin.

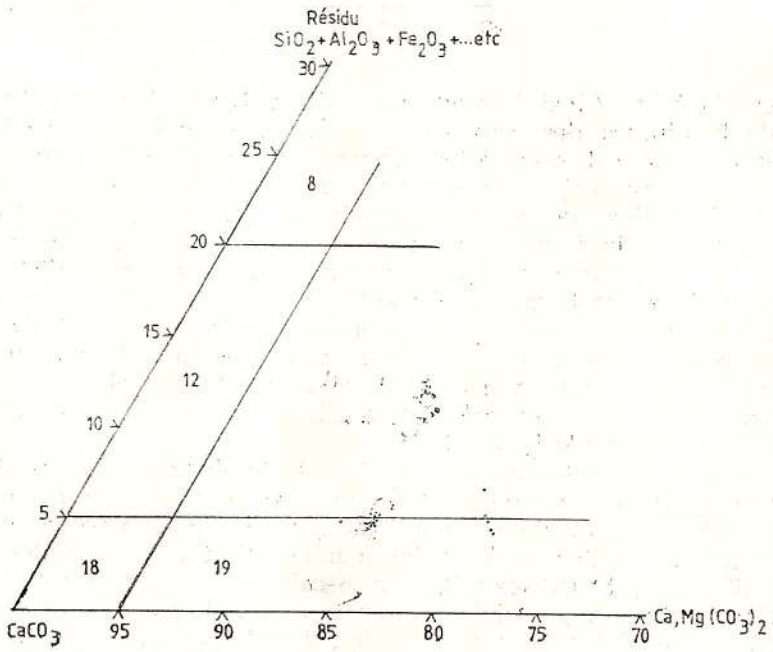


Fig. 3. — Distribution des échantillons collectés de la zone méridionale (416 échantillons) dans le diagramme Ruhin.

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$CaCO_3$ et $Ca.Mg(CO_3)_2$, et par la perte du groupe hydroxyle, au lieu de $Mg(OH)_2$ — calculs rationaux, $Mg(OH)_2$ — déterminé par A.T.D. Ainsi, dans le diagramme de la figure 4 la distribution des échantillons de la zone septentrionale relève leur appartenance tant aux marno-calcaires à brucite qu'aux calcaires à brucite. La plupart des échan-

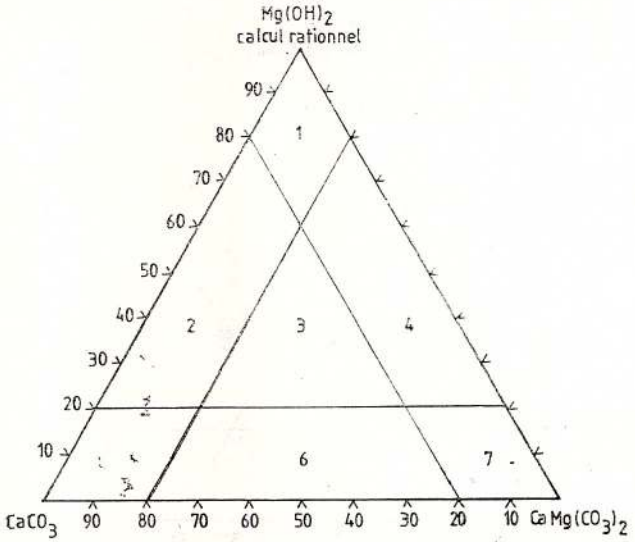


Fig. 4. — Diagramme de la distribution du $Mg(OH)_2$ (calcul rationnel) dans les roches carbonatées analysées de la zone septentrionale (124 échantillons): 1, Brucitites; 2, Marno-calcaires à brucite ; 3, Marne dolomitique à brucite ; 4, Dolomito-marne à brucite ; 5, Calcaires à brucite ; 6, Calcaires dolomitiques à brucite ; 7, Dolomites à brucite.

tillons de la zone centrale se trouvent dans le champ des marno-calcaires à brucite et dans une moindre mesure dans le champ des calcaires à brucite (fig. 5). Les échantillons de la zone méridionale se

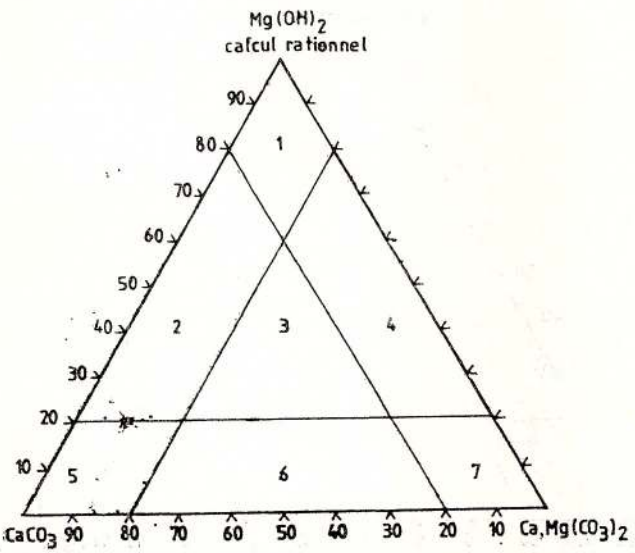


Fig. 5. — Diagramme de la distribution du $Mg(OH)_2$ (calcul rationnel) dans les roches carbonatées analysées de la zone centrale (725 échantillons).

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trouvent dans le champ des marno-calcaires à brucite et dans celui des calcaires à brucite.

Le diagramme où $Mg(OH)_2$ est déterminé par A.T.D. (fig. 7) relève pour les échantillons de la zone centrale une distribution dispersée dans le champ des marno-calcaires à brucite et celui des calcaires à

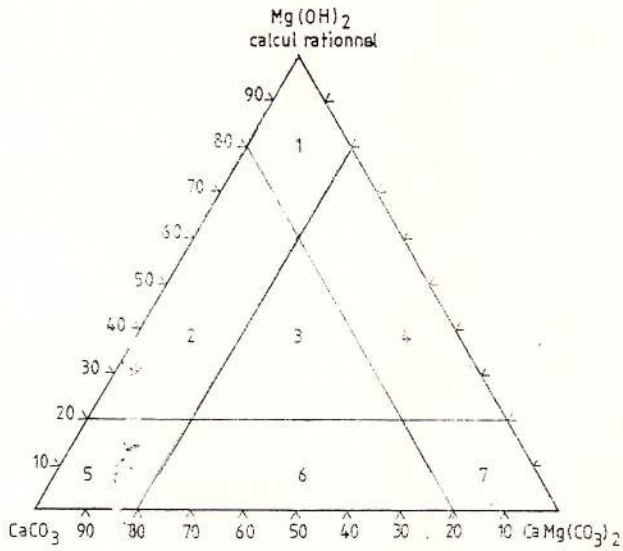


Fig. 6. — Diagramme de la distribution du $Mg(OH)_2$ (calcul rationnel) dans les roches carbonatées analysées de la zone méridionale (276 échantillons).

brucite. Les mêmes caractéristiques apparaissent aussi pour les échantillons prélevés de la zone méridionale (fig. 8), où il y a aussi des échantillons dans le champ des calcaires dolomitiques à brucite.

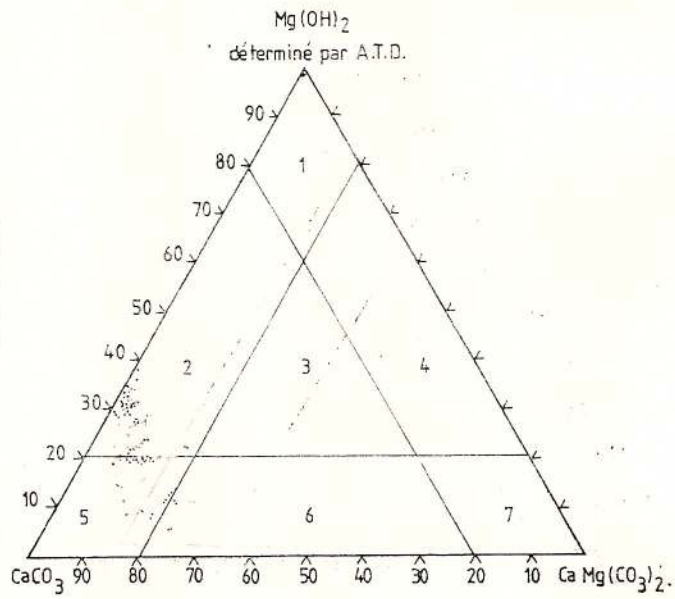


Fig. 7. — Distribution du $Mg(OH)_2$ déterminé par A.T.D. des échantillons collectés de la zone centrale (378 échantillons).

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Considérations génétiques. Dans la littérature de spécialité sont mentionnés des gisements de roches carbonatées à brucite dans les Etats Unis (Gabbs Nevada), Canada, R.P.D. Coréenne et en Union Soviétique Le Grand Hingan et Le Petit Hingan, région de Habarovsk). La genèse du gisement de Gabbs est hydrothermale, liée à l'intrusion des

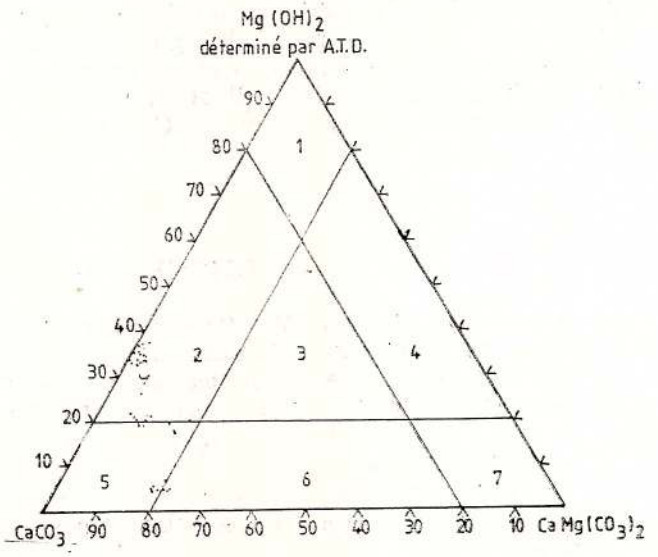


Fig. 8. — Distribution du $Mg(OH)_2$ déterminé par A.T.D. des échantillons collectés de la zone méridionale (78 échantillons).

certains granitoïdes dans un complexe dolomitique et de magnésite. Nous n'avons pas de données sur la genèse des gisements de Canada et de R.P.D. Coréenne. En ce qui concerne l'Union Soviétique, on pense que la formation de la brucite n'est pas générée par les processus de contact métasomatique.

Toujours de la littérature on connaît les expériences de laboratoire sur la décomposition de la dolomie en périclase et calcite. Celles-ci ont conduit à obtenir la courbe monovariante d'équilibre de la réaction : dolomie-périclase + calcite + CO_2, qui passe par les points 700° et P_{CO_2} = 200 barys ; 820° et 1000 barys, avec P_{H_2O} diminué. Pour réaliser ces conditions il faudrait exister une pression moyenne de poids de 500-600 barys, qui devrait représenter une épaisseur des roches du toit de 1,5-2,0 km.

Sauf la brucite, nos recherches ont mis en évidence des granoblastes de périclase ± pseudomorphoses de brucite, ainsi que des intercalations lentilliformes de périclase et de quartz. On a observé aussi des filons constitués de α-sépiolite, qui intersectent la masse des nodules et des nids de brucite et la masse carbonatée, celle-ci avec une genèse typiquement hydrothermale.

Les gisements connus dans le monde apparaissent comme des accumulations locales ayant des réserves réduites. Dans notre région les roches carbonatées à minéralisations magnésiennes constituent des couches considérables, qui présentent une distribution assez uniforme du contenu en MgO dans toute la formation. Ce fait, de même que la

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présence de la périclase, de la α-sépiolite et l'épaisseur réduite (700-800 m) des formations du toit, nous déterminent d'émettre l'hypothèse d'une genèse mixte : syngénétique (pour la périclase et le quartz) et hydrothermale, phase vadeuse (pour la brucite et la α-sépiolite).

L'appartenance des formations carbonatées à minéralisations magnésiennes des trois zones étudiées, aux types lithologiques calcaire argileux et calcaire dolomitique, ainsi que l'appartenance des roches à brucite aux mêmes types lithologiques, démontrent l'existence d'un seul bassin de sédimentation qui a fonctionné pendant le Trias et le Lias et d'une source unique d'apport pour les composants principaux : des minéralisations magnésiennes ; $CaCO_3$ et Ca, $Mg(CO_3)_2$.

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CRETACEOUS AND PALEOGENE FLYSCH OF THE ROMANIAN CARPATHIANS: PALEOCURRENTS, SOURCE-AREAS, PALEOGEOGRAPHY [1]

BY

NICOLAE MIHĂILESCU [2]

The paleotransport maps for Cretaceous-Paleogene molasse and flysch deposits from the Romanian Carpathians area represent an attempt to synthetize the existing data and to obtain a general paleogeographic image of this area.

In front of the Romanian Carpathian arc there are two rigid zones, the East-European Platform, facing the East Carpathians and the Moesian Platform, facing the southern zone of the East Carpathians and the South Carpathians. The marginal rim of the East-European Platform was formed, during Cretaceous and Paleogene times, of the Green Schists and of the North Dobrogean deposits, joined together (Dumitrescu et al., 1962). The East-European Platform was covered as well by the Upper Cretaceous-Lower Paleogene deposits (Patrulius, Chiriac, 1965).

Within the East Carpathians, from the sedimentation processes point of view, two distinct structural units do appear:

— the internal zone of the East Carpathians (median Dacides — Transylvanian domain), namely Transylvanian Nappes and their Mesozoic cover, and

— the East Carpathian Flysch zone (marginal Dacides and Moldavides — the Carpathian flysch domain), namely the Baraolt Nappe the Ceahlău Nappe, the Bobu Nappe, the Convolute Flysch Nappe (Teleajen), the Macla-Zagon Nappe, the Audia Nappe, the Tarcău Nappe and the Marginal Zone (Săndulescu, 1975).

Within the South Carpathians (South Carpathian domain) the main units are: the Getic Nappe and the Danubian Autochthon (Codarcea, 1940).

It must be underlined that both the Getic Nappe and the Danubian Autochthon contain several other distinct units, with different paleogeographic and paleotectonic evolutions. This is the reason

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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for which the term of "South Carpathian domain" suggests a false image of a single unit.

Within the Apuseni Mountains (Apusenide domain) the two main units are the North Apuseni and the South Apuseni, with a different paleogeographic evolution (B l e a h u, 1974).

During the Upper Tithonian, the Romanian Carpathian sediments do not show a flysch character, except pelitic flysch deposits of the lower Sinaia Beds (A v r a m, 1980) and of the flysch deposits of the Finiş Unit.

At the beginning of the Berriasian-Valanginian stage, within the area of the Carpathian geosyncline (Pl. I), there is, on the one hand, a gradual passage from the Upper Jurassic to the Lower Cretaceous, and on the other hand, with rare exceptions, the facies of these deposits maintains its characteristics sometimes up to the end of the Hauterivian.

First we shall refer to the Berriasian-Valanginian, as this time marks, within the Romanian Carpathians, the showing up of some flysch deposits which will continue, with different facies, up to the end of the Paleogene.

During the Berriasian-Valanginian time, the Romanian Carpathian geosyncline was limited westwards by the Transylvanian massif, eastwards by the East-European Platform and southwards by the Moesian Platform. The sedimentation zones, for flysch deposits, were represented by :

— the East Carpathians trough, which finds its continuity in the South Carpathians (Danubian Autochthon),

— the Codru zone trough in the North Apuseni, and

— the Mureş trough (South Apuseni).

These troughs are bordered either by emerged territories (northern and eastern promontories of the Getic Nappe), or by the "sub-Bukovinian fold", or by shallow water zones (epicontinental or lagoonal deposits).

On the western border of the East Carpathians there were formed marly-limy deposits and fine wildflysch sandstones, sometimes with numerous olistoliths and flysch type sediments (Lunca Beds).

Within the East Carpathians trough, there deposited westwards as well, turbidites of the Sinaia Beds which were components of the Ceahlău Nappe, and eastwards, the argillo-laminated flysch (Black Schists) of the Audia and Tarcău Nappes and of the Marginal Zone.

The current directions within the Sinaia Beds suggest the existence of a display area of the detrital material (Pl. I), at the East Carpathians bend, and of some longitudinal currents, from south to north and from north to south, in the northern zone.

In the western area of the Black Schists the current directions show orientations from west to east in the southern area, and orientations from east to west in the northern area. In the eastern area of the Tarcău Nappe and of the Marginal Zone the main orientations are from east to west.

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No matter the present-day structure of the Black Schists deposits, sedimentological observations have shown that there are no proofs to sustain the hypothesis of the existence of a cordillera, in this period, within the East Carpathians trough.

The source-areas originate thus from the eastern promontory of the Getic Nappe (Făgăras promontory) and the western border of the East-European Platform. The existence of the Sinaia Beds within the Severin Nappe (South Carpathians) indicates a source-area located southwards.

In the Apuseni Mountains, the flysch deposits appear in the Codru Nappes (North Apuseni) and in the Mureș trough (South Apuseni).

At the beginning of the Hauterivian, the sedimentation conditions are rather similar to those of the Valanginian, so that we comment only on the main differences.

We mainly refer to the dominance, within the upper horizon of the Sinaia Beds, of detrital material supplied from south to north, transported by transversal currents (marginal threshold).

The presence of green schists fragments within microconglomerates of the external slope deposits of the East Carpathians trough shows their presence somewhere in the east of the Carpathian area (P a t r u l i u s, C h i r i a c, 1965).

During the Barremian-Aptian, the Romanian Carpathians trough was limited westwards by the Transylvano-Pannonian Massif, eastwards by the East-European Platform and southwards by the Moesian Platform. Thus the crystalline core of the East Carpathians (Carpathian fold) was attached to the Transylvano-Pannonian Massif, and the eastern area of the Getic Nappe (South Carpathians) was emerged.

The sedimentation zones, for flysch deposits, were represented by the East Carpathians trough and by the South Apuseni trough.

In the East Carpathians trough there accumulated westwards, the wildflysch formation, with olistostromes, flysch packets and tilloid conglomerates, and in the central and eastern zones, namely in the two main formations, it was laid down the turbiditic flysch (Ceahlău Nappe, Convolute Flysch Nappe) and the argillo-laminated flysch (Audia Nappe, Tarcău Nappe, Marginal Zone).

The main source-areas originate from the crystalline central Carpathian core attached to the Transylvano-Pannonian Massif, from the eastern area of the Getic Nappe (Făgăraș promontory), from the East-European Platform and from the Moesian Platform (the Olt marginal threshold included — D u m i t r e s c u et al., 1962).

Within the bend zone of the East Carpathians, the "haut fond" (Zamora) is covered westwards and northwards by the Piscu cu Brazi Beds (material supplied by the Făgăraș promontory) and southwards by the Comarnic Beds (J i p a, 1961).

In the South Apuseni domain there continues as well the process of sedimentation of two distinct troughs, separated by the "haut fond" Techereu-Drocea continued by the Trascău peak.

During the Albian, the Romanian Carpathians geosyncline was limited westwards by the Transylvano-Pannonian Massif, eastwards by the East-European Platform and southwards by the Moesian Platform.

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The crystalline core of the East Carpathians (Carpathian fold) was situated between the Carpathian troughs. The sedimentation zones for flysch deposits were represented by :

— the East Carpathians troughs which found their continuity in the South Carpathians (Danubian Autochthon), and

— the South Apuseni trough.

In the southern area of the Transcarpathian trough (Mihăilescu in Slaczka, 1976) the Albian deposits form the molasse of the Bucegi Conglomerates (Mihăilescu, 1971).

These conglomerates are a gravel nappe deposited in marine environment and represent a fan-shaped accumulation. Their formation represents the consequence of the emergence of the central part of the Getic promontory, at the beginning of the Albian, namely at the beginning of the Recent Austrian phase, an emergence which influenced the whole zone westwards of the present-day area of the Piatra Craiului Massif.

On the eastern edge of the crystalline core of the East Carpathians there continues the sedimentation of the wildflysch formation.

In the external trough of the East Carpathians there deposited, westwards, turbidites participating in the formation of the Bobu and the Teleajen Nappes, and eastwards of the argillo-laminated flysch (Black Schists) of the Albian of the Macla-Zagon, Audia, Tarcău and Marginal Zone Nappes.

The source-areas originate from : the Transylvano-Pannonian Massif, the crystalline central Carpathian core, the East-European Platform and the Moesian Platform.

In the South Apuseni trough, an "haut fond" inwards delimits turbidites transported from the south, and outwards, wildflysch deposits, transported from the north to the south.

As compared to the Albian, the widespreading area of the Vraconian-Senonian deposits points out their transgressive character.

The Vraconian-Cenomanian flysch deposits in the central zone of the East Carpathians trough and in the Mureș trough :

— In the central zone of the East Carpathians trough there form turbiditic deposits composing the convolute flysch (Teleajen Nappe) and the upper Tisaru Beds (Macla-Zagon Nappe, Audia Nappe). In the external zones there form either coarse-grained deposits (Ceahlău Nappe) westwards, or fine-grained deposits (Tarcău Nappe, Marginal Zone), eastwards.

In this eastern external area of the East Carpathians there appear red and green lutites, "exotic rocks" which in Murgeanu's opinion (1973) are the result of destruction during the Upper Cretaceous of a relief (Cuman cordillera), which was present along the flysch trough.

The source-areas for the detrital material of the flysch sequences, limited by shallow marine water, are represented by the Transylvano-Pannonian Massif, the Făgăraș and the Leaota massifs.

— In the Mureș trough there continues the sedimentation which started during the Albian.

In the Turonian-Senonian, the flysch sedimentation zones occupy surfaces by far larger, represented by : the East Carpathians trough,

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which finds its continuity in the Danubian Autochthon (South Carpathians), in the Haţeg trough (the post-tectonic cover of the Getic Nappe) and in the Mureş trough (South Apuseni).

These zones are bordered either by emerged territories (Transylvano-Pannonian Massif, the central crystalline core of the South Carpathians), or by shallow water zones.

On the eastern border of the Transylvano-Pannonian Massif, there deposited, during the Turonian-Senonian, northwards, Puchov Marls (Botiza Nappe), and southwards, in the Vlădeni couloir, in the Perşani Mountains and in the Ceahlău Nappe, marls and variegated marl-limestones (P a t r u l i u s et al., 1968).

Within the East Carpathians trough there deposited, westwards, turbidites (Teleajen Nappe, Macla-Zagon Nappe, Audia Nappe) and eastwards, coarse-grained turbidites (Tarcău Nappe and Marginal Zone).

The source-area originates from : the Transylvanian Massif, the Central Carpathian crystalline core (northern and southern zones) and the East-European Platform.

Within the South Carpathians trough, where turbidites have formed, during the Turonian-Senonian, the post-tectonic cover overlay large surfaces. The source-areas originate from the central crystalline core of the South Carpathians (the Călimăneşti outcropping area), and from the western area of the Supragetic Nappe.

In the South Apuseni there continues the existence of two troughs, separated by an "haut fond", the Sălciua-Gilău trough was made both westwards (Gilău Massif) and eastwards (Trascău Peak). In the Mureş trough the detrital material comes as well from the Transylvanian Massif zone and from the central crystalline core of the South Carpathians.

In the geosynclinal zones of the Romanian Carpathians sedimentation is continued during the Danian-Paleocene, on a somehow restricted area as compared to the Upper Maestrichtian.

Only a sedimentation zone, for flysch deposits is represented in the East Carpathians trough, by turbiditic deposits (Audia Nappe, Tarcău Nappe, Marginal Zone). During this period the Audia and the Tarcău Nappes were supplied by the central crystalline core of the East Carpathians, and the Marginal Zone by the East-European Platform.

The flysch deposits are represented during the Eocene by the East Carpathians troughs. In the northern area of the Transcarpathian trough (Maramureş) the Eocene deposits from restricted domains (J i p a, M i h ă i l e s c u, P a n i n, 1963). In the East Carpathian trough there deposited turbidites which were forming (1) the Ceahlău and the Convolute Flysch Nappes (Teleajen), southwards and (2) the Audia and the Tarcău Nappes, outwards : coarse-grained turbidites, microconglomerates with green schists fragments were forming the Marginal Zone eastwards.

The source-areas originate from : the Transylvano-Pannonian Massif, the Carpathian Core, the East-European Platform and the Moesian Platform.

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During the Lower Oligocene, the sedimentation conditions are not too different from those of the Eocene. In the Transcarpathian trough (Maramureș-Bîrgău) the current directions show a prolongation of these deposits, south-eastwards, probably hidden by Neogene eruptions (Murgeanu, Patruliu s, 1960).

In the external part of the Tarcău Nappe and in the Marginal Zone there appear, during the Oligocene, conglomerates with green schists elements. They form the lower part of the graded beds, Kliwa type arenites or thick banks. The measured current directions from the east to the west, show that the detrital material comes from the East-European Platform (Pl. II).

During the Upper Oligocene the transport directions have several distinct features as compared to the Paleogene rest of the East Carpathians. There takes place a sudden change of the current sense, which carries detrital material, most of which moving this time from north to south (Tarcău Nappe, in Bukovina and in the Carpathian bend zone).

The fact that the whole system of current directions is changed with 180°, can have the following significances :

— a tipping of the inclination of the sedimentation basin axis, at the beginning of the Upper Oligocene ;

— a complete change of detrital material sources, when we imagine the sedimentation basin bottom as horizontal.

In the first case, there can be admitted an imobility of the eastern and southern borders of the sedimentation basin and a modification of morphology of the Carpathian area, due to a sudden disappearance of several source-areas which existed during the Lower Oligocene.

In the second case, we must admit a flat relief of the sedimentation basin bottom, which is hard to believe, taking into account the dimensions and shape of the Carpathian area.

There can be noticed that the facies of the Cretaceous-Paleogene flysch deposits appear in the Romanian Carpathians at the end of the Upper Jurassic. They occupy important surfaces during the Cretaceous time and during the Upper Paleogene and end their sedimentation during the Upper Oligocene.

As it was stated before (Contescu, Jipa, Mihăilescu, Panin, 1966) the system of current directions is the same at the beginning of the Miocene while sediment dynamics and the environment (paleoclimate, paleosalinity etc.) are completely changed.

The present data represent a stage of the knowledge of paleogeographic evolution of Cretaceous-Paleogene flysch deposits of the Romanian Carpathians.

It is a stage, because the results of such researches are reported to two factors :

— accumulation of data concerning directions of transport of the detrital material, and

— progress obtained in biostratigraphic researches and of geological mapping which allow the location on maps, more and more precisely, of sedimentological data.

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PALAEOCURRENT DIRECTIONS OF THE BERRIASIAN-VALANGINIAN FLYSCH DEPOSITS OF THE ROMANIAN CARPATHIANS

0 15 30 45 60 Km

LEGEND

- Flysch deposits
- Epicontinental deposits
- Continental deposits
- Source areas
- Current directions
- Nappe overthrust
- Recent border of Moesian and East-European platforms
- Source area boundary

HUNGARY
U. S. S. R.
YUGOSLAVIA
BULGARIA
BLACK SEA
PANNONIAN MOUNTAINS
APUSENI MOUNTAINS
EASTERN CARPATHIANS
SOUTHERN CARPATHIANS
SATU MARE
BAIA MARE
ORADEA
CLUJ-NAPOCA
TIRGU MURES
ALBA IULIA
ARAD
TIMISOARA
DEVA
SIBIU
BRASOV
PETROSANI
DROBETA-TURNU-SEVERIN
CRAIOVA
PITESTI
BUCUREȘTI
GIURGIU
PLOIEȘTI
BUZAU
BACAU
DOROHOI
BOTOȘANI
SUCEAVA
IAȘI
GALAȚI
BRĂILA
TULCEA
CONSTANȚA
Mangalia
Bazias
Tisa
Somes r.
Barcau r.
Crisul Repede r.
Crisul Negru r.
Crisul Alb r.
Somesul Mic r.
Somesul Cald r.
Somesul
Mureș r.
Tîrnava Mică r.
Tîrnava Mare r.
Olt r.
Birzava r.
Lotru r.
Gilort r.
Oltet r.
Motru r.
Jiu r.
Argeș r.
Dîmbovița r.
Ialomița r.
Buzău r.
Bistrița r.
Siret r.
Prut r.
Putna r.
DANUBE R.
DANUBE RIVER
Chilia Br.
Sulina Br.
St. Gheorghe Br.

Imprim. Atel. Inst. Geol. Geof.

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N. MIHĂILESCU

PALAEOCURRENT DIRECTIONS OF THE LOWER OLIGOCENE DEPOSITS OF THE EAST CARPATHIANS

0 4 6 8 10Km

LEGEND

- Green schists conglomerates
- Kliwa Sandstone
- Fusaru Sandstone
- Pucioasa Beds
- East-European Platform
- Crystalline schists

S. R. S. U.

Siret r.
Suceava
Moldovita
Cirlibaba
Moldova r.
Cimpulung
Gura Humorului
Vatra Dornei
Glod
Bistrita r.
Tg. Neamt
Moldova r.
Piatra Neamt
Bicaz
Bistrita r.
Mures r.
Trotus r.
Comănești
Tazlău r.
Tirgu Ocna
Gh. Gheorghiu - Dej
Oituz r.
Trotus r.
Olt r.
Olt r.
Tg. Secuiesc
Negru r.
Covasna
Putna r.
Bisca Mică r.
Zăbala
Bîrsa r.
Brașov
Bisca Mare r.
Predeal
Bisca Chiojdului r.
Sinaia
Mineciu
Cimpulung
Comarnic
Buzău r.
Pietrosita
Valeni de Munte
Cimpina
Buzău
Dîmbovița r.
Teleajen r.
Tîrgoviște
Ploiești
Ialomița r.
Prahova r.

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LOWER DANUBE RECENT ALLUVIA: SEDIMENTS AND SEDIMENTARY FACTORS [1]

BY

NICOLAE MIHĂILESCU [2]

This paper presents the results of a general study concerning sediment composition and sedimentary conditions in the lower course of the Danube river.

The early information about the Danube river comes from antiquity; during the 19th century the information number increases (de Marigny, 1850; Hartley, 1862), while starting from the 20th century (Antipa, 1912) specialized studies are bringing more and more interesting details.

From the physico-geographical and hydrographical points of view, along the Danube river three sectors can be separated: the upper sector (from the sources to Bratislava), the middle sector (between Bratislava and the Porțile de Fier Dam) and the lower sector (from the Porțile de Fier Dam to the river's mouth).

Hydrography. As compared to the Danube flow when entering the Porțile de Fier Defile (5390 m^3/s), that of the tributaries from the lower course totalizes about 1000 m^3/s and it does not change quantitatively the outflow discharge.

The most important discharge supplies are those of the Timok (40 m^3/s), Jiu (90 m^3/s), Isker (57 m^3/s), Olt (160 m^3/s), Iantra (42 m^3/s), Argeș (65 m^3/s), Siret (210 m^3/s) and Prut (86 m^3/s) rivers which down to Ceatal Ismail rise the Danube flow at 6330 m^3/s.

The study of the Danube sediment discharge in a longitudinal profile has shown that the bed load increases downstream from 225 mg/l at Drencova, to 375 mg/l at Brăila, namely from an annual sediment discharge of 35 million tons at Orșova, to approximately 70 million tons at Ceatal Ismail, at an increase of only 13.5% of the water flow (Stănescu et al., 1967).

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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The extreme values of the measured Danube multiannual water flows were of 1500 m^3/s and 13,000 m^3/s (B o n d a r, 1972).

Measurements of the secular variation of the Danube silt charge at influx, as a result of harnessing the hydrotechnic works from the afferent basin, represent during 1861-1900, 232 g/m^3, during 1901-1940, 202 g/m^3 and during 1941-1968, 179 g/m^3.

Up to 1969 when the storage basin from Porţile de Fier was formed, the water flow of the Danube river was distributed as follows in the Danube Delta : the Chilia Branch, 62.5%, the Sulina Channel, 17.7% and the Sf. Gheorghe Branch, 19.8%. The sediment discharge in suspension of the Danube river stands for 65.7 million tons yearly, of which 60.5 million tons annual sediment discharge in suspension is flown in the Black Sea. To this volume there adds the Danube bed load evaluated at 4.96 million tons yearly, of which 3.1 million tons on the Chilia Branch, 0.99 million tons on the Sf. Gheorghe Branch and 0.87 million tons on the Sulina Channel.

Hydrological measurements (Drobeta-Turnu Severin), immediately downstream the Porţile de Fier Dam, during 1971-1975, have shown that the sediment discharge of the Danube is of 414 kg/s (164-890 kg/s) at 73 g/m^3 (34-139 g/m^3), and at Ceatal Ismail, during the same period of time, it amounts at 1,304 kg/s (1120-1740 kg/s) at 199 g/m^3 (157-219 g/m^3) (B o n d a r and S t a t e, 1977).

If at Drobeta-Turnu Severin measurements indicate a lessening of the sediment discharge, at Ceatal Ismail the values are relatively constant. This equilibration process of the lower Danube sediment discharge is a result of accentuating the erosion phenomena of the bed and the islands (islets), then of the banks and of the river tributaries.

The building up of the Porţile de Fier Dam has modified the sediment discharges, as the lacustrine conditions from upstream the dam have as a result the deposition of most of the bed loads and of the suspension loads, that is of a large part of the 35 million tons yearly. Thus, the Carpatho-Balkan area supply becomes the main source of detrital material for the lower course of the Danube.

Grain Size Distribution. The grain size, petrographic and chemical study (M i h ă i l e s c u et al., 1972) of bottom sediments from the Danube river and its main tributaries, as well as of the main branches of the Danube Delta has shown that there are several causes and processes contributing to the formation, accumulation and erosion of sediments.

According to the rudite repartition in the Danube sediments, there can be separated the following zones :

I. The zone between Baziaş and Orşova (Fig. 1), namely the former zone of Cataracts (Cazane), contains frequent coarse grained rudites which before building up the Porţile de Fier Dam, formed the Danube bed sediments in strong stream conditions. After building up the Porţile de Fier Dam (1971), this zone has changed into a lake, where, at least between Moldova Nouă and Orşova, the water current is very weak. In these new conditions, the Danube river has started

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to deposit coarse grained sediments at the lake entrance and covered with a mud layer the old gravels.

This is the case, for example, of the Dubova-dam zone, where coarse grained sediments have already been covered by fine mud, mainly the easily flooding zones, the former depression reliefs and sometimes the former minor stream bed of the Danube river.

These sedimentation processes are not uniform within the zones where the Danube bed narrows, namely at a smaller section, the water velocity is enough to maintain in suspension the sediment discharge (Cazanele Mari, Greben).

II. Downstream the Porțile de Fier Dam where the water velocity is high, a zone which before building up the dam represented the place where the Danube was going out of cataracts, the bottom sediments are formed of heterogeneous gravels. Within the river channel the cobbles are angular, poorly sorted, with dimensions of 1-3 cm and very well rounded.

Downstream the dam zone to downstream the Timok mouth the Danube bed sediments are formed of gravels. Sometimes there appear islands made of coarse grained deposits, such as the Țigănușul and the Șimian islands. The coarse grained sediments between the dam and the Timok mouth represent most of all sediments of the "former" Danube river, new supplies being very low. For the downstream part of this zone, the Timok river which crosses the Balkans near the Danube river brings an important sediment discharge, well rolled, heterogeneous from the petrographical point of view, mainly made of coarse detritus (Fig. 1).

The 1979 studies have shown that the Danube sediment discharge, downstream the dam is very low and connected with the water velocity, controlled by the dam operating conditions the Danube water has a tendency to recover the bed and suspended load, characteristic of different phases of water velocity.

This process has as a result the fact that within the Danube bed there are successive erosion, removal and redeposition phenomena of sediments already existing within the river bed.

III. The third zone (Fig. 1) is formed of different sectors (a, b and c) characterized by the formation of some coarse grained deposits, located mainly towards the right bank of the river, to the Lom, Ogosta and Isker river-mouths or in the navigation channel where the bed narrowing has as a result the differential transport of the fine sediment fraction.

As concerns the accumulation way of these deposits it is interesting to notice the situation at the Lom river mouth. The detritus transported by the Lom is formed of coarse grained sands with gravel elements, without constituting a proper gravel. This detritus brought in the Danube river gradually enriches in ruditic elements, due to the strong current of the Danube river which can rise in suspension only the sandy fraction while the coarse grained elements are left where they are.

IV. Downstream the Lom mouth, the existence of gravels is connected to different local causes.

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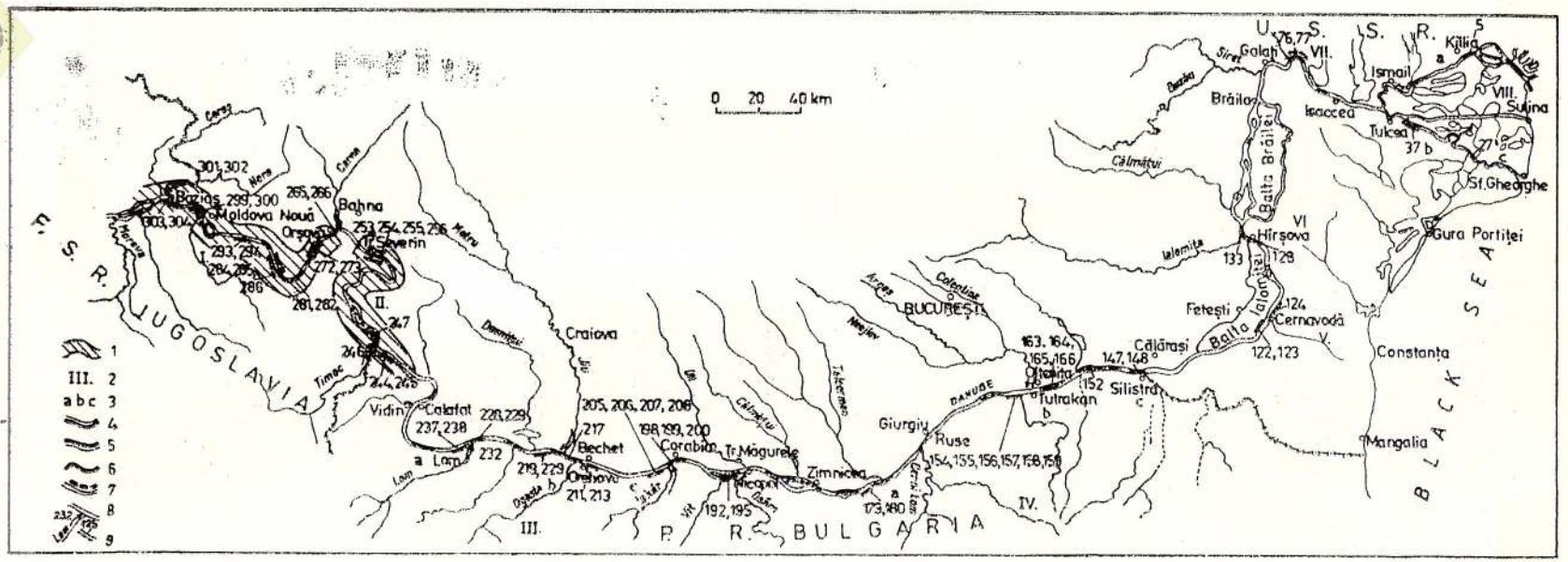


Fig. 1. — Distribution of rudite accumulations along the Romanian course of the Danube: 1, gravel zone ; 2, number of the gravel zone ; 3, restricted gravel accumulations ; 4, gravel deposits on the right side bank ; 5, gravel deposits on the left side bank ; 6, gravel deposits in the river channel ; 7, rocky bank without sediments ; 8, gravel sediments brought in by a tributary river ; 9, sample number.

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V. From the Danube Delta we have collected rudites only in three sectors where they show on very small surfaces. This material consists of either clay cobbles resulted from the pulling out of some fragments from the Chilia Branch bed, or quartzite cobbles resulted from the Dobrogea Devonian deposits, or of polygenous cobbles, a result of erosion of some fossil littoral belts intersected by the Sulina Channel and the Sf. Gheorghe Branch.

The arenites from the Danube river bed show various grain size and mineralogical composition, in connection with depth the samples were collected from, and with their position as compared to the main morphological elements of the Danube bed.

The distribution pattern of the main grain size fractions, shows the following :

— along the Danube river the clay fraction percentage varies between 0.07 and 5.6% (J i p a, 1974), except two sectors : the Porțile de Fier Lake (1-53.0%) and the Danube Delta (0.8-63.0%). The largest quantities of clay are to be found, due to gravitational processes of deposition, in the large bed linear sectors and within the downstream zone of the Porțile de Fier Lake. The amount of the clay fraction is, as well, important at the Danube mouths where fine sediments deposit first at the junction of fluviatile waters with the salt sea water (M i h ă i l e s c u et al., 1974).

— the variation of the siltic fraction along the navigation channel of the linear Danube is constant (0.05-1.0%) (J i p a, 1974). Within the lake sediments at Porțile de Fier the silt fraction reaches 80.5% and along the banks of the Sulina Channel and of the Sf. Gheorghe Branch the siltic fraction of sediments reaches 71.2%. In the quiet zones of Dunărea Veche (Danube Delta) the siltic fraction varies between 49.6% and 72.6% (M i h ă i l e s c u et al., 1974).

— the arenitic fraction has variable importance, connected with sediment position as compared to the main morphological elements of the channel. In the Porțile de Fier Dam Lake, the arenite varies between 0.26% and 98.0%. In the Danube navigation channel, between the Porțile de Fier Dam and Ceatal Ismail, the sand varies between 15.4% and 98.0% (J i p a, 1974). Variations of sand percentage within sediments of the Danube Delta main branches are by far larger, partly due to a larger scale of hydrological conditions.

Mineralogical Parameters. From the mineralogical point of view, considering the arenites of the Lower Danube, we can state the following :

— Quartz varies between 28.40% and 32.88% in the zone placed upstream the Porțile de Fier Dam, as compared to the Lower Danube zone where this variation amplitude is by far larger (26.47-87.41%).

The large amplitude of quartz amount variations (Fig. 2) within Lower Danube arenites is mostly given by important variations of hydrological conditions, and due to the various origin of material carried into the Danube river by different tributaries. This statement is confirmed by the diagram in Fig. 2, where samples collected downstream the Jiu (D 217), Iantra (D 172) and Ialomița rivers (D 133) junctions, have a larger quartz percentage.

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— Plagioclase feldspars, the microcline and the orthose appear rather seldom and in small amounts (0.12-0.50%). The feldspar granules, generally angular to sub-rounded are frequently altered. Within the Porțile de Fier Lake sediments, feldspars represnt 3.50-10.00% of arenite composition, along the Lower Danube 2.68-12.73%, while in the pre-deltaic zone their percentage is 0.68-7.10%.

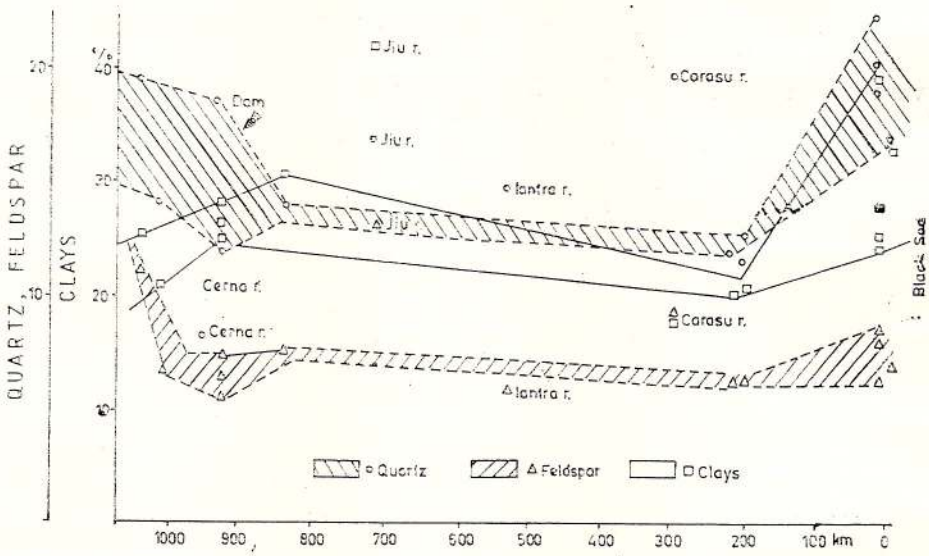


Fig. 2. — Mineralogical composition of the lower course of the Danube river sediments (quartz, feldspars, clays).

— Micas, represented by muscovite, biotite and chlorite, with percentages below 6%, appear irregularly in the Lower Danube zone, excepting the main branches of the Danube Delta. Within the Porțile de Fier Lake sediments, the amount of micas increases (3-10%) due to the low water velocity.

— Heavy minerals in the Lower Danube sediments are represented by : garnets, amphiboles (green hornblende, actinolite), pyroxenes, epidote, zoisite, disthen, staurolite, tourmaline, rutile, titanite, zircon and opaque minerals. The variation curve of the heavy minerals percentage from the arenites of the Danube navigation channel is, in the Lower Danube zone, relatively uniform with maxima which do not overpass 2.5%, and in the Porțile de Fier Lake zone it has variations between 2.50 and 8.87%.

Several factors contribute to the formation and modification of the Danube arenite composition :

A) As concerns the source rocks supplying the detrital material that comes to the Danube, it must be pointed out that they belong to various categories. The presence of diopside, disthen and sillimanite indicates their provenance from metamorphic rocks ; the presence of andalusite, microcline, orthose, acid plagioclases, sphene, tourmaline

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and zircon indicates igneous acid or metamorphic rocks as source rocks ; the presence of epidote, zircon, serpentiniform minerals indicates eruptive basic or metamorphic rocks as source rocks and finally the rather sporadical presence of glauconite and Miocene and Pliocene fauna indicates sedimentary rocks contributing as well to the formation of the Danube arenites.

This association of mineral species, characteristic for the Danube arenites show however that they mostly come from metamorphic rocks.

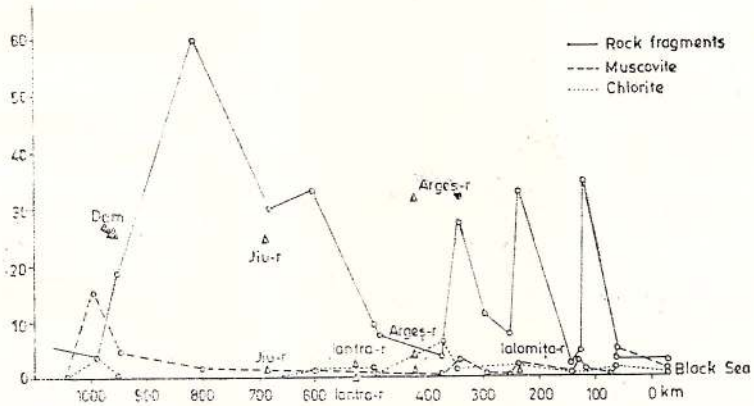


Fig. 3. — Distribution of rock fragments and micas in the lower course of the Danube river sediments.

The presence, although in low percentages of microcline, diopside, disthen and sillimanite pleads for this hypothesis. There adds, downstream the junction with the Timok river, an important amount of orthose grains associated with acid plagioclases, sphene, tourmaline and zircon, probably originating from the Belogradcic granite zone. The presence of epidote and zoisite within the arenites of the middle sector of the Lower Danube, indicates as well the influence of some areas covered by basic rocks.

The grain size and petrographic study of gravels and sands of the Danube tributaries has shown that only the Nera, Lom and mainly Timok rivers can be considered as having an important contribution in the rudite supply, while the Jiu, Isker, Olt, Iantra, Argeș rivers and most of all the Prut river are carrying arenitic material. From all the Danube tributaries, the Ialomița river is the one that carries the most diminished and fine sediment discharge, but which in exchange carries an important amount of organic materials.

B) From the examination of a large number of mineralogical analyses there can be stated that in connection with a mechanical alteration processes predominance (in the linear sectors of the Danube river, with narrow bed) or a chemical one (the storage lake from Porțile de Fier, Balta Ialomiței, Balta Brăilei and the Danube Delta), the mineralogical composition can sensibly vary. This can be seen, for example, while examining the presence of muscovite (sometimes with important participation), and we can see that (Fig. 3) :

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— due to the high values of the flatness index, it appears in sediments of still water zones (Porţile de Fier Lake, Măcin Branch) and

— due to resistance to chemical alteration it can be found at large distances from the source area.

C) Another important factor concerning composition of the Danube sediments is the stability of flowbed.

The Quaternary map (G h e n e a et al., 1971) indicates for the Danube course a translation movement from north to south. The only proof of this "migration" of the Danube bed is formed by the fossil

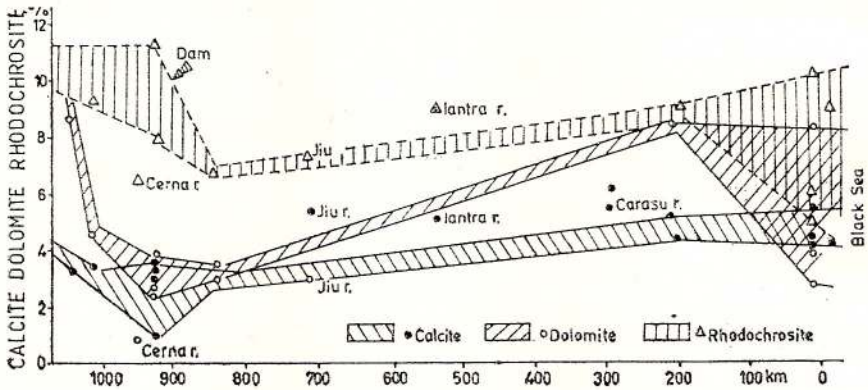


Fig. 4. — Mineralogical composition of the lower course of the Danube river sediments (calcite, dolomite, rhodochrosite).

terraces on the left bank which are left "behind", those on the right bank being mostly eroded.

During translation of the Danube flowbed, southwards, the terrace on the left bank and the alluvial fans of rivers coming from the Balkans were partly eroded and the detrital material deposited, either in the river bed, or in the new terraces. At the same time, a part of these terraces and alluvial fans which were uneroded, were left "behind", namely on the left bank of the Danube river. This hypothesis [3] raises the question of some future evaluations of the contribution of the Carpathian and Balkan rivers to the formation of fossil terraces of the Danube river.

The mineralogical study of Danube lutites has shown the existence of some large variations within their content (Fig. 1). As well as for the arenites, these variations are due both to supplies, and to the influence of some local physico-chemical conditions.

As it was shown before (R ă d a n in M i h ă i l e s c u et al., 1972), the presence of quartz, plagioclase feldspars and calcite within the lutitic fraction is constant. There appear variations due to the sediment "ageing" along 1,100 km, and to local causes as for example the enrichment in calcite of the Danube Delta sediments, due to shell abundance. Lutites contain as well dolomite (2.7-9.5%), siderite (2.4-4.8%), rhodochrosite (6.0-12.5%), hematite (1.2-3.6%), pyrite (1.3-7.7%) and clay minerals (6.4-39.0%) (Fig. 4).

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Organic Compounds. If we examine the participation of organic matter within the fluviatile sediments, we can separate as well the above mentioned sectors (Fig. 5) :

I. From Bazias downstream, the average content in organic carbon increases to a maximum of 2.29% in the storage lake of Porţile de Fier.

II-III. Downstream the dam, between Drobeta-Turnu Severin and Silistra, the water flow is faster, sediments are coarser and the average

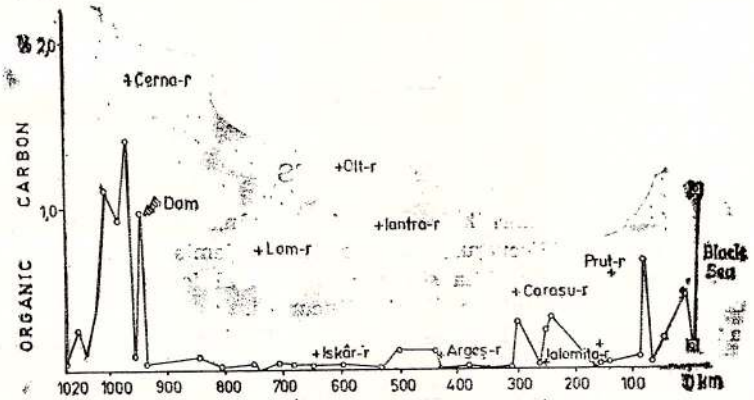


Fig. 5. — Distribution of organic carbon in the lower course of the Danube river sediments.

content of organic carbon diminishes to 0.08% ; although in this sector there are registered some high values for the organic carbon percentage to the mouths of the Lom (0.79%), Jiu (2.55%) and Iantra (0.99%) rivers.

IV. In the zone between Silistra and Brăila, the Danube river, parting into several secondary branches, contributes to the decrease of outflow velocity, which favours on the one hand the deposition of some finer sediments, and on the other hand the increase of organic carbon content, which reaches 0.11%.

V. At the Delta beginning, the organic carbon percentage varies between 0.005% and 0.10% (Fig. 5).

As concerns the organic nitrogen from sediments, its percentage varies between 0.08% and 0.20%.

The fact that most of the C/N values are below 12 shows that organic nitrogen is autochthonous. The C/N values variation — 7.70-10.00 — indicates the origin of organic carbon from vegetal substances decomposition.

The transformation processes of the Danube river and the Danube Delta were accelerated during the last ten years, on the one hand due to human activity, and on the other hand due to intensification of colmatation processes.

The results of some of these activities are contradictory in effects. Even since 1912, A n t i p a has shown the important part of the Danube flood plains and of the Danube Delta in compensating the highest discharges. In time, most of these zones were dammed up, having as a result water sewerage and directing the sediment discharges down-

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stream. This process is compensated by the building up of dams in the Danube valley, whose storage lakes cause particle deposition, decreasing thus the sediment discharge of the river. The building up of some new dams, both on the middle course of the Danube river and in the lower sector of the Danube will modify more and more the sedimentation conditions within the lower course of the Danube river sector.

[3] Prof. G. Murgeanu, verbal communication.

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MODERN SEDIMENTATION IN THE RAZELM-SINOE LACUSTRINE COMPLEX [1]

BY

NICOLAE MIHĂILESCU, SILVIU RĂDAN, LUCIANA ARTIN, SORIN RĂDAN, MARIA RĂDAN, IULIAN VANGHELIE [2]

Introduction. The southern zone of the Danube Delta is formed of a vast lake system resulted of the Danube and the Black Sea interaction during the Holocene. This large lacustrine area (867 km^2) consists of four major units (Razelm, Golovița, Zmeica and Sinoe) and various small satellite lakes (Babadag, Ceamurlia, Leahova etc.), characterized by a permanent or ephemeral water circulation. The most important water flow is directed from north (Lake Razelm) to south (Lake Golovița), going further south-eastwards (Lake Sinoe) and south-westwards (Lake Zmeica).

Lake Razelm receives the main supply (water and sediment discharge) from the Sf. Gheorghe Branch, mostly through the Dunavăț and Dranov Channels (30-90 m^3/s), and subordinately from the Taița and Telița valleys (0.4-0.5 m^3/s) through Lake Babadag. Lake Golovița is supplied with water from Lake Razelm and provides water and sediments for Lakes Sinoe and Zmeica. As concerns Lake Sinoe, this is supplied as well with brackish water from the Black Sea, through the breaches of the beach ridge.

The sediment discharge of the lacustrine complex results from:

— detritus of fluviatile origin ;

— detritus brought in the lacustrine basin by torrents and rain wash water from the ante-Quaternary formations ;

— detritus resulted from erosion of fossil beach ridges which form the basement of the lacustrine basin ;

— detritus reworked by waves and wind during the storms, resulted from the present-day beach ridges and redeposited in lakes ;

— detritus, most of all organic matter, resulted from the marsh zones bordering the lakes and resedimented by waves during strong storms.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981, September 8—13, Bucharest, Romania.

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During storm periods, the superficial bottom sediment layer is removed in suspension by the ground swell, subsequently generating graded bedded deposits by gradual loss of water turbidity.

Sediments of the Razelm-Sinoe complex are built up, most of all, of fine sands and silts. Clays appear only at the remote limit of the settling area of suspended material brought by fluvial channels. The sediment distribution pattern shows the importance of the control, on the one hand, of fluvial sediment discharge and, on the other hand, of reworking processes of detritus from the fossil beach ridges included in the Danube Delta basement (Pl. I).

Littoral erosion is active in the vicinity of headlands (Cape Iancila, Cape Dolojman) and has a tendency to remove the detritus derived from the old and recent formations cropping out in lake shores ; the high cliff demolition (for instance, the western coast of Lake Razelm between Cape Dolojman and Enisala) provides sometimes coarse grained elements. It is difficult to estimate the loess cliff supply, but it is still present, contributing with fine granular quartz and clay minerals (mainly illite).

The underwater vegetation layer is hydrodynamically important, preventing erosional phenomena and accelerating colmatage processes. The northern and eastern coast of Lake Razelm, as well as the north-western one of Lake Zmeica are nothing but walls made of reed stems ; rhizome ramifications form a net in which vegetal and mineral detritus is trapped. This process is the main cause of development, in time, of the firm ground in spite of the lacustrine area.

Mineralogy of Lake Sediments. The mineralogical composition of sediments is represented by 30-90% light minerals (quartz 12.0-65.0%, feldspars 5.0-20.0%, micas 0.025-6.0%, calcite 6.0-10.2%, aragonite 5.0-43.0%, dolomite 2.8-8.6%), 0.001-3.25% heavy minerals and 2.0-42.0% clay minerals. It must be underlined that carbonates resulted most of all from shell trituration (8.8-18.8%).

According to its mineralogical composition, the sandy fraction of the Razelm-Sinoe bottom sediments originates from :

— arenites brought from the Sf. Gheorghe Branch through the Dunavăț and Dranov Channels ;

— arenites resulted from erosion of beach ridges included within the lake shores ;

— arenites reworked from Holocene sediments of lake basement and introduced into the lacustrine basin.

In the group of heavy minerals the percentage of the opaque grains, represented by magnetite, hematite, ilmenite and limonite, varies between 4.6-38.8% in Lake Razelm, 1.7-18.0% in Lake Golovița, 1.4-32.6% in Lake Sinoe and between 4.3-57.8% in Lake Zmeica. Opaque mineral distribution is connected with redeposition of Holocene detritus which forms the lake substratum.

As concerns the distribution of clay minerals within the lake bottom sediments, this is generally controlled by fluviatile supplies,

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being influenced by the material removed from the shores during rainfalls, redistribution of suspended sediments by currents, differential sedimentation and, possibly, early diagenesis.

The mineralogical composition of the clay fraction ($< 2\,\mu$) of superficial sediments from Lakes Goloviţa, Zmeica and Sinoe varies as shown in the following table :

Clay mineralogy	Lake Goloviţa	Lake Zmeica	Lake Sinoe
Illite	38 % (33—50 %)	44 % (21—56 %)	43 % (33—53 %)
Smectite	40 % (29—49 %)	38 % (23—55 %)	36 % (22—46 %)
Kaolinite	22 % (18—27 %)	19 % (13—26 %)	21 % (16—29 %)
Chlorite	sporadic	sporadic	sporadic
Mixed layers	ubiquitous (generally of the 10—14M type)		
Illite crystallinity (Kubler, 1966)	5.2 (3—7)	6.0 (5—7)	5.0 (3—7)

Although average mineralogical compositions are rather similar for the three lakes mentioned above (except Goloviţa where illite is dominated by smectite), areal distribution of clay minerals shows several interesting features (Pl. II).

The settling velocity of clay particles is different, smectite having a strong tendency to remain longer in suspension. The transport from the Danube to Lake Razelm and mainly from Razelm to Goloviţa, Zmeica and Sinoe being made by weak currents, with low turbidity, the fine suspended fraction is gradually impoverished in illite and relatively enriched in smectite. The presence of smectite maxima ($S/I > 1$) in the area between Dolojman, Bisericuţa and Channel 5 (in Lake Goloviţa), at the mouth of Channels 2 and 5 (in Lake Sinoe), and northwards Lake Zmeica (in front of an important junction channel with Goloviţa) suggests that the main supplies of smectite in suspension are directed from Razelm to Goloviţa, from Goloviţa to Zmeica and Sinoe, and from Zmeica to Sinoe (Pl. II). The distribution pattern of smectite/illite values reflects the main trends of water circulation in the Razelm-Sinoe lake complex. Other inflexions of the S/I contours as those between Lunca and Jurilovca (Lake Goloviţa) are explained by protection of the firm land by a marsh zone which plays the part of a filter for "heavier" clay minerals, favouring a preferential accumulation of smectite.

If for smectite the outspreading peculiarities are explained by preferential transport in suspension (by the low turbidity water) and differential settling, the illite and partially the kaolinite mainly depend on the land supplies (the mouth of Jurilovca Channel dug near the loess cliff, the Lupilor Ridge, the island system from the north-western

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zone of Lake Zmeica, the beach ridge separating Lake Sinoe from Black Sea, the Chituc Formation etc.).

The distribution pattern of clay minerals in the superficial layer of bottom sediments of Lakes Goloviţa, Zmeica and Sinoe is mainly controlled by transport and differential settling of the clay material brought through channels from the Danube or supplied by land leaching (reworking). Reworking phenomena are also confirmed by distribution of grain size classes, the areas rich in smectite being superposed on the finest sediments, and the illite and kaolinite zones generally corresponding to the sandy or silty areas (see Pl. I and II). The high gradient of illite enrichment in the Periboina zone (Lake Sinoe) and increase of illite contents towards Portiţa (Lake Goloviţa) are certainly a consequence of an early diagenetic transformation of smectite into illite under the influence of interstitial waters with higher salinity in these areas close to the seacoast. For the same cause plead as well the values of K u b l e r crystallinity indexes, lower — therefore higher crystallinity degree — in Lake Sinoe, as compared to the other lakes.

Chemistry of Lake Sediments. The bottom sediments showed as main chemical constituents silica, alumina, iron oxides, lime, magnesia and alkaline elements.

Silica, organized as quartz and opal, included in the clay mineral and feldspar lattices, as well as in external frustules of diatoms and silicoflagellates, is present between the following limits : 20-70% in Lake Razelm, 34.40-58.53% in Lake Goloviţa, 36.38-68.98% in Lake Sinoe and 35.69-68.51% in Lake Zmeica.

Alumina content varies between 0.83-19.45% for Lake Razelm, 3.79-14.29% for Lakes Goloviţa and Sinoe and 4.34-12.50% for Lake Zmeica ; it is mainly controlled by the amount of the clay minerals and subordinately by feldspars and micas.

Within the sediments of the studied area the iron appears as mineral (iron oxides), constituent of clay minerals, and in aqueous solutions (as a result of aquatolysis of mineral detritus from the sediment discharge of fluviatile origin). In Lake Razelm sediments FeO varies between 0.65-2.98% and Fe_2O_3 between 0.66-5.68%, Lake Sinoe sediments contain 0.34-3.55% FeO and 0.34-5.16% Fe_2O_3, in Lake Goloviţa the variation limits are 1.01-2.90% FeO and 2.63-5.92% Fe_2O_3, and in Lake Zmeica 0.57-3.68% and 0.25-2.63% respectively.

The alkaline-earth carbonates are most of all connected with the presence of shells in sediments, and sometimes they are also the result of land erosion and depositional processes. The variation limits are 2.17-30.50% for Razelm, 12.16-33.00% for Goloviţa, 13.40-50.59% for Sinoe and 7.96-28.09% for Zmeica.

Malacological Parameters. The malacofauna structure of the Razelm-Sinoe lakes is characterized by the existence of two complexes corresponding to two successive phases of population : a thanatocoenose formed of species which supported a large variation of salinity and a

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complex formed of thanatocoenoses and biocoenoses of some species of Ponto-Caspian and fresh-water type with a general tendency towards completely fresh-watered waters.

The first thanatocoenose complex is dominated by polyhaline molluscs of Mediterranean origin : *Cerastoderma edule-lamarcki, Abra ovata, Mytilaster lineatus, Lentidium mediterraneum, Mya arenaria, Nassarius reticulatum, Rissoa membranacea, Bittium reticulatum, Retusa truncatula.* In addition there is *Mytilus galloprovincialis* with diminished populations and a widespreading area reduced to Lakes Razelm, Golovița and Sinoe.

Within Lake Sinoe, besides these species there appear as well low euryhalinity forms : *Spisula subtruncata triangula, Solen vagina, Barnea candida, Cyclope donovani, Pronerithula westerlundi,* and in Lake Golovița, the Mediterranean species *Lenibulus pela* is present. Their sensibility to a strong or sudden lowering of salinity has not allowed them to migrate and adapt themselves in the rest of the lacustrine complex, a fact which can be connected with salinity conditions rather fluctuant in these areas, generally situated below 10‰.

The important changes in the hydrochemical conditions of Lake Razelm, due on the one hand to its separation from the Black Sea and, on the other hand, to the partial break of connections with the Danube, have first led to an increase of water salinity. It was normal that in these conditions some marine faunas with a high degree of euryhalinity and euryoxiphyly should have proliferated — since the abundance of populations of *Cerastoderma edule, Abra ovata, Mytilaster lineatus, Hydrobia ventrosa,* whose biocoenoses are quoted by B o r c e a (1926) in some areas of Lakes Golovița and Sinoe.

The increasing importance of fresh water character by resuming the connection with the Danube has changed the malacologic background, the polyhaline forms being replaced by oligohaline species of Ponto-Caspian and fresh-water type which populate this area at present.

The spatial distribution of limnocardiids of Ponto-Caspian type *(Monodacna pontica, M. colorata, Adacna laeviuscula fragilis, Hypanis plicatus relictus)* is almost uniform, with some concentrations mainly encompassed around the shores.

While comparing the present data on biocoenoses with limnocardiids with data provided by B o r c e a (1926) one can notice a withdrawal of areas and a decrease of population density in the eastern zone of Lake Golovița and a beginning of the populating process in Lake Sinoe.

Petromagnetic and Magnetometric Results. As regards geophysical methods, two complementary techniques were used for the study of the Razelm-Sinoe lacustrine complex : petromagnetism and submerse magnetometry.

The use of the first method was limited, because of metrological reasons, to the study of magnetic susceptibility of bottom sediments on the basis of determinations performed in laboratory on representative samples. These were collected from the first 5 cm below the water/

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sediment interface — when we had in view the areal distribution of susceptibility — and from cores — when we had in view the vertical distribution of the above mentioned petromagnetic parameter.

The magnetic susceptibility of bottom sediments of Lakes Golovița, Zmeica and Sinoe varies between the limits indicated in histograms on Plate III. The areal distribution pattern of magnetic susceptibility values, represented on the isosusceptibility map (Pl. III), points out a good correlation with grain size, mineralogical and geochemical data, as well as with morphostructural details of the emerged adjacent areas, suggesting some connections with sedimentogenetic implications.

Therefore, the junction zones between Lakes Golovița and Zmeica, characterized by stronger currents transporting from northwards a rather coarse grained material provided by the still forming sand barrier between the two lakes, control as well the maximum susceptibility zone in the northern part of Lake Zmeica. The maximum area within the south-east Zmeica, which seems to delimit on a small distance the Lupilor Ridge, can be explained by a possible reworking of the sandy material from the ridge. The minimum areas pointed out in Lake Zmeica coincide with the offshore zones characterized by a quieter sedimentation. The western part of this lake is peculiarly rich in subaquatic vegetation, which explains better the low level of magnetic susceptibility values determined from these zones (very rich in organic detritus).

While comparing the maximum zones from the isosusceptibility map with the structure of the surrounding sand ridges, a particularly clear connection between them can be observed (Pl. III). Thus, susceptibility maxima on the Pricop-Histria line (Lake Sinoe) are parallel to the Chituc Formation revealing the structural continuity of these sand bar deposits below the immerged zone. Also, some maxima along the north-western shore of Lake Sinoe mould, in the water-covered zone, the fan-like structure of the Lupilor Ridge, suggesting its continuity southwards the Channel 5 up to Portița. The prolongation of the same sand ridge towards Lake Leahova is clearly pointed out by the susceptibility contours from northwards Channel 5. Similar parallelisms can be also noticed along the beach ridge between the Black Sea and Lake Sinoe and along the sand ridge separating Lakes Zmeica and Golovița (between the northern mouths of Channels 2 and 5).

As concerns the vertical distribution of the magnetic susceptibility in the sediments of the Razelm-Sinoe lacustrine complex, some diagrams of susceptibility showed the existence of an interesting correlation with data obtained by radiographs or by lithological and mineralogical study of the cores.

The second geophysical method mentioned above, was applied in the Razelm-Sinoe lacustrine complex by carrying out 15 magnetometric profiles which have brought supplementary elements for identifying the structures of the submerged zone. As it has already been mentioned, the fossil ridge alignments on the lake bottom are pointed out by areas with particular heavy mineral assemblages. The records

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achieved by means of a protonic magnetometer with subaquatic sensor have revealed variations of the geomagnetic field which can be finally interpreted in sedimentological terms.

Summary of Geologic History. Some considerations concerning the evolution of sedimentary processes in the deltaic area can be made on the basis of the results presented above, correlated with data from literature.

The Razelm, Golovița, Zmeica and Sinoe lake sediments are the result of some complex changes of the southern area of the Danube Delta during the Holocene. If at the beginning of the Holocene the present-day territory of the Danube Delta, Razelm-Sinoe lacustrine complex included, was part of the marine domain, the "littoral ridge" (Antipa, 1914; Vîlsan, 1934) which barred the Danube gulf has modified the sedimentary conditions for the whole north-western area of the Black Sea.

It is already known that the basement of the Danube Delta depositional system is formed by a Pleistocene loess layer, cropping out in the northern (Chilia Veche) and southern zones of the Danube Delta (western border of Lake Razelm, Popina Island and northern border of Lake Golovița) (Mihăilescu, 1974).

Thus, the "initial ridge" was supported by loess deposits, but between the Dunavăț Promontory and these beach ridges there formed the Sf. Gheorghe I Delta (Panin, 1974), its northern area being represented by the present-day Caraorman Formation, while the southern part represents deposits included within the basement of Lake Razelm and the northern side of Lake Golovița (Pl. I).

During the Phanagorian regression, at the same time with the formation of the Sulina Delta edifice, there formed as well the Coșna Delta (Panin, 1976) by the supplies of a fluvial channel (Paleo-Dunavăț) which separated from the Sf. Gheorghe Branch (Pl. I).

At the beginning of the Histrian transgression (Bleahu, 1963), the Sinoe Delta was formed (Panin, 1974), covering the older deposits (ante-Holocene).

Complex researches carried out in the Razelm-Sinoe lacustrine complex (Mihăilescu, 1976—1979, in Szász et al., 1980) bring several new data concerning dynamics of modern sedimentation processes, confirming and completing concomitantly the image of time and space evolution of the Danube Delta depositional system.

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GEOLOGICAL SKETCH OF THE RAZELM-SINOE LACUSTRINE COMPLEX

0 1 2 3 Km

Lake Agighiol
o Sarinasuf
Popina Is.
Sarichioi o
LAKE RAZELM
Dunavăț Channel
Mustaca Channel
LAKE BABADAG
o Enisala
Cape Iancila
Lake 6 Martie
6 Martie o
Dranov C.
Periteașca
Lake Coșna
Jurilovca
Cape Dolojman
Bisericuța Is.
o Lunca
Lake Ceamurlia
LAKE GOLOVITA
Lake Leahova
Channel 5
LAKE ZMEICA
Portița
Ridge
Lupilor
Channel 2
SEA
LAKE SINOE
Periboina
BLACK
Pricop
Lake Histria
Histria
Chituc Formation

LEGEND

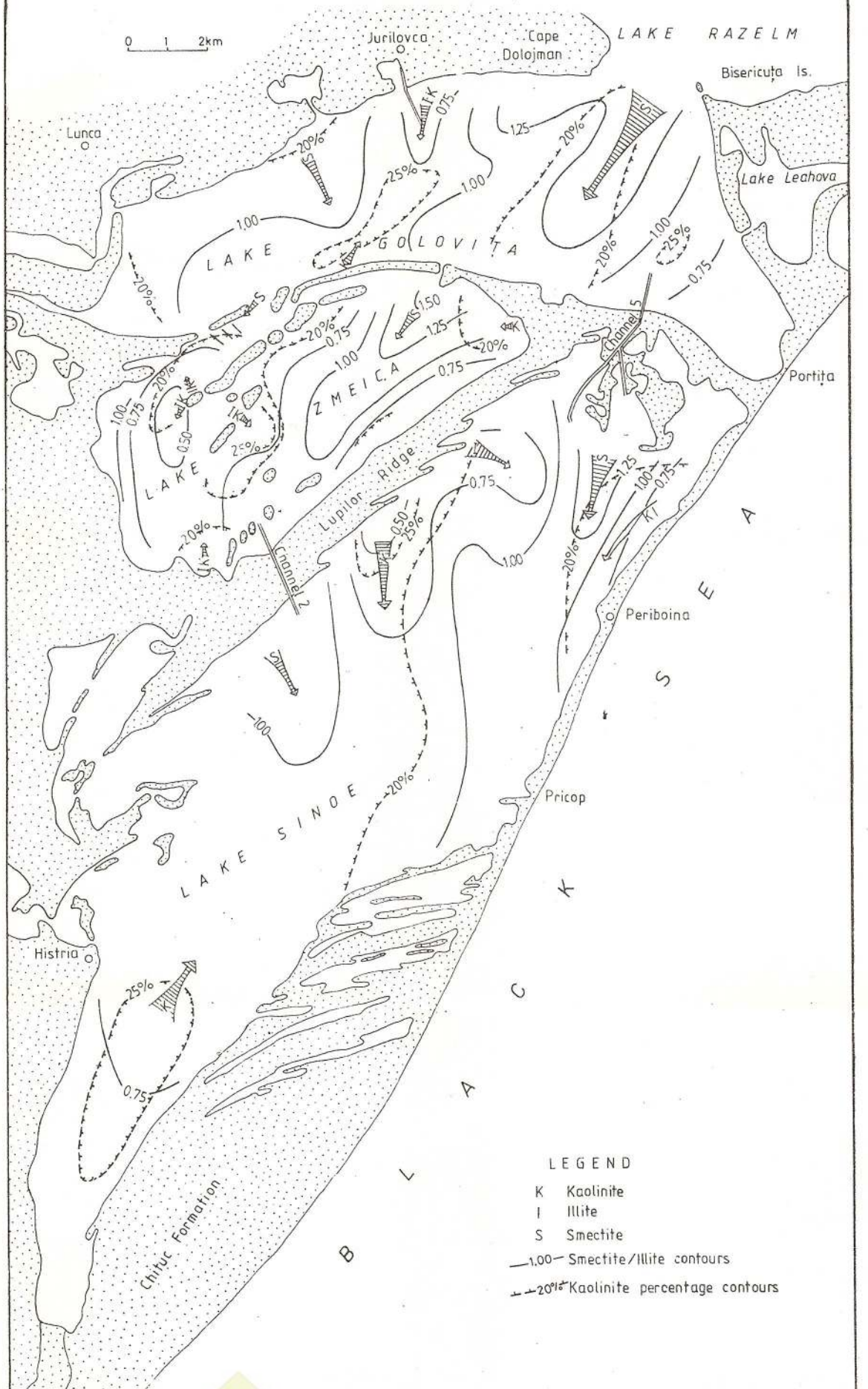
- Clay
- Silt
- Sand
- Loess deposits
- Paleo-Dunavăț Branch
- Fossil lacustrine ridges
- Fossil beach ridges

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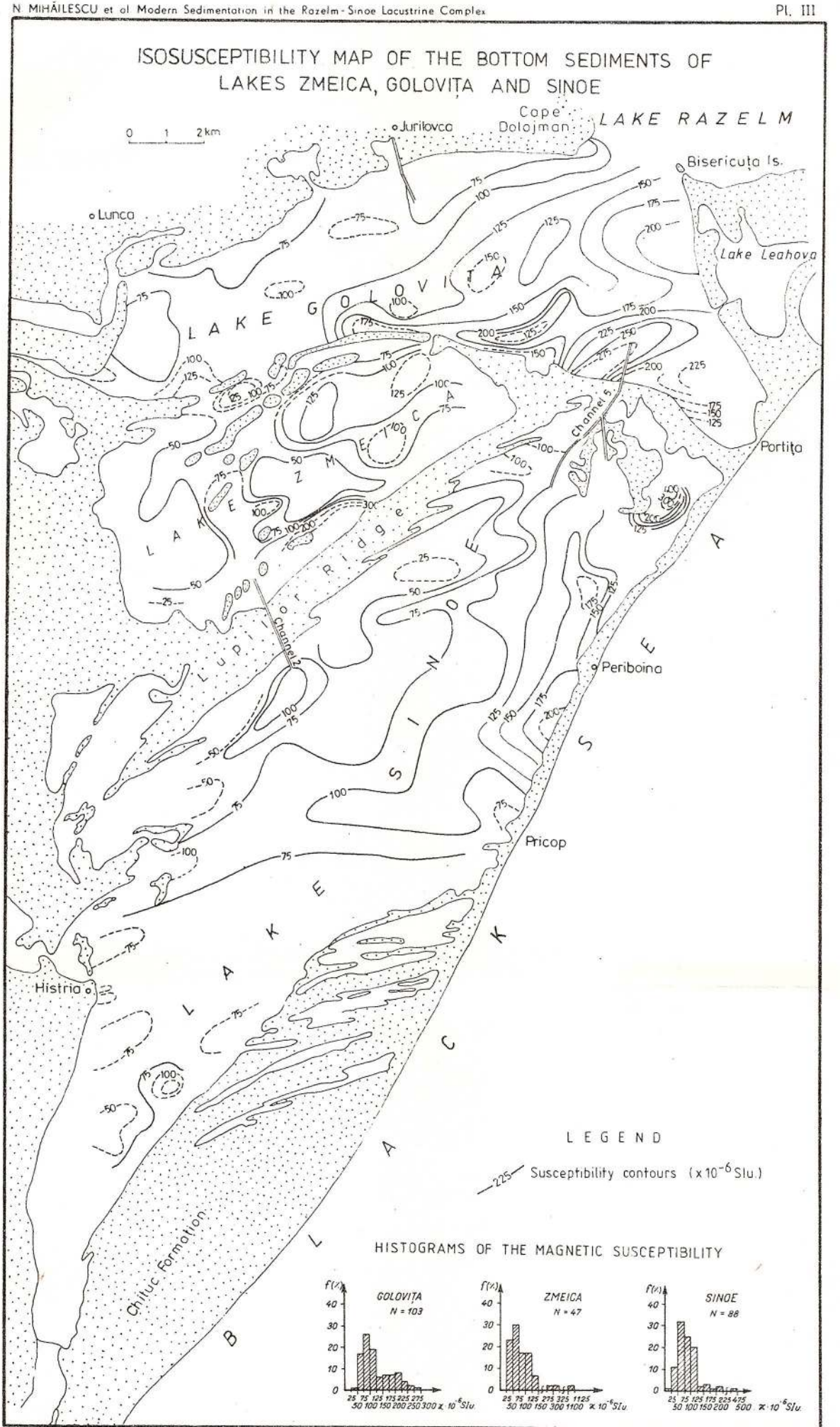
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CLAY MINERAL DISTRIBUTION IN THE BOTTOM SEDIMENTS OF LAKES ZMEICA, GOLOVIȚA AND SINOE



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ISOSUSCEPTIBILITY MAP OF THE BOTTOM SEDIMENTS OF LAKES ZMEICA, GOLOVIȚA AND SINOE



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UPPER CRETACEOUS TEPHRA RE-SEDIMENTATION IN THE SREDNOGORIE TROUGH [1]

BY

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Tephroidal rocks resulting from the re-sedimentation of tephra from synchronous subaqual volcanism in the Srednogorie trough in Bulgaria are discussed. Sedimentological studies revealed that part of the so called "Senonian tuffs and tuffites" are components of the tephroidal flysch (Nachev, 1976; Nachev et al., 1980), are of dominantly turbidite character (Nachev, 1978; Nachev et al., 1981) have flysch hieroglyphs and internal structures (Nachev, 1978; Nachev et al., 1981), are composed of volcanogenic components — lithoclasts, crystalloclasts, volcanic glass and matrix, but show textures analogous to clastic rocks (Nachev, 1978) and originated as a result of the re-sedimentation of tephra from synchronous subaqual volcanism (Nachev, 1976, 1978; Nachev and Sultanov, 1979; Nachev et al., 1980) in an epicontinental intra-arc trough with subaqual volcanism (Nachev, 1978, 1980; Nachev and Ianev, 1980; Nachev et al., 1980).

Tephroidal rocks are of interest in connection with the problem of sedimentation and volcanism or the influence of volcanism on the origin of flysch (Nachev, 1976, 1978; Aiello et al., 1977; Hvorova, 1980; Markevich, 1980).

Genetic Types of Tephroidal Rocks

The results of the sedimentological studies (Fig. 1) and the data on the mineralogic composition, textures and structures showed that the tephroidal rocks are determined by different re-sedimentation processes. They may be referred to four genetic types — tephra olistostromes, tephra fluxoturbidites, tephra turbidites with tephra laminites and tephra contourites.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, September, 8—13, 1981, Bucharest, Romania.

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Tephra Olistostromes. They are of local occurrence and are found in the Coniacian, Santonian and Campanian. The rocks comprise olistoliths of effusives or tuffs, small lithoclasts and arenitic to ashy matrix. Commonly they contain olistoliths of marls, limestones, tephroidal flysch. The structure is chaotic. The lower contact is mainly uneven and erosional while the upper one is sedimentary. The tephra olisto-

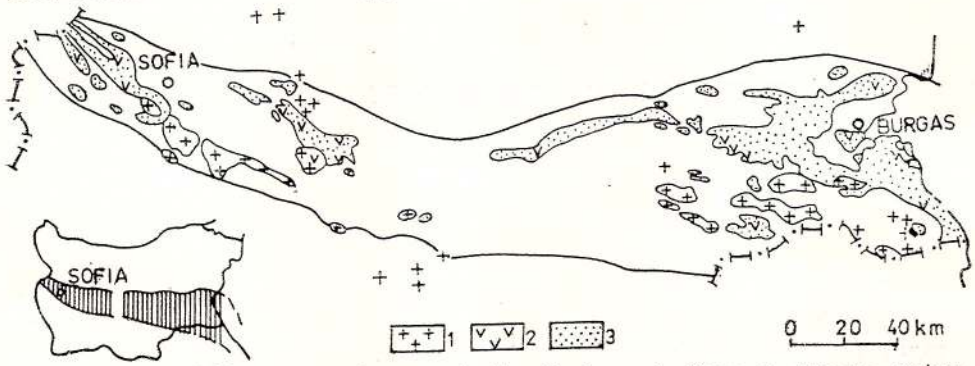


Fig. 1. — Distribution of rock types in the Srednogorie Zone. 1, igneous rocks; 2, volcanoes; 3, tuffs, tephroidal rocks.

stromes are found as beds and packets up to 100 m thick (Fig. 2). They originated as a result of submarine slumping of coarse tephra from volcanic centres towards the volcanic raises. They are of intraolistostrome character.

Tephra Fluxoturbidites. They are widespread in the Coniacian, Santonian and Campanian. The rocks are composed of lithoclasts of effusives, tuffs and tephroids, crystalloclasts of pyroxenes, plagioclases and rare hornblende, volcanic glass. The matrix is arenitic to ashy, rarely with admixtures of clayey and calcareous substance. The texture is ruditic to arenitic. The sorting is weak. The internal structures are indistinct, massif, rarely with weak graded bedding. Spherical weathering is typical and common. The lower contact is uneven with channels to regular. Tephra fluxoturbidites occur in beds, layers and packets ranging from 1 to 20 m thick, commonly from 5 to 10 m (Fig. 2). They were formed through the re-sedimentation of the ruditic-arenitic tephra. The mobilization occurred in the confines of volcanic centres. The transport was in the form of density grain flows along canyons in the slope. The re-sedimentation took place in the environment of slopes, volcano raises and in part depressions between volcanic centres.

Tephra Turbidites and Tephra Laminites. They are widespread and occur in the Coniacian, Santonian and Campanian. Contain a tephroidal component of basaltic, andesitic and trachyandesitic (latitic) composition. According to fragments they are litho-, crystallo- and vitroclastic (Fig. 2).

The lithoclastic tephroidal rocks are composed of fragments of effusive rocks (basalts, andesites, trachyandesites), volcanic glass and

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clayey-calcite or ashy cement. The volcanic glass is commonly altered to zeolites, chlorite, calcite, etc.

The crystalloclastic tephroidal rocks comprise mainly crystalloclasts of intermediate plagioclases (andesine, labrador), monoclinic

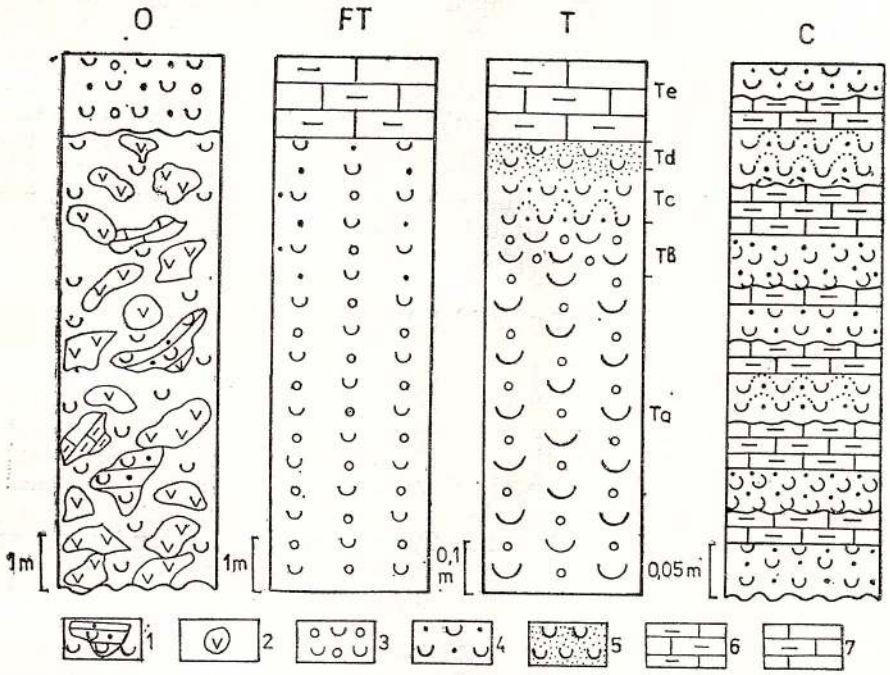


Fig. 2. — Genetic types of tephroidal rocks: O — tephra olistostromes ; FT — tephra fluxoturbidites ; T — tephra turbidites ; C — tephra contourites ; 1, breccia-conglomerates (olistostromes) ; 2, olistolites of effusive rocks ; 3, lithoclastic tephroidal rocks ; 4, crystalloclastic tephroidal rocks ; 5, vitroclastic tephroidal rocks ; 6, marls ; 7, argillaceous limestones

pyroxenes (augite, hypersthene), hornblende, biotite, fragments of volcanic glass, magnetite, etc. The cement is ashy or clayey-calcitic.

The vitroclastic tephroidal rocks are composed of fragments of volcanic glass, secondary chlorite, zeolites, albite, quartz, but comprise also crystalloclasts of plagioclases, augite, hornblende, etc.

The texture is arenitic to silty (2-0.1 mm), litho-, crystallo- and vitroclastic or mixed. The sorting is weak to good. The internal structures are massif, commonly graded bedding, lower parallel lamination, cross-stratification and convolution and upper parallel lamination. The structures on lower surface are channels, load casts, flute casts, bioglyphs, etc.

The tephroturbidites occur in the form of layers, beds and packets. The thickness is from 1 cm to 2 m, but commonly 0.1-0.7 m. The tephrolaminites show a thickness ranging from 1 cm to 0.1 m. They originated through the transport of tephra from volcanic centres,

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trough turbidity currents and deposition in volcano raises and in the depression parts of the basin.

Tephra Contourites. They are widespread in the Coniacian, Santonian and Campanian and comprise tephroidal components — crystalloclasts of plagioclases, pyroxenes, biotite, magnetite, volcanic glass and much calcite. The texture is fine-arenitic, silty and pelitic, crystallo-vitroclastic to vitroclastic. The sorting is good. The structure is fine-laminated, banded. The internal structures are parallel lamination, single-sloped cross stratification, wavy stratification, etc. The lower contact is irregular with channels and load casts. The beds are irregular, commonly pinching out, and the thickness is ranging from 1 mm to 4 cm (Fig. 2). The tephrocontourites are formed as a result of the transport and deposition of tephra by deep-sea bottom currents.

Tephroidal Flysch

The tephroidal flysch is composed mainly of tephroidal rocks with repeated alternation of marls, argillaceous limestones, tuffites and cherty rocks. The tephroidal rocks comprise re-deposited tephra ("pyroclastics") with the participation of lithoclasts of effusive rocks, tuffs, tuffites, volcanic glass, crystalloclasts of intermediate plagioclases, monoclinic pyroxenes, hornblende, biotite and magnetite, and ashy, clayey-calcitic or calcitic cement. There are basalts, andesites and trachyandesites lithoclasts. The crystalloclasts are broken, and the plagioclases commonly show zonal strucure. The volcanic glass is mainly sideromelane. The vitroclasts are commonly strongly porous — scoriae. Tachylitic glass is rare. As a result of halmyrolysis the sideromelane is partially or totally palagonized. The volcanic ash is in most places turned to zeolites. Part of the volcanic ash is partially altered to montmorillonite. These processes are diagenetic.

The relations between the rock components are strongly varying and the amount of cement is up to 40%. Lithoclasts dominate in tephroidal rocks with ruditic to coarse arenitic texture, crystalloclasts — in those with arenitic to silty texture and vitroclasts — in those with fine-silty and pelitic (ashy) texture (Fig. 3). According to the texture the tephroidal rocks are blocks, agglomeratic, lapillic, ruditic, arenitic, silty and ashy.

The tephroidal rocks form layers, beds and packets. They have a well expressed stratification. The lower surface shows erosional channels, load casts and flute casts. The internal structures are graded bedding, lower parallel lamination, cross stratification, convolution and upper parallel lamination. The tephra olistostromes have a chaotic structure. In tephra fluxoturbidites graded bedding is lacking or indistinct. The tephroidal rocks occur in the lower part of the flysch rhythms. The rhythms are of varying composition and structure. They are complete (Ta-e), truncated (Ta-d, Ta-c, Ta-b, Ta) or base cut-out (Tb-a, Tc-e). The thickness varies from 1 mm to 1 m ; for the tephra fluxoturbidites it is 10 m, and for the tephra olistostromes — up to 50 m (Fig. 2).

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In the thick tephroidal beds and packets there is a gravity to flotation distribution of the lithoclasts in the lower part, of the crystalloclasts — in the middle part and of the vitroclasts — in the upper

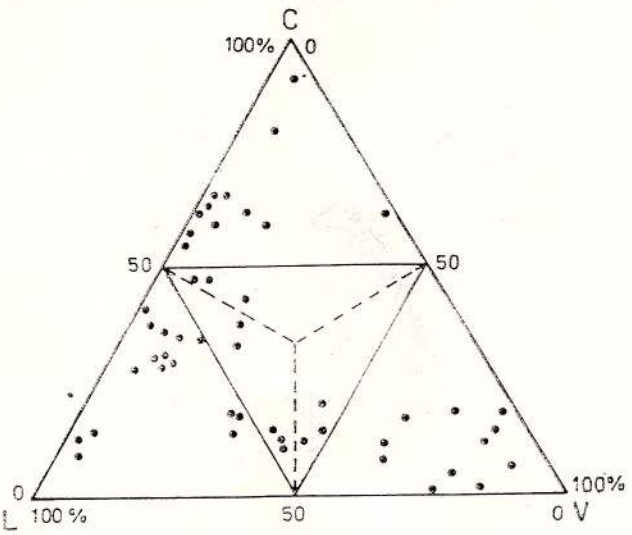


Fig. 3. — LCV diagram of tephroidal rocks : L — lithoclasts ; C — crystalloclasts ; V — vitroclasts.

part. Incomplete from top rhythms terminate with tephroidal rocks and the complete ones — with beds of marls or argillaceous limestones. The tephroidal flysch forms local rhythms and packets up to 2 000 m in thickness. It associates with marls, limestones cherty rocks (jaspers), tuffites, tuffs and effusive rocks, commonly showing features of pillow-lava flows.

Sedimentation Processes

The hemipelagic sedimentation from the Coniacian to the Campanian was a background process. It determined the deposition of marls and calcareous deposits in the Srednogorie trough.

The submarine Ca- to K-alkaline volcanism, mainly of explosive character, determined the formation of many tuffs and a small amount of effusive rocks. The explosive volcanic activity favoured the accumulation of huge masses of nonlithified tephra in the confines of the volcanoes. Individual volcanic centres were sources of tephra. The tephra was intensively mobilized, re-transported and re-deposited. The processes of superimposed tephra re-sedimentation were casually related to the seismic activity of the trough. The bottom currents were the main agent for the paleotransport of tephra. Paleocurrents formed above volcanic edifices. They flowed down along the slopes of the volcanoes.

Based on the genetic types of tephroidal rocks and tephroidal flysch four types of bottom paleocurrents have been distinguished — (1) tephra submarine slumping, (2) tephra grain flows, (3) tephra tur-

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bidity currents and (4) tephra contour bottom currents. The paleocurrents were the mechanical form of tephra transport. They were of different character and scale. In parts they were avalanches, which carried huge chaotic masses of tephra. Others were density grain flows.

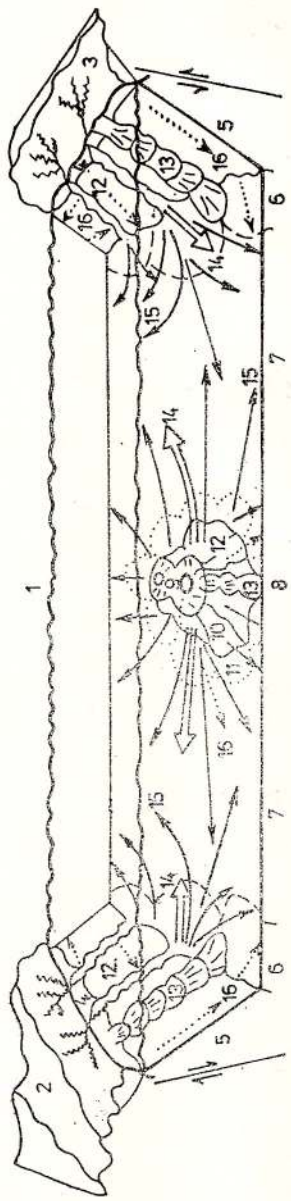


Fig. 4. — Model of the Srednogorie intra-arc trough : 1, sea level ; 2, southern, Macedonian-Rhodope arc ; 3, northern, Balkanide arc ; 4, shelves ; 5, trough slopes ; 6, trough raises ; 7, bottom part of the trough (depressions) ; 8, volcanic edifices ; 9, volcanoes ; 10, volcanic slopes ; 11, volcanic raises ; 12, canyons ; 13, submarine slumpings olistostromes ; 14, density grain flows (fluxoturbidites) ; 15, turbidity currents (turbidites and laminites) ; 16, deep-sea bottom currents (contourites).

The third had the character of turbidity currents. Probably the bottom paleocurrents carried the minimum amount of arenitic to silty tephra material.

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The paleocurrents transported the tephra from volcanic centres to inter-volcanic depressions. Probably episodic submarine canyons formed along the slopes. The individual paleocurrents had different directions. The radial and fan-like model of paleocurrents is indicated by data on paleotransport directions (Fig. 4).

The re-sedimentation of tephra occurred after the paleocurrents lost their transportation ability. This took place after a progressive decrease of the transport velocity.

The rate of tephra re-sedimentation was extremely high for the submarine slumping. It is high for the grain and turbidity currents and low for the deep-sea bottom currents. It determined the chaotic structure of the tephra olistostromes, the indistinct (tephra fluxo-turbidites) and distinct (tephra turbidites) graded bedding, as well as the structures of laminites and contourites.

The tephra re-sedimentation was a discrete process in time. It is superimposed upon the background clay-limestone sedimentation. This is indicated by the alternation of rhythms of tephroidal rocks with marls, limestones and lava flows.

Paleogeodynamic Environments

In the confines of the intra-arc Srednogorie trough (N a c h e v, 1978, 1980) the re-sedimentation of tephra was a discrete process in space. It was of perivolcanic (up to 50 km) localization. The paleo-currents re-deposited tephra on the volcanic slopes, the volcanic raises, intra-volcanic depressions and adjacent bottom parts of the trough. In case of close volcanic centres there was an interference of areas of tephroidal sediments. This phenomenon is well known from the eastern part of the Srednogorie trough. Distally from volcanic centres the tephroidal rocks interfinger and are replaced by marls and limestones or by deep-sea fans of greywacke-siltstone flysch which were deposited in northern and southern trough raises.

Through canyons huge masses of tephra accumulated in the volcanic raises. The re-sedimentation occurred from avalanche submarine slumping (tephra olistostromes) and density grain flows (tephra fluxo-turbidite). The chaotic pattern, the indistinct thick bedding and the large thickness of these lense-like bodies are characteristic of deep-sea fans, close to the source ("proximal"). The distal tephroturbidites, tephrolaminites and tephracontourites are characterized by distinct thin bedding and rhythmicity as well as by many flysch features. They were deposited in distal parts of the volcanic raises, intravolcanic depressions and the bottom part of the trough (Fig. 4).

The spatial localization of tephroidal rocks and flysch in the Srednogorie zone indicates as source of tephra volcanic centres in the axial bottom part of the trough but not in its southern marginal part (A i e l l o et al., 1977, p. 66, Fig. 20).

Conclusions

In the Srednogorie zone in Bulgaria there are diverse tephroidal rocks. In genetic respect they are tephra olistostromes, tephra fluxo-

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turbidites, tephra turbidites, tephra laminites and tephra contourites. They associate wtih marls, argillaceous limestones, cherts and other rocks and form packets of tephroidal flysch. Four interpretative types of bottom currents have been distinguished — submarine slumping, density grain flows, turbidity currents and contour bottom currents. The processes of tephra re-sedimentation are superimposed upon a background of hemipelagic clay-calcareous sedimentation. Volcanic centres with submarine, mainly explosive volcanism were the sources of tephra. The mobilized tephra was re-transported by paleocurrents with fan-like to radial directions. The re-sedimentation occurred upon volcanic slopes, volcano raises, intra-volcanic depressions and bottom parts of the intra-arc Srednogorie trough. The tephra re-sedimentation is determined by the subaqual volcanism and the seismicity of the trough. The subaqual volcanism had a strong influence on the sedimentation. The synchronous volcanism predestined the formation of the tephroidal rocks and the flysch as packets and zones around volcanic centres in the Srednogorie trough. The submarine volcanism within the intra-arc troughs was predestining the origin of tephroidal flysch.

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CONSIDÉRATIONS SUR LA GENÉSE DES SCHISTES ARGILEUX BIGARRÉS (VRACONIEN-TURONIEN) DU FLYSCH DES CARPATHES ORIENTALES DE ROUMANIE [1]

PAR

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Considérations géologiques sommaires. La formation des schistes noirs (=couches d'Audia, couches de Sărata ou couches de Streiu) du flysch des Carpathes Orientales est surmontée stratigraphiquement, dans les trois unités structurales (Audia, Tarcău et l'Unité des plis marginaux) par une autre formation, dont le coloris est à dominance rouge-vert, ce qui lui imprime le caractère spécifique de „série bigarrée". Dans la littérature géologique, la formation des schistes argileux bigarrés est connue sous différentes dénominations locales : la série des argiles bigarrées (Băncilă, 1958), les couches de Zagon (Filipescu, 1957) ou les couches de Bota (Marinescu, 1962) dans l'unité d'Audia, couches de Lupchianu (Dumitrescu, 1952) ou couches de Cîrnu-Şiclău (Băncilă, 1955), dans l'unité de Tarcău et les „argiles bigarrées" (Mirăuță et Mirăuță, 1964) ou couches de Tisaru „pro parte" (Dumitrescu, 1952, 1963) dans l'Unité des plis marginaux (les demi-fenêtres de Bistrița et de Putna-Vrancea).

La formation des schistes bigarrés de toutes les trois unités structurales est constituée surtout de schistes argileux rouges et verts, quelquefois gris ou noirâtres, auxquels s'ajoutent sporadiquement des arénites muscovitiques, des microrudites ou même des rudites minces, à l'exception de ceux de l'unité des plis marginaux (la demi-fenêtre de Bistrița).

À la partie inférieure des schistes argileux bigarrés, surtout dans les unités d'Audia et de Tarcău, se trouvent des tuffites et des tufs de nature probablement andésitique (le tuf de Poiana Uzului), avec une répartition spatiale remarquable. En étroite connexion avec le matériel cinéritique des tuffites et des tufs, on rencontre des roches sili-

[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

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ceuses (jaspes et radiolarites) en couches minces de 1-15 cm, renfermant de nombreuses concrétions de rhodocrosite, qui abritent des tests de radiolaires admirablement conservés et qui ont été assimilés — faute d'autres éléments paléontologiques — à un „fossile caractéristique" (P a p i u et al., 1976).

L'âge de la formation des schistes argileux bigarrés a été établi antérieurement, en vertu des restes d'organismes (*Belemnites*, foraminifères calcaires etc.) et a été attribué à l'intervalle Vraconien-Turonien (F i l i p e s c u, 1957 ; M a r i n e s c u, 1962 ; A l e x a n d r e s c u et S ă n d u l e s c u, 1973 ; A l e x a n d r e s c u et al., 1974, etc.).

Des études sur la lithologie de la formation des schistes argileux bigarrés ont été effectuées par B ă n c i l ă et P a p i u (1962) et, sur la géochimie, par S a v u l et B o t e z - P o s t e l n i c u (1950) et, plus tard, par I d r i c e a n u et al. (1967).

Les échantillons destinés à l'étude chimico-minéralogique proviennent des parties septentrionales et centrales des Carpathes Orientales, d'entre les vallées de Suceava et de Bistrița, surtout de la partie inférieure des schistes bigarrés. Le matériel rudito-arénitique, ainsi que les marnocalcaires de la partie supérieure de cette formation ne font pas l'objet de la présente étude.

Considérations chimico-minéralogiques. On a exécuté sur les échantillons prélevés des analyses chimiques complètes, des analyses thermo-différencielles (DTA) et RX. La corrélation de ces données nous a permis d'en déduir la constitution minéralogique. Dans le tableau 1 sont présentées les limites de variation et les moyennes pour les roches étudiées ; dans le tableau 2 sont présentées les valeurs récalculées pour la „fraction argilo-hématitique", après ce qu'on a déduit la teneur apportée par les minéraux clastiques et ceux carbonatiques. À la composition des schistes argileux de cette formation participent donc trois composants : le premier (clastique) est représenté par du quartz de dimensions siltiques jusqu'à luthitiques, de nature cristallophyllienne et des feldspaths (calculés sous forme d'albite), de nature autant détritique que pyroclastique. La fraction carbonatique est de nature organogène, provenant des restes d'organismes entièrement diagénisés, insaisissables au microscope et peut-être de nature organo-chimique aussi, résultant des processus de réduction des sulfates (pour les roches ferreuses).

Le composant argilo-hématitique, qui fait en effet l'objet de cette étude, est représenté par des hydromicas (présentés sous forme „d'illite"), kaolinite et chlorites de 14 Å. On a reconnu ça et là des structures mixtes (illite-chlorite et illite-montmorillonite). Il faut remarquer que les smectites ne sont rencontrées dans aucun échantillon bien que dans la formation apparaissent des intercalations pyroclastiques.

L'hématite apparaît exclusivement dans les roches de couleur rouge. À partir de la valeur du rapport Fe_2O_3 : FeO, les schistes argileux de cette formation ont été classifiés en deux groupes, notamment : les schistes argileux ferriques de couleur rouge, dont la valeur est plus grande que 3 (moyenne 6,5) et schistes argileux ferreux (dans

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TABLEAU 1

Limites de variation et moyennes

	Schistes argileux ferriques		Schistes argileux ferreux		Schistes argileux ferriques		Schistes argileux ferreux		
	Limites de variation	Moyennes	Limites de variation	Moyennes	Unité d'Audia	Unité de Tarcău	Unité d'Audia	Unité de Tarcău	Unité des Plis Marginaux
					Moyennes	Moyennes	Moyennes	Moyennes	Moyennes
SiO_2	55.5—78.2	62.91	57.1—72.3	64.72	60,29	70,12	64.60	63.49	66.20
Al_2O_3	8.7—20.5	17.88	7.2—21.4	15.91	19.72	12.81	17.27	17.54	12.46
Fe_2O_3T	3.0— 9.4	6.93	2.4— 9.5	5.10	7.28	5.96	4.56	6.72	4.79
Fe_2O_3	2.6— 8.4	5.69	1.0— 5.1	2.78	6.05	4.70	2.60	3.47	2.94
FeO	0.4— 1.8	1.12	1.3— 4.0	2.09	1.11	1.14	1.78	2.93	1.67
MgO	1.5— 3.1	2.12	1.3— 3.1	2.13	2.12	2.13	2.07	2.67	1.78
CaO	0.7— 2.1	1.04	0.7—13.0	2.21	1.08	0.95	1.18	1.13	4.67
Na_2O	0.4— 1.0	0.71	0.4— 1.2	0.73	0.73	0.65	0.74	0.63	0.58
K_2O	2.2— 3.7	3.22	1.8— 3.5	2.86	3.38	2.77	2.98	2.78	2.76
TiO_2	0.4— 0.8	0.63	0.4— 0.8	0,53	0.69	0.54	0.59	0.54	0.46
P.C.	3.3— 6.3	4.90	3.3—11.0	5.68	5.12	4.31	5.56	4.34	6.71
Illite	29.4—55.0	47.54	24.4—60.3	42,17	51.88	35.60	44.73	41.52	39.41
Kaolinite	5.8—16.8	9.57	0.0—17.4	7,28	10,93	5.82	8.89	10.21	2.21
Chlorite	1.3— 5.7	3.11	3.6—10.5	5.88	3.11	3.35	5.04	8.21	4.75
Hématite	1.0— 5.0	3.03	0.0— 2.4	0.23	3.16	2.67	0.49	0.72	0.18
Calcite	0.0— 3.7	0.91	0.0—23.2	3.25	0.86	1.05	1.12	1.03	8.30
Dolomite	0.0— 3.0	0.20	0.0— 3.6	0.65	0.27	0.00	1.17	0.60	0.00
Quartz + Calcédoine	17.0—59.2	27.03	15.8—53.3	35,22	21.06	43.42	31.80	29.53	40.45
Feldspaths	3.4— 8.5	6.08	3.8—10.4	6.04	6.62	4.60	6.31	6.86	4.93

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TABLEAU 2

Limites de variation et moyennes (composants argilo-hematitiques)

	Schistes argileux ferriques		Schistes argileux ferreux		Schistes argileux ferriques				Schistes argileux ferreux					
					Unité d'Audia		Unité de Tarcău		Unité d'Audia		Unité de Tarcău		Unité des Plis Marginaux	
	Limites de variation	Moyennes	Limites de variation	Moyennes	Limites de variation	Moyennes	Limites de variation	Moyennes	Limites de variation	Moyennes	Limites de variation	Moyennes	Limites de variation	Moyennes
SiO_2	55.1—60.4	56.8	53.1—60.8	57.7	53.9—60.4	56.1	57.0—62.6	59.3	55.1—60.3	58.1	53.1—59.0	56.1	57.7—60.8	58.9
Al_2O_3	24.7—33.1	30.6	28.7—36.3	31.2	30.3—33.1	31.6	24.7—29.5	27.8	30.2—36.3	32.3	29.4—33.9	31.2	28.7—32.3	30.2
Fe_2O_3T	11.8—15.2	13.0	6.8—16.7	11.2	11.7—15.0	13.6	12.2—13.4	12.7	6.8—13.8	9.8	8.1—16.9	12.8	9.3—15,7	11.5
Fe_2O_3	6.7—12.0	9.0	3.2—15,7	5.5	6.7—11.2	9.0	3.2—12.0	10.7	4.0— 5.0	4.3	3.2—15.7	7.1	3.9— 8.3	5.3
FeO	0.6— 2.9	1.8	2.4— 6.2	3.6	0.6— 2.9	1.7	1.7— 2.6	2.0	2.4— 3.6	2.8	3.2—3.6	3.4	3.0— 4.4	4.3
Illite	72.0—83.2	78.9	57.9—90.0	77.6	72.0—81.3	78.4	78.0—81.0	78.7	70.5—89.8	77.7	57.9—77.4	69.0	87.7—90.0	86.1
Kaolinite	10.2—25.3	16.1	0.0—21,5	12,1	12.8—20.3	18.1	10.4—17.7	14.1	13.0—21.5	14.5	11.2—17.9	15.9	0.0—12.4	3.2
Chlorite	2.2— 8.3	5.0	6.7—17.8	10.8	2.0— 8.3	4.7	4.3— 5.2	5.9	6.7—12.1	8.6	9.0—17.8	13.6	8.1—14.4	10.7
Hématite	2.3— 7.8	5.1	0.0—11.8	1.2	2.3— 7.1	4.8	5.1— 7.8	6.4	— —	—	— —	—	8— —	—

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lesquels cette valeur diminue), la moyenne étant de 1,3, leur couleur variant entre vert, gris et noir.

Il est à noter que, dans toutes les trois unités structurales (Audia, Tarcău et les Plis Marginaux), les valeurs des composants chimiques et minéralogiques sont du même ordre de grandeur, sauf les minéraux de fer (silicates, oxydes), les différences essentielles étant données par la variation des additions de matériel clastique et carbonatique. La différence principale entre les schistes argileux ferriques et ferreux est donnée par les formes minérales du fer. L'examen du tableau 2 met en évidence des valeurs moyennes rapprochées pour la silice et l'alumine, composants qui se trouvent en rapport inverse. Le fer total a une valeur plus élevée dans les schistes ferriques — dans lesquels il est sous forme d'oxyde — que dans ceux ferreux où la teneur en silicates (chlorites) est dominante. En ce qui concerne l'hématite, elle apparait pratiquement seulement dans les schistes rouges, dans lesquels elle est sédimentogène, les petites quantités trouvées en des certains schistes ferreux provenant de l'altération des chlorites.

Le chlorite et l'hématite présentent un rapport inverse, la kaolinite présentant, de l'autre part, la valeur moyenne plus élevée plutôt dans les schistes ferriques que dans ceux ferreux, dans lesquels elle manque de 5 échantillons.

L'illite présente des limites de variation plus grandes dans les schistes ferriques que dans ceux ferreux, mais les moyennes sont rapprochées, un peu plus petites dans les roches ferreuses.

Considérations pétrologiques. De la figure résulte le champ restreint de projection dans le cadre des principaux minéraux argileux des schistes argileux ferriques et le champ beaucoup plus large de répartition de ceux ferreux. Nous considérons que cette situation re-

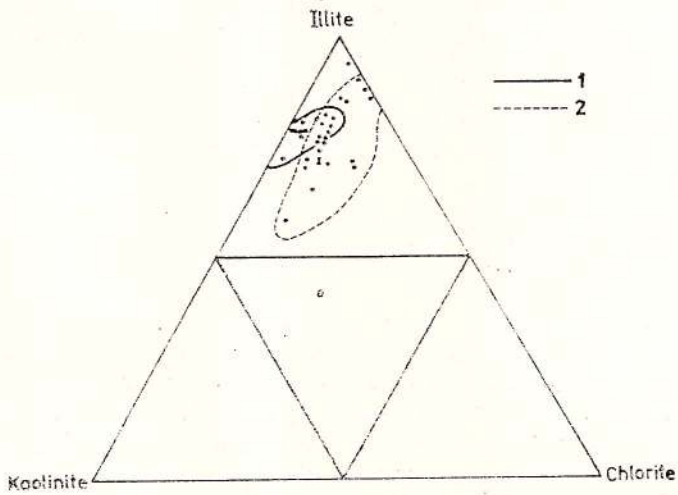


Fig. — 1, Champ de projection des schistes argileux rouges ; 2, Champ de projection des schistes argileux vert-noirs.

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flète, pour les premières, le caractère primaire des composants, et pour ceux ferreux — le degré d'évolution diagénétique.

À la lumière de ces données et tenant compte du fait que les schistes rouges et ceux verts — jusqu'aux noirs — alternent sur des épaisseurs assez petites, ainsi que du fait que la couleur verte „pénètre" parfois dans la masse des roches rouges, nous sommes arrivés aux conclusions pétrogénétiques suivantes.

Le matériel argilo-hématitique qui, près de celui clastique et de celui carbonatique autigène, a participé à la formation des sédiments qui sont la source des schistes argileux, provient d'une aire continentale à roches cristallophylliennes, sédimentaires et éventuellement pyroclastiques, issue des éruptions continentales, un peu avant la sédimentation.

L'altération latéritique sous régime sidérolitique avec des alternances de périodes chaudes sèches et humides déterminait des processus de kaolinisation et d'accumulation d'oxyde ferrique (hématogel) avancés. Ce matériel était déversé par voie fluviatile et peut-être éolienne dans le bassin de la mer vracono-turonienne, où il s'accumulait à côté du matériel détritique et de celui pyroclastique.

À cause de l'altération latéritique avancée, il est possible que les smectites, même si elles avaient existé, soient dégradées engendrant de la kaolinite, elles apparaissant seulement dans les quelques structures mixtes mentionnées.

Sous conditions oxydantes, le fer se maintenait sous forme d'hydroxyde et la kaolinite et l'illite s'accumulaient comme tel. En conditions réductrices, la forme ferrreuse dominait et se déroulaient des processus d'agradation, les kaolinites, les smectites et même les hydromicas évoluant vers des chlorites ferrifères. De tels sédiments sont issues les argiles vertes et grises. Si les conditions réductrices étaient plus avancées, dans la présence de la substance bitumineuse et de la monosulfure ferreuse, se formeraient des sédiments pélitiques qui auraient engendré les schistes argileux noirs, rappelant la formation sous-jacente des schistes noirs — couches d'Audia. Cette dernière situation a caracterisé à prédilection, semble-t-il, la partie du bassin de sédimentation duquel ont résulté les schistes argileux dans l'Unité des plis marginaux, où les schistes argileux rouges sont moins représentés.

En phase de diagenèse primaire et sous des influences lithostatiques, les solutions réductrices ont migré dans la masse des sédiments hématitiques, en réduisant le fer et donnant naissance à des zones chloritiques de couleur vert-gris.

Pour conclure, dans la mer du flysch crétacé (Hauterivien supérieur-Albien), après la sédimentation anaérobe de la formation des schistes noirs (=couches d'Audia) au niveau du Vraconien-Turonien suit, en continuité de sédimentation, l'accumulation des dépôts argilo-détritiques en conditions variables dans lesquelles les phases aérobes oxydantes alternent avec des phases plus pauvres en oxygène, aspects réflétés par la constitution chimico-minéralogique et la couleur des dépôts argileux. En même temps, avaient lieu des apports pyroclastiques qui s'accumulaient soit directement en milieu marin, soit sur

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le continent, où l'altération sidérolitique les réduisait à kaolinite et oxydes ferriques. Telles ont été les conditions d'accumulation du matériel originaire qui, dans le milieu marin, évoluaient par agradation, vers illite et éventuellement chlorite, selon le potentiel redox des eaux au moment considéré. L'illite peut donc être remanié et formé aussi par voie autigène, par agradation.

La partie supérieure de la formation des schistes argileux bigarrés (couches de Bota — couches de Cîrnu-Şiclău) finit avec des sédiments à dominance calcaire, accumulés sous des conditions d'oxygénation variables. Les organismes calcaires trouvent des conditions favorables de développement (foraminifères calcaires du type des globotruncanes), à différence de la partie inférieure mentionnée, où les conditions de développement des organismes ont été beaucoup limitées.

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QUESTIONS

Gr. Pop. 1. Si les auteurs ont reconnu d'autres produits de l'altération continentale accumulés conjointement avec l'hématite et la kaolinite ?

2. Il est intéressant de savoir également si l'hématite est accompagnée par d'autres oxydes de fer ?

Réponse : 1. On a mentionnée dans l'exposé que dans la composition des roches apparaissent aussi d'autres minéraux argileux et de précipitation, comme par exemple les hydromicas (illite) mais nous ne pouvons pas mentionner s'ils proviennent des processus d'altération continentale ou sont remaniés des dépôts préexistents (ce qui est plus probable).

2. L'hématite est accompagnée quelquefois de la goethite, produit secondaire d'altération hypergène.

E. Dudich : Est-ce qu'il y a une connection observée entre la teneur en substances organiques et en soufre et l'EH ?

Réponse : Evidemment ! Mais, dans nos études nous n'avons pas fait de déterminations d'EH qui nous permettent une analyse minutieuse du problème.

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CONSIDÉRATIONS GÉNÉRALES SUR LA CONSTITUTION ET SUR LA GENÈSE DES BAUXITES DE ROUMANIE [1]

PAR

VICTOR C. PAPIU [2], VASILE IOSOF [3], SILVIA MÎNZATU [2], GHEORGHE MANTEA [2], CONSTANȚA UDRESCU [2]

Les bauxites de Roumanie sont cantonées dans le secteur occidental des Carpathes (Monts Apuseni et partie occidentale des Carpathes Méridionales) (fig. 1). Elles reviennent en exclusivité aux bauxites karstiques et sont d'âge crétacé, tout en marquant, pendant cette période, une série d'intervalles continentaux caractérisés par des processus d'altération et de sédimentation de type sidérolitique. Tenant compte des critères minéralogiques, stratigraphiques et génétiques on a établi deux grands groupes de bauxites :

A) *Bauxites autochtones* — résultées des précipitations physico-chimiques dans les dépressions paléokarstiques ; ce sont des roches sans stratification, dépourvues de matériel détritique, en exclusivité diasporiques, d'âge néocomien inférieur (faciès wéaldien), plaquées aux calcaires récifaux de la partie supérieure du Malm (faciès de Stramberg). Il s'agit des bauxites du massif de Pădurea Craiului, de Remeți, du Bihor Central, du Bihor Septentrional-Vlădeasa (synonyme du Graben de Someșu Cald, Monts Apuseni) et probablement de celles du massif de Poiana Ruscă (Carpathes Méridionales).

B) *Bauxites allochtones ou détrito-chimiques* — résultées de la consolidation des boues bauxitiques (ou latéritiques) auxquelles s'ajoutent des minéraux résultés des précipitations ; ce sont des roches exclusivement bœhmitiques, rarement stratifiées ou schisteuses, comportant des minéraux détritiques et parfois de l'argile en quantité élevée. Elles sont plaquées aux calcaires de différents âges, marquant deux

[1] Note présentée au 12ème Congrès de l'Association Géologique Carpatho-Balkanique, 8—13 septembre 1981, Bucarest, Roumanie.

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niveaux sidérolitiques dans le Crétacé supérieur. Elles comportent deux groupes de bauxites :

a) bauxites d'âge albien accumulées pendant une phase sidérolitique précédant la transgression cénomanienne de la partie occi-

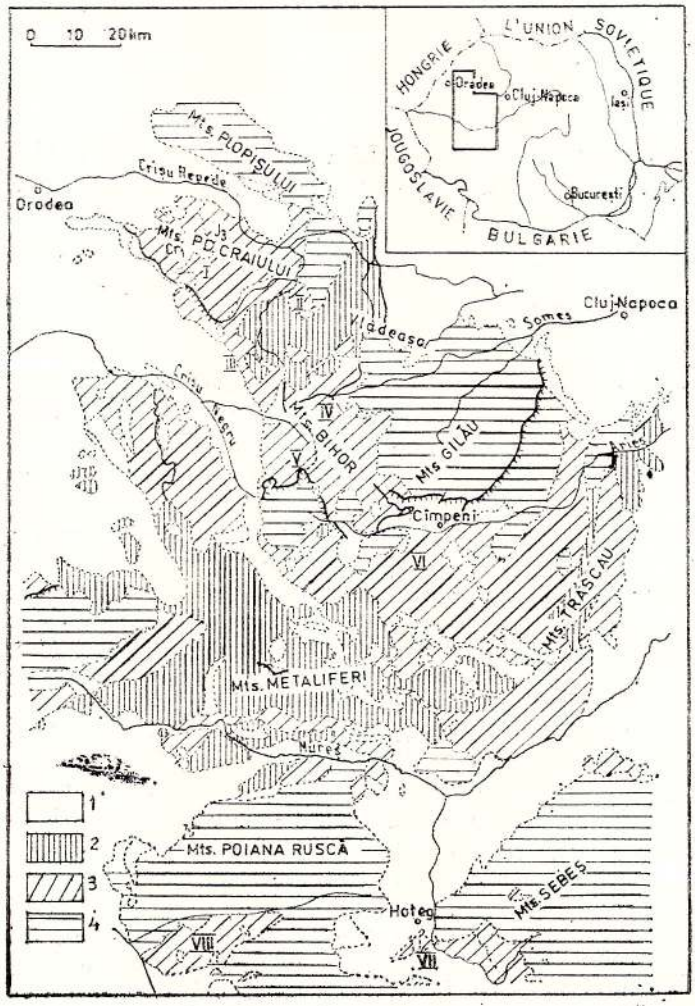


Fig. 1. — Emplacement structural-géologique des bauxites de Roumanie : 1, Formations tertiaires et quaternaires ; 2, Roches magmatiques hercyniennes ; 3, Formations paléozoïques et mésozoïques ; 4, Formations cristallophylliennes et granitoïdes ; Localisation des accumulations de bauxite. I. Partie centrale et nord-ouest des Monts Pădurea Craiului ; II. Grabenul Remeți (Monts Pădurea Craiului, est) ; III. Région de Meziad (Monts Pădurea Craiului, sud) ; IV. Vlădeasa septentrionale (Monts Bihor) ; V. Bihor Central ; VI. Zone de Sohodol-Cimpeni (Monts Metaliferi) ; VII. Bassin de Hațeg ; VIII. Bassin de Rusca-Montană (Monts Poiana Ruscă).

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dentale des Carpathes Méridionales (bassin de Haţeg). Le mur de ces dépôts est représenté soit par des calcaires récifaux d'âge jurassique supérieur sous faciès de Stramberg, soit par des calcaires récifaux urgoniens, en temps que le toit est représenté par des dépôts argilo-détritique dont débute le Cénomanien marin ;

b) bauxites d'âge santonien de Cîmpeni-Sohodol (district d'Alba), situées à la partie basale de la transgression du Crétacé supérieur des Monts Apuseni. Elles sont plaquées aux calcaires cristallophylliens de la série de Baia de Arieş et sont surmontées par des sédiments de molasse, tantôt détritocharbonneux, tantôt à récifs d'hippurites.

Cette classification est valable pour les bauxites *str. s.* à „caractères primaires", sédimentogènes, avec une diagenèse avancée ou avec un faible début de métamorphisme.

Opposé à ce groupe, est le groupe des bauxites qui ont subi des modifications fondamentales et qui ont une constitution chimico-minéralogique résultée soit à la suite des influences endogènes (thermo-métamorphisme ou apports hydrothermaux), soit à la suite des influences exogènes (déferrifiées).

Au premier type reviennent les bauxites compactes, parfois corindoniques, du massif de Pădurea Craiului et de Remeţi autant que les roches kaoliniques, plus ou moins diasporiques, de ce même massif et tout spécialement les corindonites pyriteuses de Poiana Ruscă. Au second type reviennent les bauxites déferrifiées, fréquentes dans le massif de Pădurea Craiului.

Les bauxites à „caractères primaires" du premier groupe ont été attribuées, en fonction du rapport $Fe_2O_3 : FeO$, à trois sous-groupes géochimiques : ferriques (plus de 20), ferroferriques (20-4) et ferreuses (moins de 4). Ces groupes sont évidents dans le massif de Pădurea Craiului. Les roches sont caractérisées par des couleurs définies : celles ferriques sont rouge foncées ; celles ferroferriques sont rouges ou brunes (à hématite et goethite) ; celles ferreuses sont vertes ou noires (à chlorites ou à hydrotroïlite accompagné de matériel charbonneux et de bitume). Les bauxites à „caractères sécondaires" du Bihor Central et du Bihor Septentrional-Vlădeasa, présentent ce caractère imprimé par un faible métamorphisme thermique, rattaché au magmatisme banatitique qui a engendré la chlorite aux dépens de l'hématite et de la kaolinite. Les bauxites ferreuses de Poiana Ruscă, comportent de la chlorite, malgré leur couleur rouge imposée par le pigment hématitique.

Les bauxites allochtones, ferriques et ferreuses, de Cîmpeni-Sohodol, présentent le caractère sédimentogène primaire, alors que celles ferroferriques sont partiellement déferrifiées.

Les bauxites en exclusivité ferriques du bassin de Haţeg presentent des transitions jusqu'aux argiles proprement-dites, plus ou moins bœhmitiques passant vers la partie supérieure, à des grès et des microconglomérats à ciment argilo-ferrugineux (complexe bauxitifère).

Du point de vue minéralogique, les bauxites de Roumanie sont constituées par les minéraux de la triade : aluminium — fer — titane,

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auxquels s'ajoute la silice (dans les minéraux argileux) et, moins souvent, le soufre (dans les sulfures ferreux). Les oxyhydroxydes d'aluminium prépondérants sont : le diaspore et la bœhmite. Sporadiquement apparaît la gibbsite, secondaire.

Le minéral argileux omniprésent est la kaolinite et rarement la dickite (dans les argiles bauxitiques de Haţeg) auxquelles s'ajoutent, tout spécialement dans les bauxites ferreuses, les septéchlorites.

Le fer apparaît, de manière prépondérante, fixé sous forme d'hématite (hématogel) et de manière subordonnée sous forme de goethite dans les bauxites oxydées et sous forme de sulfure ou de sidérite (Sohodol-Cîmpeni) et de chlorite, dans les bauxites ferreuses.

Le titane apparaît exclusivement sous forme d'anatase et subordonnée de rutile dans les roches plus ou moins métamorphisées. Les bauxites de Sohodol renferment parfois des charbons à côté de teneurs élevées en pyrite.

La structure ooïdale est caractéristique pour les bauxites du Crétacé inférieur, alors que dans celles du Néocrétacé la structure est pélitomorphe et, dans quelques cas, comme dans celles schisteuses de Poiana Ruscă, vaguement détritique.

Le tableau compréhensif révèle les teneurs moyennes des principales bauxites du territoire de Roumanie :

La teneur en alumine varie faiblement : entre 50 et 60% dans les bauxites wéaldiennes ; entre 45-52% dans celles crétacées supérieures ; supérieure à 70% dans celles déferrifiées et supérieure à 60% dans celles intensément métamorphisées de Poiana Ruscă.

Les mêmes conclusions sont valables aussi pour les minéraux de l'alumine, le diaspore dans les premières (la bœhmite n'apparaissant que dans les bauxites ferroferriques et tout spécialement ferreuses du massif de Pădurea Craiului), et la bœhmite dans les secondes où, par contre, le diaspore est sporadique. Les bauxites faiblement métamorphisées à la suite des processus thermique et hydrothermaux sont, en exclusivité, diasporiques. Dans celles profondément métamorphisées apparaît en abondance le corindon (Poiana Ruscă). Dans les bauxites normales de Pădurea Craiului l'alumine est en rapport direct avec la silice et en rapport inverse avec le fer total et naturellement en rapport direct avec le fer bivalent dans les bauxites à caractère ferreux. Le rapport entre le fer bivalent et celui trivalent est inverse dans tous les cas. La corrélation inverse se manifeste aussi dans les bauxites faiblement métamorphisées de Meziad et du Bihor Central, déterminée par des apports secondaires de fer bivalent (à côté de la silice), et une baisse dans le Bihor Septentrional-Vlădeasa et dans les bauxites de Poiana Ruscă, par rapport aux autres bauxites (nous avons admis l'existence de quelques processus de déferrification).

Dans les bauxites détritochimiques de Sohodol le taux en alumine baisse proportionellement avec le degré de déferrification, par rapport auquel le fer total monte et le fer bivalent augmente remarquablement. On constate une indépendance entre le taux en alumine et celui en silice. Les bauxites de Haţeg sont toutes ferriques et contiennent le

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plus élevé taux en fer de toutes les bauxites examinées, présentant des transitions jusqu'aux argiles kaolinitiques ; la limite a été tracée, de manière arbitraire, à 50%. Les bauxites détritochimiques sont plus pauvres en alumine et plus riches en silice que celles autochtones.

Les plus élevés taux en alumine présentent les bauxites déferrifiées du massif de Pădurea Craiului et de Sohodol ; parfois les premières sont déferrifiées à cause de la lévigation du fer, conduisant soit à d'authentiques „diasporites" soit à des argiles kaolineuses (déferrification hydrothermale accompagnée de silication). Dans les bauxites ferriques prédomine l'hématite ; la goethite a le caractère secondaire, engendré par hydratation aux dépens du précedent. La goethite présente un caractère primaire seulement dans les bauxites brunes, ferroferriques et dans celles noires, ferreuses du massif de Pădurea Craiului (non-métamorphisées). Il y a des bauxites, tout spécialement celles ferreuses, où le fer bivalent est lié soit aux silicates (chlorite), soit à la pyrite, tandis que dans quelques bauxites de Sohodol il est lié à la sidérite.

Les minéraux argileux constituent le second groupe minéralogique dans lequel l'alumine est fixée, la kaolinite étant constamment présente (entre 2 et 10%). Font exception les métabauxites pyriteuses à corindon, de Poiana Ruscă et celles ferroferriques du Bihor Central.

Les chlorites, principaux minéraux à fer bivalent, sont représentées par les septéchlorites dans les bauxites sédimentogènes et dans le cas des bauxites ferreuses vertes du massif de Pădurea Craiului, auxquelles impriment cette couleur. Dans les bauxites faiblement métamorphisées apparaissent des chlorites de 14 Å, formées probablement aux dépens de la kaolinite et de l'hématogel. Leur taux varie, dans les bauxites néocomiennes, des valeurs sous-unitaires, dans les bauxites ferriques de Pădurea Craiului (et dans celles déferrifiées — environ 1%) jusqu'au maximum 30%, dans les bauxites faiblement métamorphisées ferreuses de Poiana Ruscă. Dans les bauxites allochtones, les chlorites font défaut ou présentent des valeurs sous-unitaires, excepté dans celles ferreuses de la région de Cîmpeni-Sohodol.

La pyrite est un minéral primaire seulement dans les bauxites ferreuses à charbons de la région susmentionnée et probablement dans celles ferreuses noires de Pădurea Craiului (à hydrotroïlite). Dans les autres bauxites elle est d'origine hydrothermale, rattachée au magmatisme banatitique.

Le métamorphisme thermique est responsable de l'apparition du corindon aux dépens du diaspore dans les bauxites massives pyriteuses, métamorphisées, de Poiana Ruscă.

Le titane présente une remarquable uniformité. Il est présent sous forme d'anatase, fin, dispersé dans toutes les bauxites et tout spécialement dans les bauxites métamorphisées, sous forme de rutile.

Dans les bauxites de Cîmpeni-Sohodol, dans les roches argilo-bauxitiques de Haţeg et dans les roches bauxitiques schisteuses de la partie supérieure des bauxites normales de Poiana Ruscă on trouve du matériel détritique représenté tout spécialement par des micas (muscovite, biotite plus ou moins chloritisée), du zircon, de la tourmaline,

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du rutile et rarement, à Sohodol, du quartz. La présence de ce matériel montre le caractère détritochimique des bauxites du Crétacé supérieur et de la phase finale d'accumulation des bauxites de Poiana Ruscă qui, outre la présence du matériel détritique, montrent aussi une texture stratifiée (schistes bauxitiques).

Dans les bauxites métamorphisées de cette région qui présentent une structure typique intersertale (baguettes diasporo-corindoniques et espaces intersticiaux comblés de pyrite) seule la présence de quelques lames remaniées de muscovite et des granules sporadiques de zircon, nous ont porté à conclure que nous n'avons pas affaire à une roche „saprolitique" résultée des diabases ayant subi le métamorphisme thermique et hydrothermal, mais à une bauxite *str.s.* métamorphisée.

Généralement, les ooïdes des bauxites autochtones présentent des formes normales, plus ou moins isométriques, constituées d'une à plusieurs couches concentriques. Les ooïdes de forme dénaturée due aux phénomènes de contraction ou de pression (spastoïdes) ainsi que les coïdes fragmentées à la suite des processus de remaniement, sont caractéristiques pour la coupe de Schireaua (massif de Pădurea Craiului). Ici, dans un affleurement épais d'environ 1,75 m et dépourvu de stratification, on a observé un passage graduel des bauxites rouges ferriques (hématitiques) de la partie basale, à des bauxites ferreuses vertes vers la partie supérieure, fait qui indique une baisse graduelle de la teneur en oxygène dans le milieu de sédimentation depuis le commencement jusqu'à la fin. Graduellement gagne la teneur en septéchlorites formées aux dépens de l'hématite ; le diaspore de la phase nettement oxydante fait place à la bœhmite qui, selon toute vraisemblance, caractérise la phase réductrice finale. En même temps apparaissent des fragments de bauxite ou d'ooïdes remaniées et de faibles teneurs en substances organique, révélant génétiquement la transition d'un milieu palustre, ou débute la sédimentation, à un milieu lacustre qui va culminer avec l'accumulation des calcaires micritiques à Carophytes, uniformément répandus dans le toit des bauxites de ce secteur des Carpathes.

Les bauxites détritochimiques présentent deux situations différentes. Celles santoniennes de Cîmpeni-Sohodol répètent en quelque sorte le schéma du rédoxypotentiel ci-dessus. À la partie basale on trouve des bauxites ferriques rouges hématitiques, alors que vers la partie supérieure apparaissent des bauxites ferreuses à sidérite ou à pyrite et charbons, indiquant des milieux nettement réducteurs de marais avec une végétation abondante. Leur structure est pélitomorphe, sans contenir les ooïdes pluriminérales propres aux bauxites wéaldiennes. Ce matériel détritique, parfois en quantités importantes (micas), autant que l'association avec des roches argileuses portent à conclure qu'elles se sont formées aux dépens des boues latéritiques rattachées au cristallin et aux granitoïdes voisins de Muntele Mare.

Les „complexes bauxitiques" albiens du bassin de Hațeg sont généralement associés à des argiles hématito-kaoliniques ; elles sont bœhmitiques et ferriques. Les successions lithologiques montrent des alternances de bauxites et d'argiles, dont les dernières apparaissent

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généralement à la partie inférieure et supérieure des complexes. Elles supportent des grès et des conglomérats fins à matrice argilodétritique. Cette situation suggère des séries gravitationnelles inverses.

Généralement, la teneur en éléments mineurs bauxitophiles se situe dans les bauxites de Roumanie, entre les limites de variation reconnues pour les bauxites karstiques. On remarque des teneurs plus élevées en zircon, les teneurs maxima étant dans les bauxites de Bihor Septentrional-Vlădeasa. Dans le cadre des bauxites de Roumanie se manifeste une distinction fréquente entre celles santoniennes de Sohodol, d'une part, et les autres bauxites d'autre part, différence mise sur le compte du caractère des roches primaires qui les ont engendré (granitoïdes). Ainsi dans ces roches prédominent quantitativement, par rapport aux autres éléments : le béryllium, l'étain et à coup sûr le lithium. Par contre, le chrome et le vanadium apparaissent comparativement en proportions réduites. Dans les bauxites de Roumanie, excepté celles de Sohodol, le gallium, le chrome, le vanadium et le nickel présentent une évidente corrélation positive par rapport à l'aluminium. Le métamorphisme, accompagné par des apports hydrothermaux de sulfures, entraîne, dans les bauxites de Poiana Ruscă des taux sensiblement supérieurs en nickel et cobalt.

Le lithium, dont la présence en quantités très variées se rattache tout d'abord au matériel argileux, présente la corrélation inverse vis-à-vis du rapport minéraux bauxitiques/minéraux argileux. Dans les bauxites de Sohodol cet élément a été concentré de manière remarquable indépendamment de la présence de l'argile, fait corrélable aux minéraux lithinifères de la roche mère.

Au point de vue génétique nous avons admis que les bauxites autochtones ont résulté de précipitations, de solutions électrolites ou colloïdales par le mélange avec les eaux bicarbonatées des calcaires karstifiés. Nous avons supposé que les bauxites allochtones proviennent de l'accumulation, dans des dépressions paléokarstiques, des boues initialement latéritiques ou bauxitiques, accompagnée aussi de processus de précipitation. En ce qui concerne les bauxites du Crétacé inférieur nous avons présumé que le matériel initial a été de nature pyroclastique, rattaché au magmatisme ophiolitique mésozoïque, caractéristique des Monts Apuseni. Nous admettons que les bauxites du Crétacé supérieur et quelques bauxites autochtones des Monts Bihor ont été engendrées aux dépens d'un matériel latéritique d'origine granitique ou gneissique.

Le diagramme de la fig. 2 (d'après O z l ü, 1978) met en évidence cette constatation. Le décalage qu'on remarque entre la ligne de corrélation tracée par l'auteur et celle obtenue pour les bauxites de Roumanie (en pointillé) vient de l'excès en zirconium qui a été introduit dans le calcul du coefficient (R) d'accumulation des éléments mineurs.

Les intervalles post-orogènes pendant lesquels ont pris naissance les bauxites du territoire de Roumanie se rattachent, dans le cas des bauxites autochtones, aux mouvements orogéniques cimmériens récents (bauxites wealdiennes) et, dans le cas des bauxites allochtones, aux

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TABLEAU SYNTHETIQUE

La constitution chimique et mineralogique et le contenu en elements mineurs des bauxites roumaines

	BAUXITES AUTOHTONES													BAUXITES ALLOHTONES			
	Pădurea Craiului Nord			Pădurea Craiului Sud Meziad			Bihor Central			Bihor septentrional Vlădeasa			Poiana Ruscă		Sohodol			Haţeg
	Ferriques	Ferro-ferriques	Fer-reuses	Ferri-ques	Ferro-ferriques	Fer-reuses	Fer-riques	Ferro-fer-riques	Fer-reuses	Ferri-ques	Ferro-ferri-ques	Fer-reuses	Fer-reuses	Meta-mor-phis-ées*	Fer-riques	Ferro-ferriques**	Fer-reuses	Fer-riques
Al_2O_3	53,6	56,3	59,4	59,8	58,8	56,0	55,9	60,9	51,2	57,2	53,0	51,4	54,4	61,6	52,2	49,9	44,5	50,5
Fe_2O_3	27,4	18,4	13,6	18,7	18,0	18,2	21,3	19,6	16,2	25,0	24,3	16,4	10,2	1,8	23,7	14,0	6,2	29,8
FeO	0,5	3,2	5,2	0,3	1,6	5,2	0,7	2,2	7,5	0,7	1,7	6,3	16,3	2,7	urme	0,4	10,0	0,2
TiO_2 **	2,7	3,0	3,3	2,9	2,4	2,7	2,7	3,1	2,7	2,5	2,5	2,6	2,6	3,0	2,7	2,6	2,1	3,6
SiO_2	3,9	5,7	7,9	5,5	5,6	5,3	3,8	1,5	8,5	3,7	3,5	8,0	8,9	1,1	6,7	14,7	7,6	2,8
Fe_2O_3T	27,9	21,9	14,2	19,0	19,4	24,2	22,1	22,0	24,5	25,8	26,2	23,4	21,8	19,4	23,7	15,3	21,7	30,0
Al_2O_3/SiO_2	13,7	9,9	7,5	10,9	10,5	10,6	14,7	40,6	6,0	14,2	15,1	6,4	6,1	56,0	7,8	3,4	5,8	18,0
Diaspore	51,6	42,4	19,3	66,3	64,1	61,9	62,0	69,9	53,4	59,6	59,4	53,9	55,0	36,7	5,3		0,7	
Boehmite	7,5	18,4	43,0										1,2		49,2	45,7	45,7	57,6
Kaolinite	8,1	9,1	11,7	8,4	9,5	2,6	7,0	0,9	5,9	6,8	4,2	6,5	2,5		11,7	30,3	7,0	7,1
Chlorite	0,5	6,2	10,2	0,8	4,4	14,6	2,1	6,3	20,4	2,1	4,2	17,9	29,2	8,1		0,4	4,0	0,6
Hematite + Goethite	25,3	18,3	8,6	10,1	11,5	5,8	21,5	19,7	16,2	25,7	25,1	17,1	8,9	1,5	23,7	15,6	6,0	30,9
Ga	43	44	44,6	63	51	47	58	49	55	62	62	60	47	54	51		57	46
Sn	11,9	13	13,8	14	7	7,7	18,6	9,5	15	18	17	17	8,4	9,3	34		37	8,2
Cr	405	409	483	408	365	352	392	388	378	286	272	231	244	227	120		97	216
V	372	339	496	382	312	286	401	357	406	356	361	364	562	593	238		206	370
Sc				44	43	49	44	47	48	51	51	40	54	54,5				
Be	10,5	11,7	8,2	10	8,2	8,5	6,9	7,5	6	8,7	7,5	6,8	5,4	7	13		9	7
Zr	808	815	713	720	625	661	822	762	784	1550	1564	1202	585	807	625		723	733
Nb				73	72	66,5	52	81	60	64	62	57	50,5	61				
Ni	138	249	136	93	120	137	97	125	85	80	134	144	195	462	130		149	134
Co	<20	<20	20	21	19	17	11,5	26	10	12	21,5	22	31	50	32		10,5	17,5
	−72	−66	−47														−70	−74
Li	<5− 675	22− 198	14− 198	16−86	36−86	67− 110	5−24	10−72	13−86	4−315	56−88	61− 126	93− 400	34−67	270− 6600		88− 1200	6−650

* Contient 29,4 % Corindonj 22,6 % Pyrite (10,8 % Fe et 11,8 % S).
** TiO_2 sous forme d'Anatase.
*** Partiellement dèferrifiées.

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mouvements autrichiens (mésocrétacés), en ce qui concerne les bauxites albiennes (Haţeg), et aux mouvements laramiens en ce qui concerne les bauxites santoniennes (Cîmpeni-Sohodol).

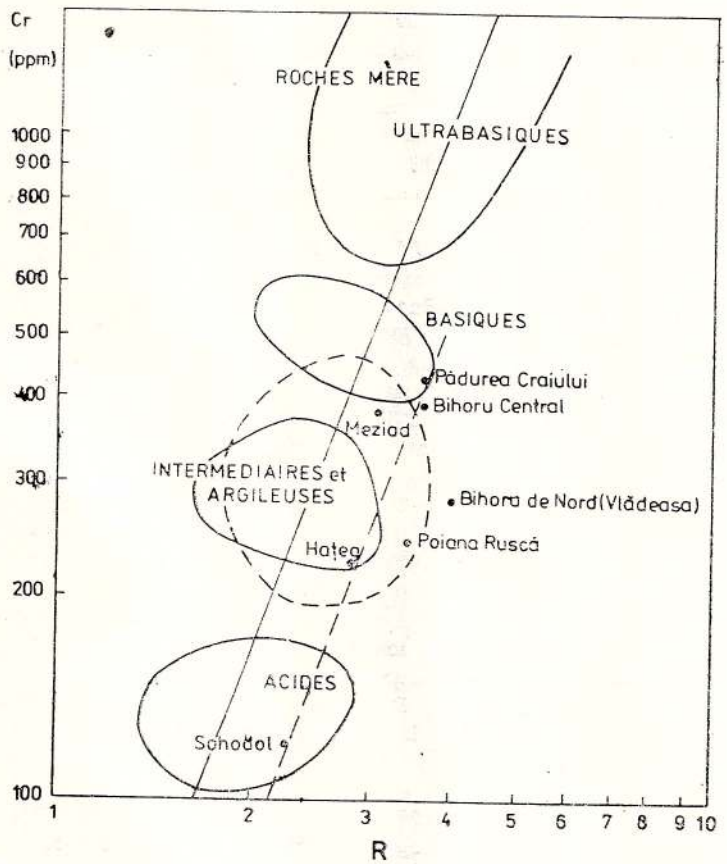


Fig. 2. — Emplacemnt des bauxites roumaines dans le diagramme Cr-R (coeffiicient d'accumulation d'Ozlü, 1978).

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QUESTIONS

E. Dudich: V. Papiu et coll., ont fait des études complexes et exemplaires sur les bauxites de la Roumanie. En Hongrie nous sommes très intéressés de la comparaison entre les bauxites de deux pays. On sait que les différences entre les bauxites de la Montagne Centrale de Transdanubie et celles de la Tran-

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sylvanie sont considérables. Cette année nous avons eu l'opportunité de faire une étude préliminaire sur les bauxites des Monts Villány (SE de Transdanubie) et des Monts Apuseni. J'invite les collègues roumaines à une collaboration pour comparer les bauxites de Sohodol, Haţeg, etc., avec quelques gisements plus ou moins analogues de la Hongrie.

Réponse : Nous serons enchantés de connaître les résultats de cette étude comparative et même de collaborer.

G. Pop : Il est intéressant de savoir d'une manière plus détaillée le milieu physico-chimique de la concentration de l'aluminium du matériel latéritique accumulé dans les dépressions karstiques.

Réponse : On trouve des détails dans les travaux anterieurs de notre collectif.

A. Mindszenty : La classification présentée est fondée principalement sur la composition chimique et la distribution des éléments-trace. Nous voulons savoir s'il existe des différences de texture et de structure entre les groupes définis par les auteurs.

Réponse : Les bauxites néocomiennes-inférieures ont toujours une structure ooïdale et sont massives (pas stratifiées). Les très rares exceptions, celles crétacées, moyen-supérieures, ne présentent pas cette différenciation corpusculaire spécifique ; quelquefois, surtout dans la partie supérieure, elles présentent des indices d'orientation jusqu'à des aspects schisteux. Au contraire, la plupart des bauxites de Haţeg, principalement celles santoniennes de la région de Sohodol-Cîmpeni sont parfois stratifiées.

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INTERPRETATION AND RELATIONS OF DEVELOPMENT FOR PANNONIAN LITHOFACIES OCCURRING IN THE SOUTHERN PART OF THE GREAT HUNGARIAN PLAIN [1]

BY

ISTVÁN RÉVÉSZ [2]

The studied area is situated from the line of the river Körösök southwards (Fig. 1). The encircled area indicates the area of idealized block section.

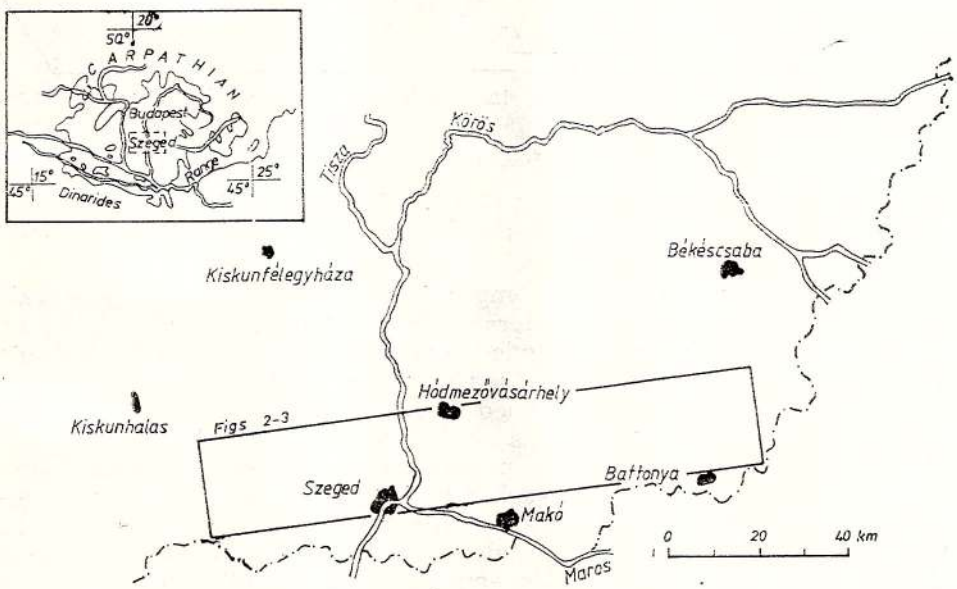


Fig. 1. — Sketch with the location of the studied area.

The bottom of the basin is composed of (Precambrian) metamorphic rocks, Paleozoic granites, quartz porphyries and Mesozoic sedimentary

[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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rocks (in depth about between 1000-1600 m). The sediments of the Miocene island-sea superimposed on these rocks with high sediment insufficiency (Fig. 2). Inundation of the area took place from the northwest direction.

The Miocene rocks have extremely varying nature from coastal conglomerates to pelites accumulated in the reductive deep water environment or rather to different carbonates.

Owing to relations on these rocks in history, it is particularly remarkable the existence of flysch type sediments characteristic of

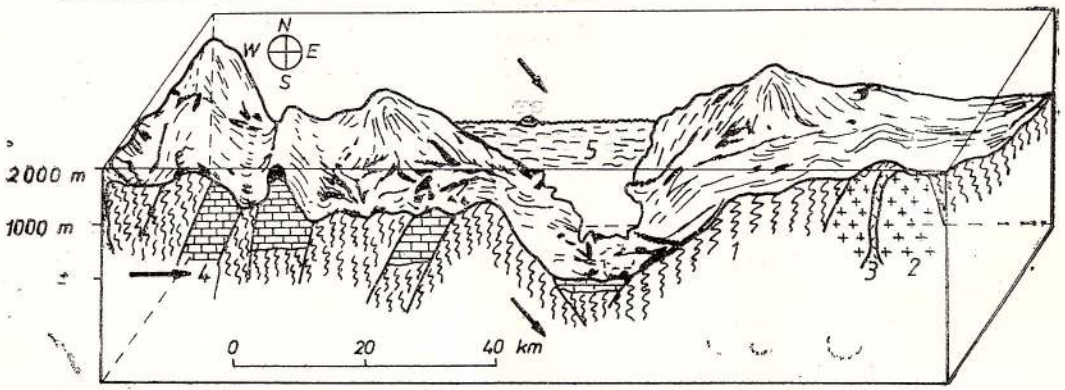


Fig. 2. — Schematic block section in the initial stage of the Miocene transgression (in Mucsi, Révész, 1975). 1, metamorphic; 2, granite; 3, quartz, porphyry; 4, sedimentary; 5, sea.

areas having deep structural position at that time and at present. The coarser sediments of deep areas were probably accumulated by turbidite flows.

The present faciological composition, grain size distribution bedding structures of them are referring to turbidite flow as well. Often angular, or rather slightly rounded quartz, quartzite and metamorphic pebble occurring in the fine-grained matrix are all related to a rapidly subsiding basin. It may be assumed that these pebbles, as regards their origin, are connected with islands of the Miocene sea and its coast lines. The marl and argillaceous marl pebbles have also frequent occurrence. The turbidite flows carrying such pebbles have ripped previously deposited clay sediments off their initial depositional place. The joint presence of two pebble types is also frequent. In the core descriptions all members of Bouma series do appear. Graded bedding, laminite, undulated and convoluted lamination alternate with nonstratified marl, argillaceous-marl and lime-marl strata. During the Badenian the turbidite flow was initiated by crust movements taking place in many stages, earthquakes connected with them and slope of the sea floor. At the intermediate rest periods the formation of argillaceous marl and marl may be connected to mainly geochemical causes source area, etc.

At the Sarmatian stage (sensu Suess), the formations of limestones, lime-marls and coastal conglomerates have been described. In

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the region of our deep basins, Sarmatian formations, as well as the boundary of Badenian and Sarmatian stages and especially the relation of two stages were not managed yet to determine. As regards classification into Sarmatian stage, this is carried out on the basis of decrease of individuals in faunal assemblages due primarily to the dominance of fresh-water influx.

We should say, the most part of the area has been permanently subsiding. The rate of the subsidence was variable in space and time. According to its environment, the Great Hungarian Plain has been

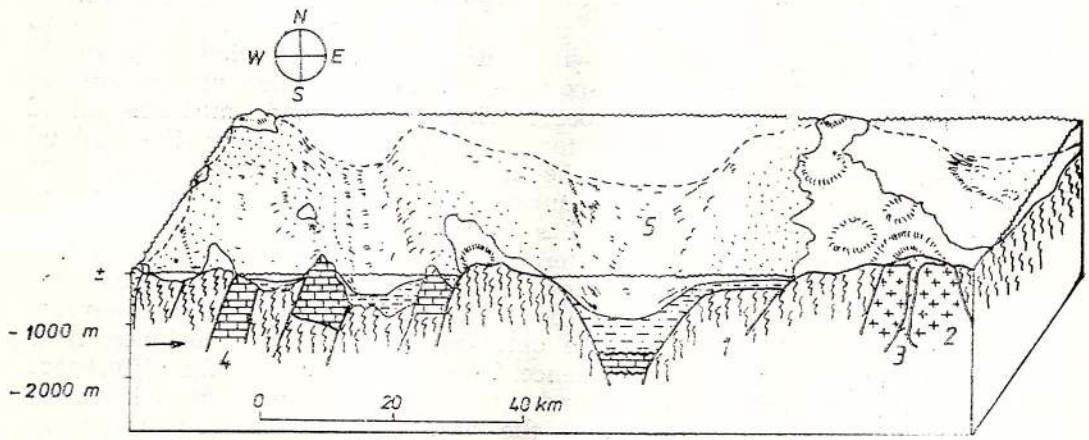


Fig. 3. — Initial stage of the Lower Pannonian. Schematic block section (in Mucsi, Révész, 1975). Legends : see Fig. 2.

considered until now as a depocenter. In the Carpathian Basin, the emergence of range of mountains resulted in depositional environments differring from that of the Great Hungarian Plain. This is the cause, that in this depocenter the counterparts of the fairly classical, well described series of the Middle Mountain area cannot be identified. It is considered unjustified to assume erosion periods and emergences on the basis of lack of marginal facies. We especially contradict to this, because the absence of the Sarmatian stage has been supposed primarily in the region of deep basins.

At the Miocene-Pannonian *(sensu lato)* boundary the absence of sediments, especially abrasion — erosion cannot be proved on the stratigraphical basis (Fig. 3). The boundary was dated by appearance of Limnocardies and Congeries, and by disappearance of Foraminifers The alteration of biofacies is not necessarily accompanied by change of lithofacies.

Our experience shows that other possible way of distinction can be based on the disappearance of pebble intercalations — disseminations connected with turbidite flows.

The disappearance of pebbles has not been caused by disappearance of turbidite flows, because this type of transportation continues to play an important part in the infilling the inner part of basin. The argillaceous-marl pebbles continuing to be present, as well

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as the grain size composition also refer to the presence of turbidite flows. It may be imagined, although a further consideration is required, that it has been caused by submergence of islands.

From among formations of earliest Lower Pannonian stage the coarse detritus is associated with islands of the Miocene island sea. Elsewhere, the earliest Pannonian formations of a borehole may be represented by sandstones, marls and argillaceous marls close to each other in space, but depending on facies.

In the studied area, the Pannonian basal conglomerate was intersected by a number of wells. Considering its grain size composition, in most cases this formation proved to be only coarse-grained — to medium-grained sandstones with pebbles. This formation only rarely close to the bottom of the sequence reaches the class of fine-grained conglomerates. Sometimes occur fine-grained and medium-grained conglomerate, even boulders too. In the sequence some fine-grained sandstones can be found, by the help of which the seemingly uniform sequence can be divided into sub-rhythms. In certain subrhythms, the whole conglomerate sequence has an upward fining tendency. In some places, subdividing the conglomerate is facilitated by impermeable intercalations with carbonate cement. As regards disposition of pebble materials with proportion of 1-40 per cent, orientation cannot be observed. Stratification (bedding) can be detected only in the sandstones, near to the upper boundary of sequence. This is due partly to the differences in grain-size distribution and partly to the presence of mica lamellae. The non-stratified nature and the grain size composition could be considered as an evidence of deposition in the abrasion zone. In the bore-holes drilled in deeper structural position a decrease in grain size distribution as well as reduction of pebble-fraction could be observed. Vertically, approaching the top of the sequence, similar changes could be observed. All these prove the increasing depth of the depositional agent or the changing conditions of the transporting energy. The formation of conglomerate strata is considered as a long lasting process. We are of the opinion that this process has begun along the coast of the Miocene islands in parallel to the gradual subsidence of the basin areas with variable rate, and this process has been transmitted to the beginning of the Pannonian sequence.

This conglomerate stratum is overlapping overlain by a calcareous marl containing pyritic plant residues, bacteriopyrite nodules. This stratum is separated from the coarse grained beds by transitional section with some metres thick (1-2 m) materials, composed of fine-grained sandstones, with carbonate matrix fine, and coarse-grained aleurolites and marls. The bedded, continuous transition is of frequent occurrence. As to the upper boundary, the stratification is also continuously bedded towards overburden with the dominance of argillaceous marl beds. Here the marl and calcareous marl alternate with continuous transitions, with the preponderance of argillaceous marl, then marl stripes also appear.

While the coarse-grained sedimentary sequence is related to relative elevations of the basement complex, the argillaceous marl is considered as a widespread formation. Where the Pannonian is thin

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(Ásotthalom, Kelebia, Battonya etc.) it has a bright-yellowish-grey colour and presumably it has formed not so far from the coast. In the deep structural regions, the blackish-grey, bacteriopyritic and pyritic marls and calcareous-marls with plant residues belong to the earliest Lower Pannonian sediments. These rocks were formed in the deep water, Euxinic environment, inherited from the Miocene.

The time range of the calcareous-marl formation also was determined by regions — islands, which successively had been submerged.

Summing up the calcareous marl as a chemical sediment is typical for shallow, medium deep and deep regions respectively and it has been formed during a long lasting period in the Lower Pannonian. The reduction — Euxinic — depositional environment is supposed only at the formation of calcareous-marls of medium-deep and deep zones.

The studies show that during the accumulation of Lower Pannonian sediments, the formation of the sediments has been determined by predominantly two flows systems, namely the system parallel to strike of the basin and following the morphology of the bottom and the turbidite flows more and less perpendicular to this system. The effects of these two flow systems are mixing with each other in the sandstone sediments. The sediments of "free" of flow periods, are argillaceous marl and siltstone beds. The proportion of the sandstone beds in the sequence amounts about 15 per cent.

Studying the grain size compositions in the deep basins, it appears that the sandstone beds at the end of the lower third of the Lower Pannonian have a finer nature. This is attributed partly to the disappearance of the pebble materials, and simultaneously it represents, or rather means more compensated energy conditions. It is probable that the accelerated subsidence at the beginning of Lower Pannonian period, the rate of which considerably exceeded the rate of deposition, had reduced to the middle third part of the Lower Pannonian, but the influence of the subsidence still had predominant feature.

The sediments (deposits) continued to be transported by deep lake — axial — flows and turbidite flows. The subsidence of the basin had continued longer, but the rate of the deposition more and more approached the speed of the subsidence.

The course of the evolution in the upper third part of the Lower Pannonian period has changed and the infilling of the basin from the coastlines is beginning with high rate. On the margins of the basin the rate of the deposition is higher at this time than that of the subsidence. It has been proved by occurrence of the siltstone pebble and imprint of the ardous leaf in the similar core from the interval between 2800 to 3000 meters of bore-hole No. Hód-I. Above 2800 m, the siltstone pebbles disappear, indicating the decrease of the role of the turbidite flows, the leaf-imprints however of the calmer and shallower waters, could be found in a number of cores.

The thin Lower Pannonian sequences of the southern part of the Great Hungarian Plain do not contain, or rather scarcely contain sandstone interbeddings. The cause of this can be explained that these regions were the underwater ridges of the inland lake, probably far from the coast. Therefore only the pelites and chemical sediments got

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through flow zones of the surrounding deeper regions to these elevations, which served as flotation site for sandy sediments.

The studies of the grain size composition show that the Lower Pannonian sandstone sediments of the deeper zones have a finer grain size composition that that of the Lower Pannonian sediments from the regions Algyő, Ferencszállás. It is obvious that the coarser Lower Pannonian sediments of the medium deep regions could get only to their depositional place, when the surrounding deep regions already had been infilled (probably from NW-direction). Otherwise the Dorozsma trench and the Makó — Hódmezővásárhely depression would have been served as settling pond and there the coarser sediments would have been deposited by flow.

On the basis of bedding marks a —"transgressive" — sequence of relatively deep water turbidites and a relatively shallow water "regression" phase have been consecutively distinguished in the region medium deep and deep structures.

At the upper third part of the Lower Pannonian there appear the 20-50 cm thick upward coarsening rhythms. These small rhythms of "regression" type also unanimously indicate the vicinity of coastline.

In the practice of the oil industry the boundary of Lower and Upper Pannonian is given by sudden increase of the percentage of the sandstone strata.

The quartz pebbles, the vertically situated plant residues occurring above the mentioned boundary, the regional extension of the coal grain composition, the horizontal and vertical change of the thickness of sandstone strata, the alternation of the bedding phenomena, the horizontal and vertical arrangement of the fauna-elements within a

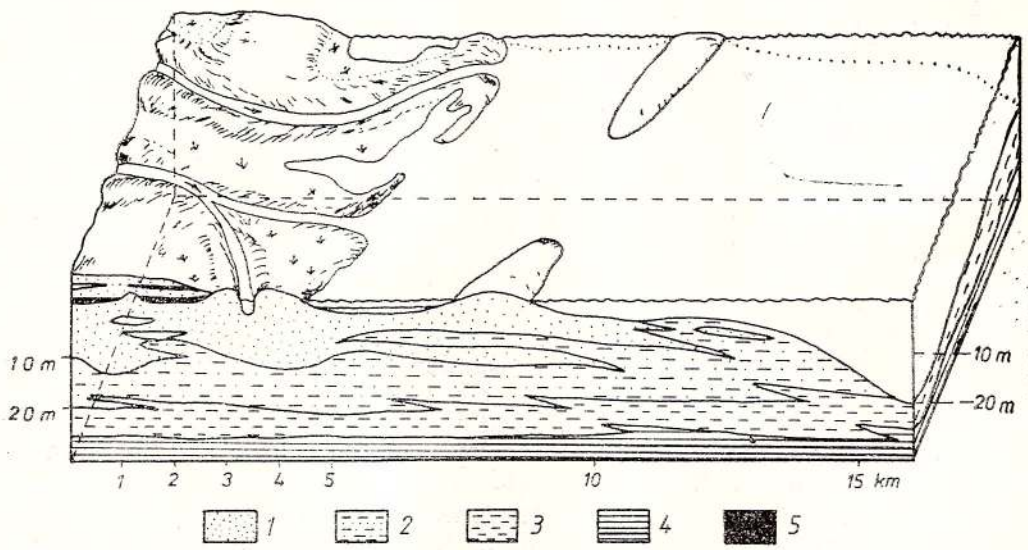


Fig. 4. — Schematic block section for illustrating the sedimentary environments of the initial stage of the Upper Pannonian (in Mucsi, Révész, 1975). 1, sandstone ; 2, sandstone and aleurolite ; 3, aleurolite ; 4, clayey marl ; 5, coal.

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sedimentary rhythm are all referring to delta sedimentation (Fig. 4) (Révész, 1976).

Considering the Great Hungarian Plain as a sedimentary basin, it can be supposed that with the previous accumulation of the Lower Pannonian sediments, the expansion of the Upper Pannonian environments has begun from the margins of the basin. Time limit cannot be delineated on this basis. The cause of the angular unconformity between the Lower and Upper Pannonian sediments can be explained by facies discordance between delta front and delta slope sediments. The degree of stratification increases towards the margin of the delta front. Closer to the coast the gradually accelerating flow (as a result of advance of the coastline) is effective, being the cause of the upward coarsening sedimentary rhythms. Some intercalating argillaceous marls indicate a periodical, local advancement of lacustrine sedimentation. Owing to damming effect of the channels the delta front is forced back for a while, or will be formed elsewhere.

According to our knowledge obtained hitherto, two types of the delta sedimentary deposit can be studied. In the more slowly subsiding regions the delta is mainly advancing horizontally, with creating fewer and thinner rhythms. In the case of more rapidly subsiding basin parts the delta has a considerable vertical extension (Algyő).

Over the delta front sediments the Upper Pannonian sequence was composed of lacustrine, fluviatile continental and flood basin, or rather swamp sediments.

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SOME DEEP-SEA FANS FROM THE POLISH FLYSCH CARPATHIANS [1]

BY

ANDRZEJ ŚLACZKA [2]

The study of sedimentation in ancient and modern submarine fans have significantly contributed to our present understanding of flysch basin sedimentation (Mutti, Ricci Lucchi, 1972, 1978; Normark, 1970; Ricci Lucchi, 1978; Stanley, Palmer, Dill, 1978; Walker, 1978). Especially the works of Mutti and Ricci Lucchi presented the criteria for recognizing fans and their subenvironments. They worked out the classical model with channelized inner and outer fans with sandstone lobes and interlobe sediments.

The detailed studies of the sediments of the Northern Carpathian flysch basin has allowed us to distinguish more types of deep-sea fans: classical ones, fluxoturbiditic fans, and basin-plain turbidite-like fans. The above mentioned types are strongly dependent upon the nature and influx of clastic material from source areas which was subsequently involved in mass flows (debris flow, grain flow, turbidite flow etc.).

The most common is the classical type where it is possible to distinguish at least portions of inner and especially outer fan facies associations. Gradual changes in the structure of sandstone bodies, changes of their thickness, grain size etc., can be observed as well as changes in the sandstone/shale ratio. In these types of fans there is a more or less gradual passage into basin-plain sediments. In some cases however, the mineralogical composition of turbidites from the basin plain are different and there is no connection between the two sediments.

From the analysis of redeposited material the conclusion can be drawn that the formation of the classical fans took place when there were clastics of differentiated size (from pebbles to pelite) in the source areas.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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One such example is the Oligocene Cergowa sandstones (Ślączka, Unrug, 1976), see Fig. 1. Other examples are the Oligocene Krosno sandstones, Eocene Magura sandstones or the Upper Cretaceous Inoceramian Beds.

The shapes of these fans were controlled by the basin morphology and it is possible to distinguish two basic subtypes : one in which

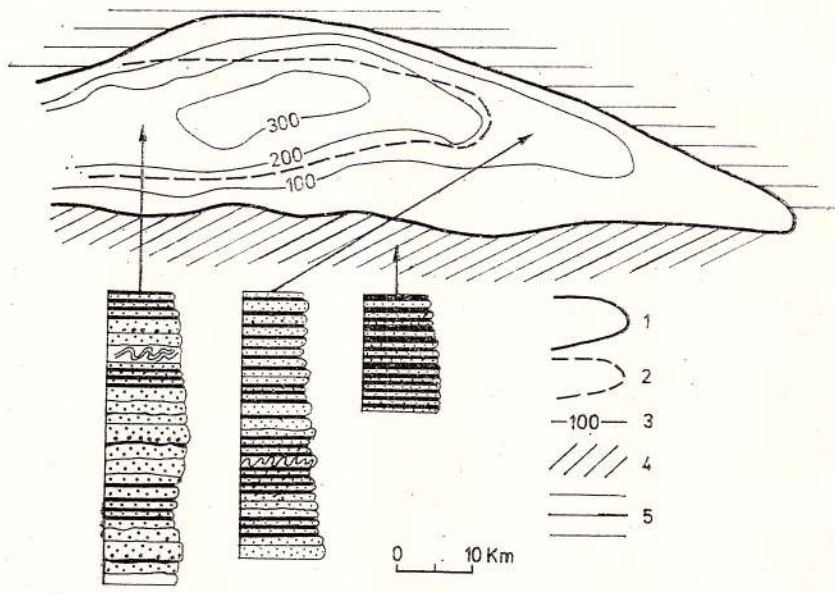


Fig. 1. — Reconstruction of the Cergowa deep-sea fan : 1, Limit of thick- and medium-bedded sandstones ; 2, Limit of very thick beds ; 3, Isopachytes ; 4, Outer fan interlobe facies ; 5, Basin plain facies with sandstones of other mineralogical composition than the Cergowa sandstones (Menilite beds).

the changes in facies associations took place radially (symmetrically) and the second in which changes took place along one direction only. In the latter case, the fan is elongated according to the basin shape.

In the examples cited above, outer fans are predominantly present. Inner fans are preserved only partially. Probably this is caused by the destruction of the marginal parts of the basin during overthrusting movements.

Less common are fluxoturbiditic fans. In these fans, facies associations typical for channelized bodies of inner fan (channel fill and channel-bar) embrace practically the whole fan. The sandstones show fabrics and structures characteristic for deposition from gravity flows, massive grain flow, liquefied sediment flow or sometimes debris flow. Upper parts of the beds were deposited by turbidity currents (Ślączka, Thompson, 1981). The major depositional type is a thick nongraded or poorly graded massive pebbly sandstone, coarse grained sandstone and in smaller amounts orthoconglomerates and paraconglomerates (pebbly mudstones). Beds are thick, in some cases up

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to 20 m, usually amalgamated and lenslike. Some of the coarse-grained sandstones and conglomerates show large scale cross bedding, probably as a result of turbulent tractive current. Coarser parts of the beds are poorly sorted whereas other parts are well sorted and in some places grain segregations exist. Matrix is dominantly sandy, and quite often there are interclasts of shales.

The lower parts of the beds show traces of strong predepositional erosion. The visible depth of erosional channels is up to two meters, but according to well-log data this depth can be even greater than 10 metres.

The coarse-grained beds usually show a thinning upwards sequence and sandstone beds a thickening upwards one (Leszczyński, in press). In fluxoturbiditic fans aside from thick bedded sandstones there exist thin intercalations (less than 5% of whole thickness) of thin and medium bedded, fine- and medium-grained sandstones. Their mineralogical composition is similar to the composition of the thick beds and probably they represented sediments of an interchannel area or a level. The thickness of fluxoturbiditic fans reach 1000 metres.

Although all structures mentioned above are present in the whole fan, there are differences in their relative proportion (Fig. 2).

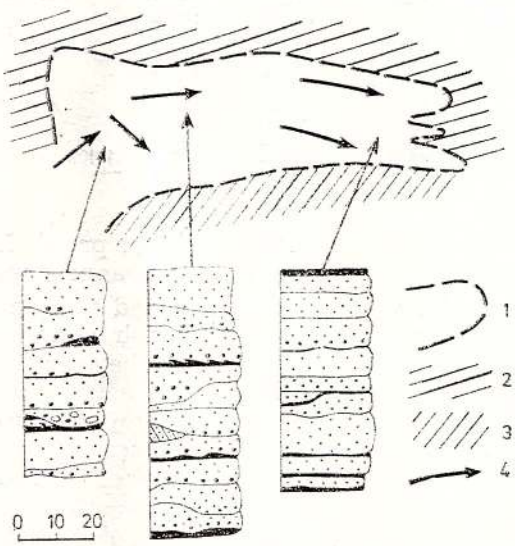


Fig. 2. — Reconstruction of Ciężkowice deep-sea fluxoturbiditic fan: 1, Limit of the fan ; 2, Red shales and marls ; 3, Green shales, thin and medium-bedded, glauconitic sandstones ; 4, Current directions.

Near the source area, washouts, conglomerates and pebbly mudstone are more frequent, nevertheless the channel facies association is present up to the margin of the fan, and the outer fan, if it exists, is limited only to a very thin belt. For example in the Ciężkowice sandstone fan, the width of the outer fan is not greater than one kilometer, whereas the part built up by facies typical for the inner fan extends over a distance of a hundred kilometers.

The fluxoturbidite beds wedge out very quickly between shales, or series of thin and medium-bedded turbidites and shales. These

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turbidites however have a different mineralogical composition and therefore they cannot be regarded as more diluted parts of fluxoturbidites beds, e.g. thinner turbidites surrounding the Ciężkowice fluxoturbidite fan are characterized by the occurrence of glauconite completely absent in the fluxoturbidites even in their fine part. The fluxoturbiditic fans could be formed when in the source areas the main bulk of the material was represented by coarse material with finer material being scarce. This influenced the mode of transport and deposition. One other factor was the probably quick lateral shifting of

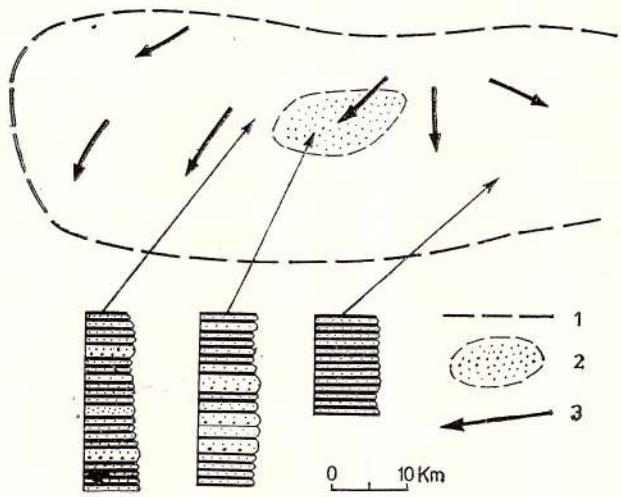


Fig. 3. — Reconstruction of the Hieroglyphic fan from the Dukla basin : 1, Approximate limit of the fan ; 2, Sandstone lobe ; 3, Current directions.

channels (L e s z c z y ń s k i, in press). In the previously mentioned fans the system of distributory channels was more or less stable.

It ought to be mentioned that the development of the fluxoturbiditic fans was connected with a period of increased tectonic activity. In the Polish Carpathians they are correlated with tectonic activity during the uppermost Cretaceous, Paleocene and lowermost Oligocene. Examples of such fans are Lower Istebna Sandstones, Ciężkowice Sandstones and Mszanka Sandstones. It ought to be stressed, however, that not all fluxoturbidites in the Carpathians are associated with only fluxoturbiditic fans. In many cases they compose the inner part of normal fans. The third type of fan, contrary to the previous one, is built up mainly by a facies association similar to that described as the basin-plain and interlobe outer fan turbidites. Outer fan sandstone lobes are very scarce and subordinate, whereas the inner fan facies association is usually entirely absent or restricted to a very small area (Fig. 3). It could be partly caused by anihilation of the marginal parts of the basin during the overthrusting movements. The main reason, however, was the lack or scarcity of coarser material in the source area. As an effect these fans are built up by thin- and medium-bedded usually laminated sandstones passing upwards into mudstones. Sandstones with graded bedding occur sporadically. The turbidites are se-

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parated by hemipelagic shales. The relation of turbidites to the hemipelagic sediments is dependent upon the distance from the source area, farther from it there are more hemipelagic shales and sediments pass laterally into deposits which may be regarded as typical basin plane ones. They are hemipelagic shales with very thin-bedded or lenslike sandstones, probably contourites.

Field observations show that the frequency of occurrence of turbiditic currents in a given time was often greater in fans described above than in normal or fluxoturbiditic ones. The thin intercalation only, or lack of hemipelagic sediments in the later ones were caused by much greater erosion, which removed part of the hemipelagic sediments.

The examples from the Polish Carpathians are the Upper Albian Lgota Beds and the Eocene Hieroglyphic Beds.

Data from the Carpathians show that at least two types of fans could be formed simultaneously, interfingering with one another.

In these cases, especially when one of them is a fluxoturbiditic fan it looks that there exists only one classical fan with inner and outer parts. Detailed studies of current directions and especially of mineralogical compositions can, however, show that there exist different fans, usually connected with different source areas.

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QUESTIONS

I. Berczi : 1. Is there any possibility to distinguish the "molase type" upper part of the fan sequence from that of the lower part of "classical flysch" type ?

2. Considering the feldspathic nature and texturally less mature character of the sandstones in these fans, what about their petrophysical parameters ? I mean porosity and permeability.

Answers : 1. Yes. In the "molase type" there are more sediments deposited by slumps, gravel and sandy flows, the corrosional channels are frequent.

2. I. cannot give now the exact data, but the sandstones from the fluxoturbiditic fan display under greater porosity and permeability than normal turbidites.

E. Dudich : Could you give us some information about material transport and current directions for actual cases of various fan types in the Northern Carpathians ?

Answer : The current directions are chiefly parallel to this axis of basin and elongation of fan ; only near the presumed source area the directions are perpendicular to the axis.

D. Jipa : On what criteria could you define the prograding character of some deep sea fans ?

Answer : The progradation could be established on the basis of microfauna from shales intercalations and data from geological maps and deep borings.

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SEDIMENTOLOGICAL AND RAW MATERIALS PROBLEMS IN THE PLANNED BANK OF SURFACE GEOLOGICAL DATA FOR THE POLISH FLYSCH CARPATHIANS [1]

BY

TADEUSZ SŁOMKA, ANDRZEJ J. KRAWCZYK, JANUSZ KOTLARCZYK, RYSZARD MYSZKA, ELŻBIETA SŁOMKA [2]

In the last years a considerable increase of interest on the computer data bank is noted among Polish geologists. This is manifested by numerous interesting conceptions and definite programmes and systems. They are used for archivization and processing of data, concerning different branches of geology and of various regions of Poland. Usually, these systems are intended to archivise the data from deep petroleum (SAGWiG) and hydrogeological (HYDRO) boreholes or, more rarely, mining data (eg. CYNK-1, GEO-WĘGIEL, IOS-10, ZASOBY, APIGEOKS) (Kunstman, Urbańczyk, 1976; Sokołowski, 1978; Stenzel, 1978; Stenzel, Berestka, 1979). Besides, short discussions on these subjects are contained in the Proceedings of V — IXth Symposiums on the Application of Mathematical Methods and Computers in Geology held in the Mining and Metallurgical Academy in Kraków in 1976-1980.

It should be emphasized that there were no attempts of such approach in the Carpathian geology, no matter of enormous amount of the accumulated primary data. Because of this fact, as well as of considerable diversity of forms of storage of informations and their dispersion in various research and industrial centres and even private hands, it is very difficult or even impossible to make acquaintance with all the available data when solving a new scientific problem. The use of so heterogeneous archival data in computer systems does not seem to be possible. However, in the present authors opinion, it is necessary to standardize the documentation of at least some research works in the future. Consequently, the authors initiated the studies on pre-

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liminary conception of bank of surface geological data for the Polish Flysch Carpathians.

The present paper presents the English translation of basic proposals contained in a more detailed Polish publication (S ł o m k a et al., 1981). Particular attention is paid here to the fundamental geological, sedimentological and raw material data.

The essential element of informations coded in this system is an individual geological observation, localized in space by its coordinates (geographical or topographical) and in time (geological) — by its stratigraphic appertainment. Individual observations may have — from geological viewpoint — different character (observations of various properties of rocks; geomorphological, hydrogeological, engineering-geological and other observations). Consequently, it is necessary to classify them properly. Such classification would directly be reflected in the organization of the storage of the system.

Thus, the basic classification of the whole set of elementary observations of geological objects and phenomena would consist in a subdivision into main structural-tectonical units i.e. nappes of the Polish Flysch Carpathians. This is justified by the fact that individual research problems refer usually to definite units. Consequently, the vast majority of questions put to the system will be connected with definite units and it would not be economic to search mixed informations each time.

Elementary geological observations within each unit will have their consecutive numbers and the data included in these observations will be subdivided into blocks, arranged according to substantial criterion (Fig. 1). It is proposed that to each block there would correspond one standardized source document (or its distinctly isolated fragment), from which the information can be transferred on perforated cards.

The basic block of the system will be the one of the localization-information data (supervisory block). It will embrace the data localizing each observation in time (geological) and space, as well as other data of general character. Therefore, this block will play the role of the first selector of informations, stored in the system, from the point of view of the question content. Further searching would refer to appropriate topical blocks.

It is proposed to put a constant length of record for each observation in the supervisory block, in which the following data will be coded : observation number, localization of observations in space (sheet number of the map 1 : 50 000 and coordinates) and in time (system, series, stage, substage, as well as the name and rank of corresponding lithostratigraphic units), general data on the content of observation (eg. the presence of results of various laboratory analyses, data on raw materials etc.) and information on the author of observation, its date and localization of archives of documentation in traditional form.

Supervisory block, unlike the other ones, will possess no own separate source sheet. The above mentioned informations will be recorded in appropriate places of sheets of individual thematic blocks (Figs. 2, 4, 5).

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In the block of basic geological data, those referring to both natural and artificial outcrops will be stored. Individual observations (maintaining superior classification into structural-tectonical units) will be recorded on magnetic tape in the succession determined by their numeration, whereby variable length of the record is proposed. As fol-

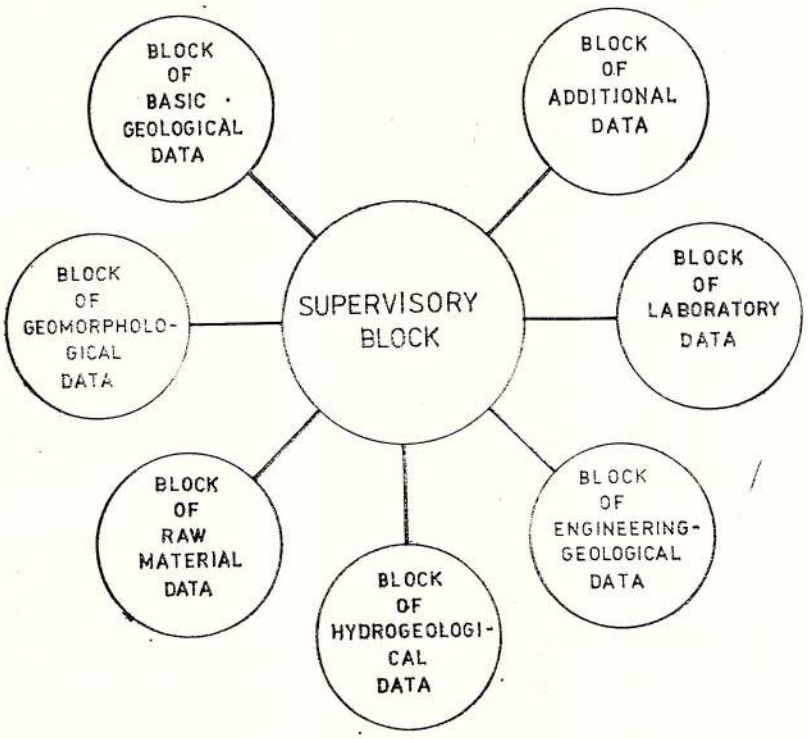


Fig. 1. — A scheme of the blocks of the proposed system.

lows from this fact, the description of each outcrop will contain : 1) the data concerning this outcrop as a whole (first of all — mesotectonic) which will be coded in the same number of columns for all the observations, and 2) mineralogical-petrographical, lithological, sedimentological-paleontological and other data concerning different rocks occurring in the outcrop. Since the number of rock types described will be different for various outcrops, individual fragments of the record will be repeated several times, giving totally the variable length of the whole record.

We may judge on the range of information, destined for coding in the block of basic geological data, on the basis of the project of source document, presented in Fig. 2. It should be admitted that in the original the sheets of all the documents should be coloured. The positions referring to different grades of hierarchy of descriptions should be marked by different colours. Moreover, all the source docu-

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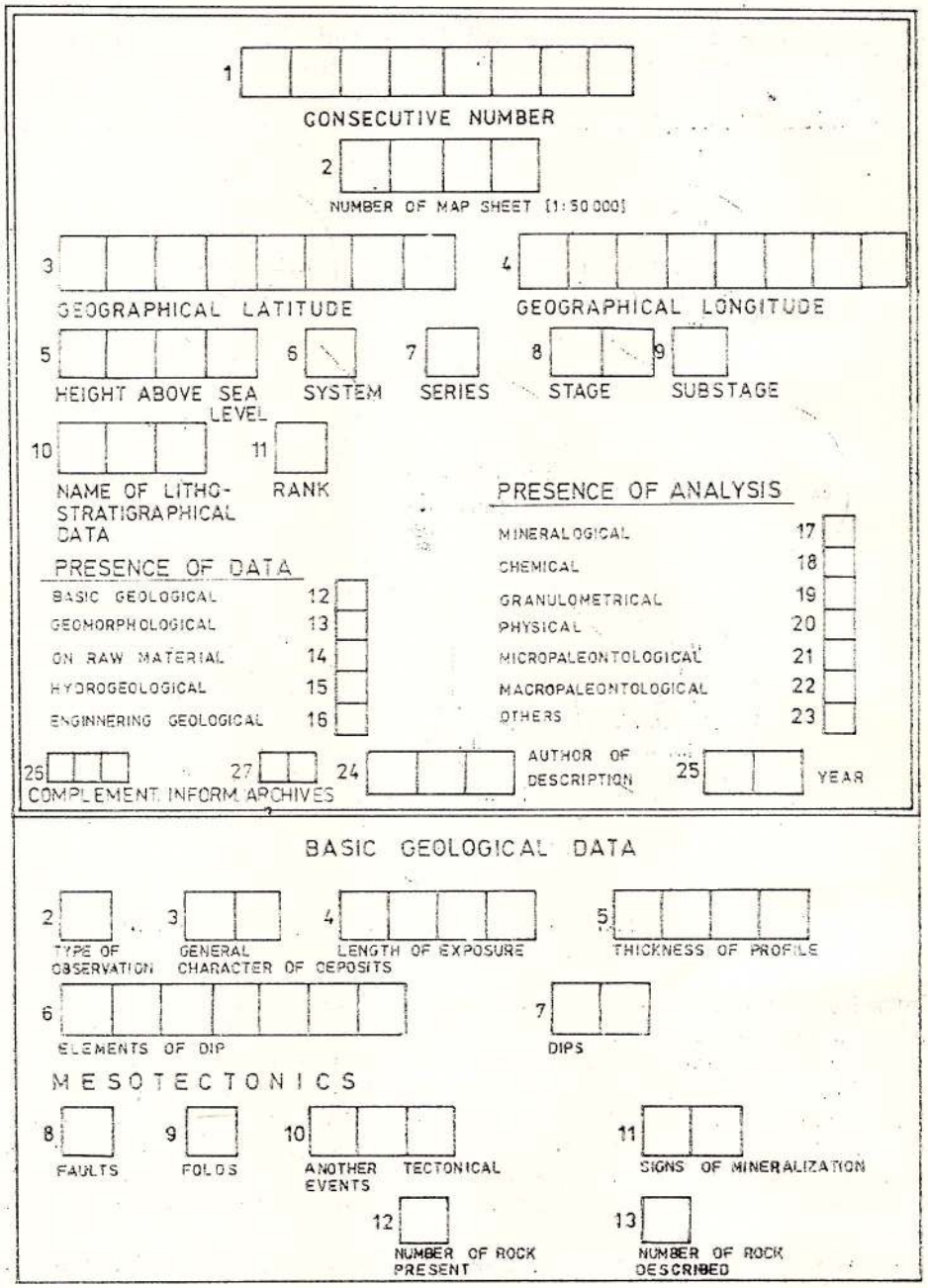


Fig. 2. — Source document for basic geological data — the complete version.

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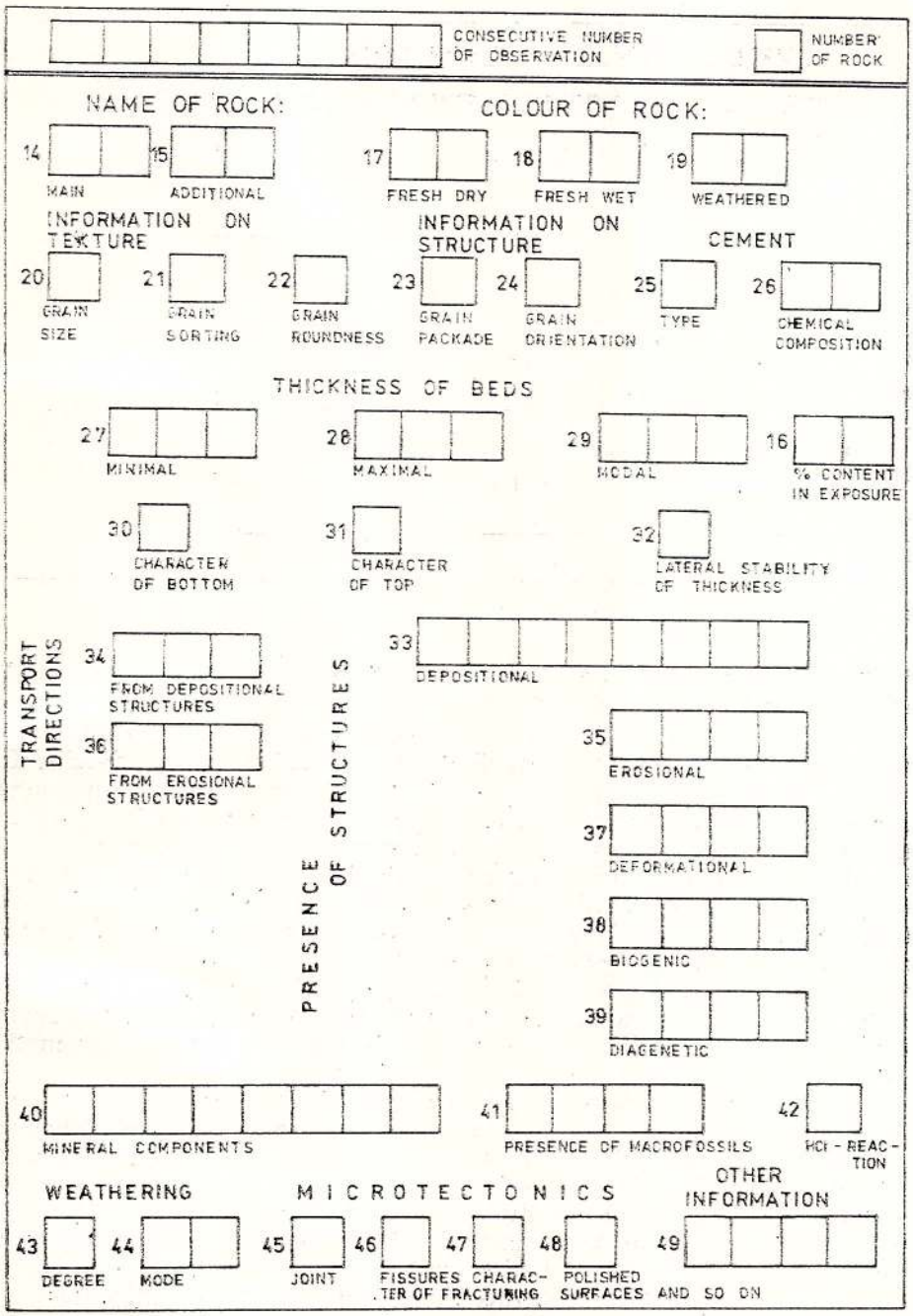


Fig. 2 a.

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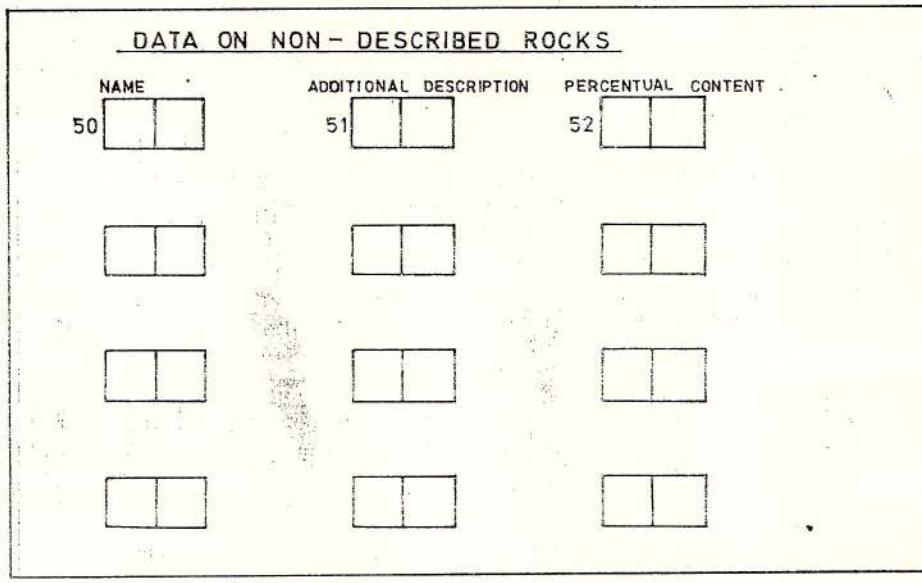


Fig. 2 b.

ments should be coded in sheets of the same size. This allows to collect their appropriate set in the form of a booklet.

It is very often observed that in the course of geological field works the descriptions of successive outcrops differ but in details. In order to eliminate manifold repetition of nearly identical and long descriptions, two forms of records in the block under consideration are proposed : complete and short. In the latter one there would be coded only the following data : observation number, number of "parent" complete observation, number of rock (in parent observation), to which the coded information is referred, number of changing position and, finally, the content of newly introduced observation. The scale of simplification obtained is visible in Fig. 3, presenting the project of a source sheet. Due to technical reasons (mainly because of search rate), complete and short descriptions will be stored on separate magnetic tapes.

In the range of data of raw material block, there are contained observations of all the indirect and direct mineralization phenomena and their traces, as well as general data on actually exploited deposits. Because of considerable diversification of raw material data, collected in various outcrops, four variants of record (each of constant length) are proposed : 1) (for quarries) in which informations on the kind, basic properties and destination of the material are coded, as well as on the state of exploitation, accompanying raw materials, thickness of overburden, resources etc. (Fig. 4) ; 2) for natural outcrops (including small quarries and pits) (Fig. 5) ; 3) for gravel pits and 4) clay pits, in which all the information on the kind of raw material and its most important properties are coded.

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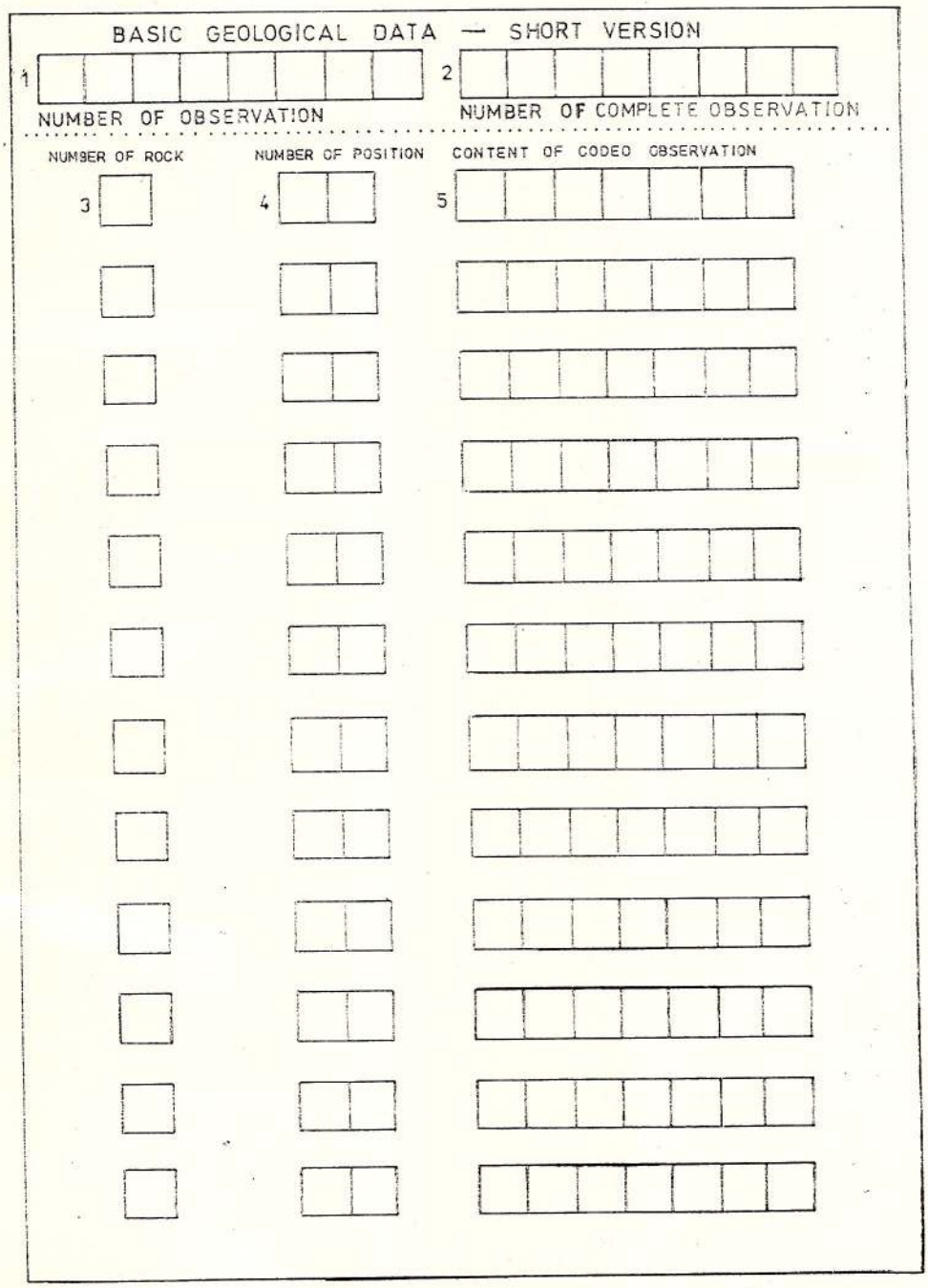


Fig. 3. — Source document for basic geological data — the short version.

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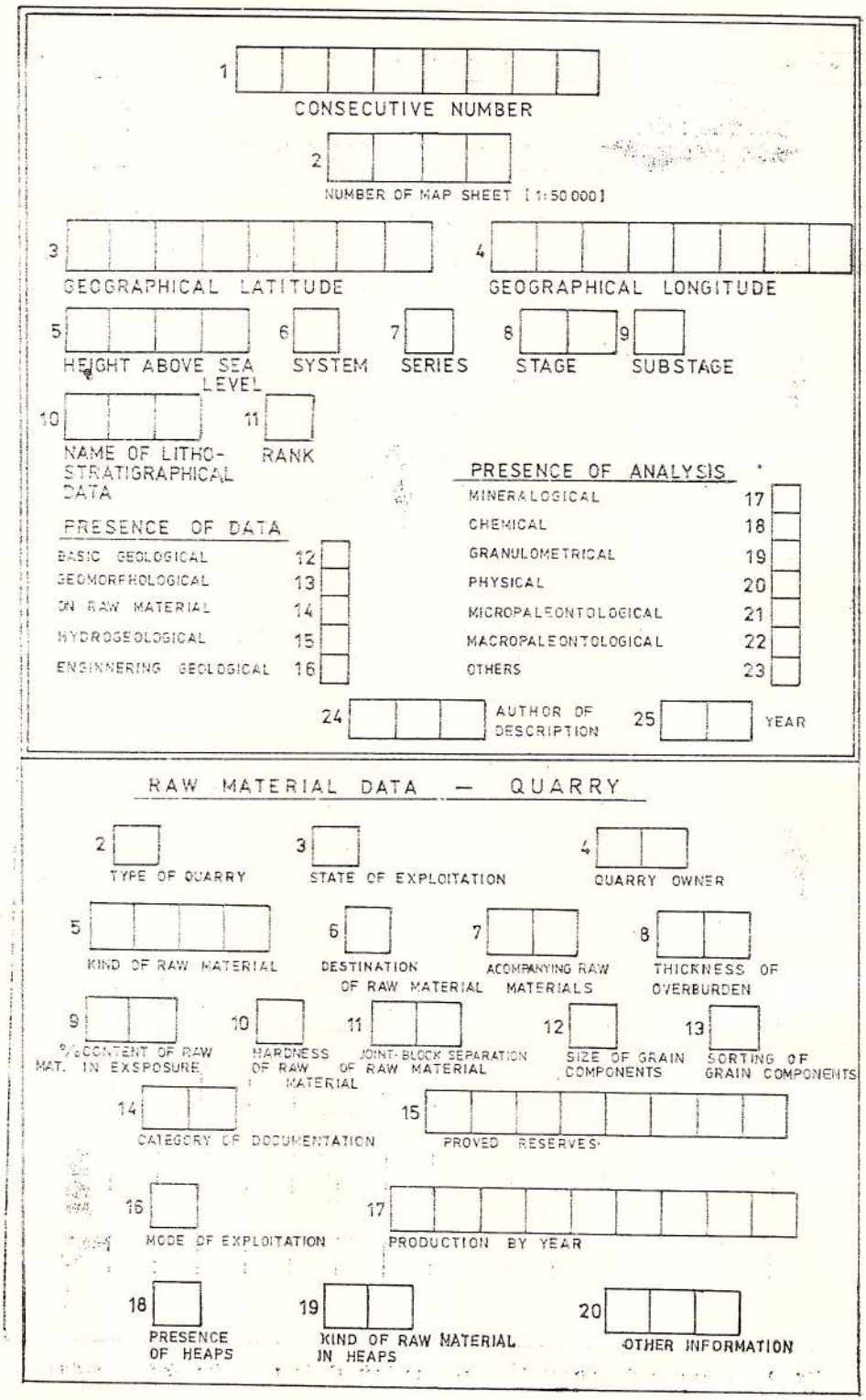


Fig. 4. — Source document for raw material data — description of a quarry.

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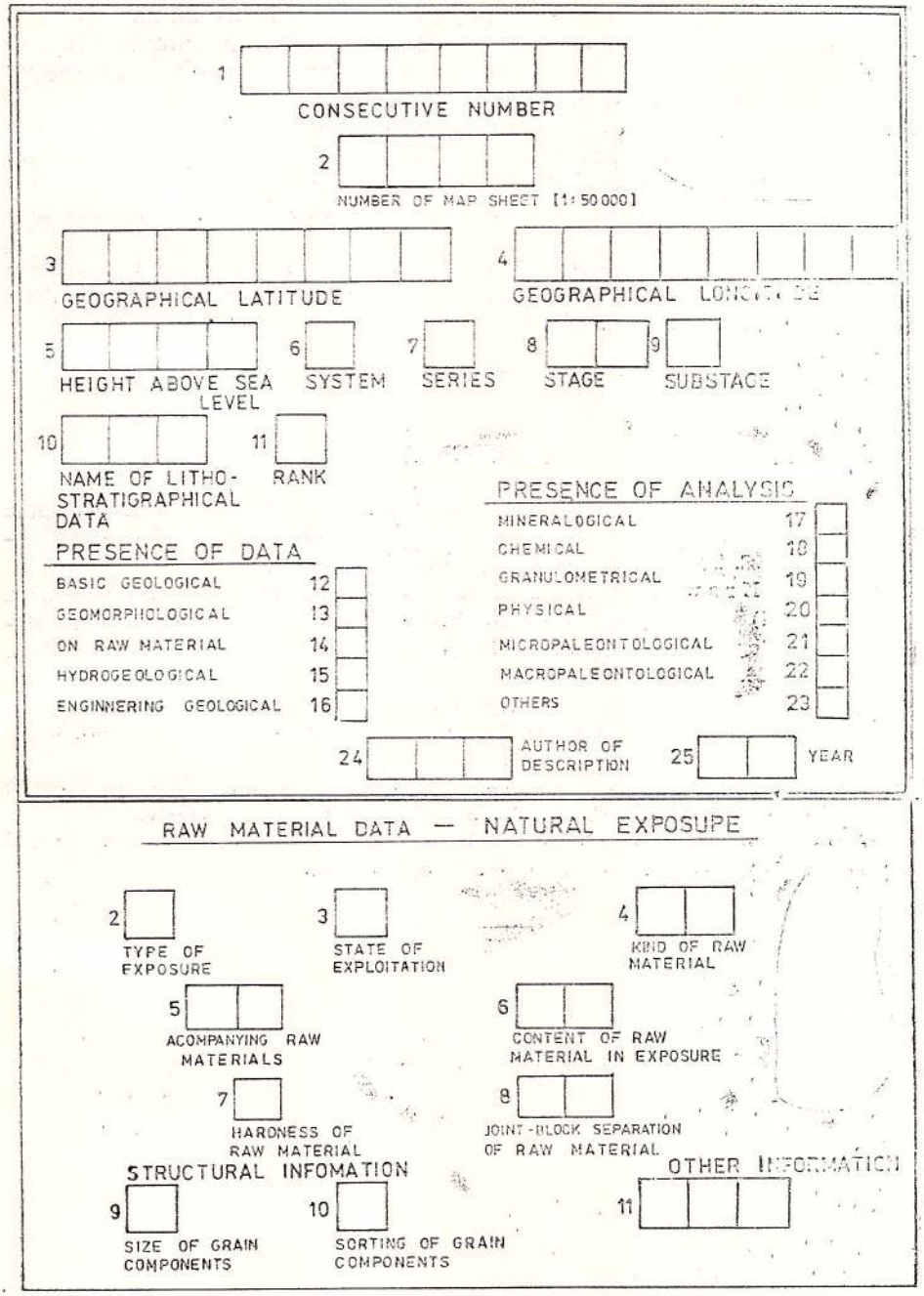


Fig. 5. — Source document for raw material data — description of a natural outcrop.

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The present authors would like to discuss the preliminary project of the system among Carpathian geologists in order to improve it and to get its approval. It is quite obvious that further work is necessary to archivize the data in the proposed system. Another condition of success of this initiative is to incorporate the studies on this system into the working programme of the Geological Institute and to get financial support of the Central Geological Office. This refers both to further research works on the system (vocabularies, software) and to its application in praxis.

The final aim consists in the application of the system for processing of geological surface data in automatic construction of geological maps, cross-sections etc.

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A COMPLEX EVALUATION OF NONMETALLICS FROM THE COAL-BEARING KOLUBARA NEOGENE BASIN (SERBIA, YUGOSLAVIA) [1]

BY

BRANIMIR VAKANJAC [2], MILOJE ILIĆ [2], JELKA SPASOJEVIĆ [3]

Main Geological Characteristics of the Coal-bearing Kolubara Basin

The coal-bearing Kolubara Basin represents, in the geological sense, the southern rim of the great Kolubara Bay of the Pannonian Basin (or the Kolubara Basin *sensu lato).* The remaining part of this bay is made up of the non-productive Kolubara Basin which, northwards, stretches up to the Sava River.

The coal-bearing Kolubara Basin is situated in the region of the Kolubara River (the lower and middle reaches) and its tributaries: the Tamnava, the Ub, the Kladnica, the Vraničina, the Turija, and the Peštan. The basin is elongated in the west-east direction: its longer axis is 55 km and shorter axis — about 16 km. The area of the basin amounts to about 600 sq km (Fig. 1).

Geographically, the coal-bearing Kolubara Basin is divided into two parts by the Kolubara River — the eastern and western parts. The eastern part has an area of about 120 sq km and is the site of the coal-bearing fields A, B, C, and D. The western part is 480 sq km in the area and in it there is the Tamnava coal field, which is nevertheless partially located in the eastern part of the basin.

From the geomorphological point of view, the location of the coal-bearing Kolubara Basin is an area which ranges from flat to gently undulating, with land at 90-250 m above the sea level.

The coal-bearing sequence in the Kolubara Basin is made up of brackish (caspibrackish) Lower Pliocene (Pontian) sediments. These sediments deposited in the southern rim of the Kolubara Bay of the Pannonian Sea which once stretched over the sunken parts of the Inner Dinarides.

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[1] Paper presented at the 12th Congress of the Carpatho-Balkan Geological Association, 1981 September 8—13, Bucharest, Romania.

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The productive sequence of the basin is edged on the southern side by various older formations : Paleozoic (Devonian, Carboniferous and Permian) formations, Mesozoic (Triassic and Cretaceous) sediments, Tertiary plutonic and volcanic rocks (intermediate) and Miocene sediments.

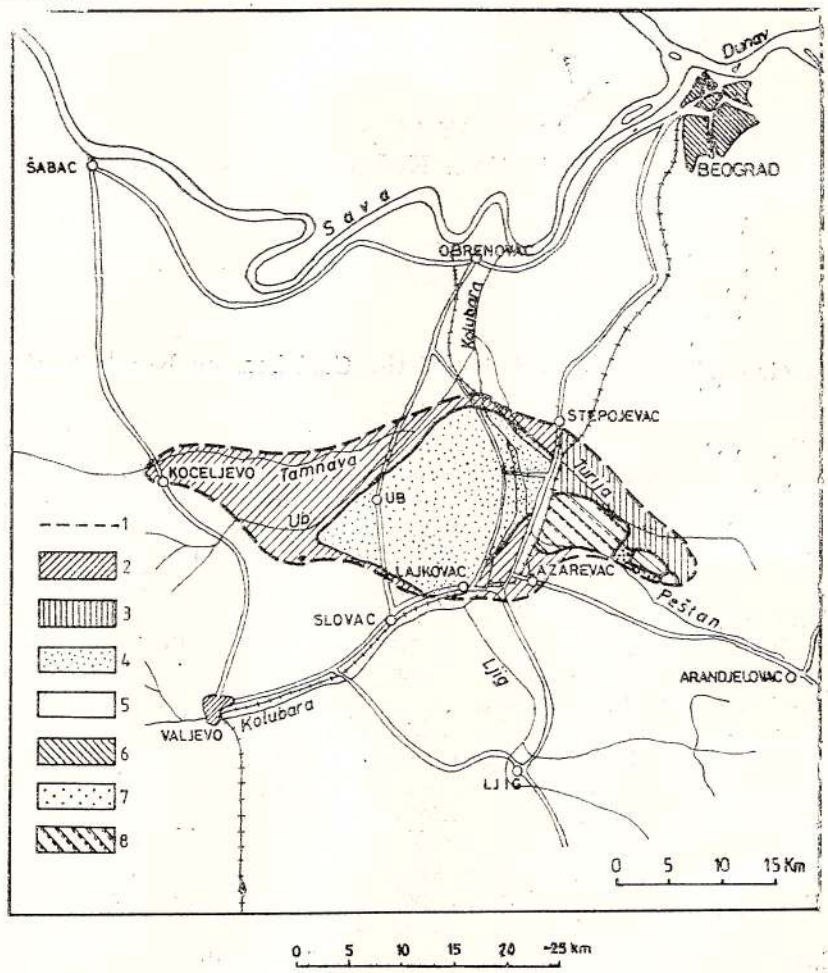


Fig. 1. — Sketch showing the geographic position of the coal-bearing Kolubara Basin : 1, geologic boundary of the basin ; 2, western part of the basin ; 3, eastern part of the basin ; 4, Tamnava coal field ; 5, coal field A ; 6, coal field B ; 7, coal field C ; 8, coal field D.

The Lower Pliocene (Pontian) series lies transgressively and concordantly over the Pannonian sediments and intermittently over the older formations, described in earlier expositions.

In the non-productive Kolubara Basin, the Pontian sediments are deep-water (neritic) and are of greater total thickness. Both Lower and

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Upper Pontian are represented. The Lower Pontian age is developed in the clay-marl facies ; these sediments contain fossil lamellibranchiata fauna : *Congeria praerhomboidea, C. zagrabiensis, Limnocardium asperocostatum, Paradacna abichi* and others. The Upper Pontian age is re-

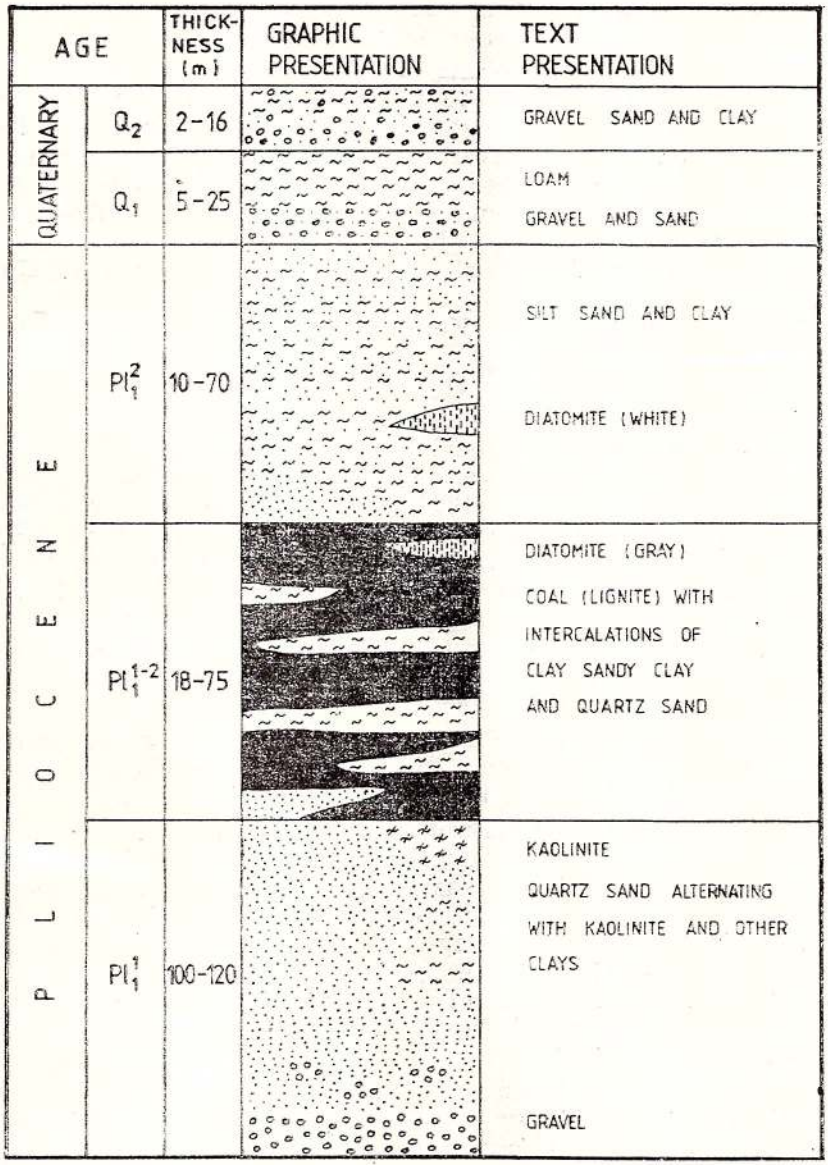


Fig. 2. — A schematic lithostratigraphic column of the coal-bearing Kolubara Basin.

presented in the lower part by marls and clays with *Congeria rhomboidea, C. croatica, Limnocardium mayeri* and *Valenciennensia reussi,* and in the upper part by fine-grained sand with *Budmania histiophora.*

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In the coal-bearing Kolubara Basin, shallow (paralic) sediments are found, represented by sand, gravel and clay, by coal and intermittent occurrences of diatomite. The total thickness of the coal-bearing Pontian sequence is 250-300 m (Fig. 2).

In both the non-productive and the coal-bearing Kolubara Basin, the Pontian sequence is caspibrackish in character.

In most of the coal-bearing Kolubara Basin, the coal horizon is found as a uniform seam, 18-45 m in thickness, in which there are layers and lenses of basin sediments (clay, sand). In the region of field B, however, there are two coal seams, and in the northern part of field C we find one thinner coal seam in the roof. West of Skobalj and Mali Borak, the coal seam splits into three or four thinner seams, separated by basin sediments ; the total thickness of the coal horizon is then 70-75 m. Such a coal horizon stretches as far as Ub and Zvizdar.

Coal exploitation in the Kolubara Basin is carried out in great open pits. The coal mined is used mostly for thermpower plants within the Kolubara Mining, Energy and Industrial Combine.

Kolubara coal (lignite) represents a paralic formation, which came into being in swamp of a coastal type. The material from which the coal was created was plant vegetation which, according to Pantić, Ercegovac and Pantić (1967), was made up of coniferous trees *(Taxodium, Glyptostrobus)*, deciduous trees *(Nyssa)* and bushes *(Myrica, Cyrilla, Salix* and others). In the southern (coastal) part of the coal-bearing Kolubara Basin there are trunks and roots of trees in an upright position, pointing to the fact that the coal is autochthonous. Going towards the north, the coal is allochthonous (and increasingly sorted according to its particle size) and the coal seam splits and gradually pinches out.

The floor of the coal horizon is composed of quartz sand and gravel, and in the far eastern part of the basin (in the region of Rudovci-Prkosava-Baroševac) kaolin and other clays occur.

The roof of the coal horizon is made up of clay, silt and sand, and in the far eastern part of the basin (near Baroševac) there are occurrences of diatomite. In the eastern part of the basin, the roof clay, directly overlying the coal seam, is burned in many places as a result of self-ignition of coal ; this clay has a characteristic red dye. In the roof sediments, especially in the region of Veliki Crljeni, the Upper Pontian Lamellibranchiata fauna is represented by *Congeria rhomboidea, Limnocardium zagrabiense, I. riegeli, Budmania histiophora, Paradacna okrugići* and other shells.

Since the floor sediments belong to the Lower Pontian, and the roof sediments to the Upper Pontian, Stevanović (1977) believes that the coal horizon was formed at the transition between the Lower and Upper Pontian.

The tectonic structure of the coal-bearing Kolubara Basin is comparatively simple : the Lower Pliocene sequence was subjected only to disjunctive tectonics (which took place during the Middle and Upper Pliocene) and it was divided into a system of blocks which moved in

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different directions (the so-called "parquet" structure). Within the individual blocks, the sediments are either horizontal or gently tilted (1-5°, more rarely 5-15°), and only near the faults, the dip of the seams can be even steeper.

In both the eastern and western parts of the basin, the coal horizon occurs as shallow, asymmetrical synclines, whose rims have been reduced by the action of erosion. In the Tamnava coal field, for example, the coal horizon makes up one shallow syncline, whose axis lies in the WNW-ESE direction. Its north-eastern wing has been greatly reduced by erosion, while its south-western wing lies on Triassic sediments.

Quaternary (Pleistocene and Holocene) sediments lie discordantly over the Pontian roof sediments.

Pleistocene sediments build up the highest parts of the land in the coal-bearing Kolubara Basin (180-250 m above sea level) and yellowish-brown loam of 5-25 m in thickness lying below. These sediments are the erosion remains of Pleistocene lacustrine terraces.

Holocene sediments are represented by alluvial deposits (gravel, sand and clay) of the Kolubara River and its tributaries. These sediments vary greatly in thickness, ranging from a few metres to some 15 metres.

Nonmetallic Mineral Raw Materials

Exploration and exploitation of the Kolubara Basin have shown that there are rocks representing nonmetallical mineral raw materials in the coal-bearing Pliocene (Pontian) sequence and in the Quaternary roof sediments. According to the main areas of their use, they can be classified in the following way (going downward in the stratigraphic column) : (1) brick clay, (2) gravel and sand — natural building materials, (3) silt — raw materials for the production of expanded materials and gas-formed concrete, (4) diatomite — raw materials with varied industrial use, (5) fire-ceramic clay and (6) quartz sand — raw materials for the glass and foundry industries.

Brick Clay

Brick clay is widespread among the Quaternary sediments (which lie over the coal-bearing Pontian sequence), occurring as a permanent member of the Pleistocene terrace lacustrine deposits and the Holocene alluvial deposits of the Kolubara and its tributaries.

The terrace clay in the western part of the Kolubara Basin is particularly widespread — this is yellowish-brown loam which builds up a continuous seam 5-25 m in thickness, which lies above the layer of terrace gravel of 1.5-5 m in thickness.

Granulometric analysis of this clay shows that it contains up to 8 % of sand fraction, 9-40 % of clay fraction and that the remainder is made up of silt fraction. The mineral content of the clay is as follows : montmorillonite, illite, quartz, carbonates and organic matter (0.1-1 %).

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Laboratory examination of this clay shows that it stands up well to firing and that it represents a high quality raw material for brick production (whether full, hollow or facing bricks), tiles and other products of rough building ceramics.

Gravel and Sand

Gravel and sand are also widespread among Quaternary sediments, occurring as a permanent member of the Pleistocene terrace deposits and the Holocene alluvial deposits.

In the western part of the basin, sand and gravel which occur in the form of a continuous layer 1.5-5 m in thickness and intermittently lying directly over the coal are widespread. These sediments represent a natural gravel-sand mixture in which gravel predominates (constituting 70-75 % of the mixture).

The petrographic constitution of this gravel-sand mixture is complex — fragments of magmatic, sedimentary and metamorphic rocks occur within it. Of the magmatic rocks, diabase is the most frequent, but porphyrite, melaphyre, and andesite and gabbro as well as some altered magmatic rocks occur ; these rocks constitute about 30 % of the natural mixture. Of the sedimentary rocks, chert and sandstone are the most frequent ones, with limestone and shale occurring more rarely ; these rocks represent 20-30 % of the natural mixture. Of the metamorphic rocks, quartzite is predominant, while serpentinite is represented to a subordinated degree ; serpentinite constitutes up to 15 % of the natural mixture. Of the fragments of minerals, the most frequent is quartz, constituting 30-35 % of the natural mixture. Besides this, feldspar, pyroxene, mica and metallic minerals occur in fine fractions. This natural mixture has an increased mud content as well as a clay lamp content amounting to 2-11 %.

Gravel grains are cubical or elliptical in shape, and the content of elongated and flattened grains is minimal.

Investigation of the quality of Kolubara gravel has shown that as a raw material it satisfies all the technical demands for production of concrete aggregate, as well as for use in road-building, except in the mud and clay lump content which are above the permitted level. For that reason, this gravel must be subjected to beneficiation before use, i.e. the natural mixture must be washed and separated.

Silt

The Upper Pontian silt sediments are overlying the coal seam and underlying the Quaternary gravel. They represent the predominant member of a heterogeneous sequence consisting of three components : silt, sand and clay. These components are usually mixed in different proportions (but in most cases silt is a prevailing component). Pure quartz sand occurs in separate places in the lowermost part of the sequence, most frequently lying directly on the coal.

The maximal thickness of the sequence is about 70 m.

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The sand-silt-clay sediments contain up to 22 % of sand, 44-89 % of silt and 9-51 % of clay. The following minerals are represented in their composition : quartz, feldspars, mica, hydromica, kaolinite, montmorillonite, vermiculite, chlorite, carbonates, limonite, and organic matter. The Fe_2O_3 content varies from 2.4-8.4%, the MgO content from 0.2-2.20 %, the CaO content from 0.4-3.1 %, the alkali from 2-3 % and the organic matter from 0.1-3.1 %. Certain varieties of silt expand at a temperature of 1,100-1,200°C, and the material obtained has a volume of mass of 0.8 t/m^3.

By hydro-separation of silt sediments, a fine-grained quartz product has been obtained (consisting of silt and fine sand of a grain size below 90 μ).

Kolubara silt is a potential raw material for brick production (as a processing agent), and in the production of keramzite and agloporite, for obtaining gas-formed concrete and other silicate autoclave building materials (in which it replaces ground quartz), depending on the predominance of sand, silt and clay and on the suitable technological treatment in certain cases of use.

Diatomite

Diatomite occurs in the roof of the coal-bearing Pontian sequence in the eastern part of the Kolubara Basin — in field B near Baroševac.

Diatomite is found as a continuous seam about 3 km in length and 0.5-0.9 km in width. The maximal thickness of the seam is about 3 m, and the average thickness is some 1.3 m. The diatomite seam is a direct floor of the upper coal seam (the grey variety) in one case, and is in a higher roof of the main coal seam (white variety) in the other.

Two industrial types of ore occur in the deposit :

— *grey diatomite* of poorer quality, unpurified of organic matter (about 25 %) and other admixtures. It occurs on the surface in about 0.9 sq km, and with an average thickness of the layer of about 1.6 m.

— *white diatomite* of standard quality, with up to 6 % content of combustible matter, occurring on the periphery of the deposit on the surface in about 0.6 sq km, and with an average thickness of the layer of about 0.8 m.

Baroševac diatomite is distinguished by the following physical characteristics : a volume mass of 0.45-0.53 t/m^3, dimensions of the grain varying from 0.08-0.002 mm, porosity of 76-81 %, SiO_2 content of 76-85 %, while the remainder are admixtures (quartz grains, mica, feldspar, mineral clay and so on).

During recent coal exploration in the eastern part of the Kolubara Basin, new outcrops of diatomite were found, but they are insufficiently studied.

The diatomite of the Kolubara Basin could be used as a filter, as a filler, as an absorbent, as an abrasive, for heat insulation in building and as an active hydraulic (pozzolan) additive to cement and for many other purposes.

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Fire-Ceramic Clay

For the most part, fire-ceramic clay occurs in the Kolubara Basin between the coal seams. It is distinguished by its relatively poor quality (with a high content of organic matter, sand and silt particles). Its thickness is usually about 1 m in this part. In the eastern part of the basin, however, where the coal pinches out, there is much better quality clay, 3-11 m thick. In this part of the basin, the deposits of mainly fire-ceramic clay of Rudovci and Baroševac and the ceramic clay deposits of Lukavički potok and Dren have been studied in detail.

The Rudovci deposit has been actively exploited since the inter-war years. Kaolinite predominates in the mineral content of the clay. In the floor of the fire clay, there is sandy clay and clay-quartz sand, and in its upper part, which is intermittently uneven and eroded, there are gravel, sand and sandy clay.

The Rudovci fire clay contains 85-88 % of clay material, 3.8-8.2 % of quartz, 3.3-6.3 % of feldspar and 1.8-1.9 % of 0.06 mm remainder on the sieve. The clay is extremely fine-grained and plastic (98 % of the particles are smaller than 0.06 mm ; the plasticity varies from 55-75 MPa). The clay is 31-33/34 SK refractory and is mainly used in the firebrick industry in Arandjelovac.

The Baroševac deposit contains illite-kaolinite clay ; both vertically and laterally, the quality of the clay varies ; it is 26-30 SK refractory. The deposit is not presently being exploited.

The Lukavički potok deposit is occasionally exploited for the requirements of the ceramics industry at Mladenovac. The deposit contains typical hydromica clay with little kaolinite. Besides the basic fatty and relatively low-sandy clay in the deposit, there are considerable quantities of extremely sandy clay and clay sand.

The Dren deposit also contains hydromica clay, fatty and relatively low-sandy, which is associated with sandy clay and clayish sand. The clay has increased contents of Fe_2O_3 and alkalies (about 4.5 %), which severely restrict their application in the ceramics industry.

Quartz Sand

Quartz sand is widespread in the Kolubara Basin. It occurs within Pontian sediments which lie : (1) in the roof of the coal, (2) between the coal seams and (3) in the direct floor of the coal. Two types are represented from the granulometric point of view : medium-grained and fine-grained, with fine-grained sand usually located below medium-grained.

(1) Roof quartz sand alternates laterally with silt-clay sediments. It is found in the form of elongated lens-like bodies whose thickness reaches up to 30 m.

Medium-grained quartz sand is light grey or yellow in colour and the medium size of the grain is 0.28 mm. Grains of medium size make up about 75 % of the sand and fine-size grains — about 25 %. Besides quartz, the other minerals present are feldspars (up to 10 %), mica and a minimum quantity of accessory minerals. Washed quartz

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sand has the following chemical composition : SiO_2 — 91-95 %, Al_2O_3 — 3-5.9%, TiO_2 — 0.10-0.16%, Fe_2O_3 — 0.18-0.48%, Na_2O — 0.46-0.69 %, K_2O — 0.77-0.85 %, LOI — 0.32-0.57 %. With the corresponding treatment (washing and flotation), this sand yields a product which satisfies the demands of foundry work, glass production as well as of some other industrial branches.

Fine-grained quartz sand is greyish-blue, compact and has a greater clay content than the medium-grained sand. It contains 75-95 % of fine grains and 5-25 % of medium-sized grains. The mean size of the grains is 0.09 mm. Quartz, feldspars, mica and a minimum quantity of accessory minerals make up the mineral content. Fine-grained quartz sand grades into silt-clay sediments.

(2) Quartz sand alternates laterally with clay between the coal seams. The thickness of this quartz sand is up to 15 m and the granulometric composition shows a predomination of medium-grained varieties, while coarse-grained sand is of less significance. It is distinguished by its grey colour, its compactness and occasional coal-containing character. Besides quartz, feldspars, mica and minimum accessory minerals are found. This sand is insufficiently studied to determine its possible applications.

(3) Floor quartz sand occurs directly below coal with a thickness of over 100 m, and includes medium-grained and fine-grained varieties. It is greyish-green in colour, compact and occasionally clay-bearing.

Floor quartz sand has been studied in detail in field D of the Kolubara Basin. Crude sand had the following chemical composition : SiO_2 — 93.90 %, Al_2O_3 — 2.65 %, TiO_2 — 0.40 %, Fe_2O_3 — 1 %, Na_2O — 0.13%, K_2O — 0.30%, S — 0.74%, organic matter — 0.38%, LOI — 0.38%. This sand belongs to the medium-grained variety, in which 78 % of its mass belongs to the 0.21-0.42 mm class ; it is poor in the silt-clay component as well as in grains of over 1 mm in size. Its grains are spherical and well-formed. Quartz is the basic mineral component. Besides quartz, we find feldspars, muscovite, tourmaline, amphibole, rutile, sphene, ilmenite, zircon, chromspinel, apatite and locally coal-containing clay and grains of coal.

After the sand has been washed and flotated, the end-product contains SiO_2 — 98.51%, Al_2O_3 — 0.90%, TiO_2 — 0.13% and Fe_2O_3 — 0.06 %, with 98 % utilization.

The quartz sand from the coal floor is a raw material which, by a simple process of washing and mud-removing with classing, can be prepared into a high quality product for casting and for the glass industry (for the production of semi-milk and packaging glass) ; after further flotation, a concentration highly suitable for the production of sheet glass can be obtained.

The complex geological-economic evaluation of the nonmetallic mineral raw materials of the coal-bearing Kolubara Basin, made by the authors of this paper and a team of associates, has shown that exploitation of these raw materials simultaneously with coal has yielded

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very favourable economic results so that exploitation is planned in the development programme of Kolubara Mining, Energy and Industrial Combine which has been adopted.

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О ГЕОХИМИЧЕСКОЙ СПЕЦИАЛИЗАЦИИ ФЛИШЕВЫХ ТОЛЩ СЕВЕРНОГО СКЛОНА СОВЕТСКИХ КАРПАТ [1]

И. М. АФАНАСЬЕВА [2]

Распределение редких и рассеянных элементов в породах флишевой формации северного склона Карпат находится в тесной связи со сложным комплексом геологических процессов, определивших характер формирования этой осадочной толщи.

На рис. 1 и 2 приведены средние значения содержаний редких и рассеянных элементов в песчаниках и глинистых породах мелового и палеогенового возраста Скибовой и Силезской зон, где по вертикальной оси в хронологической последовательности отложены средние величины концентраций элементов в породах. Изучались элементы, образующие железомарганцевую группу, которая объединяет группу мало геохимически подвижных гидролизатов (Al, Ti, Zr, Ga), подгруппу железа (Fe, V, Cr, Ge), подгруппу халькофильных элементов (Cu, Zn, Pb, As) и подгруппу марганца (Mn, Ni, Co, Mo).

Рассматривая содержание элементов первой подгруппы, можно наблюдать отчетливо выраженный максимум содержания титана и циркония в породах верхнего мела: в песчаниках из отложений Скибовой зоны и в аргиллитах Силезской зоны.

Кривые распределения циркония во многом напоминают кривые распределения титана, что свидетельствует о закономерном колебании количеств титана и циркония. Содержания галлия в разрезе характеризуются незначительными пределами колебаний. Наибольшие его концентрации связаны с породами эоцена и олигоцена Силезской зоны. Преимущественная приуроченность концентраций циркония к песчаным породам связана с его миграцией в составе обломков минералов и механических взвесей. Иногда находящийся в растворе цирконий выпадает вместе с гидроокислами железа, марганца и алюминия.

Содержание титана в песчаниках обычно превышает кларковый уровень. Максимальные его концентрации отмечаются в породах верхнего мела. В морских условиях обычно максимальные его количества приурочены к прибрежным либо прикордильерным участкам геосинкли-

[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г, сентябрь 8—13, Бухарест, Румыния.

[2] СССР

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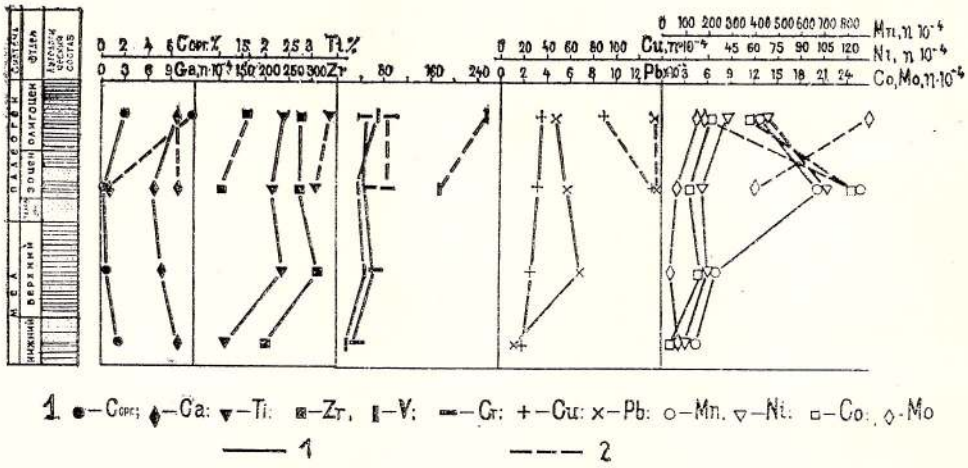


Рис. 1. — Распределение главнейших акцессорных элементов в породах мелового и палеогенового флиша Скибовой зоны

нальных бассейнов, устьям рек, т.е. районам с максимальным поступлением терригенного материала.

Данные распределения элементов — гидролизатов свидетельствуют о преимущественном нахождении их в кристаллической структуре минералов и весьма ограниченном развитии в породах их свободных форм. Нахождение в виде свободных форм в какой-то мере свойственно галлию и титану, относительное накопление которых в глинистых породах свидетельствует о его большой подвижности и позволяет предположить его частичную миграцию в коллоидах или растворах. Наиболее высокие содержания титана (6000—8000·10⁻⁴%) установлены в глинистых породах олигоцена северо-западного района Силезской зоны и в отложениях менили-

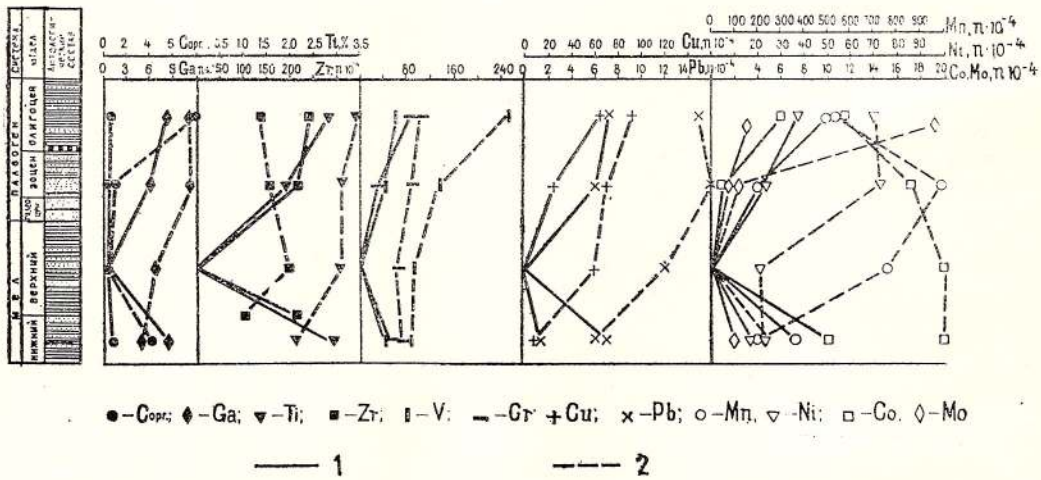


Рис. 2. — Распределение главнейших акцессорных элементов в породах мелового и палеогенового флиша Силезской зоны.

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товой свиты центрального района Скибовой зоны. В последних содержится значительная примесь пирокластического материала.

Самые высокие концентрации элементов подгруппы железа — ванадия и хрома — связаны в основном с глинистыми породами. Содержание ванадия почти повсеместно превышает кларковый уровень. Эта закономерность сохраняется в целом как для терригенных, так и для глинистых пород. Наиболее высокие концентрации ванадия — $300—400 \cdot 10^{-4}\%$ — отмечаются в глинистых породах менилитовой свиты, развитой в пределах Субсилезской зоны и в северо-западном и центральном районах Скибовой и Силезской зон. Кроме органического материала, эти породы содержат примесь пирокластики. На рис. 1 и 2 наблюдается прямая корреляционная связь ванадия с $C_{орг.}$. Основная масса ванадия находится в глинистых породах, где его накопление происходит благодаря сорбции глинистыми частицами. Ванадий вместе с медью, свинцом и хромом также сорбируется органическим веществом, присутствующим в дисперсной форме в глинистых породах. Наибольшие концентрации ванадия наблюдаются в сильно битуминозных разностях ($C_{орг.}$ — 11— 16%). Гольдшмидт (1954) пришел к выводу о том, что ванадий, очевидно, является также катализатором при конденсации и формировании углеводородов. В битуминозных сланцах концентрация ванадия происходила биохимическим путем. Он входил в биохимический цикл, переходя из V^{+3} в V^{+5}. Этот элемент образует стойкие метало-органические соединения, которые никаким образом не преобразуются ни в процессах диагенетических, ни даже метаморфических. В изученных породах намечается прямая связь между содержанием ванадия и титана (особенно в отложениях Скибовой зоны). Такая же связь отмечается и в современных морских осадках — Емельянов и др. (1979). В связи с этим можно предположить, что ванадий, особенно V^{+4}, может замещать Ti^{+4} в титансодержащих минералах. Часть ванадия в определенных условиях (в основном при высоком содержании органического вещества) становится подвижной. Возможно именно в этих условиях образуются ванадийорганические соединения.

Кривые распределения хрома в песчаниках в целом подобны кривым распределения ванадия и титана. Средние содержания его в песчаных породах колеблются от 30 до $80.10^{-4}\%$. Максимальные содержания хрома отмечаются в песчаниках из флишевых отложений центрального района Силезской зоны ($300.10^{-4}\%$) и в глинистых отложениях северозападного района этой зоны ($150.\ 10^{-4}\%$). В песчаниках и аргиллитах менилитовой свиты, развитой в центральном районе Скибовой зоны, содержание хрома нередко достигает $200.10^{-4}\%$. В этих геохимически аномальных зонах наряду с повышенными содержаниями хрома наблюдается увеличение концентраций титана (до $8000.10^{-4}\%$) и ванадия (до $300.10^{-4}\%$).

Наиболее вероятной формой миграции хрома являются коллоиды и тонкие взвеси пород, а также возможен перенос в виде комплексов с органическим веществом. Основными носителями хрома являются ультраосновные породы, содержащие хромшпинелиды. Разрушение хромшпинелидов при эпигенезе сопровождается выносом хрома. Приуроченность повышенных содержаний хрома к песчаным и глинистым породам олигоцена связана с его миграцией в составе обломков минералов (в основном шпинели) и механических взвесей. Его поведение в данном

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случае напоминание поведение титана в этих породах — содержание обоих элементов достигает максимума в аргиллитах и несколько падает в сторону песчаников.

Элементы халькофильной подгруппы (свинец и медь) также изменяют свои содержания в зависимости от стратиграфического положения. Кривые распределения меди и свинца в песчаниках в целом напоминают кривые распределения ванадия и хрома. Среднее содержание меди в песчаниках колеблется в пределах 20—66.10^{-4}%. В глинистых породах оно составляет 60—136.10^{-4}%, в карбонатных породах — 50—100.10^{-4}%, в туфогенных породах менилитовой свиты повышается до 100—200 . 10^{-4}%. Такие же величины содержаний меди характерны для глинистых пород эоцена Субсилезской единицы, где она вместе со свинцом образует геохимически аномальную зону. Еще одна зона геохимической аномалии установлена в глинистых породах эоцена Скибовой зоны (довжинская свита), где содержание меди достигает 500 . 10^{-4}%.

В целом содержание меди увеличивается в глинистых породах. В связи с этим можно предположить, что в морских илах она в основном связывалась с глинистыми минералами, которые являются хорошими сорбентами меди. Кроме того, она хорошо сорбируется гелями гидратов окиси железа, марганца, алюминия, кремнезема. Органические компоненты, как известно, играют большую роль в миграции не только медино всей группы халькофильных элементов. Содержание меди находится в прямой зависимости и от количества органического вещества. Она дает соединения с гуминовыми кислотами, которые удерживают ее в растворенном состоянии. Некоторая часть меди, видимо, содержится в сульфидах.

Таким образом, концентрация меди контролируется количеством глинистых минералов, органического вещества и пирита, а в толщах, обогащенных марганцем, количеством гидроокислов марганца, сорбирующих медь.

Средние содержания свинца в песчаниках составляют 2—7 . 10^{-4}% в глинистых породах — 12—18 . 10^{-4}%, повышаясь в карбонатных породах до 11—20 . 10^{-4}%. В глинистых породах менилитовой свиты, где установлена примесь пирокластического материала (северо-западный район Скибовой зоны) количество свинца составляет 20—30 . 10^{-4}% Как уже отмечалось, наибольшие содержания свинца (100 . 10^{-4}%). отмечаются в глинистых породах верхнего эоцена Субсилезской зоны. Здесь он вместе с медью образует зону геохимической аномалии. Максимум содержания свинца в песчаниках верхнего мела Скибовой зоны связан, вероятно, с их высокой карбонатностью. Кривая распределения свинца в глинистых породах Силезской зоны соответствует кривым распределения марганца и никеля в этих породах.

Преимущественное накопление свинца в глинистых породах, а местами и в карбонатах, свидетельствует о том, что он мигрирует главным образом в виде истинных и коллоидных растворов.

Элементы марганцевой подгруппы — марганец, никель, кобальт, молибден — пользуются повсеместным распространением, и их содержание часто превышает кларковый уровень. Кривые распределения этих элементов в песчаниках обладают большим сходством. Максимальные содержания их отмечаются в глинистых породах. Особенно резко увели-

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чивается содержание молибдена в глинистых породах олигоцена. Кривые распределения этого элемента напоминают кривые распределения $C_{орг.}$

Марганец является наиболее активным мигрантом в марганцевой подгруппе, на что указывает его повышенное содержание в глинистых и карбонатных породах. Заметные концентрации образует марганец в глинистых и песчаных породах Скибовой зоны и в глинистых породах Силезской зоны (см. рис. 1 и 2). Самые высокие содержания марганца наблюдаются в эоценовых глинистых породах Силезской зоны, которые в отдельных участках, расположенных в пределах Голятинского поднятия, достигают $5000—10000 \cdot 10^{-4}\%$. Песчаники из этих же отложений содержат максимально не более $1500 \cdot 10^{-4}\%$ марганца. Сравнительно высоким ($2000—2500 \cdot 10^{-4}\%$) содержанием марганца обладают глинистые породы эоцена северо-западной части Скибовой зоны и Субсилезской зоны.

В песчаниках манявской, выгодской и особенно быстрицкой свит из северных скиб центрального района Скибовой зоны и отдельных участках Силезской зоны содержание марганца достигает $3000—5000.10^{-4}\%$.

Высокие концентрации марганца сохраняются и в олигоценовых отложениях северо-западной части Силезской и Субсилезской зон. В отложениях менилитовой свиты повышенные содержания марганца в песчаниках (до $3000 \cdot 10^{-4}\%$) приурочены к туфогенным разностям пород.

Таким образом, наиболее обогащены марганцем эоценовые отложения Скибовой, Субсилезской и особенно Силезской зон. Геохимическая особенность этих толщ выражается в региональной повышенной марганценосности, которая проявляется в виде высокого кларкового фона и появлении накоплений с высокими концентрациями марганца.

Изучение современных морских осадков показало, что в открытых областях моря основная часть марганца представлена различными гелями и гидроокислами, образовавшимися в самом водоеме независимо от терригенного стока—Емельянов и др. (1979). Обогащение марганцем глубинных слоев воды некоторых водоемов подмечено многими исследователями. В Средиземном море оно происходит скорее всего за счет поглощения растворенного и коллоидного марганца гидроокислами железа и глинистыми минералами.

В изученных породах существует прямая связь между содержанием железа и марганца. Этот факт, а также приуроченность наиболее высоких концентраций марганца к глинистым породам свидетельствует о том, что в глубинных слоях эоценового моря, содержащих высокие концентрации марганца, он, вероятно, адсорбировался гидроокислами железа и глинистыми частицами, а также пелитоморфным кальцитом. Таким образом, осаждение марганца на дно происходило, вероятно, за счет коагуляции и осаждения сгустков марганца, так и за счет поглощения его различными твердыми частицами.

Никель и кобальт сопутствуют обычно друг другу в породах, хотя несколько отличаются по своим геохимическим свойствам. Следует отметить, что количество никеля в породах зависит как от его содержания в седиментационном бассейне, так и от состава глинистых минералов в аргиллитах. Никель чаще всего адсорбируется глинистыми минералами, обладающими различными адсорбционными свойствами. Гидрослюды обладают низкими адсорбционными свойствами, смешаннослойные минералы и монтмориллонит — наиболее высокими. Кроме присутствия в

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породах в виде адсорбированных ионов, никель входит в состав решеток глинистых минералов, замещая алюминий.

Кобальт способен к более активной миграции. Он нередко мигрирует в виде истинных растворов, о чем свидетельствует местами увеличение его содержаний в известняках (до $20 \cdot 10^{-4}\%$).

Иногда никель и кобальт концентрируются в пиритах. Эти элементы имеют близкие к железу ионные радиусы и образуют группу изоморфных элементов. Видимо, никель и кобальт изоморфно замещают железо в структуре дисульфида, в отличие от меди, которая образует самостоятельные фазы сульфидов, находящихся в срастании с пиритом. Основным источником никеля и кобальта являются продукты выветривания основных пород. Оба элемента в бассейне седиментации сорбируются окислами марганца, железа, захватываются коллоидами кремнезема и глинозема. Большую роль в переносе растворенного никеля играют гуминовые кислоты.

Еще одним, весьма геохимически подвижным элементом этой подгруппы является молибден, который концентрируется в породах всего разреза мела и палеогена в количествах, превышающих кларковые. В песчаниках его количество составляет $1-3 \cdot 10^{-4}\%$ (в песчаниках олигоцена повышается до $5 \cdot 10^{-4}\%$); в глинистых породах содержание молибдена увеличивается, достигая максимума в породах олигоцена менилитовой свиты — $30 \cdot 10^{-4}\%$ (в среднем). В отдельных участках в пределах южных скиб центральной части Скибовой зоны, содержание молибдена в битуминозных аргиллитах составляет $100 \cdot 10^{-4}\%$ (в 50 раз превышает его кларковое содержание). Повышенные содержания молибдена ($40-60 \cdot 10^{-4}\%$) отмечаются в менилитовых аргиллитах Покутскобуковинских складок (юго-восточная часть Внутренней зоны Предкарпатского прогиба). Кривые распределения молибдена подобны кривым распределения ванадия и $C_{орг.}$. Наиболее высокие концентрации его наблюдаются в наиболее битуминозных разностях глинистых пород, что объясняется сильной восстановленностью этих осадков, содержащих много органического вещества и пирита.

Данные изучения распределения и концентрации элементов в главных типах пород, слагающих карпатский флиш, в разрезе и на площади дают возможность выделить группу руководящих корреляционных элементов, характерных для определенных стратиграфических уровней. Для флишевой формации северного склона Карпат такими корреляционными элементами являются марганец, ванадий и молибден. Это послужило основанием для выделения эоценовой марганцевой и олигоценовой ванадий-молибденовой геохимических провинций, в пределах которых выделяются зоны геохимических аномалий. Среди эоценовых отложений геохимические аномалии образуют свинец и медь, которые, видимо, являются элементами, сингенетичными марганцу, основная масса которых сорбировалась гидратами окиси марганца. В районе Голятинского поднятия геохимически аномальную зону образуют барий, стронций и мышьяк. Здесь содержание стронция в песчаниках равно 0,2—0,4%, бария — 3,5—7,5%, мышьяка — 0,2—0,6%, что в сотни, а для мышьяка в тысячи раз, превышают их кларковые содержания. Концентрация этих элементов связана с более поздними наложенными процессами стадии гипогенного эпигенеза. Превращение Карпат в горно-складчатую систему (неоген) повлекло за собой резкое изменение длительно существовавшего гидродина-

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мического режима водоносных комплексов. Развитие тектонических нарушений в пределах Голятинского поднятия вызвали появление очагов разгрузки хлор-кальциевых мышьяк-барионосных растворов и сероводородных вод. Миграция растворов осуществлялась по трещиноватости пород. Этим объясняется развитие оруденения по сети трещин отдельности, кливажа, брекчирования.

В толщах олигоцена в битуминозных аргиллитах геохимически аномальные зоны образует уран.

Наиболее высокие содержания молибдена и ванадия приурочены к битуминозным породам, развитым в районах сочленения Скибовой зоны с Предкарпатским прогибом и Скибовой зоны с Силезской зоной. Повышенные содержания урана приурочены к зонам тектонических нарушений в районах сочленения Скибовой и Субсилезской зон с Силезской зоной.

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ВОПРОСЫ

Лозыняк 1. При характеристике распределения кварца Вы упоминали южный и северный борта геосинклинали. Что это за борта?

2. При расчете принималась ли во внимание Бориславско-Покутская зона?

Ответы 1. В составе северного склона Карпат мы рассматриваем зоны Скибовую , Силезскую и Субсилезскую, в составе южного склона — все что южнее их.

2. При исследованиях принимались во внимание отложения Поляницкой свиты Покутской зоны.

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МИНЕРАЛЬНЫЕ АССОЦИАЦИИ ФЛИШЕВЫХ КОМПЛЕКСОВ СОВЕТСКИХ КАРПАТ — ИНДИКАТОРЫ ПРОЦЕССОВ СЕДИМЕНТОГЕНЕЗА И ЛИТОГЕНЕЗА[1]

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Количественные и качественные соотношения минералов во флишевых толщах мела и палеогена дают возможность выделить характерные минеральные ассоциации, включающие седиментогенные минералы, минералы-индикаторы стадий диа- и катагенеза, а также наложенные минеральные образования, связанные с процессами регрессивного и гипогенного эпигенеза. Установленные типы минеральных ассоциаций являются основой для познания эволюции вещественного состава пород на различных этапах геологического развития карпатской складчатой области в целом и отдельных структурно-фациальных зон, а также отражает постседиментационную геологическую историю флишевых образований.

Характер распределения седиментогенных минералов в разрезе и на площади показывает, что ассоциации этих минералов (различные типы кварца, полевых шпатов, минералы группы микоидов) имеют как общие, так и отличительные черты. Это объясняется явлениями неоднократного переотложения материала и поступлением в область размыва новых порций пород из областей питания, отличающихся по своему петрографическому составу.

Кварц является наиболее распространенным минералом в составе обломочных пород. Он имеет самую разнообразную форму, по степени окатанности бывает угловатый, полуугловатый и окатанный. По морфологическим особенностям и с учетом его нахождения в обломках пород различного петрографического состава были выделены наиболее часто встречаемые шесть типов терригенного кварца (таблица 1).

Распределение выделенных типов кварца в породах мел-палеогеновой флишевой формации Советских Карпат показывает неоднородный характер источников питания и своеобразие гидродинамики морского бассейна.

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[1] Доклад прочитанный на XII-ом Конгрессе Карпато-Балканской Геологической Ассоциации, 1981 г., сентябрь 8—13, Бухарест, Румыния.

[2] СССР

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ТАБЛИЦА 1

Типы кварца в породах флишевой формации Советских Карпат

Тип №№	Характер угасания	Тип включений	Распределение включений в зерне	В обломках каких пород наблюдается
1	нормальное	точечные газовожидкие	равномерное	магматические
2	,,	точечные + циркон, апатит, магнетит, ильменит	,,	,,
3	волнистое	точечные + рутил, гранат, силлиманит, мусковит	,,	метаморфические
4	,,	точечные газовожидкие	струйчатое	,,
5	,,полосчатое''	,,	равномерное	,,
6	мозаичное или блоковое	,,	,,	жильные образования

Полевые шпаты пользуются в обломочных породах повсеместным распространением, но в отличие от кварца их содержание ограничено и не превышает 30% общего объема породы (в среднем 10—12%). Они представлены плагиоклазами и микроклинами, причем, последние играют обычно подчиненную роль. Среди плагиоклазов выделяются альбит, олигоклаз-альбит, олигоклаз, андезин, в редких случаях анортит и гиалофан. Калишпаты представлены решетчатым микроклином и микроклин-пертитом. По данным изучения основных морфологических признаков полевых шпатов были выделены их основные типы (таблица 2) и изучено распределение по площади флишевого бассейна как в мелу, так и в палеогене.

ТАБЛИЦА 2

Типы полевых шпатов в породах флишевой формации Советских Карпат

Тип №№	Состав	Степень измененности	Тип двойникования	Характер включений
1	Олигоклазальбит № 27—28	Серицитизированный	Простые двойники	точечные
2	Альбит № 2,5	Свежий	Тонкая двойниковая штриховка	,,
3	Андезин № 35—37	,,	Широкие полисинтетические двойники	точечные + графические вростки кварца, апатит, гранат, сфен, турмалин, мусковит
4	Олигоклаз № 28—32	,,	,,Висячие двойники''	точечные
5	Альбит № 5,.	,,	Деформированные двойники	,,
6	Микроклин и микроклин-пертит	,,	Решетчатый	,,

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Минералы группы слюд представлены биотитом, мусковитом и гидробиотитом. Биотит наблюдается в подчиненном количестве и только в породах палеогена. Гидробиотит и мусковит пользуются повсеместным распространением.

Ассоциации акцессорных седиментогенных минералов представлены группой таких устойчиво доминирующих минералов, как гранат, рутил, циркон, турмалин, апатит. Кроме того, отмечается присутствие в виде незначительной примеси сфена, ильменита, шпинели, ставролита, лейкоксена, эпидота, гиперстена, роговой обманки. Каждая структурно-фациальная зона характеризуется определенным количественным соотношением минералов. Пестрота состава этих зон обусловлена смешанным характером пород областей питания. Распределение их по структурным единицам в конкретные периоды геологической истории неравномерно и подчиняется некоторым закономерностям: в южной части флишевого бассейна отмечено большее разнообразие акцессориев, на северном — значительно меньше.

Глинистые минералы составляют основную массу глинистых и глинисто-кремнистых пород, входят в состав мергелей, а также в состав цемента обломочных пород. В составе цемента глинистые минералы чаще всего в различной степени перекристаллизованы. Глинистая составляющая большинства из изученных пород представлена характерной для геосинклинальных областей гидрослюда-хлоритовой ассоциацией, либо ассоциацией смешаннослойный минерал типа гидрослюда-монтмориллонит (обычно с преобладанием гидрослюдистых слоев) + хлорит.

Данные рентгеноструктурного анализа позволяют наметить по количественному соотношению основных глинистых минералов семь ассоциаций: 1. гидрослюда + хлорит; 2. гидрослюда; 3. смешаннослойные минералы + хлорит; 4. смешаннослойные минералы + каолинит; 5. монтмориллонит + хлорит + каолинит; 6. монтмориллонит + + гидрослюда + каолинит; 7. смешаннослойные минералы + монтмориллонит + каолинит.

Парагенетические ассоциации глинистых минералов отражают определенный этап постседиментационного преобразования пород. Смешаннослойные фазы и монтмориллонит исчезают в породах, претерпевших стадию глубинного катагенеза, давая начало диоктаэдрической гидрослюде и хлориту. Следует отметить, что в пределах Восточных Карпат граница зон начального и глубинного катагенеза не совпадает с определенным стратиграфическим уровнем. Переход начального катагенеза в глубинный в одних структурно-фациальных зонах происходит в нижнем мелу, в других — в эоцене.

Главнейшими аутигенными минералами стадий диа- и катагенеза являются карбонаты, минералы кремнезема, пирит, глауконит.

Карбонатные минералы образуются на всех этапах формирования карбонатных пород. Наибольшим распространением пользуется кальцит наиболее чистые разности которого содержатся в перекристаллизованных и вторичных песчаных известняках, а также в кальцитовых прожилках. В перекристаллизованных известняках иногда развиваются светлобурые кристаллы анкерита. При сравнительно высоких содержаниях магния и железа наблюдается кристаллизация двух карбонатных фаз — анке-

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рита и кальцита. Карбонаты входят в состав диагенетических конкреционных образований, сложенных поликомпонентными изоморфными смесями карбонатов железа, кальция и магния. Ведущая роль в составе карбонатной составляющей конкреций из флишевых толщ южного склона Карпат принадлежит сидериту (иногда магниевому сидериту), при этом наблюдается примесь кальцита, анкерита, родохрозита. В конкреционных образованиях, развитых во флише северного склона Карпат, преобладает доломит.

Кремнезем является широко распространенным веществом, слагающим основную массу кремнистых пород и конкреционных образований, входящим в состав цемента обломочных пород, а также выполняющим трещины, поры и пустоты в породах и замещающим органические остатки.

Среди минеральных форм кремнезема установлены опал, кристобалит и кварц, различающийся по величине „структурного совершенства". Местами в единой толще (например, в менилитовой толще олигоценового возраста), претерпевшей в одинаковой степени раннекатагенетические преобразования, существуют все три минеральные формы SiO_2.

Изучение структурных особенностей кварца позволило установить, что наиболее высокой степенью кристалличности обладает кварц эпигенетический, образовавшийся в трещинах и пустотах в условиях свободного роста, затем, в порядке убывания степени кристалличности следует кварц органогенно-хемогенного происхождения, составляющий основную массу фтанитов. Еще меньшей степенью кристалличности обладает диагенетический кварц, входящий в состав кремнистых конкреционных образований и туфогенных силицитов (продукт гальмиролитического разложения пирокластики). Самая низкая степень кристалличности оказалась у кваца предположительно хемогенного происхождения из кремней ассоциирующих с туфами. Таким образом, намечается определенная зависимость между генетической принадлежностью кремнезема и степенью кристалличности его твердой модификации — кварца.

Пирит в меловых и палеогеновых породах пользуется повсеместным распространением. Чаще всего он замещает обломки углефицированных растительных остатков с сохранением структуры древесины, либо инкрустирует растительные остатки. Пирит также развивается в виде микроконкреций, иногда образует цемент песчаников. В битуминозных породах пирит обычно диагенетический, но может быть и эпигенетическим.

Глауконит отмечается в породах повсеместно в разрезе от нижнего мела до олигоцена. Наблюдаются три разновидности глауконита: густо-зеленая, светлозеленоватая, почти бесцветная и синевато-зеленая, отличающиеся различными показателями преломления.

Аутигенный полевой шпат пользуется довольно ограниченным развитием и отмечается главным образом в меловых породах южного склона Карпат. Он образует две формы выделения: 1. — идиоморфные зерна кислых плагиоклазов в карбонатных породах и 2. — регенерационные каемки вокруг зерен обломочного плагиоклаза.

Минералы наложенных процессов характеризуют стадию гипогенного эпигенеза. В отдельных участках идет образование наложенной минеральной ассоциации: барит + реальгар + пирит + кварц + озокерит. Это связано со сложными гидрохимическими процессами, которые были

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обусловлены тектонической активизацией. Главным фактором, определяющим рудоотложение, было сопряжение разгрузок хлоркальциевых и сероводородных вод. Со стадией гипогенного эпигенеза мы связываем образование иодистой ртути, найденной впервые в Карпатах во флишевых породах палеогена южного склона, где она в виде отдельных кристаллов и корочек наблюдается в микропрожилках и пустотах в ассоциации со смолисто-черными битумами.

Исследование аутигенных минеральных ассоциаций показало, что такие минералы, как карбонаты, кварц и пирит являются полистадийными образованиями.

Изучению минеральных ассоциаций предшествовали детальные исследования пород и их взаимоотношений в составе флишевой формации, что отражало определенные физико-географические и тектонические обстановки на различных стадиях развития геосинклинали. Эти исследования создавали необходимый ,,геологический фон'' для познания сложных и разнообразных процессов минералообразования.

В таблице 3 в обобщенном виде представлены главнейшие комплексы минералов (седиментогенных, глинистых и аутигенных) во флишевых породах различных стратиграфических уровней.

В породах нижнего мела ассоциация породообразующих седиментогенных минералов представлена главным образом кварцем метаморфических пород, реже — жильным. Плагиоклазы в отложениях южного склона наблюдаются в виде 4-х разновидностей, из микоидов отмечается мусковит и гидробиотит. В породах северного склона Карпат уменьшается количество разновидностей плагиоклаза, появляется микроклин. Набор главных акцессорных минералов и их количественные взаимоотношения в целом сходны в породах как южного, так и северного склона. Для обоих склонов характерен одинаковый состав глинистых и аутигенных минералов.

Для пород из верхнемеловых толщ южного склона Карпат характерно присутствие всех выделенных разновидностей кварца и плагиоклаза, в заметном количестве встречается микроклин, в составе слюд отмечается мусковит и гидробиотит. В породах верхнемелового возраста северного склона сокращается количество разновидностей кварца и плагиоклаза. В породах северного склона, кроме повсеместно развитой ассоциации гидрослюда+хлорит, в составе глинистой составляющей появляются монтмориллонит и смешаннослойные минералы. Более широкий спектр аутигенных минералов отличает породы южного склона от северного.

Анализ обломочного материала позволяет установить, что наряду с преобладающими метаморфическими породами, в область размыва включались гранитоиды, пегматиты, а также эффузивы основного состава. Распределение обломочного материала свидетельствует о появлении нового внутрибассейнового источника питания.

Ассоциации породообразующих седиментогенных минералов пород нижнего и среднего палеогена также отличаются большим разнообразием типов кварца и плагиоклаза, количество которых сокращается в отложениях северного склона. Характерным является появление биотита а в группе акцессорных минералов — эпидота, ильменита и гиперстена. Большим разнообразием отличаются ассоциации глинистых минералов

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породах южного склона, где, кроме обычной ассоциации гидрослюда + хлорит, заметную роль в составе глинистой составляющей играют монтмориллонит и каолинит. Характерной чертой пород среднего палеогена является широкое развитие наложенных аутигенных минеральных

ТАБЛИЦА 3

Главнейшие комплексы минералов в породах флишевой формации Советских Карпат

Основные характеристики		Нижний мел		Верхний мел	
		Южный склон	Северный склон	Южный склон	Северный склон
Породообразующие седиментогенные минералы *		кварц 3, 4, 5, 6 типов; плагиоклаз 1, 2, 4, 5 типов; мусковит, гидробиотит.	кварц 2, 3, 4, 6 типов; плагиоклаз 2,5 типов; микроклин; мусковит.	кварц 1, 2, 3, 4, 5, 6 типов; плагиоклаз 1, 2, 3, 4, 5, типов; микроклин; мусковит, гидробиотит.	кварц 3, 4 типов; плагиоклаз 2, 3, типов; микроклин; мусковит, гидробиотит.
Акцессорные седиментогенные минералы **		гранат циркон турмалин рутил апатит (сфен)	циркон турмалин; рутил (сфен ильменит).	гранат турмалин рутил циркон апатит (сфен, лейкоксен).	циркон турмалин рутил гранат (сфен, ильменит).
Ассоциации глинистых минералов		1. гидрослюда + хлорит, 2. гидрослюда.	1. гидрослюда + хлорит. 2. гидрослюда	1. гидрослюда + хлорит.	1. гидрослюда + хлорит, 2. гидрослюда + хлорит + монтмориллонит. 3. смешанно-слойный минерал + хлорит.
Аутигенные минералы	Минералы стадий диа-и катагенеза	кварц, плагиоклаз, кальцит, сидерит, пирит, глауконит.	кварц, кальцит, сидерит, пирит. глауконит.	кварц, плагиоклаз, кальцит, сидерит, пирит	кальцит, пирит. глауконит.
	Минералы наложенных процессов	кальцит, кварц	кальцит, кварц,	кальцит кварц битумы.	кальцит
Породообразующие седиментогенные минералы		кварц 1, 2, 3 4, 5, 6 типов плагиоклаз 1, 2, 3, 4, 5 типов микроклин; мусковит, гидробиотит, биотит.	кварц 1, 2, 3, 4 типов; плагиоклаз 1, 2, 5 типов; микроклин; мусковит, биотит.	кварц 1,2,3, 4, 5, 6 типов; плагиоклаз 2,3 типов; микроклин; мусковит.	кварц 1,3 типов; плагиоклаз 1, 2, 4 типов; микроклин; мусковит, гидробиотит, биотит

Примечание: * Смотри таблицу 1 и 2; ** В скобках заключены второстепенные акцессорные минералы.

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продолжение таблицы 3

Основные характеристики		Палеоцен — Эоцен		Олигоцен	
		Южный склон	Северный склон	Южный склон	Северный склон
Акцессорные седиментогенные минералые		турмалин гранат циркон рутил (сфен, эпидот, ильменит, гиперстен)	апатит турмалин гранат циркон рутил.	рутил циркон турмалин апатит гранат (шпинель, гиперстен, монацит).	циркон гранат турмалин апатит рутил (шпинель, гиперстен, рог. обманка, эпидот)
Ассоциации глинистых минералов		1. гидрослюда + хлорит, 2. смешаннослойный минерал + + хлорит +каолинит, 3. монтмориллонит + +хлорит + каолинит, 4. монтмориллонит + гидрослюда + каолинит.	1. гидрослюда + хлорит, 2. смешаннослойный минерал + хлорит	1. гидрослюда + хлорит + каолинит, 2. смешаннослойный минерал + монтмориллонит + каолинит.	1. гидрослюда — хлорит монтмориллонит. 2. смешаннослойный минерал + + монтмориллонит + каолинит.
Аутигенные минералы	Минералы стадий диа-и катагенеза	кальцит, кварц, сидерит, родохрозит, пирит.	кальцит, доломит, пирит, глауконит.	Кальцит, сидерит, пирит, глауконит.	опал, кристобалит, кварц, кальцит, доломит, пирит, ломонтит, глауконит.
	Минералы наложенных процессов	кальцит, битумы, иодистая ртуть.	кальцит, кварц битумы, барит, реальгар, пирит.	кальцит, кварц битумы, пирит.	кальцит, кварц, битумы, пирит.

ассоциаций, формирование которых связано с проявлениями тектоно-магматической активизации.

Судя по составу обломочного материала, материнскими образованиями были метаморфические, магматические и осадочные породы активно разрушающихся южного и северного бортов геосинклинали, а также внутрибассейновые поднятия.

Наиболее резкие отличия в составе породообразующих седиментогенных, глинистых и аутигенных минералов отмечаются в породах южного и северного склона Карпат в завершающий этап развития геосинклинали — в олигоцене. В породах южного склона Карпат в ассоциациях породообразующих седиментогенных минералов присутствуют все разновидности кварца, при этом в заметном количестве появляются переотложенные разности. Плагиоклазы представлены двумя разновидно-

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стями, из слюд присутствует лишь мусковит. В породах северного склона количество разновидностей кварца сокращается до 2-х. Здесь большим разнообразием отличаются ассоциации глинистых и аутигенных минералов, что, вероятно, можно связывать с процессами разложения тонкой пирокластики.

Среди всего многообразия разновидностей седиментогенных минералов можно выделить так называемые ,,сквозные'' минералы, развитые повсеместно в разрезе и на площади. Это метаморфическая разновидность кварца 3-го и 4-го типа (см. табл. I), плагиоклаз 2-го типа (см. табл. 2), решетчатый калишпат и мусковит, что, во-первых, свидетельствует о преобладающей роли метаморфических пород в областях питания, а, во-вторых, о стойкости этих разновидностей минералов в процессе переноса.

Анализ минерального состава ассоциаций различных генетических групп минералов дает основание считать, что основные источники питания располагались в пределах южного борта геосинклинали (большое значение имеют метаморфические породы, в меньшей степени — осадочные). Заметная роль в осадконакоплении принадлежит также метаморфическим породам низких ступеней метаморфизма, входящих в состав областей питания северного борта геосинклинали. В олигоцене отмечается большое влияние на процессы осадкообразования вулканического фактора.

Следует отметить, что латеральная смена одновозрастных минеральных ассоциаций породообразующих седиментогенных минералов связана, скорее всего с процессами дифференциации терригенного материала в бассейне седиментации и вряд ли определялась зрелостью рельефа области сноса. На протяжении всего мела и палеогена вблизи источников сноса (особенно на южном склоне) формировались осадки более разнообразные по минералогическому составу.

Исследование процессов минералообразования, включая анализ взаимоотношений всех составных компонентов пород, на фоне геологической истории карпатской геосинклинальной области имеет большое значение для познания геодинамической минералогии (геоминералогии) региона — направления в литологической науке, которое успешно развивается в настоящее время.

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Traducători : A. BRATU, A. BĂJENARU, A. LUPAN, A. NĂSTASE, M. TOPOR, S. ȚOCU
Ilustrația : V. NIȚU

Dat la cules : iulie 1983. Bun de tipar : aprilie 1984. Tiraj 750 ex. Hirtie scris I A. Format 70×100/56 g. Coli de tipar : 24. Comanda : 226. Pentru biblioteci indicele de clasificare 55(058).

Tiparul executat la Întreprinderea Poligrafică „Informația" str. Brezoianu nr. 23—25. București, România

Institutul Geologic al României

Institutul Geologic al României

L'Annuaire de l'Institut de Géologie et de Géophysique a été publié le long des années sous les titres suivants:

Anuarul Institutului Geologic al României, t. I - XV (1908-1930)

Anuarul Institutului Geologic al României (Annuaire de l Institut Géologique de Roumanie) t. XVI - XXII (1931 - 1943)

Anuarul Comitetului Geologic (Annuaire du Comité Geologique) t. XXIII - XXXIV (1950 - 1964)

Anuarul Comitetului de Stat al Geologiei (Annuaire du Comité d'Etat pour la Géologie) t. XXXV-XXXVII (1966 - 1969)

Anuarul Institutului Geologic (Annuaire de l'Institut Géologique) t. XXXVIII - XLII (1970 - 1974)

Anuarul Institutului de Geologie şi Geofizica (Annuaire de l'Institut de Geologie et de Géophysique) depuis le vol. XLIII-1975

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