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2. ZĂCĂMINTE

BARITINA DE LA CÎRJELARI, DOBROGEA [1]

DE

ION BERBELEAC [2], CONSTANTIN LAZĂR [3], AVRAM ȘTEFAN [3], EMILIAN ROȘU [3]

Barite deposits. Devonian. ***Paleozoic limestone.*** *Alkaline rhyolite. Mineralogical study Contact metamorphism. Dobrogea — Central Dobrogea.*

Abstract

Cîrjelari barytine, Dobrogea. Near Cîrjelari, south of Valea Satului, in the neighbourhood of the contact between Paleozoic alkaline rhyolites (± riebeckite) on one side and Devonian limestones together with Presilurian phyllitic shales on the other side, on about 200 m^2 area, several baryitine and limestones blocks and fragments occur. In the area with barytine blocks as well as in the whole region, rhyolites are strongly laminated and show a lamination lineation oriented N20°–40°W and obvious inclinations eastwards. Baritine, which is yellow-brown at the surface and grey-yellow in the fresh break, is displayed in a parallel-banded and fine-granular structure. Sometimes here, there are noticed spongeous aspects caused by levigation of primary minerals, possibly sulphides. Baritine microscopic study points out the presence of stratified relict structures with obvious dynamo-metamorphic modifications of cataclastic, protoclastic, mylonitic and blastomylonitic type; the main minerals are baritine and quartz, subordinately occurs a micaceous mineral too. The presence of baritine blocks at Cîrjelari implies the existence in North Dobrogea of some baritine lenses or beds with or without sulphides, probably in the lower part of Devonian limestones.

Résumé

Barytine de Cîrjelari, Dobrogea. Aux environs de la localité de Cîrjelari, au sud de Valea Satului, près du contact entre les rhyolites alcalines (± riebeckite) paléozoiques, d'une partie et les calcaires dévoniens associés aux schistes phylliteux présiluriens d'une autre partie, on a

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[2] Intreprinderea de Prospecțiuni Geologice și Geofizice, str. Caransebeș nr. 1, București 32.

[3] Institutul de Geologie și Geofizică, str. Caransebeș nr. 1, R 79678, București, 32.

rencontré, sur une étendue de 200 m² environ, plusieurs blocs et fragments de barytine e-calcaires. Les rhyolites de la zone d'affleurement de la barytine et de toute la région, sont fortet ment laminées ; les linéations de laminage sont orientées N20—40°W et pendage accentué vers l'est. La barytine, jaunâtre-brunâtre à la surface et grisâtre-jaunâtre en cassure fraiche, est disposée en rubans parallèles à structure à grains fins où on remarque des corps spongieux engendrés par la lévigation de certains minéraux primaires, possiblement sulfures. L'étude microscopique de la barytine met en évidence la présence des structures reliques stratifiées à des modifications accentuées dinamométamorphiques du type cataclastique, protoclastique, mylonitique et blastomylonitique ; les minéraux principaux sont la barytine et le quartz, y apparaît aussi subordonnément un minéral micacé. La présence des blocs de barytine à Cîrjelari pose le problème de l'existence en Dobrogea de Nord, probablement dans la base des calcaires dévoniens, de quelques lentilles ou couches de barytine avec ou sans sulfures.

Pînă în prezent, la Cîrjelari n-a fost semnalată prezența baritinei. În cursul cercetărilor noastre de teren din 1984 a fost constatată existența mai multor blocuri și fragmente de baritină și calcare, toate situate în dealul de la sud de Valea Satului, în apropierea contactului dintre rocile riolitice și formațiunile presiluriene și devoniene (figura). Aici, la cca 150 m de contactul amintit, în versantul vestic al dealului constituit din riolite alcaline, pe o arie de cca 200 m², s-au întîlnit fragmente și blocuri de baritină și calcare cu conture angulare și dimensiuni centimetrice rar pînă la 1 decimetru. În general fragmentele și blocurile de baritină predomină asupra calcarelor. Notăm faptul că în rocile riolitice din jur, în general masive, nu s-au observat fragmente și blocuri de baritină și calcare. Riolitele în această zonă, ca de altfel în întreaga regiune, sînt puternic laminate, lineația de laminare avînd orientare N 20—40° W și înclinări accentuate spre nord-est. Aici, pe alocuri și mai ales în regiunea Piatra Roșie — Muchia Mare, riolitele sînt puternic silicifiate și mineralizate cu hematit și pirită. Zonele alterate se asociază sistemului de fracturi cu orientare NW-SE și NE-SW.

Formațiunile presiluriene aparțin probabil seriei superioare slab metamorfozate (Mirăuță et al. 1968) reprezentată de cuarțite albe, filite sericitoase, filite grafitoase, subordonat șisturi verzi tufogene. Devonianul este reprezentat de calcare albe și cenușii recristalizate (Mirăuță 1966); recristalizarea progresează de la ivirile sud-estice spre cele nord-vestice (figura) și este considerată ca fiind determinată de un metamorfism termic asociat unui magmatism probabil paleozoic.

Jurasicul cuprinde calcare tithonice alb-cenușii, ușor roșiatice și masive situate probabil transgresiv peste formațiunile devoniene. Loessul este larg răspîndit (fig.).

Două sisteme principale de fracturi afectează formațiunile din regiune : unul mai vechi, cu orientare NE-SW, anterior riolitelor și calcarelor jurasice care a determinat ridicarea formațiunilor presiluriene și altul mai recent, cu orientare NW-SE, care delimitează riolitele de formațiunile presiluriene, devoniene și calcarele jurasice ; ultimul sistem se asociază probabil zonei de fracturi Pecineaga-Camena, situată la 1,5—2 km sud-vest.

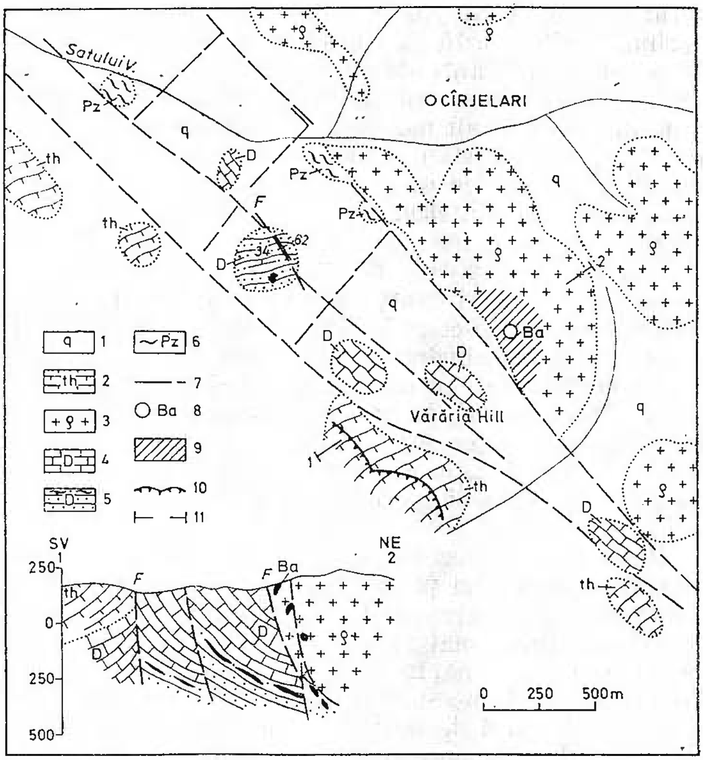

Fig. 1. Schiță geologică a zonei Cîrjelari-Dealul Vărăria : 1, loess ; 2, calcare tithonice ; 3, riolite alcaline ; 4, calcare recristalizate devoniene ; 5, roci detritice devoniene ; 6, formațiuni paleozoice nediferențiate ; 7, falie ; 8, ivirea cu blocuri de baritină ; 9, silicifieri ; 10, carieră ; 11, secțiune geologică.

Schéma géologique de la zone de Cîrjelari-Dealul Vărăria : 1, loess ; 2, calcaires tithoniques ; 3, rhyolites alcalines ; 4, calcaires recristallisés dévoniens ; 5, roches détritiques devoniennes ; 6, formations paléozoïques non différenciées ; 7, faille ; 8, affleurement à blocs de barytine ; 9, silicatizations ; 10, carrière ; 11, coupe géologique.

Mineralizația de baritină

Fragmentele și blocurile de baritină au dimensiuni centimetrice, rar ating un decimetru. Culoarea acestora este gălbuie-cafenie la suprafață și cenușie-gălbuie în spărtură proaspătă. Textura minereului este orientată, cu aspecte spongioase punctiforme provenite din levigarea unor minerale primare, probabil sulfuri. Unele blocuri se remarcă și prin prezența unor fisuri milimetrice umplute cu baritină alb-cenușie. Rar, fragmentele și blocurile de baritină sînt acoperite de cruste cu hidroxizi de fier.

Studiul microscopic al baritinei evidențiază prezența structurilor stratificate milonitice, blastomilonitice etc. Minereul cuprinde în special baritină și cuarț ; subordonat apare un mineral micaceu și sulfuri.

Structurile stratificate sînt interpretate ca reprezentînd relicte ale structurii primare. Ele constă în conservarea în materialul fragmentelor de minereu a unor alternanțe de ritmuri fine milimetrice alcătuite din baritină, cuarț ± un mineral micaceu, sau numai din baritină. Efectele metamorfismului dinamic au modificat structurile inițiale, acestea devenind cataclastice, protoclastice, milonitice și blasto-milonitice.

Structurile cataclastice se caracterizează prin lipsa oricărei orientări a mineralelor din matrice.

Structurile protoclastice sînt de asemenea frecvente, ele remarcîndu-se prin prezența în proporții de 35—50 % a matricei neorientată; porfiroclastele de baritină și cuarț nu arată orientări (Pl. I, fig. 2).

Structurile milonitice constă din porfiroclaste de baritină cu conture angulare sau alungite înglobate într-o matrice fin granulară. Tendința de orientare a porfiroclastelor de baritină ca și a mineralelor din matrice este evidentă (Pl. I, fig. 1). În acest caz granulele și agregatele de cuarț și de baritină pot sau nu prezenta extincție ondulatorie. Matricea constituită din cuarț și baritină, la care uneori sporadic se adaugă mineralul micaceu, este fin granulară și prezintă o structură granoblastică cu aspect poligonat (Pl. I, fig. 1).

În multe cazuri sînt prezente structurile blastomilonitice; ele sînt rezultatul unor recristalizări pronunțate, care au șters parțial structura milonitică a materialului original (Pl. II, fig. 1,2). Procesele de recristalizare au afectat neuniform materialul inițial : cel mai adesea au fost afectate zonele bogate în baritină, în timp ce cele mai bogate în cuarț evidențiază o blasteză slabă. În acest caz, imaginea microscopică redă contrastul dintre agregatele largi de baritină fin cristalizată, pură și transparentă și cele fine, zdrobite, nerecristalizate, care îmbracă granulele izolate de cuarț sau cimentează zonele mai bogate în acest mineral (Pl. II, fig. 2). Asemenea zone au forme insulare sau cu totul neregulate, uneori cu tendință de orientare (Pl. II, fig. 2). Recristalizările totale însă se recunosc prin existența granulelor și agregatelor de cuarț pur într-o masă de baritină transparentă relativ larg cristalizată. De asemenea, este interesant de menționat că fisurile de baritină, cuarț ± calcedonie din agregatele de cuarț sau baritină sînt neafectate sau foarte puțin afectate de recristalizări determinate de metamorfismul dinamic.

Variațiile de structuri prezentate se regăsesc de regulă în cadrul aceluiași fragment sau bloc de minereu de baritină. Tipic însă rămîne structura milonitică care local prezintă treceri spre celelalte structuri menționate și în special spre cea blastomilonitică. Asemenea variații sugerează faptul că fragmentele și blocurile de baritină provin probabil dintr-o lentilă de baritină.

Recristalizările recunoscute microscopic sînt de două tipuri : statice și dinamice.

Recristalizările statice conduc la forme poligonale atît pentru baritină cît și cuarț. Variațiile de dimensiuni ale granulelor în marea majoritate a cazurilor sînt neînsemnate în cadrul aceluiași ritm. La mineralul micaceu neidentificat, recristalizările sînt recunoscute prin prezența cristalelor fin alungite, aliniate foliației de deformare, asociate cu o matrice în care se recunosc și granule de cuarț și baritină cu tendințe de orientare.

Foarte variate sînt aspectele de deformare suferite de mineralele menționate. Astfel baritina porfiroclastică prezintă pronunțate extincții ondulatorii și maclări polisintetice iar adesea lamele de macle sînt ușor curbate. Maclările polisintetice (Pl. I, fig. 1) au o distribuție neuniformă frecvent fiind observate numai în anumite porțiuni ale granulelor. Tot frecvente sînt și maclele după două direcții, maclele ultimului sistem intersectînd pe cele anterior formate (Pl. I, fig. 1). Maclele de deformare (Pl. I, fig. 1,2), ca și liniile de alunecare cu conture curbate remarcate la unele porfiroclaste de baritină sînt, de asemenea, rezultatul deformărilor. Cuarțul porfiroclastic prezintă extincții ondulatorii, iar uneori arată substructuri de deformare. La mineralul micaceu deformările au condus la aglomerarea lui lentiliformă sau fusiformă. Finge-uri simetrice de mineral micaceu în umbrele de presiune ale cuarțului sau de baritină după mineralul micaceu, au fost de asemenea remarcate.

Sporadic în masa baritinei au fost întîlnite granule alungite de cuarț, asemănătoare celor de natură hidrotermală crescute postdeformare.

După cum s-a menționat în aria de răspîndire a fragmentelor și blocurilor de baritină s-au întîlnit și calcare cenușii gălbui ușor rozii cu entroce de crinoizi, de vîrstă probabil devoniană.

O analiză chimică a unei probe de baritină a indicat un conținut de 87,69 % $BaSO_4$ și 0,24 % $BaCO_3$. Dintre ceilalți componenți chimici cel mai important este SiO_2 ; ceilalți componenți au o pondere nesemnificativă.

Dintre elementele minore pot fi menționate Cu, Pb, Zn și Bi ; conținuturile acestora, stabilite prin analiză spectrală informativă, sînt mici (0,00x %).

Avînd în vedere caracterele structurale, texturale, mineralogice și chimice se poate presupune că materialul inițial a reprezentat un sediment format în condiții de mare puțin adîncă. Mîlul de baritină format în mediu oxidant, impurificat periodic cu cuarț detritic a condus la texturile rubanate. Procese ulterioare în special metamorfismul dinamic, au condus la aspectele structural-texturale și mineralogice actuale.

Prezența fragmentelor și blocurilor de baritină și de calcare de la Cîrjelari, întîlnite în apropierea contactului tectonic al riolitelor alcaline cu formațiunile devoniene, sugerează existența în adîncime a unor mineralizații stratiforme de baritină. Aceste mineralizații sînt probabil de vîrstă devoniană și s-ar situa în baza calcarelor (figura). Se poate presupune că baritina a fost scoasă la suprafață fie de către riolite, fie de fracturi. Notăm că în afară de ocurența menționată în regiune, blocuri de baritină, de calcare și șisturi slab metamorfozate au mai fost întîlnite în aria riolitelor din Muchia Mare, situată la cca 2 km NE.

Ocurența de baritină de la Cîrjelari, aduce în atenție pentru prima dată prezența în depozitele devoniene din Dobrogea a unor mineralizații de baritină. Acest fapt implică perspective economice favorabile pentru noi resurse de baritină.

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BARYTINE DE CÎRJELARI, DOBROGEA

(Résumé)

Au sud de Valea Satului, près du contact entre les rhyolites alcalines paléozoïques, les calcaires dévoniens et les schistes phylliteux présiluriens, on a rencontré, sur une surface de 200 m^2 approximativement, plusieurs blocs et fragments de barytine et calcaire. Ces fragments et blocs, situés à une distance de 150 m environ du contact mentionné, présentent des contours anguleux et dimensions centimétriques, rarement 1 dm ; la barytine prédomine par rapport aux calcaires.

Les rhyolites de la zone d'affleurement de la barytine, d'ailleurs dans toute la région, sont fortement laminées, à linéations de laminage orientée N20—40°W et pendage accentué vers l'est.

Les fragments et les blocs de barytine sont jaunâtre-brunâtres à la surface et grisâtre-jaunâtres en cassure fraîche. La barytine se dispose en rubans parallèles, ayant une structure à grains fins oû on observe des corps spongieux ponctiformes engendrés par la lévigation de quelques minéraux primaires, possiblement sulfures.

L'étude microscopique de la barytine relève la présence des structures reliques à des changements accentués dinamométamorphiques de type cataclastique, protoclastiques, mylonitiques et blastomylonitiques.

La barytine et le quartz représentent les principaux minéraux des blocs et fragments de barytine ; y apparaît subordonnément un minéral micacé.

Les minéraux mentionnées subissent des déformations très variées. Ainsi, la barytine porphiroclastique présente des extinctions ondulatoires, macles de déformation et zones de glissement. Les substructures de déformation sont aussi fréquentes ; le quartz porphyroclastique domine ; dans les ombres de pression du quartz apparaît le minéral micacé. Rarement, on a reconnu des cristaux prismatiques de quartz et des fissures remplies de barytine$\pm$quartz, formées probablement après la déformation.

La présence des blocs de barytine à Cîrjelari pose le problème de l'existence, en Dobrogea de Nord, possiblement dans la base des calcaires dévoniens, de quelques lentilles et lits de barytine avec ou sans sulfures. Résulte des études microscopiques que ces accumulations seraient d'origine sédimentaire. On a attribué à la barytine l'âge dévonien, grâce à l'absence de la région des dépôts triasiques qui, en Dobrogea de Nord, sont associés à des minéralisations de barytine d'origine sédimentaire et hydrothermale.

EXPLICAȚIA PLANȘELOR

Planșa I

Fig. 1 — Milonit. Matricea orientată și porfiroclaste de baritină maclate. N+ (×100).
Mylonite. Matrice orientée et porphyroclastes de barytine maclés. N+ (×100).

Fig. 2 — Protoclasit. Porfiroclastele de baritină și cuarț și matricea nu prezintă orientări. N+ (×100).
Protoclasite. Les porphyroclastes de barytine et quartz et la matrice ne présentent pas des orientations. N+ (×100).

Planșa II

Fig. 1 — Blastomilonit și fisură post metamorfism dinamic cu cataclasite. N+ (×100).
Blastomylonite et fissure post-métamorphisme dinamique à cataclasites. N+ (×100).

Fig. 2 — Resturi milonitice de baritină și cuarț (cenușiu-negru) în agregate largi de baritină fin granulară (cenușiu). NII (×80).
Débris mylonitiques de barytine et quartz (grisâtre-noirâtre) dans des agrégats larges de barytine finement granulaire (grisâtre). NII (×80).

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2. ZĂCĂMINTE

LARAMIAN HYDROTHERMAL ALTERATION AND ORE DEPOSITION IN THE ORAVIȚA—CICLOVA AREA. SOUTH-WESTERN BANAT [1]

BY

EMIL CONSTANTINESCU [2], GHEORGHE ILINCA [3], AURORA ILINCA [3]

Hydrothermal alterations. Mineralizations. Scheelite. Molybdenite. Tellurides. Sulphosalts. Kobellite. Electron microprobe analyse. Microtectonics, South Carpathians, Getic and Supragetic Sedimentary Domains. Reșița-Moldova Nouă Zone. Neocretaceous-Paleogene magmatites. Hornfelses. Skarns. Oravița-Moldova Nouă.

Abstract

In the Oravița-Ciclova area, the following mineralization types were identified: Cu+Mo (in granodiorites), Cu+Bi+W (in garnetiferous skarns, granodiorites, and hornfelses), Cu+pyrite (in recrystallized limestones), Cu+Mo+W (in garnetiferous-vesuvianitic skarns and monzodiorites), Cu+Co+As (in propylitized skarns and monzodiorites), Cu+Pb+Zn (in monzodiorites). Within the mineralization, a mineral was pointed out for the first time in our country: kobellite $5PbS \cdot 4(Bi, Sb)_2S_3$. Although the ore deposits, in their large majority, are hosted by skarns, they are genetically related to the hydrothermal evolution stage. The identified hydrothermal assemblages (i.e. tourmaline-orthoclase-quartz; potassium feldspar (orthoclase-adularia)-biotite; quartz-epidote-actinote-chlorite-calcite; quartz-sericite; zeolites-calcite) reflect for the study area as a whole, a relatively continuous evolution of hydrothermal solutions from an acid-oxidating to a basic-reducing character. Spatial-genetic correlations between the tourmaline-orthoclase-quartz assemblage and the scheelite mineralization from Chinisea Valley as well as between the propylitic association with its passings to phyllic facies and the Cu+Bi+W, Cu+Mo+W and Cu+Co+As mineralizations can be established.

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Résumé

Alterations hydrothermales et des minéralisations laramiennes dans la zone de Oravița — Ciclova, le Banat de sudouest. Dans la zone d'Oravița-Ciclova on a identifié les suivants types de minéralisations : Cu—Mo (dans les granodiorites), Cu+Bi+W (dans les skarns granatifères, granodiorites et cornéennes), Cu+pyrite (en des calcaires recristallisés), Cu+Mo+W (en des skarns propylitisées et monzodiorites), Cu+Pb+Zn (en des monzodiorites). Dans le cadre de la minéralisation on a mis en évidence, pour la première fois dans notre pays, la kobellite $5PbS . 4(Bi, Sb)_2S_3$. Bien que la majorité des minéralisations soient cantonnées dans les skarns, elles sont associées, du point de vue génétique, au degré d'évolution hydrothermale. Les associations hydrothermales identifiées (tourmaline-orthose-quartz, feldspath potassique-biotite, quartz-épidote-actinot-chlorite-calcite, quartz-séricite, zéolithes-calcite), reflètent, dans l'ensemble de la région, une évolution relativement continue du pH des solutions hydrothermales de l'acide vers basique. On peut établir des corrélations spatial-génétiques entre l'association tourmaline-orthose-quartz et la minéralisation de scheelite de la vallée de Chinisea, tout comme entre l'association propylitique à des passages vers des faciès phylliteux et les minéralisations de Cu+Bi+W, Cu+Mo+W et Cu+Co+As.

Although known and mined in a rudimentary manner as far back as in antiquity, the Oravița-Ciclova mineralizations became the subject of some early geological mentions not before the second half of the 18th century.

Within the mineralization, several rare minerals were described, namely scheelite, wolframite, argentite, cubanite, bismuthinite, native bismuth, bismite, cobaltite, smaltite, glaucodot, erythrite, löllingite, hoernesite, native tellurium, tetradymite (Marka—1869, Zepharovich——1859, 1875, 1893, Cădere—1925, 1926, 1927, 1928).

In 1948, Koch described for the first time in samples from Ciclova, a bismuth telluride, which he called csiklovaite. In the case of two minerals which have remained unidentified, i.e. a Ni and Co sulphoarsenide and a Bi telluride, only the chemical analyses carried out by Sipocz and Grasselly (1886 respectively 1948, fide Rădulescu, Dimitrescu 1966) are available.

A complex view of the Oravița-Ciclova ore deposits and their relations with the intrusive bodies and contact aureole has been given by means of the last decades studies (e.g. Gheorghițescu, 1974 ; Cioflica et al., 1976 ; Constantinof, 1980).

In 1977, Popescu and Constantinescu made detailed studies on the mineralization, emphasizing the physiographic relationships between the ore minerals as well as the main hydrothermal replacement features. Five types of mineralizations have been outlined : (1) copper in crystalline schists, (2) copper-molybdenium, (3) copper-bismuth-tungsten and subordinately gold, (4) copper in hornfelses and (5) titanium in crystalline schists.

A complex study of the metallogenesis related to Ciclova Laramian magmatism and its contact aureole, by Cioflica and Vlad (1981), has pointed out the main types of mineralizations (Cu+Mo, Cu+Co+As, Cu+W, Cu+Pb+Zn), the ores deposition sequence and their essential geochemical and genetic characters.

1. General Data

The Oravița-Ciclova ore deposits are mainly hosted by the pyrometasomatic contact zone, in association with skarns.

The main types of skarns are given by the following assemblages : *(1) grandite (grossular 30—50 and), (2) wollastonite-grandite-tremolite, (3) wollastonite-grandite, (4) grandite-scapolite (meionite) (5) wollastonite-diopside-grandite-vesuvianite-clintonite, (6) grandite-vesuvianite, (7) diopside-melilite (gehlenite), (8) wollastonite-diopside-humite (chondrodite) — grandite-vesuvianite.*

Subordinately, the ore deposits are associated with thermal contact metamorphism produces represented by : orthoclase-quartz-biotite-andalusite (±corundum, cordierite), hornfelses, quartz-acid plagioclase--biotite-clinozoisite hornfelses and recrystallized micro- or mesoblastic limestones with rare separations of epidote, quartz and pyrite. To the same effect, ores are to be found in association with Laramian magmatites (hornblende-biotite granodiorites and porphyritic microgranodiorites, monzodiorites, porphyritic monzodiorites).

2. Hydrothermal alterations

The Laramian igneous rocks, the skarns and hornfelses are marked by intense hydrothermal alterations. We shall proceed to a brief description of the identified hydrothermal assemblages.

The *tourmaline-orthoclase-quartz I* assemblage is developed in the upper course of Chinisea Valley against the background of garnetiferous skarns and porphyritic granodiorites. A correlation may be assumed between the Chinisea Valley tourmaline and the scapolite occurrences in the Rîndunicii Brook, as they could signify a first wave of high temperature, acidic and rich in mineralizers solutions, which are, to all appearances transitional from pneumatolytic to hydrothermal conditions.

Tourmaline occurs as tiny radiated crystal aggregates with a marked pleochroism showing maximum absorption when the elongation of the crystal is perpendicular to the vibration plane of the polarizer. It shows pink, greenish-yellow and greenish-blue as colours of pleochroism, indicating a member of schörl-elbaite series. Tourmaline constantly appears associated with sericitized orthoclase and quartz, but the mutual relations are wavering.

The *potassium feldspar (orthoclase II-adularia)-biotite* assemblage (K-silicate facies) is confined to a small part of the intrusive bodies, partially affecting the porphyritic granodiorites from Chinisea Valley and Racilor Brook. The alteration consists in hornblende biotitization processes as well as in replacements and corrosions of plagioclase by orthoclase. Locally, along the fissures, potassium feldspar is represented by adularia, which occurs as limpid euhedral crystals. In the Chinisea Valley granodiorites, adularia replaces orthoclase.

The *quartz II-epidote-actinote-chlorite-calcite I (± albite)* assemblage defines the propylitic facies for the Oravița-Ciclova area. Propylitization affects a wide spectrum of rocks : porphyritic granodiorites, diorites, monzodiorites, skarns and hornfelses, often being superposed on other assemblages which were already mentioned.

Epidote mainly occurs at the expense of skarn minerals, i.e. garnets, wollastonite, vesuvianite, which it replaces peripheraly or along fissures. Such processes are locally resulting in pseudomorphs after garnets. Epidote also appears against the background of Laramian magmatites, especially sienites, where it substitutes potassium feldspar along fissures and cleavages. Within propylitized recrystallized limestones from the northern and northeastern slopes of Tîlva Mică, epidote frequently forms monomineral concretions ranging from 1 to 10 cm in diameter.

Chlorite is abundant in skarns and Laramian magmatites and its occurrence at the expense of tourmaline-orthoclase-quartz and potassium feldspar-biotite assemblages, is always typical. Within the magmatites, chlorite replaces hornblende and biotite, often resulting in pseudomorphs. The chloritization of magmatic primary biotite (in order to distinguish it from the biotite in the K-silicate assemblage), is accompanied by a detitanization process which is marked by the appearance of sphene or rutile.

Actinote occurs frequently as inclusions in quartz and calcite or as small monomineral veinform accumulations within porphyritic granodiorites.

The *quartz III-sericite* assemblage (phyllic facies) develops in the porphyry-microgranodioritic and dacitic apophyses of the Chinisea Valley intrusive body and more frequently in the Ciclova monzodiorites and dykes. Members of quartz-sericite facies overlap the tourmaline-orthoclase-quartz assemblage and often obscure the effects generated by propylitization.

The *zeolite-calcite II* assemblage is ascribable to the lowermost temperature phase of the hydrothermal alteration. Zeolites are represented by stilbite, thomsonite, scolecite-which occur mainly in skarns-and by laumontite which is to be found mostly in Laramian magmatites.

3. Description of ore minerals

Scheelite forms millimetric disseminations in a body of tourmalinized and feldspathized granodiorites in Chinisea Valley as well as of monzodiorites and garnet-vesuvianite skarns at Ciclova. Quite seldom, scheelite nodules over 1 cm in diameter can be observed.

Under the microscope, scheelite appears as anhedral, high relief crystals, associated with tourmaline, potassium feldspar and quartz or with anisotropic garnets and vesuvianite. Sometimes, crystals are rounded or peripheraly corroded by calcite or adularia. In the Ciclova zone, two generations of scheelite can be emphasized.

Molybdenite appears in the following characteristic assemblages:
— in granodiorites: +chalcopyrite, pyrite, zeolites, calcite;
— in skarns and monzodiorites: +chalcopyrite, quartz.

Molybdenite occurs as veinlets, fine films or discrete flakes. Mutual relationship with chalcopyrite provides evidence for the tardy character of molybdenite (Plate I, Fig. 1).

Chalcopyrite is the most wide-spread among the ore minerals. Its characteristic associations are:

— in granodiorites: + molybdenite, pyrite, zeolites, calcite;

— in garnetiferous skarns, granodiorites and hornfelses (north of Oravița Valley): + glaucodot, cobaltite, enargite, tetrahedrite, tetradymite, tellurobismuthite, kobellite, sphalerite, chalcocite, covellite, cuprite, malachite, azurite, erythrite, goethite, lepidocrocite, epidote, quartz, calcite, actinote, chlorite;

— in garnetiferous skarns and monzodiorites (Ciclova): (a)+cubanite, molybdenite, pyrite, azurite, malachite; (b) + glaucodot, pyrite, arsenopyrite, tetrahedrite, tennantite, bornite, covellite, chalcocite, native copper, erythrite, scorodite;

— in recrystallized limestones: + pyrite, pyrrhotite, cobaltite, marcasite;

— in phyllitized monzodiorites: + galena, sphalerite, pyrite.

Chalcopyrite exhibits numerous mineralogical particularities, mainly referring to Vickers hardness variation, optical anisotropy and relations with other ore minerals.

The early chalcopyrite generations which are associated with garnetiferous skarns and monzodiorites, are represented by crystals with relative strong birefringence, in dark brown hues, thereby revealing a multiple twinned structure. After Uytenbogaard and Burke—1971, an increase in the birefringence of chalcopyrite is dictated by a higher iron content. The Vickers hardness measurements in these particular cases, show very high values: $VHN_{20} = 195-221$ kg/mm^2, i.e. at the uppermost limits of the chalcopyrite microhardness range.

The appearance of strong anisotropic chalcopyrite pleads for its genesis at high temperatures which characterize the first stages of hydrothermal process. At the same time, a direct correlation between the iron content and microhardness number may be reasonably inferred.

The high temperature chalcopyrite replaces or cements glaucodot and cobaltite. Sometimes it shows exsolutions of cubanite which are believed to occur at temperatures ranging between 235 and 450°C (Borchert 1934, Ross 1934 fide Schwartz 1955). High temperature chalcopyrite is frequently substituted by copper sulphosalts, native bismuth, bismuth tellurides and sulphosalts.

As concerns the late chalcopyrite generations, optical anisotropy is invisible and the Vickers hardness values are appreciably lower: $VHN_{20} = 169-182$ kg/mm^2.

Low temperature chalcopyrite forms borders around enargite and tetrahedrite being in its turn replaced by native bismuth and bismuth tellurides and sulphosalts. Within the mineralization associated with the monzodiorites from south of Oravița Valley and with propylitized skarns from the Floreana, Țiganilor and Ciclova Valley chalcopyrite is replaced by tetrahedrite, tennantite and quite locally by galena and sphalerite. Within the ores associated with the Ciclova Valley monzodiorites, there are frequent exsolutions of chalcopyrite in sphalerite. In recrystallized limestones, mutual relationships between chalcopyrite and other ore minerals are hesitating. Within the supergene enrichment zone, chalcopyrite is replaced by bornite, chalcocite, covellite and in the oxidized zone by goethite and lepidocrocite.

Glaucodot seems to be the most abundant ore mineral in the Ciclova Valley monzodiorites, its share being somehow reduced in the mineralization associated with the Chinisea Valley garnetiferous skarns and magmatites and with the Tilva Mică hornfelses. Characteristic assemblages :

— in garnetiferous skarns, granodiorites and hornfelses :1 + cobaltite, chalcopyrite, copper and bismuth sulphosalts, pyrite ;

— in propylitized skarns and phyllitized monzodiorites (Ciclova) : + pyrite, chalcopyrite, arsenopyrite, gersdorffite, copper sulphosalts, sphalerite, galena.

Glaucodot forms euhedral crystals with seeming prismatic or rhombic outline (Fig. 1A) and more frequently anhedral ones. They are brilliant-white coloured and their anisotropy is invisible even under strongest lightings. The Vickers hardness values are high : $VHN_{70-100} = 900-1000$ kg/mm^2, but it is difficult to establish a true hardness range due to the intense fractured identitation. Glaucodot is penetrated and cemented by chalcopyrite (Fig. 1B) as well as by copper or bismuth sulphosalts (Fig. 1C). In the oxidized zone, glaucodot passes into erythrite and iron oxides and hydroxides.

Cobaltite (Pl. I fig. 2) seldom occurs as euhedral crystals, with high relief and visible anisotropy in grey and brownish-grey hues. It is associated with chalcopyrite, pyrrhotite and pyrite in the mineralization hosted by recrystallized limestones.

Gersdorffite appears quite locally as low relief inclusions in a body of glaucodot and arsenopyrite. Its colour is white with a weak yellowish tint as compared to that of glaucodot or arsenopyrite and in crossed polars is isotropic. The Vickers hardness at 100 g loading ranges between 730 and 910 kg/mm^2. Measured reflectances for 487, 552, 591 and 658 nm are : 47,48 ; 46,52 ; 46,35 ; 46,87 %. The reflectance spectrum is rendered in fig. 2.

Arsenopyrite occurs in association with glaucodot, cobaltite, gersdorffite, tetrahedrite, tennantite and skorodite. It forms anhedral crystals with marked anisotropy. In the oxidized zones, replacements of arsenopyrite by skorodite are commonly (Fig. 1D).

Skorodite $Fe(AsO_4) \cdot 2H_2O$ is a typical mineral of the arseno-pyrite-bearing oxidized zones in the Ciclova area. This occurrence, previously not mentioned, is significant as it provides evidence for supergene alteration processes, carried on in a warm and moist climate. X-ray diffraction

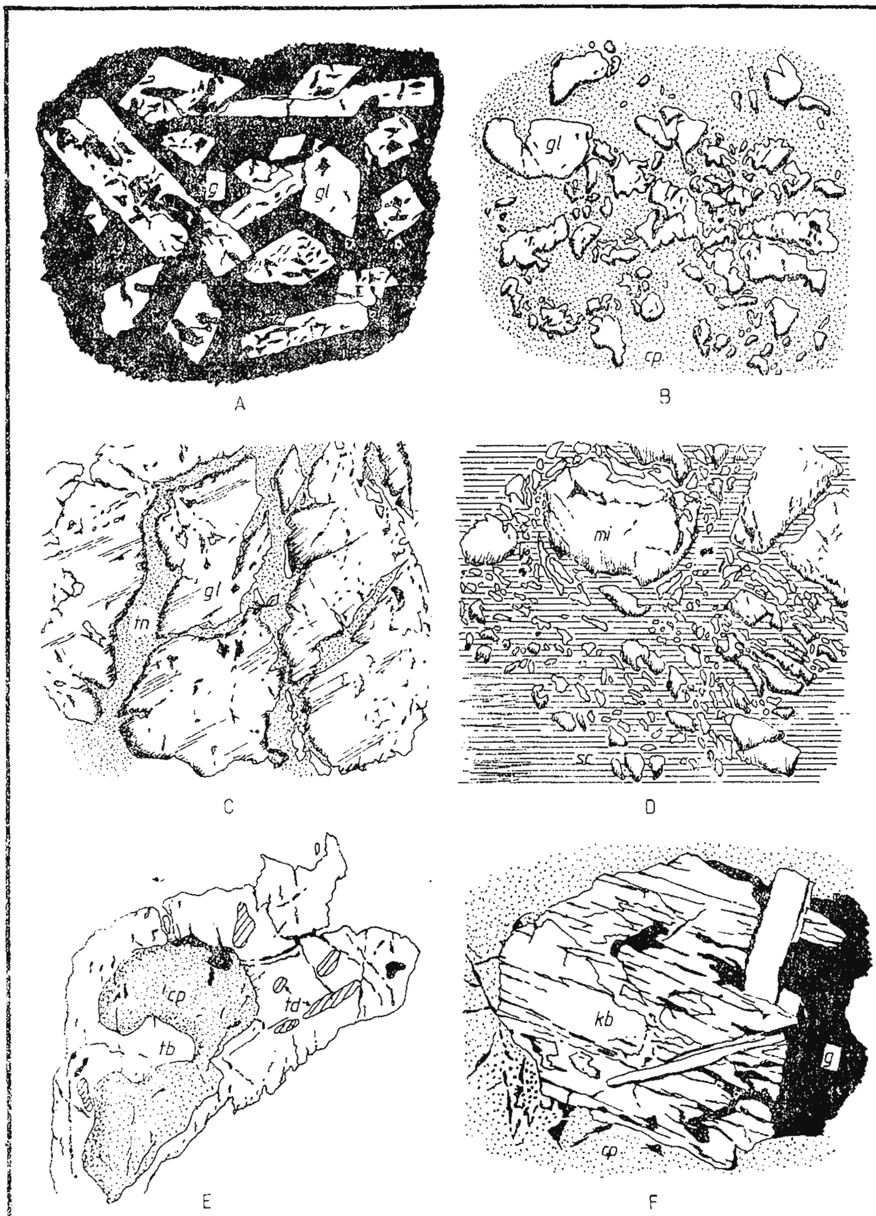


Fig. 1—A, Glaucodot crystals (gl) in a quartz gangue (g) (Trei Crai gallery-Ciclova); B, glaucodot (gl) penetrated and cemented by chalcopyrite (cp), (Emil gallery-Chinisca Valley); C glaucodot (gl) penetrated by tennantite (tn), (Lobkowitz gallery-Ciclova); D, arsenopyrite (mi) replaced by skorodite (sc) (Trei Crai gallery-Ciclova), E, tellurobismuthite (tb) with tetradymite (td) inclusions forming a border around chalcopyrite (cp) (Emil gallery-Chinisca Valley); F, kobellite (kb) associated with chalcopyrite (cp) and quartz gangue (g), (Emil gallery-Chinisca Valley).

study of skorodite was accomplished and the obtained d/n values are rendered in table 1.

TABLE 1

Calculated d/n and I values for a skorodite and arsenopyrite mixture (Trei Crai gallery)

d/n	I	d/n m [1]	d/n s [2]	
5.5672	56		5.56	s
4.9509	19		4.95	s
4.4541	100		4.44	s
4.0720	22		4,06	s
3.7891	22		3.78	s
3.6584	30	3.669		m
3.3623	19		3.36	s
3.1662	90		3.16	s
3.0516	63		3.05	s
2.9867	34		2.98	s
2.8455	22	2.843	2.84	s, m
2.7863	20	2.783		m
2.7191	16			
2.6503	100	2.662		m
2.5785	47		2.58	s
2.4951	31		2.50	s
2.4471	80	2.443		m
2.4047	73	2.412		m
2.2132	33	2.206		m
2.1126	19		2.11	s
2.0480	25		2.04	s
1.9998	22		2.00	s
1.9467	32	1.943		m
1.8135	70	1.817		m
1.7945	16		1.79	s
1.7659	28			
1.7502	28		1.75	s
1.6606	28		1.66	s
1.6321	29	1.629		m
1.6255	29	1.629		m

1) d/n m — d/n values for arsenopyrite (from Miheev — 1957)
2) d/n s — d/n values for skorodite from Durango — Mexico (Miheev — 1957).

Copper sulphosalts are represented by *tetrahedrite, tennantite* and *enargite*. Characteristic associations :

— in garnetiferous skarns and hornfelses : + chalcopyrite I, II, bismuth sulphosalts ;

— in propylitized skarns and monzodiorites : + glaucodot, chalcopyrite, sphalerite, galena, arsenopyrite.

Obtained Vickers hardness values are as follows : tetrahedrite $VHN_{40-50} = 380-403$ kg/mm^2 ; tennantite — $VHN_{40} = 270-335$ kg/mm^2 ; enargite $VHN_{50} = 290-360$ kg/mm^2.

Tetrahedrite and enargite replace high temperature chalcopyrite within the mineralization associated with the Chinisea Valley skarns and magmatites and with Tîlva Mică hornfelses (Plate II, fig. 1, fig. 2), being in their turns substituted by low chalcopyrite or by bismuth sulphosalts and tellurides. In the mineralization hosted by the Ciclova Valley monzodiorites and skarns, tetrahedrite and tennantite in association with sphalerite, replace glaucodot and arsenopyrite.

Native bismuth occurs in the Chinisea Valley mineralized skarns, opening the deposition sequence of the bismuth minerals. It has a bri-

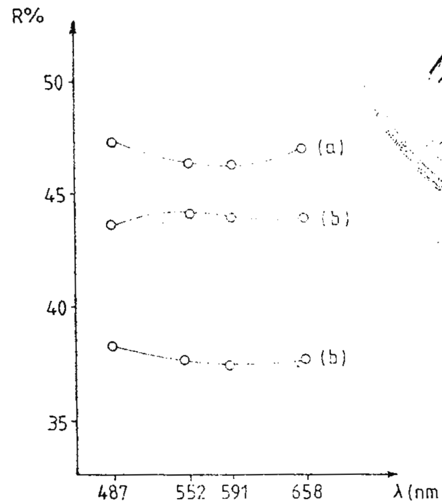


Fig. 2 — Reflectance spectra of gersdorffite (a) and kobellite (b).

lliant creamy-pink colour and strong optical anisotropy. The grains are frequently anhedral, but tiny euhedral, short prismatic crystals, often localized along fissures in tetrahedrite can be identified, too. The VHN_{10} values range between 21 and 24 kg/mm². Native bismuth is corroded by tetradymite what states precisely their sequence of deposition.

Bismuth tellurides and *sulphosalts* are represented by *tetradymite*, *tellurobismuthite* and *kobellite*. Tetradymite and tellurobismuthite are associated with chalcopyrite and copper sulphosalts, the later being penetrated along fissures and bordered by the former. Sometimes, tetradymite forms inclusions in tellurobismuthite (fig. 1E). The Vickers hardness values are as follows: tetradymite — $VHN_{10} = 35-69$ kg/mm²; tellurobismuthite — $VHN_{10} = 52-87$ kg/mm². Kobellite — in fact, an intermediary member of kobellite — tintinaite series ($5PbS\text{-}4Bi_2S_3\text{-}5PbS\text{-}4Sb_2S_3$) characterized by a Bi/Sb ratio greater than unity (Uytenbogaard, Burke — — 1971) — was identified only in the Emil gallery waste in Chinisea Valley. This mineral is now pointed out for the first time in our country. As the available amounts of kobellite proved insufficient for a chemical analysis, informations about the chemical compositions were obtained by aid of electron-microprobe investigations (Plate III and IV). Kobellite (fig. 1F) shows a weak bireflectance in white and greyish-white with pale violaceous tints. It occurs as tabular or columnar crystals with good cleavage, aligned to elongation (Plate V, fig. 1). Optical anisotropy is strong (Plate V fig. 2) in greyish-brown hues and has straight extinction in all sections parallel to the cleavage. The Vickers microhardness values are $VHN_{10} = 65-164$ kg/mm². Measured reflectances Rg-Rp for 487, 552, 591 and 658 nm wavelenghts are 43,70—38,23 ; 44,19—37,79 ; 44,00—37,49 ; 43,81—37,64% the reflectance spectrum is rendered in fig. 2. Kobellite is associated with chalcopyrite, tetradymite, tellurobismuthite and native bismuth.

Native gold appears sporadically as minute grains associated with tetradymite and tellurobismuthite.

4. Discussion

The identified ore minerals in correlation with their country rock and spreading area, outline the following types of mineralization :

— Cu + Mo : associated with hornblende-biotite granodiorites from Maidan zone (chalcopyrite, molybdenite, pyrite);

— Cu + Bi + W (± Te, Pb, Co, Ni, As, Zn, Au): associated with garnetiferous skarns and granodiorites from Chinisea Valley as well as with the Tîlva Mică hornfelses (scheelite, glaucodot, cobaltite, chalcopyrite I, enargite, tetrahedrite, chalcopyrite II, native bismuth, tetradymite, tellurobismuthite, kobellite, native gold and in the supergene enrichment and oxidized zones, chalcocite, covellite, cuprite, malachite, azurite, erythrite, goethite, lepidocrocite);

— Cu + pyrite (± Co) : represented by small lenticular bodies associated with recrystallized limestones in the Forviz-Kiesberg gallery zone (pyrite, pyrrhotite, chalcopyrite and subordinately cobaltite and marcasite);

— Cu + Mo + W : associated with the garnetiferous-vesuvianitic skarns and with the monzodiorites in Floreana-Ciclova Valley zone (scheelite I, scheelite II, chalcopyrite, cubanite, molybdenite, pyrite and in the oxidized zone : azurite, malachite, goethite, lepidocrocite);

— Cu + Co + As (± Ni, Sb, Pb, Zn): associated with propylitized skarns in the Floreana, Ţiganilor Valley and Ciclova Valley zones, as well as with the monzodiorites from south of Oraviţa Valley (glaucodot, pyrite, chalcopyrite, arsenopyrite, gersdorffite, tetrahedrite, tennantite and quite subordinately sphalerite and galena ; in the enrichment and oxidized zones occur : bornite, covellite, chalcocite, native copper, azurite, malachite, erythrite and skorodite);

— Cu + Pb + Zn : less developed, is associated with the Ciclova zone monzodiorites (galena, sphalerite, chalcopyrite I, chalcopyrite II, pyrite) [4].

It may be noticed that the Cu + Bi + W mineralization is preponderent at north of Oraviţa Valley, whereas the Cu + Mo + W and Cu + Co + As ones are prevailing in the Ciclova zone.

Although the Oraviţa-Ciclova ore deposits, in their large majority, are hosted by skarns, they are genetically related to the hydrothermal stage of postmagmatic evolution.

The described hydrometasomatic assemblages, as seen from the angle of deposition temperatures, of acidity degree which they reflect (Schwartz, 1955) and of specific superposition relationships, suggest for

4) Minerals were mentioned according to their deposition sequence.

the whole area a relatively continuous evolution of the hydrothermal solutions pH from acid to basic (fig. 3).

The recurrence described sometimes by the repeated appearances of quartz and potassium feldspar within the hydrothermal assemblages suite, could be explained by taking in account both pH and Eh variation

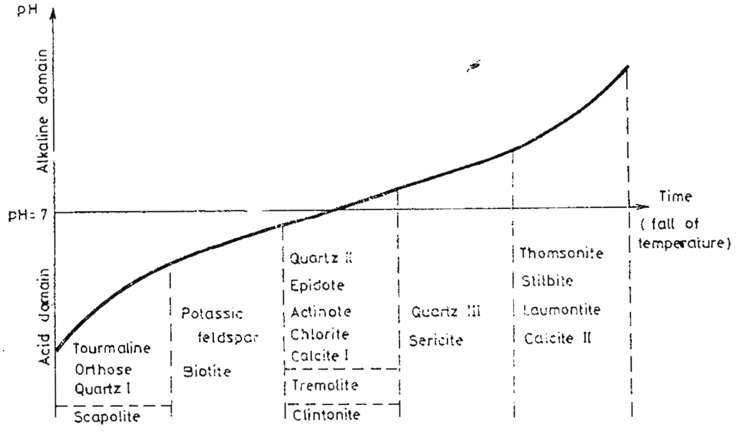
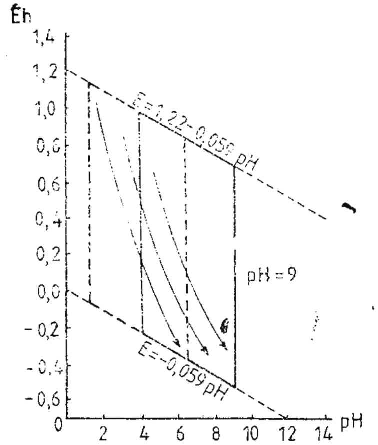


Fig. 3 — Evolution of the hydrothermal solutions pH.

ranges (fig. 4). Commonly, these ranges are given for exogene conditions (Ianovici et al., 1982), but we have considered that at high temperatures which involve a higher dissociation degree of water, the state of the variation limits of Eh and pH may be described in a similar manner, considering the exogene conditions field as being shifted to the diagram's

Fig. 4 — Variation limits of pH and Eh at high temperatures (interrupted line) and in exogene conditions (uninterrupted line).



upper left area. Thus, the whole variation field moves to the bottom-right area as the hydrothermal solutions evolved from acid-oxidating to basic-reducing conditions.

Several spatial-genetic correlations may be established between the tourmaline-orthoclase-quartz assemblage and the scheelite occurrences from Chinisea Valley, as well as between the propylitic assemblage with its frequent passings to phylic facies and the Cu + Bi + W mineralization from north of Oraviţa or the Cu + Mo + W and Cu + Co + As mineralization in the Ciclova zone. Mutual replacing relations occurring between the ore minerals or between these and the gangue ones, are relevant for polyascending character of the mineralizing fluids materialized by successive crystallizing moments separated by intense fracturing stages.

Based on about 2200 measurements, a computer microtectonic study was carried out. Thus, it became obvious that the ore distribution was subordinated to a strict structural control. The main tension fracture system which controls the disposition of both some igneous dykes and mineralization, trends NW—SE. This fact is pointed out by the disposition of molybdenite and chalcopyrite-bearing fissures in the Maidan granodiorites, of pyrrhotite and chalcopyrite bodies in the Kiesberg zone, of the glaucodot lensform bodies from Ţiganilor Valley as well as of chalcopyrite and glaucodot veinlets from Floreana Hill. This tension fracture system can be emphasized all over the study area and its development within the Laramian magmatites, aureole formations, sedimentary deposits and crystalline schists pleads for an exokinetic character. The system intensely affects the skarns and hornfelses thus providing evidence for being active even after the emplacement of the main intrusive bodies.

5. Acknowlegements

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ALTERAȚII HIDROTERMALE ȘI MINERALIZAȚII LARAMICE ÎN ZONA ORAVIȚA-CICLOVA. BANATUL DE SUD-VEST.

(Rezumat)

Mineralizațiile de la Oravița și Ciclova sînt cantonate predominant în zona de contact pirometasomatic, în asociație cu skarne. Subordonat apar asociate cu corneene, roci eruptive laramice și șisturi cristaline.

Mineralele metalice identificate, în corelație cu formațiunile gazdă și aria de răspîndire, conturează pentru zona Oravița—Ciclova, următoarele tipuri de mineralizații :

— *Cu + Mo:* în granodioritele cu hornblendă și biotit de la Maidan (calcopirită, molibdenit, pirită);

— *Cu + Bi + W* (± *Te*, *Pb*, *Co*, *Ni*, *As*, *Zn*, *Au*) : în skarnele granatifere și granodioritele din valea Chinisea și în corneenele din nordul Tîlvei Mici (scheelit, glaucodot, cobaltină, calcopirită I, enargit, tetraedrit, calcopirită II, bismut nativ, tetradimit, telurobismutit, kobellit, aur nativ, calcozină, covelină, cuprit, malachit, azurit, eritrină, goethit, lepidocrocit);

— *Cu + pirită* (± *Co*) : în calcarele recristalizate din zona Forvizgalería Kisberg (pirită, pirotină, calcopirită, cobaltină, marcasită);

— *Cu + Mo + W:* în skarnele granatifer-vezuvianice și monzodioritele din zona Floreana-valea Ciclova (scheelit I, scheelit II, calcopirită, cubanit, molibdenit, pirită, azurit, malachit, goethit, lepidocrocit);

— *Cu + Co + As* (± *Ni*, *Sb*, *Pb*, *Zn*) : în skarnele propilitizate din zona Floreana, valea Țiganilor și valea Ciclovei precum și în monzodioritele de la sud de valea Oravița (glaucodot, pirită, calcopirită, mispichel, gersdorfit, tetraedrit, tennantit, blendă, galenă, bornit, covelină, calcozină, cupru nativ, azurit, malachit, eritrină, scorodit);

— *Cu + Pb + Zn* : în monzodioritele din zona Ciclova (galenă, blendă, calcopirită I, calcopirită II, pirită).

În ansamblu, se poate remarca preponderența mineralizației de Cu + Bi + W la nord de valea Oravița și a celei de Cu + Mo + W și Cu + Co + As la Ciclova.

Deși în marea lor majoritate mineralizațiile sînt cantonate în skarne, ele sînt asociate genetic stadiului de evoluție hidrotermală.

Asociațiile hidrometasomatice identificate (turmalină-ortoză-cuarț, feldspat potasic (ortoză-adular)-biotit, cuarț-epidot-actinot-clorit-calcit (± albit), sericit-cuarț, zeoliți-calcit), privite prin prisma temperaturilor de formare, a gradului de aciditate pe care îl reflectă precum și a relațiilor specifice de suprapunere, sugerează pe ansamblul regiunii, o evoluție relativ continuă a pH-ului soluțiilor hidrotermale de la acid la bazic.

Se pot stabili corelații spațial-genetice clare între asociația turmalină-ortoză-cuarț și mineralizația de scheelit din valea Chinisea, precum și între asociația propilitică cu frecventele ei treceri la faciesuri filice și mineralizațiile de Cu + Bi + W la nord de valea Oravița, Cu + Mo + W și Cu + Co + As la Ciclova.

Studiul microtectonic relevă existența unui sistem tensional de fracturi care jalonează atît dispunerea unor roci eruptive cu caracter filonian cît și a mineralizației. Avînd o orientare NV—SE, acest sistem poate fi identificat în tot cuprinsul regiunii, dezvoltarea sa atît în cadrul banatitelor și șisturilor cristaline, relevînd caracterul său exocinetic în raport cu eruptivul.

EXPLANATION OF PLATES

Plate I

Fig. 1 — Molybdenite (mo) associated with chalcopyrite (cp) in porphyritic granodiorite. Maidan quarry : N ||, 160 ×

Fig. 2 — Cobaltite (co) in chalcopyrite. Emil gallery, Chinisea Valley : N ||, 250 ×

Plate II

Fig. 1 — Tetrahedrite (te) associated with chalcopyrite (cp) and tetradymite (td). Emil gallery Chinisea Valley : N ||, 160 ×

Fig. 2 — Veinform enargite (en) in chalcopyrite (cp). Prinz Albert gallery, Tîlva Mică ; N ||, 160 ×

Plate III

Fig. 1 — Kobellite (kb) associated with chalcopyrite (cp) and glaucodot (gl) ; the electron microprobe investigated field : N ||, 300 ×

Fig. 2 — Electron image of composition : 300 ×

Fig. 3 — X-ray scanning image showing distribution of Bi ; 300 ×

Plate IV

Fig. 1 — X-ray scanning image showing distribution of Pb ; 300 ×

Fig. 2 — X-ray scanning image showing distribution of Sb ; 300 ×

Fig. 3 — Variation of Sb content : 300 ×

Plate V

Fig. 1 — Kobellite (kb) associated with chalcopyrite (cp) (Emil gallery — Chinisea Valley) ; N||, 250 ×

Fig. 2 — Kobellite (kb) associated with chalcopyrite (cp) (Emil gallery — Chinisea Valley) ; N +, 250 ×

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2. ZĂCĂMINTE

CONTRIBUTIONS TO THE STUDY OF THE ORAVIȚA – CICLOVA SKARN OCCURRENCE, SOUTHWESTERN BANAT[1]

BY

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Skarns. Garnets. Vesuvianite. Chemical composition. Scapolite. Gehlenite. Chondrodite. Pyroxenes. Wollastonite. Petrogenesis. South Carpathians – Sedimentary Getic and Supragetic Realms – Reșița–Moldova Nouă Zone. Neocretaceous-Paleogene magmatites – Oravița – Moldova Nouă.

Abstract

The Oravița-Ciclova skarns are developed at the contact between the Laramian magmatites and the Upper Kimmeridgian-Valanginian limestones, marls and calcareous clays. The main types of skarns are defined by the following assemblages: grandite (grossular$_{30-50}$ and); wollastonite-grandite-tremolite; wollastonite-grandite; grandite-scapolite (meionite); wollastonite-diopside-grandite I-grandite II-vesuvianite-clintonite; grandite I-grandite II-vesuvianite; diopside-melilite (gehlenite); wollastonite-diopside-chondrodite-grandite-vesuvianite. Skarns were formed in a medium rich in mineralizers (F, Cl, B), suggested by the appearance of vesuvianite, chondrodite, scapolite and, probably, asharite. According to the more basic character of the Laramian magmatites occurring here, the temperature reached in the contact aureole was, in all probability, higher (750°) than in case of other skarn occurrences in Banat. The sequence of skarn minerals at the contact of the Oravița Valley diorites indicates the existence of two main phases in the evolution of the temperature: a heating phase (diopside-gehlenite) and a cooling phase (wollastonite-diopside II-grandite-vesuvianite-clintonite).

Résumé

Contributions à l'étude des skarns d'Oravița et de Ciclova. Les skarns d'Oravița-Ciclova se développent au contact des magmatites laramiennes à argiles calcaires, marnes et calcaires qui couvrent l'intervalle Kimméridgien supérieur-Valanginien. Les principaux types de skarns sont définis par les associations suivantes: grandite (grossulaire$_{30-50}$ and); wollastonite-gran-

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dite-trémolite ; wollastonite-grandite ; grandite-scapolite (méïonite), wollastonite-diopside-grandite I-grandite II-idocrase-clintonite ; grandite I-grandite II-idocrase ; diopside-mélilite (géhlenite) ; wollastonite-diopside-chondrodite-grandite-idocrase. Les skarns se sont formées dans un milieu riche en minéralisateurs (F, Cl, B), suggéré par l'apparition de l'idocrase, de la chondrodite, de la scapolite et peut-être de l'asharite. Selon le caractère plus basique des magmatites laramiennes d'ici, la température atteinte dans l'auréole de contact a été, selon toutes les probabilités, plus grande (750°C) que pour les autres occurrences de skarns de Banat. La succession des minéraux de skarn du contact des diorites de la vallée de l'Oraviţa indique l'existence de deux phases principales dans l'évolution de la température : une phase d'échauffement (diopside-géhlenite) et une phase de refroidissement (wollastonite-diopside II-grandite-idocrase-clintonite).

1. Introduction

Remarkable for their mineralogical complexity, the pyrometasomatic produces related to the Oraviţa—Ciclova Laramian magmatites were the subject matter of numerous researches. Beside the pioneering works of earlier authors : Born (1774, 1780), Cotta (1865), Castel (1869), Marka (1869), Halaváts (1884), Koch (1885), it is worth mentioning the important contributions of Koch (1924), Superceanu (1958), Pieptea (1964), Mînzatu (1964), Gheorghiţescu (1974), Cioflica et al. (1976, 1977, 1980), Popescu, Constantinescu (1977), Constantinof (1980), Cioflica, Vlad (1981), by which a marked advance in the geological knowledge of this region was attained.

The rich mineralogical list of the Oraviţa-Ciclova thermal and metasomatic contact zone is broadly represented in the earlier or later literature, e.g. Marka (1869), Zepharovich (1859, 1875, 1883), Koch (1885), Cădere (1927), Koch (1948), Rădulescu, Dimitrescu (1966).

This paper is intended to offer the main typological and mineralogical aspects of the skarns in the Oraviţa—Ciclova area. By means of these observations, an outlining of the essential petrogenetic features is attempted.

2. General Data on the Geology and Petrology of the Region

2.1. **Crystalline schists.** The regional metamorphic rocks in the Oraviţa—Ciclova area belong to the southern part of the Bocşa Montană—Oraviţa Ilidia Crystalline Massif (Codarcea, 1931 ; Constantinof, 1980), namely to the complex of retromorphosed micaceous gneisses of the Bocşiţa—Drimoxa Series (Constantinof, 1980). Muscovite-biotite paragneisses with gradual transitions to muscovite schists with albite porphyroblasts may be emphasized as the background petrographic element of the crystalline schists suite. The frequency of the muscovite schists increases towards the Oraviţa overthrust line. Quartz-feldspathic gneisses, amphibolites and amphibolic gneisses, muscovite-bearing quartzites and granite gneisses occur subordinately as intercalations.

Eastwards, along the Oraviţa tectonic line, the crystalline schists overlap Paleozoic and Mesozoic deposits of the Reşiţa—Moldova Nouă sedimentary zone.

2.2. **Sedimentary deposits.** The Paleozoic formations are represented by grey lithic sandstones with subrounded lithoclasts of quartzites and micas alternating with brown-violaceous or black-violaceous clay slates of Permian age. They form a band of variable thickness, extending north-southwards near the Oraviţa overthrust line (Fig. 1).

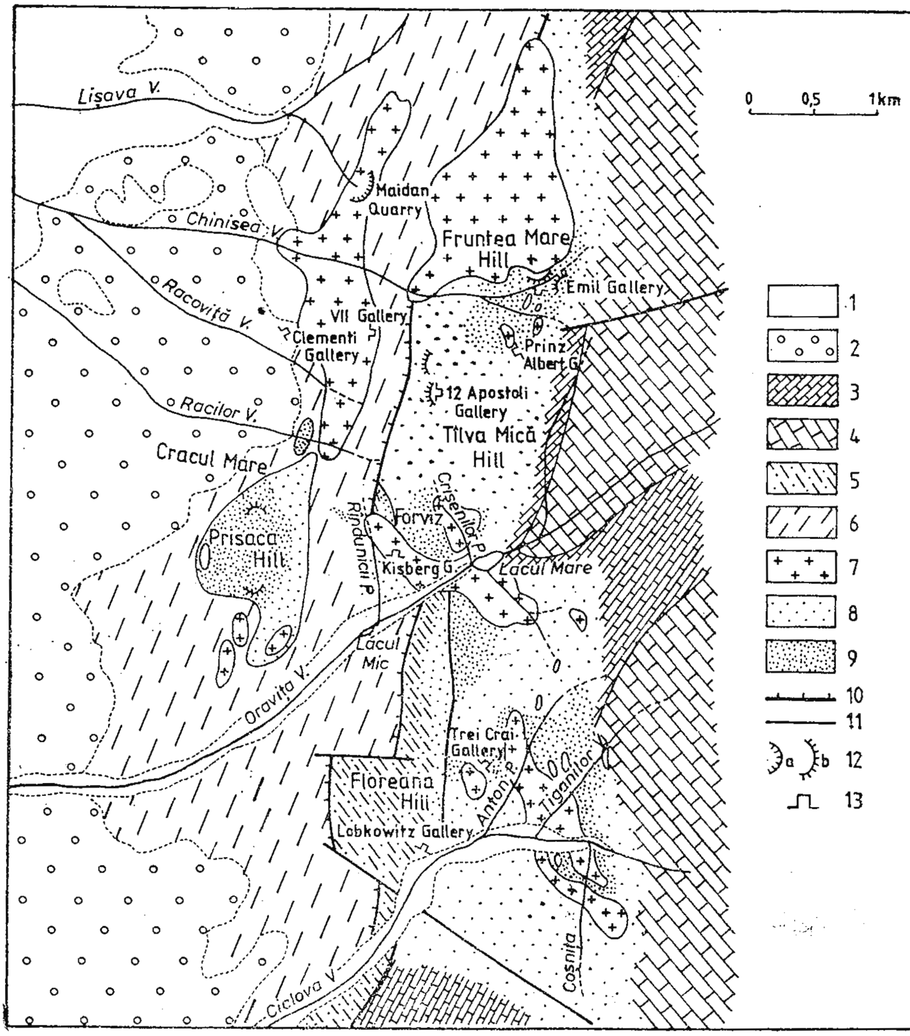

Fig. 1 — Geological sketch of Oraviţa-Ciclova zone. 1, Pleistocene (gravel, sand, clays); 2, Miocene (conglomerates, sandstones); 3, Cretaceous (marls, calcareous clays, chert-bearing limestones, reef limestones); 4, Jurassic (chert-bearing limestones, sublithographic limestones); 5, Permian (lithic sandstones, clay slates); 6, Precambrian (muscovite-biotite paragneisses, chlorite-muscovite schists with albite porphyroblasts, amphibolites, muscovite-bearing quartzites); 7, Laramian magmatites (granodiorites, diorites, monzodiorites); 8, hornfelses; 9, skarns; 10, Oraviţa tectonic line; 11, faults; 12 a, quarry; b, waste. 13 gallery.

The Mesozoic sedimentary is widely spread in the area of study; it is included in the Natra anticlinal structure and in the Cornetul Mare and Jitin synclines, covering the Upper Oxfordian—Lower Aptian interval. It is represented by limestones with stratiform or lens-shaped siliceous intercalations (Valea Aninei limestones, Upper Oxfordian-Lower Kimmeridgian), micrites with rare bioclasts and centimetric separations of schistous marls (Brădet limestones, Upper Kimmeridgian—Lower Tithonian), yellowish-grey sublithographic limestones with marl intercalations in the upper part (Marila limestones, Upper Tithonian—Berriasian), marls and calcareous clays [4] (Crivina Beds, Valanginian), blackish-grey calcareous clays with ellipsoidal silicolite concretions and marly and calcareous intercalations which grade upwards into massive limestones with numerous bioclasts of requiens and corals (Plopa limestones, Barremian—Lower Aptian).

The Mesozoic deposits are mainly carbonatic, certain compositional particularities being given both by silicolite intercalations and by the wide development of calcareous clays and marls within the Crivina Beds and the Hauterivian formations.

2.3. **Laramian magmatites.** Beside the similar occurrences at Tincova—Nădrag, Bocșa Montană, Ocna de Fier, Dognecea, Sasca Montană and Moldova Nouă, the Oravița—Ciclova igneous rock series belong to the western principal alignment of the Laramian magmatites in Banat (Cioflica et al., 1977), parallel to the Oravița line trending.

In the Oravița—Ciclova area, the outcrop pattern displays several main intrusive bodies both within the crystalline schists and the sedimentary rocks.

In the north-easternmost part of the study area, between the Cuptorului Brook and Chinisea Valley, there is a large-sized body, chiefly consisting of biotite and green hornblende porphyritic granodiorites, within which numerous transitions to microgranodiorite-porphyritic and dacitic apophysis facies may be observed. Quite locally, small separations of porphyritic diorites, e.g. those of Popii Brook spring zone, are occurring.

Between the Popii Brook and Racilor Brook, west of the Oravița fault, there is a N—S elongated body, entirely situated in crystalline schists. Here, granodiorites with biotite and green hornblende are transitional from equigranular or megaporphyritic phaneritic structures, characteristic of the northern part, to marked porphyritic structures in the southern part.

South of Poiana Crucii Hill, in the Forviz area, occurs a body with a relatively complicated morphology, trending approximately WNW—ESE; it crosses Oravița Valley and can be followed up to the spring zone of Coliliilor Brook. Within this body there is a great petrographic variety, with a stronger basic character as compared with the above-mentioned intrusive bodies: diorites with green and/or brown hornblende, porphyritic diorites, quartz-microdiorites, monzodiorites and syenites.

In the Anton Brook spring zone, crossing Ciclova Valley and reaching the area of Coșnița Brook, develops a body, also with a complicated morphology, mainly constituted of monzodiorites, within which there are local gradings into hornblende + biotite diorites. A similar composition is observed for small-sized bodies occurring in Floreana area and Poienilor Brook.

The intrusions in Oravița Valley and Ciclova Valley are considered to represent a unique body (Cioflica et al., 1980), the existent discontinuities depending on the actual level of erosion.

The main intrusive bodies occur in association with small-sized satellite bodies as well as numerous dykes of porphyritic diorites (Oravița Valley), biotite granodiorites (Anton Brook and Coliliilor Brook), hornblende latiandesites (Racilor Valley, Țiganilor Valley), quartz-syenites (Oravița Valley), augite-aegirine bearing alkali-feldspathic syenites (Țiganilor Valley), augite-aegirine bearing albitized oligoclase akerites (Coșnița Brook, Anton Brook) and micrographic alkali-feldspathic granites (Țiganilor Valley).

2.4. **Hornfelses.** They are produces of the thermal contact metamorphism, developed around all intrusive bodies, irrespective of the country rock characters and ascribable to the albite + epidote hornfelses and hornblende hornfelses facies.

Within the crystalline schists were emplaced hornfelses with orthose, quartz, biotite and andalusite, sporadically accompanied by corundum and cordierite.

The contact processes underwent by the Permian sedimentary are materialized by the appearance of quartz, acid plagioclase, biotite and clinozoisite hornfelses or of mostly biotitic hornfelses. Also produced by the isochemical contact metamorphism, the micro- or mesoblastic recrystallized limestones, formed against the Mesozoic carbonatic deposits, are widely spread. Separations of clay minerals, epidote, quartz and pyrite are found locally in association with calcite, which is the main mineralogical component.

3. Skarns

3.1. **Petrographic types, spreading.** Results of complex metasomatic reactions triggered by the Laramian igneous rocks emplacement, the skarns outcrop on large areas in the Oravița—Ciclova zone.

The main types of skarns, according to mineralogical criteria are defined by the following assemblages [5] :

— *grandite (grossular* $_{3-50}$ *and)* : widespread in Chinisea Valley and in the NW side of Tîlva Hill and Anton and Ciclova valleys zone ;

— *wollastonite-grandite-tremolite*[6] : visible in the upper course of Chinisea Valley and in the southern side of Fruntea Mare Hill ;

— *wollastonite-grandite* : in Lacul Mare-Crișenilor Brook area ;

— *grandite-scapolite*[6] : first outlined as such in the skarn vein body in the spring zone of Rîndunicii Brook ;

— *wollastonite-diopside-grandite I-grandite II-vesuvianite-clintonite* [6] : in Lacul Mare-Crișenilor Brook zone ;

— *grandite I-grandite II-vesuvianite* : in the middle and lower course of Anton Brook, in Țiganilor Valley and in the Coșnița Brook zone ;

— *diopside-melilite (gehlenite)*: identified in the right side of Crişenilor Brook;

— *wollastonite-diopside-chondrodite-grandite-vesuvianite* : in the right side of Ţiganilor Valley.

Skarns form columns and irregular bodies and are locally found as veins within the crystalline schists. The appearance of the vein body in Rîndunicii Brook seems to be conditioned by the existence of a limestone lamina planed in front of the Oraviţa overthrust and brought in an unconformable position against the crystalline schists.

The field observations indicate sometimes a certain tendency of zoning given by the peripheral disposition of the garnetiferous skarns as compared with the garnetiferous-vesuvianitic ones.

3.2. **Mineralogy of skarns.** *Garnets* predominante over the other skarn minerals. Macroscopically, they exhibit a great morphological and colour variety. Garnets can form monomineral accumulations within which the crystal sizes vary from 2—3 mm to 8—10 cm; other times they constitute nests, small voids and veinlets or they can occur as dodecahedral crystals within a groundmass of calcite or quartz. The colour varies from brown and reddish-brown to honey yellow, yellowish-green and China green. It is difficult to establish a correlation between the variation of the colour and that of the chemism; however, the appearance of the green colour at andradite-rich terms can be outlined as a tendency.

The chemistry of garnets was followed by means of several chemical analyses on the basis of which the percentage compositions were established

TABLE 1

Chemical analyses of the garnets from the skarns in the Maidan—Tilva Mare — Oraviţa zone

Oxides	151 A *	151 B *	67 *	C_2	68	O_2	O_1
SiO_2	38.10	39.26	37.36	34.90	32.30	35.38	34.36
TiO_2	0.18	0,04	2,08	0.13	0.10	0.35	0,45
Al_2O_3	17.12	20.26	12.38	16	13.80	16.58	18.24
Fe_2O_3	4.08	2.07	10.99	11	18	3.66	4.69
FeO	2.96	1.17	0.71	0.70	0.34	0.29	0.42
MnO	0.03	0.05	0.44	0.38	0.40	0.10	0.10
MgO	1.35	2.20	0.89	2	1.22	5.20	4.50
CaO	35.53	34.12	34.23	31.36	32.76	35.01	34.03
H_2O^+	0·15	0·18	0·17	—	—	—	—
H_2O^-	0·75	0·41	0·30	0·34	0·26	1·12	0,16
Total	100·55	99.79	99.55	100.04	99.98	99.77	99.73

* from Popescu, Constantinescu (1977).

in end members (Tab. 1 and 2). The resulting values, plotted on Boecke diagram (1914 from Winchell, 1958), point out their appurtenance to the grandite fields (Fig. 2). The significant participation of the pyralspitic terms

TABLE 2

Ion number versus basis 24 (o)

	151 A	151 B	67	C_2	68	O_2	O_1
Si	6.02	6.00	5.877 } 6.00	5.4594 } 6.00	5.1777 } 6.00	5.4527 } 6.00	5.4029 } 6.00
Al	—	—	0.123	0.5406	0.8223	0.5473	0.5971
Al	3.001 } 3.48	3.722 } 3.94	2.164 } 3.71	2.4066 } 3.7138	1.7993 } 3.9904	2.4639 } 2.9277	2.7621 } 3.3661
Fe^{3+}	0,464	0.222	1.304	0.2923	2.1780	0.4233	0.0532
Ti	0,0018	—	0.246	0.0149	0.0125	0.0405	0.5508
Mg	0.323 } 6.61	0.491 } 6.03	0.208 } 6.12	0.4667 } 5.8712	0.2928 } 6.0608	1.1945 } 7.0316	1.0494 } 6.8258
Fe^{2+}	0.570	0.092	0.094	0.0911	0.0462	0.0377	0.0551
Mn	—	—	0.057	0.0502	0.0549	0.0129	0.0131
Ca	5.663	5.420	5.764	5.2632	5.6669	5.7895	5.7082

Percentage participation of end members (mole %)

	151 A	151 B	67	C_2	68	O_2	O_1
andradite	13.7	5.623	31.6	31.79	54.6	14.46	16.36
grossularia	68.7	84.559	55.319	54.87	38.9	67.84	67.27
almandine	11.2	1.550	1.813	1.55	0.76	0.54	0.81
pyrope	6.3	8.226	3.99	7.95	4.83	16.98	15.37
spessartine	—	—	1.092	0.85	0.91	0.18	0.19

is obvious, three of the analysed samples following the limit of the miscibility gap between grandites and pyralspites. High contents in pyralspitic moles were observed in other occurrences too : Ocna de Fier (Kissling, 1967), Dognecea (Vlad, 1974), Sasca Montană (Constantinescu, 1980). This fact can be retained as a remarkable mineralogical particularity of the garnetiferous skarns in Banat, the more so as the grandite-pyralspite miscibility is considered, on the basis of numerous experimental data (Schreyer, 1976), to be hardly achievable under thermo-baric conditions of the pyrometasomatic reaction zones.

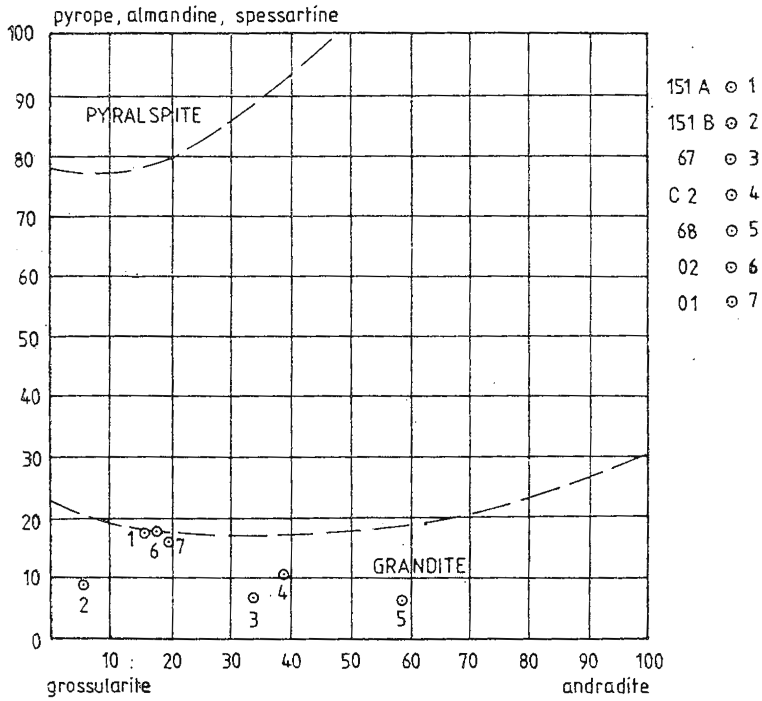

Fig 2 — Boecke diagram (1914): plots of the values representing the percentage participation of end members (mol %) obtained for garnets in Oravița zone: 151 A — green-yellowish garnet, Oravița Valley, 151 B — brown garnet — Oravița Valley: 67 — dark green garnet-Chinisea Valley (Gh. Popescu, E. Constantinescu — 1977), C2 — dark green garnet — Rîndunicii Brook, 68, dark green garnet — Chinisea Valley, 02 brown-yellowish garnet — Crișenilor Brook, 01 — light green garnet — Crișenilor Brook.

Microscopically, garnets occur as xenoblastic or idioblastic crystals, colourless or of a brown-yellowish colour, with a high relief. Generally, two garnet generations can be emphasized :

— generation I — colourless garnet as seen in plane polarized light, usually displaying idioblastic forms;

— generation II — brown-yellowish garnet with a higher refringence than the first one, commonly showing xenoblastic forms.

Rather as a rule than as an exception, the garnets from Oravița-Ciclova skarns display an anomalous optical anisotropy, locally very obvious, certain morphological particularities of the anomalies allowing the separation of the following types :

— sectorial anomaly (Pl. I, Fig. 1) : crystalloblasts sectioned in a median plane reveal a structure divided into six triangular-shaped birefringent sectors, with the peak in the centre of the crystal ;

— concentric anomaly (Pl. I, Fig. 2) : lamellae of variable sizes, alternatively isotropic and anisotropic, parallel to the crystal faces ; the crystalloblasts with a concentric anomaly reveal sometimes the evolution of the crystallographic form from rhomboidal dodecahedron to trapezohedron (Pl. II, Fig. 1), a fact also observed in case of Ocna de Fier garnets (Kissling, 1967) ;

— mixed anomaly : a complex joining of the two mentioned types : the anizotropic sectors are divided by lamellae parallel to the margin of the grain.

The birefringence of the sectorial areas and of the anisotropic lamellae is generally low (order I) ; a positive or negative biax character, with a variable angle of the optical axes ($2V = 23-30°$) can be observed. The main plane of optical symmetry of the lamellae from the concentric anomaly is approximately parallel to the crystal faces but, however, there is not a perfect coincidence. In accounting for the appearance of the double refraction at these grandites it may be appealed to internal tensions due either to forced isomorphic mixtures between the pyralspitic and granditic terms or to particular processes connected with the skeletal growth. In some cases, certain morphological features of the garnets, difficult to infer from a selective substitution suggest an incomplete skeletal development (Pl. II, Fig. 2).

Garnets replace wollastonite, diopside and chondrodite and are substituted by vesuvianite. There were observed significant structures of metasomatic substitution of plagioclases from monzodiorites by garnet, perfectly comparable, in morphological respect, to the quartz-feldspar micrographic intergrowths (Pl. III, Fig. 1). In the hydrometasomatic phase, garnets are replaced by calcite, epidote, scapolite and quartz. Locally, pseudomorph epidote after garnet idioblasts, preserving a mixed-type divided structure, was identified.

Vesuvianite is, after grandites, the most frequent mineral in the Oravița-Ciclova skarns. It forms compact masses, locally with a vein character, within granditic accumulations or crystal agglomerations with sizes up to 10 cm (Țiganilor Valley). It is brown or yellowish-brown, and hence its macroscopic separation from grandite , particularly when its crystallographic shape is not obvious becomes, to a great extent, difficult.

Vesuvianite crystals show a typical bipyramidal habitus (Pl. III, Fig. 2), characterized by the disappearance of the prism faces (100) and (110), the development of the tetragonal bipyramid faces (101), as well as of the basal pinacoid (001) (Fig. 3).

The chemistry of the Ţiganilor Valley vesuvianite points out, in comparison with other chemical analyses on samples from known occurrences, average values of the main cations. The relatively high amount of Fe_2O_3 is not connected with a decrease of the content in Al_2O_3, as in the case of other types of high-iron vesuvianite. The Al_2O_3/Fe_2O_3 ratio in the

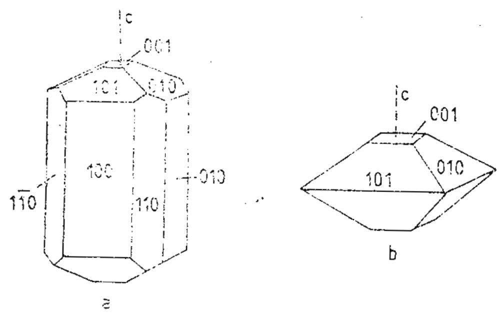

Fig. 3 — Habitus of vesuvianite crystals: a) forms specific to Sasca Montană vesuvianite (Oraşului Hill), b) forms specific to Oraviţa and Ciclova vesuvianite.

Ciclova vesuvianite is 20.38—5.15% in comparison with 17.29—4.87% (FeO 0.36%) in the Sasca Montană vesuvianite (Constantinescu, 1980), 12.66—4.36 % (FeO 1.55%) in Akhmat-Ural (Miaşnikov, 1940, in Deer et al. 1965), 13.36—4.15% (FeO 2.15%) in the Iron Mountains vesuvianite (New Mexico, Deer et al., 1965) and 15.62—2.81% (FeO 2.96%) in the Turnback Lake vesuvianite (Canada; Meen, 1968 in Deer et al., 1965).

TABLE 3

Chemical analysis of the Ţiganilor Valley vesuvianite

Oxides	Content %	Ion number in base 76 (0.OH, F)		
SiO_2	37.64	Si	18.01	18.00
TiO_2	0.121	Al	—	
Al_2O_3	20.38	Al	11.50	15.53
Fe_2O_3	5.15	Ti	0.04	
FeO	—	Fe^{3+}	1.85	
MnO	0.08	Fe^{2+}	—	
MgO	2.72	Mg	1.94	
CaO	33.19	Ca	17.03	
Na_2O	0.03	OH	0.97	
K_2O	—			
H_2O^+	0.303			
H_2O^-	0.192			

In comparison with the mentioned occurrences, the Ciclova vesuvianite is characterized either by the absence of FeO or by extremely small amounts of it : 0.58 or 0.25% (Cioflica et al., 1980).

Under the microscope vesuvianite displays a xenoblastic or idioblastic contour and a high refringence. Its colour, in plane polarised light, is almost brown yellow; in crossed polars crystalloblasts show a low birefringence in anomalous colours : Prussian blue, purple, light yellow and brown. The disposition of the birefringence colours frequently induces a marked zoning in the plane perpendicular to (001). Both negative uniaxial crystals and anomalous negative biaxial crystals were identified; in the later cases the optic plane is parallel to (110).

Vesuvianite replaces all the other associated skarn minerals, providing evidence for its appurtenance to the late phases of the pyrometasomatic process. The replacement of the high-andradite garnets by vesuvianite determines a significant increase of the birefringence in the reaction zone between the two minerals and, implicitly, a change of colour towards light hues corresponding to an enrichment in Fe (Pl. IV, Fig. 1). Similar situations were described for the Sasca Montană vesuvianite (Constantinescu, 1980).

During the hydrometasomatic phase vesuvianite is highly substituted by clintonite, epidote, calcite and quartz.

Very interesting mineralogical aspects were observed in the contact zones of the Țiganilor Valley skarns with the alkali-feldspar syenites. Pseudomorph vesuvianite after a fibrous-radiar mineral was identified (Pl. IV, Fig. 2). The X-ray diffraction investigation, carried out on such samples, pointed out traces of serpentinite and asharite.

Wollastonite occurs frequently in the Oravița-Ciclova skarns.

Macroscopically, wollastonite can be easily distinguished due to the long prismatic habitus, locally needle-shaped, as well as to its bright white or white-grey colour. Commonly it forms monomineral accumulations within which the crystals are longer than 5—6 cm (Chinisea Valley, Crișenilor Brook, Țiganilor Valley).

Microscopically, wollastonite occurs as hipidioblastic or xenomorphic crystals due to marginal corrosion. The optic angle is $2V = 39 - 40°$, the extinction angle $\alpha \wedge c = 30°$ and the optic sign is negative.

Wollastonite is replaced by all the other associated skarn minerals, marking the early stages of the pyrometasomatic process. In the hydrometasomatic phase, wollastonite is very sensitive to the substitution of calcite, quartz and epidote.

Pyroxenes belong to the diopside-hedenbergite series and are comprised in the skarns with a complex composition from Crișenilor Brook and Țiganilor Valley.

In thin sections, clinopyroxenes form hipidioblastic crystals with short-prismatic habitus and a good cleavage which is parallel to the prism face. The measurements of the extinction angle $\gamma \wedge c$ and of the optic angle carried out for 17 crystals from different thin sections indicate, by plotting on Hess diagram (1949-in Troger, 1952), a significant concentration of the values in the diopside field (Fig. 4).

In the Crișenilor Brook-Lacul Mare skarns, diopside is replaced by melilite and within the other mentioned assemblage in this zone it is formed after wollastonite and is corroded by garnet and vesuvianite, indicating the presence of two generations. In Ciclova zone the diopside contemporaneous with chondrodite also replaces wollastonite, being substituted by garnet and vesuvianite. In the hydrometasomatic phase, diopside is corroded by calcite and quartz.

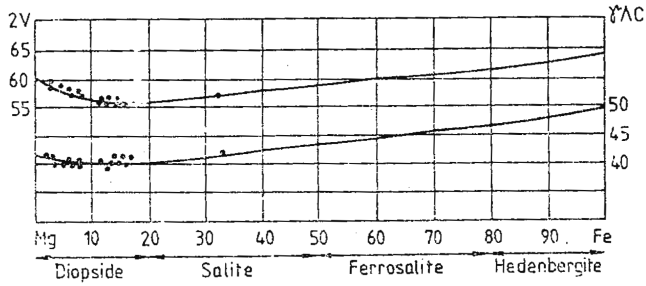

Fig. 4 — Plotting of 2V and γ Λ c values measured for calcic pyroxene from the Oravița-Ciclova skarns on Hess diagram (1949).

Melilite was identified in association with diopside or forming small monomineral accumulations in the skarns from Crișenilor Brook.

Macroscopically, it occurs as crystals (up to 0.5 cm) of a dark green colour with brownish spots, trapped in a groundmass of diopside and clay minerals. Microscopically (Pl. V, Fig. 1), it displays xeno- or hipidioblastic outlines, with a visibly lower relief as compared with garnets and vesuvianite.

In comparison with vesuvianite, melilite differs clearly due to the quality of the cleavage—medium towards good — along two orthogonal directions. Melilite occurs frequently in normal birefringence colours of the first order; some thin sections reveal anomalous hues of lavander-blue. The extinction occurs after both directions of cleavage. The uniaxial character has been checked; the optic sign is negative indicating the presence of gehlenite. Locally, crystals are covered by a brown-greenish pigment, resembling a clay mineral which is, however, undeterminable.

Humites were identified in the Țiganilor Valley skarns. Microscopicaly, they occur as idioblastic crystals, locally isometric or short prismatic, with a weak pleochroism in yellow and light brown hues. The cleavage parallel to (001) is poor, often unseen. The relief is medium to high, conferring a shagreen-like aspect similar to that of olivine. Chondrodite is positive biaxial; the values of the optic angle range between 68° and 75° and the extinction angles $\beta \wedge c$ are large (25—27°), differentiating chondrodite from the other minerals in the humite group. The radiar intergrowths of chondrodite with diopside are characteristic and they indicate their simultaneous appearance in the pyrometasomatic process (Pl. V, Fig. 2). Chondrodite is corroded by garnet, vesuvianite, epidote, calcite and quartz.

Clintonite was first described at Oravița (Popescu, Constantinescu, 1977); it was identified in association with brown-yellowish, xenoblastic vesuvianite and with grandite in the skarns from Crișenilor Brook. This mineral was also found in the waste of gallery II Clementi, but in this case, its source place could not be established.

Macroscopically, it occurs as green, leafy, pseudohexagonal crystals. The crystals usually underwent a supergene decolouring, locally with a wider extension, conferring a muscovite-like aspect. In thin sections it shows a light green colour, with a strong positive relief and a perfect cleavage parallel to (001).

The birefringence colours are vivid, nonhomogeneously spread. The optic angle is small, and the optic sign is negative; the optic plane is perpendicular to (010), which differentiate clintonite from xantophyllite where the optic plane is parallel to (010). Clintonite is preferentially developed along some fissures in garnets or vesuvianite (Pl. VI, Fig. 1) proving its late position versus the other two minerals.

Scapolites are associated with grandite (35 and), epidote, calcite and zeolites in the skarn vein body at Rîndunicii Brook.

Scapolites form colourless, limpid hipidioblastic or idioblastic crystals, with a marked pseudoabsorption; the relief is weakly positive after ω, decreasing sensibly after ε. The cleavage parallel to the prism face is good and in basal sections one can observe two orthogonal cleavage directions, typical for minerals in the tetragonal system. The stages of growth and evolution of the crystals from a tetragonal prism to a ditetragonal one by the development of the face (110) (Pl. VI, Fig. 2) can be distinguished in basal sections. Birefringence is very high, according to the appearance of the pseudoabsorption. The relief variation and the high birefringence indicate a term closer to meionite.

Meionite represents a subsequent phase versus garnet, being, in its turn, replaced by calcite and zeolites.

Tremolite occurs as crystals with a long prismatic up to acicular habit, of a greyish-white colour, spotted by iron oxides as superficial depositions. Microscopically, it forms needle-shaped or radiar fibrous aggregates, colourless or of a light green colour, which cement or corrode garnet crystalloblasts. Extinction $\gamma \wedge c$ is 16—18°, with lower values at the coloured terms. Tremolite is corroded by quartz and opacized by iron oxide depositions.

3.3. **Petrogenetic considerations.** The intrusion of the Laramian magmatic bodies was accompanied by the release of significant amounts of post-magmatic fluids with a pneumatolytic and hydrothermal character.

The Mesozoic sedimentary, with a mostly carbonatic nature, was sensitive to the action of the pneumatolytic fluids, and thus the pyrometasomatic products are preferentially linked to it. The Permian deposits and the crystalline schists underwent only thermal metamorphism therefore they display an isochemical character.

The main petrogenetic factors whose influence is proved by observation data refer to : petrographic and chemical features of the paleosome, circulation possibilities of the post-magmatic fluids, chemical composition of these solutions, pressure and temperature under which the metasomatic reactions took place.

The influence of the paleosome is well illustrated by the fact that the skarns with complex mineralogical associations are developed only on the background of Crivina Beds, mostly with a marly and clay-calcareous character, whereas the zones presumed to exist in the extension of the Brădet and Marila limestones include skarns with a relatively simple composition. In this latter case, a diversification of the mineralogical associations seems to be the result of the existence of marly intercalations at the upper part of the Marila limestones. The absence of periplutonic zoning, the skarn development as columns, veins or irregular bodies as well as the petrographic characters of the Mesozoic paleosome, plead for processes of metasomatosis by infiltration and quite locally by diffusion at the contact between the marly and calcareous levels.

The access ways opened to metasomatosis by infiltration were represented by fissures, fractures, bedding planes, as well as separation planes between the calcareous levels and the marly or siliceous ones.

The tendency of zoning, locally manifested within pyrometasomatic deposits, indicates the local preponderance of a bimetasomatosis-type mechanism related, in this case, to the development of Brădet and Marila limestones. The zoning displayed by the disposing of the garnetiferous skarns versus the garnetiferous-vesuvianitic ones is a result of the different relative mobility of the chemical components within the changes of substances yielded between the eruptive mass and the calcareous paleosome.

The chemical components of the system within which the pyrometasomatic processes took place are very numerous as one can see from the described mineralogical associations : $SiO_2-Al_2O_3-CaO-MgO-Fe_2O_3-FeO-CO_2$, H_2O, etc., and they cannot be assigned entirely by the Mesozoic paleosome. In this respect there is the fluid composition whose substance supply is always significant, justifying more than the paleosome composition the diversity of the skarn minerals and the particularities of their succession in time, that must be taken into account.

Pressure and temperature played an important role in establishing the succession of the skarn minerals. As regards pressure, one shall distinguish the lithostatic pressure corresponding to the pyrometasomatic reaction zone level and given by the Laramian overlying rocks and, on the other hand, the fluid pressure.

It may be reasonably inferred that the lithostatic pressure corresponding to pyrometasomatic reaction zones — at depths of 1—1.5 km and with an average specific weight for the overlying rocks of 2.5—2.6 — was approximately of 250—400 bar. This approximation is due to the impossibility of an exact estimation of the overlying deposits erosion rate and of the load induced during the Laramian by the eastward extension of the crystalline schists in the Bocşa Montană—Oraviţa—Ilidia massif.

A notable permeability of the reaction system for the volatile components is suggested by certain particularities of the succession of skarn minerals, i.e. the preferential replacement of mineralogical phases along geometric discontinuities. Thus, it may be accepted that the total pressure of the fluids was subordinated to the lithostatic one, and it ranged between a maximum value close to the lithostatic pressure and a minimum value corresponding to the atmospheric pressure.

Like the fluid pressure, temperature constituted a variable factor in time and space as it ranged between a minimum value corresponding to the geothermal degree of the reaction zone (ca 50°C)[7] and a maximum value corresponding to the intruded magma. Giving a prime clue about the maximum value of the temperature in the Oraviţa Valley contact aureole, there are the frequent transitions from ferrotschermakite to brown hornblende which are considered to occur at temperatures of 750°. In perfect agreement with the strong basic character of the Laramian magmatites in this zone the reaching of so high values conditioned the appearance of gehlenite which differentiates the Oravița skarns from other occurrences in Banat.

The crystallization sequence of the skarn minerals illustrates the variability in time of the temperature factor. Thus, the associations identified in the aureole of the Oravița body indicate the existence of two main stages in the evolution of temperature :

— a progressive (heating) phase represented by diopside I-melilite association ;

— a regressive (cooling) phase during which were formed wollastonite-diopside II + calcite — garnet I — garnet II — vesuvianite — clintonite — quartz — calcite — epidote (Fig. 5 A).

In case of the Țiganilor Valley skarns there are no elements to suggest the manifestation of the two main phases in the evolution of temperature and therefore the existence of the progressive phase can be only presumed (Fig. 5 B).

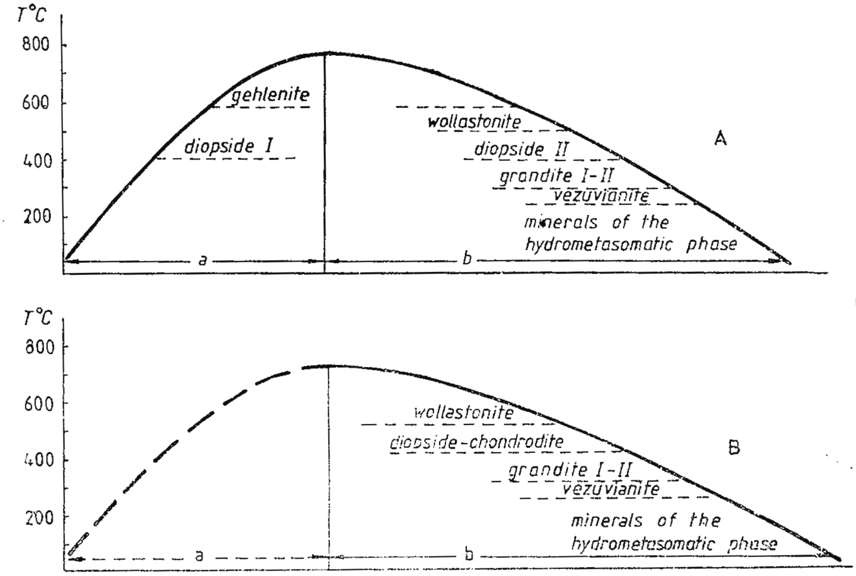

Fig. 5 — Evolution of the temperature described by the sequence of skarn minerals for the contact aureoles in Oravița Valley (A) and Țiganilor Valley — Ciclova (B).

4. Conclusions

The ample pyrometasomatic process generated by the intrusion of the Oravița—Ciclova magmatites differentiatedly affected the pre-existent formations. Skarns are confined to the impact zones between the intrusions and the Mesozoic sedimentary represented by the Crivina Beds, Marila and Brădet limestones.

Within the crystalline schists, the Permian sedimentary and partly the Mesozoic one, produces of isochemical metamorphism, were generated which can be referred to the facies of hornblende hornfelses or of albite and epidote hornfelses.

The particularities of the Oraviţa—Ciclova skarn occurrence refer to:

— the presence of mineralizers of F, Cl, B type in the reaction medium, materialized by the appearance of minerals such as: vesuvianite, chondrodite, scapolite and probably asharite;

— the appearance of gehlenite as a result of the high temperature (ca 750°C) reached in the contact aureole from Oraviţa Valley, in perfect agreement with the more basic character of the Laramian magmatites occurring here;

— the confining of the substitution zones of the early skarn minerals by more recent mineralogical phases along microfissures and cleavages, indicating a good permeability of the reaction medium for the volatile components;

— the frequent absence of a clear periplutonic zoning beside the development of skarns as irregular bodies or columns indicating metasomatosis by infiltration and, subordinately, bimetasomatosis as mechanisms of emplacement;

— the development of skarns with a complex composition against the background of a marly of clay-calcareous paleosome and of those with a simple composition against a calcareous paleosome;

— the microfissures occurring in skarn crystals which represent hosts of the late depositions of vesuvianite and minerals of the hydrometasomatic phase, indicating a general tendency of contraction manifested towards the end of the pyrometasomatic process;

— the existence of two main phases in the temperature evolution, at least in case of the contact zone of the Oraviţa Valley diorites: a heating phase, represented by the diopside I — melilite association, and a cooling phase, represented by the wollastonite — diopside II + calcite — garnet — vesuvianite — clintonite succession.

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[4] According to the nomenclature of the transition terms from the clay-silica-carbonate ternary system; Scolari, Lille (1973).

[5] The order in which the minerals are mentioned corresponds to their formation sequence.

[6] The associations also include some minerals of the hydrometasomatic phase: tremolite, scapolite, clintonite, which by their widespreading can individualize the respective association.

[7] The value of the temperature at the geothermal degree corresponding to a depth of 1000 m.

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CONTRIBUȚII LA STUDIUL SKARNELOR DE LA ORAVIȚA—CICLOVA

(Rezumat)

Transformările pirometasomatice generate de intruderea banatitelor de la Oravița și Ciclova au afectat în mod diferențiat formațiunile preexistente. Skarnele se dezvoltă exclusiv în zonele de contact ale intruziunilor cu sedimentarul mezozoic reprezentat prin stratele de Crivina (argile calcaroase, marne), calcarele de Marila (calcare sublitografice) și calcarele de Brădet (calcare micritice cu rare bioclaste și separații de marne șistoase).

Principalele tipuri de skarne separate după criterii mineralogice sînt definite de următoarele asociații :

— *grandit (grossular*$_{30-50\ and}$*)* ;
— *wollastonit-grandit-tremolit* ;
— *wollastonit-grandit* ;

— *grandit-scapolit (meionit)*;
— *wollastonit-diopsid-grandit I-grandit II-vezuvian-clintonit*;
— *grandit I-grandit II-vezuvian*;
— *diopsid-melilit (gehlenit)*;
— *wollastonit-diopsid-chondrodit-grandit-vezuvian*.

Particularitățile ocurenței de skarne de la Oravița-Ciclova sînt următoarele:

— prezența în mediul reacțional a unor mineralizatori de tipul F, Cl, B, materializată de apariția unor minerale ca: vezuvian, chondrodit, scapolit și probabil asharit;

— apariția gehlenitului, ca o reflectare a temperaturilor ridicate (cca 750°C), atinse în aureola de contact din valea Oravița, în perfect acord cu caracterul pronunțat mai bazic al magmatitelor laramice de aici;

— concentrarea zonelor de substituție a mineralelor de skarn timpurii de către faze mineralogice mai noi, la nivelul microfisurilor și clivajelor, sugerînd o bună permeabilitate a mediului de reacție pentru componenții volatili;

— absența unei zonalități periplutonice clare, alături de dezvoltarea skarnelor sub formă de corpuri neregulate sau coloane, ceea ce pledează pentru un mecanism de punere în loc de tipul metasomatozei prin infiltrație și cu totul izolat a bimetasomatozei;

— dezvoltarea skarnelor cu compoziție complexă pe fondul unui paleosom marnos și argilo-calcaros, iar a celor cu compoziție simplă, pe seama unui paleosom calcaros;

— microfisurile existente la nivelul cristalelor din skarne și care se constituie în gazde ale depunerilor tardive de vezuvian și minerale ale fazei hidrometasomatice, relevînd tendința generală de contracție manifestată spre finele procesului de skarnizare;

— existența a două faze principale în evoluția temperaturii, cel puțin pentru zona de contact a dioritelor din valea Oravița: o fază de încălzire materializată de asociația diopsid I-gehlenit și o fază de răcire dată de succesiunea wollastonit-diopsid II-granat-vezuvian-clintonit.

EXPLANATION OF PLATES

Plate I

Fig. 1. — Sectorial-type optical anomaly of garnets (Anton Brook-Ciclova) N +, 250 ×.

Fig. 2. — Concentric-type optical anomaly of garnets (Chinisea Valley) N +, 250 ×.

Plate II

Fig. 1. — Evolution of a garnet crystalloblast from rhomboidal dodecahedron to trapezohedron (Prisaca Hill) N +, ca 300 ×.

Fig. 2. — Skeletal garnet crystalloblasts (Chinisea Valley) NII,60 ×.

Plate III

Fig. 1. — Substitution structures of monzodiorite plagioclase feldspar by garnet (black) (Țiganilor Valley) N +,150 ×.

Fig. 2. — Bipyramidal crystals of vesuvianite (Țiganilor Valley).

Plate IV

Fig. 1. — Remnants of andraditic garnet in vesuvianite; a marked increase of the vesuvianite birefringence in the reaction zone is visible (Țiganilor Valley) B +, 250×.

Fig. 2. — Vesuvianite pseudomorph after a fibrous-radiar mineral (Țiganilor Valley) N +, 160 ×.

Plate V

Fig. 1. — Gehlenite (Crișenilor Brook) N +, 60 ×.

Fig. 2. — Radiary intergrowths of chondrodite (ch) and diopside (di). (Țiganilor Valley) N +, 160 ×.

Plate VI

Fig. 1. — Clintonite (cl) in vesuvianite (v) (Crișenilor Brook) N II, 300 ×.

Fig. 2. — Basal section of a scapolite crystal; the stages of growth and evolution from tetragonal prism to ditetragonal prism by the (110) face development are visible. N II, 300 ×.

D. S. Inst. Geol. Geofiz., vol. 72–73/2 (1985 1986), 1988, pag; 47–64

2. ZĂCĂMINTE

DATE ASUPRA COMPOZIȚIEI MINERALOGICE ȘI A TEMPERATURILOR DE CRISTALIZARE A MINERALELOR DIN ZĂCĂMÎNTUL BĂIȚA-NISTRU (JUD. MARAMUREȘ) [1]

DE

VASILE MANILICI [2]

Hydrothermal processes. Mineralogical composition. Native elemets. Sulphides. Sulfosalts. Oxides. Tellurides. Crystal forms. Crystal growth. Habit. Geologic thermometry. East Carpathians — Neogene-Quaternary eruptive rocks-Gutin.

Abstract

Data about mineralogical composition and crystallization temperature of Băița-Nistru ore-deposit (Maramureș district). This paper presents new data about mineralogical composition of Băița-Nistru ore-deposit, insisting on the characteristics of component minerals, on which account physico-chemical conditions of mineralization formation are found. Afterwards, there are shown some data about crystallization temperature of main minerals which are determined through the homogeneity and decrepitation method, this adds to the image of chemical evolution of hydrothermal generating solutions of mineralization, that of the evolution of power level of these solutions.

Résumé

Données sur la composition minéralogique et les températures de cristallisation du minerai du gisement de Băița-Nistru (département de Maramureș). La présente note apporte des nouvelles données sur la composition minéralogique du gisement de Băița-Nistru, insistant sur les particularités des minéraux composants, ayant comme but la détermination des conditions physiques et chimiques de la formation de la minéralisation. On présente aussi des données sur les températures de cristallisation des principaux minéraux, qui ont été déterminés par la méthode de l'homogénéisation de décrépitation, et qui complètent l'image de l'évolution du chimisme des solutions hydrothermales qui ont engendré la minéralisation avec l'évolution du niveau énergétique de ces solutions.

[1] Depusă la 6 martie 1979, acceptată pentru publicare la 13 mai 1980, comunicată în ședința din 13 aprilie 1979.

[2] Institutul Politehnic București, Splaiul Independenței nr. 313.

Ca şi celelalte zăcăminte din zona Baia Mare, cel de la Băiţa-Nistru are caracter complex, la alcătuirea sa participînd după datele de literatură : Zepharovici (1859, 1893), Hauer et al. (1855), Ackner (1895), Stoicovici (1950), Cădere (1925), Ianovici et al. (1961), Butucescu et al (1963) şi Rădulescu et al (1966) circa 55 de minerale în care se includ şi cele identificate cu ocazia cercetărilor noastre. În cadrul lucrării se aduc noi date asupra naturii mineralelor şi a raporturilor lor spaţiale care permit stabilirea ordinei de depunere a acestora, inclusiv asupra temperaturilor de formare a acestora.

După compoziţia lor chimică, deosebim în acest zăcămînt următoarele grupe de minerale :

a) Elemente native : aur, argint, stibiu, cupru ;

b) Sulfuri, sulfosăruri şi compuşi similari : galenă, blendă, wurtzit, pirotină, pirită, calcopirită, covelină, calcozină, marcasită, mispichel, tetraedrit, stibină, freibergit, pirargirit, proustit, şi stefanit ;

c) Telururi : altait, hessit, petzit şi sylvanit ;

d) Halogenuri : fluorină ;

e) Oxizi şi hidroxizi : cuarţ, calcedonie, opal, oligist, magnetit (muschetovit), goethit, tenorit şi limonit ;

f) Sulfaţi : baritină, goslarit, chalcantit, hexahidrit, melanterit, anglezit, mallardit şi gips ;

g) Fosfaţi : apatit şi vivianit ;

h) Carbonaţi : calcit, dolomit, siderit, rodocrozit, azurit şi malachit ;

i) Silicaţi : adular, sericit, clorit, illit, montmorillonit, dickit şi caolinit.

Urmărirea repartiţiei mineralelor componente în cuprinsul umpluturii filoniene, a asociaţiilor caracteristice diverselor etape de mineralizare, inclusiv a particularităţilor cristalografice şi microscopice ale acestora permit descifrarea condiţiilor fizico-chimice de depunere a mineralizaţiei şi evoluţia chimismului soluţiilor hidrotermale din perioada de mineralizare. După modul lor de formare, deosebim minerale hipogene formate pe seama soluţiilor hidrotermale şi supergene formate sub acţiunea apelor de infiltraţie.

Dintre componentele hipogene, *pirita*, semnalată de Cădere (1925), Rădulescu (1958) şi Butucescu et al (1963), are răspîndirea cea mai largă, participînd la alcătuirea celor trei tipuri de mineralizaţie cunoscute ca şi a impregnaţiilor. Se prezintă sub formă de mase compacte ori cristale izolate de 1—5 mm, atingînd local chiar 5 cm. Frecvent, pe feţele sale se observă coroziuni şi tremii concave, indicînd fluctuaţii importante ale temperaturii de cristalizare.

La cristalele bine dezvoltate se identifică formele : (100) şi (210), mai rar (110), (111), (140), (122) (221), (320), (421), (513), (756) şi (11 4 0) ; ultimele mai frecvente în cuprinsul mineralizaţiei piritocuprifere. Urmărirea frecvenţei feţelor (100) şi (210), respectiv a asociaţiei acestora (tabelul 1) arată că în culcuşul şi coperişul filoanelor predomină net faţa de cub, în porţiunile mediane asociaţia (100), (210), pe cînd în porţiunile centrale ale filoanelor faţa (210). Admiţînd valabilitatea concluziilor

TABELUL 1

Variaţia habitusului cristalelor de pirită

Filonul	Tipul de mineralizaţie	Frecvenţa formelor cristalografice %		
		(100)	(100) (210)	(210)
	Mina 11 Iunie			
	culcuşul şi coperişul filonului			
Nepomuc	pirito-cupriferă	67	25	8
	porţiunile mediane ale umpluturii filonului			
Nepomuc	pirito-cuprifer	16	53	31
	partea centrală a umpluturii filonului			
Nepomuc	pirito-cupriferă	4	23	73
	culcuşul şi coperişul filonului			
142	plumbo-zinciferă	70	23	7
	porţiunile mediane ale umpluturii filonului			
142	plumbo-zinciferă	27	65	8
	partea centrală a umpluturii filonului			
142	plumbo-zinciferă	16	27	57
	Mina 9 Mai			
	culcuşul şi coperişul filonului			
Sofia	plumbo-zinciferă	79	19	2
	porţiunile mediane ale filonului			
Sofia	plumbo-zinciferă	37	52	11
	partea centrală a filonului			
Sofia	plumbo-zinciferă	25	22	53

lui Sunagawa (1957) asupra zăcămîntului cercetat, rezultă că în etapele incipiente ale procesului de mineralizare cristalizarea mineralelor componente s-a realizat într-un regim de răcire rapidă, la o alimentare insuficientă cu soluţii, deci condiţii puţin favorabile depunerii minereului. În etapele următoare se ajunge la un regim mai lent de răcire, fără fluctuaţii mari de temperatură şi concentraţie, cu o alimentare constantă şi suficientă de soluţii, condiţii specifice ultimelor etape. Creşterea în ambele tipuri de mineralizaţie a frecvenţei feţei (210) în detrimentul feţei de cub, indică menţinerea în ambele cazuri a condiţiilor stabilite de Sunagawa şi evoluţia lor în acelaşi sens.

Urmărirea frecvenţei formelor cristalografice în diferite stadii de dezvoltare ale cristalelor de pirită, arată că la cristalele de 0,03—0,07 mm se identifică în exclusivitate forma (100), la cele de 0,12—0,25 mm predomină asociația (100), (210) iar la cele de peste 1 mm forma (210) asociată deseori cu forma (111).

În cuprinsul mineralizației pirito-cuprifere și a celei plumbo-zincifere se identifică cîte trei generații de pirită. Cea din prima generație, localizată în culcușul și coperișul filoanelor este asociată în cuprinsul mineralizației pirito-cuprifere cu calcopirită$_1$, cuarț$_1$ cenușiu, clorit, și local pirotină, iar în cadrul celei plumbo-zincifere cu cuarț$_1$ fin granular, cenușiu, adular monoclinic, mai rar blendă$_1$ și galenă$_1$. Probabil că acestei generații îi aparține și pirita cubică ce impregnează roca gazdă a filoanelor. Ea include adesea cristale de oligist, fiind adesea diaclazată și cimentată de calcopirită$_1$ care o și corodează. Pirita$_2$ din porțiunile mediane ale filoanelor este asociată cu cuarțul$_2$ fibros, blendă$_2$ galenă$_2$ și marcasită. Cea din a treia generație din porțiunile centrale ale filoanelor este asociată în cadrul mineralizației pirito-cuprifere cu cuarț$_3$, hidromice și carbonați, iar în cuprinsul celei plumbo-zincifere cu cuarț$_3$, caolinit, calcedonie și baritină. La toate generațiile de pirită din cuprinsul filoanelor minei 11 Iunie se observă uneori o slabă anizotropie, asemenea efecte observîndu-se mai ales la pirita concrescută cu mispichel.

Calcopirita, citată de Zepharovici (1859), Stoicovici (1950), Ianovici et al (1961) și Butucescu et al (1963), cea de a doua componentă principală a mineralizației pirito-cuprifere și plumbo-zincifere, se concentrează în culcușul și coperișul filoanelor. Ea însoțește mineralele specifice celor trei generații ale ambelor tipuri de mineralizație, fiind mai bine reprezentată în depunerile care cimentează minereul diaclazat ori brecifiat din primele două generații.

Blenda, citată de Ianovici et al. (1961), și Butucescu et al. (1963), furnizează alături de pirită, numeroase date asupra condițiilor fizice de formare a zăcămîntului. Este un mineral reprezentativ al minereului plumbo-zincifer, fiind rar întîlnită în cuprinsul celui pirito-cuprifer și numai în porțiunile centrale ale acestuia. Ea apare concentrată, de obicei, în porțiunile mediane ale filoanelor plumbo-zincifere, cea mai mare parte a ei cristalizînd în cea de a doua generație. Caracteristică acestui mineral este frecvența ridicată a incluziunilor de calcopirită, deseori cu dispoziție zonară, în care alternanțele cu și fără incluziuni sînt adesea paralele cu fețele cristalografice. Mărimea acestor incluziuni variază între 1 mμ și 40—50 mμ, cele mai fine întîlnindu-se în culcușul și coperișul filoanelor, iar cele mai dezvoltate în porțiunile mediane și centrale ale acestora. Fără îndoială că prezența incluziunilor fine indică o răcire rapidă a umpluturii filoniene, proprie etapei incipiente a procesului de mineralizare, pe cînd a celor mai dezvoltate arată instaurarea unui regim lent de răcire, propriu etapei finale a mineralizării.

În afară de incluziunile de calcopirită din blendă provenite din procesul de dezamestec, se identifică și incluziuni rezultate din difuziunea celei dintîi în cea de a doua, care apar totdeauna în porțiunile marginale ale granulelor de blendă în contact cu calcopirita masivă. Conform rezultatelor experimentale obținute de Filimonova (1964), apariția acestora din urmă se explică prin menținerea agregatului mineral nou format o perioadă îndelungată de timp la o temperatură ridicată — probabil apropiată de cea de formare. Atît în porțiunile marginale cît și în cele mediane, blenda feriferă de culoare brun-închisă cu numeroase incluziuni de calcopirită, este brecifiată şi cimentată de o varietate de blendă neferiferă de culoare gălbuie lipsită de incluziuni de calcopirită, indicînd o diminuare a conţinutului de Fe şi Cu din soluţiile stadiului final de mineralizare.

Spre deosebire de blendă, *wurtzitul*, are o perioadă mai scurtă de cristalizare, fiind întîlnit printre ultimele componente ale mineralizaţiei plumbo-zincifere. El acoperă sulfurile principale, fiind acoperit de calcedonie, cuarţ tardiv ori calcit. Deseori el se întîlneşte în depuneri alternante cu $blenda_3$, indicînd variaţii ale pH-lui soluţiilor de la sfîrşitul perioadei de mineralizare.

Galena, semnalată de Zepharovici (1859), Cădere (1925), Stoicovici (1950) şi Ianovici et al (1961), reprezintă alături de blendă, componenta principală a minereului plumbo-zincifer, fiind însă subordonată cantitativ acesteia. În cuprinsul mineralizaţiei pirito-cuprifere ea apare în cantităţi mici în porţiunile centrale ale filoanelor, în timp ce în cuprinsul celei plumbo-zincifere ea este răspîndită pe toată grosimea acestora, concentrîndu-se mai ales în porţiunile mediane. Ca şi la pirită şi blendă, dimensiunile cristalelor cresc de la pereţi spre centrul filoanelor, indicînd încetinirea regimului de răcire al soluţiilor, inclusiv o atenuare a variaţiilor de concentraţie. Frecvent, în cuprinsul mineralizaţiei plumbo-zincifere $galena_1$ corodează cristalele de pirită, în schimb $galena_2$ asociată cu $cuarţ_2$ fibros, marcasită, wurtzit şi sericit din porţiunile mediane corodează $blenda_2$. $Galena_3$ din porţiunile centrale ale filoanelor include sporadice cristale de pirargirit, indicînd o îmbogăţire a soluţiilor finale în Sb şi Ag. La suprafaţă ea trece în *anglezit*, iar acesta în *ceruzit*.

Marcasita, mai puţin răspîndită, se identifică microscopic printre ultimele componente sulfuroase ale ambelor tipuri de minereu, fiind acoperită de calcit şi caolinit. Local se întîlnesc şi depuneri alternante de cuarţ fibros, calcedonie şi marcasită. Microscopic se identifică şi marcasită secundară, formată pe seama piritei, indicînd instaurarea în ultima fază a procesului de mineralizare a unor condiţii oxidante.

Tetraedritul, semnalat de Zepharovici (1859), identificat în cîteva secţiuni provenite din filoanele 50, 60 şi 141, alcătuieşte umplutura unor filonaşe ce străbat blenda şi calcopirita ultimelor generaţii din minereul plumbo-zincifer. Absenţa lui în cuprinsul minereului pirito-cuprifer indică un conţinut scăzut în Sb al soluţiilor generatoare, fapt confirmat şi de raritatea stibinei.

Mispichelul, identificat numai microscopic, apare răspîndit pe toată grosimea filoanelor.

Oligistul, cunoscut în filoanele din mina 11 Iunie, se identifică şi el pe toată grosimea acestora, imprimînd minereului local culoare roşcată ori cenuşie. Deseori este parţial muschetovitizat.

Pirargiritul se identifică sub formă de incluziuni în ultima generaţie de galenă din mina 11 Iunie. Este posibil ca tot spre sfîrşitul perioadei de mineralizare să se fi depus şi stefanitul semnalat de Cioflică (1956) în acelaşi grup filonian.

În cuprinsul filonului 143 din aceeaşi mină, minereul plumbo-zincifer este străbătut de filonaşe cu umplutură de telururi semnalate de Butucescu et al (1963). Macroscopic printre acestea se identifică altaitul sub formă de mase compacte de culoare albă, mai rar în cristale cubice fixate pe galenă ori pirită. Este acoperit sau cimentat de hessit anizotrop care-l corodează. Microscopic, în asocierea acestora se mai întîlnește petzit și sylvanit. Relațiile lor spațiale permit stabilirea succesiunii : altait → → hessit → petzit → sylvanit, indicînd o scădere treptată a conținutului de Pb și Ag, însoțită de o îmbogățire în Au și Tl.

Variata gamă a componentelor metalice este însoțită de un număr important de minerale de gangă, a căror cunoaștere întregește imaginea condițiilor de formare a zăcămîntului.

Cloritul, reprezentat prin pennin, este unul dintre principalele componente ale mineralizației pirito-cuprifere, fiind adesea prezent și în culcușul și coperișul celei plumbo-zincifere.

Adularul monoclinic se întîlnește în asocierea mineralelor din prima generație a minereului plumbo-zincifer și mai rar a celor din a doua generație. În cuprinsul celei pirito-cuprifere, el se întîlnește numai în asocierea blendei și galenei din centrul filoanelor, unde a fost depus probabil în timpul formării filoanelor plumbo-zincifere.

Cuarțul este mineralul de gangă cel mai răspîndit, cu cea mai lungă perioadă de cristalizare. În cele două tipuri de minereu care au putut fi mai bine studiate, se disting cîte trei generații de cuarț. Cel din prima generație a minereului pirito-cuprifer apare în asocierea piritei$_1$, calcopiritei$_1$ și cloritului, pe cînd în minereul plumbo-zincifer cu adularul monoclinic, blendei$_1$ și galenei$_1$. Obișnuit, mărimea granulelor sale nu depășește decît rareori 0,2 mm. Cel din a doua generație, alcătuiește împreună cu sulfurile corespunzătoare umplutura porțiunilor mediane ale filoanelor, prezentîndu-se sub formă de mase compacte cu o granulație ce oscilează între 0,3—1 mm. Cuarțul din ultima generație, alcătuind umplutura părților centrale ale filoanelor, este asociat în cadrul mineralizației pirito-cuprifere cu illit, pirită și calcopirită, respectiv cu caolinit, dolomit și calcit în cuprinsul celei plumbo-zincifere. Dimensiunile granulelor sale ating 10—12 cm. Este posibil ca această dezvoltare să fi fost determinată și de prezența anumitor microelemente.

Microscopic, pe lîngă cuarțul granular omogen, se recunoaște și o varietate fibroasă, mai frecventă la cuarțul$_2$, între aceste două varietăți existînd și termeni de tranziție cu extincție ondulatorie. Se întîlnesc și cazuri de supracreștere, varietatea fibroasă acoperind cristalele omogene, adesea idiomorfe, cît și depuneri alternante ale acestora. Admițînd că varietatea fibroasă a rezultat din transformarea unor geluri de silice, reiese că în timpul procesului de formare a mineralizației au existat intervale de cristalizare normală cît și „momente" de depunere de geluri silicioase. Faptul că în cuprinsul filoanelor nu se întîlnește opal ci numai calcedonie ori cuarț fibros, arată că gelurile de silice au fost transformate pe parcurs.

Calcedonia se întîlnește rar în porțiunile mediane și centrale ale filoanelor plumbo-zincifere în asocierea mineralelor din ultimele două generații.

Illitul (fig. 1) este larg răspîndit în porțiunile mediane și mai ales centrale ale filoanelor pirito-cuprifere.

Mallarditul a fost identificat de D. Todor (I.P.G.G.) prin efectul endoterm de la 700 – 750°C în probele de illit provenite de pe filoanele Nepomuc (fig. 1), efect care dispare la spălarea probei.

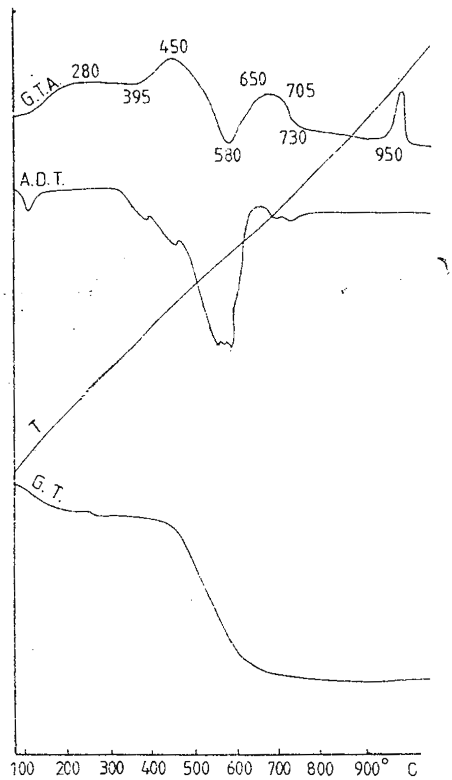

Fig. 1. Diagrama termică diferențială a unei probe de illit de pe filonul 172.
Diagramme thermique d'un échantillon d'illite du filon 172.

Fluorina, identificată microscopic în asocierea mineralelor din primele două generații ale minereului plumbo-zincifer, se prezintă sub formă de cristale submilimetrice izolate ori mici aglomerări în cuarț.

Sericitul este frecvent întîlnit în asocierea mineralelor din a doua generație a minereului plumbo-zincifer, asociat de regulă, cu cuarț fibros.

Montmorillonitul apare rar în minereul pirito-cuprifer, fiind mai frecvent în cuprinsul ultimelor depuneri ale minereului plumbo-zincifer. Este frecvent în piroclastitele de la contactul filoanelor. El acoperă sulfurile și fluorina, fiind acoperit de caolinit.

Baritina, semnalată de Cădere (1925) și Stoicovici (1950), se identifică în cuprinsul filoanelor din mina 9 Mai acoperind sulfurile principale din a doua generație, fiind acoperită de componentele celei de a treia generații. La cristalele bine dezvoltate se determină formele : (001), (110), (010), (100), (011), (101), (111) și (102).

Carbonații, reprezentați prin ***siderit***, ***dolomit*** și ***calcit*** se întîlnesc în porțiunile centrale ale filoanelor, în asocierea ultimelor depuneri din cea de a treia generație.

Vivianitul, întîlnit în filoanele plumbo-zincifere din mina 11 Iunie, se prezintă sub formă de cristale de 1—3 cm lungime, fixate pe sulfurile ce

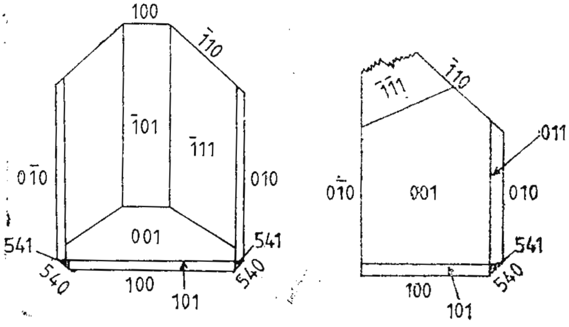

Fig. 2. Cristale de vivianit de pe filonul 141.
Cristaux de vivianite du filon 141.

tapițează pereții geodelor, fiind acoperit de caolinit. Măsurătorile goniometrice permit determinarea formelor : (100), (010), (001), și (111), bine dezvoltate, asociate cu (101), (540), (541), (121) și (221) mai slab dezvoltate. (fig. 2). În secțiuni mai groase este bine vizibil pleocroismul : γ = = albăstrui, α = incolor. 2V = 84°. Analiza termică diferențială și cea dilatometrică scot în evidență corelația dintre efectele exoterme, endoterme și dilatație.

Caolinitul, asociat local cu dickit, montmorillonit și beidelit, toate verificate termic diferențial, este bine reprezentat în cuprinsul filoanelor plumbo-zincifere și la contactul acestora.

Gipsul sub formă de cristale cu lungimi de 0,5—1 cm, are două proveniențe ; una hipogenă a cărui cristale tapițează pereții geodelor și alta supergenă a cărui cristale sînt fixate pe pereții galeriilor vechi. Se identifică prin spectrul său de absorbție în infraroșu cu valorile de : 3547, 3400, 2629, 1141, 1115, 661 și 601 ν (cm^{-1}) și prin liniile sale de difracție de la : 1,62 ; 1,78 ; 1,81 ; 1,87 ; 1,90 ; 1,99 ; 2,07 ; 2,21 ; 2,68 ; 2,78 ; 2,87 ; 3,06 ; 3,87 și 4,29 dn.

Pe lîngă mineralele prezentate, la nivelul orizonturilor superioare a mai fost semnalată prezența stibiului (Hauer et al 1855), argentitului și rodocrozitului (Ackner 1895), stefanitului, stibinei și proustitului (Zepharovici 1893).

Diagramele de cristalizare ale mineralelor componente din cele două tipuri de mineralizație studiate sînt prezentate în figurile 3 și 4.

Ca minerale supergene se identifică :

Covelina, semnalată de Stoicovici (1950), acoperă sub formă de pojghițe calcopirita din zona de oxidație, fiind asociată cu malachit și azurit.

Limonitul, întîlnit sub formă de stalactite și stalagmite pe galeriile vechi sau pseudomorfozează pirita din zona pălăriei de fier a cărei grosime depășește local 30 m. La nivelele superioare ale filoanelor plumbo-zincifere

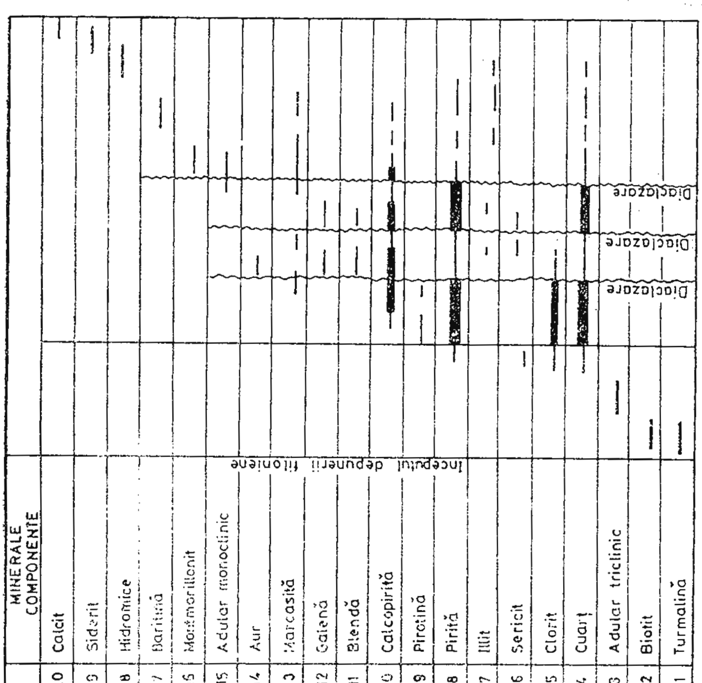

Fig. 3. Diagrama de cristalizare a mineralelor din cuprinsul mineralizației pirito-cuprifere.
Diagramme de cristallisation des minéraux compris dans la minéralisation pyrito-cuprifère.

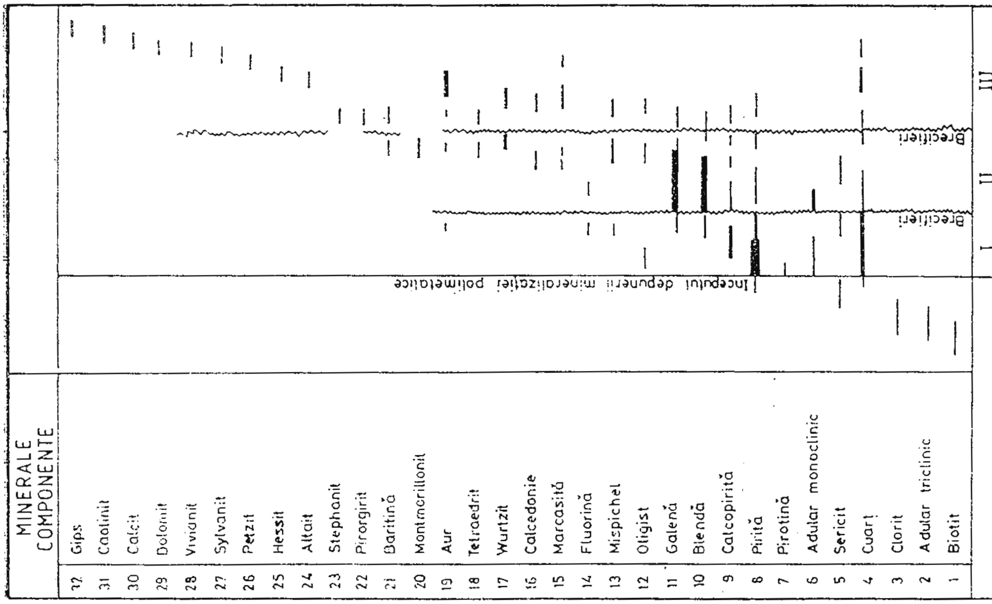

Fig. 4. Diagrama de cristalizare a mineralelor din cuprinsul mineralizației plumbo-zincifere.
Diagramme de cristallisation des minéraux compris dans la minéralisation plombo-zincifère.

el poate fi găsit și sub formă de depuneri alternante cu cuarțul$_3$, ceea ce arată că depunerea sa a început încă la sfîrșitul perioadei de mineralizare.

Goslaritul și *hexahidritul*, alb-lăptoase, verzui, brune ori albăstrui acoperă sub formă de cristale fibroase de 1—5 cm lungime, pereții galeriilor vechi. Microscopic, se determină două minerale; unul rombic cores-

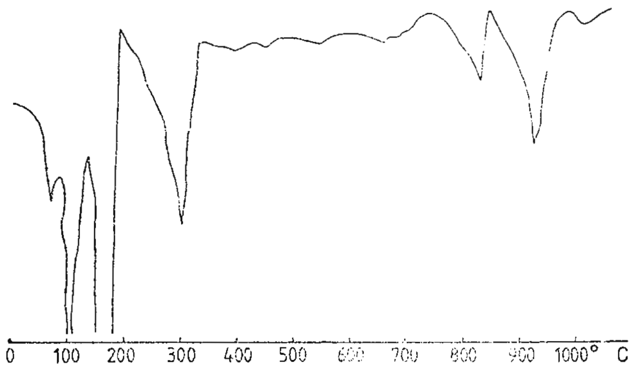

Fig. 5. Curbe termice diferențiale a asociației goslarit-hexahidrit de pe galeria direcțională a filonului 142, orizont superior.
Courbes thermiques différentielles de l'association goslarite-hexahydrite située dans la galérie le long du filon 142, horizon supérieur.

punzînd goslaritului și altul monoclinic cu c : $\alpha = 20°$; $\beta = 94°$; (100) : :(001) = 86°, maclat polisintetic, corespunzînd hexahidritului. Prezența acestor două minerale este confirmată și prin analiza termică diferențială (fig. 5).

Melanteritul, verzui-albastru, alcătuiește frecvent depuneri stalactitice și stalagmitice pe traseul galeriilor părăsite. Natura acestui mineral se verifică prin analiza termică diferențială, cu efecte endoterme la: 220°, 325°, 645°, 800° și 900°C, corespunzînd după A. Dinescu și T. Dene (I.P.B.) formulei: $Zn_{0,53}Fe_{0,34}Mn_{0,14}Cu_{0,03}SO_4 \cdot 7H_2O$.

Acest mineral este un termen intermediar din seria izomorfă goslarit-melanterit-mallardit-pisanit.

Pentru explicarea formării mineralelor supergene prezentate, au fost executate de către D. Țintilă și D. Dobrotă (I.P.G.G.) două analize chimice a două probe de apă de mină colectate de pe filonul Nepomuc (A) mina 11 Iunie și filonul 50 din mina 9 Mai (B), ambele provenind de pe orizonturile inferioare.

Se constată o strînsă legătură între natura mineralizației, chimismul apei de mină și natura mineralelor supergene. Conținutul ridicat în Cu și Zn al acestor ape (tabelul 2), pune problema valorificării lor.

Pentru explicarea mecanismului de solubilizare al elementelor chimice din zăcămînt, s-au efectuat la catedra de microbiologie a Universității din București analize ale apelor evacuate prin galeriile Cîmpurele și 9 Mai (tabelul 2), identificîndu-se *Thiobaccillus feroxidans* și o varietate de *Ferrobaccillus feroxidans*, care pe lîngă solubilizarea chimică contribuie la eliberarea elementelor chimice din mineralele primare.

TABELUL 2

	A	B
pH	6	7.5
Reziduu fix la 180 °C	648,0 g/kg apă	536,0 g/kg apă

Componente	Conținutul			
	g/l	milivali	g/l	milivali
Anioni				
Cl^-	7,1	0,2000	7,1	0,2000
SO_4^{--}	376,8	7,8146	200,7	4,5948
HCO_3^-	134,2	2,2000	231,8	3,8000
Cationi				
Na^+	3,0	0,1459	8,9	0,3899
K^+	7,5	0,1917	5,7	0,1458
NH_4^+	3,0	0,1662	abs	—
Ca^{++}	134,0	6,6000	132,2	6,6000
Mg^{++}	31,6	2,6000	15,5	1,2800
Fe^{++}	15,1	0,5408	5,0	0,1791
Al^{+++}	0,7	0,0258	0,2	0,0074
Cu^{++}	9,5	0,1492	2,3	0,0362
Pb^{++}	0,1	0,0004	1,6	0,0077
Zn^{++}	0,2	0,0031	6,5	0,1003
Duritatea în grade germane:		26		22

Date de geotermometrie

Continuînd cercetările paleogeotermometrice începute de Pomîrleanu et al (1961) și Borcoș (1964), efectuate asupra cristalelor de cuarț și blendă, în cadrul lucrării de față se aduc noi date geotermometrice, extinzîndu-se asupra calcitului, baritinei, galenei și vivianitului din mina 11 Iunie. Măsurătorile efectuate prin metoda omogenizării asupra mineralelor din umplutura filoniană și pereții filoanelor sînt prezentate în tabelul 3, iar cele prin metoda decrepitării în tabelul 4.

Se vede că temperaturile de cristalizare ale mineralelor din cuprinsul mineralizației pirito-cuprifere, cu excepția calcitului, au cristalizat între 260° și 360°C, cele ale componentelor mineralizației plumbo-zincifere între 240° și 330°C, iar a celei auro-argentifere între 219° și 280°C; potențialul energetic scăzînd în ansamblu paralel cu evoluția procesului de depunere a mineralizației. Este demn de remarcat faptul că baritina, calcitul și vivianitul au cristalizat la nivelul de temperatură al mineralizației auro-argentifere. Aceeași scădere se urmărește și la fiecare tip de mineralizație de la prima la ultima generație; în cuprinsul mineralizației pirito-cuprifere temperatura scăzînd de la prima la a doua generație în medie cu 20°C, iar de la a doua la a treia generație în medie cu 25°C; în timp ce în cuprinsul celei plumbo-zincifere aceasta scade în medie de la prima la a doua generație cu 27°C, pe cînd de la a doua la a treia în medie cu 31°C. Este evident că cele două tipuri de mineralizație s-au format în condiții

TABELUL 3

Temperaturile de cristalizare ale mineralelor, determinate prin metoda omogenizării

Proveniența probelor (filonul)	Mineralul analizat, parageneza	Nr. de determinări	Temperatura °C		
			Media	Minima	Maxima
1	2	3	4	5	6
Mina 11 Iunie A. *Mineralizația pirito-cupriferă*					
171—172 culcuș-coperiș	Cuarț$_1$, P$_1$, C$_1$, Cl	49	319	269	352
171, zona mediană	Cuarț$_2$, P$_2$	24	302	285	330
171—172 centru	Cuarț$_3$	23	267	254	298
Media ponderată orizont superior		96	300	266	336
171—172 culcus-coperiș	Cuarț$_1$, P$_1$- C$_1$, Cl	67	323	302	357
171—172 zona mediană	Cuarț$_2$, P$_2$, Cl	24	304	284	325
172 centru	calcit, P$_3$	5	182	160	206
Media ponderată orizont zero		131	303	285	332
171—172 culcuș-coperiș	Cuarț$_1$, P$_1$, C$_1$, Cl	57	343	317	>360
171 zona mediană	Cuarț$_2$, P$_2$, C$_2$	21	320	296	340
171—172 Centru	Cuarț$_3$	42	308	285	339
171 centru	Baritină, P$_3$	19	236	193	303
172 centru	Calcit, P$_3$	12	186	180	196
Media ponderată orizont intermediar		151	304	280	303
171—172 culcuș-coperiș	Cuarț$_1$, P$_1$, C$_1$, Cl	66	353	313	>360
171—172 zona mediană	Cuarț$_2$, P$_2$, C$_2$	53	331	304	356
171—172 centru	Cuarț$_3$	126	298	281	323
Media ponderată orizont inferior		245	319	294	348

Continuare tabelul nr. 3

1	2	3	4	5	6
		B. *Mineralizaţia plumbo-zinciferă*			
141, 143 culcuş-coperiş	Cuarţ$_1$, P_1, B_1, G_1 Ad	95	289	271	312
141, 143 zona mediană	Cuarţ$_2$, P_2, B_2, G_2, Sr	55	275	258	297
141, 143 centru	Cuarţ$_3$, Cd	47	241	228	266
Media ponderată orizont superior		197	272	257	298
141, 143 culcuş-coperiş	Cuarţ$_1$, P_1, B_1, Ad	80	310	291	335
141, 143 zona mediană	Cuarţ$_2$P, B_2, G_2	92	278	259	308
141, 143 centru	Cuarţ$_3$, P_3, B_3, Ca	111	262	238	276
Media ponderată orizont zero		283	280	259	303
142 culcuş-coperiş	Cuarţ$_1$, P_1, C_1	45	314	284	338
142 zona mediană	Cuarţ$_2$, P_2, B_2	21	291	267	307
142 centru	Cuarţ$_3$	17	279	245	294
142 centru	Vivianit	10	215	258	285
Media ponderată orizont intermediar		93	291	262	314
142 culcuş-coperiş	Cuarţ$_1$, Cl, Ad	42	334	300	360
142 zona mediană	Cuarţ$_2$, B_2, G_2	53	312	296	348
142 centru	Cuarţ$_3$	38	297	283	315
Media ponderată orizont inferior		133	314	293	357
		C. *Mineralizaţia auro-argentiferă*			
Aflorіment Tarniţa	Cuarţ	93	219	198	246
Afloriment Carolina	Cuarţ, Ad	45	281	234	309
Halda Galbena	Cuarţ	61	244	214	276
Halda Mihai	Cuarţ	25	234	216	265
Halda Cîmpurile	Cuarţ, B, Sr	26	248	218	281
Halda Nepomuc	Cuarţ, P, Ad	35	247	205	297
Media ponderată mineralizaţie auriferă		285	241	211	268

Prescurtări : 1, 2, 3 generaţii de minerale ; P — pirită ; C — calcopirită ; B — blendă ; G — galenă ; Cl — clorit ; Sr — sericit ; Ad — adular ; Ca — calcit ; Cd — calcedonie.

TABELUL 4

Temperaturile de cristalizare determinate prin metoda decrepitării

Proveniența probei, filonul, orizontul	Mineralul analizat, parageneza	Temperatura de decrepitare în grade C			Temperatura de omogenizare în grade C		
		Începutul	Primul maxim	Al doilea maxim	Media	Minima	Maxima
142 inferior	Calcit, P_3,*	162	234	265	—	—	—
170 inferior	Baritină*	161	237	264	236	193	303
60 intermediar	Baritină *	122	160	233	260	217	304
50 intermediar	Calcit *	156	230	264	253	218	291
140 inferior	Vivianit, P_3 **	170	210	250	204	165	252
142 inferior	Vivianit P_3 **	190	215	255	234	210	265

*) Determinările efectuate de V. Pomîrleanu și D. Filipescu, **) Determinările efectuate de V. Manilici, P_3 — pirită din generația a treia.

termice diferite. Asemenea estimări nu se pot face pentru mineralizația auro-argentiferă, exploatată în trecut.

În cadrul generațiilor, respectiv al pulsațiilor se constată că întotdeauna temperatura la care începe cristalizarea unei anumite generații, separată de cea precedentă prin diaclazări ori fisurări ale umpluturii filoniene, este mai ridicată decît temperatura la care se termină cristalizarea generației ori pulsației precedente. Această situație se corelează bine cu textura rubanată, respectiv cea brecioasă a filoanelor, indicînd caracterul pulsatoriu al procesului de mineralizare. Se semnalează însă și cazuri izolate de creștere a temperaturii de cristalizare la nivelul ultimei generații față de a doua sau chiar prima generație. Astfel, pe filoanele 140 și 142 la nivelul orizonturilor intermediare, s-au întîlnit cristale de cuarț, formate în jurul temperaturii de 285°C, cele din a doua generație la 270°C, pentru ca la cuarțul$_3$ să se determine o temperatură medie de 301°C. Local, o asemenea creștere se urmărește și la nivelul unor cristale izolate de cuarț (fig. 6), temperatura medie crescînd de la centru (273°) spre zona mediană (294°C) pentru a atinge la periferie o medie de 322°C. Incontestabil că paralel cu ridicarea temperaturii soluției, pentru continuarea creșterii unor asemenea cristale era necesară o creștere corespunzătoare a concentrației de SiO_2. Admițînd după Dekeyser et al (din Millot et. al. 1959) că soluțiile hidrotermale conțin 7—140 p.p. m. SiO_2 și că după Sunagawa

(1957) concentrația de silice scade de la prima spre ultima generație, apariția unor asemenea cristale la care se constată o creștere a temperaturii de la centru spre periferie, ne obligă să admitem și unele fluctuații ale concentrației de SiO_2. Avînd în vedere caracterul pulsatoriu al procesului de mineralizare, evidențiat atît prin textura filoanelor cît și măsurătorile geotermometrice, asemenea fluctuații apar posibile. După toate probabilitățile, cristalul în cauză s-a format pe seama unei pulsații noi venite din adîncime.

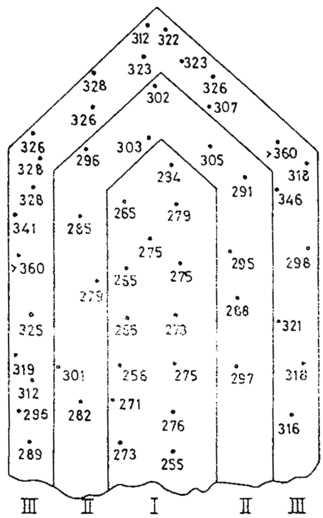

Fig. 6. Cristal de cuarț din partea centrală a filonului 142, cu distribuție zonară a temperaturilor de cristalizare, zona I temperatura medie 273° C, zona II 294° C, iar zona III 322° C. Cristal de quartz de la partie centrale du filon 142, à distribution zonale des températures de cristallisation, zone I température moyenne de 273° C, zone II 294 C et la zone III 322 C.

Urmărirea variației temperaturilor de cristalizare pe verticală, arată că în mina 11 Iunie, în cadrul mineralizației plumbo-zincifere pe o diferență de nivel de 235 metri se înregistrează o creștere de temperatură de 39°C, pe cînd în cazul celei pirito-cuprifere pe o diferență de 150 metri o creștere de temperatură de 41°C. Rezultă pentru mineralizația plumbo-zinciferă o creștere de 16,6°C la 100 m adîncime, iar pentru cea pirito-cupriferă 27,3°C la 100 m adîncime. Treptele geotermice corespunzătoare sînt de 6,00 m/1°C în cazul mineralizației plumbo-zincifere și de 3,65m/1°C al celei pirito-cuprifere. Luind în considerare temperaturile de cristalizare ale cuarțului din a treia generație a mineralizației plumbo-zincifere din aceeași mină, cu conținuturi valorificabile de aur, la o diferență de nivel de 235 m se înregistrează o creștere de temperatură de 33°C, ceea ce revine la o creștere de 14°C la 100 m, respectiv un gradient geotermic de 7, 12 m/1°C. Aceste elemente coroborate cu relațiile spațiale ale tipurilor de mineralizație prezentate, arată că depunerea lor s-a realizat în condiții fizice și chimice deosebite.

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DONNÉES SUR LA COMPOSITION MINÉRALOGIQUE ET LES TEMPÉRATURES DE CRISTALLISATION DU MINERAI DU GISEMENT DE BĂIŢA-NISTRU (DÉPARTEMENT DE MARAMUREŞ)

(Résumé)

Le gisement de Băiţa-Nistru, comme tous les autres gisements de la région de Baia Mare, présente un caractère minéralogique complexe. Il comporte approximativement 55 minéraux et variétés de ceux-ci, représentés par des éléments natifs, sulfures, tellures, halogénures, oxydes, sulfates, phosphates, carbonates et silicates. L'observation de leur distribution dans les filons permet la détermination de l'évolution du chimisme des solutions hydrothermales pendant la minéralisation ; les particulari-

tés cristallographiques et microscopiques des minéraux y compris indiquent les conditions physiques et chimiques qui ont déterminé la formation du gisement.

La pyrite et le quartz sont les plus répandus de tous les minéraux du gisement et les plus importants, en même temps, pour la détermination des conditions de métallogenèse. De toutes les 11 formes cristallographiques de la pyrite, les faces 100 et 210 ont la fréquence la plus élevée. Selon on observe dans le tableau 1, dans le nid et le toit des filons prédomine la forme cubique, dans les zones médianes du remplissage des filons prédomine l'association de la face cube avec le dodécaèdre pentagonal et dans les parties centrales des filons les faces en dodécaèdre pentagonal. Selon Sunagawa (1957), au début du processus de minéralisation, le dépôt des minéraux s'est formé pendant un régime de refroidissement rapide, une alimentation insuffisante en solutions hydrothermales et grandes variations de température et concentration; au contraire, vers le final, le refroidissement devient plus lente, sans des variations de température et concentration trop grandes, enregistrant une alimentation suffisante . La même évolution est enregistrée pendant le développement des cristaux de pyrite; à ceux de 0,03 —0,07 mm on observe exclussivement des faces en cube, à ceux de 0,12 à 0,25 mm l'association de cube avec dodécaèdre pentagonal et à ceux de plus d'un millimètre prédomine la face en dodécaèdre pentagonal associée à celle en octaèdre.

Pour la blende, la galène et le quartz on observe le même développement des dimensions des grains, partant des parois des filons vers le centre, déterminé par la même évolution du régime de refroidissement des solutions hydrothermales. La même conclusion dérive de la variation des dimensions des inclusions de chalcopyrite des cristaux de blende, qui, dans le nid et le toit des filons ont un rayon d'approximativement 1 mμ pendant que dans le centre des filons arrive jusqu'à 40 —50 mμ. Exceptant les inclusions de chalcopyrite de la blende, issues du processus d'exsolution du genre de ceux présentées, on doit considérer aussi les inclusions de chalcopyrite de la masse de la blende située au contact de celle-ci avec la chalcopyrite massive. Des auréoles de telles inclusions sont observées aussi dans la blende dépourvue d'inclusions à l'intérieur, étant le résultat d'un processus de diffusion. Selon Filimonova (1964) la présence de ces auréoles indique le maintien de l'agrégat minéral pendant un laps de temps plus long à une température élevée, probablement près de celle de la formation de la minéralisation.

Quant au quartz, exceptant une variété homogène résultée de la cristallisation de certains solutions à caractère électrolytique on observe aussi une autre variété fibreuse à extinction ondulatoire, issue de la cristallisation de quelques gels siliceux. Ce fait indique que pendant la formation du gisement ont existé aussi des périodes de sédimentation de certains gels siliceux. Tels gels sont observés dans les sulfures aussi.

La succession des minéraux dans la minéralisation pyrito-cuprifère est représentée dans la fig. 3 et celle plombo-zincifère dans la fig. 4.

Dans les galeries anciennes on a identifié comme minéraux supergens : covelline, goslarite, hexahydrite (fig. 5) et mélantérite, leur apparition étant expliquée par le chimisme des eaux de mine (tableau 2).

On a effectué des déterminations de température par la méthode de l'homogénéisation et de la décrépitation sur le quartz, la calcite, la barytine, la galène et la vivianite. Les résultats sont présentés dans les tableaux 3 et 4.

On observe que la minéralisation pyrito-cuprifère s'est formée entre 260 et 360°C, celle plombo-zincifère entre 240 et 330°C et celle auro-argentifère entre 190 et 280°C ; le potentiel énergétique diminue en rapport avec l'évolution du processus de minéralisation de la première à la dernière génération. La température à laquelle commence la cristallisation d'une génération est toujours supérieure à la température à laquelle termine la cristallisation de la génération antérieure. On a enregistré aussi des cas d'élévation de la température au niveau de la dernière génération : le $quartz_1$ cristallise à 285°C, le $quartz_2$ à 270°C et le $quartz_3$ à 301°C. La même élévation de la température est enregistrée aussi au niveau de quelques cristaux isolés (fig. 6), la température augmentant du centre, à une moyenne de 273°C, vers la zone médiane à une moyenne de 294°C, pour arriver, vers les bords, à une moyenne de 322°C.

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2. ZĂCĂMINTE

ELEMENTE STRUCTURALE ŞI MINERALIZAŢII ÎN FĂGĂRAŞUL DE EST[1]

DE

LIVIU NEDELCU[2], GHEORGHE ILINCA[2]

Structural controls. Laramid orogenesis. Overthrust. Tension fracture. Austrian tectogenesis. Tectonic controls. Epigenetic processes. Spatial distribution. South Carpathians Getic and Supragetic crystaline domains — Făgăraş Mountains; Getic and Supragetic sedimentary domains — Bîrsa Fierului Zone — Şinca

Abstract

Structural elements and mineralizations in East Făgăraş. Spatial distribution of polymetallic mineralizations in Eastern Făgăraş reveals a direct correlation with that of Austrian and Laramian (?) structural elements in the region. Analysis of ore deformations, which have occurred during these tectogeneses, shows that they have been produced under a compressive regime; thus, the ore features evolved up to the level of tectonite. Structural control of mineralizations is pointed out by their spatial coincidence with the main tectonic lines (overthrust plane faults) and by a stronger dismembering of ore bodies eastwards and westwards, together with an increased frequency of tectonic elements. Therefore, as a result of deformations, subsequent reorganizations allow neither the constitution of ore deposition sequence in the classical sense, nor any signs of ore zoning.

Résumé

Eléments structuraux et des minéralisations des monts Făgăraş de l'est. La distribution spatiale des minéralisations polymétalliques des monts Făgăraş de l'est indique une corrélation directe avec la distribution des éléments structuraux autrichiens et laramiens (?) de la région.

L'analyse des déformations subies par les minéralisations, pendant les tectogenèses autrichienne et laramienne (?), indique que les deux ont actionné dans un régime compressif; les

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déformations évoluent jusqu'au niveau de tectonite. Le contrôle structural des minéralisations se manifeste tant dans la coïncidance spatiale de celle-ci avec les principales lignes tectoniques (plans de charriage, failles), que dans le développement de la dispersion des corps de minerai, de l'ouest vers l'est, parallèlement à l'augmentation de la densité des éléments tectoniques. Par conséquent, les réorganisations subséquentes, comme effet des déformations, ne permettent pas la réconstitution de la succession de dépôt dans le sens classique ni la réconstitution de la zonalité des minéralisations.

Lucrarea își propune, pe baza unui cadru structural în mare măsură cunoscut (Săndulescu, 1976, 1980; Nedelcu, Anton, 1984; Nedelcu et al în Vâjdea, Udubașa et al., 1984; Balintoni et al., 1986), să încerce o reconstituire a istoriei proceselor de deformare și implicit și a elementelor structurale care controlează localizarea mineralizațiilor din Făgărașul de est.

Principalele unități structurale ale Făgărașului de est (Nedelcu, Anton, 1984; Nedelcu în Vâjdea, Udubașa et al, 1984), a căror continuitate a fost recunoscută și în restul masivului (Balintoni et al, 1986), aparțin, după Săndulescu (1976, 1980), pînzei supragetice. Succesiunea acestor unități de jos în sus și respectiv de la sud spre nord, se prezintă astfel (Planșa): pînza de Argeș, pînza de Moldoveanu, unitatea de Bîrsa Fierului, pînza de Strîmba.

Imaginea repartiției regionale a mineralizațiilor polimetalice din Munții Făgăraș de est (Nedelcu și Balaban în Udubașa et al, 1985), în relație cu elementele structurale recunoscute, evidențiază cîteva aspecte particulare ale acesteia (Planșa):

— mineralizațiile se concentrează în două unități tectonice: în pînza de Moldoveanu (circa 60 %) și în pînza de Argeș (aproximativ 40 %);

— distribuția lor este controlată de factori structurali (structura în pînze de șariaj, sistemele de falii). Astfel, ele sînt localizate fie de-a lungul unor falii direcționale majore, mineralizațiile de la pîrîul Gherdana-pîrîul Dracului, Platin, situate în zona faliei văii Holbavului, mineralizațiile de la pîrîul Ciorogarului de-a lungul faliei Morișoara, fie în vecinătatea unui plan de șariaj: corpurile de minereu de pe valea Morișoara, valea Mesteacăn, valea Răchitei, valea Șutilei, pîrîul Orzului, pîrîul Cabanei și probabil Nimaia, aflate sub incidența planului de șariaj al pînzei de Moldoveanu. De asemenea, mineralizații au mai fost întîlnite pe traseul unor falii transversale: ivirile de pe valea Vulcănița, valea Cetățelei, valea Bîrnei;

— frecvența dimensională a mineralizațiilor variază și ea de la vest la est astfel: pentru zona Nimaia-Morișoara frecvența cea mai mare o au mineralizațiile a căror lungime însumată a corpurilor de minereu este cuprinsă între 10 m și 300 m, pe cînd pentru zona Ruda-Holbav maximul de frecvență (80 %) este dat de ivirile a căror lungime este sub 10 m. Această descreștere dimensională a mineralizațiilor de la vest spre est se corelează însă cu o creștere a frecvenței elementelor structurale (falii, plane de șariaj) fapt care explică astfel și dispersarea mare a corpurilor de minereu spre est;

— distribuția regională a mineralizațiilor nu reflectă un control litologic evident al acestora, ele putînd fi întîlnite în formațiuni cristaline cu litologii diferite (micașisturi, paragnaise, gnaise albe, amfibolite, gnaise migmatice ale grupurilor Făgăraș și Cumpăna).

În consecință, se remarcă faptul că numai anumite elemente structurale au jucat un rol de factor de control al mineralizațiilor. Evidențierea lor s-a făcut pe harta distribuției mineralizațiilor din Făgărașul de est (Nedelcu, Balaban în Udubașa et al, 1985). Pentru control am făcut apel la elementele furnizate de galeriile și de forajele din regiune, precum și la datele prospecțiunilor geochimice și geofizice recente.

Imaginea rezultată relevă aspecte semnificative ale distribuției spațiale a elementelor structurale care controlează localizarea mineralizațiilor, precum și unele indicații referitoare la istoria evenimentelor deformaționale care au avut loc în acest teritoriu. Din analiza structurală regională rezultă că elementele susceptibile de a da un răspuns sînt sistemele de cute, de falii și planele de șariaj. Astfel, au fost recunoscute două sisteme de cute și falii care definesc, prin caracterul particular al deformărilor, două stadii distincte.

A. *Primul stadiu/sistem* este legat de compresiunile austrice care au generat șariajele, cutele și faliile longitudinale. În acest caz, dacă se are în vedere faptul că scurtarea structurii s-a produs pe direcție NV-SE, corespunzătoare axei C a elipsoidului de deformare, se poate presupune că vectorii forțelor de compresiune austrice au avut aceeași direcție (planșa). Apartenența elementelor rupturale la acest sistem este dovedită și de evidentul lor paralelism cu axele cutelor și orientarea generală a planelor de șariaj. În cadrul sistemului au fost recunoscute șapte linii tectonice importante care controlează localizarea principalelor mineralizații din regiune :

Falia I (Nimaia) cu poziția cea mai nordică, orientată aproximativ E-V, cuprinde corpurile de minereu cercetate în lucrările miniere vechi, precum și indicii de mineralizare din galeria I — pîrîul Spirtului. Întrucît această falie este întreruptă spre est de falia transversală de pe pîrîul Cenușa, corelarea ei cu falia Morișoara, care controlează o mineralizație preponderent piritoasă, poate fi făcută doar pe criteriul poziției spațiale.

Falia II este marcată de ivirile și indicii de mineralizare de pe pîraiele Hîrsan, Bolovanului, Scradei și valea Ruda Mică. Toate aceste iviri sînt caracterizate de predominanța mineralelor de gangă (cuarț, carbonați) față de cele metalice. Traseul său este de asemenea jalonat de anomalii electrometrice și geochimice. Este posibil ca și mineralizațiile de carbonați cu sulfuri de pe pîrîul Fierului, exploatate pentru fier în secolul XV (Hauer și Stache, 1863), să se înscrie pe aceeași falie.

Falia III cuprinde corpurile de minereu din galeriile vechi de pe pîrîul Hîrsănel, ivirile de pe pîrîul Hîrsan, pîrîul Ursului, pîrîul Motoanu și mineralizațiile de la pîraiele Ciorogarului și Iuzii. Spre est, în bazinul văii Șinca, pe această fractură s-ar situa lentila de sulfuri din galeria 3 — pîrîul Sărat și probabil mineralizația de baritină și sulfuri de pe valea

Ruda Mică. Extinderea faliei pînă în valea Găunoasa ar putea fi sugerată de prezența, în malul stîng al acestei văi, a unei iviri de carbonați de fier într-o zonă de tectonizare. Totodată, tronsonul vestic al faliei este evidențiat de anomalii de polarizație indusă și de anomalii geochimice.

Falia IV se poate urmări de la pîrîul Cabanei (corpurile de minereu de la suprafață și indicațiile de la nivelul galeriei 3), prin valea Rușească (carbonați și cuarț în frontul galeriei 4), pîrîul Crăiesei (carbonați în descoperta 3), pînă la izvoarele pîrîului Șutila (corpul de sulfuri de Pb și Zn din descoperta 2). Corelarea acestei falii cu mineralizația din galeriile de pe valea Mesteacăn este mai mult ipotetică, ea rezultînd doar din poziția spațială similară.

Falia V ar corespunde următoarelor indicații de mineralizare : ivirile de carbonați de fier cu sulfuri (galenă, pirită) de pe pîrîul Șipot ; lentilele de minereu de la nivelul galeriei I (veche) și galeriei 4 valea Rușească ; corpul de cuarț, carbonați și baritină din descoperta 1 — pîrîul Crăiesei ; corpul de carbonați și cuarț cu blendă și galenă din descoperta 3 — pîrîul Șutila. Spre est traseul său a fost marcat ipotetic pe baza lentilelor de sulfuri (galenă, pirită) cu carbonați și cuarț din galeriile 1 și 2 — pîrîul Răchitei.

Falia VI este materializată de un set de trei lentile de minereu din galeria 4 — valea Rușească care s-ar putea eventual corela cu setul de trei lentile interceptate de laterala 350 stînga din galeria 2 — pîrîul Orzului. Echivalentul estic presupus al acestei falii ar putea fi fractura pe care se localizează mineralizațiile de la gura galeriilor 1 și 2 — pîrîul Răchitei, precum și corpul filonian de sulfuri (blendă, galenă) din pîrîul Cărbunari.

Falia VII a putut fi evidențiată doar în partea estică a regiunii, începînd de la valea Mărului pînă în valea Holbavului. Falia este marcată în principal de mineralizațiile de galenă argentiferă de pe pîrîul lui Frenz, pîrîul Gherdana și pîrîul Dracului, exploatate în secolul trecut (Giușcă, 1942).

B. *Al doilea stadiu/sistem* este caracterizat de deformări compresive subsecvente celor austrice, posibil laramice, după cum rezultă din relațiile sale cu primul stadiu. Din poziția axelor cutelor majore și a faliilor de încălecare cu vergență estică, rezultă că scurtarea structurii s-a produs pe direcția NE-SV. Acest fapt conduce la ideea că elipsoidul de deformare a avut axa C orientată pe direcția respectivă și deci că vectorii forțelor de compresiune laramice (?) ar fi avut aceeași direcție. Deși intensitatea deformărilor din acest stadiu a fost mai mică decît în primul, manifestarea lor pe direcții transversale față de cele austrice a condus la o complicare a imaginii structurale regionale.

Deformările s-au manifestat prin cutări transversale însoțite de forfecări care, în situațiile extreme, au condus la încălecări. Astfel, se constată o recutare a planelor de șariaj austrice pe direcția NV-SE generînd o serie de structuri anticlinale și sinclinale (Planșa) :

1) anticlinalul Valea Mare — Bîrsa lui Bucur ; de formarea sa este legată cutarea planului de șariaj al pînzei de Moldoveanu și a minera-

lizaţiilor de la pîrîul Cabanei. De asemenea au fost generate şi faliile de forfecare ale căror efecte asupra mineralizaţiilor de la Nimaia şi pîrîul Cabanei sînt deja cunoscute;

2) anticlinalul Strîmba — Bîrsa Fierului este evidenţiat de o puternică ondulare a planului de şariaj al pînzei de Moldoveanu. Intersecţia acestui anticlinal cu una din structurile anticlinale longitudinale a condus la formarea domului structural din zona vf. Ciuma, care scoate în fereastră gnaisele de Glimeea;

3) anticlinalul Strîmbişoara — valea Mărului; intersecţia acestuia cu anticlinalul Morişoara a determinat ridicarea în fereastră tectonică a gnaiselor de Cumpăna;

4) sinclinalul Ciuta-Găunoasa este definit de puternica modificare a direcţiei formaţiunilor, de la poziţia NE-SV la NV-SE. Intersecţia sa în partea nordică cu o structură sinclinală din sistemul longitudinal este marcată de peticul de acoperire din dealul Ţilfa, unde apar resturi ale unităţii de Bîrsa Fierului şi ale pînzei de Strîmba.

De asemenea, considerăm că poziţia lentilelor de sulfuri din galeria Ruda Mică, precum şi cea a corpului de pirită de pe valea Găunoşiţa este determinată, ca şi în cazul celor de la Nimaia (galeria X) şi pîrîul Scurt, de transpunerea şi concentrarea tectonică pe faliile de forfecare conjugate din sistemul transversal.

Pe măsură ce avansăm spre est, începînd de la confluenţa valea Găunoasa — valea Holbav, se constată o accentuare a dinamicii deformărilor din acest stadiu care, depăşind limitele de forfecare trec la încălecări cu vergenţe nord-estice. Aceste încălecări cu orientare NV-SE, sînt paralele cu fruntea „liniei Holbavului", considerată laramică de către Săndulescu et al (1972), şi prind sub planul lor depozite triasice inferioare şi medii şi depozite apţiene superioare. Faptul că încălecările respective intersectează liniile de contur ale planelor de şariaj austrice (i.e. planul de şariaj al unităţii de Bîrsa Fierului în zona Dealului Mare) vine, alături de celelalte observaţii, în sprijinul considerării lor drept laramice. Efectele lor asupra mineralizaţiilor este cel de transpunere şi dezmembrare avansată. Acesta este se pare, deci, motivul pentru care majoritatea mineralizaţiilor din extremitatea estică a regiunii prezintă o dispersie mare însoţită de scăderea dimensională a corpurilor de minereu.

Unele din faliile importante, care ar aparţine sistemului transversal, falia Dealul Mare şi falia Bîrsei (= falia Branului, Patrulius et al, 1967) par să fi fost active şi după tectogeneza laramică întrucît afectează depozite paleogene. După Săndulescu (în Vâjdea et al, 1984) aceste falii au putut funcţiona înainte de prima tectogeneză (mezocretacică), ele putînd fi însă mişcate şi recent (Pliocen?, Pleistocen?).

În concluzie, putem spune că suprapunerea mai multor stadii de deformare, generate de tectogenezele amintite, a avut un efect negativ asupra mineralizaţiilor filoniene preexistente dezvoltate pe fracturi de tensiune. Regimurile de compresiune, atît cel austric cît şi parţial cel laramic (?), au generat cutări, forfecări şi în final încălecări sau şariaje, al căror efect distructiv şi limitativ asupra mineralizaţiilor a fost evidenţiat aproape în majoritatea lucrărilor miniere executate pînă în prezent în regiune. În aceste condiții reorganizările subsecvente, ca efect al deformărilor, nu mai permit reconstituirea succesiunii de formare în sensul clasic și nici a zonalității mineralizațiilor. Realizarea însă a unor progrese în decelarea faliilor longitudinale de compresie, care au implicații importante în deformarea și perspectiva economică a mineralizațiilor din regiune, s-a dovedit ca și în cazul recunoașterii pe teren a planelor de șariaj, extrem de dificilă. Aceasta în primul rînd pentru că faliile au un caracter intraformațional, punînd în contact formațiuni cu litologii și grade de metamorfism similare. În al doilea rînd, datorită caracterului compresiv ele generează milonite și filonite, în general confundate cu metamorfitele pe care le afectează. În al treilea rînd, pentru că mai există încă tendința de a minimaliza importanța factorilor compresivi ca factori de control tectonic al mineralizațiilor.

În schimb, faliile de forfecare, transversale pe structură, sînt în general ușor de recunoscut tocmai datorită faptului că pun în contact formațiuni cu litologii diferite. Ele produc deformări reduse ale mineralizațiilor (pipe de falii, ferestre, fragmentări) iar uneori, la intersecții sub unghi mic, chiar o transpunere a acestora (i.e. terminația vestică a filonului Nimaia).

Ca o remarcă generală este faptul că faliile de tensiune și o parte din cele de forfecare transversale, post-tectogenetice în raport cu tectogenezele amintite, sînt sterile din punct de vedere al prezenței mineralizațiilor, chiar dacă spațial, uneori, li se asociază iviri sau corpuri de minereu cum sînt cele dispuse paralel cu faliile Morișoara, Holbavului, Vulcănița.

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STRUCTURAL ELEMENTS AND MINERALIZATIONS IN EAST FĂGĂRAŞ

(Summary)

The history of deformation events in the north-eastern part of the Făgăraş Mountains is closely connected with the structural evolution of this region as it was accomplished during two main tectonic cycles : Austrian and Laramian.

The Austrian paroxysmal tectogenesis worked in a field of compressive forces which generated the known overthrust sheets and the NE—SW shear-faults system. The effects upon the existing mineralizations — localized along tension fractures parallel to the overthrust lines — were mainly represented by breccias, boudins, transpositions and extreme, tectonitic type deformations.

The Laramian (?) tectogenesis acted in a compressive regime, too, but with the compression forces differently directed, as compared to the Austrian ones. This tectogenesis may be inferred to be responsible for the emplacement of some transverse faults and folds. Related deformations were less marked than the Austrian ones engendering few anticlinal and synclinal structures, directed NW—SE (Valea Mare—Bîrsa lui Bucur and Strîmba Mare—Bîrsa Fierului anticlines and Ciuta—Găunoasa syncline), which evolve eastwards to small overthrusts. The effects upon the mineralizations were therefore reduced, being materialized mainly by shear fracturing, transpositions under a small angle, fault bendings, tectonic windows.

The overimposing of the Laramian (?) foldings upon the Austrian ones led to the emplacement of some dome-shaped structures (i.e. the dome in the Ciuma peak area, with Glimeea gneisses in tectonic window).

The analysis of the spatial distribution of mineralizations in the north-eastern part of the Făgăraş Mountains reveals a direct correlation with that of Austrian and Laramian (?) structural elements. Thus, it follows that :

— the distribution of epigenetic mineralizations is mainly controled by the overthrust sheets and the fault systems ;

— the actual control exerted by the overthrust sheets upon the mineralizations was effected by important deformation of the ore bodies and by the limitation of their extent (i.e. Pîrîul Orzului, Nimaia) ;

— the main epigenetic mineralizations are confined along older longitudinal tension fractures ; their taking over in a compressive regime during the Austrian tectogenesis explains their spatial coincidence with the tectonic lines and, as well, their deformations and dismembering along the compression faults ;

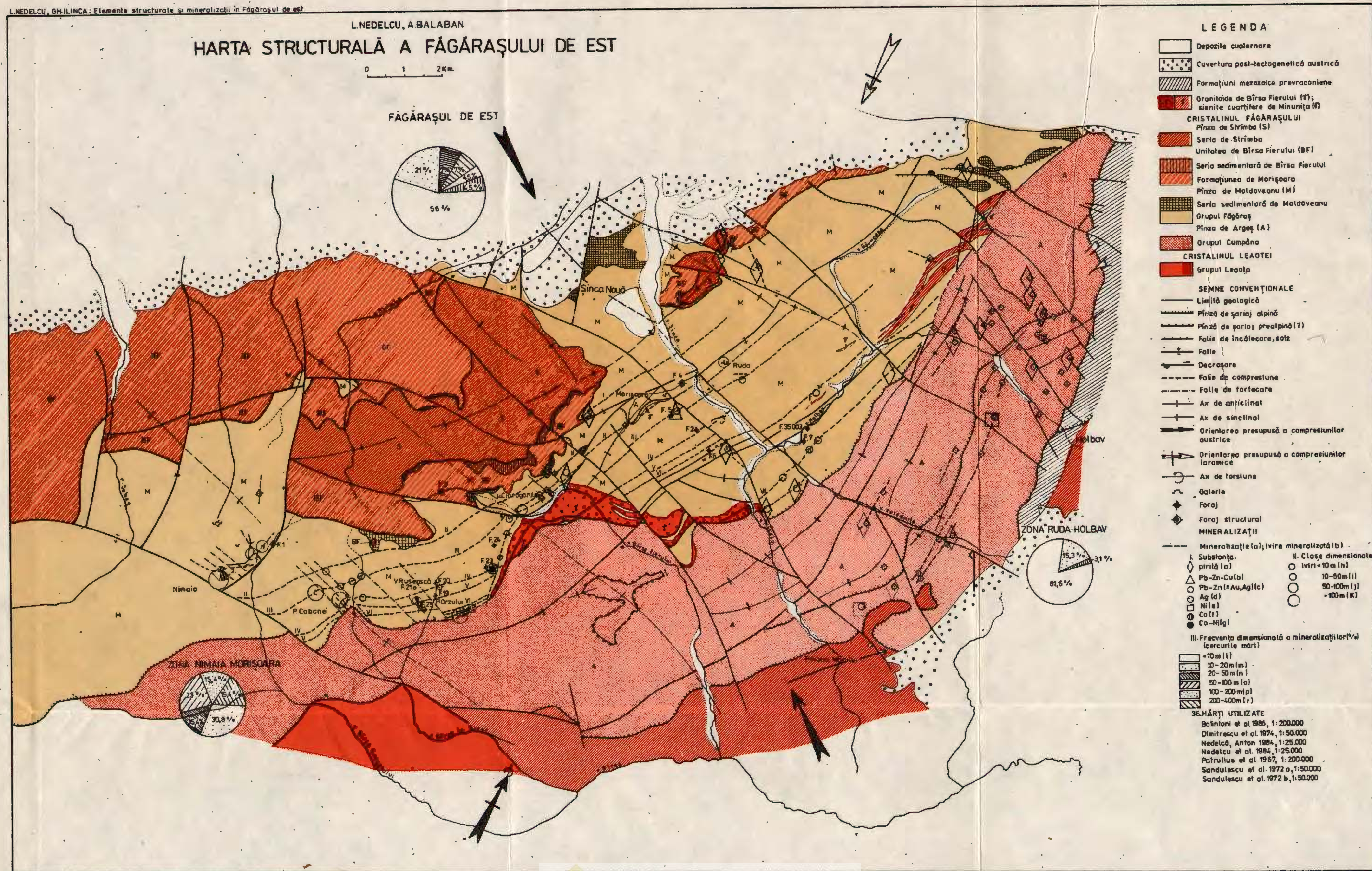
— the eastward dimensional decrease of the mineralizations correlates with an increased frequency of tectonic elements as well as with a more prominent dismembering of ore bodies ;

— the distribution of mineralizations does not reveal any obvious lithological control; therefore the ores are to be found in crystalline formations with different lithology, belonging to the Făgăraş Group (60%) and Cumpăna Group (40%);

— subsequent reorganizations of ore bodies, as a result of deformations allow neither the reconstitution of ore deposition sequence in the classical sense, nor the ascertainment of any ore zoning.

EXPLANATION OF PLATE

Structural map of East Făgăraş. 1, Quaternary deposits; 2, Austrian post-tectogenetic cover; 3, Pre-Vraconian Mesozoic formations; 4, Bîrsa Fierului granitoids; Minuniţa quartziferous syenites; 5, Făgăraş Crystalline; 6, Strîmba Nappe (S); 7, Strîmba Series; 8, Bîrsa Fierului Unit (BF); 9, Bîrsa Fierului sedimentary Series; 10, Morişoara Formation; 11, Moldoveanu Nappe (M); 12, Moldoveanu sedimentary Series; 13, Făgăraş Group; 14, Argeş Nappe (A); 15, Cumpăna Group; 16, Leaota Crystalline; 17, Leaota Group; 18, Conventional symbols; 19, Geological limit; 20, Alpine overthrust nappe; 21, Pre-Alpine overthrust nappe; 22, Overthrust fault, scale; 23, Fault; 24, Slip; 25, Compression fault; 26, Shearing fault; 27, Anticlinal axis; 28, Synclinal axis; 29, Supposed orientation of Austrian compressions; 30, Supposed orientation of Laramian compressions; 31, Torsion axis; 32, Gallery; 33, Drilling; 34, Structural drilling; 35, Mineralizations: I Substance: pyrite (a); Pb—Zn—Cu (b); Pb—Zn—(±, Ag) (c); Ag (d); Ni (e); Co (f); Co—Ni (g); II Dimensional classes: occurrences < 10 m (h); 10—50 m (i); 50—100 m (j); > 100 m (k); III Dimensional frequency of mineralizations (%) (big circles): < 10 m (l); 10—20 m (m); 20—50 m (n); 50—100 m (o); 100—200 m (p); 200—400 m (r).



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2. ZĂCĂMINTE

CONSTITUTION AND GENESIS OF THE LOWER JURASSIC FIRECLAY FORMATION OF THE PĂDUREA CRAIULUI MASSIF[1]

BY

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Lower Jurassic. Fireclay Formation. Detrital Rocks. Ferruginous Siltstones. Genesis. Ore minerals. Chemical-mineralogical composition. Heavy minerals. Lenticular deposits. Apuseni Mountains-North Apuseni — Pădurea Craiului Mountains

Abstract

The fireclays of the Pădurea Craiului Massif (Apuseni Mts — Romania) make up lenticular bodies within the Liassic deposits (Hettangian — Sinemurian) in Gresten facies. These rocks are associated with arenites and, sometimes, with orthoquartzitic microconglomerates and with coal. The clays are prevailingly made up of kaolinite with subordinate mixtures of hydromicas, Fe- and Mg-rich chlorites and detrital quartz and, especially in the case of non-refractory clays, with few percents of hematite, ferrous monosulphide, organic matter, goethite, siderite, dickite, smectite, gibbsite. It is admitted that the fireclays were formed in palustrine up to lacustrine environments, engendered at the surface of the Rhaeto-Liassic paleokarst developed on the marmorean limestones and the massive Ladinian dolomites. During the long lasting continental phase at the end of the Triassic, an advanced weathering of lateritic type (siderolitic facies) took place, leading to the formation of great quantities of kaolinite. This one was accumulated afterwards, possibly also with hydromicas, in lakes and heterotrophic marshes with very acid pH. Under such conditions, the hydromicas and the smectites were degraded, forming kaolinite which possibly evolved up to refractory kaolinite. The degradation of clay minerals also released important amounts of silica which cemented afterwards the detrital quartzose arenites, engendering orthoquartzitic rocks associated with fireclays.

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Résumé

Composition et genèse de la formation des argiles réfractaires jurassiques inférieures du massif de Pădurea Craiului. Les argiles réfractaires du massif de Pădurea Craiului (Monts Apuseni — Roumanie) forment des corps lenticulaires dans la formation liasique (Hettangien — Sinémurien) en faciès de Gresten. Ces roches sont associées à des arénites, parfois à des microconglomérats orthoquartzitiques et des intercalations de charbon. Les roches argileuses sont prépondéremment constituées de kaolinite associée à des quantités subordonnées de hydromicas, chlorites ferrifères et magnésiennes et de quartz détritique et, surtout les non-réfractaires, à pourcentages réduits de hématite, monosulfure ferreuse, substance organique, goéthite, sidérite, dickite, smectite, gibbsite. Quant à la genèse, on admet que les argiles réfractaires sont formées dans des environnements palustres jusqu'à lacustres, installés à la surface du paléokarst rhéto-liasique développé au dessus des calcaires marmoréens et des dolomies massives ladiniennes. Pendant la longue phase continentale de la fin du Trias a eu lieu une altération avancée de type latéritique (faciès sidérolitique) qui a engendré une grande quantité de kaolinite. Celle-ci s'est accumulée ensuite, peut-être aussi à apports de hydromicas, dans des lacs et des marécages hétérotrophes à des pH très acides. Dans telles conditions les hydromicas et les smectites se sont dégradées, en formant de la kaolinite qui a évolué eventuellement jusqu'à la kaolinite réfractaire. Le processus dégradatif des minéraux argileux a libéré également une quantité importante de silice qui a cimenté ensuite les arénites quartzeuses détritiques, formant les roches orthoquartzitiques qui accompagnent les argiles réfractaires.

The Lower Liassic formations of Romania often show the specific Gresten continental facies in which detrital deposits, prevailingly quartzitic arenites, are associated with clayey, mostly refractory rocks and with coal interbeds.

It is the fireclay sequence—industrially mined in certain areas of the Piatra Craiului Massif — that is typical in this respect. The fireclays are mentioned and even investigated in view of their utilization since the past century. These rocks have been studied so far by a great number of researchers who have approached problems related both to their stratigraphy and to their chemical-mineralogical composition, first of all with economic purposes in view, but also with genesis ones.

The Lower Liassic Formation is cited as such as early as 1852 by Hauer, but it is Hoffmann (1879) who identified fireclays here. Matyasovszky (1879, 1884), Màrtonfi (1882) and Szontagh (1901) pointed out their association with quartzitic sandstones and mentioned rudimentary mines at Şuncuiuş and Bratca. Between the two world wars, Fisch's studies (1924) and especially Kräutner's ones (1939, 1941), the latter including the first structural and stratigraphic image of the Pădurea Craiului Mts, are worth mentioning. After the Second World War, a number of studies and researches were carried out, many of them with economic purposes, largely contributing to the knowledge of the formation lithology. In this connection we should mention Codarcea (1948) and especially Patrulius (1952, 1956) the main prospector of the region, on whose data, systematically presented in the geological map of Romania, scale 1 : 200 000 (Şimleul Silvaniei Sheet) are based our researches (Patrulius et al., 1968). A series of field and laboratory works follow, carried out by Drăghici (1953) Dumitriu, Dumitriu (1963), Naghel, Naghel (1963), Bulgăreanu (1964), Stănoiu, Diaconu (1965, 1966), Diaconu, Ionescu (1966), Diaconu (1967), Treiber, Bedelean (1967). Neacşu (1966) and Ianovici, Neacşu (1968) described certain types of fireclays and identified the presence of diagenetic nacrite on fissures. In a complex study with economic purposes, Mălin et al. (1967) separated four groups of clays — aluminous, siliceous, ferruginous and carbonaceous. Semaka (1969) identified in the Lower Liassic fireclay complex of Pădurea Craiului a flora including *Solenocarpus* that is specific to fresh water lacustrine areas, in wet and warm climate (analogous to present day tropical zones).

The present paper is based on the chemical-mineralogical study carried out at the Geological Institute in 1968—1969 and presented as a report (Papiu et al., 1969).

The Lower Liassic Series, in typical Gresten facies, containing the fireclays of the Pădurea Craiului Massif, is built up of a sequence of prevailingly detrital rocks (Fig. 1) i.e. sandstones and quartzitic microconglomerates with clayey sandstones and ferruginous siltstone interbeds,

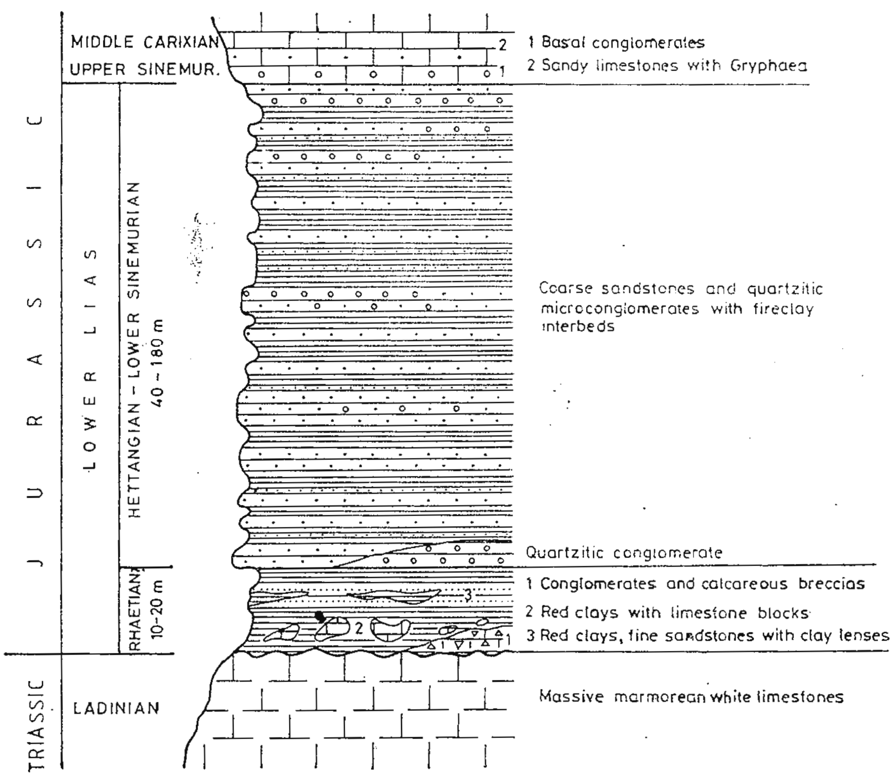

Fig. 1. — Generalized stratigraphic column of the Lower Lias in the Pădurea Craiului Massif

usually red, rarelier black in colour. These ones are associated with kaolinitic and kaolinito-illitic clays of various colours (most of them grey, subordinately red ones — with ferruginous pigment, and black ones — with carbonaceous pigment, which often grade into coaly intercalations). Associated with grey clays, fireclays develop, especially as lenticular interbeds, whose structure is never stratified. In the Măgura Hill, at the boundary with the Neogene Borod Basin, there occur a mixture of clays and rounded and sharp-edged blocks of quartzites, which could be considered a chaotic material, formed following breaking-down processes at the border of the Pannonian Lake. These rocks would represent, therefore, a secondary deposit.

The detrital-quartzitic formation lies at the base of the Lias, normally or unconformably overlying the Upper Triassic deposits assigned to the Rhaetian, constituted of argillo-detrital rocks of red colour (rich in hematite), indicating a continental weathering phase of siderolitic type. According to Patrulius et al. (1968) the Carnian and the Norian are absent from the Triassic sequence, the above described deposits lying directly over Ladinian dolomites. The formation containing fireclays is Hettangian—Sinemurian (Rhaeto—Liassic) in age, as was proved by Patrulius (1956) — on paleontological criteria, Semaka (1969) — on paleobotanical data and Antonescu (in Papiu et al., 1969) on palynological datings.

The clays collected both from outcrops and from underground workings were subjected to chemical analyses : 18 on bulk sample and 6 on the clay fraction (less than 2 microns) obtained by pipette-method (table 1). Thermodifferential, roentgenographic and infra-red analyses were correlated with the chemical data, establishing the mineralogical composition of the clays (table 2). The variation range and the means of these analyses are shown in table 3. To these data, the microscopic study of the quartzitic sandstones is added, accompanied by only one chemical analysis.

A. Detrital rocks

The main characteristic feature of the Lower Liassic Formation of the Pădurea Craiului Massif, as, in fact, of all the series of this age in Gresten facies in the Carpathian Orogen, is the existence of arenites and ortho- and protoquartzitic microconglomerates together with kaolinitic fireclays. As already told, fireclays appear as large lenticular bodies intercalated between detrital siliceous deposits. The clays sometimes include generally centimetric interbeds of siltstones and hematitic sandstones and, at their upper part (Banlaca Area), carbonaceous black sandstones.

1. *Conglomerates and quartzitic sandstones* (*orthoquartzites*)

The miscroscopic study of these rocks shows a peculiar uniformity and mineralogical simplicity, being built up almost exclusively of quartz of metamorphic origin and subordinately of metaquartzitic grains, with sinuous sutural outlines, reminding by their textural characters, sometimes up to identity, of the metaquartzites *stricto sensu*. The size of these

TABLE 1

Chemical composition of the Lower Jurassic clays of the Pădurea Craiului massif (%)

No	Sample no.	Location	Type of clay	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	H_2O^+	CO_2	S
								Bulk sample									
1	16a	Măgura Hill	Refractory = Fireclays, Grey	49.66	1.45	32.45	0.17	1.71	0.25	0.34	0.15	1.50	0.19	0.12	12.32	—	0.12
2	36a	Recea G. VII		49.09	1.45	30.75	4.18	traces	0.05	0.25	0.06	1.79	0.13	0.10	12.03	—	—
3	33b	Banlaca G. XV		46.09	1.50	31.68	2.51	—	0.05	0.25	0.02	2.41	0.21	0.14	14.08	—	—
4	MII	Banlaca		49.11	1.65	30.61	1.88	1.12	traces	0.20	0.07	2.01	0.27	0.10	13.03	—	—
5	M I	Banlaca		52.79	1.45	28.09	2.30	—	—	0.23	0.08	2.03	0.22	0.10	12.26	—	—
6	323	Bratca F33802		52.95	0.80	27.40	2.32	1.65	0.08	0.36	0.20	2.61	0.16	0.06	10.42	—	0.28
7	15b	Recea G. P102	Non-refractory kaolinitic = Common, Grey	53.93	1.06	27.09	6.39	traces	—	0.34	0.12	1.61	.013	0.11	8.98	—	traces
8	4	Recea G. XI		56.56	1.85	25.19	2.29	0.73	0.14	0.14	0.04	0.87	0.13	0.16	11.63	—	0.35
9	16b	Măgura Hill		53.16	1.15	28.53	3.12	traces	0.18	0.26	0.02	1.21	0.13	0.14	10.95	—	0.16
10	6	Recea G. XI		60.61	1.10	24.87	0.98	0.16	traces	0.21	0.03	1.26	0.18	0.06	10.47	—	traces
11	8	Recea G. XI		58.02	0.93	24.84	5.51	traces	—	0.18	0.04	1.73	0.66	0.10	7.94	—	—
12	471	Bratca F33810	Red	50.79	0.80	26.91	3.15	2.98	traces	0.20	0.27	2.66	0.27	0.06	11.35	—	traces
13	28	Banlaca L. 900		49.69	1.00	30.21	5.60	0.20	traces	0.34	0.16	2.00	0.16	0.14	10.50	—	traces
14	36b	Recea G. VII		47.16	1.95	26.73	8.16	1.50	traces	0.24	0.12	1.79	0.21	0.14	12.43	—	—
15	20	Banlaca G. 6PI	Black	51.82	1.14	27.82	—	0.22	traces	0.29	0.01	0.32	0.05	—	7.61	—	3.25
16	7	Recea G. XI		48.51	1.00	26.91	3.55	traces	traces	0.14	0.04	1.15	0.16	0.16	13.79	—	traces
17	33a	Banlaca G. XV		46.77	1.31	31.71	2.50	1.49	0.10	0.16	0.01	2.91	0.13	0.21	9.26	—	0.21
18	19	Banlaca G.G.		46.83	1.50	29.19	2.51	6.41	0.21	0.55	0.10	2.61	0.27	0.10	11.92	—	0.14
								Clay fraction (less than 2 microns)									
1	33b	Banlaca G. XV	F—g	46.29	0.98	38.67	0.74	—	—	0.23	0.01	1.83	0.12	—	10.63	—	—
2	15b	Recea G. P102	N—g	49.59	1.27	34.56	3.06	—	—	0.33	0.12	0.72	0.08	—	9.85	—	—
3	4	Recea G. XI	N—g	46.25	1.26	39.29	1.78	—	—	0.14	0.04	0.46	0.20	—	11.09	—	—
4	6	Recea G. XI	N—g	46.41	1.29	37.19	1.72	—	—	0.20	0.03	0.97	0.10	—	14.35	—	—
5	36b	Recea G. VII	N—r	47.70	1.54	35.26	3.33	—	—	0.25	0.12	1.44	0.14	—	10.60	—	—
6	20	Banlaca G. 6PI	N—b	46.47	1.04	34.42	4.32	—	—	0.29	0.02	0.43	0.07	—	10.75	—	1.73
7	33e	Balanca G.XV	N—b	44.90	1.09	38.63	1.61	—	—	0.15	0.01	1.75	0.09	—	11.80	—	—

F = Fireclay; N = Non-refractory clay; g = Grey; r = Red; b = Black.

TABLE 2

Mineralogical composition of the Lower Jurassic clay of the Pădurea Craiului Massif (%)

No	Sample no.	Type of clay	Gb	K	D	Hd	M	Ch	H±G	G	P	S	O.M.	Q
Bulk sample														
1	16a	Refractory = Fireclays Grey	—	67.5	—	12.7	—	4.8	—	—	0.2	—	—	11.0
2	36a		—	63.2	—	15.0	—	—	4.2	—		—	—	12.9
3	33b		—	59.2	—	20.1	—	3.2	2.5	—	—	—	—	8.6
4	MII		—	58.5	—	16.8	—	—	1.9	—	—	—	—	14.3
5	MI		—	52.5	—	16.9	—	4.7	2.3	—	—	—	—	19.4
6	323		—	47.5	—	22.4	—	—	2.0	—	0.5	—	—	20.6
7	15b	Non-refractory kaolinitic = Common Grey	—	57.0	—	13.6	—	2.1	2.9	3.9	—	—	—	19.7
8	4		1.2	55.3	—	7.5	—	—	1.9	—	0.6	—	—	26.8
9	16b		—	62.0	—	10.4	—	0.4	2.9	—	0.3	—	—	20.0
10	6		—	52.4	—	10.8	—	—	1.0	—	—	—	—	31.3
11	8		—	44.4	—	14.6	—	8.4	2.6	3.2	—	—	—	28.4
12	471		—	45.7	—	22.8	—	0.6	3.1	6.2	—	—	—	19.0
13	28	Red	—	58.0	6.2	16.7	—	4.2	0.4	—	—	—	—	13.9
14	36b		—	43.5	—	15.0	—	0.6	8.2	—	—	—	—	19.9
15	20	Black	—	67.9	—	2.5	4.3	0.6	—	—	—	—	2.8	20.0
16	7		—	58.5	—	9.9	—	—	3.5	—	—	—	4.0	21.3
17	33e		—	56.2	—	24.7	—	4.2	2.2	—	—	—	3.0	19.4
18	19		—	52.2	—	22.4	—	18.2	—	—	—	2.6	—	17.5
Clay fraction (less than 2 microns)														
1	33b	F—g	—	77.2	—	21.5	—	—	0.5	—	—	—	—	—
2	15b	N—g	—	79.4	—	8.9	—	—	3.0	—	—	—	—	—
3	4	N—g	—	94.6	—	3.9	—	—	1.8	—	—	—	—	—
4	6	N—g	—	83.2	—	12.0	—	—	1.6	—	—	—	—	1.8
5	36b	N—r	—	73.0	—	17.8	—	—	3.2	—	—	—	—	5.3
6	20	N—b	—	82.3	—	5.3	—	—	4.3	—	—	—	—	5.7
7	33c	N—b	—	74.2	—	21.6	—	—	1.4	—	—	—	—	—

F = Fireclay; N = Non-refractory clay; g = Grey; r = Red; b = Black; Gb = Gibbsite; K = Kaolinite; D = Dickite; Hd = Hydromicas; M = Montmorillonite; Ch = Chlorite; H = Hematite; G = Goethite; P = Pyrite; S = Siderite; O.M. = organic matter; Q = Quartz.

grains vary largely, even within the same thin section, from millimetric up to ± 0.2 mm. In most cases there are neither cement or overgrowth zones around the quartz grains nor diagenetic corrosion traces. However, thin zones or files of neoformation microquartz are individualized sometimes (reminding to a certain extent of the quartz of hydrothermal origin), spread among detrital grains, from which the mineral generally differs by its normal extinction (Banlaca Area).

In certain samples from the Banlaca Area, equigranular zones also appear, with coarse psammitic grains (0.5—1.5 mm). Some other times (Recea Area) there are arenites referred to two grain-size classes, that is: a coarse phase (D = 0.5—1.5 mm), mostly (about 70%) made up of metaquartzite grains, rather varied in size (unequigranular) and a fine-grained phase (about 30%), with grains of less than 0.5 mm. Among quartz grains, there occur scarce bent or fractured muscovite flakes, fresh or partially argillized (loss of birefringence colour and dim aspect). Muscovitic metaquartzite grains are observed sporadically and some heavy mineral grains are encountered accidentally. The heavy minerals are more or less fragmented but still preserve their originary habitus (yellow tourmaline) or, rarelier their outlines are slightly modified by reworking (staurolite).

As regards the cementing material and the authigene minerals, it is worth noticing that in all the investigated cases no other quartz than that in the sporadic zonal microquartz concentrations could be found.

The grains generally show sinuous or interlocking outlines, often looking like microsutures or microstylolites. Some other times, the grains penetrate one another, indicating advanced diagenetic solubility. These characters generally reflect a high purity material generated by strong chemical alteration processes (platform facies). Rarely, close to the grain boundary there are unclear areas that indicate the presence of clay material mixed with neoformation quartz of cement. This also results from the chemical analysis and mineralogical composition (deduced by calculation) of an orthoquartzite sample from the Banlaca Area: SiO_2 = 93.60%, Al_2O_3 = 2.64%, Fe_2O_3 = 0.17%, FeO = 0.73%, MgO = 0.45%, CaO = 0.09%, Na_2O = 0.07%, K_2O = 0.58%, TiO_2 = traces, MnO = 0.05%, P_2O_5 = 0.12%, S = 0.09%, CO_2 = absent, H_2O = 0.68%, C = absent, kaolinite = 2.22%, illite + muscovite = 4.62%, hematite = 0.06%.

These data show that, beside quartz, these apparently extremely pure rocks, also contain 9.15% prevailingly clay minerals, micas and hydromicas being the most important of them. It is also worth noticing that often in the quartz mass there occur pyrite framboides, either in concretions circularly shaped in section or, more often, in concentrations ramified among the quartz grains, the framboidal character being obvious in both instances. The concretions have a clayey core and submillimetric sizes. Sometimes around them and in fact also in the corpuscles mass, a kind of „powder", of idiomorphic, cubic little crystals of pyrite, looking like diffuse tiny clouds is observed. The more compact zones that surround the quartz grains like a real cement, sometimes closely following their outlines, have a strictly local character. In the Banlaca Area, the passage between clays and the uppermost quartzites is made through 0.20 m thick sandy clays currently named the „false roof", which is removed during the mining process. In fact, at the upper part of the clays under this deposit, there also occurs a black pyritous sandstone interbed. The presence and the quantity of framboidal pyrite suggests a genesis controlled by an obviously reducing lacustrine environment or by reducing sulphurous solutions migrated from upper horizons, which subsequently evolved in an anadiagenetic phase to framboidal pyrite.

The rocks correspond to certain proto- up to orthoquartzites, according to Pettijohn's classification (1957).

2. *Ferruginous siltstones*

The microscopic study of certain ferruginous siltstones coming from a lens only a few centimeters thick intercalated in the mass of Banlaca fireclays shows 60—70% angular quartz grains, alongside 30—40% hematitic, sometimes slightly translucent clay, indicating maybe incipient recrystallization (hydrohematite or goethite). Most of the detrital quartz (80%) is characterized by fine silty dimensions (D less than 0.05 mm), the remaining particles ranging between 0.08 and 0.2 mm.

We have equally cited above the existence of fine black coloured sandstones, indicating a reducing sedimentary environment, unlike the preceding ones, that illustrate the most genuine oxidizing conditions.

B. Chemical-mineralogical composition of the clays

The clays have been divided after the mineralogical criterion correlated with that of colour. The first criterion is illustrated in Fig. 2 where, considering the participation of three main components-kaolinite, illite + chlorite + smectites (non-kaolinitic clay component) and quartz — in a simple triangular diagram, four types of clay were established, i.e. : kaolinitic, illito-chloritic (± smectitic [4]), quartzose and mixed. Three types were distinguished according to colour : grey (refractory and non-refractory) clays, red clays (pigmented with hematite) and black clays (pigmented with organic matter ± hydrotroilite). In what follows we shall treat of fireclays and common (non-refractory) clays.

1. *Chemistry of clays*

On examining the data concerning the bulk sample (tab. 1), first of all a reversed ratio results between silica and alumina, the most kaolinitic being those rich in alumina and poorer in silica, the quartzose ones showing the reversed case. The average contents also indicate this ratio, the values being of the same order of magnitude (tab. 3).

As natural, the trivalent iron in oxides (our analyses also including the iron in sulphides) shows a much larger variation range in common clays (which they pigment) than in fireclays, although for total iron (Fe_2O_3 T) they are of close values, a little bit higher in the case of non-refractory clays. Ferrous oxide (present especially in septechlorites and possibly in illite and smectites) shows a greater affinity for certain black clays and is subordinate or even absent from fireclays.

TABLE 3

Variation range and average contents of the main chemical and mineralogical components of the Lower Jurassic clays of the Pădurea Craiului Massif (%)

Component	Refractory clays = Fireclays			Non-refractory clays = Common			
	Bulk sample n = 6	Clay fraction n = 1		Bulk sample n = 12		Clay fraction n = 6	
	Δ	$\bar{x}$		Δ	$\bar{x}$	Δ	$\bar{x}$
Chemistry							
SiO_2	46.1–53.0	50.0	46.3	46.8–60.6	52.0	44.9–49.6	46.9
Al_2O_3	27.4–32.4	30.2	38.7	24.8–31.7	27.5	34.4–39.3	36.6
Fe_2O_3	0.2– 4.2	2.2	0.7	0.0– 8.2	3.6	1.6– 4.3	2.6
K_2O	1.5– 2.6	2.1	1.8	0.3– 2.9	1.7	0.4– 1.8	1.0
H_2O	10.4–14.1	12.4	10.6	7.6–13.8	10.6	9.9–14.3	11.4
Fe_2O_3T	2.1– 4.2	3.1	0.7	1.2– 9.8	4.9	1.6– 4.3	2.6
Mineralogy							
Kaolinite	47.5–67.5	58.1	77.2	43.5–67.9	54.4	73.0–95.6	81.3
Hydromicas	12.7–22.4	17.3	21.5	2.5–24.7	14.2	3.9–21.6	11.6
Chlorites	0.0– 4.8	2.1	—	0.0–18.2	3.3	—	—
Quartz	8.6–20.6	14.4	—	13.9–31.3	21.4	0.0– 5.7	2.1
Hematite ± goethite	0.0– 4.2	2.2	0.5	0.0– 8.2	2.4	1.4– 4.3	2.5

n = Number of samples; Δ = Variation range; $\bar{x}$ = Arithmetic mean.

Magnesium oxide (MgO), which in fact originates equally in chlorites and sometimes in smectites, or results from adsorbtive bonding, is sometimes higher than 1%, showing in all types of clays analogous average contents, slightly decreasing in quartzose clays.

Sodium (Na_2O) generally less than 0.3%, but actually present in all samples, maybe partially originates in the small content of detrital feldspars, undetected by X-rays, or is adsorbed in the clay complexes, just like calcium.

Calcium oxide (CaO) is subunitary in all the analysed samples, being probably linked to phosphates — P_2O_5 participates in percentages smaller than 0.2% or is absent — or absorbed in clay complexes.

Potassium (K_2O), whose source is represented by muscovite or illite, appears in all the samples, in 1—3% (with two subunitary exceptions), surprisingly indicating a slight tendency of augmentation in the clays rich in detrital material (orthose ?).

Titanium (TiO_2) is fixed in the crystal lattices of clay minerals, replacing aluminium, and participates below 2% in all the samples, being subunitary in a few cases and thus indicating its reversed relation with the content of detrital material.

Sulphur, that originates in sulphides and sometimes in secondary ferric sulphates, is absent from many samples, showing an affinity for the black clays accumulated in strongly reducing environments.

Organic matter appears only in the black clays.

A comparison with the chemical composition of the clay fraction (Tab. 1 and 3) leads to the following conclusions.

Most clays contain higher silica, iron, magnesium and potassium percents in the bulk sample than in the clay fraction (less than 2 microns), because of the detrital supplies (quartz, micas and possibly feldspars). In exchange, the fine fractions are excedentary in aluminium compared with the bulk sample, reflecting the concentration of clay minerals in the fraction less than 2 microns. The (trivalent and total) iron content diminishes sensibly in comparison with the bulk sample. Potassium has close average values in the case of fireclays, which also have smaller variation range than common clays, with larger variation range and lower average K_2O contents in the fraction less than 2 microns than in the bulk sample.

2. *Mineralogical composition*

The clay minerals are represented by kaolinite, illite (hydromicas [5] more exactly), magnesium and iron-rich chlorites and, only in one case, by smectites (fig. 2, tab. 2 and 3). The first three appear in all samples, while

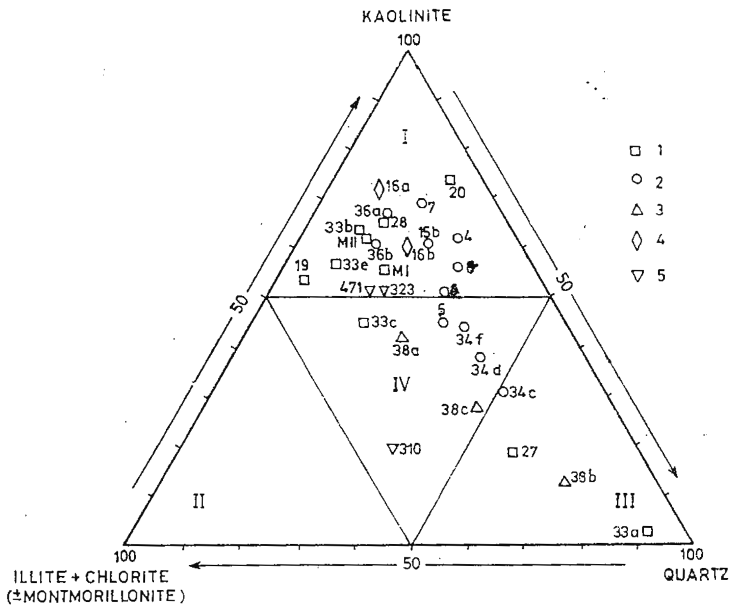

Fig. 2. — Mineralogical classification of the clays of the Lower Jurassic fireclay Formation of the Pădurea Craiului Massif.

1, Banlaca Area ; 2, Recea Area ; 3, Damiș Area ; 4, Măgura Hill Area ; 5, Bratca Area ; I Kaolinitic clays ; II, Illitic (Montmorillonitic) clays ; III, Quartzose clays ; IV, Mixed clays.

the minerals of the chamosite group (septechlorites) occur in about half of them. Between kaolinite and hydromicas there is a slightly reversed ratio, maybe also indicating a kaolinite genesis from hydromicas. No fire-clay kaolinite was found in (refractory and non-refractory) clays.

In the case of common clays, hydromicas show in the bulk sample larger variation range and lower average content than in fireclays while chlorites, although have large variation range in common clays show in both cases quite close average values.

Magnesian montmorillonite was identified in two samples at Banlaca one (20, tab. 2) containing 4.3% and the other, unincluded in this paper, 16% (silty-quartzose clay). In this area dickite was also found in a sample (28, tab. 2). It is also worth mentioning that a bulk sample of fireclay at Banlaca shows free gibbsite probably formed through continental lateritic material reworking.

Iron oxides are represented by hematite and goethite which generally occur together; they are absent only from certain black clays and reach maximum percentages (up to 8%) in red clays, which they pigment.

Iron sulphides were identified only in a few samples, in which pyrite often appears as framboids, being probably also present as colloidal monosulphide (hydrotroilite), undetectable by X-rays, that accounts, together with the carbonaceous pigment, for the black colour. Neither intermediate sulphide forms, such as greigite and makinawite were identified roentgenographically.

Finally we also point out the presence of siderite (2.6%) in one of the black clays in the Banlaca Area.

By comparing the mineralogical composition of the bulk sample with that of the clay fraction, we can see that it is in the latter that kaolinite is massively concentrated, while hydromicas have higher (average) values in fireclays and lower ones in common clays. Chlorites are no longer found in the clay fraction and hematite has smaller variation range in common clays, where the average content remains practically the same, and is more than three times lower in refractory clays.

3. *Study of heavy minerals*

The study of the heavy minerals in the Liassic clays of Pădurea Craiului Massif has led to the conclusion of a double origin: allogenic (detrital) and authigenic. The most important of the second group is neoformation pyrite that can make up almost the whole heavy fraction in some black clays, masking the presence of the other heavy minerals, and sulphates, identified in certain fireclays under idiomorphous forms or submillimetric concretions. Detrital minerals have mesometamorphic crystalline origin and show the following frequence in the analyzed samples: 1) brown tourmaline (in 94% of the samples); 2) zircon (88%); 3) staurolite (76.5%); 4) rutile (35%); 5) epidote + zoizite (23.5%); 6) clinozoizite +; 7) colourless garnet +; 8) green hornblende (17.5%); 9) biotite (sp.).

As can be seen, heavy minerals are represented by few mineral species and their penury must be completed with the quantitatively reduced participation of this fraction (generally much below 1%). The black, carbonaceous clays which sometimes contain pyrite in great quantities, as it results from chemical analyses, are an exception. Pyrite as well as sulphates represents the diagenetic neoformation product and generally show framboidal structures or replaces vegetal fragments. It is sometimes oxidized, hematite being formed at its periphery or on fissures.

Genetic interpretation

The argillo-detrital formation in the base of the Liassic of the Apuseni Mts appears in the specific continental Gresten facies and overlies the ravined karstic paleorelief of Ladinian limestones, sometimes having residual Rhaeto—Liassic deposits in its base (red clays corresponding to old „terra rossa" deposits).

According to Patrulius (1956) the sedimentation of these rocks took place after a hiatus which started as far as the Carnian. The exclusively continental lacustrine and palustrine character is specific to Liassic fireclay occurrences in Gresten facies of all the regions of Romania and is given by the assemblage of mature detrital rocks with clays characterized by the presence of kaolinite (possibly refractory) — and with minable coal (Holbav and Codlea—Brașov, Anina—Banat or Schela—Gorj). As in this last zone the rocks are affected by a slight Alpine metamorphism, it is pyrophyllite-bearing schists (improperly called „refractory clays") that correspond to fireclays.

There are very frequent facies variations, depending on the nature of the material and on the conditions of accumulation, and the sequence of deposits indicates a sedimentary periodicity or even rhythmicity.

The lenticular character of the fireclay bodies as well as the lithological composition and the paleontological contents, with frequent lateral lithofacies variations, show that the accumulation took place in waters with minimum salinity, virtually in fresh waters of not very large lakes, on whose banks grows a specific flora, first of all of Pteridophyta. Nowadays certain Osmundacea species of Pteridophyta are characteristic of the vegetation of totally fresh water lakes (Semaka, 1970). The most suggestive sequence, reflecting the mentioned rhythmicity is the following:

1. sandstones and orthoquartzitic conglomerates („lacustrine detrital phase");

2. grey or red clays of various types, prevailingly kaolinitic, sometimes refractory („argillo — palustrine phase");

3. black clays with carbonaceous interbeds („local palustrine phase with peat-bogs" supplying the material in which originated the present day coals).

In the first phase the accumulation of argillo-detrital materials, denoting very advanced chemical alteration, was controlled by fluviatile supplies. This alteration is likely to have taken place in a warm wet climate, which has been confirmed by lithology as well as by the mentioned vegetal forms. The quartz grains, prevailingly of psammitic sizes were usually deposited in the base of the cycles, as more or less continuous layers. The clay material, with silty and pellitodetrital supplies in which quartz and muscovite were the dominant minerals remained in suspension for a longer while, determining a certain turbidity of the waters and consequently, a quite high density, all this leading to a sedimentation often characterized by true precipitation processes. The clay mineralogy dominated by kaolinite as well as the scarcity in ions resulted from alteration, indicate both the very advanced degree of weathering on the initial continental area and the prevailingly low pH of the waters. The detrital material shows the direct or indirect origin from crystalline schists and granitoids: metamorphic quartz, alkaline feldspar and muscovite in various degrees of kaolinization. The clay material is mainly reworked from preexisting sedimentary rocks : illite, smectites, chlorites to a great extent and maybe even some of the kaolinite. The kaolinization process might have taken place both in the primary phase of continental weathering and during transport and continued in the lacustrine acid environment, rich in CO_2, humic acid and sometimes H_2S (heterophic lakes with waters and sediments characterized by important bacterial processes and variable degree of oxygenation). Under conditions of high redox potential, syndiagenetic ferric oxides were formed and the ferric oxides derived from continental lateritic sediments were preserved and fixed in muds, in the phase of anadiagenesis, if oxidizing conditions were dominant (red clays).

The presence of decaying organic matter sometimes creates more or less marked reducing conditions in the interstitial waters of the originary muds favouring, in progressive order, the linkage of iron silicates (leptochlorites), carbonates (siderite, in only one case), or colloidal ferrous monosulphide (syn. hydrotroilite). The last one is generally associated with the carbonaceous pigment determining the black colour of some clays. During the syn- and anadiagenetic phases the three-layer clay minerals were probably subject to characteristic transformations controlled by the low pH of lacustrine and palustrine waters. It is in this way that the kaolinization of smectites, hydromicas and chlorites took place, and this process was accompanied by massive elimination of silica. It could subsequently migrate in the subjacent quartzo-detrital horizon, silicifying the sands accumulated in the previous phase and leading to the formation of siliceous sandstones that evolved, forming proto- and orthoquartzites. Analogous processes were supposed to take place also in other regions of the earth, for explaining the genesis of certain quartzitic sandstones associated with illitic clays resulted from the diagenesis of smectites, which implies removal of silica (Lahan, 1980). The same processes are to be supposed for explaining to a great extent the silicification of menilites and maybe of the Kliwa Sandstone (Papiu et al., 1982, 1983).

On the other hand, in the lacustrine but especially in the palustrine acid environment and then mainly in the subsequent epidiagenetic-metamorphic phase, kaolinization could also take place directly at the expense of feldspars, especially of the potash ones, this *in situ* argillization being cited in fact in other regions as well (Elsinger and Sellar, 1981). The formation of authigenic kaolinite associated with pyrite in the primary diagenesis phase can be explained by the elimination of potassium from the pyroclastic material and the formation of an aluminous gel accumulated in foraminifera tests, followed by its transformation in kaolinite (by reacting with silica), polycristalline aggregates being consequently formed. The bacterial reduction of sulphates and the formation of framboidal pyrite would be simultaneous with the kaolinite crystallization. As regards the illite of the fireclays, it can be generated to a certain extent at the expense of detrital muscovite, by the partial loss of potassium ions.

The formation of refractory kaolinite marks a more advanced phase in the strongly acid environment in which these processes take place. Although not proved by X-rays, refractory kaolinite (syn. mellorite, livesite, pM kaolinite, fire-clay kaolinite) could be formed under hyperacid conditions, by chemical alteration, directly at the expense of kaolinite supplied by continental waters as well as at the expense of primary minerals, by breaking their original structures. Oberlin et al. (1962) experimentally obtained refractory kaolinite by treating normal kaolinite with sulphuric acid at pH 2 for a long period of time. Electron micrographs illustrate this transformation by the appearance around the mineral of fringes produced by alteration, followed by the epitaxy of refractory kaolinite on the faces of the previous one. The authors admit that the formation of the new kaolinite (refractory) is preceded by the random solution of a number of kaolinitic layers and the consecutive silica and alumina removal. Finally a certain number of staking sequences of disordered layers is obtained, distributed between the untouched kaolinite units. In fact the formation of kaolinite at the expense of muscovite can be preceded by the appearance of ambiguous mineral complexes, initially considered distinctive minerals and called ,,leverrierite" by Termier (in Millot, 1964). These forms were also identified in the clays occurring in the ,,Albian bauxite complexes" in the Haţeg Basin (Papiu et al., 1971 a).

Dickite and gibbsite — sporadic minerals — can originate in the initial products of lateritic continental weathering. Dickite, formerly considered a typical mineral of hydrothermal alteration, has later been proved to be able to form under exogenous conditions. In fact dickite was identified as well in the Albian bauxitic complexes of the Haţeg Basin (Papiu et al., 1971 a) and in Liassic fireclays of the Anina Region (Banat) and Cristian—Holbav (Papiu et al., 1970). Gibbsite, a mineral also found in other fireclays can be inherited or can directly result from the lateritic weathering of the silicates in the crystalline rocks on the originary continental area.

The lack of stratification of the Liassic clays in the Pădurea Craiului Mts proves a rapid accumulation, maybe equally some precipitation processes. Probably bicarbonated karstic water supplies augmented the pH of the palustrine or lacustrine very acid environments rich in suspended, silica-aluminous matter, determining the coagulation of the argillaceous mass (kaolinite).

In the same way was explained the genesis of some ,,detritochemical" (clayey) bauxites, identified in the Haţeg Basin (Papiu et al., 1971) and in the Sohodol—Cîmpeni Region (Apuseni Mts) (Papiu et al., 1975).

In conclusion, the Liassic Formation in Gresten facies of the Apuseni Mts (Pădurea Craiului) starts with continental lacustrine-palustrine sediments, characterized by the association of silicarenites (orthoquartzites) with more or less pure kaolinitic clays, subordonately pigmented with ferric oxides or with the association ferrous monosulphide-organic matter. Such an occurrence shows very strong weathering of siderolitic type on the originary continental area. These rocks are associated with coal intercalations, as was observed in fact in all the Carpathian areas on the territory of Romania where the Lias appears in Gresten facies.

It is also worth mentioning that the series of Jurassic deposits of the Apuseni Mts ends just like it starts, that is by a siderolitic continental phase but which, this time, is characterized by the accumulation of karstic bauxites (Wealdian facies) (Papiu and Mînzatu, 1969).

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[4] Not represented among the studied rocks.

[5] Illites *str.s.* up to muscovite, proper or in various stages of hydration (hydromuscovite), were referred to by this term.

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ALCĂTUIREA ŞI GENEZA FORMAŢIUNII ARGILELOR REFRACTARE JURASIC INFERIOARE DIN MASIVUL PĂDUREA CRAIULUI

(Rezumat)

Liasicul inferior (Hettangian—Sinemurian) din masivul Pădurea Craiului este reprezentat printr-o formaţiune detrito-cuarţitică în facies tipic de Gresten, constituită din gresii şi microconglomerate cuarţitice cu intercalaţii de gresii argiloase, siltite şi argile refractare, acestea din urmă dezvoltîndu-se sub forma unor corpuri lentiliforme de dimensiuni variabile şi cu textură masivă. Formaţiunea cu argile refractare este dispusă normal

sau discordant peste depozite argilo-detritice roșii atribuite Rhetianului, situate la rîndul lor direct peste dolomitele ladiniene (fig. 1).

Studiul microscopic al conglomeratelor și gresiilor cuarțitice (ortocuarțite) arată o remarcabilă uniformitate și simplitate mineralogică, fiind alcătuite aproape în exclusivitate din cuarț de origine metamorfică și subordonat din granule de metacuarțite cu contururi sinuoase, suturale, fără ciment și fără zone de supracreștere evidente. Sporadic, apar lame de muscovit proaspete sau în curs de argilizare, granule de minerale grele și aglomerări de pirită cu caracter framboidal.

Studiul geochimic al rocilor argiloase arată procente de SiO_2, Fe_2O_3, MgO și K_2O mai ridicate în proba brută decît în fracția argiloasă (sub 2 microni), datorită adaosurilor detritice (cuarț, mice și eventual feldspați), fracțiile fine fiind în consecință excedentare în alumină în urma concentrării mineralelor argiloase (tab. 1 și 3).

Din punct de vedere mineralogic, rocile argiloase sînt constituite preponderent din caolinit, cu adaosuri subordonate de hidromice, clorite ferifere și magneziene și cuarț detritic, la care se adaugă (mai ales în argilele nerefractare), procente reduse de hematit, monosulfură feroasă, substanță organică, goethit, siderit, dickit, smectit, gibbsit (tab. 2 și 3). Clasificarea mineralogică a rocilor argiloase arată concentrarea preferențială a argilelor refractare în domeniul argilelor caolinitice (fig. 2). Studiul comparativ al probelor brute și fracțiilor argiloase evidențiază creșterea conținuturilor de caolinit în fracțiile fine însoțită de reducerea corespunzătoare a participării hidromicelor și cuarțului detritic.

Mineralele grele participă cu un număr restrîns de specii și cu o pondere foarte mică (în general sub 1%) la constituția argilelor liasice. Mineralele detritice au originea cristalofiliană mesometamorfică (turmalină brună, zircon, staurolit, rutil, epidot + zoizit, clinozoizit, granat incolor, hornblendă verde și biotit), iar cele autigene sînt produse de neoformație diagenetică (pirită, sulfați).

Sub raport genetic se admite că argilele refractare au luat naștere în medii palustre pînă la lacustre, instalate la suprafața paleocarstului rheto-liasic dezvoltat pe calcarele marmoreene și dolomitele masive ladiniene. În timpul îndelungatei faze continentale de la finele Triasicului a avut loc o alterare avansată de tip lateritic (facies siderolitic) care a generat mari cantități de caolinit, acumulat ulterior — poate și cu unele adaosuri de hidromice — în lacuri și mlaștini heterotrofe cu pH-uri foarte acide. În asemenea condiții hidromicele și smectitele s-au degradat cu formare de caolinit, iar acesta din urmă a evoluat eventual pînă la caolinitul refractar. Ritmicitatea remarcată adescori : (1) gresii și microconglomerate ortocuarțitice, (2) caoline refractare și nerefractare, (3) argile negre cărbunoase, ar reflecta următoarele faze sedimentogene : 1 — faza lacustră detritică ; 2 — faza lacustră argiloasă ; 3 — faza palustră cu turbării, urmată de carbonificare.

Procesul degradativ al mineralelor argiloase (hidromice, smectite) care avea loc în lacurile cu pH-uri scăzute (generînd o parte din caolinit) a eliberat și o cantitate importantă de silice, care a cimentat apoi arenitele cuarțoase detritice, dînd naștere rocilor ortocuarțitice care însoțesc argilele refractare.

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2. ZĂCĂMINTE

CHEMICAL-MINERALOGICAL STUDY OF THE LOWER JURASSIC FIRECLAY FORMATION OF ANINA (BANAT)[1]

BY

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Lower Jurassic. Chemical-mineralogical study. Fireclay Formation. Kaolinitic clays. Detrital rocks. Orthoquartzites. Quartzitic microconglomerates. Lithofacies. Clay minerals. Palustrine environment. South Carpathians — Getic and Supragetic Sedimentary Domains — Reșița — Moldova Nouă Zone.

Abstract

The Lower Liassic fireclays of Anina are associated with coal and orthoquartzitic arenites specific to continental lacustrine accumulations. Subordinately there occur quartzitic microconglomerates, quartzito-kaolinitic sandstones, clayey-silty shales and kaolins with sideritic concretions. The main mineralogical feature of the Anina fireclays is the massive presence (up to 30%) of dickite, accompanying kaolinite, the dominant mineral. The average kandite contents are of 72% in the bulk samples of fireclays and exceed 90% in the fraction less than 2 microns. Hydromicas, chlorites and mixed-layer minerals appear subordinately. The Middle Liassic bituminous shales overlying the fireclay formation have a similar mineralogical composition. The Lower Liassic deposits in Gresten facies are connected with a continental regressive phase, starting with macroclastic lacustrine sedimentation (sandstones and microconglomerates), followed by a clayey-microclastic lacustrine accumulation. The kaolinite and dickite in fireclays originated in reworking the lateritic material of the weathering crusts and in the degradation of hydromicaceous minerals in the palustrine acid environment.

Résumé

Etude chimique-minéralogique de la formation des argiles réfractaires jurassiques inférieures d'Anina (Banat). Les argiles réfractaires liassiques inférieures d'Anina sont associées aux gisements de charbons et d'arénites orthoquartzitiques spécifiques aux accumulations à caractère

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continental-lacustre. Des microconglomérats quartzitiques, grès quartzito-kaolinitiques, schistes argilosiltiques et kaolins à concrétions sidéritiques apparaissent subordonnément. Le trait minéralogique principal des roches argileuses est la présence massive (jusqu'à 30 %) de la dickite qui accompagne la kaolinite — le minéral dominant. Les kandites représentent en moyenne 72 % de l'échantillon brut et dépassent 90 % dans la fraction sous 2 microns. Subordonnément apparaissent des hydromicas, des chlorites et des minéraux interstratifiés. Les schistes bitumineux du Lias moyen suprajacents à la formation des argiles réfractaires ont une composition minéralogique similaire. Les dépôts du Lias inférieur en faciès de Gresten sont le résultat d'une phase regressive continentale qui débute par une sédimentation lacustre macroclastique (grès et microconglomérats) suivie d'une accumulation lacustre argilo-microclastique. La kaolinite et la dickite des argiles réfractaires proviennent de l'héritage du matériel latéritique des couvertures d'altération environnantes et de la dégradation des minéraux hydromicacés dans le milieu acide palustre.

The investigation of the Liassic kaolinitic clays of Anina, Banat, has been one of the main research activity as part of the systematic study initiated by the Institute of Geology and Geophysics on the fireclays in Romania. Fireclays as well as certain accompanying rocks—non-refractory clays, bituminous shales (one sample), silty clays, orthoquartzitic arenites, sideritic kaolins — have been collected from the drift tunnels and the stopes of the Mining Enterprise Anina—Uteriş and Covăcia mining fields.

The clays were investigated by chemical analyses on bulk sample and clay fraction (less than 2 microns), X-ray and DTA techniques. Associated rocks were analyzed only microscopically.

1. Brief History of Research

The fireclays in the Anina region have been investigated since the past century, but only in general geological terms, as part of the deciphering of the stratigraphy of this complex of formations in Banat, in which the main economic stress lies on the well known bituminous coal deposits. It is Kudernatsch's paper (1857) that is worth mentioning first of all, followed by Roth von Telegd's stratigraphic studies (1886, 1890), and after World War I, by the synthesis concerning the Carpathians of the Banat area elaborated by Codarcea (1940). After World War II, Banat's complex study elaborated mainly by researchers of the State's Committee of Geology, includes papers by Răileanu, Năstăseanu, Mutihac, Boldur (1954—1964), synthetically presented afterwards (Năstăseanu, Savu, 1968) in the geological map of Romania, scale 1 : 200 000 drawn up at the Institute of Geology and Geophysics. Mineralogical studies are carried out by Neacşu (1965) who identifies by X-ray analyses the presence of kaolinite (80 %) and illite (20 %) as well as of sericite (in bulk samples). Kaolinite is well crystallized. In bituminous shales montmorillonite (ca. 30 %) and bitumens (15—20 %) are also mentioned. The formation of kaolinite is related to a weathering of tropical type followed by palustrine sedimentation, which explains the coal deposit proximity. For bituminous shales an euxinic sedimentation is admitted, with considerable continental supplies from an area of wet and warm climate, alternating with periods of dryness (siderolitic environment).

New data on the chemistry, mineralogy and genesis of the Anina fireclays were presented in a geological report elaborated by Papiu et al. (1970). These data are summarized in the present paper. The image of the investigations carried out on the fireclay formation of Anina is to be completed with the remarkable coal petrography studies of Mateescu (1932) and the paleobotanic studies of Semaka (1962, 1964) and Oarcea and Semaka (1962) as well.

2. Geologic setting

The Eo-Jurassic Formation of the Anina region starts with coarse conglomerates containing well-rounded fragments of crystalline schists and quartz, and subordinately feldspars. The thickness of this sequence ranges between 10 m at Anina and 100 m at Doman. These rocks are Rhaeto—Liassic (Codarcea, 1940) or Lower Liassic (Semaka, 1964) in age. They are overlain by an argillo-detrital formation, 250 m thick, built up of interbeddings of micaceous clayey sandstones, carbonaceous shales, coals and fireclays. Răileanu et al. (1957) refers this formation, as well as the mentioned basal deposits to the so called ,,coaly horizon''. Laterally, especially eastwards, these deposits are replaced by a gritty facies, lacking in fireclays, representing torrential deposits. As a whole, "the coaly horizon" is assigned to the Lower Lias by Semaka (1964) which confirms, on paleobotanic criteria (a rich Pterodophites flora), Roth von Telegd's (1886) conclusions. This horizon is overlain by the horizon of bituminous shales, Middle—Upper Liassic in age, 200 m thick. This horizon is characterized by spherosideritic concretions (sometimes more than 1 m in diameter) and coaly intercalations, which can be more than 20—30 cm thick. At its upper part the horizon passes towards a sequence about 10 m thick dominated by grey sandy clays and representing the Upper Lias.

3. Occurrence of fireclays

The fireclays are related to the coal-bearing lower horizon and are followed on both limbs of the Anina anticline, along ca. 2 km. The bituminous coal and fireclay deposits of Anina are intensely folded and faulted, especially in the eastern limb of the anticline, where there are three main slices affected by a system of transverse faults with varying slips and strikes, delimiting a series of tectonic blocks grouped in a few mining fields. Because of the intense folding and faulting the clays show numerous slickensides, and their continuity is very difficult to establish by mining works.

Just like all fireclay deposits in the Lower Liassic formation of Gresten facies of Romania, the fireclays at Anina are associated with coal and orthoquartzitic arenites specific to the continental lacustrine accumulations (Papiu et al., 1969, 1970).

The fireclays were sampled only in two areas : Uteriș and Covăcia. The material from the Uteriș mining field was collected from mining works (drift tunnels and stopes), the sample position being shown in the synthetic stratigraphic column in fig. 1. Under the fireclay there is an orthoquartzite bed, underlain by few metres of quartzose conglomerates,

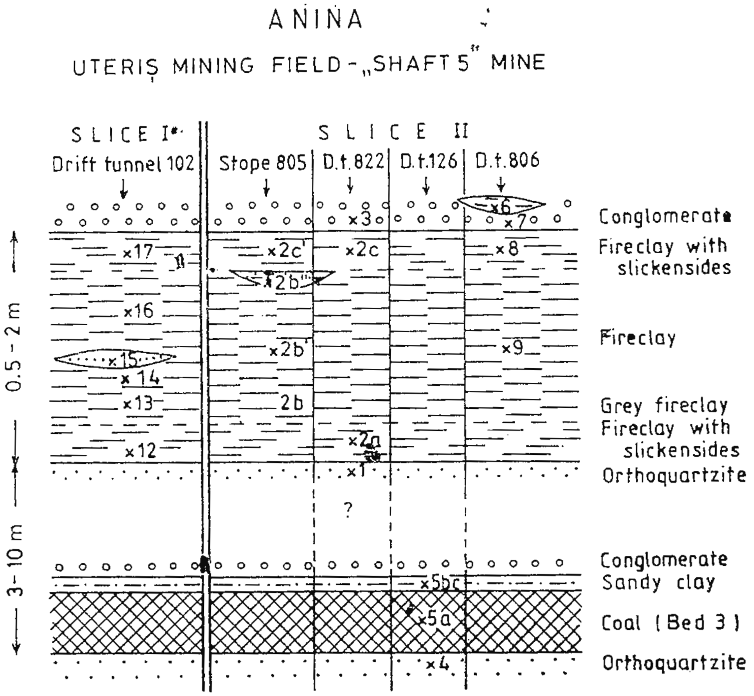

Fig. 1. — Generalized stratigraphic column of the Lower Jurassic fireclay Formation and location of samples in the Uteriș mining field

variable in thickness, followed by a decimetric bed of sandy clay, underlain by coal bed 3, whose foot-wall is built up of orthoquartzites. The thickness of the sequence overlain by fireclays ranges between 3 and 10 m, and that of the fireclay sequence between 0.5 and 2 m. The clays are compact, locally lithified as claystones, grey in colour and show slickensides, especially within the zones adjacent to the foot-wall and the roof.

The stratigraphic column of the Covăcia mining field (Fig. 2) shows a first grey clay intercalation in the mass of the siliceous conglomerate in the foot-wall, above which the gritty-conglomeratic deposit develops massively on 3—4 m thickness and shows (other) two clayey interbeds : one in the basal part (50 cm) and the second in the middle part (80 cm). There follow the fireclays, represented by a bed of grey clay, partly lithified, rich in slickensides (sample 25 a), with local lenticular decimetric interbeds of brown-grey clays and followed finally in the top by quartzitic sandstones which end the sequence investigated underground. In this series is also intercalated a bed of sandy, laminated, brittle coal, 1 m thick, not minable (bed 7) and which is not represented in the column in figure 2. In the base of the quartzitic sandstone there are numerous vegetal remains (sample 27). This sequence may be considered particularly illustrative for genetic interpretations, indicating an obvious cyclic lacustrine — palu-

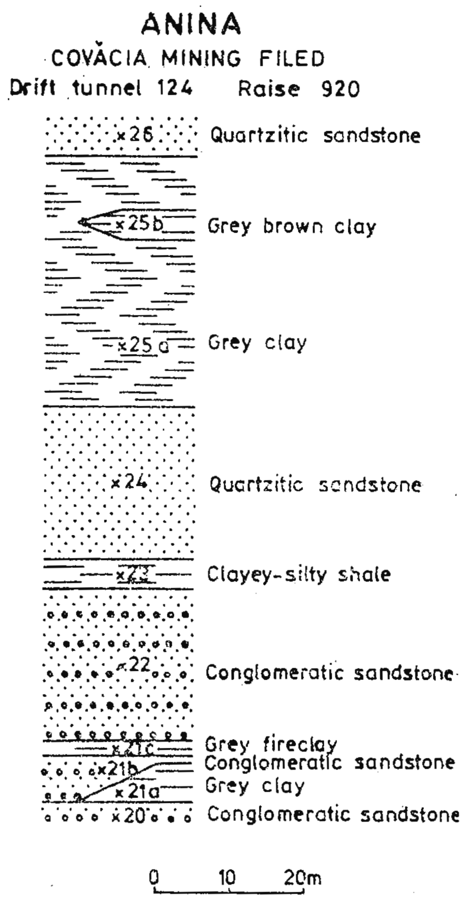

Fig. 2. — Stratigraphic column of the Lower Jurassic Fireclay Formation and location of samples in the Covăcia mining field.

strine evolution, from the clayey kaolinitic deposit, accumulated in waters with low pH, to a more or less normal sedimentation influenced by the hydrophyte vegetation of the palustrine-limnic environment.

4. Petrographic study of the detrital rocks associated to fireclays.

The microscopic studies pointed out the prevalence of the quite mature sediments (orthoquartzitic) associated with Anina fireclays, which suggests obvious resemblances with Lower Liassic deposits in Gresten facies of other areas : Pădurea Craiului (Papiu et al., 1969), Holbav—Cristian (Papiu et al., 1970). The following lithologic types were studied :

a) orthoquartzites, b) quartzitic microconglomerates, c) quartzito-kaolinitic sandstones, d) clayey-silty shales, e) coarse kaolins with sideritic concretions.

a) *Orthoquartzites*

Orthoquartzites *str.s.* are generally arenitic and subordinately finely ruditic rocks. Their psammitic texture shows almost the whole granulometric range, grains of silty sizes occurring sometimes (sample 2—27 %). Their mineralogical composition is extremely uniform, metamorphic quartz generally representing 95 % of the rock mass and fresh muscovite or muscovite under various degrees of illitization or kaolinitization, the remaining percents. Muscovite reaches the maximum percentage in the Covăcia mining field (10—20 %), in an arenitic orthoquartzite, followed by a silty-psammitic orthoquartzite from the base of coal bed 7, — Covăcia field as well — and by an orthoquartzite from the Uteriș mining field, the last two containing 15 % muscovite. The coarsest grains (D more than 0.75 mm) are often polymineral, represented by small fragments of vein quartz or of crystalline schists (quartzites, micaschists). As for grain size, two more frequent types of distributions are observed : heterogranular, which, in the arenitic material, shows a great variety of grain sizes and bimodal, in which there are sometimes obvious trends of local sorting and graded bedding. Isogranular orthoquartzites occur subordinately. Samples 1 (D = 0.025—0.20 mm), 14 (D = 0.5—1 mm) and 26 (D = 0.17—0.75 mm) are classed as heterogranular orthoquartzites. Most samples have bimodal distributions. Thus, sample 7 shows graded bedding on millimetric scale, fine zones (D = 0.10—0.50 mm) alternating with coarse grained zones (D = 0.50 — 1 mm) in which polymineral grains (metaquartzites) also appear. In sample 20, two grain size phases of quartz are recognized — a coarse one (D = ± 0.10 mm) and a silty one -(D = 0.02—0.04 mm) — the ratio between these two fractions being approximately 1 : 4. Sample 21 b contains a finer quartz fraction (D = 0.08—0.24 mm) and a coarser one (D > 0.75 mm) that prevails (more than 60 % of the grains). A remarkable zonation appears in sample 27 : fine-arenitic microzones of millimetric thicknesses and thicker (up to 1 cm) fine silty zones, in which the psammitic material represents no more than 10 %, the remaining material being silty (less than 0.05 mm). Coarse silty quartz (D = 0.05—1 mm) represents only 2—5 %. There is an obvious reversed ratio between the grain sizes and the degree of roundness ; some grains show platy or rod-like forms inherited from the crystalline schists they originate in. Samples 27 (in the microzones) and 2 b (D = 0.35—0.37 mm) represent two cases of isogranular orthoquartzites.

The muscovite is fresh or in various degrees of kaolinization ; no correlation was established between the mineral size (which can exceed 1 mm) and the degree of alteration. The kaolinization develops epitaxitically or as cryptocrystalline haloes around micas (40—50 %). The muscovite flakes mould upon the quartz grain outlines or appear fractured under the latter's presure. The biotite as well as the chlorite formed at its expense appear only in places, and heavy minerals are found only extremely rarely (an idiomorphic rutile grain in sample 20, epidote in sample 27). The complete absence of feldspars is worth mentioning.

As regards neoformation minerals, it is quartz, which cements orthoquartzites, that should be mentioned first of all. But neoformation quartz can be recognized only rarely and imprecisely, and therefore, the sizes and outlines of the initial quartz grains can be established approximately, only in exceptional cases. Sometimes the intergranular spaces are filled up with microquartz or cryptocrystalline kaolinite concentrations. Isolated grains or tiny siderite agglomerations (sample 14) or fine-grained pyrite, sometimes associated with calcite, as well as secondary ferric oxides powder are observed sporadically. The presence of very small carbonaceous fragments, which appear almost everywhere in the series, and of bituminous matter, sometimes insinuated along fissures or along cleavage directions of micas, in fact just like ferric oxides, complete the petrographic picture of these rocks.

b) *Quartzitic microconglomerates*

These rocks (collected only from the Uteris mining field) can be somehow assimilated to the orthoquartzites, the grains being replaced by small (millimetric up to centimetric) fragments of metaquartzites and vein quartz that come into touch, protecting the interfragmentary spaces filled with a quartzitic gritty matrix. The fragments are covered with a fine film of ferric oxides, overgrowth quartz being very rarely identified. Just like in the case of orthoquartzites, the grain interlock along sinuous lines. Muscovite, less than 15%, shows various degrees of kaolinization, and biotite, sporadic, is partly chloritized or kaolinized, ferric oxides being removed in the process. Locally there occur small independent kaolinite patches and, quite rarely, an idiomorphic zircon grain released by biotite alteration.

c) *Quartzito — kaolinitic sandstones*

These rocks, identified in the foot-wall of coal bed 3, show similar grain size and composition to those of orthoquartzites and orthoquartzitic microconglomerates. The difference consists in the presence in higher quantities of kaolinite, which makes up a pellicular cement or fills the intergranular spaces. Muscovite is, in this case, as well, kaolinized, intermediate stages being noticed sometimes, with the extremities open in a fan or even reaching the stage of millimetric worm-like particles. These forms, called „leverrierite" by Termier (1890) were also described in the clays accompanying the bauxites in the Haţeg Basin (Papiu et al., 1971). The mineralogical composition of these rocks is dominated by lithic grains (D = 0.5 — 2 mm) 50 — 60 %, followed by quartz grains (D = = 0.12—0.75 mm) 25—45 %, with subordinate cryptocrystalline kaolinitic cement 5—25 %, and tourmaline and pyrite in places.

d) *Clayey — silty shales*

Silty clay interbeds, more or less indurated and even laminated, are sometimes associated with fireclays or with quartzitic arenites. The samples from the Uteriş mining field consist of an intimate mixture of clay and detrital material of silty sizes. So, sample 12 is built up 70% of finely triturated muscovite, fresh in proportion of 30 %, the remaining part being to a great extent kaolinized. Detrital quartz is also found, represented by a dominant silty fraction, subordinately accompanied by psammitic grains (D = 0.1—0.25 mm) relictly elongated, angular or even splintery. The argillaceous matter is pigmented in greenish, probably due to the presence of fine dispersion chlorites. Star-like and partly oxidized sphenosiderite concretions, 1—1.5 mm in diameter, also appear in the rock, representing 2—3 % of its mass. In the clayey — silty shales of the Covăcia mining field, these formations are missing, and detrital quartz has, to a greater extent, arenitic dimensions, the rock also containing quartzite grains. The muscovite, in various degrees of kaolinization, shows a large grain size range, from fine sericitic powder (less than 0.015 mm) up to flakes of 0.30 mm.

e) *Coarse kaolin with sideritic concretions*

The rock makes up an intercalation in the clays in the Uteriş mining field and is made up of well crystallized kaolinite, associated with sericite, probably engendered from the „in situ'' alteration of a feldspathic deposit. The large-sized kaolinite (or maybe dickite) crystals are probably generated from diagenetic recrystallization. Quartz grains occur sporadically in these rocks. The muscovite flakes are more frequent (10—15%), and usually partly kaolinized, argillization taking place from the periphery towards the centre.

5. Chemical-mineralogical study of clays

The samples collected from the two mining fields were analyzed with respect to the chemical (tables 1 and 3) and mineralogical (tables 2 and 3) composition. A sample of bituminous shale (table 4) was also analyzed from the chemical-mineralogical point of view (only on the bulk sample).

a) *Chemical composition*

The main oxides making up clays — silica and alumina — represent, in most cases, 80—90% of the rockmass. The contents have orders of magnitude sensibly close for the bulk sample and the fraction under 2 microns and show average values similar to fireclays and common clays (tables 1 and 3). In the case of silica, fireclays have a somehow lower mean, with more reduced variation range (mean 49.6% as compared

TABLE 1

Chemical composition of the Lower Jurassic clays of the Anina fireclay deposit (%)

No.	Sample no.	Location	Type of clay	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	H_2O^+	CO_2	S
								Bulk sample									
1	2c	Uteriș	Refractory = Fireclays	51.91	1.40	33.77	0.38	0.20	traces	0.21	0.05	0.93	0.03	0.06	11.24	—	0.10
2	2c′	— ,, —		48.04	0.96	36.67	0.88	traces	traces	0.30	0.04	1.36	0.30	traces	11.63	—	0.06
3	2a	— ,, —		50.02	1.06	32.48	1.97	0.69	0.04	0.26	0.06	2.14	0.40	0.07	10.23	—	traces
4	2b	— ,, —		48.53	1.01	35.97	0.94	traces	traces	0.26	0.06	1.33	0.38	traces	11.57	—	0.05
5	2b′	— ,, —		50.66	1.06	34.33	0.90	traces	traces	0.23	0.05	1.52	0.38	traces	11.10	—	0.06
6	8	— ,, —		48.83	1.00	36.15	0.23	0.08	traces	0.24	0.06	2.08	0.16	0.06	10.91	—	0.09
7	9	— ,, —		48.28	0.72	35.66	0.78	0.08	traces	0.48	0.05	2.14	0.16	0.06	11.60	—	0.12
8	16	— ,, —		50.66	1.00	34.49	0.17	0.70	traces	0.24	0.03	1.69	0.13	0.05	10.62	—	0.12
9	17	— ,, —		51.69	0.96	32.93	1.07	0.22	0.05	0.29	0.02	1.80	0.18	0.06	10.40	—	0.12
10	21a	Covăcia		47.49	1.00	35.88	1.65	0.27	traces	0.31	0.04	2.01	0.16	0.08	10.73	—	0.09
11	21c	— ,, —		50.39	1.21	33.95	1.21	0.08	traces	0.30	0.04	1.83	0.16	0.07	10.91	—	0.32
12	5c	Uteriș	Non-refractory = Common	50.83	1.00	33.36	0.49	0.24	traces	0.25	0.04	2.00	0.16	0.05	11.56	—	0.11
13	6	— ,, —		51.89	1.18	32.07	2.06	0.09	traces	0.22	0.05	1.62	0.10	1.18	10.57	—	0.04
14	23	Covăcia		52.68	1.17	32.63	1.58	0.08	0.05	0.30	0.04	1.91	0.21	0.11	9.74	—	traces
15	25a	— ,, —		54.83	1.05	31.13	0.54	0.55	0.05	0.21	0.06	2.17	0.22	0.08	9.13	—	0.03
16	25b	— ,, —		56.28	0.85	29.45	1.40	0.11	0.08	0.25	0.05	1.80	0.27	0.09	9.16	—	0.07
								Clay fraction (less than 2 microns)									
1	2c′	Uteriș	Refractory	46.19	0.80	38.33	1.13	undt.	—	0.21	0.06	0.46	—	—	12.65	—	—
2	2a	— ,, —		45.61	0.36	38.84	0.72	0.33	—	0.23	0.07	1.68	—	—	12.75	—	—
3	2b′	— ,, —		45.53	0.89	38.08	0.75	0.22	—	0.22	0.05	1.07	—	—	13.14	—	—
4	8	— ,, —		45.74	0.98	38.20	1.13	undt.	—	0.19	0.07	1.06	—	—	12.10	—	—
5	9	— ,, —		47.54	0.79	37.51	1.04	undt.	—	0.21	0.05	0.89	—	—	12.18	—	—
6	16	— ,, —		47.34	0.89	37.46	1.20	undt.	—	0.20	0.06	0.54	—	—	11.57	—	—
7	17	— ,, —		46.80	0.85	37.82	1.38	undt.	—	0.21	0.05	1.27	—	—	12.20	—	—
8	21a	Covăcia		44.65	1.10	38.82	0.47	0.29	—	0.19	0.07	1.41	—	—	12.59	—	—
9	21c	— ,, —		45.24	1.37	38.70	0.35	0.27		0.20	0.07	1.33	—	—	11.47	—	—
10	23	Covăcia	Non-refractory	45.57	0.92	37.86	0.77	0.38	—	0.17	0.07	0.74	—	—	13.31	—	—
11	25a	— ,, —		46.68	0.96	37.69	0.70	0.25	—	0.18	0.06	0.65	—	—	12.55	—	—
12	25b	— ,, —		45.33	1.13	38.46	0.92	0.19	—	0.14	0.05	1.34	—	—	12.73	—	—

TABLE 2

Mineralogical composition of the Lower Jurassic clays of the Anina fireclay deposit (%)

No.	Sample no.	Type of clay	Kaolinit*	Dickite	Hydromicas	Chlorites	Hematite	Pyrite	Feldspars	Quartz
			Bulk sample							
1	2c		46.4	30.0	7.8	—	0.2	0.3	—	10.9
2	2c′		52.5	27.7	11.5	1.9	0.7	0.2	2.5	4.4
3	2a		41.4	20.5	18.1	—	2.0	—	3.4	8.8
4	2b		50.5	28.2	11.2	—	0.8	0.1	3.2	4.8
5	2b′	Refractory=	45.1	28.1	12.8	—	0.8	0.2	3.2	8.7
6	8	Fireclays	47.8	25.4	17.6	—	0.2	0.1	1.3	5.1
7	9		42.0	29.8	18.1	—	0.8	0.2	1.3	5.4
8	16		63.4	7.8	14.2	2.0	—	0.3	1.1	8.4
9	17		45.0	23.3	15.2	0.6	0.7	0.3	1.5	12.8
10	21a		50.1	19.5	16.9	0.8	1.4	0.3	1.3	4.6
11	21c		49.1	20.6	15.4	—	1.2	0.9	1.3	9.0
12	5c	Non	45.7	20.6	16.9	0.7	0.4	0.3	1.3	10.1
13	6	refrac —	41.2	22.7	13.7	—	2.0	0.1	0.8	14.4
14	23	tory=	45.3	20.4	16.1	—	1.6	—	1.8	13.0
15	25a	Common	46.6	13.1	18.3	1.6	0.2	0.3	2.0	17.5
16	25b		38.4	20.0	15.2	0.3	1.4	0.1	2.4	20.5
			Clay fraction (less than 2 microns)							
1	2c′		91.8	—	5.7	—	0.9	—	—	0.7
2	2a		76.0	—	20.7	0.9	0.5	—	—	—
3	2b′		82.9	—	13.2	0.6	0.6	—	—	—
4	8	Refrac-	84.7	—	13.1	—	1.0	—	—	—
5	9	tory	84.5	—	11.0	—	0.9	—	—	2.7
6	16		88.7	—	6.7	—	1.1	—	—	2.8
7	17		78.9	—	15.7	—	1.2	—	—	2.5
8	21a		77.5	—	17.4	0.8	0.3	—	—	—
9	21c		80.4	—	16.4	0.8	0.3	—	—	—
10	23	Non-re-	87.0	—	9.1	1.1	0.6	—	—	0.5
11	25a	fractory	87.7	—	8.0	0.7	0.6	—	—	1.7
12	25b		82.0	—	16.5	0.5	0.7	—	—	—

* = For the clay fraction the values also include the dickite contents.

to 53.3%) for the bulk sample, due, of course, to the presence of a higher content of detrital material in common clays; the clayey fraction shows almost identical means (46 %). A similar, but reversed situation is noticed in the case of alumina, which, in bulk samples is to be found in a little higher proportion in fireclays (mean 34.7%) than in common clays (mean 31.7 %), while in fine fraction, the means are practically identical (38%) for both types of clay. Although the variation range of alumina is smaller than that of silica, a reversed ratio is noticeable between these

TABLE 3

Variation range and average contents of the main chemical and mineralogical components of the Lower Jurassic clays of the Anina fireclay deposit (%)

Component	Refractory clays = Fireclays				Non-refractory clays = Common			
	Bulk sample n = 11		Clay fraction n = 9		Bulk sample n = 5		Clay fraction n = 3	
	Δ	x̄	Δ	x̄	Δ	x̄	Δ	x̄
Chemistry								
SiO_2	47.5–51.9	49.6	44.7–47.5	46.1	50.8–56.3	53.3	45.3–46.7	45.9
Al_2O_3	32.5–36.7	34.7	37.5–38.8	38.2	29.5–33.4	31.7	37.7–38.5	38.0
Fe_2O_3	0.2– 2.0	0.9	0.3– 1.4	0.9	0.5– 2.1	1.2	0.7– 0.9	0.8
K_2O	0.9– 2.1	1.7	0.5– 1.7	1.1	1.6– 2.0	1.9	0.7– 1.3	0.9
H_2O^+	10.2–11.6	11.0	11.5–13.1	12.3	9.1–11.6	10.0	12.6–13.3	12.9
Fe_2O_3T	0.3– 2.7	1.2	0.6– 1.4	1.0	0.8– 2.2	1.5	1.0– 1.2	1.1
Mineralogy								
Kaolinite *	41.4–63.4	48.5	76.0–91.8	82.8	38.4–46.6	43.4	82.0–87.7	85.5
Dickite	7.8–30.0	23.7	—	—	13.1–22.7	19.4	—	—
Hydromicas	7.8–18.1	14.4	5.7–20.7	13.3	13.7–18.3	16.0	8.0–16.5	11.2
Chlorites	0.0– 2.0	0.5	0.0– 0.9	0.3	0.0– 1.6	0.5	0.0– 1.1	0.8
Hematite	0.0– 2.0	0.8	0.3– 1.2	0.8	0.2– 2.0	1.1	0.6– 0.7	0.6
Pyrite	0.0– 0.9	0.3	—	—	0.0– 0.3	0.2	—	—
Feldspars	0.0– 3.4	1.8	—	—	0.8– 2.4	1.7	—	—
Quartz	4.4–12.8	7.6	0.0– 2.8	1.0	10.1–20.5	15.1	0.5– 1.7	0.7

* = For the clay fraction the values also include the dickite contents; n = number of samples; Δ = Variation range; x̄ = Arithmetic mean.

two main oxides. Thus, the maximum quantity of silica (55.3%) is found — in bulk sample — in common clay, the poorest in alumina (29.5 %), from the Covăcia mining field and conversely, the maximum content of alumina (37 %) appears in a fireclay from the Uteriș mining field, where is also found one of the most reduced silica percentage (48 %). That is due to the supply of detrital material which diminishes the clay content to a greater extent in common clays than in fireclays and justifies the two remarks concerning the clayey fraction, namely :

— extremely close values to both types of clays, for both oxides;

— extremely small variation range (sometimes practically absent) in the case of the clayey fraction, in comparison with the bulk samples.

In conclusion, the difference between fireclays and common clays of the Anina region consists in the presence of detrital material, particularly of quartz, in higer percentages in common clays as compared with fireclays.

With the exception of H_2O, the other oxides composing the fireclays and the common clays of Anina vary around 1% (TiO_2, Fe_2O_3, Fe_2O_3 T) or are clearly subunitary, at the first decimal (MgO, Na_2O) or

TABLE 4

Chemical-mineralogical composition of a Middle Liassic bituminous shale of the Anina area (Banat) (%)

Chemical analysis			Mineralogical analysis			Bituminological analysis	
Oxide	Bulk sample	Devoid of organic matter	Mineral	Bulk sample	Devoid of organic matter	Component	Bulk sample
SiO_2	39.48	49.91	Kaolinite	60.5	76.5	Bitumen A	0.9368
TiO_2	0.78	0.99					
Al_2O_3	26.57	33.59	Hydromicas	6.3	8.0	Loss in HCl	1.6
Fe_2O_3	2.02	2.55	Chlorites	1.1	1.5	Bitumen C	0.1309
FeO	0.12	0.15	Hematite	2.0	2.5	Organic carbon	11.87
CaO	0.10	0.13	Pyrite	—	—		
MgO	0.36	0.46	Feldspars	—	—	Kerogen	14.48
MnO	traces	traces	Quartz	8.0	10.2	Bituminization degree	7.9
K_2O	0.75	0.95	Organic matter	20.7	—	Bituminization index	106.8
Na_2O	0.13	0.16					
P_2O_5	0.09	0.11	TOTAL	98.6	98.7	Total organic matter	15.55
S	traces	traces					
CO_2		—					
H_2O^+	8.65	11.21					
Organic matter	20.70	—					
TOTAL	99.75	100.21					

at the second, with insignificant exceptions (FeO, P_2O_5, S) or with no exception at all (MnO and especially CaO). The minimum participation of Ca correlated with the total lack of CO_2 emphasizes the general absence of calcite and of other carbonates, although the fireclay formation is underlain by the Triassic paleokarst. This situation resembles that of the Wealdian bauxites of the Pădurea Craiului Massif, with Upper Jurassic limestone bedrock.

The only constant element in all samples, supraunitary and with extremely small variation range (1—2% in the bulk sample and 0.5—1.7% in the fine fraction) is potassium (K_2O). It is linked with illites and with detrital muscovite, probably rather abundant in the bulk sample in comparison with the clayey fraction (where it is diminished by pipetting).

Iron, the main indicator of the chemical conditions of sedimentation and diagenesis shows for the total content (Fe_2O_3T), similar variation range and means at both types of clay and indicates, of course, the same continental source area (table 3). FeO, linked in silicates (prevailingly chlorites), is only poorly represented in fireclays, especially in the fine fraction, being more frequent in common clays. Na_2O, linked with feldspars (detrital albite) is altogether absent from the fraction under

2 microns. Sulphur, present as pyrite in the bulk sample and phosphorus, correlatable with the contents in organic matter of the originary muds, are also missing. TiO_2, about 1%, is related to the presence of aluminium as prevalent element and, to a certain extent, also to the detrital material, which would justify a certain superiority in the bulk sample, compared with the clayey fraction. Mn and Ca show insignificant contents, the former being practically absent from the clayey fraction. They are of exogene origin or are adsorbed as exchangeable cations by clay minerals.

b) *Mineralogical composition*

The main mineralogical feature of the Anina fireclays is the massive presence (up to 30%) of dickite, accompanying kaolinite, the dominant mineral (table 2). Dickite was also identified in the other Lower Liassic fireclays and common clays, but in much lower percentages, at Cristian-Holbav (Brașov) and only accidentally in the Pădurea Craiului Massif (Papiu et al, 1969, 1970). Kandites represent therefore, the main minerals in these rocks, with means of 72% in the bulk samples of fireclays and of 63% in common clays. In the fine fraction, kaolinite + dickite exceed 90% (sample 2 c) in fireclays and reach 88% in common clays, the means being 83% and 85% respectively (table 3). In bulk samples, the kaolinite content is about twice higher than the dickite content. In fact, the latter considered in the past to be related exclusively to the magmatic activity, is proved by recent researches to be also exogene. With a similar genesis, dickite was also mentioned in the Albian clayey-bauxitic complexes of the Hațeg Basin (Papiu et al., 1971).

Illite + detrital muscovite, minerals referred to by the generical name of „hydromicas", include all the silicates of „muscovite type". As a matter of fact, the whole quantity of illite from the Lower Jurassic lacustrine clays of Anina is probably inherited. Hydromicas occur in smaller quantities in the fine fraction in which kandites are about 4 times more abundant. Chlorites (both ferrous and magnesian), present in less than half of the investigated samples, do not exceed 2 %. It is possible that, at least partly, the kaolinite from these clays should be born by processes of degradation in lacustrine or palustrine environment, following the pH reduction due to an intense bacterial activity. The presence of mixed-layer minerals, identified by X-ray in small quantities in the clayey fraction, confirms that such degradation processes took place in the environment of accumulation of these rocks. Moreover, these processes could release important amounts of free silica that cemented the orthoquartzitic rocks. The possible presence of the refractory kaolinite (pM, fire-clay kaolinite) identified in X-ray only by Neacșu (1965) would suggest the existence of some strong acid lacustrine or palustrine episodes, according also to experimental data (Oberlin et al., 1962).

The reducing environment as well as the proximity of the coal sequences are indicated by the presence of pyrite, in small supplies, but in almost all the samples (with the exception of a fireclay from the Uteriș mining field and a common clay from the Covăcia mining field).

Considering the contents in kanditic minerals (kaolinite + dickite), the hydromicas + chlorites and the supply of granular detrital material (quartz + feldspars), a ternary diagram has been drawn up (fig. 3), from which results a quite similar composition with a slight tendency of concentration of aluminous minerals in refractory clays. The fact that a num-

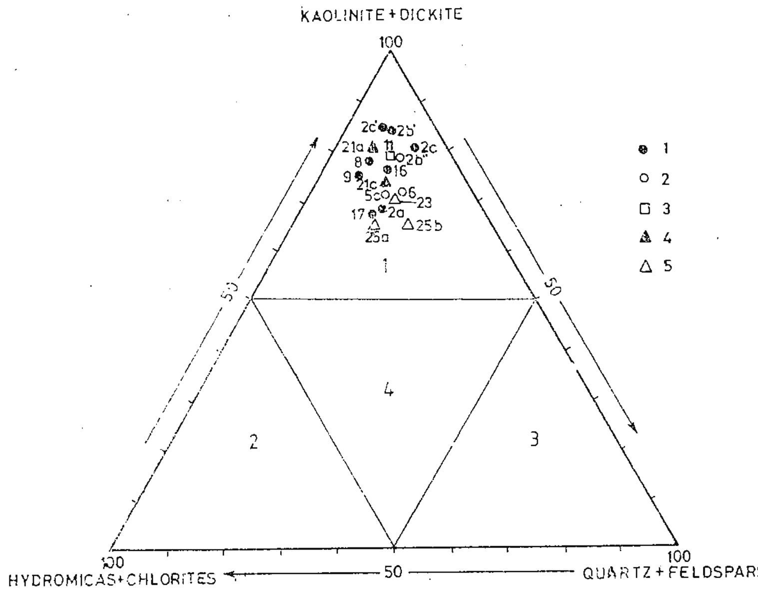

Fig. 3. — Mineralogical classification of the clays of the Lower Jurassic Fireclay Formation of Anina (Banat). 1, Uteriș mining field (fireclays); 2, Uteriș mining field (non-refractory clays); 3, Uteriș mining field (bituminous shale); 4, Covăcia mining field (fireclays); 5, Covăcia mining field (non-refractory clays).

ber of common clays show higher percentages of kaolinite in comparison with certain fireclays, would represent an argument for explaining the refractoriness by the presence of pM-kaolinite.

c) *Bituminous shals*

Besides the Lower Liassic refractory and common clays a Middle Liassic bituminous shale sample, containing 20% organic matter, was also analysed. The chemical analysis recalculated in the absence of organic matter, is approximately ranging in the limits of variation of the chemistry of the refractory and common clays previously examined, and also, the mineralogical composition is quite similar to that of fireclays (table 4).

These results point out the possibility of a complex utilization of this type of rocks, after extracting the organic matter. As for the bituminological constitution (determined by dr. eng. M. Filipescu), it does not correspond to an oil source rock, but indicates the bituminous shales for being used as fuel rocks.

G. Genetic considerations

The Lower Liassic fireclays of Anina, just like the other fireclays in Romania, are characteristic of the Gresten continental facies and are associated with common silty rocks, with sandstones and orthoquartzitic microconglomerates and with coal beds. The pyrophyllitic formation at Schela-Gorj, accompanying the anthracite deposits, corresponds to deposits synchronous and isopical with the above mentioned ones, affected by a slight metamorphism in an Alpine orogenic phase.

We consider these deposits to make a continental regressive phase at the end of the Triassic and the beginning of the Jurassic, starting with a macroclastic lacustrine sedimentation (sandstones and microconglomerates) followed by a clayey microclastic lacustrine accumulation. This much longer phase is characterized by a water environment with intense bacterial activity, its features varying in time and space. On the crystalline area in which originated the material supplied in these lakes, a vast lateritic alteration took place, which generated a great quantitiy of kaolinite. It accumulated at the same time with the hydromicas supplied by the preexisting clays, both being subsequently subject to a series of primary diagenetic processes. The kaolinitic clayey material, as well as the dickitic one (maybe of volcanic origin) could possibly evolve in refractory kaolinite, under the conditions of a very low pH and equally of a low redoxipotential. As for illite and the other minerals of the muscovite type, they were probably subject to a degradation process leading to kaolinite neoformation. Vatan (1962) shows that the transformation of illite in kaolinite is accompanied by the release of free silica (about 20%) which can quartzify the nearby sands, as well as by alkalis (ca. 15%). That is how can be explained in our case the silicification of the orthoquartzitic rocks at the base of the formation. At the same time, in a first phase, iron can be linked under the form of leptochlorite, possibly also by reacting with the released silica. In a more advanced reducing stage, the conditions have been met for the precipitation of siderite, identified in places, and in the last phase, after the decomposition of the organic matter and the bacterial activity that characterize the passage to the final, palustrine stage, pyrite and ferrous monosulphide were formed. The last ones pigment in black the clays, together with the bituminous and carbonaceous organic matter. This final palustrine phase with peat bogs is reflected in the present-day coal deposits.

In more advanced diagenesis phases descendant infiltrations of reducing solutions could have been produced, that might have reduced iron, with local formation of ferrous minerals. Red clays and silty clays correspond either to clearly oxidizing episodes or to synchronous and heteropical local facies. The succession of these processes can be summed up in the following way :

$Fe_2O_3 \cdot nH_2O$ $\longrightarrow$	$+SiO_2$ $\longrightarrow$	$+CO_2$ $\longrightarrow$	$+H_2S$ $\longrightarrow$	$+O_2$
(primary supply)	(leptochlorite) slightly reducing environment	(siderite) reducing environment	(sulphide) ultra-reducing environment	(oxide) secondary oxidizing environment

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STUDIUL CHIMICO-MINERALOGIC AL FORMAŢIUNII ARGILELOR REFRACTARE JURASIC INFERIOARE DE LA ANINA (BANAT)

(Rezumat)

Formaţiunea eojurasică în facies de Gresten din regiunea Anina debutează cu conglomerate grosiere, peste care se dispune o secvenţă argilodetritică alcătuită din alternanţe de gresii micacee, argiloase, şisturi cărbunoase, cărbuni și argile refractare („orizontul cărbunos"). Urmează „orizontul șisturilor bituminoase" cu concrețiuni sferosideritice și intercalații cărbunoase, care trece la partea superioară la argile nisipoase cenușii.

Argilele refractare sînt legate de orizontul inferior cu cărbuni, fiind urmărite pe ambele flancuri ale anticlinalului Anina. Zăcămîntul de huilă și argilă refractară de la Anina este puternic tectonizat, determinînd delimitarea mai multor blocuri tectonice grupate în cîteva cîmpuri miniere. Materialul studiat provine din lucrările cîmpurilor miniere Uteriș și Covăcia. Argilele refractare sînt asociate cu ortocuarțite, microconglomerate cuarțitice, gresii cuarțito-caolinitice, șisturi argilo-siltitice și caoline grosiere cu concrețiuni sideritice (fig. 1 și 2).

Studiul petrografic al rocilor detritice grosiere arată o mineralogie uniformă, dominată de granule sau elemente de cuarț metamorfic și metacuarțite, la care se adaugă în mod constant muscovitul proaspăt sau în diferite grade de illitizare sau caolinitizare. Este notabilă totala absență a feldspaților. Cuarțul de neoformație apare arareori. Sporadic apar granule izolate sau minuscule aglomerări de siderit sau pirită fin granulară, asociată uneori cu calcit, precum și pulberi de oxizi ferici de natură secundară. Cîteodată se întîlnesc fragmente cărbunoase, precum și substanțe bituminoase. Rocile mai fin granulare prezintă amestecuri intime de argilă și material detritic angular de dimensiuni siltice.

Compoziția chimică a rocilor argiloase se caracterizează prin valori ale conținuturilor sensibil apropiate pentru proba brută și fracția sub 2 microni și prezintă medii asemănătoare la argilele refractare și la cele comune (tab. 1 și 3). Argilele refractare sînt totuși mai bogate în alumină și mai sărace în silice decît cele comune, deosebirea fiind determinată de prezența în cantități mai ridicate a materialului detritic (în special cuarț) în acestea din urmă.

Caracteristica principală a rocilor argiloase de la Anina este prezența masivă (pînă la 30%) a dickitului alături de caolinit — mineralul dominant (tab. 2). Kanditele constituie în medie 72% din proba brută și ajung la peste 90% în fracția sub 2 microni. Subordonat apar hidromice, clorite și minerale interstratificate. Prezența piritei în mici cantități, dar aproape în toate probele, sugerează caracterul reducător al domeniului de sedimentare și apropierea domeniului cărbunos. Clasificarea mineralogică prezentată sub forma unei diagrame ternare (fig. 3) indică o alcătuire foarte asemănătoare pentru toate rocile argiloase, cu o ușoară tendință de concentrare a mineralelor aluminoase în argilele refractare. Este interesant de notat că șisturile bituminoase supraiacente formațiunii cu argile refractare au o compoziție mineralogică și chimică asemănătoare cu a argilelor descrise mai sus (tab. 4).

Depozitele liasic inferioare în facies de Gresten de la Anina sînt rezultatul unei faze regresive continentale, care debutează printr-o sedimentare lacustră macroclastică (gresii și microconglomerate) urmată de o acumulare lacustră argilo-microclastică. Această fază se caracteriza printr-un mediu cu ape cu pH scăzut, în care se manifesta o intensă activitate bacteriană. Pe aria cristalină de pe care provenea materialul sedimentar avea loc o vastă alterare lateritică generatoare de caolinit, care se acumula odată cu hidromicele din rocile argiloase preexistente, suferind apoi o serie de procese diagenetice primare. Illitul şi celelalte minerale de tipul muscovitului sufereau probabil un proces degradativ cu transformare în caolinit. În acest fel caolinitul şi dickitul din argilele refractare provin atît prin remanierea materialului lateritic cît şi prin neoformare pe seama mineralelor hidromicacee degradate în mediul acid palustru. Acest ultim proces era însoţit totodată de eliberarea de silice care putea produce silicifierea rocilor ortocuarţitice din baza formaţiunii. În acelaşi timp fierul poate fi legat într-o primă fază sub formă de leptoclorit, reacţionînd eventual şi cu silicea eliberată. Ulterior, într-un stadiu reducător mai avansat au fost realizate condiţii pentru precipitarea sideritului, iar în ultimul stadiu, în urma descompunerii materiei organice şi activităţii bacteriene, care caracterizează trecerea la stadiul final palustru, au luat naştere pirita şi monosulfura feroasă. Această fază este reflectată în orizonturile cărbunoase actuale. Rocile argiloase de culoare roşie corespund fie unor episoade net oxidante, fie unor faciesuri locale sincrone şi heteropice. Succesiunea acestor procese poate fi sistematizată după cum urmează :

$Fe_2O_3 \cdot nH_2O$	$\rightarrow$	$+SiO_2$	$\rightarrow$	$+CO_2$	$\rightarrow$	$+H_2S$	$\rightarrow$	$+O_2$
(aport primar)		(leptoclorit) mediu slab reducător		(siderit) mediu reducător		(sulfură) mediu ultra-reducător		(oxid) mediu oxidant secundar

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2. ZĂCĂMINTE

CHEMICAL-MINERALOGICAL STUDY OF THE LOWER JURASSIC FIRECLAY FORMATION OF CRISTIAN-HOLBAV (BRAŞOV DISTRICT)[1]

BY

VICTOR CORVIN PAPIU[2], VASILE IOSOF[3], SILVIU RĂDAN[2]

Lower Jurassic. Fireclays. Clays. Chemical and mineralogical study. Kaolinite. Dickite. Detrital material. Lacustrine detrital phase. Cyclic sedimentation. East Carpathians-Crystalline-Mesozoic Zone — Braşov Mountains — Codlea Zărneşti Zone

Abstract

The paper presents a chemical and mineralogical study of the Lower Liassic fireclays and common clays accompanying them, as well as a microscopic study of associated rocks (quartzitic sandstones, clayey siltstones and silty-clayey shales with pyroclastic material). The main clay minerals are kaolinite, dickite (sometimes in quite high amounts — — 21%), with subordinate hydromicas and chlorites. Kandites generally represent more than 50% of the composition of clays. The detrital material (quartz, feldspars, micas) is totally subordinate and is followed by organic debris (+ bitumen) and precipitation minerals (hematite, goethite, pyrite). The association of these deposits with coal suggests a more or less cyclic sedimentation, represented by a lacustrine-detrital phase during which the future quartzitic arenites were accumulated, followed by a palustrine microclastic phase in the course of which clays were deposited probably in a very acid environment, and finally by a palustrine one, with peat bogs where coal was formed.

Résumé

Étude chimique-minéralogique de la formation des argiles réfractaires du Jurassique inférieur de Cristian-Holbav (district de Braşov). L'ouvrage présente une étude chimique et minéralogique des argiles réfractaires du Lias inférieur et des argiles communes qui les accompagnent,

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ainsi qu'une étude microscopique des roches associées (grès quartzitiques, argilites et schistes siltito-argileux à matériel cinéritique). Les principaux minéraux argileux de ces roches sont la kaolinite et la dickite (celle-ci parfois en quantités assez grandes — 21 %), avec hydromicas et chlorites subordonnées. Les kandites représentent généralement plus de 50 % de la composition des roches argileuses. Le matériel détritique (quartz, feldspath, micas) est tout-à-fait subordonné, et il est suivi par le détritus organique (+ bitumes) et les minéraux de précipitation (hématite, goéthite, pyrite). L'association de ces dépôts à charbon nous mène à la conclusion de l'existence d'une sédimentation plus ou moins cyclique, dans laquelle, après une phase lacustrino-détritique pendant laquelle se sont accumulées les futures arénites quartzitiques, a suivi une phase microclastique palustre, pendant laquelle se sont déposées les argiles, probablement dans un milieu très acide et la phase finale palustre, à turbières où se sont formés les charbons.

The Cristian-Codlea-Vulcan-Holbav region is situated in the Brașov district, in a very accessible area, well known for its coal and fireclay deposits and investigated, for this reason, since the second half of last century (Brem, 1854). It was Stur (1860) who, based on paleoflora, established the Liassic age of the Mesozoic deposits at Holbav and Meschendörfer (1860) who delineated the geology of the formations at Cristian and Vulcan. In their well known synthetic paper on the geology of Transylvania, Hauer and Stache (1863) presented a series of rather advanced data on this region, but the first systematic study, accompanied by a sketch of geological map and by geological sections was that by Wachner (1913) who also referred to a series of mining works that had been carried out in the region. It is Jekelius (1915, 1923, 1927) who thoroughly investigated this area of the East Carpathians, whose studies largely contributed to the knowledge of the geology of the Brașov-Codlea region. Ample paleobotanic studies as well as systematic data on the fireclays of this region are due to Semaka (1954, 1956, 1957, 1962, 1965, 1967) who also approached economic aspects. That author established the stratigraphic sequence of the Liassic formation of the Vulcan-Holbav region, showing that the basal transgressive conglomerates, 10 m thick, are supported by Triassic limestones and overlain by the complex with clays and coals (30 m). The clay and coal complex contains a coal bed between two beds of fireclay associated with common clays, followed by an upper sequence (100—200 m) of gritty-argillaceous rocks with local interbeds of fireclays. The geology of the deposits is complicated and there are frequent facies variations. Năstăseanu (1958) carried out a stratigraphic study insisting on the frequent facies variations which make it practically impossible to establish a clear synthetic stratigraphic column, and emphasized the lithological resemblances of this formation with the Liassic formation at Anina. The region was subsequently studied by Vîlceanu (1960), Săndulescu (1964), Patrulius et al. (1968, 1969) who established, among other things, the ages of the three complexes building up the Liassic formation whose basement does not crop out, being encountered only in boreholes and mining workings. Antonescu presented a series of novel stratigraphic data, resulted from palynological investigations and included in a complex and detailed chemical-mineralogical study of this fireclay-bearing formation (Papiu et al., 1970). The mining activity in the Cristian-Holbav zone has been stopped in 1983 when, the last fireclay mine — Poiana Poienița — was closed because of working difficulties.

I. Geological setting

The fireclays at Cristian-Holbav belong to the Liassic formation in Gresten facies and are associated with coal deposits, like most fireclays on the territory of Romania. The Eo-Jurassic deposits in the region unconformably overlie the Triassic formation, reaching about 500 m in thickness and are included in the northern zone of the Dîmbovicioara Couloir, being referred to two zones : a western one (Holbav-Vulcan-Codlea) and an eastern one (Cristian). In the western zone, the Liassic deposits start with a lower complex with coals and fireclays, associated with conglomerates, sandstones and common clays, overlain by an effusive-pyroclastic complex with porphyry and trachytic tuffs and tuffites, crossed by keratophyre, trachyte and basic porphyrite veins. After a disconformity, the sequence ends with „the upper coaly complex", characterized by fossiliferous quartzitic and conglomeratic sandstones. The presence of the *Pseudogrammoceras* and *Ptygmatoceras* species at the upper part of the complex indicates the Upper Toarcian age. According to Jekelius (1915), Săndulescu (1964) and Semaka (1965), the Eo-Jurassic formation in the Cristian area (eastern zone) is built up of five terms grouped in three complexes with the following succession : (1) clays with blocks of Triassic limestones followed by fireclays with small coal lenses and plant debris, correlated with „the lower coaly complex" of the Vulcan region (Sinemurian) ; (2 a) marly sandstones and arkoses associated with fossiliferous siltstones with *Griphaea cymbium* Lk. (Lower Carixian) and (2 b) spathic sandy limestones and calcareous sandstones containing *Liparoceras sp.*, *Pholadomya idaea* d'Orb. and brachiopods (Middle and Upper Carixian) ; (3 a) clayey and marly shales with *Amalteus margaritatus* Mont. and brachiopods (Domerian) and (3 b) calcareous sandstones and clayey-marly siltstones containing belemnites and the genus *Dactiloceras sp.* (Toarcian), overlain by quartzitic coarse sandstones which, according to Jekelius (1915) on paleontological criteria, ends the Toarcian complex.

Antonescu's palynological data (in Papiu et al., 1970) lead to the conclusion that in the Holbav-Codlea region there are two horizons of fireclays : (1) a lower one, corresponding to the „lower coaly complex" at Cristian (zone with *Nilsonia orientalis*) and (2) an upper complex corresponding to the shaley-sandy complex (Toarcian-Aalenian) at Cristian.

II. Occurrence of fireclays

The lower complex with fireclays of the Cristian zone unconformably lies on Anisian limestones and is included in two synclines, overturned and laminated on the eastern limb, cropping out in the Joader Valley and, more eastward, at Poiana Poienița and the Căldarea Brook. The samples have been collected from the old mining works open in the western limbs of those synclines.

At Poiana Poienița, the producing horizon shows 9 fireclay beds. The sequence examined in the section of the Poiana Poienița adit (fig. 1) includes a clayey horizon, 5 m thick, lying on the erosion surface of the

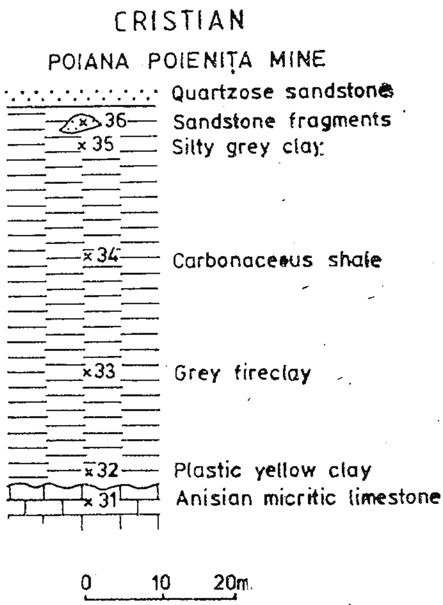

Fig. 1. — Lithologic column of the basal part of the Lower Jurassic fireclay Formation of Cristian-Poiana Poienița Mine and the location of samples.

Anisian micritic limestones and having plastic yellow clay in its base, overlain by carbonaceous clayshales (2.5 m) and then by unstratified grey fireclay (1.5 m) in whose upper part quartzitic sandstone blocks and fragments are included.

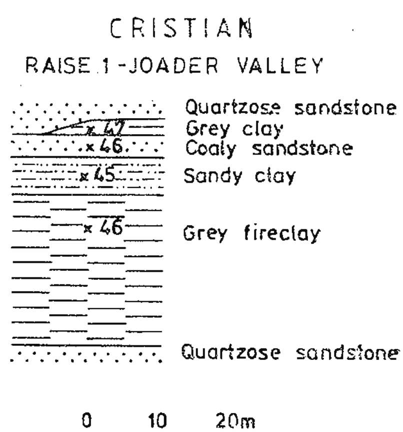

Fig. 2. — Lithologic column of the deposits of the Lower Jurassic fireclay Formation intersected by raise 1 of Cristian-Joader Valley and location of samples.

The producing horizon of the Joader Valley contains 2—5 discontinuous fireclay beds, difficult to correlate because of the intense faulting of the fireclay formation. The sequence traversed by the mine raise no. 1 (fig. 2) shows a quartzose sandstone in the base supporting the fireclay horizon (3 m), followed by another quartzose sandstone with clay intercalations.

In the Holbav area, the development of fireclays is very irregular; the formation shows a comprehensive lithological range, from clays str. s. up to coarse sandy clays and carbonaceous clays. There are 2—5 fireclay intercalations, from a few centimeters up to 2 m thick.

III. Petrographic study of associated rocks

A) *Quartzitic sandstones*

The orthoquartzites of the Cristian-Holbav area are present both in the footwall and at the upper part of the Gresten fireclay Formation, showing rocks of a great uniformity and a peculiar resemblance with the rocks of the same type associated with the similar Liassic fireclays of Anina or of the Pădurea Craiului Massif.

The orthoquartzitic rocks in the footwall of the fireclay bed at Holbav show grey colour and consist of grains of metamorphic quartz, oblong at times but generally isometric, interlocked after sinuous outlines. Two grain-size classes can be observed, sometimes with graded bedding trends, in which the fine material forms microzones about 0.5 mm thick. Thus, a sample of fine silty sandstone shows a bimodal grain-size distribution, characterized by 80—90% grains with D = 0.17—0.34 mm and 10—20 % grains with D = 0.025—0.050 mm. Like in the case of other quartzites accompanying the Liassic fireclays in Romania, no overgrowth cement is identified, and the quartz grains are locally surrounded by limonitic pigment probably formed at the expense of certain granular pyrites. Muscovite flakes, usually fresh, rarelier in various stages of kaolinization, often crushed and fractured between quartz grains, appear subordinately. Among heavy minerals, tourmaline has been identified only sporadically.

The quartzitic sandstones and the quartzites of the hanging wall and those included in the fireclay mass at Cristian (Fig. 1 and 2) contain fragments of carbonaceous grains, disposed on more or less continuous millimetric zones, sometimes corresponding to more argillaceous areas. Unlike the basal quartzites, the cement of these rocks is usually discernible. It consists of kaolinite associated with specific quartzose cement which is not microscopically identifiable.

The sandstones of Poiana Poienița are very heterogranular (D = = 0.17—0.70 mm) and contain fresher or partially epitaxically kaolinized muscovite (5—10%), of much larger sizes than that in the footwall of the fireclays. Cement-neoformation quartz is discernible neither in this case. Locally, scaly kaolinite occurs, filling the pores of rocks, sometimes associated with sericite or coating the quartz grains, just like a fine pellicular cement.

The deposits of the upper part of the Joader Valley sequence show a detrital, arenitic up to silty component (D = 0.08—0.25 mm) building up 70% of the rock mass and kaolinito-quartzitic precipitation cement. Muscovite occurs sporadically (up to 1%), fresh or slightly kaolinized, fan-like swollen at the extremities, like in most previously mentioned cases. Detrital biotite (sporadically chloritized), tourmaline (somehow more frequent than in previously mentioned lower quartzites) and acicular rutile (sometimes occurring as inclusions in the quartz grains) complete the list of minerals present in these mature rocks. Organic matter can also be encountered coating the grains like an opaque cement.

B) *Clayey siltstones*

These rocks appear as lenticular bodies in the fireclay mass and are built up of an intimate mixture of clay (40–60%), finely triturated muscovite (20–30%) and quartz grains (20–30%), less than 0.01 mm in size, pigmented by fine bituminous-carbonaceous material. Small coal and granular pyrite fragments and, on fissures, bitumen concentrations occur sporadically.

C) *Silty-clayey shales with pyroclastic material*

In the Holbav area silty-clayey shales with laminae of rather coarse detrital material and rich in pyroclastic material have been studied. Their stratigraphic position cannot be rigorously established. The rocks show remarkable graded bedding and banded structure pointed out by the alternation of submillimetric zones with clastic (silty up to arenitic) material with argillaceous microzones. The argillo-lutitic laminae are impregnated with bituminous-carbonaceous pigment, which account for the black colour of the rock. Sometimes the banded structure is determined only by a few quartz grains disposed in rows or small muscovite concentrations, as usual, in various degrees of kaolinization. These local microfacial characters result from the lacustrine or palustrine sedimentation of the deposit. The pyroclastic material constitutes 20–40% of the rock and is represented by feldspar crystalloclasts with shapes resulted from fragmentation, from almost idiomorphic grains up to fine splinters, 0.01–0.02 mm in size. They are accompanied by rare lithoclastic grains, less than 1.2 mm in size, in which fluidal structure can be observed sometimes with difficulty. The opaque, argillo-silty mass impregnated with bitumen and especially its finer zones probably contain a certain amount of vitroclastic material, but not optically identified.

IV. Chemical-mineralogical study of clays

The petrologic study of Liassic clays of the Cristian-Holbav region (Brașov district) is based on chemical, thermodifferential and X-ray analyses, carried out on 18 samples. Only 8 of them represent fireclays (5 from Cristian and 3 from Holbav). The clayey fractions (less than 2 microns) have been analyzed only for 6 samples of the Cristian area (3 fireclays and 3 common clays). The mineralogical qualitative analyses performed by physical methods were correlated with the chemical quantitative data (tab. 1) to obtain the probable mineralogical composition of these rocks (tab. 2). Some clays, especially those from Holbav have high con-

TABLE 1

Chemical composition of the Lower Jurassic clays of the Cristian — Holbav region (Brasov district) (%)

No.	Sample no	Location	Type of clay	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	H_2O^+	CO_2	S	Organic matter
							Bulk sample											
1	33	Cristian P.P.	Refractory = Fireclays, Grey	51.47	1.53	31.96	0.95	traces	traces	0.41	0.14	—	0.33	traces	12.50	—	0.05	—
2	48	Cristian J.V.	Refractory = Fireclays, Grey	54.69	1.16	26.78	2.41	0.70	0.07	0.30	0.20	2.03	0.17	0.10	10.69	—	0.65	—
3	43	— „ —	Refractory = Fireclays, Grey	59.76	1.18	26.27	2.39	0.44	traces	0.55	0.17	0.63	0.08	0.04	8.22	—	0.15	—
4	948A	— „ —	Refractory = Fireclays, Carbonaceous	47.61	1.96	24.86	3.60	1.63	0.10	0.60	0.18	1.96	0.27	0.08	7.35	—	0.84	9.09
5	949A	— „ —	Refractory = Fireclays, Carbonaceous	53.96	1.76	23.77	2.65	0.33	—	0.52	0.20	1.63	0.22	0.10	7.00	—	0.08	7.61
6	951A	Holbav	Refractory = Fireclays, Carbonaceous	46.00	1.95	33.21	1.26	1.56	—	0.30	0.18	1.70	0.22	0.09	11.32	—	—	1.90
7	952	— „ —	Refractory = Fireclays, Carbonaceous	52.33	1.16	20.63	5.26	1.72	—	0.27	0.23	1.71	0.24	0.10	7.04	—	—	7.83
8	954	— „ —	Refractory = Fireclays, Carbonaceous	27.92	1.18	21.01	4.81	1.66	traces	0.55	0.17	1.00	0.14	0.06	8.82	—	—	29.11
9	35	Cristian P.P.	Non-refractory = Common, Grey	64.92	2.34	18.73	1.14	0.55	0.05	0.29	0.16	1.44	0.21	0.08	6.36	—	0.23	4.00
10	32	— „ —	Non-refractory = Common, Grey	50.98	1.53	31.10	3.63	0.06	traces	0.56	0.24	1.98	0.21	0.06	9.70	—	0.07	—
11	40	Cristian J.V.	Non-refractory = Common, Grey	49.36	1.28	32.38	0.86	0.18	0.05	0.47	0.22	1.13	0.16	0.04	10.95	—	0.17	3.00
12	12	— „ —	Non-refractory = Common, Grey	66.83	1.26	21.27	2.71	0.24	traces	0.35	0.13	0.72	0.08	traces	6.24	—	0.10	0.08
13	47	— „ —	Non-refractory = Common, Grey	54.77	1.32	28.73	0.51	2.03	traces	0.79	0.17	—	0.39	traces	9.28	—	0.10	—
14	34	Cristian P.P.	Non-refractory = Common, Carbonaceous	45.00	1.15	29.66	2.62	0.20	traces	0.37	0.22	1.01	0.13	0.02	9.61	—	0.73	9.90
15	52	Holbav	Non-refractory = Common, Carbonaceous	46.01	1.39	26.56	5.18	0.10	traces	0.22	0.10	0.32	0.16	0.11	9.38	—	traces	9.91
16	53	— „ —	Non-refractory = Common, Carbonaceous	46.72	1.59	28.65	1.65	0.16	traces	0.39	0.14	0.61	0.24	0.08	9.01	—	0.10	10.50
17	54	— „ —	Non-refractory = Common, Carbonaceous	34.91	1.09	28.20	1.59	0.70	traces	0.18	0.10	0.97	0.14	0.07	9.51	—	0.17	22.07
18	56	— „ —	Non-refractory = Common, Carbonaceous	42.60	0.94	25.38	1.88	0.05	traces	0.20	0.04	—	traces	0.04	9.12	—	traces	19.72
							Clay fraction (less than 2 microns)											
1	33	Cristian P.P.	Refractory	46.15	0.93	35.19	0.72	0.57	—	0.40	0.14	1.75	—	—	13.29	—	—	0.76
2	48	Cristian J.V.	Refractory	46.58	1.01	35.24	2.43	—	—	0.25	0.08	0.90	—	—	12.98	—	—	0.94
3	43	— „ —	Refractory	46.62	0.97	34.84	2.68	—	—	0.29	0.10	1.29	—	—	12.12	—	—	1.19
4	35	Cristian P.P.	Non-refractory	47.57	2.49	34.10	1.63	—	—	0.31	0.07	0.78	—	—	11.94	—	—	1.74
5	32	— „ —	Non-refractory	44.69	0.40	36.03	1.89	0.22	—	0.28	0.18	1.80	—	—	14.06	—	—	—
6	47	Cristian J.V.	Non-refractory	45.73	1.06	34.68	3.08	—	—	0.38	0.11	1.95	0.07	—	11.98	—	—	1.53

P.P. = Poiana Poienița; J.V. = Joader Valley.

TABLE 2

Mineralogical composition of the Lower Jurassic clays of the Cristian region (Braşov district) (%)

Bulk sample

No.	Sample no.	Location	Type of clay	K*	D	Hd	Ch	ML	H	P	S	OM	F	Q
1	33	CPP	Refractory = Fireclays, Grey	79.5	—	—	—	n.d.	0.9	0.1	—	—	2.8	12.5
2	48	CJV		36.5	13.1	17.2	2.0	n.d.	2.4	1.8	—	—	1.4	22.3
3	43	CJV		48.5	12.0	5.3	1.2	n.d.	2.4	0.4	1.5	—	0.7	27.7
4	948A	CJV	Refractory = Fireclays, Carbonaceous	43.6	—	16.6	4.6	n.d.	3.6	1.5	—	10.5	2.3	17.0
5	949A	CJV		44.4	—	13.8	0.9	n.d.	2.6	0.2	—	7.8	1.9	25.4
6	951A	Hb		67.3	—	14.4	4.4	n.d.	1.2	0.8	—	1.9	1.9	5.7
7	952	Hb		35.0	—	14.4	4.9	n.d.	5.2	3.9	—	7.8	2.0	25.8
8	954	Hb		37.0	—	8.5	4.7	n.d.	4.8	6.7	—	29.1	1.2	4.7
9	35	CPP	Non-refractory = Common, Grey	34.0	—	12.2	1.6	n.d.	1.4	0.6	—	4.0	1.8	38.0
10	32	CPP		61.9	—	16.7	—	n.d.	3.6	0.2	—	—	1.8	13.4
11	40	CJV		71.8	—	9.6	0.5	n.d.	0.8	0.5	—	3.0	1.3	10.5
12	42	CJV		41.3	6.0	6.1	0.7	n.d.	2.7	0.3	—	—	0.7	40.4
13	47	CJV		54.0	14.5	—	5.8	n.d.	0.5	0.3	2.7	—	3.3	20.0
14	34	CPP	Non-refractory = Common, Carbonaceous	65.8	—	8.5	0.6	n.d.	2.6	2.0	—	9.9	1.1	9.6
15	52	Hb		63.8	—	2.7	0.3	n.d.	5.2	—	—	9.9	1.3	13.7
16	53	Hb		45.5	20.8	5.2	0.4	n.d.	1.6	0.3	—	10.5	2.0	12.0
17	54	Hb		61.8	—	8.2	0.7	n.d.	1.6	0.5	—	22.1	1.2	1.1
18	56	Hb		64.3	—	—	—	n.d.	1.9	—	—	19.7	—	12.7

Clay fraction (less than 2 microns)

No.	Sample no.	Location	Type of clay	K*	D	Hd	Ch	ML	H	P	S	OM	F	Q
1	33	CPP	Refractory	68.6	—	21.6	1.6	3.7	0.5	—	—	0.8	—	3.4
2	48	CJV		79.1	—	11.1	—	2.9	2.3	—	—	0.9	—	4.4
3	43	CJV		73.6	—	15.9	—	3.2	2.5	—	—	1.2	—	4.7
4	35	CPP	Non-refractory	77.5	—	9.6	—	2.9	1.5	—	—	1.7	—	6.9
5	32	CPP		70.6	—	22.2	0.6	10.4	1.7	—	—	—	—	1.0
6	47	CJV		65.8	—	24.1	—	2.2	2.9	—	—	1.5	—	3.6

K = Kaolinite; D = Dickite; Hd = Hydromicas; Ch = Chlorite; ML = Mixed layers; H = Hematite; P = Pyrite; S = Siderite; OM = Organic matter; F = Feldspars; Q = Quartz; * = For the clay fraction the values also include the dickite contents; CPP = Cristian—Poiana Poieniţa; C JV = Cristian—Joader Valley; Hb = Holbav; n.d = not determined.

TABLE 3

Variation range and average contents of the main chemical and mineralogical components of the Lower Jurassic clays of the Cristian Holbav region (Braşov district) (%)

Component	Refractory clays = Fireclays							Non-refractory clays = Common			
	Bulk sample					Clay fraction		Bulk sample		Clay fraction	
	Cristian n = 5		Holbav n = 3		Cr + Hb n = 8	Cristian n = 3		Cristian + Holbav n = 10		Cristian n = 3	
	Δ	$\bar{x}$	Δ	$\bar{x}$	$\bar{X}$	Δ	$\bar{x}$	Δ	$\bar{X}$	Δ	$\bar{x}$
Chemistry											
SiO_2	47.6—59.8	53.5	27.9—52.3	42.1	49.2	46.2—46.6	46.5	34.9—66.8	50.2	44.7—45.7	46.0
Al_2O_3	23.8—32.0	26.7	20.6—33.2	25.0	26.1	34.8—35.2	35.1	18.7—32.4	27.1	34.1—36.0	35.0
Fe_2O_3	0.9— 3.6	2.4	1.3— 5.3	3.8	2.9	0.7— 2.7	1.9	0.5— 5.2	2.2	1.6— 3.1	2.2
K_2O	0.0— 2.0	1.3	1.0— 1.7	1.5	1.3	0.9— 1.8	1.3	0.0— 2.0	0.8	0.8— 2.0	1.5
H_2O^+	7.0—12.5	9.2	7.0—11.3	9.1	9.2	12.1—13.3	12.8	6.2—11.0	8.9	11.9—14.1	12.7
Fe_2O_3T	0.9— 5.4	3.1	3.0— 7.2	5.6	4.0	1.4— 2.7	2.2	1.1— 5.3	2.7	1.6— 3.1	2.3
SiO_2/Al_2O_3		2.0		1.7	1.9		1.3		1.9		1.3
Mineralogy											
Kaolinite *	36.5—79.5	50.5	35.0—67.3	46.4	49.0	68.6—79.1	73.8	34.0—71.8	56.4	65.8—77.5	71.3
Dickite	0.0—13.1	5.0	—	—	3.1	—	—	0.0—20.8	4.1	—	—
Hydromicas	0.0—17.2	10.6	8.5—14.4	12.4	11.3	11.1—21.6	16.2	0.0—16.7	6.9	9.6—24.1	18.6
Chlorites	0.0— 4.6	1.7	4.4— 4.9	4.7	2.8	0.0— 1.6	0.5	0.0— 5.8	1.1	0.0— 0.6	0.2
Mixed layers	—	—	—	—	—	2.9— 3.7	3.3	—	—	2.9—10.4	5.2
Hematite	0.9— 3.6	2.4	1.2— 5.2	3.7	2.9	0.5— 2.5	1.8	0.5— 5.2	2.2	1.5— 2.9	2.0
Pyrite	0.1— 1.8	0.8	0.8— 6.7	3.8	1.9	—	—	0.0— 2.0	0.5	—	—
Organic matter	0.0—10.5	3.7	1.9—29.1	12.9	7.1	0.8— 1.2	1.0	0.0—22.1	7.9	0.0— 1.7	1.1
Feldspars	0.7— 2.8	1.8	1.2— 2.0	1.7	1.8	—	—	0.0— 3.3	1.5	—	—
Quartz	12.5—27.7	21.0	4.7—25.8	12.0	17.6	3.4— 4.7	4.2	1.1—40.4	17.1	1.0— 6.9	3.8

Cr = Cristian; Hb = Holbav; n = Number of samples; Δ = Variation range; $\bar{x}$ = Arithmetic mean; $\bar{X}$ = General arithmetic mean (Cristian + Holbav); * = For the clay fraction the values also include the dickite contents

tents of organic, mainly carbonaceous matter and are called, for this reason, „carbonaceous clays". The rocks show rather heterogeneous compositions, according to the general data synthesized in table 3, because of the mixture in various proportions of clayey, detrital and organic material as well as of the mineralogical diversity of clay minerals.

A) *Chemical composition*

1. *Bulk sample.* First of all it is worth mentioning that, although variation intervals of common clays are larger than those of fireclays, their average values are rather close or anyhow, of the same order of magnitude. Reverse correlation between alumina and silica generally reported in the case of clays and especially of fireclays can be hardly noticed, the general means for quartz being practically identical and that of silica only 1% higher for common clays. Average contents of alumina are higher at Cristian (26.7%) than at Holbav (25.0%) in the case of fireclays and generally a little bit higher for common clays. The more aluminous character of common clays is only apparently anomalous, the explanation being given by the reduction of the percentages of chemical constituents of mineral origin by the organic matter present in large amounts in the fireclays at Holbav (Tab. 1). The SiO_2/Al_2O_3 ratio appears with general average values identical for fireclays and common clays (1.9). The fireclays show a little bit higher average ratios at Cristian (2.0) than at Holbav (1.7) because of the higher contents of detrital quartz at Cristian (Tab. 2 and 3). All these data suggest the common geochemical origin of the fireclays and non-refractory Lower Liassic clays.

Trivalent iron (Fe_2O_3 in the table also including the iron in pyrites) shows a large variation range both for fireclays (0.9—3.6 % for Cristian and 1.3—5.3 % for Holbav) and for common clays (0.5—5.2 %), controlled by the variation of sulphide contents. For both types of clays, the highest values are found at Holbav (up to 5.3 %). Ferrous iron (FeO), originating in silicates, more exactly in chlorites, is supraunitary only in the fireclays at Holbav and in a fireclay (sample 948 A) and a common clay (sample 47) at Cristian, in the last mentioned one reaching 2.03 % (Tab. 1). The consequence is the very large range of total iron contents, with high values especially at Holbav (7.2% in sample 952), related to the high values for both forms of iron (Tab. 1 and 3). The average values increase in the order: common clays, fireclays — Cristian and fireclays — Holbav. This situation suggests either the existence of different source areas of material, with variable importance in space and time, or rather, certain variations in the geochemical environment of sedimentation, the muds containing H_2S, fixing high quantities of iron as ferrous sulphides.

Potassium (K_2O), controlled by illite and detrital muscovite contents has similar restricted variation ranges for the two types of clays, with lower means for common clays (0.8 %) than for fireclays (1.3 %).

Sodium (Na_2O), although ubiquitous, has in all samples subunitary values, more exactly lower than 0.4 % (Tab. 1 and 3), indicating the presence in these rocks of small quantities of unaltered feldspars, but that are no longer present in the clay fraction (Tab. 2 and 3).

Manganese (MnO) is practically missing except for three samples in which it appears in a few hundredths of a percent.

Magnesium (MgO), originating in chlorites and maybe, to a less extent, in adsorbed ions, is subunitary, but present in all samples, with at most 0.79% in a common clay at Cristian.

Calcium (CaO) appears in all the samples with values lower than 0.25 %, without differences for various types of clays.

Phosphorus (P_2O_5) is equally ubiquitous, but in very small, insignificant quantities (less than 0.10%).

Sulphur, fixed in pyrite, is generally subunitary and completely missing in the fireclays at Holbav (although they are the richest in organic matter).

Organic matter, probably mainly carbonaceous, is missing in 5 of the 12 samples from Cristian, where it reaches almost 10% in a non-refractory clay (sample 34) and is present in all the samples from Holbav in high percentages (up to 29.11 % in sample 954), the mean reaching 12.9 % (Tab. 3). These data suggest that the presence within certain limits, of finely dispersed organic matter, has no influence on the refractoriness of clays.

2. *Clay fraction*. The fraction less than 2 microns was extracted only for 6 samples from Cristian, so that the discussion of the results will strictly refer to this area. The trends of geochemical evolution suggested by the comparison of the bulk sample and clay fraction chemistry have a more general validity and can be extended to the whole area of study.

So, unlike the bulk sample, the clay fraction shows both for silica and for alumina a very narrow variation range, the means for fireclay being practically identical with those for common clays. The clay fraction of fireclays and common clays contains significantly lower percentages of silica and consequently higher amounts of alumina as compared to the bulk sample (Tab. 3). The SiO_2/Al_2O_3 ratio is, therefore, much lower in the clayey fraction (1.3) than in the bulk sample (2.0) and identical for both types of clays (1.3). The Fe_2O_3 contents have more limited variation ranges for both types of clays, showing more marked tendencies of diminution in the case of fireclays (from 2.4 to 1.9 %). Ferrous oxide, with low subunitary values, was identified only in two cases (sample 33 — refractory and sample 32 — non-refractory), an increasing trend being observed in both of them (Tab. 1). The contents in total Fe_2O_3 is also characterized by a reduction of the variation range, by diminution tendencies and by practically identical means in the clayey fraction of both types of clays.

Potassium (K_2O) reduces its variation range in both types of clays, the average values remaining unchanged for fireclays and increasing sensibly in the case of common clays (from 0.8 to 1.5 %).

MgO and CaO show clear diminution trends in the fraction less than 2 microns in comparison with the bulk sample in both types of clays and Na_2O, MnO, P_2O_5 and S are removed from the clayey fraction.

B) *Mineralogical composition*

The rockforming minerals of the Liassic clays in the Cristian – Holbav area are genetically classified in two groups : reworked (allogenic) and authigenic minerals. The main mineral constituents, the clay minerals, probably belong to both categories : some of them show a primary character resulted from continental weathering or from reworking preexisting clays, and others are formed *in situ* from feldspars or at the expense of previous clay minerals, by degradation in acid continental environment or diagenetic processes.

1. *Bulk sample.* Fireclays are above all kaolinitic clays. In this case the feature is proper to both types of clays (fireclays and common clays), kaolinite being present in comparable amounts. Beside kaolinite, a few samples of fireclays (48 and 43) and common clays (42, 47 and 53) show large quantities of dickite (6.0–20.8 %) (Tab. 2). This mineral was also noticed in the other Lower Liassic clays in Gresten facies, being present in all the samples from Anina-Banat, where it reaches contents up to 30% (Papiu et al., 1970) and, in places, in the samples from Pădurea Craiului (Papiu et al., 1969).

In the Cristian-Holbav area kaolinite has similar variation ranges in both areas, showing a higher mean in common clays (56.4 %), followed by the fireclays of Cristian (50.5 %) and of Holbav (46.5 %). If dickite is also included in the calculation, the general average values are of 60.5 % kandites for common clays and 52.1% for fireclays (Tab. 3).

Under the term of „hydromicas" we referred to the whole series of minerals, from illites of micronic sizes up to macroclastic flakes of detrital muscovite. With a rather large variation range, hydromicas are missing only from three samples (33, 47 and 56) and reach their maximum content (17.2 %) in a fireclay sample (48) from Cristian.

Chlorites (both magnesian and ferrous) amount to 5.8 % in a sample of non-refractory clay (47) from Cristian and are missing from some samples of refractory (33 – Cristian) and non-refractory (32–Cristian and 56–Holbav) clays. It should be mentioned that in common clays, the chlorite average content is lower than that in fireclays. The general average content in clay minerals reaches close values in two types of clays : 66.2 % in fireclays and 68.5 % in common clays.

Undoubtly, authigenic minerals are iron minerals : hematite, siderite, pyrite. Fe-rich chlorites can be equally referred to the authigenic and to the allogenic origin. Hematite can also be both a primary and a secondary mineral, generated by chemical alteration. In only one sample (32–Cristian) was identified by X-ray a very low percentage (2.1 %) of hydrated ferric oxide (hydrohematite-goethite), the remaining Fe_2O_3 in clays being fixed as hematite. It is worth mentioning that the fireclays of Cristian contain less hematite (mean 2.4 %) than those at Holbav (mean 3.7%). These observations, correlated with the similar concentration trend of pyrite (0.8 % at Cristian and 1.9 % at Holbav) suggest more reduced iron supplies in the sedimentary basin in the Cristian area than at Holbav. Although common clays have a variation range altogether analogous with that of fireclays, their average hematite content is lower (2.2%). As for the pyrite content, we mention first of all its almost total independence from the content in organic matter, a direct correlation between them seeming to exist only for the carbonaceous fireclays at Holbav. The lowest average pyrite content is found in common clays (0.5%), followed by the Cristian (0.8 %) and Holbav (3.8%) fireclays. Siderite was identified only in places, in reduced quantities, uniquely in the Cristian area, in a fireclay sample (sample 43—1.5 %) and in a common clay (sample 47—2.7 %).

Detrital material is represented by quartz, feldspars (calculated as albite) and, to a certain extent also by muscovite, more or less altered to kaolinite or, rather to hydromuscovite — illite. Quartz shows a very large variation range for common clays (1.1—40.4 %) in comparison with fireclays (4.7—27.7 %), but with practically equal general means (17.1 % and 17.6 % respectively). Feldspars, typically detrital minerals, appear in quantities comparable, in variation range, and show slightly lower average values in common clays.

The organic matter is characteristic of the Holbav clays, where the content varies between 1.9 and 29.1%, with rather high means — 12.9% — for fireclays and 15.6 % for common clays. Less than half of the samples of Liassic clays of Cristian contain organic matter, so that, although the content can reach 10.5 % (sample 948 A), the maximum mean is only 3.6 % for fireclays and 2.8 % for common clays. All the clays in the Holbav area are carbonaceous and show an average content of organic matter about 4 times higher than that of the fireclays at Cristian and about 6 times higher in the case of common clays.

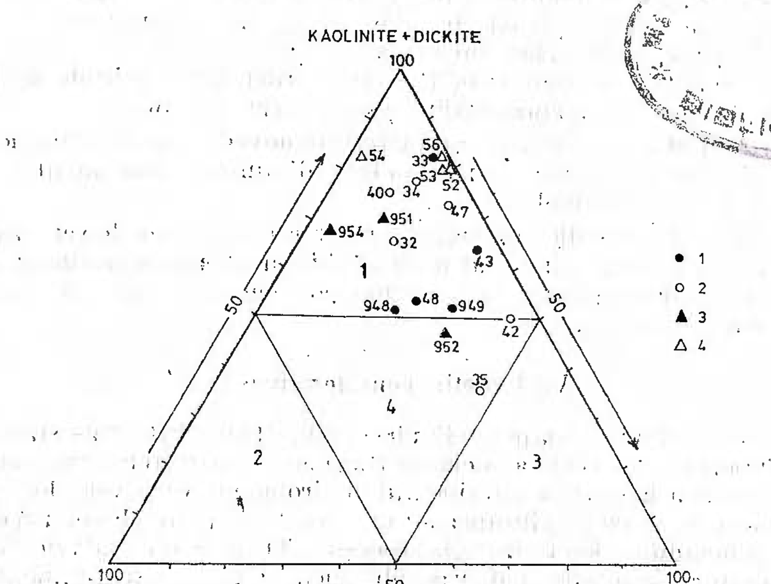

Fig. 3. — Mineralogical classification of the clays of the Lower Jurassic fireclay Formation of Cristian-Holbav : 1, Cristian (fireclays) ; 2, Cristian (non-refractory clays) ; 3, Holbav (fireclays) ; 4, Holbav (non-refractory clays).

A general mineralogical classification of the clays presented in the ternary diagram in Figure 3 shows that almost all the studied clays are situated in the field of kanditic clays, with two exceptions : sample 952 — Holbav, which is refractory and sample 35 — Cristian, non-refractory, plotted in the central field of mixed clays.

2. *Clay fraction*. Like in the case of the chemical composition, the comparison with the bulk sample will be made only for the Cristian area. The first thing worth noticing, which is in fact quite normal, is the great increase of the content in clay minerals and the reduction of the variation range of mineralogical and chemical components in the fraction less than 2 microns (tab. 2 and 3). So, kaolinite (+dickite) increases from 55.5 % to 73.8 % in fireclays and from 66.5 % to 71.3% in common clays.

Hydromicas show a less important increase in fireclays, that is due, of course, to the removal of a certain amount of detrital muscovite of silty sizes. In common clays, the increase in the hydromica content is more important (more than twice, the general means being relatively close for the two types of clays (16.2 %and 18.6%).

Chlorites appear only in two clay fraction samples (33 — refractory and 32 — common), which implies the lowering of the means as compared to the bulk sample. Much of the chlorite is probably derived from altered femic minerals, eliminated by pipetting.

Mixed-layers are present in all the analyzed clay fractions, with contents frequently ranging from 2.2 to 3.7 %, accidentally reaching 10.4 % (sample 32 — non-refractory) and reflecting, of course, the degradation processes produced in the lacustrine environment at the expense of pre-existing clay minerals.

The hematite content is of the same order of magnitude as in the bulk sample but the average values are a little bit lower.

Pyrite and feldspars are completely removed from the fraction less than 2 microns and the quartz content diminishes considerably (from 21.0 % to 4.2 % in fireclays).

Finally, the supplies of organic matter have much lower values in the clay fraction, indicating that most of this substance is granular or even fragmentary carbonaceous, being removed together with the fractions larger than 2 microns.

V. Genetic considerations

In some previous papers (Papiu et al., 1969, 1970) was stated that Liassic fireclays and their associated rocks of the Gresten formation were sedimented in a lacustrine-continental environment with very low pH, in which fine triturated phyllosilicates of mica type (three-layer type) were subject to degrading kaolinization processes. There is no analytic evidence that refractory kaolinite (pM) was obtained. The chemical-mineralogical similarity between fireclays and common clays suggests nevertheless that refractoriness is imposed by pM kaolinite and therefore, that the acidity of the sedimentation environment was very high, according to the experimental data of Oberlin et al. (1962). The association of clays with orthoquartzitic arenites is due, in a first phase, to macroclastic detrital sedimentation in which arenites and fine rudites were gravitationally separated, resulting a horizon of lacustrine sands. The suspended clay material would have precipitated subsequently, at the same time with the modification of the pH, maybe under the influence of bicarbonated karstic waters, in the same way in which karstic bauxites of the Apuseni Mts and the East Carpathians precipitated (Papiu et al., 1983). In this stage probably the transition took place from the lacustrine to the palustrine phase, during which vegetal remains were accumulated generating coal-forming peat-bogs. An approximate cyclic evolution is thus established, reflecting the succession of continental sedimentation of the Lower Liassic formation.

In certain diagenesis phases, within the clayey muds took place a strong degradation of illites or smectites, accompanied by silica release. Silica diffused in the arenitic subjacent deposits, cementing them and generating the orthoquartzitic sandstones associated to the fireclays of this formation.

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STUDIUL CHIMICO-MINERALOGIC AL FORMAŢIUNII ARGILELOR REFRACTARE JURASIC INFERIOARE DE LA CRISTIAN-HOLBAV (JUD. BRAŞOV)

(Rezumat)

Asemenea majorităţii argilelor refractare de pe teritoriul ţării noastre, argilele de la Cristian-Holbav se găsesc cuprinse în formaţiunea liasică în facies de Gresten şi sînt asociate cu zăcăminte de cărbuni. În zona Cristian complexul cu argile refractare este prins în două sinclinale deversate şi laminate pe flancul estic, care aflorează în Valea Joaderului (fig. 1) şi, mai la est, la Poiana Poieniţa (fig. 2) şi Pîrîul Căldării. Lucrările miniere din care a fost recoltat materialul studiat sînt în prezent abandonate. În regiunea Holbav dezvoltarea argilelor refractare este foarte capricioasă, formaţiunea prezentînd o întinsă gamă litologică, cu treceri de la argile *str. s.*, pînă la argile nisipoase şi argile cărbunoase.

Studiul rocilor detritice mai grosiere, care sînt asociate în mod obişnuit argilelor din formaţiunile liasice în facies de Gresten, a evidenţiat o mare uniformitate şi o asemănare remarcabilă cu rocile de acelaşi tip din depozitele similare de la Anina sau din masivul Pădurea Craiului. Gresiile cuarţitice şi argilo-siltitele de la Cristian şi Holbav prezintă în secţiuni subţiri caracterele petrografice bine-cunoscute: predominarea granulelor de cuarţ metamorfic, absenţa cimentului de supracreştere, prezenţa lamelor de muscovit proaspete, mai rar în diferite stadii de caolinizare. Caolinitul poate constitui uneori cimentul acestor roci. Rocile mai fine pot fi bogate în material cărbunos şi/sau bituminos. În regiunea Holbav au fost studiate şi o serie de şisturi siltito-argiloase cu material cineritic, cu aspect rubanat datorat unei succesiuni de lamine cu stratificaţie gradată la scară milimetrică sau submilimetrică, deseori impregnate preferenţial cu pigment bituminos-cărbunos. Materialul piroclastic reprezintă 20—40% şi este constituit din feldspaţi, rare granule litoclastice în care uneori se disting texturi fluidale şi probabil material vitroclastic, acesta din urmă mascat de prezenţa substanţelor bituminoase.

Analizele chimice arată că rocile argiloase studiate au un caracter destul de heterogen, datorită amestecului în diferite proporţii al materialului argilos cu cel detritic şi organic, precum şi participării cu ponderi variabile a diferitelor minerale argiloase (tab. 1 şi 3). Conţinuturile de alumină sînt în general mai mari la Cristian decît la Holbav, ceea ce se explică prin „diluarea'' ponderii componenţilor chimici de origine minerală de către substanţa organică prezentă în procente ridicate în argilele refractare de la Holbav. Datele chimice nu permit în acest caz trasarea unei limite clare între argilele refractare şi cele nerefractare.

Compoziţia mineralogică a argilelor (tab. 2 şi 3) este dominată de caolinit+dickit (acesta din urmă fiind recunoscut în cca 50% din eşantioane şi atingînd uneori procentaje ridicate), cu care se asociază în cantităţi subordonate hidromicele şi cloritele. Dintre mineralele argiloase, kanditele reprezintă în general peste 50% din compoziţia argilelor refractare. Materialul detritic (cuarţ, feldspaţi, mice) este net subordonat, fiind urmat de detritusul organic (+bitumene) şi mineralele de precipitaţie chimică (hematit, goethit, pirită). Conţinuturile de substanţă organică ating valori ridicate la Holbav (pînă la 29%), de 4—6 ori mai mult decît la Cristian. O clasificare mineralogică generală arată că aproape toate argilele studiate se încadrează în cîmpul argilelor kanditice (fig. 3).

Asocierea argilelor refractare de la Cristian şi Holbav cu depozite de cărbuni sugerează formarea lor în urma unor procese sedimentare mai mult sau mai puţin ciclice, în care după o fază lacustro-detritică în care se acumulează viitoarele arenite cuarţitice, urmează o fază palustră microclastică în care are loc depunerea argilelor, probabil într-un mediu foarte acid. În prima fază diagenetică mineralele filitoase cu trei strate sufereau procese degradative cu generare de caolinit şi silice liberă. Aceasta din urmă putea migra apoi în orizonturile arenitice cimentîndu-le şi dînd naştere rocilor ortocuarţitice. Fazei lacustre îi urmează faza finală palustră, cu turbării din care vor rezulta cărbunii.

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2. ZĂCĂMINTE

FLUID INCLUSIONS IN THE MINERALIZATIONS FROM THE VALEA LITA — BĂIŞOARA — CACOVA IERII AREA (APUSENI MOUNTAINS)[1]

BY

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Fluid inclusions. Geological thermometry. Hydrothermal minerals. Banatitic rocks. Mineralogenetic processes. Ore forming solutions. Apuseni Mountains — North Apuseni — Gilău Massif; Neocretaceous — Paleogene magmatites — Băişoara

Abstract

Fluid inclusions in some skarn and hydrothermal minerals genetically related to the banatitic rocks from the Valea Lita — Băişoara — Cacova Ierii area as well as the fluid inclusions from the quartz phenocrysts occurring in banatite rocks and inclusions from some recrystallized metamorphic rocks have been studied. There is a correspondence between the known ore deposits and the occurrences of the ore-forming solutions of the highest salinity (30—50 wt% NaCl). The latter may be followed from Valea Lita through Băişoara and Maşca to the Vadu Valley. Based on the study of fluid inclusions and on microscopic investigations, the mineralogenetic stages, the mineral assemblages, the peculiarities of ore forming solutions, the decrepitation and/or homogenization temperatures and the sequence of the main minerals have been determined. Using the mentioned results a model of the mineralogenetical processes developed in the investigated area has been sketched.

Résumé

Inclusions fluides dans les minéralisations de la vallée Lita—Băişoara—Cacova Ierii (monts Apuseni). On a étudié les inclusions fluides des skarns, les minéralisations pyrométasomatique-hydrothermales des roches des intrusions banatitiques, tout comme des métamorphites. Les solutions engendrant des minerais à salinité la plus élevée (30 à 50% NaCl) sont disposées horizontalement, dans la direction du système de fractures NNE—SSW. Sur base

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des inclusions fluides et des observations minéralogiques concernant les associations de minéraux, on a déterminé les phases, les stades, la nature des solutions de minéralisation, la température et la succession de formation des principaux minéraux. Tous ces facteurs ont contribué à l'ébauche d'un model minéralogique dans la zone investiguée.

1. Introduction

The data obtained in recent years by the study of fluid inclusions have an increasing significance as regards the genesis and prospecting of the ore deposits.

The first studies on the fluid inclusions from mineralizations related to some skarn deposits of Rumania (Pomârleanu, 1968; Kissling, Pomârleanu, 1970) have aroused the interest of several scientists (Takenouchi, 1971; Takenouchi, Imai, 1971; Schröcke, 1973; Takenouchi, 1973 etc.). Such studies have been recently made on the fluid inclusions from magnesian skarns occurring in the Ţibleş Mountains (Pomârleanu et al., 1982; Pomârleanu et al., 1986) as well as on those from porphyry copper mineralizations at Lăpuşnicu Mare (Pomârleanu, Întorsureanu, 1982, 1985).

Taking into account the above-mentioned results, similar studies have been recently made on the fluid inclusions from the mineralizations related to the banatitic (Laramian) rocks occurring in the eastern part of the Gilău Mountains (Lazăr et al., 1981, 1984).

In addition to the data concerning the geologic setting, the skarns and ore deposits from the Valea Lita-Băişoara-Cacova Ierii area, the characteristics of the ore-forming solutions are presented in this paper based on the fluid inclusions. At the same time some remarks regarding the temperature and salinity of the ore-forming fluids are made and finally a model for the evolution of the mineralizing processes in the investigated area is proposed.

2. Geologic setting

The Valea Lita-Băişoara-Cacova Ierii area consists of metamorphic sedimentary and banatitic igneous rocks (Fig. 1).

The metamorphics are assigned to the Baia de Arieş, Biharia and Vulturese-Belioara Series (Lazăr et al., 1984) and represent formations of Precambrian-Paleozoic age which were affected by regional metamorphism. The metamorphic rocks comprise many types of crystalline schists, limestones and dolomites.

The sedimentary rocks belong to the Permian, Cretaceous, Paleogene and Quaternary.

The pre-Paleogene formations are penetrated by granodiorite intrusions as well as by numerous dikes and sills of andesites, dacites, rhyolites and seldom of lamprophyres. A large number of small sized banatitic bodies could not be represented on the annexed geological sketch map (Pl. 1). The banatitic bodies are marked by an obvious mineralogical and textural inhomogeneity.

The various types of banatitic rocks (Lazăr et al., 1972; Ştefan et al., 1985) were formed by the consolidation of a calc-alkaline quartz dioritic-granodioritic magma.

Thermal metamorphism, metasomatic processes and ore deposition developed especially in the surrounding rocks of the plutonic intrusions. The identified marbles and hornfelses formed in the contact aureole of the granodioritic bodies.

The products of the pyro- and hydrometasomatism are the most important considering the intensity of transformations, the diversity of the neoformation minerals and associated ore (Lazăr, Intorsureanu, 1982).

In agreement with the previous investigations it was noticed that the oldest formations, especially those belonging to the pre-alpine metamorphosed basement, have been affected by folding.

It should be noted that in a complexly folded region several dislocations of strata can be distinguished. The fractures of Laramian age are largely developed, numerous N-S striking faults being formed.

Pre-, syn- and post-ore deposition zones of fracturing, faults, fissures and minute cracks have been described.

3. Skarns and mineralizations

In the Valea Lita-Băişoara-Cacova Ierii area the skarns and the associated iron ore deposits are largely developed. They were generated by the infiltration and diffusion metasomatism in the contact aureole of the intrusive granodioritic bodies.

Skarns frequently occur in the Dealul Grecului, Maşca and Cacova Ierii iron ore deposits and subordinately at Valea Lita.

The skarns were commonly formed by the replacement of the crystalline limestones and dolomites in the vicinity of the granodioritic bodies, closely connected with their apophyses. Calcic and magnesian skarns were identified in the investigated area.

The main minerals of the magnesian skarns are: spinel, forsterite, diopside, phlogopite and clinohumite. The characteristic mineral assemblage of the calcic skarns consists of pyroxene (diopside-hedenbergite), garnets (grossularite-andradite, vesuvianite, wollastonite, scapolite and ilvaite (Lazăr, Intorsureanu, 1982).

Mineralizations related to banatitic rocks have a prevailingly transition character (pneumatolytic-hydrothermal). The ore occurs as irregularly-shaped metasomatic ore-bodies. Impregnations and metalliferous veins rarely occur.

The hypogene ore minerals are represented by iron oxides (magnetite, maghemite, hematite), iron sulphides (pyrrhotite, pyrite, marcasite), boron minerals (ludwigite, szaibelyite), common sulphides (sphalerite, chalcopyrite, galena) and sporadically arsenopyrite, molybdenite, cubanite, tetrahedrite, boulangerite, mackinawite etc. Supergene minerals are: goethite, bornite, covellite, malachite and azurite.

Magnetite and pyrrhotite are associated with calcic skarns, whereas the boron minerals with the magnesian ones (Lazăr, Întorsureanu, 1982).

The hydrothermal mineral assemblages occur both in and out of the skarn bodies. The hydrothermal minerals are mainly developed by replacement, the deposition in open spaces being subordinate.

The following hydrothermal minerals, subsequently deposited with respect to the skarn formation, are distinguished : amphiboles (actinolite, tremolite, ferrohastingsite), biotite, sphene, epidote, zoisite, albite, chlorite, quartz, carbonate, sericite, clay minerals, minerals of the serpentine group, vermiculite, sepiolite, palygorskite, chalcedony and zeolites.

In the pyrometasomatic magnetite concentrations of the iron ore deposits from Dealul Grecului, Maşca and Cacova Ierii the sulphides occur subordinately. Unlike these, the Valea Lita polymetallic ore deposits are characterized by a zinciferous mineralization (Gheorghiţescu et al., 1979).

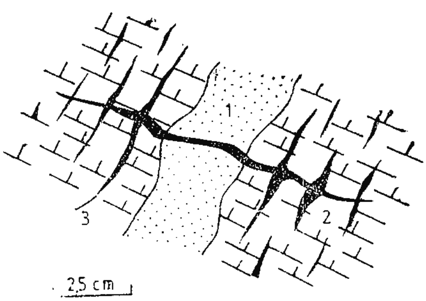


Fig. 1. — Unconformable quartz vein (1) in albite gneiss (2) crossed by two systems of fissures filled with tourmaline (3) Vadu Valley.

Several sulphide occurrences, devoid of economic interest, are also known in the investigated area (Iara Valley, Ierţii Valley, Vadu Valley etc).

Tourmaline veinlets occur in the albite gneisses from the southwestern part of the area, in the neighbourhood of the outcrop of the banatitic body on the Vadu Valley (Fig. 1).

4. Fluid inclusions

4.1. *General considerations*

The complex character of the mineralization described above reflects the complexity of the mineralizing fluids, which have generated the ore and gangue minerals. We can obtain data on these fluids from the study of the fluid inclusions, considering that these are — according to Roedder (1960) — "samples of the ore forming fluids".

The various types of the investigated fluid inclusions show that a certain mineral, belonging to the pyrometasomatic or hydrothermal paragenesis, after its deposition, frequently underwent the action of the ascending solutions. This aspect is confirmed by the presence of the secondary fluid inclusions of several generations in the skarn and ore minerals as well as in quartz and feldspar crystals within some banatitic rocks (granodiorite, rhyolite etc.).

Another evidence of the activity of the post-ore deposition solution is the recrystallization of calcite in marble and of quartz of concordant vein from crystalline schists or of quartz phenocrysts from banatitic rocks.

The occurrence of negative crystal-shaped fluid inclusions proves the presence of recrystallization (Roedder, 1967 — fide El Shatoury et al., 1975). We have also found two-phase (liquid-vapour) inclusions as negative crystal in intensely recrystallized quartz from conformable lenses within metamorphic rocks, near banatitic apophyses (Pl. III, Fig. 2).

The necking-down phenomenon, which leads to the separation of the primary fluid inclusion into secondary fluid inclusions exhibiting a varying degree of filling, also reveals the partial or total recrystallization of the minerals in the investigated area. Inclusions of this type were found in the recrystallized quartz from the quartzites occurring between the Grecu Hill and Mașca (Pl. V, Fig. 3) and sometimes in the vein quartz within the banatites on the Ierții Valley (Pl. V, Fig. 4).

The existence of the secondary fluid inclusions of several generations within minerals occurring in the investigated area shows that the post-magmatic processes gradually ceased during a long time period without any recurrence.

4.2. *Types of fluid inclusions*

Several types of fluid inclusions are found by microscopic observations of the doubly-polished plates, prepared from over 200 samples, collected from the various, mines, boreholes and outcrops in the investigatied area.

Type I is characterized by glass inclusions. These inclusions are primary in origin and considered to be samples of the magmatic melts from which the banatitic rocks crystallized. Such inclusions occur in some quartz phenocrysts within banatites from the Valea Lita deposit (Pl. II, Fig. 1). These inclusions contain sometimes, in addition to glass (St), a gas bubble (G) surrounded by a liquid phase (L). This fact indicates that the melt initially contained also volatile components such as : CO_2, H_2O etc.

Type II, commonly occurring in many skarn and ore minerals as well as in some minerals of banatite and metamorphic rocks, is represented by two-phase inclusions (liquid+gas), which, depending on the degree of filling, can be classified into two groups :

Group A. Fluid inclusions in which the gas phase occupies less than 30% of the volume of microcavities (Pl. II, Figs. 2—4). Figure 2 from Plate II shows a primary fluid inclusion, shaped as a negative crystal, in the late calcite, which includes sphalerite and chalcopyrite crystals, in a sample from the Valea Lita ore deposits. The liquid-gas inclusions as shown on Figures 3 and 4 of the same plate are interesting. They belong to the garnet-calcite mineral assemblage of the calcium skarns from the Grecu Hill ore deposit. Here andradite garnets are surrounded by large crystals of calcite, which sometimes penetrate the fissures in garnets. According to the degree of filling, that is the gas/liquid ratio, the inclusions within garnets (Fig. 3) are identical with those within calcite crystals (Fig. 4). But from the genetic viewpoint, these inclusions are different : they are primary in calcite, formed simultaneously with the host mineral, while those in garnets are secondary with respect to the crystallization of garnets.

Group B. In the fluid inclusions belonging to this group the gas phase exceeds 30% of the total inclusion volume (Pl. III, Figs. 1,2,3 and 4).

There are frequent instances when a mineral in the same microscopic field contains simultaneously formed inclusions; some of them are prevailingly liquid, others are prevailingly gaseous (Pl. III, Figs. 2,3 and 4). This fact proves that the solutions were boiling liquids at the time when they were included in minerals. The essential liquid inclusions become homogeneous in the liquid phase, while the prevailingly gaseous ones become homogeneous in the gas phase. The similar temperatures determined in such inclusions indicate the real temperatures for a given mineral. If the inclusions are situated on postmineralizing fissures cross-cutting the minerals within ores, they are of secondary character and will indicate the temperature of formation of other minerals, which belong to the later generations.

Type III is represented by monophase gaseous inclusions (Pl. IV, Fig. 1) occurring frequently in the quartz phenocrysts from the banatites.

Type IV is characterized by three – and polyphase inclusions, which preserve in their microcavities, in addition to liquid and gas, one or several crystalline phases. These inclusions can be further divided into four groups as follows:

Group A – inclusions consisting of liquid+gas + halite crystal; it is the most frequent (Pl. IV, Fig. 2).

Group B – three-phase inclusions, in which the volume of the gaseous phase prevails over the liquid phase. In addition to these two phases, one small halite crystal also occurs in this inclusion. Inclusions of this kind were found in the quartz of unconformable veinlets within albite gneisses near the contact of banatites from the Vadu Valley (Pl. IV, Fig. 3).

As shown in Figure 1, both the quartz veinlets and the albite gneisses were affected by B-rich pneumatolytic fluids with tourmaline deposition on fissures.

Group C – polyphase fluid inclusions consisting of liquid (L), gas (G), halite (H) and sylvite (S) were noticed both in the quartz veinlets from banatites and in the quartz phenocrysts within these rocks (Lita and Ierii Valleys) (Pl. IV, Fig. 4). According to Roedder (1981) halite and sylvite have formed a continuous liquid solution at high temperature, which was separated into two independent phases only by a gradual cooling.

Group D – inclusions which contain, in addition to liquid, gas, sylvite and halite, some other crystalline phases, as was the case of the quartz from the conformable lenses in hornfelses and in the crystalline schists occurring near the banatite bodies (Pl. V, Fig. 1).

Inclusions similar to those belonging to the groups A, C and D were noticed also in the porphyry copper mineralization at Lăpușnicu Mare (Pomârleanu, Întorsureanu, 1982, 1983).

Type V is represented by three-phase inclusions belonging to the CO_2-H_2O system. They contain aqueous solution, liquid and gaseous carbon dioxide. This type of inclusion was found in the quartz from the conformable lenses in the crystalline schists which were not affected by the banatite intrusion (e.g. Purcăreț Brook) (Pl. V, Fig. 2).

4.3. *Thermal regime*

In order to determine the temperature of formation of minerals occurring in the investigated area, the homogenization and the decrepitometric methods were applied.

The variation of the thermal regime is illustrated by some characteristic diagrams. The histogram of the homogenization temperatures of

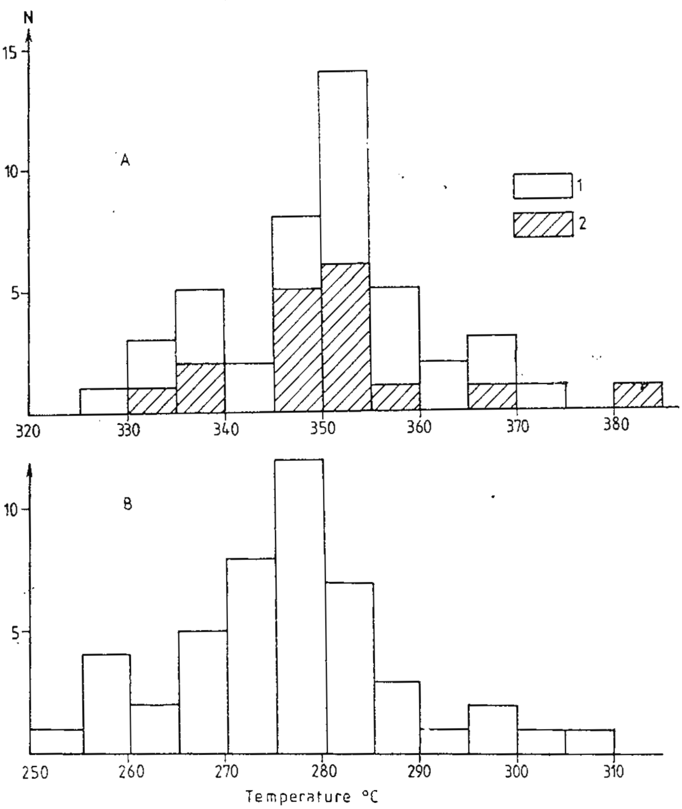


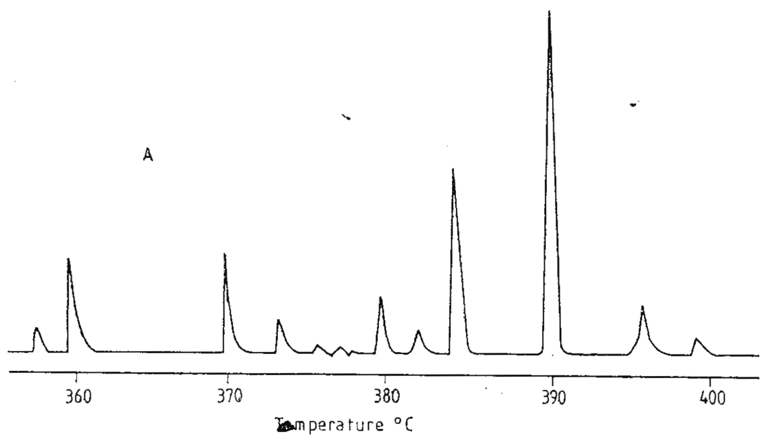
Fig. 2. — Diagram of filling temperatures of the secondary fluid inclusions in quartz from rhyolite. A — histogram of early liquid and vapour inclusions ; B — histogram for the inclusions of later generation ; 1 — homogenization in the liquid phase ; 2, homogenization in the gas phase.

the secondary fluid inclusions of the first generation is significant. These inclusions being prevailingly liquid and predominantly gaseous, have been formed simultaneously in the quartz phenocrysts of the rhyolite piercing the granodiorite body on the left slope of the Vadu Valley (Fig. 2 A).

The diagram shows that the homogenization temperatures range, with a few exceptions, within the same interval for both types of inclusions. The difference lies in the fact that the prevailingly liquid inclusions become homogeneous in the liquid phase (between 325°C and 375°C), while the prevailingly gaseous ones homogenize as a vapour phase (in the range from 330° to 385°C).

The secondary fluid inclusions of later generation occurring in the same phenocrysts exhibit lower homogenization temperatures (250° — —310°C) with a frequency maximum ranging between 275°C and 280°C (Fig. 2B).

Similar temperature ranges were also obtained for the primary fluid inclusions in calcite and quartz from the pyrometasomatic-hydrothermal ore deposit.



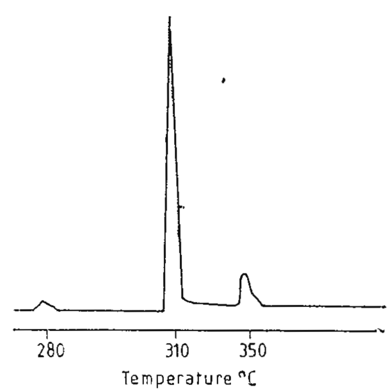


Fig. 3. A — Decrepitogram of quartz within the unconformable vein from the albite-gneisses occurring near banatictic rocks (Vadu Valley); B — Decrepitogram of tourmaline occurring on the fissures in the quartz veins from albite gneiss. Vadu Valley.

The quartz from the discordant vein in albite-gneisses occurring close to the contact of banatites and displaying two-phase inclusions (liquid + gas) show homogenization temperatures ranging between 280°C and 360°C. The upper limit of this temperature interval corresponds on the diagram to the beginning of quartz decrepitation (Fig. 3 A). The frequency curve of the decrepitation temperature reached its maximum at

390°C. It has been previously mentioned that both the quartz veins and the albite gneisses in the vicinity of the banatitic intrusions were affected by tourmalinization (Fig. 1). The decrepitogram of tourmaline indicates a temperature range between 280°C and 350°C, reaching the frequency maximum at 310°C (Fig. 3B).

In andradite garnets and in calcite (Pl. I, Figs. 3,4) within skarn bodies occurring in the Grecu Hill iron deposit we have identified fluid inclusions which are described above (4.2.II.A). An identical interval of decrepitation temperatures (290—362°C) was determined in both minerals of this assemblage. The difference consists only in the type of inclusion (primary in calcite and secondary in garnet).

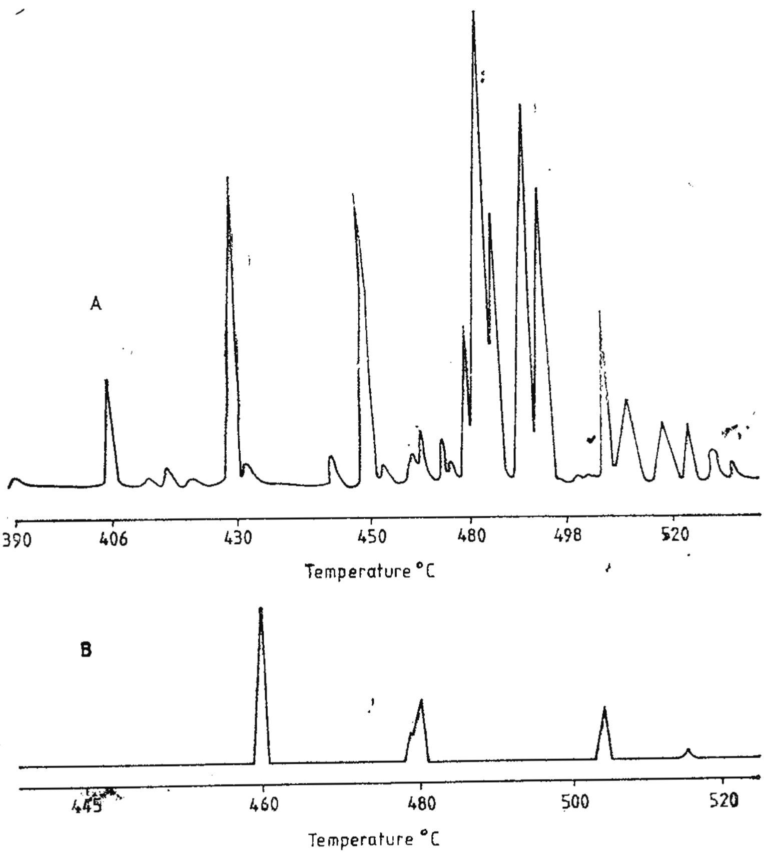


Fig.4. — Decrepitogram for garnets (A) and magnetite (B) from skarns. Cacova Ierii.

The decrepitogram of a garnet sample from the Cacova Ierii skarn bodies shows a temperature interval of 406—520°C with a maximum at 480°C (Fig. 4A), whereas those of the associated magnetite indicates temperatures ranging between 460°C and 500°C (Fig. 4B). The temperature determined for the diopside-hedenbergite assemblage ranges within wide limits (450—620°C).

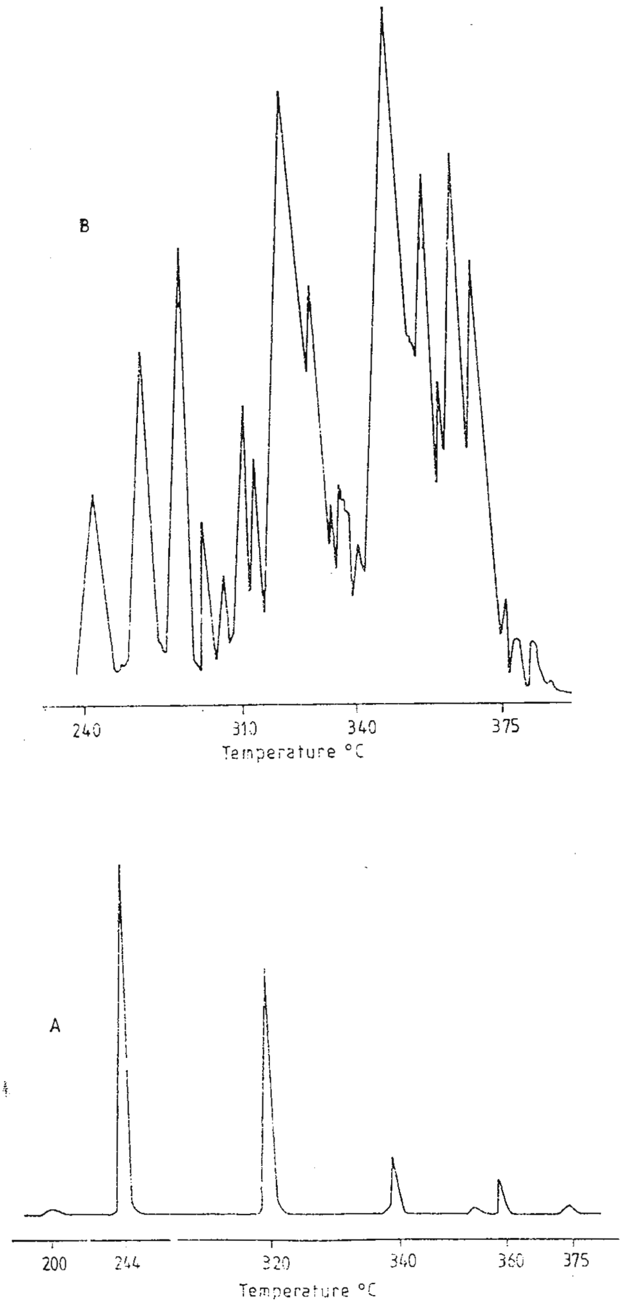


Fig.5. — Decrepitogram of epidote (A) and calcite (B) in skarns at Cacova Ierii.

The epidote associated with magnetite in skarn shows a temperature interval between 200°C and 340°C, with a maximum at 244°C (Fig. 5A), while calcite of the same mineral assemblage indicates the beginning of decrepitation at 240°C and a maximum at 350°C (Fig. 5B).

The three-phase fluid inclusions of the type : aqueous solution (L), vapour (G) and halite (H) are characterized by the same temperature intervals both in the vein quartz and the quartz phenocrysts in the granodiorite porphyry from the Lita and Iara Valleys. Thus the dissolving interval of halite ranges from 320°C to 420°C and the complete homogenization of the vapour phase in the liquid one occurred between 390°C and 420°C.

Much lower homogenization temperatures (160—220°C) were recorded for the late calcite associated with sphalerite and chalcopyrite from the **Valea** Lita deposit (Pl. II, Fig. 2).

4.4. *Salinity of the solutions*

The salinity of the solutions determined through the previously mentioned methods (Pomârleanu, Întorsureanu, 1985), depending on the characteristics of the trapped solutions in the microcavities of all the investigated minerals, varies between 3 and 12 wt % NaCl for the two-phase inclusions (liquid + vapour) and 30—50 wt % NaCl for the three- and polyphase inclusions.

The solutions of the highest salinity (30—50 wt % NaCl) have been found in the investigated area, namely in a NNE-SSW striking zone situated between the Lita Valley deposit and the confluence of the Vadu Valley with the Purcăreț Brook (Pl. I).

5. Sketch of the mineralogical model

The field observations, the study of the skarn mineral assemblages and those of the pyrometasomatic and hydrothermal ores, correlated with the results of the investigation of tluid inclusions, especially the data on the thermal regime and the salinity of the ore forming solutions, lead us to a model of the evolution of the mineralogenetical processes in the investigated area.

The model given on Figure 6 shows the genetic stages, the main mineral assemblages, the characteristics of the geochemical media (fluids) trapped in the inclusions, the temperature and succession of deposition of the main minerals.

For the diopside-hedenbergite series a temperature range from 450°C to 620°C, similar to that established by Rahmanov and Abdullaev (1980) for the same association (480—669°C) has been determined. The mineral sequence continues with ludwigite, having a formation temperature of 530°C (Ionescu et al., 1971), garnets, magnetite and probably tourmaline, which are the last known minerals of the pyroxene-garnets and magnetite assemblages. It follows the transition from pneumatolytic to hydrothermal stage and from the magnetite assemblage to the quartz--sulphides one respectively and the evolution ends in the hydrothermal (s. str.) stage, represented by the quartz-sulphides and quartz-carbonate--zeolites assemblage.

Spinel and forsterite hold a peculiar place on the sketch, being considered to be formed at temperatures above 620°C.

Based on the study of the fluid inclusions it will be noted that the first two assemblages (pyroxene-garnets and magnetite) are characterized by gaseous fluids (corresponding to pneumatolytic stage) which condense

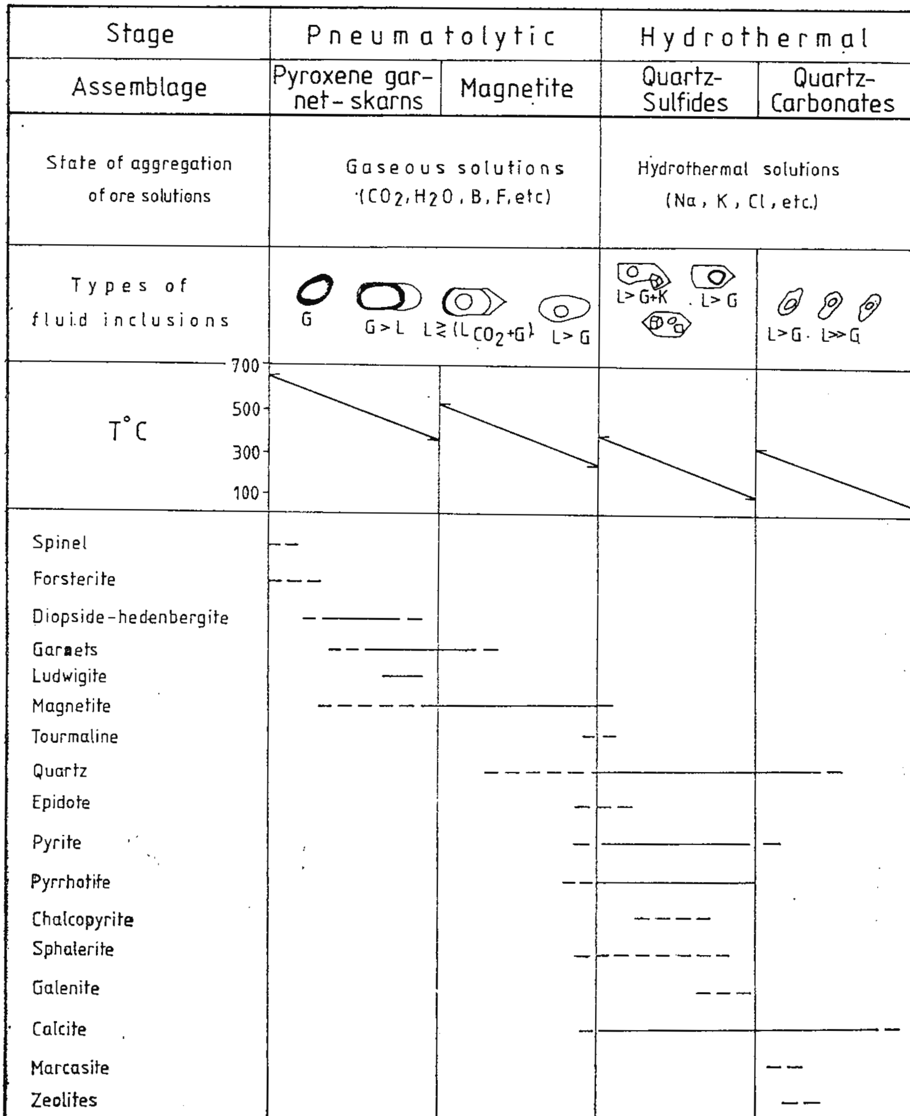


Fig. 6. — Sketch of mineralogenetical model in the Valea Lita-Băişoara-Vadu Valley area.

into liquid state of low salinity consisting of CO_2, H_2O, B, F etc., whereas the hydrothermal stage is represented by highly saline solutions (rich in H_2O, Na^+, K^+, Cl^- etc.).

6. Conclusions

Some conclusions regarding the mineralogenetic processes developed in the Valea Lita-Băişoara-Cacova Ierii area can be drawn based on the field observations, on the study of mineral assemblages and of fluid inclusions within minerals.

Pre-, syn- and post-ore forming recrystallization processes, which exhibit a partial tectonic control, are distinguished.

The coexistence of the liquid-gas fluid inclusions with the prevailingly gaseous ones exhibiting similar filling temperature intervals indicates that during the deposition of the pyrometasomatic mineralization the fluids were in a boiling state.

In the investigated area the solutions of the highest salinity (30—50 wt % NaCl) occur along the fracture system oriented NNE—SSW (Pl. 1).

Some characteristics of fluid inclusions noticed in places as well as some incipient hydrothermal alterations of the banatitic rocks suggest the existence of a porphyry copper mineralization in the investigated area.

The sketched mineralogenetic model constitutes a first attempt at synthetizing the results obtained by the study of fluid inclusions concerning the stages, mineral assemblages, features of the ore forming fluids (solutions), temperature and succession of deposition of the main minerals from the investigated area. These results are in agreement with the geological and mineralogical data.

The study of fluid inclusions provides additional data regarding the genetic relationship between the deposition of ore minerals and the banatitic intrusions as well as the pre-, syn- and post-mineralizing tectonics, explaining at the same time the nature of the mineral forming solutions.

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INCLUZIUNILE FLUIDE ÎN MINERALIZAȚIILE DIN ZONA VALEA LITA-BĂIȘOARA-CACOVA IERII (MUNȚII APUSENI)

(Rezumat)

În lucrare, paralel cu unele date referitoare la cadrul geologic, la skarnele și mineralizațiile din perimetrul Valea Lita-Băișoara-Cacova Ierii, sînt prezentate, pe baza studiului incluziunilor fluide, caracteristicile soluțiilor generatoare de minereuri. Totodată se determină regimul termic și gradul de salinitate al soluțiilor mineralizante. Pe baza observațiilor mineralogice și a studiului incluziunilor fluide se propune un model privind evoluția proceselor mineralogenetice asociate magmatismului banatitic din zonă.

Regiunea studiată, este constituită din formațiuni cristaline (atribuite seriilor de Baia de Arieș, Biharia și Vulturese-Belioara), depozite sedimentare (aparținînd Permianului, Cretacicului, Paleogenului și Cuaternarului) și o gamă variată de roci banatitice care s-au format prin consolidarea unei magme calcoalcaline, de compoziție cuarț-dioritică-granodioritică.

Skarnele și mineralizațiile asociate lor, s-au format în zona de contact a calcarelor cu rocile banatitice sub acțiunea metasomatozei de infiltrație și de difuzie.

Pe considerente de ordin mineralogic și chimic s-au separat skarne magneziene (constituite din spineli, forsterit, diopsid, flogopit și clinohumit) și skarne calcice (alcătuite din diopsid-hedenbergit, grossular, andradit, vezuvian, wollastonit, scapoliți și ilvait).

Mineralizațiile sub formă de corpuri metasomatice și mai rar filoane au un caracter pirometasomatic-hidrotermal.

Mineralele metalice primare dînt reprezentate prin oxizi (magnetit, maghemit, hematit) și sulfuri de fier (pirotină, pirită, marcasită), minerale de bor (ludwigit, szaibelyit), sulfuri comune (blendă, calcopirită, galenă) și sporadic mispichel, cubanit etc, iar cele secundare prin : goethit, hidrogoethit, bornit, covelină, malachit și azurit.

Pe lîngă acumulările pirometasomatice și hidrotermale menționate se află și turmalina depusă pe fisuri în șisturile cristaline.

În zonă s-au evidențiat mai multe tipuri de incluziuni : sticloase și fluide.

Incluziuni sticloase, care conservă topituri de silicați acum sticlă din care s-au format banatitele, apar în fenocristalele de cuarț și rareori de feldspați din banatitele de la Lita.

Incluziunile fluide comune tuturor mineralelor din skarne, mineralizații, roci banatitice și metamorfice sînt reprezentate prin incluziuni bifazice (lichid+gaz), trifazice (constituite din soluție apoasă+CO_2lichid+ +CO_2 gaz sau din soluție apoasă+gaz+halit) și polifazice (soluție apoasă +gaz+halit+silvină+unul sau mai multe faze cristaline transparente sau opace nedeterminate).

Regimul termic al soluțiilor mineralizante s-a determinat prin două metode geotermometrice, bazate pe studiul incluziunilor fluide : metoda

omogenizării şi metoda decrepitării. Datele au fost reprezentate prin histograme pentru temperaturile de omogenizare şi decrepitograme pentru cele obţinute prin decrepitare.

Temperaturile obţinute prin omogenizarea fazelor (lichid+gaz) din incluziunile fluide secundare din unele fenocristale de cuarţ, din riolite, sînt similare cu cele ale incluziunilor fluide primare din mineralizaţiile pirometasomatice — hidrotermale (325°C—385°C).

În cazul skarnelor, pentru asociaţia andradit+calcit din zăcămîntul Dealul Grecului s-a determinat un interval de temperatură de 290°C—362°C. De subliniat este faptul că în granaţi, în deplină concordanţă cu succesiunea de depunere granaţi-calcit, s-au evidenţiat incluziuni fluide secundare identice cu cele primare din calcit.

Pentru o probă de granaţi de la Cacova, prin metoda decrepitării s-a obţinut un interval de temperatură de 406—520°C cu un maximum la 480°C (fig. 4A) iar pentru magnetitul asociat cu granaţi, un interval de 460—500°C.

Temperaturi scăzute 160—220°C s-au remarcat la calcitul de ultima generaţie asociat cu blendă şi calcopirită.

Salinitatea soluţiilor din incluziuni arată variaţii mari de la 3—12 % NaCl pentru incluziunile lichid-gazoase şi între 30 şi 50 % NaCl pentru incluziunile tri-şi polifazice. Soluţiile cu salinitatea cea mai ridicată se eşalonează pe o zonă cu direcţia NNE-SSW, începînd de la zăcămîntul Lita, intersectînd corpul banatitic din Valea Ierţii (Băişoara) şi pînă în aval de confluenţa Purcăreţului cu Valea Vadului (Pl. 1).

Modelul mineralogic schiţat din fig. 6, cuprinde stadiile, etapele, starea de agregare şi caracteristicile mediilor geochimice din incluziuni, temperatura şi succesiunea de depunere a principalelor minerale asociate magmatismului banatitic din perimetru.

EXPLANATION OF PLATES

Plate I

Geological sketch map of the Băişoara—Cacova Ierii area (Gilău Mountains).

1, post-banatite formations (Quaternary, Miocene, Paleogene); 2, banatite rocks: a, granodiorite-granodiorite porphyry; b, rhyolite, dacite, andesites; 3, pre-banatite formations: sedimentary deposits (Senonian, Permian) and metamorphic rocks (crystalline schists, calcite and dolomite marble); 4, hornfelses; 5, skarn outcrops; 6, hydrothermal alteration; 7, occurrences of highly saline inclusions; 8, outline of the eruptive body; 9, transgression; 10, limits of Quaternary deposits; 11, fault; 12, bedding, schistosity; 13, shaft.

Plate II

Fig. 1. — Three-phase inclusion having glass: St (glass) + G (gas) + L (liquid) in a quartz phenocryst from the banatite in Valea Lita.

Fig. 2. — Fluid inclusions (liquid + gas) in calcite associated with sphalerite and chalcopyrite. Ore sample. Valea Lita.

Fig. 3. — Secondary fluid inclusion (liquid + gas) in garnet. Dealul Grecului, (Shaft no. 2—280 m level).

Fig. 4. — Primary fluid inclusion (liquid + gas) in a large calcite crystal associated with garnets. Dealul Grecului ore deposit.

Plate III

Fig. 1. — Secondary fluid inclusion (liquid + gas) in quartz phenocryst from rhyolite (Vadu Valley).

Fig. 2. — Two-phase (liquid + gas) fluid inclusion showing shapes of negative crystal in quartz from conformable lenses occurring in crystalline schists near the banatite apophyses (Vadu Valley).

Fig. 3. — Liquid + gas and prevailingly gaseous inclusions in a quartz phenocryst from the banatitic rock from the Ierţii Valley.

Fig. 4. — Secondary, prevaillingly gaseous fluid inclusions in a quartz phenocryst from rhyolite which crops out in the Vadu Valley.

Plate IV

Fig. 1. — Gaseous inclusion, without zoning, in a quartz phenocryst from the banatite in the Ierţii Valley.

Fig. 2. — Three-phase fluid inclusion : liquid (L) + gas (G) + halite (H) and common fluid inclusions (liquid + gas) in a quartz phenocryst from the banatitic rock in the Ierţii Valley.

Fig. 3. — Prevailingly gaseous inclusion (G) with liquid (L) and a small halite crystal (H) in quartz from a discordant veinlet in the albite gneiss affected by tourmalinization. (Vadu Valley).

Fig. 4. — Polyphase fluid inclusions : liquid (L), gas (G), halite (H) and sylvite (S).

Plate V

Fig. 1. — Polyphase fluid inclusions : liquid (L), gas (G), halite (H), sylvite (S) and an unidentified crystal (K_1) in quartz lenses within hornfelses (Cacova Ierii).

Fig. 2. — Three-phase fluid inclusions : liquid (L), gaseous CO_2 (G) and liquid CO_2 (L) in the conformable quartz lens within crystalline schists from the Purcăreţ Brook.

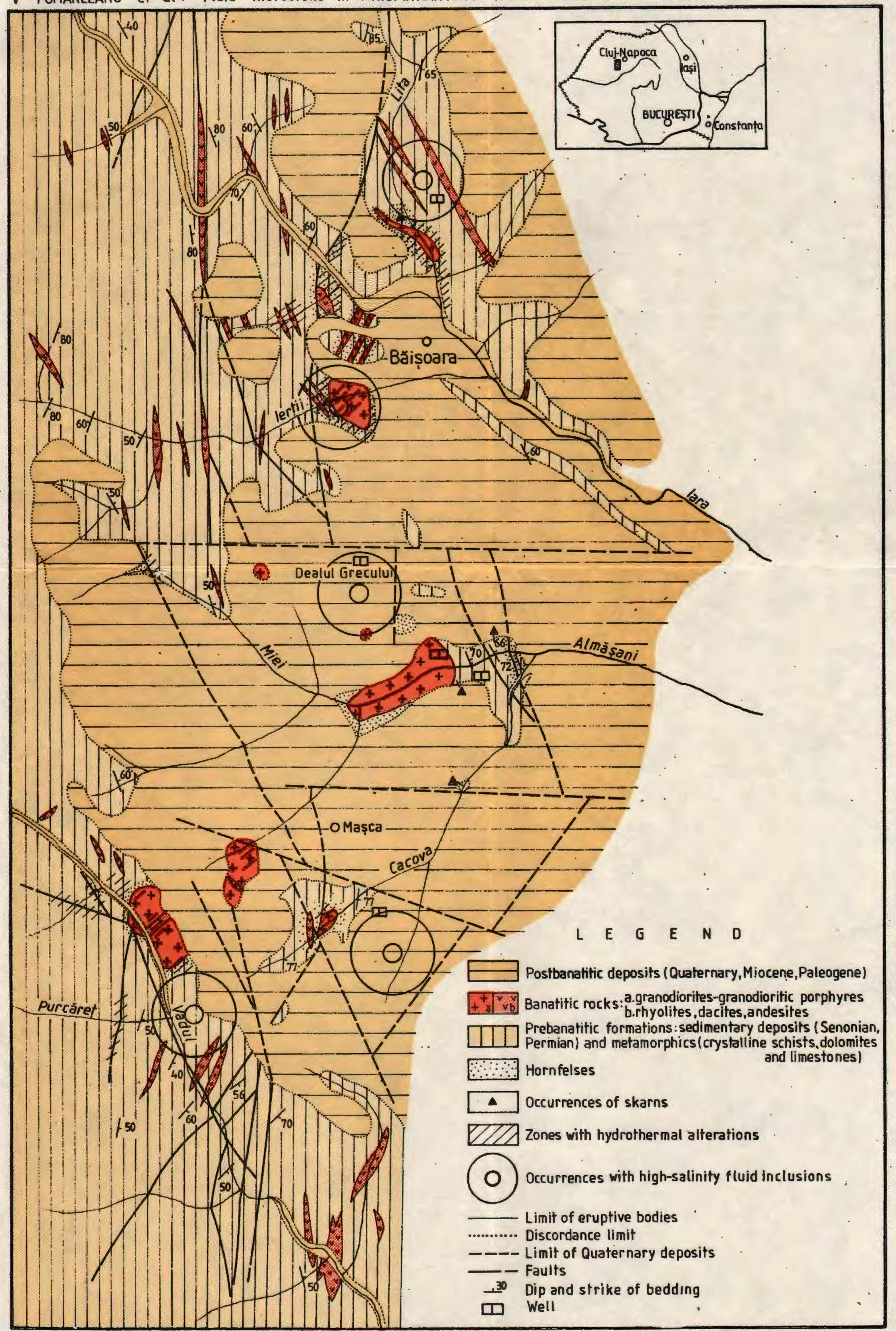
Fig. 3 and 4 — Inclusions formed by necking down in the quartz of the quarzites situated between the Grecu Hill and Maşca (Fig. 3) and in the quartz of the granodiorite body in the Ierţii Valley : the liquid inclusion communicates with the liquid-gaseous one through a capillary channel (Fig. 4).

C.LAZĂR I.ÎNTORSUREANU, V. POMÂRLEANU

GEOLOGICAL SKETCH MAP OF THE BĂIŞOARA–CACOVA IERII AREA (GILĂU MOUNTAINS)

0 250 500m

The map has beem compiled according to published (Lazăr et al 1972) and unpublished data (Lazăr et al 1980, 1984)



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2. ZĂCĂMINTE

CONTRIBUTIONS CONCERNANT LES MINÉRALISATIONS DE BOGZA (DOBROGEA DE NORD)[1]

PAR

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Fluid inclusions. Geological geothermometry. Werfenian. Copper. Barite. Epithermal deposit. Mesothermal deposit. Dobrogea — North Dobrogea — Tulcea and Consul—Niculițel Zone

Résumé

Les minéralisations cuprifères et de barytine sont localisées tant dans les grès et les conglomérats werféniens que dans les calcaires aussi. L'étude des inclusions fluides indique que les deux types de minéralisations ont une nature hydrothermale, avec des passages graduels de l'épi- à mésothermale et se sont formées dans l'intervalle de 140 à 280°C.

Abstract

Contributions on the Bogza mineralizations (Northern Dobrogea). Copper and barit mineralizations occur both in Early Werfenian sandstones and conglomerates and Spathian limestones as well. The study of fluid inclusions shows that both types are hydrothermal mineralizations. Gradually they passed from epi- to mesothermal type and deposited from 140° to 280°C.

Les premières données sur les minéralisations de barytine et sulfures de l'orogène de Dobrogea de nord ont été fournies par Peters (1867), suivi par Pascu (1904), Murgoci (1914) et Cădere (1928).

En 1951 M. Savul rédige une carte géologique de la zone de Somova—Cîșla, localisant les principaux affleurements de barytine. Cette carte a constitué la base d'un nouveau programme plus ample d'investigation par des travaux minières et forages executés dans la même zone (Bacalu,

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1957). Ce programme a été ultérieurement développé dans la zone de Marca—Malcoci (Bacalu, 1959) et plus récent dans le secteur de Beilia Mare (Vîlceanu et al., 1983).

Les minéralisations de barytine et sulfures de Somova—Cîşla ont formé l'objet de plusieurs études (Ianovici et al., 1957, 1977 ; Savul et al., 1953, 1960 ; Gurău, Gridan, 1974 ; Stiopol et al., 1976 ; Popescu, 1977 etc.). La présente note est axée sur les minéralisations de Bogza, colline située à mi-distance entre Tulcea et Malcoci.

Géologie de la région. Dans la zone dont on parle (fig. 1) affleurent des formations paléozoïques attribuées au Dévonien supérieur (Mirăuţă, 1966) et mésozoïques, respectivement triasiques inférieures (Werfénien inférieur et supérieur) et triasiques inférieur-moyennes (Werfénien terminal + Anisien basal) (Mirăuţă et Panin, 1979).

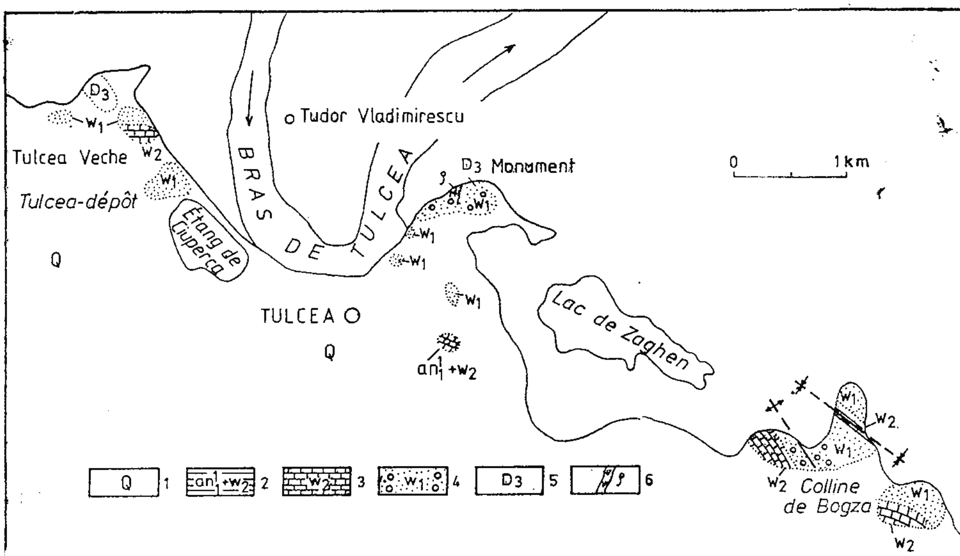

Fig. 1 — Schéma géologique de la zone de Tulcea Veche-Bogza : 1, Quaternaire (Q) ; loess ; 2, Anisien basal + Werfénien terminal ($an_1 + w_2$) : calcaires et dolomies, calcaires dolomitisés ; 3, Werfénien supérieur (w_2) : calcaires marneux grisâtres fossilifères, calcaires schisteux à sidérose ; 4, Werfénien inférieur (w_1) : conglomérats, grès, silts, argiles ; 5, Dévonien supérieur (D_3) : quartzites, schistes quartzeux verdâtres (formations anchimétamorphiques) ; 6, Paléozoïque ; rhyolites (ρ).

Le Dévonian supérieur est formé de schistes argileux, parfois faiblement quartzitiques, bruns à verdâtres, à des intercalations de roches siliceuses et plus rarement de calcaires grisâtres. Les roches sont faiblement métamorphisées (anchimétamorphisées) et, à Monument, elles sont traversées et affectées par des filons de rhyolites. Selon Vîlceanu et al. (1980) la même association de roches affleure aussi dans le soubassement des dépôts triasiques de la colline de Bogza.

Le Werfénien inférieur (W_1) est constitué de conglomérats polygéniques basals, grès quartzitiques, siltites et argilites grisâtre-violacées vers verdâtres. Elles reposent transgressivement et en discordance sur les roches dévonien-supérieures qui semblent former un paléorelief.

Le Werfénien supérieur (W_2) repose en continuité de sédimentation, visible à Tulcea et dans le déblai de la voie ferrée de Tulcea—Babadag. Le passage se fait par un paquet de siltites grisâtres à verdâtres et calcaires noirâtres à bruns avec des altérations limonitiques et des fissures à sidérose. Celles-ci forment des couches minces qui ont fourni la faune triasique inférieure identifiée par Simionescu (1908) à Tulcea Veche. Le même type de calcaires apparaît dans l'axe du synclinale de la colline de Bogza, tout comme dans le déblai aussi ; on y a identifié une espèce de Conodonte, *Neospathodus collinsoni* Solien, caractéristique pour la zone *11* à Conodontes, située à proximité de la base du Spathien. Dans la séquence calcaire apparaissent aussi des niveaux encrinitiques.

Le Werfénien terminal + Anisien basal ($W_2 + an_1$) a été identifié à base de faunes sur le territoire de la ville de Tulcea. L'intervalle comporte des calcaires, calcaires dolomitisés et dolomies. L'âge de ceux-ci a été déterminé par les espèces de Conodontes, Gondolella timorensis (Nogami) et Neospathodus homeri (Bender), caractéristiques pour cet intervalle. Dans la zone dont on parle on n'a pas observé les relations avec les dépôts sous-jacents.

Les dépôts terrigènes triasiques inférieurs se sont formés dans une mer peu profonde, agitée et représentent les conglomérats de base d'une transgréssion arrivée de l'est qui constitue le début d'un nouveau cycle de sédimentation (Mirăuță, 1967). Ultérieurement, ces dépôts ont été encadrés dans la „formation détritique bariolée dans le faciès des couches de Werfen" d'âge griesbachien (Werfénien basal) (Mirăuță in Patrulius et al., 1974), ou dans la „formation détritique inférieure" (Mirăuță, 1982). Cette formation est affectée par des filons de quartz à sulfures et des petits filons de barytine.

La structure de la colline de Bogza est considérée tel un synclinal faillée à dépôts spathiens dans l'axe, tandis que les grès et les conglomérats forment un petit anticlinal (pl. I, fig. 1). Selon Vîlceanu et al. (1980), le flanc NE du synclinal comporte un pli „parasite" engendré par l'apparition d'une fracture de type „hol". Cette fracture a facilité l'ascension des rhyolites et, ultérieurement, des minéralisations de barytine et sulfures (fig. 2).

Minéralisations. Les formations werféniennes qui forment le promontoire de Bogza sont traversées par des filons de quartz, filons de quartz à minéralisation de cuivre et filons de barytine.

Filons de quartz. Les filons de quartz stéril sont très nombreux, ayant des orientations différentes et des épaisseurs variables de 1 à 20 cm dans les grès quartzeux et microconglomérats et de 1 à 30 cm dans les roches silicifiées. Les deux types de filons comportent du quartz blanc-grisâtre compact et des géodes à monocristaux de quartz. Ceux-ci sont long-prismatiques à faces de rhomboèdre qui se trouvent parfois en des concrétions autoépitaxiales ou dans une position perpendiculaire les unes aux autres (fig. 3 B). A la différence du quartz filonien des grès, celui des roches silicifiées présente des textures endentées à faibles déformations plastiques (pl. I, fig. 2).

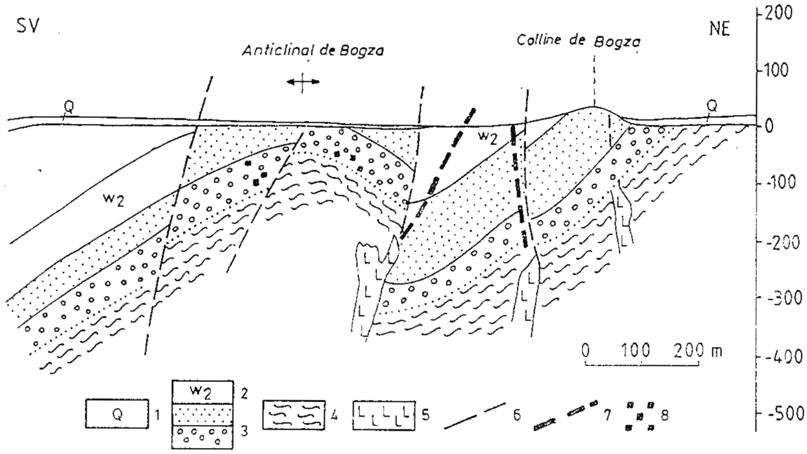

Fig. 2 — Coupe géologique par la colline de Bogza : 1, Quaternaire (Q) : loess ; 2, Werfénien supérieur (w_2) : calcaires et marnocalcaires, pélites schisteuses fossilifères ; 3, Werfénien inférieur (w_1) : conglomérats, grès bariolés et schistes ; 4, Dévonien supérieur (D_3) : schistes séricitcux, schistes siliceux, métagrauwackes ; 5, Paléozoïque : rhyolites ; 6, failles (ac) ; 7, filons de barytine ; 8, concentrations de carbonates cuprifères dans les grès werféniens.

Minéralisations de cuivre. Elles ont été identifiées à Bogza par Peters (1867) ; Murgoci (1914) mentionne des imprégnations de malachite dans quelques microconglomérats, tout comme Bacalu (1959), Savul et al. (1960), Mutihac (1964) et d'autres.

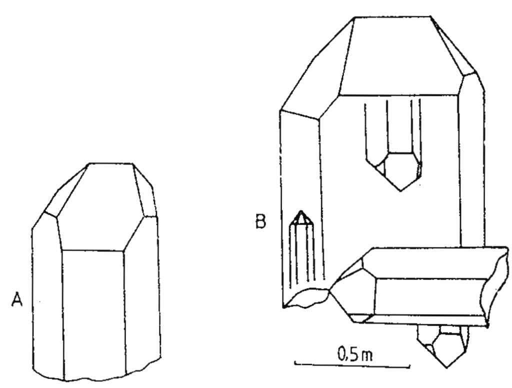

Fig. 3. Cristaux de quartz :A, dans les filons des grès et B, dans les filons des roches siliceux disposés d'une manière autoépitaxiale.

Les minéralisations de cuivre sont situées dans la partie sud du promontoire et font leur apparition dans les filons de quartz des grès et microconglomérats aussi que sous forme d'imprégnations, dans les roches qui se trouvent près des filons de quartz.

Le quartz filonien de l'affleurement est traversé par des cavités et des fissures qui comportent des cristaux et croûtes de malachite. Pendant les travaux de prospection et d'exploration on a observé que tant le quartz filonien que les microconglomérats voisins aux filons comportent des nids de chalcopyrite (Bacalu, 1959).

Filons de barytine. A différence des filons de quartz à minéralisation cuivreux, ceux de barytine se trouvent dans la partie nord du promontoire et sont localisés dans les calcaires et les grès. Ils ont une orientation N75° W et plus rare NS, ayant une épaisseur de 0,15 à 1,30 m et une longueur jusqu'à 100 m.

La barytine de ces filons est accompagnée du quartz et rarement de sidérite. Elle se présente sous forme de cristaux tabulaires divergents, ayant un aspect plumeté, telle la barytine II de Marca (pl. II, fig. 2, pl. III, fig. 1, 2) comportant quelquefois des fragments de calcaire grisâtre (pl. II, fig. 1). La barytine filonienne aussi que le quartz filonien à texture endentée ont été affectés par les déformations de croissance (pl. III, fig. 2 ; pl. I, fig. 2).

Données analytiques. Les données de difraction (Cu $K\alpha_1$, Filtre Ni, $\theta = 0{,}5°$ /min) indiquent que les „pics" de la barytine de Bogza sont identiques à ceux de la barytine des tableaux ASTM de Marca et Somova.

La téneur en BaO et en certains microéléments est notée dans le tableau I (en comparaison avec la barytine d'autres occurences).

TABLEAU I

Occurence	Concentration			
	%		ppm	
	BaO	$BaSO_4$	Cu	Mn
Bogza	61,42	93,45	120	150
Somova, + vallée de Moș Grigoraș	61,74	93,94	nd	nd
Marca	57,30	87,18	100	200
Ruda Mică (Făgăraș) **	61,31	93,27	200	100

* Berbeleac et al., 1985

** Pomârleanu, Nedelcu, 1985

Résulte du tableau que la barytine de Bogza, à une teneur moyenne de 61,42% BaO, se situe, tenant compte de la pureté, entre la barytine de Somova et celle de Ruda Mică (Pomârleanu, Nedelcu, 1985). La téneur en Cu est un peu plus élévée et celle de Mn inférieure à celle de la barytine de Marca.

Les analyses préliminaires effectuées sur les microconglomérats polymictiques à malachite indiquent des teneurs de 0,3 à 1,20% Cu.

Inclusions fluides. L'étude des sections lustrées du quartz et de la barytine, tout comme des sections minces des grès quartzifères et les microconglomérats polymictiques a évidentié de nombreux inclusions fluides. Génétiquement, celles-ci sont primaires et secondaires et du point de vue des relations de phase sont biphasiques et monophasiques.

Les inclusions fluides primaires des minéraux filoniens se sont formées pendant la cristallisation des minéraux hôtes, tandis que celles secondaires sont déterminées de plusieurs séquences de fissuration et la cicatrisation de celles-ci par des solutions hydrothermales postérieures.

Le quartz des filons stérils et de ceux à minéralisations cuprifères se caractérise par des inclusions fluides (liquide + gaz) à contours ramifiés, tubulaires ou éllipsoïdaux, à une longueur inférieure à 0,02 mm (fig. 4A).

Les cristaux de barytine sont entrecroisés par de nombreux plans à inclusions fluides secondaires. Les inclusions primaires sont similaires à celles du quartz, décrites ci-dessus, mais plus longues (fig. 4B).

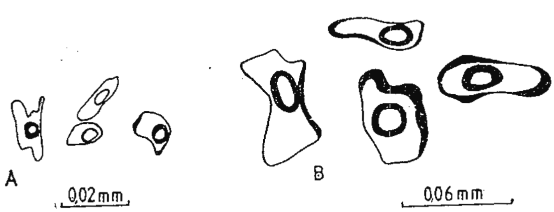

Fig. 4. Inclusions fluides : A, dans le quartz à minéralisations cuprifères ; B, dans la barytine.

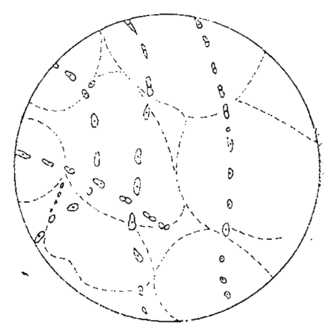

Fig. 5. Plans d'inclusions fluides secondaires disposés sur les fissures dans les grains de quartz des grès werféniens.

On a remarqué des inclusions fluides non seulement dans le quartz et la barytine filonienne mais aussi dans les grains de quartz de la masse des grès et microconglomérats werféniens. Elles sont distribuée sur les plans de fissures qui passent d'un grain de quartz à un autre grain, ayant un caractère secondaire (fig. 5)

Ce fait indique que les solutions hydrothermales, pendant leur circulation par les fissures majeures, ont engendré les minéraux filoniens : quartz, barytine, chalcopyrite, pyrite etc. Parallèlement à la formation des filons, les solutions ont pénétré, sur des certaines aires, dans les pores et les fissures des roches environnantes et se sont conservées sous forme d'inclusions secondaires dans le quartz et d'autres minéraux préexistents des microconglomérats et grès. De telles inclusions sont épigénétiques (secondaires) par rapport aux minéraux qui les renferment et syngénétiques (primaires) par rapport aux minéraux filoniens. Des inclusions similaires ont été décrites dans les grains de quartz des microconglomérats des environs du filon de Băiuț, étant considérées comme le point de départ dans l'application des recherches décrépitométriques dans la prospection (Pomârleanu, 1975).

Données géothermométriques. Savul et al. (1960) nous ont fourni les premières données géothermométriques fondées sur les inclusions fluides du quartz géodique de Bogza. Pour les monocristaux de quartz on a trouvé des températures entre 147 et 179° C, avec un maximum de fréquence entre 155 et 160° C.

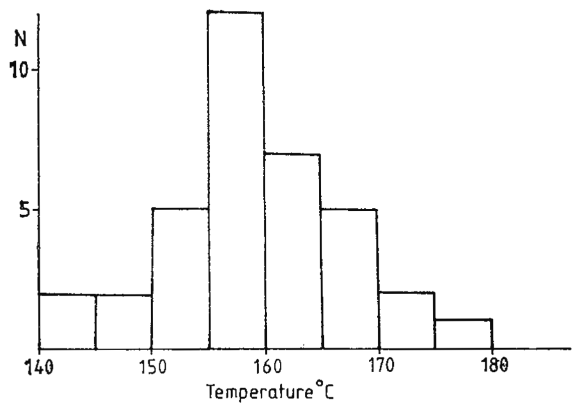

Fig. 6. Histogramme des températures d'homogénéisation des inclusions du quartz géodique.

La présente note apporte des données supplémentaires concernant le régime de température des solutions qui ont engendré le quartz géodique, aussi que des données nouvelles sur le quartz filonien massif blanc-laiteux, associé à la malachite et sur la barytine filonienne.

Le régime thermique pour la formation du quartz géodique, partant des inclusions fluides, selon résulte de la fig. 6, a varié entre 140 et 180° C et le maximum de fréquence a des valeurs similaires à celui déterminé par Savul et al. (1960).

Pour le quartz compact à malachite on constate des températures plus élevées. Les limites varient entre 210 et 275° C et le maximum de fréquence entre 240 et 250° C (fig. 7).

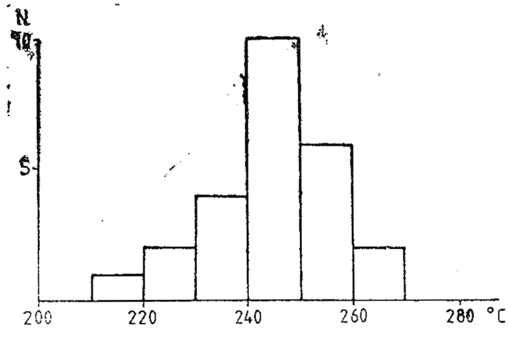

Fig. 7. Histogramme des températures d'homogénéisation du quartz blanc-laiteux associé à la minéralisation cuprifère.

Pour la barytine on a enregistré des températures plus élevées entre 250 et 280° C, à un maximum de 260 à 270° C. La température maximum d'homogénéisation des inclusions fluides primaires de la barytine corresponde à la température du début de la décrépitation de ce minéral (fig. 8).

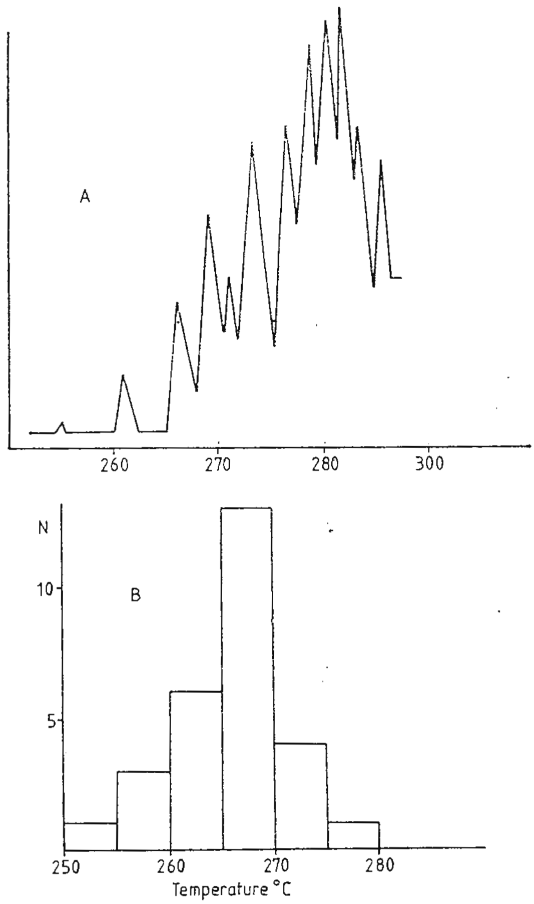

Fig. 8. Décrépitogramme (A) et histogramme (B) de la température de décrépitation et respectivement d'homogénéisation des inclusions fluides de la barytine.

Les températures spécifiques du début et du premier maximum de la décrépitation de la barytine de Bogza se situent entre les limites de la température de formation de la barytine de Somova et de Marca, limites obtenues par d'autres moyens par Manilici et Dumitrescu (1980).

Conclusions. Les données géologiques et celles sur les caractéristiques des filons de quartz et de barytine, tout comme les aspects texturaux et chimiques des minéralisations des inclusions fluides et des déterminations géothermométriques indiquent l'origine hydrothermale de tous les filons.

La formation des filons par l'action des solutions hydrothermales est soutenue par les suivantes observations :

— tant les filons de quartz que ceux de barytine comportent des géodes à agrégats monominéraux ;

— les agrégats monominéraux de barytine comportent quelquefois des fragments de calcaire gris-jaunâtre, imprimant à la minéralisation un caractère bréchique ;

— le quartz filonien blanc-laiteux à minéralisations de sulfures indique des températures entre 215 et 270° C, celui géodique entre 140 et 175° C et la barytine indique des températures un péu plus élevées, entre 250 et 278° C ;

— le quartz et la barytine comportent des inclusions fluides de solutions aqueuses et boulles de gaz a différents degrès de remplissage, caractéristiques à une action hydrothermale ;

— les cristaux de quartz des filons parallèles et discordants par rapport à la stratification des formations werféniennes, ont une orientation perpendiculaire sur les parois des géodes et les cristaux des roches siliceuses et calcaires présentent des textures endentées. Le quartz géodique appartenant au dernier type de filons, présente des orientations différentes et parfois des concrétions autoépitaxiales.

On observe la présence, dans les grès quartzeux et les conglomérats polymictiques, de quelques fragments de schistes séríciteux comportant des nids de chalcopyrite, signalés par Bacalu (1959). Ce fait indique que les agrégats de chalcopyrite, probablement d'autres sulfures aussi, ont été repris dans les conglomérats en même temps que le matériel détritogène des aires continentales exondées où on soupçonne l'existence de zones larges de minéralisations cuprifères (Vîlceanu et al., 1980).

La présence des minéralisations de sulfures et de barytine dans les dépôts werféniens de Bogza et de la minéralisation de barytine dans les brèches des formations dévoniennes de Beilia Mare (Vîlceanu et al., 1983) indique la possibilité de l'identification d'autres occurences de sulfures et de barytine dans la structure de Bogza—Colinele Mahmudiei.

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CONTRIBUȚII REFERITOARE LA MINERALIZAȚIILE DE LA BOGZA (DOBROGEA DE NORD)

(Rezumat)

Promontoriul Bogza, atribuit structurii anticlinale a Colinelor Mahmudiei, este constituit din depozite triasic inferioare. Aceste depozite, reprezentate prin microconglomerate, conglomerate, gresii, calcare, roci silicioase, marne și siltite, sînt străbătute de numeroase filoane de cuarț. Pe lîngă filoanele de cuarț steril se găsesc și filoane de cuarț cu mineralizații cuprifere, precum și filoane de baritină.

Cuarțul și baritina filoniană prezintă ușoare deformări de creștere. În cuarțul granular alb-lăptos, în acel geodic steril sau asociat cu malachit și calcopirită, precum și în cristalele de baritină s-au remarcat incluziuni fluide bifazice identice și cu diferite grade de umplere, fapt ce atestă originea hidrotermală a acestor minerale.

Determinările geotermometrice asupra generațiilor de cuarț cît și asupra cristalelor de baritină arată că aceste mineralizații au un caracter epitermal cu treceri spre mesotermal, indicînd un interval de temperatură cuprins între 140 și 280° C.

EXPLICATION DES PLANCHES

Planche I

Fig. 1. — Structure anticlinale de Bogza, dans les dépôts détritiques werféniens.

Fig. 2. — Agrégats de cristaux de quartz endentés à faibles déformations de croissance.

Planche II

Fig. 1. — Cristaux de barytine (B) lamellaires qui moulent un fragment de calcaire (C).

Fig. 2. — Agrégats tabulaires de barytine disposés d'une manière divergente.

Planche III

Fig. 1. — Agrégats tabulaires de barytine disposés d'une manière divergente.

Fig. 2. — Barytine montrant des faibles déformations de croissance.

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2. ZĂCĂMINTE

FLUID INCLUSIONS IN THE MINERALIZATIONS AT ŢIBLEŞ: IMPLICATIONS IN MINERALOGENESIS [1]

BY

VASILE POMÂRLEANU [2], ELEONORA NEAGU [3]

Fluid inclusions. CO_2/H_2O. Magnesian skarns. Porphyry copper. Salinity. Vein mineralization. Calcite. Geologic thermometry. East Carpathians — Neogene eruptive — Ţibleş

Abstract

The fluid inclusions from the vein mineralizations of the central-north-western group as well as those in some secondary minerals of the magnesian skarns have been studied. The biphasic and triphasic fluid inclusions have been pointed out. The thermal regime of solutions ranged between 400 and 230°C for the base metal mineralization and between 260—150°C for some late assemblages. The CO_2 content of solutions expressed as the CO_2/H_2O molar ratio indicates lower values 0.079 — 0.090 than in the case of some other deposits. The salinity of solutions ranges between 3—16% NaCl for the vein mineralizations. The calcite deposited on fissures in the magnesian skarn minerals is marked by a high salinity, 30—33 wt% NaCl, pressure of about 120 bars and depth of over 1000 m.

(Résumé)

Etude des inclusions fluides des minéralisations de Ţibleş: des implications dans la minéralogenèse. On étudie les inclusions fluides des minéralisations filoniennes appartenant au groupe centrale-nord-oestique et de quelques minéraux secondaires des skarns magnésiens. On a évidentié les inclusions fluides biphasiques et triphasiques. Le régime thermique des solutions a varié entre 400 et 230°C pour la minéralisation polymétallique et pour quelques associations tardives entre 260 et 150° C. La teneur en CO_2 des solutions, exprimée en molaire CO_2/H_2O, indique des valeurs basses (0,079—0,090 CO_2/H_2O) par rapport à d'autres gisements. La salinité des solutions indique des valeurs entre 3 et 16% NaCl pour les minéralisations filonien-

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nes. Dans les minéraux des skarns magnésiens, pour la calcite localisée sur la fissure, la salinité des solutions est élevée: 30 — 33 % NaCl — la pression d'approximativement 120 bars et la profondeur, supérieure à 1000 m.

Introduction

Due to their complexity and special position in the subvolcanic zone of the East Carpathians, the mineralizations from the Țibleș eruptive massif have been the object of many petrometallogenetic, geochemical and mineralogical researches in the last decade (Peltz et al., 1972; Udubașa et al., 1982, 1983, 1984; Pop et al., 1984; Pomârleanu, Neagu, 1983; Pomârleanu et al., 1984). Udubașa et al. (1984) made a critical presentation of the more than 30 papers on this massif.

Based on the study of the fluid inclusions from the vein-like mineralizations and those of the magnesian skarns this paper presents the results on the thermal regime, concentration in volatile elements and salinity of the solutions that generated the mineralizations.

The mineralizations in this zone are of vein-like, impregnation, stockwork and dissemination type.

According to Udubașa et al. (1984), the vein-like mineralizations may be separated in three groups based on paragenetic criteria: the group of central-north-western veins, the group of veins forming the external belt of mineralizations and the Măgura Neagra—Suplai vein group.

The veins belonging to the first group (Tomnatec, Preluci, Saci, 15 Rozinanta, Izvorul Băilor, Izvorul Rău), were reached by the Acer 4, and 8 Bran galleries. These veins are located within dacites (Tomnatec and Grohot types) and contain the following main metalliferous minerals: pyrrhotite, pyrite, sphalerite, arsenopyrite and galena and, as gangue minerals, quartz and calcite. The veins making up the central-western group (especially those at Izvorul Zimbrului, described in detail by Pop et al., 1984) are located in sedimentary formations and consist of bertherite associated with arsenopyrite, pyrite, silver sulphursalts and common sulphides (sphalerite and galena).

The veins of the Măgura Neagra—Suplai group are located in rocks of monzodiorite-granodiorite type and contain abundant chalcopyrite, sphalerite, bournonite and bornite.

The areas of impregnations and stockwork type mineralization extend in the upper basin of the Mesteacăn Valley and in the Izvorul Țibleș—Izvorul Neted—Măgura Neagră zone.

Fluid Inclusions

Four types of inclusions were noticed in the mineralizations of the Țibleș subvolcanic massif.

Type I, the most widespread one in all the mineralizations, is represented by biphasic inclusions, where the aqueous solution phase prevails over the gaseous one (Pl. I, Figs. 1, 2, 3, Pl. II, Figs. 1, 2).

Type II is less frequent, consisting also of biphasic inclusions marked by the prevalence of the gaseous phase (Pl. I, Fig. 4).

Type III is represented by triphasic inclusions — aqueous solution + gas + crystal (halite) belonging to the calcite from fissures in the minerals of the magnesian skarns as well as in hornfelses (Pl. I, Fig. 6).

Type IV is seldom found, consisting in triphasic inclusions : aqueous solution + gas + bitumen (Pl II, Fig. 3).

The above-mentioned types of inclusions are genetically primary and secondary. The primary ones preserve the solutions which generated the mineral containing them. The secondary inclusions (Pl. II, Fig. 2) deposited on fissures in minerals are, according to the age relations of the fissures, of several generations.

The relationship between the primary and secondary inclusions in a mineral assemblage may indicate the temperature interval of the respective mineral succession as well as its paragenetic character.

Thermal Regime of the Ore Solutions

The determinations concerning the thermal regime of the hydrothermal solutions were obtained through the study of the primary fluid inclusions from several calcite and quartz generations closely associated with pyrrhotite, pyrite, sphalerite, galena, chalcopyrite, marcasite, fluorphlogopite, chlorite, laumontite, stilbite etc. If one takes into account the structural and textural aspects of the mineralization as well as geothermometric determinations, the data obtained reflect the formation conditions of other minerals, too.

This is illustrated by the quartz + pyrite + marcasite association in the 8 Bran vein, level + 970 m (Table 1), where quartz was the first to crystallize (indicating temperatures of 390—396°C), while pyrite, which covers quartz in accordance with the temperatures determined on secondary inclusions, indicates the temperature interval of 243—285°C. Marcasite overlying the pyrite crystals probably formed at lower temperatures. Similar situations were found at the Izvorul Netedului (Suplai) vein and at Izvorul Băilor 3 vein (Table 1).

The geothermometric determinations on the veins in the central-north-western part of the deposit confirm the conclusions of Udubaşa et al. (1984) based on the study of the mineral structures, according to which the mineralizations in this sector formed at relatively high temperatures. This is suggestively noticed in the Tomnatec vein. The diagram in Figure 1 shows the frequency curves of the homogenization temperature of the primary calcite fluid inclusions. Curve 1 is for the calcite associated with pyrite, sphalerite, chalcopyrite and galena from the level of 1 019 m (1), while curve 2 is for the calcite associated with galena and chalcopyrite from the level of 970 m. By comparing the data in Table 1 with the frequency curves we infer that both the lower and mean temperatures are higher (307°C, respectively 315°C) for the lower level (970 m) than for the level of 1 019 m (300°C, respectively 310°C). If we take into account the difference of the mean temperature of 5°C and the difference in depth between the two levels (49 m), a thermal gradient of 10°C/100 m is obtained, which points to the acsending character of the solutions. In some

TABLE 1

Distribution of Homogenization Temperatures of the Fluid Inclusions in the Mineralizations at Țibleș

Location		Mineral assemblage	Sample	No.	Inclusions	Temperature °C		
Vein	Level					mean	lower	upper
Tomnatec	+IV (1019)	C+G+Sf +Cp	1861	20	primary	310	300	322
		Q+Py+Cp +Sf+G	1865	9	primary	308	272	332
		Q+Py+G	1862	13	primary	291	274	307
	+970	calcite	1866	3	primary	251	248	256
		C+G+Cp	1868	11	primary	315	307	322
		quartz	1868b	5	primary	271	251	284
Preluci	+970	quartz	1872	7	primary	232	224	246
		Q+Py+G + Sf.	1872b	12	primary	299	256	353
Saci	+1200	quartz	1894	34	primary	283	274	294
				4	secondary	229	222	237
Rozinanta	+970	calcite	1880	9	primary	252	246	258
		Q+Py+G	1885	10	primary	306	296	312
		Q+G	1893A	8	primary	322	294	353
				6	secondary	254	240	265
		Q+G+M	1893B	7	primary	315	312	317
Izv. Băilor	+970	Q+Py+M	1892	7	primary	315	307	322
				10	secondary	246	222	267
Acer 2 gallery	+970	C+G+Py	1886	21	primary	268	258	278
8 Bran	+970	Q+Py+M	1887	13	primary	392	390	396
				6	secondary	262	243	285
Saci	+970	C+F+D	1881	33	primary	318	292	340
				51	primary	217	186	260
Transversal	+970	C+Q+L +S	1882	64	secondary	186	160	220
Izv Netedului	Gallery 47	Q+Py [1])	1890	10	secondary	245	233	265
				5	primary	394	380	398
Furcituri	Valea Furcituri	Q	1895	3	primary	311	303	317
				9	secondary	271	240	303
Haba zone		Q	1888	14	primary	279	270	294

* Q = quartz, Py = pyrite, G = galena, Sf = sphalerite, Cp = chalcopyrite, C = calcite M = marcasite, F = Fluorphlogopite D = diopside, L = laumontite, S = stilbite

[1]) The samples from Izv. Netedului, Furcituri, Haba zone come from the collection of our colleague Roman Laurențiu.

portions of the Tomnatec vein the sterile quartz II indicates lower temperatures at the level of 970 m than quartz I which is associated with pyrite and galena at the level of 1019 m (251—284°C, sample 1868 and respectively 272—332°C — sample 1865 — Table 1). Relatively high temperatures were also noticed for quartz I associated with metallic sulphides in the veins Preluci and 15 Rozinanta (256—353°C and respectively 294—353°C), while somewhat lower values for the sterile vug quartz were noticed for the Saci vein (Fig. 2).

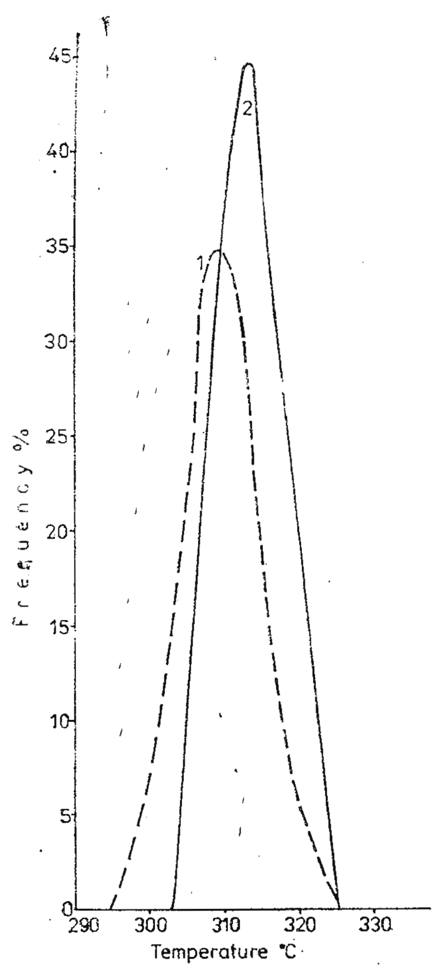

Fig. 1. — Frequency curves of homogenization temperatures of fluid inclusions in calcite, Tomnatec vein: 1, level 1019 m; 2, level 970 m.

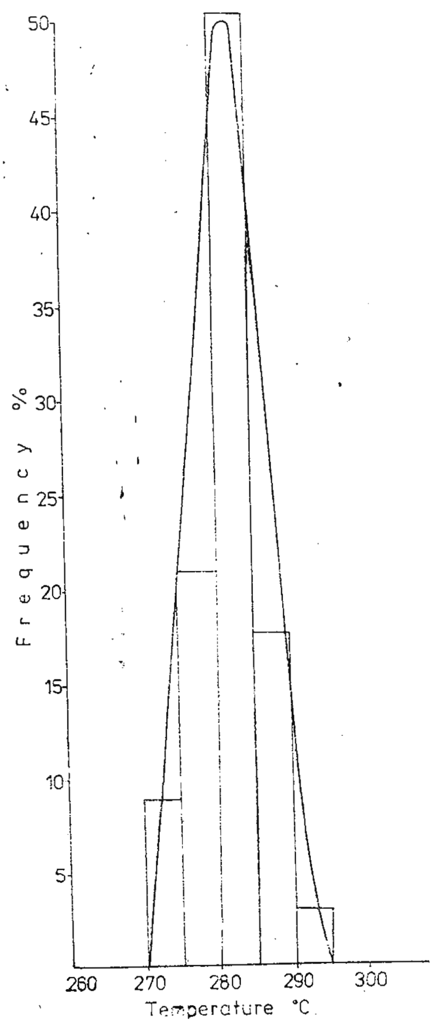

Fig. 2. — Histogram of filling temperatures of the fluid inclusions in quartz, Saci vein (horizon 1200 m).

The calcite deposited on fissures in the skarn minerals from the Saci transversal differs from the calcite type and generations belonging to the vein mineralization by the presence of fluid inclusions of the type III (aqueous solutions + gas + halite). The histograms in Figure 3 (Pomârleanu, Pomârleanu, 1982) indicate two homogenization intervals for each inclusion : one is characteristic of the dissolving of the halite crystals (170—210°C), the other is characteristic of the phase of gas in solution (290—340°C, Fig. 3).

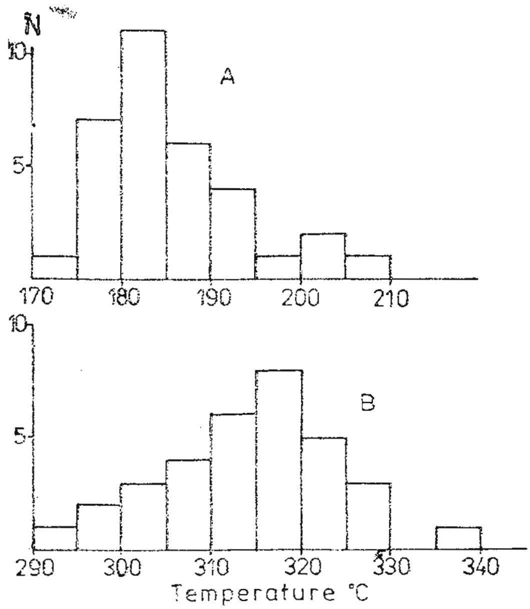

Fig. 3. — Histograms of filling temperatures of fluid inclusions in the calcite deposited on fissures from the skarn minerals ; A — temperature interval for dissolving of the halite crystals ; B — homogenization temperature of the gaseous phase.

A different thermal regime was also determined for the solutions that generated the associations of chlorite, calcite, laumontite, stilbite type in the quartz monzodiorite voids.

The diagram in Figure 4 (Pomârleanu, Neagu, 1983) was built based on the geothermometric data obtained on the primary and secondary fluid inclusions from the calcite of this assemblage.

The diagram shows the frequency curves of the homogenization temperatures of the secondary (1) and primary (2) fluid inclusions within the calcite associated with the above-mentioned minerals. According to the diagram in Figure 4, the interval of the homogenization temperatures of the primary fluid inclusions ranges between 186—260°C, while in the case of the secondary inclusions, between 160—220°C. By the superposition of the frequency curves of the respective temperature we get a common temperature interval (185—220°C) for both types of inclusions, which points to the fact that both minerals (calcite and laumontite) crystallized within this interval. Considering the order of deposition of the minerals in this association : prochlorite — calcite — laumontite — stilbite, we suppose that prochlorite crystallized at a temperature of over 250°C, calcite between 250—186°C, laumontite between 220—185°C, while stilbite at 150—100°C.

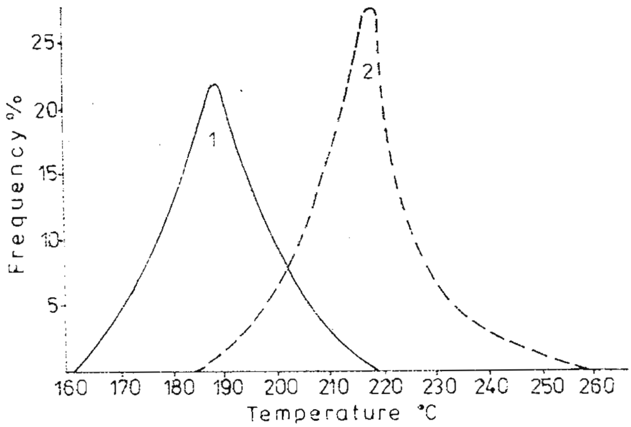

Fig. 4. — Frequency curves of homogeneization temperatures of the secondary (1) and primary (2) fluid inclusions in calcite associated with prochlorite, laumontite and stilbite from the voids within the quartz monzodiorites.

Concentration in Volatile Elements of the Solutions

The hydrothermal solutions preserved in the inclusions contain volatile elements such as : CO_2, H_2O, H_2S, hydrocarbons etc. and Na^+, K^+, Mg^{2+}, Cu^{2+}, Cl^- etc. ions.

The most widespread volatiles are : CO_2 and H_2O. The qualitative determinations have been made by means of gas chromatography. The CO_2 and H_2O release took place after the evacuation and washing with argon (repeated three times) of the samples (whose granulation ranges between 0.3 and 0.5 m and which weigh 0.5—1 g) in a special thermic decrepitation device in order to remove the adsorption gases. CO_2 and H_2O were released by a gradual heating from the quartz grains and trapped in the chromatographic column of Porapak Q type.

Table 2 presents a few preliminary data on the CO_2 and H_2O contents from the fluid inclusions of quartz associated with base metal ores from the Tomnatec and Rozinanta veins at Ţibleş, which are compared with the quartz in some deposits belonging to the Baia Mare metallogenetic province.

Table 2 shows lower CO_2 contents with respect to water for the mineralizations at Ţibleş and much higher ones for the mineralizations at Şuior and Baia Sprie. This fact is much more obvious by the comparison of the chromatograms for CO_2 and H_2O from the Rozinanta vein at Ţibleş and Şuior (Fig. 5).

Figure 5 shows that the area delimited by the CO_2 chromatogram in the Rozinanta vein (A) is much smaller than that in the case of the Şuior mineralization (B).

TABLE 2

CO_2 Contents of Hydrothermal Solutions Preserved in the Fluid Inclusions from the Vein Mineralizations at Țibleș and from Some Deposits in the Baia Mare Region

Deposit	Vein	Level	Sample	Molar ratio CO_2/H_2O	Mean Temperature °C
Țibleș	Rozinanta	970	1883	0.079	315
	Tomnatec	1019	1862	0.090	292
Șuior	Șuior	900	1835	0.218[1]	300
Baia Sprie	Main vein	+ 516	1855	0.337[1]	201

[1] Pomârleanu et al. (1985)

In the case of the Rozinanta vein at Țibleș the molar CO_2/H_2O ratio is of 0.079 and at Șuior of 0.218.

Except for the Șuior deposit, inverse correlations are obvious between the CO_2/H_2O molar ratio of solutions and the mean homogenization temperature, namely as CO_2 content increases, the temperature decreases. It has been recently concluded that high CO_2 contents of the solutions and relatively low temperatures correspond to the gold-silver

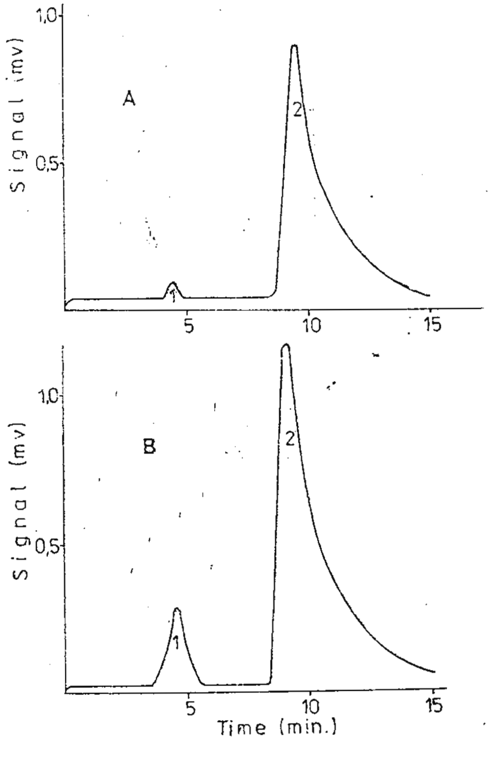

Fig. 5. — Quartz chromatogram: A — for the Rozinanta vein (Țibleș); B — for the Șuior vein; 1, CO_2 curve; 2, H_2O curve.

mineralizations, while low CO_2 contents and relatively high temperatures correspond to the base-metal mineralizations (Pomârleanu et al., 1985). This fact is confirmed in the case of the mineralizations at Țibleș, too.

Salinity of Solutions

Various methods were applied for determining the salinity of solutions depending on the types of inclusions. Thus in the case of the inclusions belonging to the types I and II the method of freezing of fluid phases from the inclusions was applied, which consists in the determination of the dissolving temperatures of the last ice crystals and the plotting of these data on equilibrium curves in the $NaCl-H_2O$ system (Roedder, 1962).

In the case of the inclusions of type III the salinity values of the solutions have been obtained from the dissolving temperatures of halite by heating and the application of the NaCl solubility curves (Sourirajan & Kennedy, 1962).

The salinity interval of the solutions determined for the inclusions of types I and II ranges between 3–16% NaCl, while for the inclusions of type III, between 31–33 wt% NaCl.

Pressure of Solutions

Several methods are known for determining the formation pressure of minerals based on the fluid inclusions. One of them, based on the data obtained on salinity and homogenization temperature of the inclusions of type III, is frequently used. Thus in the case of calcite within skarns the values of the salinity (31–33 wt% NaCl) and temperature (290–340°C) of the solutions plotted on the $NaCl-H_2O$ diagram (Cunningham, 1970) indicate the pressure of 120 bars and the depth of over 1 000 m.

Conclusions

The study of the fluid inclusions from the mineralizations at Țibleș, correlated with the mineralogical observations on the textures, structures and mineral parageneses, shows that the thermal regime of the hydrothermal solutions belonging to the vein mineralizations in the central-north-western part ranged between 400–230°C, while in the case of the chlorite-calcite-laumontite-stilbite assemblage from magnesian skarns between 260–150°C.

The CO_2 contents of the solutions from the inclusions, as shown by the CO_2/H_2O molar ratio (0.079–0.090), are much lower than those from some deposits in the Baia Mare province.

The salinity of the solutions varied within wide limits, from 3–16 wt% NaCl for the vein mineralizations to 31–33 wt% NaCl in the case of the calcite deposited on fissures in the magnesian skarns.

The pressure corresponding to the formation of calcite on fissures within skarns indicates values of about 120 bars and a depth of over 1 000 m.

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STUDIUL INCLUZIUNILOR FLUIDE DIN MINERALIZAȚIILE DE LA ȚIBLEȘ : IMPLICAȚII ÎN MINERALOGENEZĂ

(Rezumat)

În cadrul masivului eruptiv Țibleș se cunosc mai multe tipuri de mineralizații : filoniene, de impregnație și skarne magneziene (Udubașa et al. 1984).

Mineralizațiile filoniene, după poziția lor în masiv și după asociațiile de minerale, aparțin grupului central-nord-vestic, central — vestic și grupului filoanelor Măgura Neagră—Suplai.

În lucrare se studiază incluziunile fluide din mineralizațiile filoniene ale grupului central-nord-vestic (Tomnatec, Preluci, Săci, 15 Rozinanta, Izvorul Băilor, Izvorul Rău, 8 Bran). În cadrul acestei mineralizaţii s-au evidenţiat incluziuni preponderent lichide pînă la acelea preponderent gazoase (Pl. I, fig. 1, 2, 3, 4, 5). Incluziuni trifazice (soluţie apoasă + gaz + halit) s-au observat numai în calcitul depus pe fisuri în mineralele skarnelor magneziene.

Regimul termic al soluţiilor se caracterizează printr-un interval de temperatură relativ ridicat (400°—240°C), fapt ce confirmă aprecierile de temperatură făcute de Udubaşa et al. (1984), pe baza asociaţiilor şi structurilor mineralelor.

Conţinuturile în CO_2 şi H_2O ale soluţiilor, din cuarţul filonian exprimate în raport molar sînt mici (0,070—0,090 CO_2/H_2O) faţă de soluţiile hidrotermale ale zăcămintelor din provincia Baia Mare, iar salinitatea între 3 şi 16% NaCl. Calcitul din skarnele magneziene s-a depus din soluţii cu salinitate ridicată (30—33% NaCl) la presiune de cca 90 bari şi la o adîncime mai mare de 1 000 m.

EXPLANATION OF PLATES

Plate I

Fig. 1. — Biphasic fluid inclusions (liquid + gas) in calcite associated with sphalerite, galena, chalcopyrite in the Tomnatec vein, level 1019 m.

Fig. 2. — Tubular fluid (liquid + gas) inclusion in the calcite sample from Figure 1.

Figs. 3—4 — Fluid inclusion (liquid + gas) as negative crystal (Fig. 3) and predominantly gaseous inclusion (Fig. 4), both in the quartz crystals, Furcituri vein.

Fig. 5. — Fluid inclusion (liquid + gas) as negative crystal in the quartz associated with pyrite and galena (Tomnatec vein).

Fig. 6. — Triphasic fluid inclusion (liquid + gas + halite) in the calcite from the skarn minerals of the Saci gallery.

Plate II

Fig. 1. — Fluid inclusion (liquid + gas) in calcite associated with prochlorite-laumontite-stilbite from the quartzmonzodiorite voids.

Fig. 2. — Secondary fluid inclusions in the quartz associated with pyrite, Izvorul Netedului vein.

Fig. 3. — Triphasic inclusions (liquid + gas + bitumen) in the quartz from the Furcituri vein.

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2. ZĂCĂMINTE

PALEOGEOGRAPHY OF THE SUBCARPATHIAN MIOCENE AND THE GENETIC MODEL OF THE JITIA-TYPE MINERALIZATION[1]

BY

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Miocene. Sulphide. Nappe. Formations. Evaporite. Sulphur isotope. Syngenetic. Genetic model. East Carpathians — Eastern Subcarpathian area — Rîmnic Hills

Abstract

The Miocene sedimentary rocks from the Carpathian bend area contain sulphide occurrences at several stratigraphic levels (mainly Lower Miocene) and assigned to different structural units. However, the most important are the sulphide occurrences of the Subcarpathian Nappe formations, and less of the Marginal Fold Nappe. The mineralizations are spatially and genetically related to evaporite deposits — the Salt Formation and the Grey Formation with Gypsum (Stufu Gypsum Complex). The main ore minerals (pyrite, pyrrhotite, greigite, marcasite, iron-poor sphalerite and galena) form impregnations, clusters, lenses and veinlets in grey feldspathic sandstones (occurrences in Boştina brook, Sub Măgură) or thin beds in the marl blocks of the salt breccia (Argintari brook). The sulphides are commonly poor in minor elements ; however, high Tl, Mo, Mn contents are accidentally encountered. Sulphur isotopes account for different sulphur sources, $\delta\ ^{34}S$ ranging from $-31.85^0/_{00}$ to $+13.37^0/_{00}$; a gypsum sample points to $+13.47^0/_{00}$. The mineralizations are syngenetic-syndiagenetic, with greigite and framboidal pyrite firstly formed ; metals result from the transport of material from emerged areas (inner and outer). The genetic model most appropriate to the sulphide concentration in lagoon basins during the Lower Miocene is the „evaporite pan'' one, where sulphur is supplied by sulphate reduction.

Résumé

La paléogéographie du miocène subcarpathique et le modèle génétique de la minéralisation de „type'' Jitia. Dans les dépôts sédimentaires miocènes de la zone de courbure des Carpates il y a des occurrences de sulfures situées à plusieurs niveaux stratigraphiques (surtout le Miocène inférieur) et dans différentes unités structurales. Les plus importantes sont les occurrences

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de sulfures des formations attribuées à la nappe subcarpathique, et moins dans la nappe des plis marginaux. Les minéralisations s'associent spatialement et génétiquement aux dépôts évaporitiques — la formation à sel et la formation grise à gypses (le complexe du gypse de Stufu). Les principaux minéraux métallifères (pyrite, pyrrhotite, greigite, marcasite, sphalérite à peu de fer, galène) constituent des impregnations, nids, lentilles et filonnets dans les grès feldspathiques grisâtres (les occurrences dans la rivière de Boştina, Sub Măgură) ou bien des bandes minces dans les blocs de marnes de la brèche du sel (ruisseau d'Argintari). Généralement les sulfures ont peu d'éléments mineurs ; cependant les teneurs en Tl, Mo, Mn plus élevées sont accidentelles. Les isotopes du soufre suggèrent des sources diverses, $\delta^{34}S$ variant de $-31,85^0/_{00}$ à $+13,37^0/_{00}$; un échantillon de gypse indique $+13,47^0/_{00}$. Les minéralisations sont syngénétique-syndiagénétiques et la greigite et la pyrite framboïdale se sont initialement formées ; les métaux sont générés par le transport du matériel des aires émergées (interne et externe). Le modèle génétique le plus adéquat à la concentration des sulfures dans les bassins lagunaires pendant le Miocène inférieur est de type „evaporite pan" où le soufre provient de la réduction des sulfates.

The Subcarpathian Nappe is the outermost unit of the Moldavides which groups together the outer East Carpathian Miocene deformed nappes. They are (from the interior toward the exterior of the chain) the Convolute Flysch, Macla, Audia, Tarcău Marginal Folds and Subcarpathian nappes. Miocene deposits are involved in the last three nappes, predominating in the Subcarpathian one.

The Jitia-type occurrences crop out in the Miocene formations of the Subcarpathian Nappe and, partly, in those of the Marginal Folds. This is the reason to analyse the paleogeography and the palinspastics of the Lower and Middle Miocene formations, mostly within the two mentioned nappes.

Structural Framework

As mentioned, the Moldavides include nappes which were displaced (overthrust) during the Miocene time. Three tectogenetic moments which generated the successive deformation of the Moldavides were recorded (Dumitrescu, Săndulescu, 1968; Săndulescu, 1984): intra-Burdigalian („Old Styrian"), intra-Badenian („Young Styrian") and intra-Sarmatian („Moldavian"). Each of these moments involved successively more external elements of the chain, emphasizing the migration of deformation.

All the Moldavidian nappes are cover units built up only of sedimentary formations (Cretaceous—Miocene generally, Oligocene—Miocene in the Subcarpathian Nappe). The primary basements of these sedimentary formations were subducted under the Central East Carpathians, concomitantly with the underthrusting of the foreland.

The nappes with well represented Miocene deposits are the Tarcău, Marginal Folds and Subcarpathian ones. In the Tarcău Nappe the Miocene deposits are preserved in the outer structures as well as within some internal synclines. In the Marginal Folds they are involved in the synclinal structures all over the area. South of the Năruja Valley a detachment slab pulled out the Marginal Folds is preserved beneath the frontal part of the Tarcău Nappe; it is built up by the Burdigalian Salt Formation. The Subcarpathian Nappe is mainly constituted by Lower and Middle Miocene formations. It was divided (Săndulescu et al., 1980) into three digitations (subunits): Măgirești—Perchiu, Pietricica and Valea Mare (from the interior toward the exterior), which show some specific lithofacial features.

The Foredeep (s. str.) develops in front of the most external folded units of the Carpathians, namely the Subcarpathian Nappe. The inner limb of the foredeep (filled with Neosarmatian-Pliocene deposits) covers in the bend area the frontal part of the latter.

Lithostratigraphy of the Lower and Middle Miocene Formations in the Outer Moldavides

The Oligocene/Miocene chronostratigraphic boundary crosses the upper part of a bituminous succession constituted of dyssodilic shales (bituminous clays) and menilites (bituminous cherts) with interlayerings of quartzose sandstones. The first lithostratigraphic correlation level at the lowermost part of the Miocene is the Upper Menilites level. In the Marginal Folds and Subcarpathian nappe it is overlain by the Goru—Mișina Formation which still shows bituminous rocks and is also invaded by coarse-grained arenites or microconglomerates. The correspondent of the Goru—Mișina Formation in the outer part of the Tarcău Nappe is a predominantly bituminous „Supramenilitic Horizon".

A second correlation level is situated above the Goru—Mișina Formation and the „Supramenilitic Horizon", within the Lower Burdigalian and is represented by evaporitic deposits.

In the Marginal Folds and Subcarpathian nappes the Salt Formation develops at this level. The Salt Formation consists of clayey-siltic matrix with fragments of different lithologies and size, i.e. Dobrogea-type greenschists, Mesozoic and Eocene limestones, Paleogene rocks of flysch-type. Locally (Vrancea Mts. in the Marginal Folds) the lowermost part of the Salt Formation is massively conglomeratic. The salt and/or gypsum are developed discontinuously; the salt massifs are lense-like or the salt is interbedded with clay or silt layers. At the top of the Salt Formation a specific arenitic formation showing partly arcosian features — the Condor Sandstone — develops.

In the outer part of the Tarcău Nappe the Salt Formation is still present, but it is thinner, the evaporitic level being mainly represented by the „Lower Gypsum". In the frontal part of the nappe the equivalent of the Salt Formation is the „Green Series" or the Buștea Formation (gypsiferous sandstones, silts, clays and marls, conglomerates).

Above the evaporitic deposits the lithological features are more diversified with frequent lateral changes. Conglomerates develop in the outer part of the Subcarpathian Nappe (Pietricica Conglomerates rich in green schists elements). They pass laterally and upwards to sandy molasse red formations, known in different units or subunits under different names: Tescani, Măgirești, Hîrja or Tresticara (Fig. 1). The upper boundary of the red sandy molasse deposits is diachronous, being younger toward the exterior.

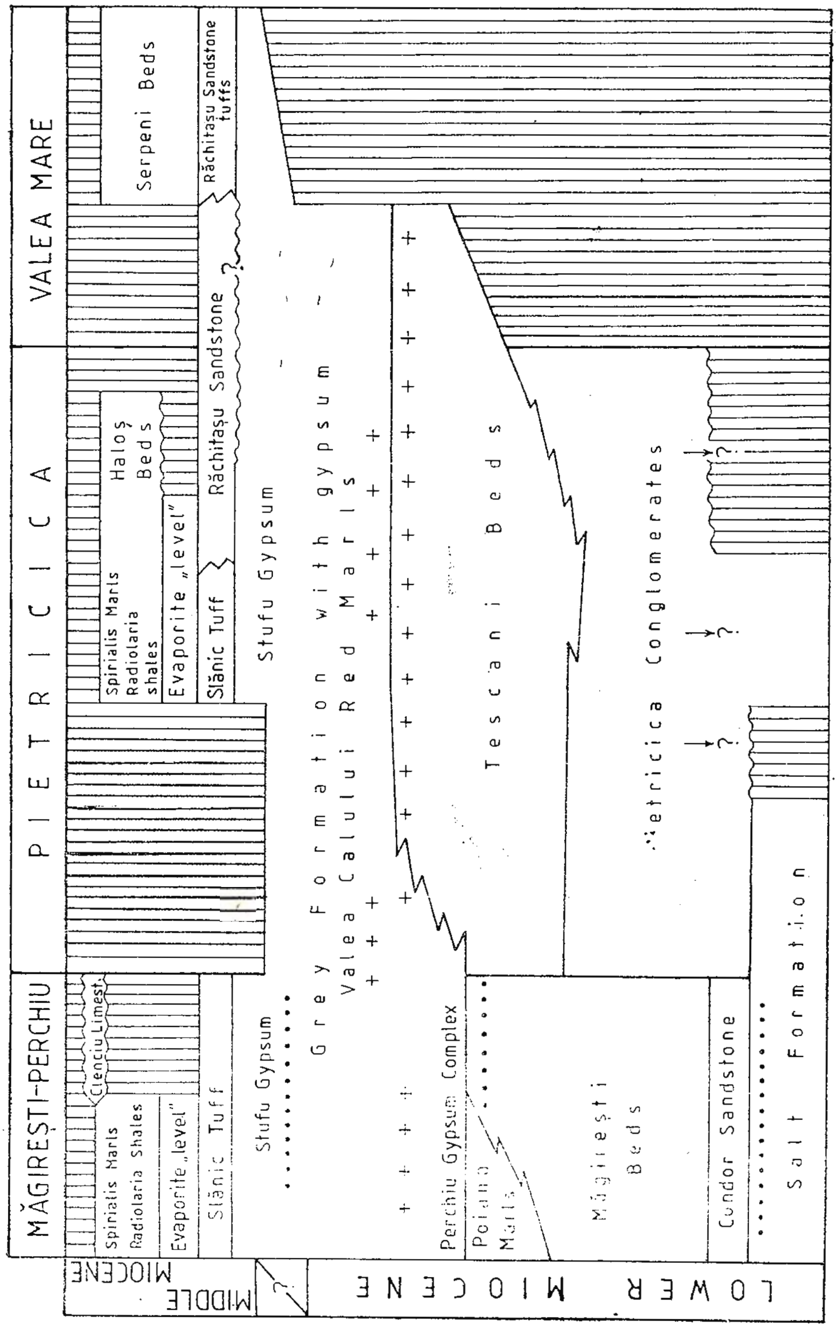

Fig. 1. — Lithostratigraphic position of base metal sulphide ores in the Subcarpathian Miocene. ... ocurrences; ++ gypsum.

The Grey Formation with gypsum develops mainly in the Subcarpathian Nappe. It is a schlier formation with marls, sandstones and sands, which shows at different levels evaporitic rocks (gypsum). There are two main evaporite levels known in this formation. The lower one — the Perchiu Gypsum — develops only in the inner part of the Subcarpathian Nappe (Măgirești Subunit) and in the outer part of the Marginal Folds Nappe. The upper level — the Stufu Gypsum — is more often developed within the Subcarpathian Nappe. The Lower/Middle Miocene boundary is situated approximately at the bottom of the Stufu Gypsum.

A very important correlation level develops in the Lower Badenian. It is represented by cinerites (Slănic Tuff) with which are associated Globigerina Marls and, towards the exterior, calcareous sandstones (Răchitașu Sandstone). Above this cinerite level is known the Middle Miocene evaporitic level which is represented by gypsum in the Moldavian area. To the south and the west (Wallachia) salt-bearing formations are also developed at this level.

Lithogenetic Remarks on the Main Rock Types of the Subcarpathian Miocene

In order to define the main features of the sedimentation environments as well as the genetic model of base metal sulphide deposits a revision of the most relevant lithogenetic features of arenites, clays and evaporites which constitute the Subcarpathian Miocene deposits from the East Carpathian bend area is needed.

Arenites and rudites

The coarse-grained (conglomerates and microconglomerates) and sandy (arenites) deposits occur in different amounts within the Miocene formations. Most of the detrital deposits occur in the Red Formation (Tescani and Măgirești beds) and in the Bîrsești Conglomerates or their equivalents. Sandy sequences are less numerous in the Grey Formation with gypsum and in the Răchitașu Sandstone.

Both the detrital rocks of the Red Formation and the Bîrsești Conglomerates are generated by an arenitic and ruditic source located outside (east) the sedimentation realm of the Subcarpathian Miocene. The greenschists of Dobrogea type occurring in both conglomerates and microconglomerates or sandstones constitute the „marker" of this source. Besides greenschists, quartz and mica fragments prevail; the lithic fragments (mainly Permian or Eotriassic red sandstones, Mesozoic and/or Eocene limestones) are sparse, being easily recognized in the foreland as outer source area.

The detrital rocks (breccias, conglomerates, sandstones) associated with the Eomiocene Salt Formation are also related to the outer source.

The external source acts on the Salt and Red formations exceeding the internal margin of the Subcarpathian realm, on the Marginal Folds area (Salt Formation, including the Piatra Geamănă Conglomerates and the Hîrja Beds) and even on the front area of the Tarcău Nappe (Salt Formation).

The transport and areal distribution of the ruditic component are represented by large fans, laterally interfingered and sometimes redistributed longitudinally. The arenitic fraction is supposed to be formerly transported with the ruditic one and then farther on, in wards. The sedimentation depth is reduced or very reduced considering the rain drops, the ripple-marks and the footprints on the upper faces of some sandstones.

The detrital rocks of the Grey Formation with gypsum depend on a different source as proved by the absence of greenschist fragments of Dobrogea type. Săndulescu (1962) supposed that the source of the detrital rocks of the Grey Formation with gypsum was located inside the sedimentation area of the Lower Miocene deposits in the Outer East Carpathians, inside the Tarcău Nappe sedimentation area respectively. This accounts, to a certain extent, for the lack of coarse-grained components from the Grey Formation of the Subcarpathian Nappe, while similar components occur inside the Tarcău Nappe (Brebu Conglomerates and their equivalents).

Within the Grey Formation of the Subcarpathian Nappe the detrital material was transported sometimes at greater depths than in the case of the Red Formation (as proved by the abundant mecanoglyphs), but in almost similar conditions (as proved by the rain drops and the ripple marks); no bird or mammal footprints similar to those known in the Red Formation have been so far reported from the Grey Formation.

It is worth mentioning that the two opposite detrital sources do not exclude each other entirely. One may speak of the prevalence of one of the two sources, as proved by the resedimentation in the Red Formation of Paleogene and Senonian microfauna from the Flysch Zone or by the presence in some areas of the Grey Formation of an external supply.

The inferences on the sources of the Subcarpathian Miocene detrital rocks are also confirmed by the heavy mineral studies (A. Popescu, in Săndulescu et al., 1978). The study of the Red Formation outcrops in the Subcarpathian Nappe (Jitia, Lopătari) pointed out greenschists which account for the important supply from the foreland in contrast with the Red Formation (Trestioara Beds) of the Tarcău Nappe with unimportant or no supply from the foreland. However the heavy mineral assemblages yielded by the red deposits of the Tarcău Nappe are similar to those of the Grey Formation, pointing to a unique distribution area, the Carpathian realm respectively.

The corroboration of all available data on the heavy mineral distribution in different Miocene formations reveals that the detrital supply from the foreland is much reduced in the sedimentation area of the Tarcău Nappe Red Formation, as compared to both the subjacent Salt Formation and the synchronous Red Formation of the Marginal Folds Nappe and the Subcarpathian Nappe.

Argillaceous rocks

The study of the argillaceous fraction of the Miocene deposits (Rădan, in Săndulescu et al.,1978,1980) has shown that the eastern source area of the foreland supplies a binary mineralogic sequence (illite+chlorite) during the deposition of the Salt Formation, of the Red Formation (Măgireşti, Tescani, Hîrja Beds) and of the Perchiu Gypsum. This material is of low maturity grade, characteristic of physical alterations, as proved by both geochemical and mineralogical features (chlorite, illite and feldspar abundances in the fine fraction).The western (inner) source area, represented by the Carpathian chain, which even if not always passive, is actively involved especially in the formations younger than the Perchiu Gypsum, while to the south of the Miocene sedimentation area its influence is marked by montmorillonite occurrences.

The argillaceous rocks supplied by this source are of intermediate nature, with medium value maturity indices.

In the Slănicul de Buzău area the mineralogic composition of the argillaceous rocks accounts for mixed influences of the main source areas during the Lower Miocene. Starting from this source westwards the mineralogic assemblages are qualitatively similar and their value as stratigraphic marker diminishes.

Gypsum

The petrogenetic studies and the paleogeographic reconstructions of Miocene evaporites are rather difficult because of the folds, faults and overthrusts which characterize these deposits. More problems arise from the outcrop discontinuities associated with an initial discontinuity and heterochrony.

The petrographic study of the Lower Miocene gypsum deposits points to several common features from both structural petrographic and textural points of view, which might show that their sedimentation conditions were similar.

The Perchiu Gypsum Complex overlies closely several layers which, according to Panin and Avram (1962) and Panin (1964), contain numerous terrestrial vertebrate imprints associated with ripple-marks. All these prove a very shallow sedimentation. Considering some structures (chicken-wire, discoidal nodules, displacement nodular structures) the Perchiu Gypsum might be considered to have formed at the boundary between the subaqueous and the subaerial environments. However, the lack of shallow carbonate sediments as well as the detrital matter related to the gypsum obviously deposited in aqueous environment do not agree with the hypothesis of subaerial sedimentation. Moreover, the massively bedded gypsum which constitutes most of the evaporites of the Perchiu Gypsum Complex are considered to represent evaporites precipitated from $CaSO_4$ supersaturated waters.

Another aspect of evaporite genesis is represented by the climate conditions. The numerous imprints of terrestrial vertebrates (birds, mammals) present below the Perchiu Gypsum Complex, as well as the abundant terrigenous matter account for warm and wet climate in an area with a relatively dense hydrographic network yielding great amounts of terrigenous matter.

It is thus supposed that the evaporite stages of the Grey Formation were related to relatively flat areas, with depressions in which massive layered gypsum did deposit. The nodular gypsum deposits resulted from the evaporation of interstitial solutions generated by adjacent aqueous basins. The aridity periods were interrupted by abundant rainfalls, when important amounts of terrigenous material covered the deposition areas and greatly changed the regional topography.

The Middle Miocene sulphate-bearing evaporite levels seem to have formed in some basins characterized by restrictive circulation. This is proved by the massive-bedded gypsum deposits and their association with laminated bituminous dolomites („calcareous shales"), which in places yield a normal marine globigerinid microfauna.

The Salt Formation

The evaporite sedimentation occurs at different levels in the Lower and Middle Miocene and might be considered as a typical recurrent event. The precipitation of soluble salts during the Lower Miocene is known at the level of the Salt Formation, widespread in Moldova and Muntenia, while in the Middle Miocene soluble salts occur mainly in Muntenia and Transylvania. While the Eomiocene salt deposits are underlain by marine deposits and overlain by red formations deposited in neritic to fluvial-lacustrine environments, the Middle Miocene Salt Formation is interlayered only in marine ones. Of interest to the present study is only the Lower Miocene Salt Formation.

The investigations carried out all over the Miocene area of the East Carpathians (Săndulescu et al., 1975—1980) have shown that the paleobasin of Lower Miocene salts was narrow, with northward communication with the open-sea, being bound to the west by the Carpathian area and to the east by the foreland, the latter with a relatively active relief. The proper evaporite sedimentation was disturbed by detrital supply from platform uplifting.

The Lower Miocene deposition of salt, more than 100 m thick (stratigraphic thickness), as well as some potash salt accumulations might be better interpreted by means of the deep basin theory (Schmalz, 1969) than by the classical theory of subsiding bottom basins. Several lagoons, resembling some satellite basins round the main deeper basin, intermittently communicating with the open-sea and thus favouring the hypersalinization of the deep-seated brines.

Just from the initial stage, small carbonate amounts did deposit, especially at the periphery of the basin, represented, for example, by the dolomite layers of the Cornu Beds in Muntenia. The euxinic stage is better represented all over the area covered by the Salt Formation, consisting of dark argillaceous, low bituminous shales, associated with gypsum crystals and sulphate efflorescences resulted from sulphide supergene alteration. During the subsequent stages, the fractional deposition took place: first of gypsum, mainly in the peripheral zones and then of salt mainly in the principal basin and in less amounts in the adjoining basins. Finally potash salts deposited in places.

As already mentioned, the precipitation of soluble salts is partially disturbed by the supply of detrital material, especially in the peripheral lagoons, where the interrupted process may start again with the precipitation of gypsum. During the final stage, the evaporites deposited in shallow waters, even in subaerial environment, as proved by the mud-cracks present in the argillaceous sediments related to the salt deposits. The detrital supply replaced, more or less gradually, the precipitation of salts during stages probably different from one lagoon to the other. Thus, it is inferred that the same paleobasin includes zones with gradual transition from salt to potash salts and zones with detrital supply which filled the lagoon and stopped the precipitation of soluble salts at the level of halite.

When the evaporite sedimentation ceased the buried deposits were subject to diagenetic changes. Among them it is to note the levigation of soluble salts from the peripheral areas of the paleobasin and their redeposition in central areas. The soluble salts are overlain by rocks, rather thick in places, of breccious or bedded character and impregnated with halite. These impregnations reach the so-called „salt mirror", which, as a matter-of-fact, is a false hanging wall covering the proper deposit and attenuating the very complicated structures of the latter.

The Mineralization from Jitia and the Adjoining Areas — Mineralogic data

The major components of ores are: sphalerite, galena, marcasite, pyrite, greigite, pyrrhotite associated — in negligible amounts — with chalcopyrite usually contained by sphalerite. Ilmenite, rutile and leucoxene, and scarce magnetite, occur sparsely in sulphides (ilmenite) or in the matrix of sandstones; fine graphite lamellae are very sparse. There are some differences of mineralogic composition (Tab. 1) among the three occurrences studied (Argintari brook, Boştina brook and „sub Măgură" area) and therefore they are to be presented independently. The occurrence in the Argintari brook differs from the other two ones owing to the type of ore deposit and mainly the stratigraphic position.

The occurrence in the Boştina brook and gallery 3. The ore is represented by fine impregnations in sandstones, difficult to note macroscopically, generating irregular veinlets perpendicular to the bedding; these veinlets become sometimes thinner within the sandstone layer unrelated to the marly-clayey interlayerings, which are usually barren. Marcasite, sphalerite and galena are the most frequent minerals; pyrite is scarce, while greigite occurs in places. Ilmenite, rutile, leucoxene, scarce titanite (on biotite cleavages) and magnetite are spread in the sandstone matrix; biotite is relatively frequent, even abundant in places, being represented by curved or U-shaped lamellae. Sulphides constitute irregular aggregates, usually of reduced size; they are mostly present in the sandstone matrix and only rarely show the tendency of substituting or corroding the detrital components (especially pyrite). Marcasite usually constitutes radial aggregates consisting of lamellae which start from a greigite core; it is juxtaposed to the other sulphides with which it associates only rarely. Sphalerite and galena are often intergrown or may form monomineral aggregates; sphalerite is nonuniformly coloured, pointing to composition variations. Pyrite is represented by subhedral grains contained by the sandstone matrix or by sphalerite. Greigite forms irre-

TABLE 1

Mineralogic Composition of the Occurrences in the Jilia and Adjoining Areas

	Boştina brook	Sub Măgură	Arginatri brook	Vintileasa
pyrrhotite			**	
pyrite	** (F)	* (F)	*** (F)	*
melnicovite pyrite			**	
marcasite	***	**	**	***
greigite	**	*		*
sphalerite	***	***	***	
galena	***	***	**	
chalcopyrite	* [1]	* [1]	* [1]	
ilmenite	*	*		
rutile		*		
titanite	* [2]			
leucoxene	*	*	**	
graphite	*			
magnetite	*	*		
hematite	* [3]			
glauconite [4]	*	*		

*** — frequent mineral
** — present
* — scarce
(F) — framboidal

[1] exclusively as inclusions in sphalerite
[2] on biotite cleavage, associated with pyrite
[3] as exolutions in ilmenite
[4] yielded by thin sections

gular, sometimes ellipsoidal patches surrounded by marcasite or pyrite. Usually it is hardly polished. The colour of greigite and of pyrrhotite is the same, the former being isotropic; it is one of the few magnetic sulphides; owing to this characteristic, a magnetic fraction was obtained from one of the samples (SC-22) and after binocular selection it was X-ray analysed. The sample diffractogram, representing a mixture (the greigite patches do not exceed 200 – 300 microns), exhibits the main diffraction peaks of greigite (d 2.97) and the main peaks of pyrite (d 2.69), sphalerite (d 3.12), calcite (d 3.02) and feldspar and/or quartz (d 3.35). As this mineral is usually metastable, its alteration into other iron sulphides is easy, as proved by the available samples; besides the marcasite rims, the central zone of greigite patches contains frequent marcasite grains or fine lamellae; owing to topotactic transformation the whole mass is slightly anisotropic.

Ilmenite constitutes small size grains (50 – 100 microns), usually unrounded; sometimes it is included in sphalerite. Some grains exhibit fine hematite exsolutions accounting for its source in metamorphics. It is seldom rutilized, more often leucoxenized.

Other features of the Boştina mineralization are: (1) pyrite and titanite occurrences on biotite cleavages: (2) the presence of foraminifera shells moulded by sphalerite; (3) fine pyrite or marcasite veinlets in the detrital grains. This last feature is due to the fact that these two sulphides are not primary, syndepositional, but have resulted during diagenesis, at the expense of preceding greigite. The sulphide, mainly galena, veinlets perpendicular to the sandstone bedding might be of the same age as the diagenesis ; in sedimentary environments with „sulphide mud" deposition, sulphides are the last to crystallize, sometimes during diagenesis, and migrate along short distances, even on fissures resulted during sediment lithification.

The occurrence in the „sub Măgură" area. Situated on the same stratigraphic level with the one in the Boștina brook and assigned to another structural unit, the mineralization in the area „sub Măgură" shows the same mineralogic characteristics ; however, galena seems to be the prevailing metalliferous mineral. There are circular or quasi-circular sphalerite and galena aggregates, rutile inclusions in the irregular sphalerite patches. Pyrite, greigite and ilmenite display the same mode of occurrence as the mineralization in the Boștina brook. The marcasite amount is slightly reduced. Pyrite is framboidal in places. The relations among sulphides are usually mutual, of juxtaposition type ; galena tends to infiltrate in sphalerite. The latter shows composition variations marked by internal reflections and „opacity degree".

The occurrence in the Argintari brook. It is situated at a stratigraphic level inferior to that of the occurrences described above (Fig. 2). This mineralization also has other specific features : it is represented by mineralized rock fragments contained by the salt breccia, its most relevant feature being the massive pyrrhotite aggregates ; framboidal pyrite is rather abundant, and marcasite often constitutes globular aggregates, while the collomorphic structures — partly „frozen" in places — contain pyrite, i.e. melnicovite-pyrite and alternating „radial" pyrite and sphalerite bands. Marcasite amounts are reduced as compared to the other two occurrences, being much more „aggressive" to the detrital grains which they frequently penetrate along fissures ; this results in the filigree-like marcasite. The rocks bearing sulphides are of very different types, while sulphide occurrences are equally different : dense ore clusters, rock fragments with extremely fine sulphide veinlets, very fine sulphide bands parallel to the rock bedding (clayey marls). Titanium minerals are scarce and mainly represented by irregular leucoxene masses. The different morphologic characteristics and the pyrrhotite occurrences point to the heterogenetic nature of this mineralisation, with a long time „evolution" ; this last feature is also proved by the complex relations among sulphides, the distinct sequence, the substitution, etc. The samples studied do not contain greigite.

The occurrence at Vintileasa, Bisericii brook. Marcasite, of prismatic-lamellar type, is the only mineral macroscopically visible in a sample collected by eng. M. Popa. Under the microscope the lamellar marcasite aggregates exhibit isolated pyrite or irregular greigite aggregates, also present at the periphery of marcasite lamellae. Some characteristic microscopic features are shown in Figure 2 and Plates I—III.

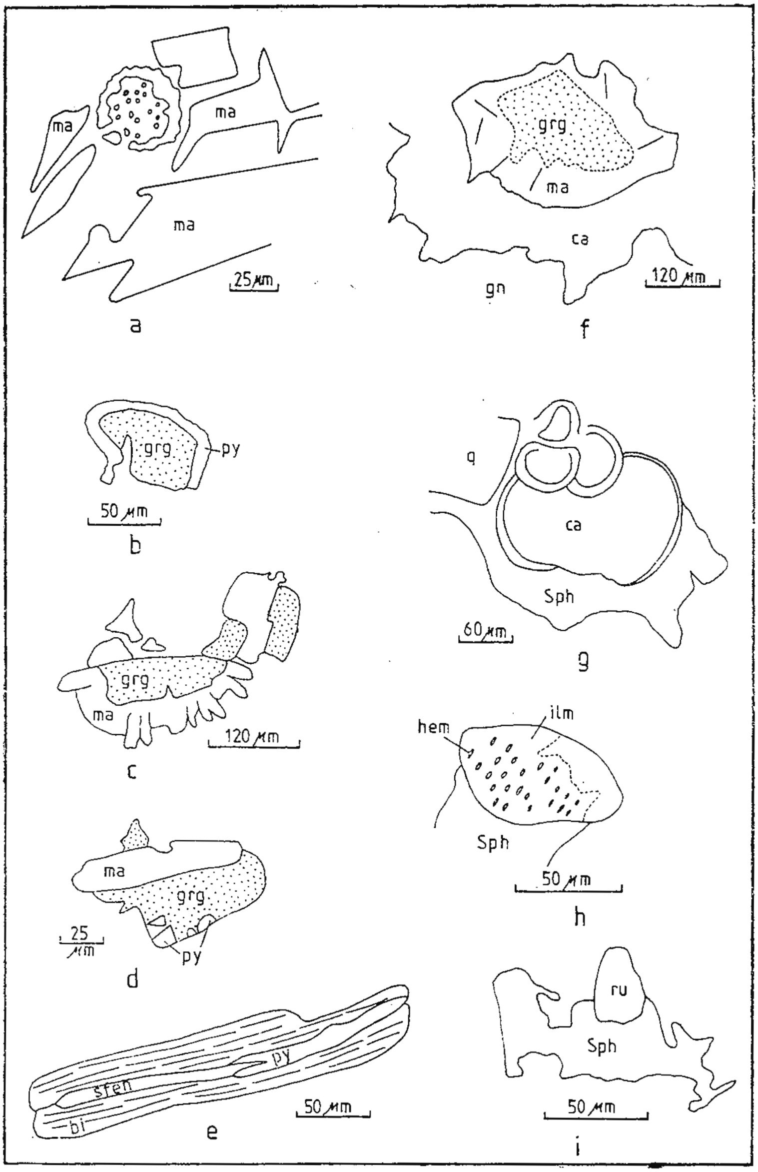

Fig. 2. — Microscopic features of ores in the Jitia area.

a, framboidal pyrite structure together with lamellar marcasite (ma). Argintari brook; b, greigite (grg) surrounded by pyrite (py) Boștina brook, gallery 3; c, greigite (grg) surrounded by lamellar marcasite (ma). Boștina brook, gallery 3; d, greigite (grg), pyrite (py), marcasite (ma) assemblage. „Sub Măgură"; e, titanite and pyrite (py) on biotite cleavage (b), Boștina brook, gallery 3; f, greigite (grg) and marcasite (ma) aggregate in calcite (ca) associated with galena (gn), Boștina brook, gallery 3; g, calcitized (ca) foraminifer shell cemented by sphalerite (sph). Nearby, quartz (q). Boștina brook, gallery 3; h, detrital ilmenite grain (ilm) with hematite (hem) exolutions, partly cemented by sphalerite (sph). Boștina brook, gallery 3; i, rutile (ru) partly included in sphalerite (sph), „Sub Măgură".

Geochemical Data on the Jitia Ores

Minor elements

The data obtained from spectrographic analyses of bulk and monomineral sulphide samples usually show reduced contents corresponding to the low mineralization degree and the type of mineralization. The bulk sample analyses (mineralized sandstones — Table 2) yield major components of low concentration. Excepting some lithophile elements (Ba, Zr, Sr), only Mo contents are somewhat higher, but varying. Both pyrite and marcasite (Tab. 3) are also lacking in minor elements; Mo and Tl occur in constant amounts, Ag and Cd are yielded only by the sample collected from Paltin, while the Ni :Co ratio is supraunitary pointing to an exogene ore deposition; Mn contents are relatively constant. Galena

TABLE 2

Minor Elements of Bulk Samples (mineralized sandstones)

Sample	Location	Pb	Cu	Zn	Sn	Ga	Mo	Ni	Co	Cr	V	Sc	Y	Yb	La	Be	B	Ba	Sr	Zr
SC-20	G—III, m315	160	22	2000	—	—	6	16	8	—	16	—	—	—	—	—	—	140	220	25
SC-25	G—III, m360	70	22	460	—	7.5	—	17	7	25	34	6	19	1.3	32	—	35	220	330	170
SC-32	Vintileasa	14	8	220	2	5	24	13	4	12	10	—	10	—	—	—	37	1000	3000	70
SC-35	G—3, m274	65	9	1000	—	11	—	16	7	25	32	6	13	1.3	—	1	40	1600	380	125

Note: In all the tables: — values below the detection limit

TABLE 3

Minor elements of pyrite and marcasite samples

Sample	Location	Cu	Pb	Zn	Ag	Cd	Tl	Mo	Ni	Co	Ti	Mn	V
U—721	Jitia	5	—	—	—	—	—	—	—	—	—	540	—
SC—6	Paltin	630	1500	1900	2.7	200	10	340	160	44	1000	410	19
SC—17	„Sub Măgură"	14	340	900	—	—	65	—	70	11	260	54	—
SC—30[1]	Vintileasa	17.5	38	200	—	—	—	—	10	—	—	10	—
SC—31[1]	G—III, m 515	75	8000	650	—	—	900	20	11	6	—	245	—
SC—32[1]	Vintileasa	13	120	120	—	—	—	13	9	—	—	11	—
U—1046	Tămașa [2]	38	26	390	—	—	—	48	55	15	50	1400	—
U—996	Balta Sărată [3]	95	130	380	32	—	—	20	185	37	550	4800	14
Detection limit					1	30	10	10	3	3	10		10

[1] marcasite

[2] pyrite concretions in the Cetate Beds

[3] small pyrite concretions in Pannonian lacustrine sedimentary deposits

Elements below the detection limit: Sb (100 ppm), As (300), Bi, Sn (10), Cr (30)

(Tab. 4) is much more strikingly lacking in minor elements ; a single sample yields Tl ; Mn and Cd — proceeding from sphalerite intergrown with the galena — occur in all the samples analysed, but their contents are

TABLE 4

Minor elements of monomineral galena samples

Sample	Location	Cu	Zn	Cd	Tl	Sb	As	Mn
SC—12	Sub Măgură	7	1600	52	30	—	—	44
SC—16	Sub Măgură	30	1700	85	—	—	—	30
SC—23	G—III, m 274	6	4700	85	—	—	—	3
SC—24	G—III	3	3000	74	—	—	—	4
SC—26	G—III, m 515	3	520	—	—	—	—	3
SC—27	G—III, m 515	8.5	4100	85	—	—	—	3
U—732	Bleiberg	—	4800	—	—	—	440	7.5
U—736	Mezica	—	1600			320	—	—
Detection limit				30	10	100	300	3

Elements below the detection limit : Ag, Ni, Co(10 ppm), Ga, Sn(3 ppm.)

commonly close to the detection limit. Sphalerite (Tab. 5) shows only Cd abundances, while Mn correlates inversely to the iron contents.

The analysed samples are marked by small amounts or by the lack of „volcanic" elements (Ag, Bi, etc.) ; there are relatively constant con-

TABLE 5

Minor elements of monomineral sphalerite samples

Sample	Location	Cu	Pb	Cd	Ag	Tl	Ge	Ni	Mn	Ti	Fe
U—974	Boștina brook	10	6700	12000	—	10.5	7	—	44	—	3%
SC—24		38	16500	7000	1.4		4	9	4600	150	1.6%
U—732	Bleiberg	—	380	7500	—		—	—	—		900
Detection limit					1	10	3	3	3	10	

Elements below the detection limit : Sb(100 ppm), As(300), Ga, Sn, In, Bi, Mo, Co(3 ppm.)

tents of elements typical of low temperature sulphides ; Tl and Mn occur in both pyrite and galena or sphalerite. Mo occurrences are worth noting as a geochemical feature of sedimentary pyrites ; in view of comparison, the tables also include contents yielded by sedimentary sulphides of different age from all over the country and abroad ; the pyrite contents presented for comparison are yielded by „purely sedimentary" occurrences lacking in volcanic supply (Cetate Beds in Transylvania — Tămașa, Pannonian lacustrine deposits at Balta Sărată-Caransebeș) ; these samples exhibit relatively constant, high manganese contents. The lack of Ag from galena and of Cu from sphalerite, which has Cd abundances both in the sulphides in Jitia area and in other occurrences, might be considered a characteristic feature of low temperature mineralizations, probably „nonvolcanic", or with very reduced igneous supply.

Isotope composition of sulphur

Besides the analyses presented by Biţă et al. (1985), new analyses have been made on sulphide and gypsum (one analysis) samples collected from gallery 3 Boştinii brook, „sub Măgură" area, Vintileasa and Paltin (one analysis) (Tab. 6). Considering that sulphides are either closely intergrown or isolated, only one pair of analysed sulphides (SC-24) was obtained; one sample yielded intergrown marcasite and gypsum bands (SC –31/A).

TABLE 6

$\delta^{34}S$ values reported for sulphides and sulphates

Mineral	Location	δ^{34} S(‰)	Reference	Sample
marcasite	gallery III, Boştina	–31.85		SC–31A
marcasite	Vintileasa	–23.54		SC–30
marcasite	Vintileasa	–23.31		SC–32
galena	Argintari	– 8.54	Biţă et al. (1985)	
galena	Boştina	– 7.90	Biţă et al. (1985)	
galena	gallery III, Boştina	– 5.50		SC–26
galena	Boştina	– 5.57	Biţă et al. (1985)	
galena	Boştina	– 1.41	Biţă et al. (1985)	
sphalerite	Faţa Cerbului	+ 0.64	Biţă et al. (1985)	
galena	gallery III, Boştina	+ 0.84		SC–24
sphalerite	Boştina	+ 2.60	Biţă et al. (1985)	
sphalerite	gallery III, Boştina	+ 4.83		SC–24
pyrite	Jitia	– 5.22		U–721
pyrite	Argintari	– 3.54	Biţă et al. (1985)	
pyrite	Paltin	– 2.87		SC–6
pyrite	Argintari	– 2.64	Biţă et al. (1985)	
pyrite	Argintari	– 2.02	Biţă et al. (1985)	
pyrite	Argintari	+ 5.59	Biţă et al. (1985)	
pyrite	Sub Măgură	+ 7.38		SC–17
galena	Sub Măgură	+ 8.72		SC–12
galena	Sub Măgură	+13.37		SC–16
gypsum	gallery III, Boştina	+13.47		SC–31A

At first, it is to note the $\delta^{34}S$ values ranging from –31.85‰ (marcasite from gallery 3 – Boştinii brook, sample SC –31/A) to +13.37‰ (galena from „sub Măgură" area, sample SC –16); the variation interval increases slightly according to the content yielded by the gypsum sample, i.e. +13.47‰.

On the whole, the $\delta^{34}S$ values account for normal isotope fractionation of sulphides (excepting marcasite), represented by gradual enrichment in the heavy isotope of the estimated sequence: galena-sphalerite-pyrite.

The sample yielding two sulphides (sphalerite/galena) shows normal fractionation. However, pyrite is characterized by a large variation range, mostly superposed on galena and sphalerite ranges accounting for different sulphur sources in pyrite genesis. In the „Sub Măgură" area galena differs from the occurrences in gallery 3 — Boștinei brook and in the Argintari brook, enriched in the heavy isotope; these galena occurrences are isotopically heavier than pyrite, which point to the different sulphur source of the different sulphide occurrences and even of sulphides of the same occurrence.

Taking into account the calculations and the experimental data, isotope fractionation is considered normal (for simultaneous deposition of both sulphides and sulphates) for $\delta^{34}S$ sulphide/sulphate ratio approximates 20. This applies to the samples collected from Jitia only to a less extent and to isolated samples. However, at temperatures below 250°C the isotope equilibrium is hardly reached or it is even absent (Schroll, 1985). The most striking feature is the difference of 45‰ (sample SC — -31/A) which informs on simultaneous processes that generated the two minerals.

Paleogeographic Environment of the Subcarpathian Miocene Deposits and the Genetic Model of Related Ores

The retrotectonic picture of the Subcarpathian Nappe associated with the lithologic features characteristic of the three main formations under discussion — the Salt Formation, the Red Formation (Tescani and Măgirești beds) and the Grey Formation with gypsum — and the characteristics of the sedimentation environments inform on the genesis of Miocene mineralizations.

A first feature to be considered is the initial width of the basin. Palinspastically defolded, the area corresponding to the Subcarpathian Nappe is of ca 60 —70 km, exceeding three times the present folded one. It is also worth mentioning that the Subcarpathian area was the outermost one of the whole Lower and Middle Miocene sedimentation realm in the East Carpathians, innwards involved in the Marginal Folds Nappe area and bounded outwards by an emerged zone, affected by erosion and supplying detrital material.

The three formations under discussion do not exhibit different areal distribution, excepting perhaps the Salt Formation. According to the model valid in the Tazlău Subcarpathians, north of the Trotuș Valley, one may consider that the Salt Formation lacks from some areas of the Pietricica digitation, due either to non-deposition or to subsequent erosion; therefore, some palinspastic sections point to the absence of the Salt Formation below the Bîrsești Conglomerates (Fig. 3).

The Red Formation and the Grey Formation with gypsum show similar areal development. The base of the former is replaced outwards by conglomerates with green pebbles.

In the Subcarpathian area, a shallow or very shallow deposition environment should be considered with respect to the Red Formation (in order to account for the widespread mammal and bird footprints at the

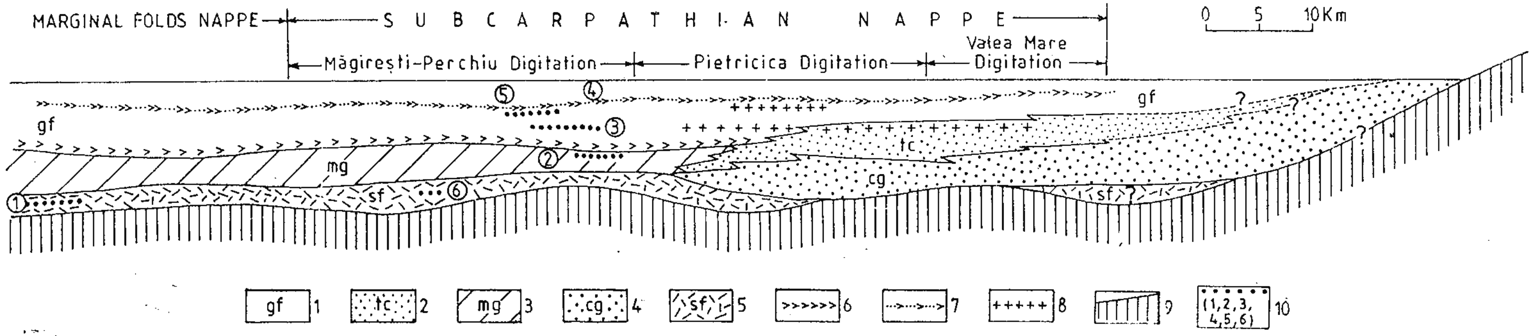

Fig. 3. — Palinspastic partial section of the Lower Miocene in the Vrancea Area; 1 — gf, Grey Formation; 2 — tc, Tescani Beds; 3 — mg, Măgirești Beds; 4 — cg, Pietricica type conglomerates and their equivalents; 5 — sf, Salt Formation; 6, Perchiu Gypsum Complex; 7, Stufu Complex; 8, tuffs; 9, nondifferentiated basement of the Subcarpathian Miocene; 10, sulphide ores: (1, Argintari brook; 2, Cerbu brook; 3, Sub Măgură; 4, Boștina brook; 5, Vintileasa; 6, Paltin).

top of arenites). A somewhat deeper depositional environment is to be supposed for the Grey - Formation.

With respect to the transversal extension of those formations baring base metal sulphides, the following are worth mentioning:

— the occurrences reported from the Salt Formation belong to the Măgirești-Perchiu (Paltin) digitation and to the salt planing slice (Argintari brook) assigned to the Marginal Folds area;

— the occurrences of the Red Formation are reduced in the Măgirești Beds (Cerbu brook) and also in the Măgirești-Perchiu digitation;

— the occurrences from the Grey Formation with gypsum (Vintileasa, Boștina brook, Sub Măgură) are reported to the Măgirești-Perchiu digitation.

It is easily noted that (1) at least so far there are no mineralizations related to the Pietricica digitation, in the outermost area of the Subcarpathian Nappe respectively, and (2) according to age distribution most of the occurrences are known in the Grey Formation with gypsum, the most relevant ones (Boștina brook) at the level of the Stufu Gypsum. Then follow the Salt Formation and the Red Formation.

Taking into account the data presented above, the genetic model of the lead-zinc mineralizations related to the Subcarpathian Miocene implies the discussion of the metal supply, its transport and concentration types.

As regards the metal supply it is to state from the very beginning that the magmatic activity cannot be considered as far as:

— all over the Moldavidian nappes area, the Subcarpathian Nappe included, and in the outer foredeep, any proof of Miocene or younger igneous activity is absent;

— tuffs and/or tuffite interlayerings in the Lower Miocene deposits are fine and very fine pointing to aerial transport on relatively long distances, excluding the possibility of a simultaneous transport of metallic components;

— hydrothermal alteration lacks even within the feldspar grains of the mineralized sandstones.

Thus, the only possible metal sources may be represented by the emerged areas which bordered the sedimentation realm of the Miocene formations. Outwards, in the Carpathian foreland areas, the main formations which might have generated metals by levigation during erosion are the greenschists and/or the metamorphics of Altîn-Tepe type. This source is mainly related to the accumulations reported to the Salt Formation and the Red Formation (Măgirești and Tescani Beds).

Innwards the Lower Miocene sedimentation area, the metal sources could be represented by the metamorphic formations which constitute the Central East Carpathian Nappes and their equivalents in the South Carpathians. Cretaceous and/or Paleogene detrital formations containing old metamorphic and/or igneous rock fragments reworked during the Miocene could also be considered. The sulphide accumulations associated with the Grey Formation with gypsum should be related to the inner source.

The transport ways of metals from their source to the sedimentation area might be the following:

— as organo-metallic components, with the metals chemically related to the organic matter;

— as metals adsorbed by some clayey minerals;

— as lithic fragments containing metallic minerals;

— as fragments originating in Miocene algal mats which usually concentrate metallic ions.

These transport ways do not exclude each other, supplying different metal amounts to the deposition area.

The concentration of sulphides should be considered by taking into account the genetic models of sedimentation. From this point of view, most of the sulphide occurrences are assigned to the evaporite formation: the Salt Formation and the Stufu Gypsum Complex (the occurrences reported from the Red Formation in the Cerbu brook and from the Grey Formation in the „Sub Măgură" area are excepted). Their association with evaporites is not accidental at all and results in defining the concentration genetic model. It is thus considered that in case of a restrictive circulation and a certain metal content, the sulphate reduction facilitates the sulphide precipitation. This process starts with the initial deposition of greigite (Fe_3S_4), a metastable component subsequently transformed into marcasite and pyrite. The lead and zinc sulphides (galena and sphalerite) are considered to have crystallized later from the sulphide-bearing mud, as also proved by their mode of occurrence compared to pyrite and marcasite (groundmass of detrital fragments or veinlets and clusters related to the fissures of the host rocks).

As already mentioned, the occurrences investigated show different composition and stratigraphic position. On the whole the sulphide assemblages are however similar, excepting the Vintileasa occurrence marked by iron sulphides only and the one in the Argintari brook where greigite is absent, but containing pyrrhotite. The structures are syn- and diagenetic, mostly similar, accounting for the non-synchronous crystallization of sulphides and their local differential mobilization. The pyrrhotite amounts of the occurrence in the Argintari brook might be due to some local conditions (iron excess, sulphur deficit) of the initial deposit. Massive pyrrhotite, partly integrown with pyrite as decimetric concretions, is reported from the Schela coal-bearing formation in the South Carpathians, proved of syndiagenetic character (Udubaşa, 1984). Considering the meso- and microscopic features of the mineralization in the Argintari brook and the sulphur isotopes data one may speak of different sources of the mineralized components of the salt breccia. Usually the mineralizing process is syngenetic as proved by the framboidal structures and the partly frozen collomorphic textures of pyrite. The relative abundance of marcasite in all these occurrences shows the acid deposition environment, which accounts also for the minor sulphide accumulations.

According to Cioflica et al. (1986) the mineralizations in the Argintari brook are epigenetic, originating in those of Boştina type due to „halotectonic" mobilisations. The circulation of brines through evaporite-rich structures could be easily taken into account even after the cessation of lithification, although it would be more appropriate to speak of peridiapir halokinetic remobilisations; the more so as the remobilization of sulphides occurred mostly as fragments of mineralized rocks and less (or none) by dissolution, transport and redeposition in the salt breccia. Considering the metal supply as exogenic and the deposition model as essentially syngenetic the Jitia mineralizations might be considered syngenetic-exogenic on the whole (according to Amstutz, 1959), with local remobilisation effects.

Two sedimentation realms could be taken into account with respect to the model presented: „sabkha" and „evaporite pan" types.

The „sabkha" type is less acceptable because of the following reasons:

— it requires in the case of the deposits containing sulphides, both in the Măgirești-Perchiu digitation and in the Marginal Folds Nappe, a transitional area between the mainland and the open sea which cannot be recognized in the paleogeographic reconstruction;

— it implies a substratum consisting of oxidized clastics of red-beds type which lacks from both the Salt Formation and the Stufu Gypsum Complex.

The only level possibly of „sabkha" type is partly represented by the Perchiu Gypsum Complex (see the preceding chapters) which so far lack in sulphide accumulations.

The „evaporite pan" type seems to be much more appropriate to the paleogeography of the Subcarpathian Miocene, the lithostratigraphic position of the evaporite levels and the location of related ores. It is to mention here that the evaporites related to most of the mineralizations have been generated by concentration and precipitation from some basins of varying size, time limited and recurrent. There was a relative communication between these basins and a weak one with the open sea.

The genetic model of „evaporite pan" type is also to be considered owing to the association of the Salt Formation and of the Stufu Gypsum Complex with characteristic carbonate rocks (dolomites and laminated limestones).

The vertical distribution and the frequency of sulphide ores seem to be due to the following factors:

— the conditions most favourable depositionally and genetically were during the sedimentation of the Salt Formation and of the Stufu Gypsum Complex;

— the presence of montmorillonite in the argillaceous fraction of the Stufu Gypsum in contrast with its absence from the Salt Formation probably favoured the transport of higher metal amounts. Unlike the other argillaceous minerals, montmorillonite has a greater capacity of metal adsorption;

— the two sources (external in the case of the Salt Formation and nternal in the case of the Stufu Gypsum Complex) supplied different metal amounts, relatively higher with respect to the internal source, but on ithe whole small in both cases.

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PALEOGEOGRAFIA MIOCENULUI SUBCARPATIC ŞI MODELUL GENETIC AL MINERALIZAŢIEI DE TIP JITIA.

(Rezumat)

Ocurenţele de sulfuri cunoscute în depozitele sedimentare miocene din zona de curbură a Carpaţilor apar la mai multe nivele stratigrafice ale Miocenului inferior şi sînt localizate în unităţile cele mai externe ale Moldavidelor, i.e. pînza subcarpatică (în special) şi pînza cutelor marginale (subordonat).

Litostratigrafia Miocenului inferior

Primul reper litostratigrafic de corelare a depozitelor miocene din unităţile sus menţionate este reprezentat de nivelul menilitelor superioare, acoperit de formaţiunea de Goru-Mişina. În succesiune urmează formaţiunea cu sare de vîrstă burdigaliană, care este constituită dintr-o brecie cu matrice argiloasă şi elemente predominante de şisturi verzi de tip dobrogean. Sarea şi gipsurile se dezvoltă discontinuu, sub forma unor corpuri lenticulare, în care se găsesc numeroase intercalaţii de argile. Formaţiunea cu sare este acoperită de o gresie arcoziană — gresia de Condor. În pînza de Tarcău, mai internă, formaţiunea cu sare este foarte subţire, nivelul evaporitic fiind reprezentat în special prin „gipsurile inferioare".

Deasupra depozitelor evaporitice litologia Miocenului este mult mai diversificată şi arată frecvente schimbări laterale de facies. În partea externă a pînzei subcarpatice se găsesc conglomerate (de Pietricica), bogate în elemente de şisturi verzi, care trec lateral şi spre partea superioară a secvenţei spre o formaţiune grezoasă roşie ce poartă denumiri locale (Tescani, Măgireşti, Hîrja etc.) în diferitele unităţi. Limita superioară a formaţiunii roşii este diacronă, migrînd în timp spre exterior.

Formaţiunea cenuşie cu gipsuri este cunoscută în special în pînza subcarpatică şi constă din marne, gresii şi nisipuri, în care la diverse nivele se intercalează gipsuri, dintre care gipsurile de Perchiu şi cele de Stufu sînt cele mai importante; sub acesta din urmă se plasează limita Miocen inferior/Miocen mediu.

Observaţii litogenetice

Arenite şi rudite. Elementele detritice din depozitele sedimentare grosiere — în special din formaţiunea cu sare şi din cea roşie — sînt reprezentate în special prin şisturi verzi de tip dobrogean, fiind prin urmare specifice unei surse externe (estice). În contrast, formaţiunea cenuşie conţine elemente detritice caracteristice unei surse interne (vestice), aparţinînd ariei carpatice. Cele două surse de material nu se exclud complet, dar materialul detritic furnizat se deosebeşte prin distanţele de transport şi adîncimea de sedimentare : mai mici în cazul materialului din sursa externă şi mai mari în cazul celui din sursa internă. Mineralele grele din aceste formaţiuni sugerează în general aceleaşi surse majore.

Rocile argiloase. Fracţia argiloasă din depozitele miocene (S. Rădan, în Săndulescu et al., 1978, 1980) arată de asemenea unele diferenţe mineralogice, dependente de sursele de material. Astfel, sursa externă a furnizat în special illit+clorit în timpul depunerii formaţiunii cu sare, a formaţiunii roşii şi a gipsului de Perchiu, materialul argilos arătînd un grad redus de maturitate. Sursa internă a fost activă în timpul depunerii formaţiunilor mai noi decît gipsul de Perchiu, furnizînd mai ales montmorillonit.

Gipsurile. Structurile observate în complexul gipsurilor de Perchiu (chicken-wire, noduli discoidali, noduli dislocaţi) sugerează o adîncime de sedimentare redusă, la limita subacvatic / subaerian, în concordanţă cu indicaţiile date de urmele de păsări şi mamifere asociate cu ripple-marks. Evaporitele din cadrul formaţiunii cenuşii s-au format în zone plate, cu mici depresiuni caracterizate de circulaţie restrictivă, în care s-au depus gipsuri masive stratificate.

Formaţiunea cu sare. Masivele de sare din Miocenul inferior sînt intercalate între depozite marine (la partea inferioară) şi neritice, fluviolacustre (la partea superioară). Paleobazinul Miocenului inferior a fost relativ îngust, spre nord comunicînd cu marea liberă, iar spre vest şi est fiind legat cu aria carpatică, respectiv cu vorlandul. Sarea şi/sau sărurile de potasiu s-au acumulat în lagune cvasiizolate, în care se ajungea la hipersalinizarea apei şi depunerea sării; periodic, în asemenea lagune — în special în cele marginale — se acumula şi material detritic.

Mineralizaţiile

Componenţii majori ai mineralizaţiilor de tip Jitia sînt sfaleritul (blenda) sărac în fier, galena, marcasita, pirita, greigitul (prima menţionare în această zonă), pirotina şi cu totul subordonat calcopirita, sub formă de incluziuni sporadice în sfalerit. Ilmenitul, rutilul, magnetitul şi grafitul apar local, fie în asociaţie cu sulfurile, fie în masa gresiilor, reprezentînd minerale detritice. Între diversele ocurenţe există unele diferenţe de compoziţie mineralogică (Tabelul 1), notabilă fiind relativa abundenţă a pirotinei în ocurenţa de pe pîrîul Argintari. În general, sulfurile formează impregnaţii fine, cuiburi, lentile sau vinişoare mai ales în gresiile cenuşii feldspatice. Interesante sînt agregatele de sulfuri de fier, în care greigitul (fin granular) alcătuieşte zona centrală, înconjurată de agregate prismatice de marcasită cu dispoziţie radiară sau de pirită granulară. Sfaleritul şi galena apar sub forma unor plaje sau granule neregulate, dispuse în matricea gresiilor, de care aparţin din punct de vedere al momentului de formare. Sfaleritul mulează uneori cochilii de foraminifere (p. Boştinei). Remarcabilă este prezenţa constantă a piritei framboidale în toate ocurenţele, care reprezintă — alături de greigit — primul moment de formare a sulfurilor. Structuri colomorfe ale agregatelor de sulfuri — în special de pirită şi macrasită — apar din abundenţă în ocurenţa de pe pîrîul Argintari, unde este foarte frecventă şi pirita framboidală. La Vintileasa (pîrîul Bisericii) marcasita apare sub forma unor cuiburi decimetrice, în asociaţie cu gips.

Gipsul apare frecvent în asociaţie cu sulfurile, cu care este deseori intim concrescut. Cioflica et al. (1986) menţionează de asemenea dolomit, calcit, anhidrit şi celestină, care aparţin în mare măsură matricei gresiilor.

Date geochimice

Mineralizaţiile de tip Jitia sînt sărace în elemente minore. Unele elemente litofile (Ba, Zr, Sr) apar la conţinuturi constant ridicate, iar Mo, Tl şi Mn sînt prezente doar în unele probe de sulfuri (tabelele 2–5).

Compoziţia izotopică a sulfului din sulfuri şi sulfaţi se caracterizează printr-un larg interval de variaţie, $\delta^{34}S$ avînd valori între $-31,85^0/_{00}$ şi $+13,47^0/_{00}$, sugerînd în primul rînd surse diferite de sulf. În ansamblu, fracţionarea izotopică pare normală, deşi numărul de analize pe perechi de sulfuri (din aceeaşi probă) este prea redus (Tabelul 6) pentru a putea generaliza o astfel de concluzie.

Modelul genetic al procesului de mineralizare

În descifrarea condiţiilor de formare a mineralizaţiilor de tip Jitia este important de menţionat faptul că lăţimea bazinului de sedimentare în timpul Miocenului inferior a fost de cca 3 ori mai mare (cca 60–70 km) decît lăţimea actuală a formaţiunilor cutate. Distribuţia areală a formaţiunii cu sare, a formaţiunii roşii şi a formaţiunii cenuşii este în general similară, exceptînd formaţiunea cu sare, care lipseşte în unele segmente ale digitaţiei de Pietricica.

Raportînd ocurenţele de sulfuri la unităţile tectonice ce conţin depozite aparţinînd Miocenului inferior se constată următoarele: (1) Ocurenţele din formaţiunea cu sare aparţin atît pînzei cutelor marginale (pîrîul Argintari), cît şi pînzei subcarpatice — digitaţia Măgireşti-Perchiu (Paltin); aceasta din urmă este de importanţă redusă; (2) În formaţiunea roşie este cunoscută o singură ocurenţă mai semnificativă (pîrîul Cerbu), situată în digitaţia Măgireşti-Perchiu; (3) Cele mai importante ocurenţe sub aspectul extinderii şi continuităţii (pîrîul Boştina, Sub Măgură) se află în formaţiunea cenuşie, la nivelul gipsului de Stufu, din digitaţia Măgireşti-Perchiu.

Din cele de mai sus rezultă că nu se cunosc, cel puţin pînă în prezent, ocurenţe de sulfuri în digitaţia Pietricica — reprezentînd cea mai externă unitate a pînzei subcarpatice.

În privinţa sursei de metale trebuie făcute următoarele precizări: (1) în întreg arealul de dezvoltare a Moldavidelor nu există dovezi pentru a susţine existenţa unei activităţi magmatice în timpul Miocenului inferior şi nici ulterior; (2) tufurile şi tufitele intercalate în depozitele sedimentare sînt foarte fine, sugerînd transportul aerian al materialului, pe distanţe relativ mari, ceea ce exclude posibilitatea transportului simultan de metale. Sursele de material şi implicit de metale trebuie astfel căutate în zonele emerse de la interiorul şi exteriorul bazinului de sedimentare, i.e. zona carpatică şi vorlandul său. Aceste zone au furnizat succesiv material detritic în timpul depunerii formaţiunii cu sare şi al formaţiunii roşii (vorlandul) şi în timpul depunerii formaţiunii cenuşii (sursa internă carpatică). Modalităţile de transport al metalelor sînt multiple, sub formă de compuşi organo-metalici, ca metale adsorbite pe minerale argiloase, ca minerale metalifere incluse în fragmentele litice, ca fragmente din pături algale (algal mats) etc.

Modelul de depunere a sulfurilor de tip ,,tipsie evaporitică" (evaporite pan) pare să fie cel mai adecvat pentru a explica particularitățile mineralizațiilor de tip Jitia; evaporitele cu care se asociază sulfurile conțin și secvențe carbonatice; precipitarea evaporitelor a avut loc în microbazine de diverse dimensiuni și cu dispoziție aleatoare în cadrul bazinului de sedimentare. Montmorillonitul este cunoscut pentru capacitatea sa mare de adsorbție a metalelor în comparație cu alte minerale argiloase, ceea ce explică în mod suplimentar relativa abundență a sulfurilor în ocurențele asociate complexului gipsului de Stufu.

Acumularea sulfurilor s-a realizat astfel în microbazine, în care formarea evaporitelor alterna cu aport de material detritic purtător de metale; sursa de sulf este asigurată de reducerea sulfaților, accidental și de sulfurile existente în fragmentele litice, ceea ce explică spectrul larg al valorilor $\delta^{34}S$ din sulfuri și sulfați. Depunerea sulfurilor poate fi imaginată ca derulîndu-se în mai multe etape: (1) formarea greigitului, a piritei framboidale și a pirotinei (probabil sincron cu depunerea sedimentelor); (2) apariția marcasitei — în mare măsură pe seama greigitului și pirotinei (diageneză timpurie); abundența marcasitei în majoritatea ocurențelor — sugerînd un mediu ușor acid — explică în parte amploarea relativ redusă a acumulărilor de sulfuri; (3) cristalizarea sfaleritului și galenei din mîluri cu sulfuri, menținute ca atare probabil pînă la instalarea proceselor diagenetice tardive, implicînd litificarea sedimentelor, apariția fisurilor transversale pe stratificație (în esență fisuri de contracție), pe care au migrat sulfurile de plumb și zinc.

EXPLANATION OF PLATES

Plate II

Fig. 1. — Biotite (black) exhibiting greigite on cleavage; greigite (porous) is associated with subhedral marcasite grains (white). Polished section (SL), oil immersion, × 350. Boștina brook, gallery 3.

Fig. 2. — Bent biotite within the mineralized sandstone matrix. SL, oil immersion, × 350. Boștina brook, gallery 3.

Fig. 3. — Semi-rolled ilmenite grain (light grey) contained by sphalerite (grey). SL, oil immersion, × 350. Boștina brook, gallery 3.

Fig. 4. — Foraminifer shell partly cemented by sphalerite (white); quartz and/or feldspar grains (of grey colour). SL, × 250. Boștina brook, gallery 3.

Plate III

Fig. 1. — Sphalerite (white) as anhedral grains or as component of the sandstone argillaceous matrix. SL, oil immersion, x350. ,,Sub Măgură".

Fig. 2. — Pyrite (white) cementing the angular detrital components of the sandstone. SL, oil immersion, x350. ,,Sub Măgură".

Fig. 3. — Pyrite (white) containing subhedral sphalerite grains (grey) and cementing the sandstone components (black). SL, oil immersion, x350. „Sub Măgură".

Fig. 4. — Lamellar marcasite aggregate. SL, x250. Vintileasa.

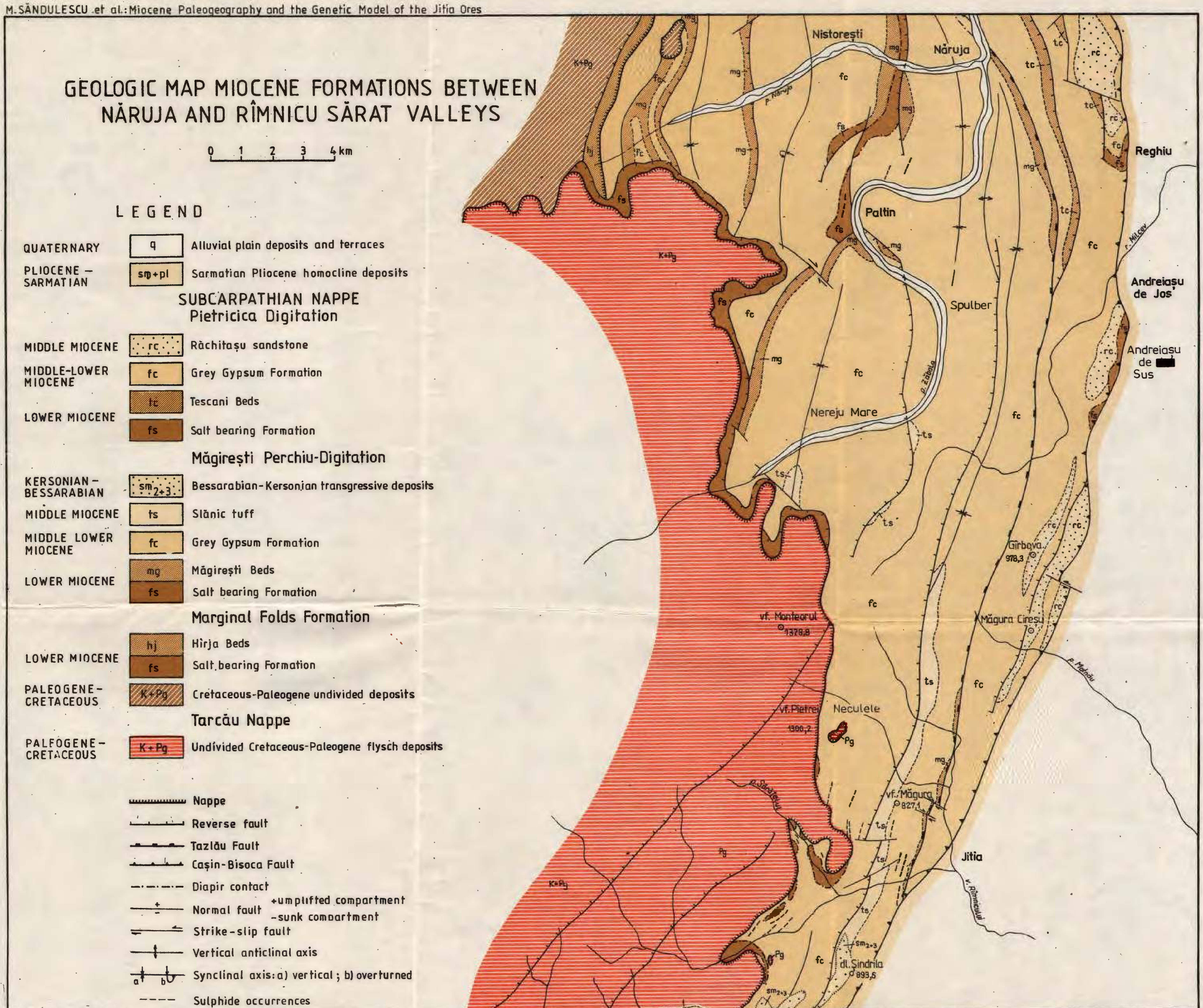
Plate IV

Fig. 1. — Greigite aggregate (grey, fine-grained, in the middle) with marcasite (white) on borders. Towards the photograph margins — galena (white). SL, × 250. Boştina brook, gallery 3.

Fig. 2. — Lamellar marcasite (white) — greigite (white, porous) assemblage. SL, oil immersion, × 350. Boştina brook, gallery 3.

Fig. 3. — Rhythmic deposition of galena (white, soft) — pyrite (white, in relief) — sphalerite (grey) with extremely fine chalcopyrite inclusions — galena (white). SL, oil immersion, × 350. „Sub Măgură".

Fig. 4. — Lamellar marcasite aggregate. SL, × 250. Boştina brook, gallery 3.



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2. ZĂCĂMINTE

EVOLUTION OF BANATITIC MAGMATISM IN THE APUSENI MTS. AND ASSOCIATED METALLOGENESIS[1]

BY

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Banatite. Metallogenesis. Calcalkaline magmatism. Igneous processes. Pyrometasomatic mineralisation. Vein hydrothermal mineralisation. Zonality. Neogene. Apuseni Mts — Neocretaceous — Paleogene magmatites.

Abstract

Evolution of banatitic magmatism in the Apuseni Mts. and associated metallogenesis. Banatitic calcalkaline magmatism (Post—Lower Maastrichtian—Paleogene) is widely developed in the Apuseni Mts. and represents the result of an eruptive activity which had two cycles : Ist cycle mostly generated lava flows, sometimes accompanied by pyroclastics as well as superficial subvolcanic bodies ; IInd cycle is characterized by important bodies of intrusive. hypabyssal and plutonic rocks, the last ones being deeply developed. Magmatic banatitic activity in the Apuseni Mts. ends with dykes of basic rocks which prevail in the Bihor Mts. and follow and partly overlie in time late alkaline vein differentiated of granodiorite-granitic magma. The metallogenesis is associated with the IInd cycle being characterized by pyrometasomatic mineralizations (which are not so widely developed in comparison with those from Banat) and vein hydrothermal mineralizations, which occur independently or overlapp the pyrometasomatic mineralizations. The geochemical spectrum of banatitic mineralizations in the Apuseni Mts. (Bi, Mo, Pb, Zn, Cu, B, Fe, W, Co, Ni, As etc.) is considerably different from those from Banat (Cu, Fe, Bi, Zn, Pb, W, Mo, Co). The metalliferous accumulations outline a regional zonality which is clearly centered on the zone of Bihor Mts. and asymmetrically developed; they especially follow the development of holocrystalline-equigranular rocks. Eastwards, the intensity of mineralizing processes decreases at the same time with the reduction of magmatites outcrop areas ; presumably in the depth there are, however, unidentified mineralized structures.

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Résumé

Evolution du magmatisme banatitique des monts Apuseni et la metalogènêse associée. Le magmatisme chalcoalcalin banatitique (Maestrichtien supérieur—Paléogène) a une large développement dans les monts Apuseni et représente le résultat d'une activité éruptive manifestée par deux cycles : le premier cycle (I) a généré des écoulements de laves, parfois accompagnés de pyroclastites et (souvent) des corps subvolcaniques. Plusieurs variétés d'andésites, dacites et rhyolites ont été mises en place successivement ; le deuxième cycle (II) est caractérisé par la mise en place d'importants corps de roches intrusives, hypabyssales et plutoniques, ces dernières avec un large développement en profondeur. Des intrusions de quartz-diorites sont suivies par des granodiorites et granites doublés par leurs variétés porphyriques. L'activité magmatique banatitique des monts Apuseni s'achève par la formation des dykes de roches basiques, très abondantes dans les monts Bihor ; ces roches sont partiellement contemporaines aux produits filoniens alcalins tardifs de la différenciation du magma granodioritique-granitique. La métalogenèse est associée au deuxième cycle étant caractérisée par des minéralisations pyrométasomatiques (plus réduites que celles de Banat) et filoniennes hydrothermales, indépendentes ou superposées aux minéralisations pyrométasomatiques. Le spectre géochimique des minéralisations banatitiques des monts Apuseni (Bi, Mo, Pb, Zn, Cu, B, Fe, W, Co, Ni, As etc). diffère sensiblement de celui des minéralisations de Banat (Cu, Fe, Bi, Zn, Pb, W, Mo, Co). Les accumulations métallifères indiquent une zonalité régionale clairement exprimée, centrée dans la zone des monts Bihor, et développée asymétriquement ; elles sont spécialement associées aux roches holocristallines-équigranulaires. Vers l'est, l'intensité des processus de minéralisation diminue parallèlement à la diminution des aires d'affleurement des roches granodioritiques-granitiques ; mais on suppose que dans la profondeur on peut trouver des minéralisations non identifiées encore.

This paper presents the evolution of the banatitic magmatism and associated metallogenesis for the whole area of the Apuseni Mts ; we also added here bentonitized rhyolites from the Chioarului Valley.

Not considered here are the granitoids from Săvîrşin, Cerbia, Pietroasa-Căzăneşti, Dealul Mare-Podele and Ampoiţa (Metaliferi Mts.) as they belong to an early magmatic activity, Lower Cretaceous in age. These rocks cut the ophiolites and the relations with the sedimentary rocks as well as the K-Ar datings indicate that their age does not fit the banatites one. In addition, the granitoids have different petrologic features (Ştefan, 1986). Savu et al. (1986) suggest these magmatites belong to the products of an island arc volcanism.

The volcanics in the southern part of the Metaliferi Mts. described by Borcoş et al. (1984) as belonging to the banatites are not included here as well. Their space distribution is still incompletely known and consequently not represented on geological maps.

This paper contains only few petrochemical data ; however, on the geological map (Plate I), there are QAP diagrams for each group of banatites in order to point out the petrotypes and to suggest the magmatic evolution.

The origin of the banatitic magmas was already discussed in relation to the subduction processes in the Carpathians (Rădulescu, Săndulescu, 1973); as no supplementary data have still appeared, this problem is here no longer treated. Although in the last decade there were obtained numerous results of isotopic analyses (Pavelescu, et al., 1975, 1985; Bleahu et al., 1984; Russo-Săndulescu et al., 1984), their bearing on the evolution of the banatitic magmatism in the Apuseni Mts. was not included because of some uncertainties concerning the interpretation such as: 1) the measured values are often discrepant both regarding the rocks' age within a certain magmatic body and/or in relation with the field data concerning the succession of magmatites; 2) just where the succession of magmatites'emplacement is very well known and the distribution area is the largest one, we have very few and unconvincing data of isotopic ages.

Previous data

There are rather numerous review papers concerning banatitic magmatic rocks, products of magmatic metamorphism and associated metallogenesis in Romania and/or in the Apuseni Mts. (Giușcă et al., 1966; Cioflica, 1967; Cioflica et al., 1973, 1980, 1985; Cioflica, Vlad, 1973, 1984; Ianovici et al., 1969, 1976; Rădulescu, 1984; Rădulescu et al., 1981).

Among the papers dealing with the study of banatitic magmatites and post-magmatic products, we mention those regarding: Vlădeasa eruptive massif (Giușcă et al., 1969; Istrate, 1978; Ștefan, 1980); Budureasa massif (Istrate, Udubașa, 1981); Fagului Valley (Udubașa et al., 1980); Bihor massif (Jude, Ștefan, 1967; Cioflica, Vlad, 1968, 1970, 1979; Cioflica et al. 1974, 1982; Proca, Proca, 1972; Giușcă et al., 1973, 1976; Lazăr et al., 1982); Bucea-Cornițel-Borod (Berbeleac et al., 1982); Mezeș-Chioarului Valley (Ștefan et al., 1986); Gilău (Borcoș, Borcoș, 1962; Gheorghițescu et al., 1979; Lazăr et al., 1972; Ștefan et al., 1985); Trascău (Bordea, Dimitrescu, 1966; Russo-Săndulescu, Berza, 1975; Russo-Săndulescu et al., 1976; Nicolae, 1985); Măgureaua Vației-Birtinului Valley (Jude et al., 1973; Ștefan et al., 1982) and Almașul Mic-Metaliferi Mts. (Berbeleac, 1975).

Evolution of banatitic magmatism

The banatitic calcalkaline magmatism (Post-Lower Masstrichtian-Palaeogene) which is widely developed in the Apuseni Mts., took place within two important cycles unequally represented from one zone to another; the most northern occurrence of such magmatic products can be met in the Chioarului Valley (Pl. I, Fig. 1).

The first cycle is characterized by lava flows (Vlădeasa, Gilău) sometimes accompanied by pyroclastics (Vlădeasa, Mezeș-Chioarului Valley); simultaneously superficial subvolcanic bodies have been emplaced (Vlădeasa, Gilău, Bihor); in some zones, the first cycle of magmatites has not been identified yet (Trascău).

Within the second main cycle there have been emplaced bodies of intrusive rocks, generally hypabyssal as well as plutonic ones which are widely developed in the depth (Proca, Proca, 1972; Cioflica et al., 1982).

Succeeding or overlying in time the late alkaline vein differentiation products of granodiorite-granitic magma, there have been emplaced dykes of basic rocks (very abundant in Bihor) which end the banatitic magmatism in the Apuseni Mts.

Well represented especially in the Vlădeasa massif and to a lesser extent in Gilău Mts. and Mezeş-Preluca, Post-Lower Maastrichtian volcanism (Istrate, 1978; Ştefan, 1980; Ştefan et al., 1982, 1985)of the first cycle of banatitic magmatism begins with lava flows of quartziferous andesites (bearing pyroxens and hornblende or only hornblende to which sometimes adds biotite). Rather abundant in the Vlădeasa (occupying 15–20% of the outcrop area of banatitic rocks), andesites have been generally emplaced at the margin of the eruptive massif, along some fractures which bordered Vlădeasa graben (Ştefan, 1980); the lava flows occupy relatively reduced areas. Subvolcanic bodies of small size as well as andesite lava flows which have been emplaced within the same I cycle, are found in the Gilău Mts. In the Bihor Mts. andesites form sills and dykes small in size (Jude, Ştefan, 1967); lava flows are not found.

In comparison with the Neogene andesitic volcanism (of central type) the banatitic andesitic volcanism (of linear type) in the Apuseni Mts.[4] is not accompanied by pyroclastic products.

In the Vlădeasa massif, andesites are followed by dacites, which cross and include them as xenoliths. Dacites constitute intrusive nappes, dykes or lava flows which cover the Upper Coniacian-Lower Maastrichtian deposits.

In Gilău, Trascău, Metaliferi and Drocea Mts. dacites from the Ist cycle of banatitic magmatism are lacking and in Bihor, they occur only within a few subvolcanic bodies of small size.

In Bihor, better represented are the rhyodacites; in the western part of Biharia massif, they form numerous sills and irregular bodies, both in the crystalline schists of the Biharia series and especially in the phyllites of the Păiuşeni series. Rhyodacites also occur in the Gilău Mts. near NE border of the massif, forming dykes, sills and irregular bodies. In all the other regions of the Apuseni Mts. rhyodacites are lacking or for the time being they have not been drawn up on the issued geological maps.

The typical development area of the first cycle volcanism — the Vlădeasa Mts. — contains the greatest volume of rhyolites forming the volcano-plutonic massif of Vlădeasa (Giuşcă et al., 1969). The rocks of the Vlădeasa main eruptive body cut and include andesites, dacites and two older rhyolite rock types producing as well contact breccias with them. Although the Vlădeasa rhyolites represent subvolcanic bodies, they exhibit ignimbritic features (Ştefan, 1980).

The (ignimbritic) rhyolites displaying ignimbritic features represent massive rocks, sometimes with cutaxitic structures, welded tuff and rarely rocks with vitrophyric structures (west of the Iadului Valley); they end the banatitic igneous activity of the first cycle in the Vlădeasa massif. However, the latest rocks of the first cycle are the banded biotite-rhyolites developed only on the western border of the massif (Istrate, 1978).

Rhyolites of ignimbritic characters similar to those in the Vlădeasa are met NE of Zalău in the Măgulicea hill and represent together with those from Puguiorul hill olistolith (near Moigrad), the northern occurrences of this type (Ştefan et al., 1986).

I^{st} cycle rhyolites forming exlusively subvolcanic bodies, intrusive nappes, sills, dykes are well represented in South Bihor and less in Gilău; in the Trascău Mts. such rocks have not been identified. It is hardly difficult to ascribe the Borod rhyolites to the first cycle volcanism although they are quite similar to those occurring in the Bihor and Gilău Mts. Andesitic, dacitic and rhyolitic volcanics on the margin of Budureasa and Pietroasa intrusive massifs in fact belong to the Vlădeasa eruptive massif.

In the Metaliferi Mts., rhyolites as well as some varieties of andesites of Upper Maastrichtian-Paleocene age (Borcoş et al., 1984), which generally correspond to the products which were previously ascribed to the I cycle of Neogene volcanism (Ianovici et al., 1976), seem to have a wide distribution; however, their distribution is as yet incompletely known, the relationships between rhyolites and andesites are still uncertain as well as their morphology. That is why they have not been included on the map (Pl. I).

Vitroclastic rhyolites intensively bentonized from the Chioarului Valley dyke, have a special mineralogical and chemical composition; they are richer in Na_2O than the other mentioned rhyolites (Ştefan et al., 1986).

The volcanics and the near-surface subvolcanic rocks belonging to the first cycle rarely produce contact phenomena. However, there exist andalusite hornfelses formed at the expense of some metamorphic rocks near the Mărgăuţa dacite dyke at Chicera Hill in North Vlădeasa. In addition, all the xenoliths are nearly completely digested and transformed to hornfelses reaching the pyroxene facies.

The products of hydrometasomatic metamorphism are rather abundant in the rhyolites of Vlădeasa main body; epidote and sometimes zeolites are very well represented. Generally the banatitic volcanics and especially rhyolites are autometamorphically changed or by a late contribution of hydrothermal solutions; excepting pyrite which is very rare, they are not accompanied by metalliferous minerals. There where such mineralizations are met in the volcanics themselves or sedimentary rocks, they should be associated to some magmatites of the II^{nd} cycle probably granodioritic-granitic in composition, situated in the depth (for instance: Ciripa zone in the basin of the Drăganului Valley, Vlădeasa).

Banatitic volcanism in the Vlădeasa massif certainly ends before the Cuisian, because blocks of andesites, dacites and rhyolites similar to those in the eruptive massif, are included as elements in the conglomerates at the base of the lower red clays complex (Paleocene-Ypresian) from Morlaca. An apparent isotopic age of 61 ± 3 mil. years (Bleahu et al., 1984) seems very close to real age of rhyolitic volcanism.

The second main cycle of banatitic magmatism contains a great deal of quartz-dioritic rocks and especially granodiorite-granitic ones accompanied and preceded in crystallization succession by their porphyritic varieties which are placed at the periphery of plutonites both as marginal facies of big bodies and as their apophyses; herein other types of subvolcanic bodies which are not so close to plutonites, can be added. Swarms of subvolcanic bodies of porphyritic, quartz-dioritic, granodioritic or granitic rocks which are drawn on the map, are supposed to be associated to some profound plutonic bodies ; such a supposition which is on account of geophysical data was confirmed by deep drillings, which were done in the area of Hălmăgel-Valea Seacă pluton (Cioflica et al., 1982). The presence of some more profound intrusions in the spring zone of Crișul Alb river, in the Trascău, Gilău, Mezeș Mts. as well as Borod or Fagului Valley, has not been proved yet, but there are geological premises supporting such an idea ; this fact is also suggested by geophysical anomalies in most cases. Nature and abundance of rock types in the satellite bodies which precede the big intrusions, indicate the relative depth of pluton and its composition.

Banatitic magmatism of the II[nd] cycle begins with quartziferous diorites and their porphyritic varieties (porphyritic microdiorites, diorite porphyres-quartziferous andesites), which, on the Țoha Valley south of Arieșul Mic river, in Bihor, cross the rhyolites of the I[st] cycle (Jude, Ștefan, 1967). In the southern part of the Bihor Mts. at Hălmăgel and Obîrșa, quartziferous diorites are crossed by granodiorite-granites and at Stînișoara, porphyritic rocks of dioritic composition in the subvolcanic bodies are thermally changed into the contact aureola of granodioritic--granitic body. In the Gilău Mts., in the Vadului Valley and at Băișoara, such rocks of dioritic composition constitute the marginal facies of the rock bodies of granodioritic composition.

In the Bihor Mts. diorites and their porphyritic varieties are displayed at the periphery of the granitic pluton or in its cover, starting from Hălmăgel and Obîrșa, at south, in the Găina Mt., at east and up to Valea Seacă at north. In this last zone, magmatites have a quartz-monzodioritic composition, being similar from this point of view with those from Măgureaua Vaței-Birtinului Valley body, which is the southernmost occurrence of banatitic magmatites in the II[nd] cycle of the Apuseni Mts.

In Pietroasa, Budureasa and Western Vlădeasa massifs, quartz-dioritic rocks occur either as some independent bodies or at the periphery of granodiorite-granitic-monzogranitic rocks ; in fact, they are included here as xenoliths. Porphyritic microdiorites are also met in the northern extremity of eastern Vlădeasa eruptive massif, north of Crișul Repede river, at the periphery and in the cover of granodiorite porphyry dyke ; in the dyke itself as well as everywhere in the rocks of granodioritic composition there are numerous xenoliths of porphyritic microdiorites.

In the Gilău Mts., south of Băișoara, there are rather continuous transitions from the granodiorites and quartz-diorites (sometime with monzodiorites characters) to their marginal counterparts. In this region, bodies of porphyritic quartz-andesitic rocks up to microdiorite-porphyres are widespread, but the Răcătău quartziferous diorites and especially those from Iara are not so extended, on account of small-sized hypabyssal granodioritic body.

Bodies of porphyritic microdiorites in the Borod zone as well as those of quartziferous andesites-porphyritic microdiorites from Mezeș, Gilău, Trascău, Bihor and Măgureaua Vaței-Birtinului Valley, which are generally automorphically changed, caused no important phenomena of contact metamorphism and are barren, excepting some isolated pyrite impregnations.

In the central part of the Metaliferi Mts. (Almașul Mic—Vălișoara), there occur dykes of quartziferous diorites passing to gabbro-diorites and monzodiorites, placed according to a system of fractures ENE—WSW oriented; a series of veins of andesitic composition add to these rocks.

On the products of contact metamorphism associated to diorites and generally to Laramian magmatism in the Apuseni Mts. already described by Cioflica et al. (1980), we do not insist reminding only that the most intensive thermal changes of surrounding rocks were caused by quartziferous monzodiorites from Măgureaua Vaței—Birtinului Valley, generating hornfelses which correspond to pyroxenic facies.

Skarns often accompanied by magnetite concentrations occur almost everywhere at the contact between dioritic and carbonate rocks, sometimes base metal sulphides associate with the skarns (Fig. 1). So, at Măgureaua Vaței skarns of a very rich paragenesis (gehlenite, spurrite, tilleyite, garnets, pyroxens, wollastonite, vesuvianite) are associated to Fe $\pm$ Ba metasomatic mineralizations in the western extremity of quartz-monzodioritic body and sulphide veins in the eastern extremity of the magmatic body, where prevail granodiorite-granites. On Martin hill at Sîrbi—Hălmăgel, in the aureola of dioritic body, which is crossed by granodiorites, there occur iron oxides and sulphide mineralizations. Magnetite associated with banatitic magmatites are also found at the spring of Arieșul Mic, Valea Seacă and Budureasa; in the last two zones, weak sulphide mineralizations overlie this kind of mineralizations as well. It is obvious that the iron oxides mineralizations are mostly associated to dioritic, quartz-dioritic and monzodioritic rocks; even in the zone of Iara—Băișoara from Gilău Mts., granodioritic rocks to which associate the well known iron mineralizations, pass to quartz-monzodiorites (see QAP diagram in Pl. I).

The Hălmăgel and Obîrșa quartziferous diorites as well as those from Găina cross Maastrichtian sedimentary rocks intensely hornfelsized; this fact pleads for their Paleogene age.

Dacites-granodioritic porphyres and porphyritic microgranodiorites as dykes, sills or apophyses of profound granodiorite-granitic bodies are sometimes thermally influenced by the latter one. These porphyritic rocks cross and include quartziferous andesites-porphyritic quartziferous microdiorites which are emplaced at the beginning of the IInd cycle. Around such rock bodies sometimes better developed, took place weak thermal contact phenomena (up to hornfelses of the albite-epidote facies) and are often accompanied by hydrometasomatic products, which are sometimes associated with weak mineralizations especially pyrite-bearing (Bihor, Vlădeasa, Gilău, Trascău, upstream of Crișul Alb river).

Granodiorite-granites in the same magmatic stage constitute main mass of banatitic bodies in the Apuseni Mts.; although they outcrop on small areas, as we already mentioned their development in the depth was proved (in the Bihor and partly in the Gilău).

The granodiorite-granitic rocks to which the main sulphide mineralizations are genetically connected, cross quartziferous diorites and porphyritic microdiorites which are often found as xenoliths at the periphery of granodiorite-granitic bodies (Budureasa, Pietroasa, Vlădeasa, Gilău, Southern Bihor).

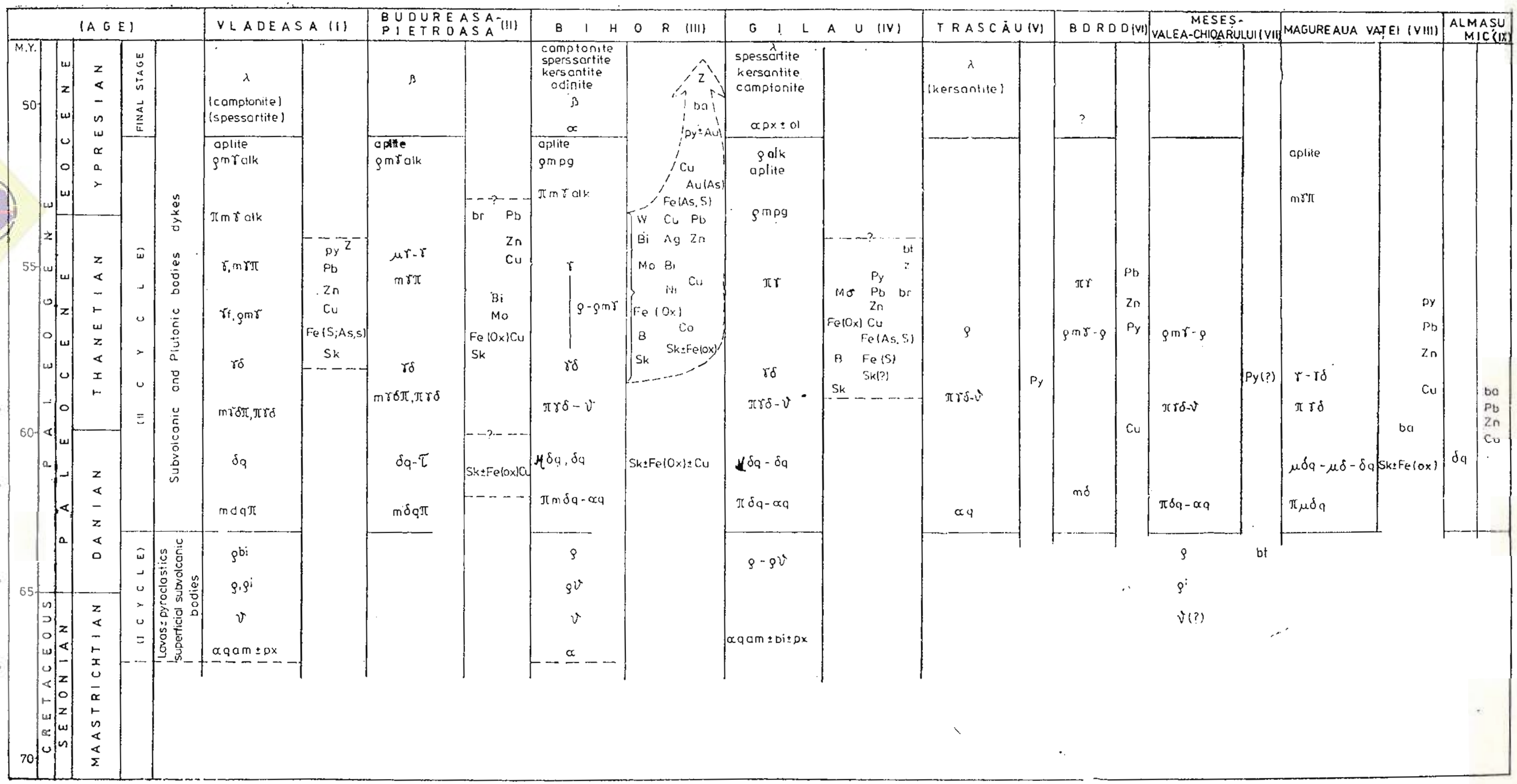

Fig. 1 — Magmatic and Metallogenetic Evolution of the Banatites in the Apuseni Mts. α andesites (q, am, px, bi : quartz, amphibole, pyroxene, biotite-bearing, alk-alkaline) ; ʋ, dacites ; ρʋ, rhyodacites ; ρ, rhyolites ; δ diorites ; μδ, monzodiorites ; δq, quartzdiorites ; πδ, diorite porphyry ; mδ, microdiorites ; γδ, granodiorites ; γ, granites ; ρmγ, microgranitic rhyolites ; ρmpg, micropegmatitic rhyolites ; λ, lamprophyres ; β, basalts (01-olivine-bearing) ; sk, skarns ; z, zeolites ; ba, barite ; py, pyrite ;, bt, bentonite.

Around big bodies of granodiorite-granitic composition, took place phenomena of thermal metamorphism which sometimes extend on 1500 m as in the Bihor, round the granitic pluton (Cioflica et al., 1974). Although products of thermal metamorphism are widely spread in the Bihor, excepting some intensely hornfelsed xenoliths (where sillimanite prevails) intensity of thermal metamorphism reached only the facies of hornblende hornfelses.

Under geologically favorable conditions, i.e. in the contact aureola of the granodiorite-granites plutons, Fe-, B-, Bi, Mo bearing skarns have been formed, locally overlapped by sulphide mineralizations, sometimes independently developed, such as the vein occurrences with Cu-, Zn- and Pb- sulphides at Valea Seacă, Valea Mare—Budureasa etc.

Subvolcanic bodies of microgranitic rhyolites, granophyres and porphyritic microgranites which form dykes and irregular bodies (in Vlădeasa, Bihor and Borod probably belong to the same magmatic episode; they are sometimes accompanied by weak sulphide mineralizations (Eastern Vlădeasa, at Scrind—Răchițele; Borod).

Granodiorite-granitic and dioritic rocks which cross the Lower Maastrichtian sedimentary deposits and as in the Vlădeasa and Budureasa, I[st] cycle volcanics at Gilău—Iara are discordantly covered by striped clays from the lower complex. This fact reduces a lot the emplacement interval of banatitic magmatites in comparison with that resulted from isotopic ages (Russo—Săndulescu et al., 1984; Rădulescu, 1984).

The II[nd] cycle of banatitic magmatism ends with alkaline differentiates rich in SiO_2 and K_2O; they form veins of aplites, microgranitic and/or micropegmatitic rhyolites, porphyritic microgranites etc. In the Bihor and Budureasa—Vlădeasa Mts. such rocks form NNW—SSE trending dykes with extension varying between hundreds of meters to some (few) kilometers. The dykes of similar composition in the Mezeș, Gilău and Trascău Mts. do not show preferential orientation. Such rocks did not generate products of thermal metamorphism to be significant and are not accompanied by mineralizations (Istrate, Udubașa, 1981).

It is likely that the isotopic age of these rocks, i.e. 47—51 m.y. (Istrate et al., 1976) is their real age.

After the consolidation of the granodiorite-granitic magma, basaltic andesites, basalts and lamprophyres have been emplaced on deep fractures; they come from a different, more deeper situated magmatic source. These basic rocks are nearly synchronous with the later differentiates of the granodiorite-granitic magma (as in the Gilău Mts.) or they are much later emplaced simultaneously with the circulating hydrometasomatic solutions associated to granodiorite-granitic plutons, e.g. Bihor Mts. The lamprophyre dykes, typically developed in the Bihor Mts. have a similar trend, i.e. NNW—SSE, to that of differentiation products of the granodiorite-granitic magma (rich in SiO_2 and K_2O); the former cut the alkaline differentiates.

Banatitic metallogenesis.

Occurrences and ore deposits which are genetically associated to banatites in the Apuseni Mts. belong to (Laramian) banatitic metallogenetic belt which extends on about N—S direction from north of the Crișul Repede up to the south of the Danube.

From genetical point of view, we distinguish mineralizations associated to skarns (especially B, Fe, Bi, Mo, W and Cu concentrations) and hydrothermal concentrations in which impregnation and substitution processes played a subordinated part. Hydrothermal mineralizations are much more diversified in comparison with pyrometasomatic ones which they often overlie.

Metallogenesis associated to banatites in the Apuseni Mts. has distinct features in comparison with that from Banat. Firstly, in the Apuseni Mts. skarns are not so developed; secondly magnetite mineralizations are only locally developed (Băişoara zone); thirdly, the main metals in the ore deposits are more diversified than in Banat; their major geochemical spectrum includes Bi, Mo, Pb, Zn, Cu, B, Fe, W, Co, Ni, As etc. while in Banat, where according to the importance there is another series of metals: Cu, Fe, Bi, Zn, Pb, W, Mo, Co. Therefore, it is suggested a metallic differentiated potential for the two major zones of banatites' development in Romania, which also have a different origin in relation with the models of plate tectonics (Rădulescu, Săndulescu, 1973; Săndulescu, 1984). Various regimes of formation and evolution of the banatites and of the associated metallogenesis are in fact reflected in the apparition of porphyry-copper systems, which are known up to now only in Banat (Cioflica, Vlad, 1980).

In the Apuseni Mts., representative bodies of skarns of very different forms and sizes are known in the Bihor—Budureasa, Gilău massifs and Măgureaua Vaţei (Fig. 1); for the time being, skarns are not known in the Plopiş, Mezeş, Trascău Mts. and in the Eastern Metaliferi Mts. as well. Skarns generation was controlled both by the circulation ways occurred near the banatitic plutons and by the paleosome nature. The limestones and dolomites both from the crystalline series and Mesozoic deposits prove to be very favorable to the substitution processes.

Regarding the types of skarns which occur, we remark on one side, prevailing infiltration skarns in relation with the contact ones (which are more characteristic for Banat), on the other side, prevailing apocarbonatic skarns in relation with aposilicate ones; calcic skarns are more developed than magnesian ones.

Mineralizations of iron oxides occur in the Apuseni Mts., especially in Băişoara—Maşca—Cacova Ierii district (Lazăr, Întorsureanu, 1982), at Măgureaua Vaţei, Martin Hill (Hălmăgel), spring of Arieşul Mic and Valea Mare (Budureasa). They associate spatially and maybe genetically either to some intrusive dioritic or monzodioritic bodies or to some basic envelopes of some granodioritic bodies. To granodiorite-granitic plutons (ex. Băiţa—Dedeş valley pluton, Bihor) are associated obviously polymetallic mineralizations, which consists mainly of sulphides and sulphosalts, more rarely sulphoarsenides and arsenides of Fe, Ni and Co.

Hydrothermal mineralizations are widely spread in the Bihor massif (Rîul Mic, Brusturi—Luncşoara, Valea Vacii, Şipot brook, Valea Mare (Poiana), Izvorul Bihorului, Gruiul Dumii, Băiţa Bihorului, Valea Seacă etc.), as well as in Budureasa, Vlădeasa massifs, at Juleşti—Valea Fagului, in Plopiş Mts. (at Bucea—Corniţel), in Gilău Mts. (Valea Lita, Băişoara), on the Birtinului Valley and at Căzăneşti and Almaşul Mic, in the Metaliferi Mts. too.

The hydrothermal minerals are frequently spatially associated with skarn and high temperature minerals (such as magnetite, ludwigite, ilvaite, scheelite, molybdenite, bismuthite, pyrrhotite) and generally succeed the skarn stage of postmagmatic mineral formation. The hydrothermal ore minerals build up mainly veins and hydrometasomatic bodies; locally there are impregnation bodies, stockworks or simple nests.

The ore veins are related to breccia zones or along fractures and their trend (especially in the Bihor Mts.) is mostly NNW—SSE, that is the same as the trend of the lamprophyres dykes closing the banatitic magmatic activity. The size of the ore veins is quite variable: hundreds of meters in length and some few meters in width. Their vertical extension varies from some tens of meters (Julești—Valea Fagului) to 100—200 m (Almașul Mic, Bucea, Cornițel) and, more rarely 300 — 500 m (Băița Bihorului, Brusturi-Luncșoara).

In the Bihor massif, the ore veins have the following characteristics: (1) both the ore vein and a lamprophyre frequently occupy the same fracture space; (2) the veins are obviously inhomogeneous as regards the distribution of the voids alternating with impregnation and substitution zones, i.e. there is a „vein zone", a name frequently used by the miners themselves; (3) the „vein zone" include ores with various structures: massive, parallel, sometimes banded (symmetrical and asymmetrical), breccious, impregnation, with mineralized caves etc. but the most common and typical are the composite structures; (4) the main fracture vein is often accompanied by veinlets and mineralized fissures, joined or not with the main veins; (5) the ore deposition was accompanyied and followed by movement along the veins, a fact proved by breccious structures and especially by longitudinal and cross-cutting faults hosting non-metalliferous minerals; (6) the vein width varies directionally; its maxima is commonly reached in the median zone; (7) there are either isolated veins or vein groups with parallel or „en echelon" distribution; (8) there exist mineralogical and chemical composition (both qualitative and quantitative) on the vertical and horizontal scale.

Some ore deposits have an obvious vertical zoning. A characteristic example is Brusturi—Luncșoara ore deposit, which was opened by means of mining works at about 350 m depth. At the upper levels, there is a lead-zinc mineralization, while at the lower levels, cupriferous character of the mineralization becomes more obvious. This modification of Cu/Pb + Zn ratio is accompanied by an increasing amount of skarn and iron oxides minerals.

Impregnation and/or substitution bodies can be sometimes lenticularly developed, being very long and flattened. They are often parallely oriented with the regional system of fractures (NW—SE), rarely about E—W (ex. Bucea—Cornițel, acc. to Berbeleac et al., 1982).

Processes of metasomatic metamorphism which influenced both crystalline formations and Pre-Paleogene sedimentary rocks and banatites are very widely spread; therefore, their products are everywhere found. The aureola of hydrothermal metamorphism is much more extended than thermal and/or pyrometasomatic metamorphism, which it some times overlies.

It is quite difficult to establish the appurtenance of minerals to the mineral associations and/or parageneses formed in the convergence zones of various factors controlling the development of the metasomatic processes; that is true especially in the marginal parts of the main plutons or in their cupolas. The contact metamorphic aureola of the granodiorite-granitic pluton in the Bihor massif has the greatest extension; on the vertical scale it reaches 2 000 m or more (Lazăr et al., 1982). The alteration processes are described in numerous papers, e.g. Gherasi, 1969; Cioflica et al., 1974, 1982; Giuşcă et al., 1976; Ionescu, Berbeleac, 1971; Lazăr et al., 1982) and typical minerals of K-feldspar-, propylitic-, sericitic- and argillitic alteration zones have been depicted; some alteration minerals occur in vugs, e.g. quartz, carbonates, feldspars, epidote, chlorite, clay minerals, zeolites, accompanying the ore minerals.

The Apuseni Mts. banatitic metallogenesis is centered on the Bihor Mts. zone with a maximum complexity in the Băiţa Bihor ore deposit. An obvious horizontal zoning appears around this important ore deposit (Fig. 2). The internal zone contains Co, Ni, Mo, Fe, Bi, Ag, Au mineralizations, the most typical being the Gruiul Dunii ore deposit, including the whole zone between the spring area of the Crişul Negru, Arieşul Mic and Arieşul Mare rivers. It follows a discontinuous zone with iron oxides (magnetite, hematite) and base metal sulphides; the typical ore deposit belonging to this zone is that at Brusturi (Dolii Hill). The external zone contains Pb—Zn and pyrite ores. All the zones may contain gold occurrences but they are typical of the external zone.

The regional zoning is however, incompletely developed and the zones show towards east uncertain boundaries. Therefore, the metallogenesis cannot be ascribed to a single magmatic body but to several ones with simultaneous mineralizing activity. The most important is the Central Bihor pluton, in whose apical zone there are a lot of mineralized structures with skarns and subsequent polymetallic mineralizations. Periplutonic zoning of the Bihor Mts. mineralizations was established both by means of metallic minerals associations and geochemical data (Lazăr et al., 1982; Cioflica et al., 1982). Northwards, the superficial pluton (Hochpluton) Budureasa—Pietroasa—Vlădeasa is accompanied by weaker mineralizations which are placed southwards. East of the Apuseni Mts., a similar pluton, the Gilălu—Băişoara zone, had a metallogenetic iron-polymetallic activity at the end of its evolution.

The most peripherical zones (Măgureaua Vaţei, Borod—Corniţel, Mezeş and Trascău) associate with some small-sized intrusions (iron mineralizations in skarns and polymetallic vein ones) or with some hidded intrusions very small in size in the depth.

Mineralized structures are displayed within an asymmetrical zoning so that western zone is much richer than eastern zone. Otherwise, in the west, on a N—S alignment, there is the great part of holocrystalline-equigranular rocks, to which the mineralizations are connected. Such an asymmetry can be associated both to a position or an asymmetrical form of central pluton and to geological structure, which is different westwards and eastwards too. It is possible that eastwards, mineralized zones whose boundaries remain opened to continue in the depth, this region becoming thus a perspective zone (eventually for the second depth stage).

Banatitic metallogenesis is characterized by ores containing Fe, B, W, Mo, Bi, Co and Ni as major elements; on the contrary Neogene metallogenesis contains significant concentrations of Au, Cu and Te. Geochemical aspects of banatitic mineralizations are given by the analysis of the distribution of minor elements in sulphides. A few examples of associations of minor elements are given in Fig. 2.

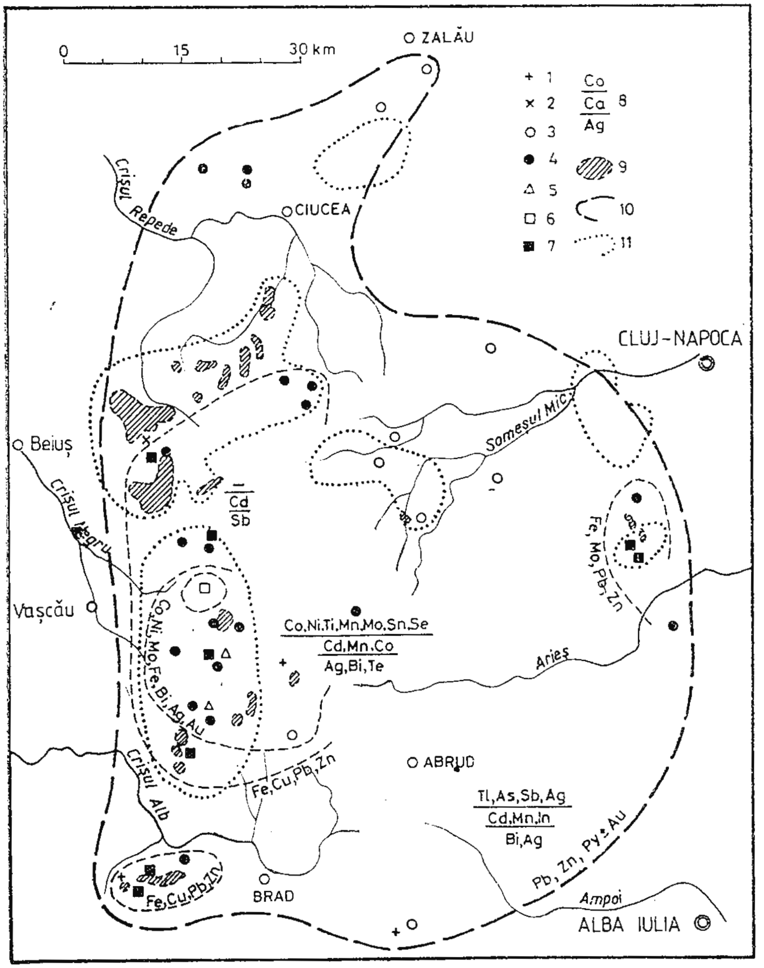

Fig. 2. — Regional distribution of the mineralization types in the Apuseni Mountains. 1, baritine occurrences; 2, brucite occurrences; 3, pyrite occurrences with or without gold; 4, polymetallic occurrences (Cu, Pb, Zn); 5, occurrences with Co, Ni, As, Bi, Ag ore; 6, Bi, Mo, W, B, Cu, Pb, Zn occurrences; 7, Fe ± Cu occurrences; 8, minor elements characteristic (downwards) in pyrite, sphalerite, galena; 9, outcrop areas of holocrystalline-equigranular rocks; 10, zones contours; 11 geophysical anomalies.

[4] We do not share Russo-Săndulescu, Berza (1976) opinion on the presence of agglomerates and of a volcano-sedimentary formation at Izvorul Muntelui in the Trascău Mts.

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EVOLUŢIA MAGMATISMULUI BANATITIC DIN MUNŢII APUSENI ŞI METALOGENEZA ASOCIATĂ.

(Rezumat)

Magmatismul calcoalcalin banatitic (post-Maastrichtian superior — Paleogene) are o largă dezvoltare în Munţii Apuseni (pl. I) şi s-a manifestat în cadrul a două cicluri importante, dar cu distribuţie inegală. Ciclul I a generat curgeri de lavă (Vlădeasa, Gilău), uneori însoţite de piroclastite (Vlădeasa, Mezeş —Valea Chioarului) şi corpuri subvulcanice s uperficiale (Vlădeasa, Gilău, Bihor); magmatitele acestui ciclu n-au fost recunoscute în Munții Trascău. Ciclul II a generat roci intrusive, hipoabisice și plutonice, acestea din urmă fiind larg dezvoltate în profunzime. Magmatismul banatitic din Munții Apuseni se încheie cu punerea în loc a unor dyke-uri de roci bazice, abundente în Munții Bihor, care succed și se suprapun în timp (parțial) peste diferențiatele filoniene alcaline tîrzii ale magmei granodiorit-granitice din care s-au diferențiat magmatitele ciclului II.

Ciclul I debutează prin curgeri de lave andezitice (andezite cuarțifere cu piroxeni și hornblendă, cu sau fără biotit), dezvoltate din abundență în masivul Văldeasa, unde ocupă 15–20% din suprafața de aflorare a rocilor banatitice. Corpuri subvulcanice se întîlnesc în special în Munții Gilău, iar în Munții Bihor andezitele formează sill-uri și dyke-uri de dimensiuni reduse.

În succesiune urmează dacite (pînze intrusive, dyke-uri, curgeri de lavă) în masivul Vlădeasa, riodacite (sill-uri, dykeuri, corpuri neregulate) în Munții Bihor și Gilău. (Fig. 1). Ciclul I se continuă cu importanta masă de riolite, în parte cu caracter ignimbritic, din masivul Vlădeasa; echivalentele lor din Munții Gilău, Munții Bihor și din cea mai nordică ocurență dealul Măgulicea de la NE de Zalău au arii mai reduse de dezvoltare și formează sill-uri, dyke-uri etc.; la Valea Chioarului sînt intens bentonitizate.

Vulcanismul banatitic din masivul Vlădeasa se încheie în mod sigur înainte de Cuisian, întrucît blocuri de andezite, dacite și riolite se găsesc în conglomeratele din baza complexului argilelor vărgate inferioare (Paleocen-Ypresian) de la Morlaca.

În legătură cu magmatitele ciclului I se cunosc iviri modeste de corneene, mai abundente în xenolite (Vlădeasa), iar produsele metamorfismului hidrometasomatic apar reprezentate mai ales prin epidot și zeoliți, rareori însoțite de pirită.

Ciclul II, principal, include un mare volum de roci cuarț-dioritice și mai ales granodiorit-granitice, însoțite sau precedate de varietățile lor porfirice; acestea sînt localizate la periferia plutonitelor, ie ca faciesuri marginale ale corpurilor magmatice mai mari și apofize ale acestora, fie sub forma unor corpuri subvulcanice qvasi-independente. Roiurile de corpuri subvulcanice de roci porfirice (cuarț-diorite, granodiorite, granite) precum și anomaliile geofizice sugerează prezența unor intruziuni profunde, de natură plutonică, în zonele Hălmăgel-Valea Seacă, în zona de izvoare a Crișului Alb, în Munții Trascău, Gilău, Mezeș, la Borod și Valea Fagului etc; plutonul Hălmăgel-Valea Seacă este singurul pînă acum confirmat prin foraje (Cioflica et al., 1982).

Ciclul II debutează cu diorite cuarțifere și varietățile lor porfirice, care pe valea Țoha (Arieșul Mic) străbat riolitele primului ciclu. La Hălmăgel și Obîrșa (sudul Munților Bihor) dioritele sînt străbătute de granodiorit-granite, iar la Stînișoara rocile dioritice porfirice sînt transformate termic în aureola corpului granodiorit-granitic; uneori asemenea roci constituie faciesurile marginale ale corpurilor granodioritice. Există numeroase cazuri cînd se poate constata trecerea gradată de la rocile granodioritice la cele cuarț-dioritice (Băișoara etc.)

Corneene corespunzătoare faciesului piroxenic sînt cunoscute la Măgureaua Vaței, asociate monzodioritelor cuarțifere, iar skarne — de regulă însoţite de concentraţii ferifere — apar la Măgureaua Vaţei, Valea Seacă, Budureasa, Iara-Băişoara etc.

Masa principală de magmatite din ciclul II este reprezentată de rocile granodiorit-granitice care, deşi aflorează pe suprafeţe restrînse, formează corpuri de mari dimensiuni în adîncime, în special în Munţii Bihor şi Gilău. Asociate lor se întîlnesc, sub formă de dyke-uri, sill-uri sau apofize, dacite-porfire granodioritice şi microgranodiorite porfirice; ele înglobează rocile andezitice cuarţifere puse în loc anterior, iar în cazul unor corpuri mai mari se observă fenomene de contact termic şi slabe mineralizaţii piritoase (Bihor, Vlădeasa, Gilău, Trascău etc.)

Xenolite de diorite cuarţifere şi microdiorite porfirice se găsesc deseori, în special în părţile periferice ale corpurilor granodiorit-granitice (Budureasa, Pietroasa, Vlădeasa, Gilău, Bihorul de sud).

Deşi extinderea produselor de metamorfism termic atinge uneori 1500 m (Bihor, în jurul plutonului granitic; Cioflica et al., 1974) intensitatea transformărilor n-a depăşit faciesul corneenelor cu hornblendă, astfel că picul transformărilor termice din arealul de dezvoltare a banatitelor din Munţii Apuseni se plasează la Măgureaua Vaţei, unde apar corneene în faciesul piroxenic şi skarne cu gehlenit, spurrit, tilleyit etc.

În legătură cu corpurile granodiorit-granitice au luat naştere mase importante de skarne şi principalele concentraţii metalifere de natură pirometasomatică (Fe ± B, Bi, Mo) şi/sau hidrotermal-filoniene (Cu, Pb, Zn etc.) din Munţii Apuseni.

Aceluiaşi episod magmatic aparţin corpurile subvulcanice de riolite micrOgranitice, granofire şi microgranite porfirice (Vlădeasa, Bihor, Borod), formînd dyke-uri şi corpuri neregulate; cu ele se asociază mineralizaţii slabe de sulfuri (Vlădeasa de est, Scrind-Răchiţele; Borod).

Rocile granodiorit-granitice şi dioritice străbat depozitele sedimentare Maastrichtian inferioare şi vulcanitele primului ciclu (Vlădeasa, Budureasa) şi sînt acoperite de argilele vărgate din complexul inferior, ceea ce restrînge mult intervalul de punere în loc a magmatitelor banatitice în comparaţie cu cel rezultat din vîrstele izotopice (Rădulescu, 1984; Russo-Săndulescu et al. 1984).

Ciclul II se încheie cu diferenţiate alcaline filoniene, reprezentate prin aplite, riolite microgranitice, riolite micropegmatitice, microgranite porfirice etc, formînd dyke-uri extinse pe sute de metri.

După consolidarea magmei granodiorit-granitice, pe fracturi adînci, dintr-o altă sursă magmatică, mai profundă, s-au pus în loc andezite bazaltoide, bazalte şi lamprofire, în mare parte concomitent cu diferenţiaele alcaline sus-amintite şi cu soluţiile postmagmatice asociate masei principale de magmatite din ciclul II.

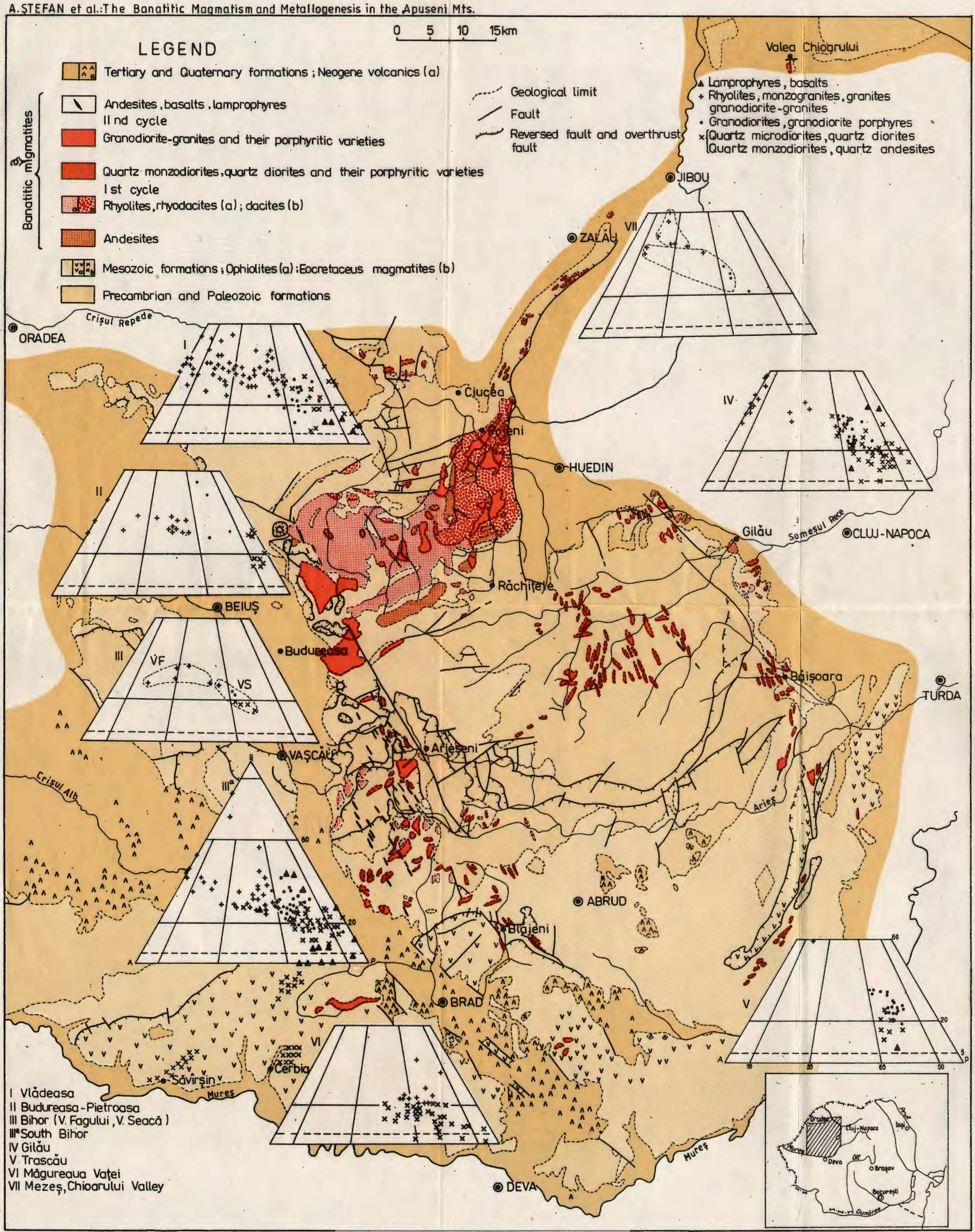
Metalogeneza banatitică din Munţii Apuseni cuprinde mineralizaţii diversificate asociate skarnelor (B, Fe, Bi, Mo, W, Cu) sau filoniene-hidrotermale (Cu, Zn, Pb, As etc), care în parte se suprapun structurilor pirometasomatice. Skarnele au o dezvoltare mai redusă în comparaţie cu structurile similare din Banat, unde şi asociaţia de metale este diferită : Cu, Fe, Bi, Zn, Pb, W, Mo, Co, şi unde există, în plus, numeroase structuri porphyry copper (Cioflica, Vlad, 1980). Potenţialul metalifer diferenţiat al celor două arii majore de dezvoltare a banatitelor din România este astfel evident, acordîndu-se cu regimul diferit de formare a banatitelor în cele două zone în raport cu modelul tectonicii globale (Rădulescu, Săndulescu, 1973; Săndulescu, 1984).

În cadrul diferitelor zăcăminte au fost evidenţiate zonalităţi verticale bine exprimate (cazul cel mai tipic: Brusturi-Luncşoara), dar este de subliniat în special zonalitatea orizontală regională (Fig. 2) majoră, în cadrul căreia se înscriu structuri zonale locale. Zonalitatea regională este însă asimetrică, fiind centrată pe extremitatea vestică, pe zona Munţilor Bihor, unde se înregistrează şi punctul de maximă complexitate metalogenetică. Spre est limitele zonelor sînt mai greu de trasat, unde de altfel şi ariile de aflorare a magmatitelor sînt mai reduse; aici se poate presupune existenţa unor mineralizaţii în profunzime, în continuarea celor cunoscute sau ca entităţi gitologice separate.

În încheiere se poate remarca suprapunerea mineralizaţiilor celor mai bogate, situate pe un „aliniament" nord-sud, pe aria unde apar cele mai multe roci holocristaline-echigranulare (Fig. 2).

MAP SHOWING THE DISTRIBUTION OF BANATITES IN THE APUSENI MTS

(after Borcoș et al 1976, modified and with additional data)



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2. ZĂCĂMINTE

REMARKS ON THE RELATIONSHIP BETWEEN THE SPATIAL DISTRIBUTION OF THE COAL COMPLEXES IN THE OLT—JIU SECTOR AND THE STRUCTURAL—GENETIC FACTORS [1]

BY

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Coal seams. Lignites. Pliocene. Spatial distribution. Structural-genetic factors. Lithostratigraphy. Biostratigraphy. Sedimentary processes. South Carpathians — Southern Subcarpathian area — Subcarpathians between Olt and Jiu rivers. Getic Plateau — Olteţ Platform.

Abstract

The authors delimited three lithostratigraphic units in the Dacian-Romanian deposits of the Olt-Jiu sector from Oltenia. Each unit contains a coal complex consisting of 1—8 coal beds. The spatial development of these coal complexes revealed the existence of two structural-genetic types of coal generating areas : the first type belongs to the Carpathian Foredeep, while the second one is specific for the Moesian Platform. A close correlation exists between the thickness of the coal complexes and their structural position, the optimum thicknesses being found on the outer and inner flanks of the foredeep. Another correlation has been established between the maximum thicknesses of the coal bed V and the thickness interval of 80—100 m of the Motru coal complex. It has also been established that a migration in time of the zone of optimum accumulation of the phytomass necessary for the coal formation took place. The differential subsidence is the main factor controlling the quantity and quality of carbogenesis through the water depth which determines the type of coal generating vegetal association.

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Résumé

Observations concernant les relations entre la distribution spatiale des complexes charbonneux du secteur Olt-Jiu et les facteurs structural-génétiques. Dans les dépôts dacien-romaniens de l'Oltenia, le secteur de l'Olt-Jiu, les auteurs ont délimité trois unités lithostratigraphiques, chacune comportant un complexe charbonneux, dans la composition duquel entrent de 1 à 8 couches de charbon. On a analysé le développement spatiale de ces complexes charbonneux et on a déterminé l'existence de deux types structural-génétiques d'aires carbo-générateures : le premier appartient à l'avant-fosse carpathique le deuxième à la plate-forme Moesienne. On observe, dans l'avant fosse, une étroite corrélation entre l'épaisseur des complexes charbonneux et leur position structurale, les épaisseurs optimum étant disposées sur les flancs intern et extern de celle-ci. On a observé aussi une corrélation entre les épaisseurs maximum de la couche V de charbon et l'intervalle de 80 à 100 m d'épaisseur du complexe charbonneux de Motru. On a établi aussi qu'il a eu lieu une migration en temps de la zone d'accumulation optimum de la phytomasse nécessaire à la formation des charbons. La subsidence différentielle représente la cause principale tant pour le contrôle quantitative de la carbogenèse que pour celui qualitatif aussi, à l'intermède des profondeurs de l'eau qui détermine le type de l'association végétale carbogénérateure.

1. Introduction

The investigations of the Pliocene coal deposits from Oltenia have been carried out for over a century. The special interest aroused by the study of these deposits is mainly due to the presence of some important coal deposits (lignites).

The knowledge of the coal accumulations in this region has recently considerably increased by the investigations through boreholes, by complex studies and by coal extractions in quarries. Several aspects regarding the genesis and spatial distribution of the coal beds have been pointed out by : Răzeşu and Biţoianu (1967) Enache (1981), Ţicleanu et al. (1982), Pauliuc and Barus (1982), Andreescu et al. (1984), Andreescu (in press), Ţicleanu et al. (1984, 1985).

2. Geological Setting

2.1. Lithostratigraphy

In the Dacian—Romanian coal deposits of the Olt—Jiu region three formations have been separated by Andreescu and Ţicleanu (in Andreescu et al., 1984), Andreescu et al. (1985) (Fig. 1) :

— Berbeşti Formation
— Jiu—Motru Formation
— Cîndeşti Formation

The Berbeşti Formation, which is lithologically characterized by the predominance of the arenitic fraction, includes sometimes siltic sand, siltic clays and coal intercalations.

The faunal content indicates that it is mostly Lower Dacian in age, being characterized by associations typical of the Getian (Pachydacna beds). The white and yellowish sands situated in the terminal part of the formation contain several mollusc species indicating the Upper Dacian (Parscovian) age (Andreescu et al., 1985). (Fig. 1).

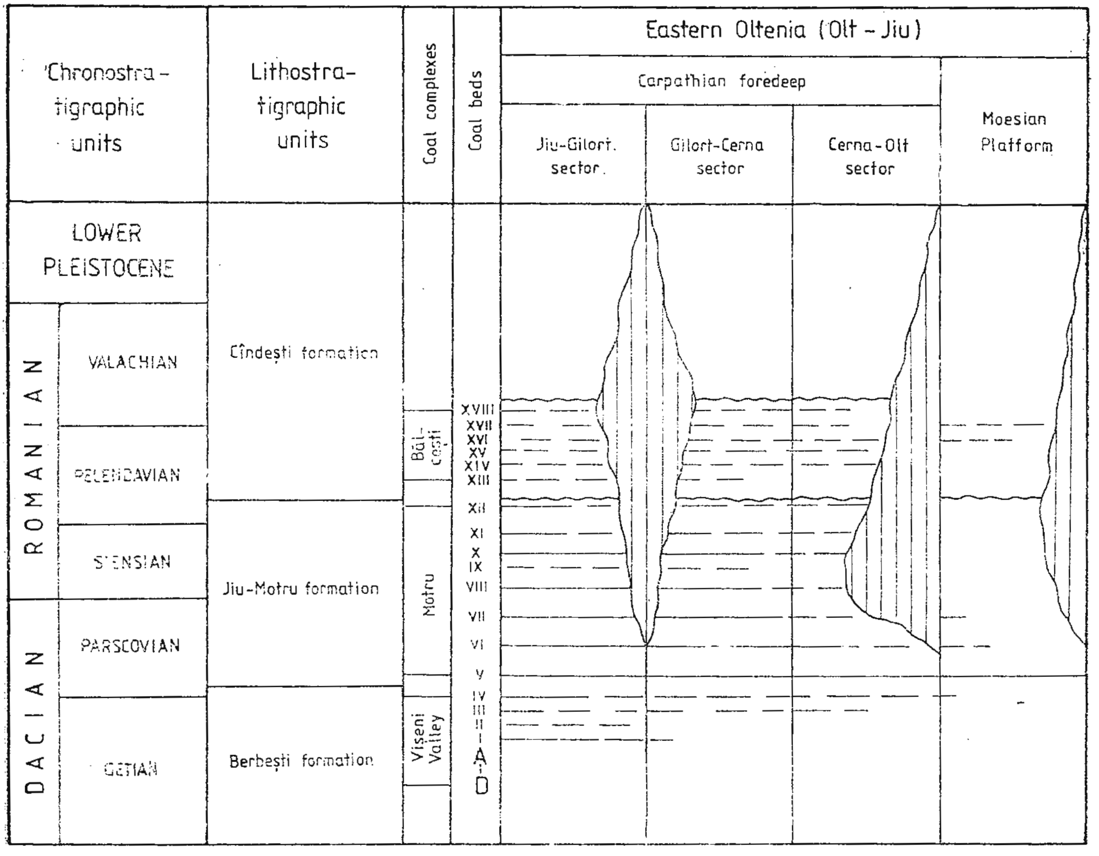

Fig. 1. — Sketch of the stratigraphic position of the Dacian-Romanian coal complexes in the Olt-Jiu sector

According to the data available, in the Motru—Danube area, the upper part of the Berbești Formation includes the coal beds I—IV characterizing the Valea Vișenilor coal complex (Andreescu et al., 1985). In the Olt—Jiu sector, in the foredeep domain, this complex is less developed, being represented by 1—2 decimetric coal beds over a restricted area (Bistrița Valley—Cerna Valley). Previous researches (Andreescu, in Andreescu et al., 1984) showed that the Berbești Formation does not include any important coal beds on the platform area, east of the Jiu Valley.

The Jiu—Motru Formation overlies seemingly conformably the Berbești Formation and is characterized by the predominance of fine facies (pelites, siltites) with arenitic intercalations and coal beds (V—XIII). This formation varies in thickness within wide limits, from about 350 m in the foredeep maximum sinking area to less than 15—20 m in the southern part of the platform. The thickness of the Jiu—Motru Formation is strongly reduced also in the northern sector of the foredeep, where its upper terms have been frequently eroded.

The lower part of the Jiu—Motru Formation, namely the interval between coal beds V—VII, belongs to the Upper Dacian. Thus we remind that the clay pile underlying the coal bed V (bed I in the local nomenclature used for the Olt—Gilort sector) includes mollusc associations indicating the Parscovian age (Pauliuc et al., 1981; Pană et al., 1981; Andreescu in Andreescu et al., 1984); Andreescu and Pană in Ţicleanu et al., 1985; Andreescu et al., 1985). The same age is supported for the interval situated between the beds V—VII by the magnetostratigraphic study carried out in the Lupoaia quarry (Andreescu et al., 1984).

Biostratigraphic and magnetostratigraphic investigations showed that the coal beds VIII—XI are of Lower Romanian age, while bed XII belongs to the lower part of the Middle Romanian (Andreescu et al., 1984).

Within the Jiu—Motru Formation the Motru coal complex (beds V—XII) was separated, whose development varies depending on the sedimentation area.

Cîndeşti Formation (Cîndeşti Beds; Mrazec, Teisseyre, 1901). Field observations showed that the coal bed XIII is often unconformably overlain by a sequence of cross-bedded medium-grained, coarse sands and tiny gravels. This coarse detrital sequence reaching 60—80 m in thickness in the foredeep area represents the lower part of the Cîndeşti Formation. Towards its median part, the Cîndeşti Formation includes a pile of deposits in which the coarse fractions are reduced, being gradually replaced by an alternation of sands, siltites, clays and sandy clays with coal clay intercalations or coal beds. This complex, which comprises the coal beds XIII—XVIII, has been named the Băleeşti coal complex (Andreescu, Ţicleanu in Ţicleanu et al., 1985).

The upper part of the Cîndeşti Formation develops prevailingly in ruditic facies (Tetoiu pebbles).

2.2. *Structural Arrangement*

The structural arrangement of the Dacian—Romanian deposits varies depending on their location in the Carpathian Foredeep or the Moesian Platform areas.

According to Săndulescu (1985), the foredeep comprises an internal zone (the northern epirogenic flank) situated north of the Pericarpathian line (Bibeşti—Tinosu line) and an external one (the epiplatform, southern flank), separated from the Moesian Platform by a flexure line, north of which the platform sinks by steps and the Neogene deposits are obviously thicker.

The Pliocene deposits on the northern flank of the foredeep generally strike south and south-east. These deposits are involved in folds with flanks dipping gently (5—10°), striking approximately east-west.

On the whole the Pliocene deposits on the southern flank of the foredeep strike northwards, several less pronounced folds being distinguished here too, striking approximately in the same direction as those on the northern flank.

In the western part of the investigated area a marked depression zone, transversal with respect to the foredeep structure is noticed, extending along the Daia — Capul Dealului alignment and continuing also on the platform towards the Terpezița—Băilești localities. The greatest thickness of the Neogene deposits in this zone (over 5 000 m) indicates the existence of a maximum subsidence area.

The Dacian—Romanian deposits on the platform are not so thick as those in the foredeep and a series of structures sketched by them represent in fact compaction structures on the vestiges of the pre-Neogene relief.

Some unconformities were noticed in the Dacian—Romanian deposits represented by the absence of the Upper Dacian and/or the Lower Romanian. But this does not affect the entity of the Jiu—Motru Formation, which is unitary over most of its developing area. This may be the result of the platform uplift as a consequence of the intra-Dacian and Wallachian orogenetic movements. A fluviatile network, formed during the glyptogenesis of the Middle Romanian — ? Upper Romanian interval in the emerged zones of the platform, led to the partial removal of the Romanian deposits and in places also of the Upper Dacian ones, the coals inclusively. Such an example is the Băilești—Negoiu deposit situated in the south-western zone of the platform.

3. Distribution of the Coal Complexes

3.1. *Valea Vișenilor Coal Complex*

This complex was drilled in the western part of the Olt—Jiu sector, being represented by the coal beds I—IV. Ghiuzeli et al. (1978) state that the beds I—III in the Peșteana area are discontinuous, while the bed IV, reached by all the boreholes, varies in thickness between 0.05—1.2 m.

The areal extension of the beds belonging to the Valea Vișenilor coal complex shows that it is formed of lenticular beds in zones of great thickness of the Berbești Formation, that is in the western and eastern parts of the Olt—Jiu region.

3.2. *Motru Coal Complex*

The specification of the stratigraphic position of the Motru coal complex and of its boundaries allowed the drawing out of an isopach map (Pl. I) showing the correlation between its thickness and structure.

Two distinct coal-generating areas corresponding to the two major structural units, the Carpathian Foredeep and the Moesian Platform respectively, could be easily noticed. The boundary between the two coal-generating areas coincides with the flexure between the platform and the foredeep.

Each coal-generating area shows characteristics specific for two structural-genetic types of carboniferous basins (according to Dorokhine, 1967): the type of premontane depression of the geosyncline group, the depression subgroup, and the erosive-tectonic platform coal basin respectively. This classification allows a more correct estimation of the coal potential of the Pliocene deposits in the investigated area.

3.2.1. *Foredeep Coal Generating Area*

North of the flexure the Motru coal complex steadily thickens along the Doba—Motoci—Breasta alignment, reaching the maximal thickness of over 300 m in the maximal sinking zone of the foredeep, on the Calopăru—Şipotu—Fărcaşu—Bălceşti—Uşurei alignment which approximately corresponds to the Pericarpathian fault. The thickness of the coal complex decreases north of the axial zone; this decrease is more rapid in the western part of the Olt—Jiu sector, where the synsedimentary rise of the Socu anticline seems to have played an important role.

The isopachs of the coal complex are on the whole parallel on the northern flank of the foredeep, except those in the Hălăngeşti—Grădiştea direction where a disturbance occurs, which was probably caused by the pre-Neogene relief. The change in the aspect of the isopachs from the Mihăiţa—Işalniţa and Oteteleşu—Susani zones on the outer flank of the foredeep, seems to be due to the same fact; here the isopachs of the coal complex are approximately parallel to the platform flexure.

An important change in the aspect of the isopachs of the Motru coal complex (Pl. I) occurs in the western part of the Olt—Jiu sector which affects both the axial zone and the external flank of the foredeep, being connected with the evolution of the Capul Dealului—Terpeziţa—Băileşti depression zone.

A gradual decrease of the thickness of the coal complex is recorded eastwards in the foredeep area: 70—100 m close to the Gilort Valley, while on the Otăsău Valley it reaches less than 10 m. Another obvious example of thickness decrease of the complex in the west-east direction is provided by the foredeep axial zone, where, at Brăneşti, between the Jiu and Gilort Valleys, a thickness of over 300 m is recorded, while to the east, at Călina, it reaches only 90—100 m.

The superposition of the isopach map of the Motru coal complex (Pl. I) upon the isopach map of bed V (Pl. II) shows that the greatest thicknesses of this bed corresponds to an interval ranging between 80—100 m in thickness.

The existence of a correlation between the thickness of the coal beds and that of the coal complex is pointed out in the case of this type of coal-generating areas as well as in other zones (Ruhin, 1967).

The main factor inducing the spatial distribution of the coal complex thickness within the foredeep is the subsidence, whose rate varied from one zone to another.

It is known that the accumulation of the phytomass takes place on condition that the accumulation rate (V_{ac}) be equal to the sinking rate (V_s) of the bottom of the coal generating swamp ($V_{ac} = V_s$). In this case the sinking rate is optimum for the coal generation. The maintenance of the equilibrium between V_a and V_s leads to the formation of a coal bed whose thickness is directly proportional to the duration of this relation. In the case when $V_{ac} < V_s$ the coal generating swamp is flooded, and a lacustrine facies sets in. On the other hand, if $V_{ac} > V_s$ the swamp becomes emerged, the organic material being subjected to rotten and erosion.

The researches carried out by Pauliuc and Barus (1982) and Andreescu (in press) show obvious differences in subsidence rates both between the two coal-generating areas and among the various areas of the foredeep.

A review of the sinking rates in the foredeep shows optimum values on the flanks and higher values in the central zone. The high values in the central zone caused the increase of the thickness of the coal complex, the digitation of the coal beds and the thickness increase of the arenitic and/or lutitic sequences.

Great sinking rates east of the Roești—Fumureni alignment led to the thinning of the coal beds and to the reduction of the coal complex. In this area the coal generating swamp facies has been replaced by a lacustrine one.

In order to follow the evolution of the coal complex the thickness map of coal beds exceeding 1 m has been drawn out (Pl. III). By comparing it with the isopach map of bed V (Pl. II) it was found that in the northern flank of the foredeep there are more beds exceeding 1 m in thickness than in the southern flank. Consequently one can conclude that their evolution in time underwent some modifications. Thus, beside the bed V, the beds VI and VII, more rarely the bed VIII (Mihăița=Ișalnița area) develop on the external flank. On the northern flank, in addition to the beds V=VII, the beds X, XI, and sometimes the bed XII in some zones, show important thicknesses. It follows that the optimum sinking rate was maintained during the Lower Romanian only on the internal flank of the foredeep.

The thickness distribution of the bed V confirms the conclusions regarding the relation existing between its position in the foredep and the thickness of the coal complex. Three, more or less parallel east-westward sectors are distinguished, two of them coinciding with the two flanks of the foredeep, where the bed V reaches maximum 5.87 m in thickness on the northern flank and 5.65 m respectively on the southern one. In the central sector bed V is 1.5 m thick except for two boreholes where the thickness reaches 2.95 m (at Bălcești). This is due to the great sinking rate in the axial zone of the foredeep which determined the digitation of the bed.

The subsidence rate determined not only the thickness of the coal beds but, indirectly, it also influenced the quality of coal. It is known that the various coal gnerating associations form ecologic series in a swamp depending on the water depth, but this depth depends first of all on the sinking rate of the basin. Each vegetal association in a coal generating swamp gives rise to a certain coal petrographic type which is characterized by its physico-chemical properties.

The impact of some synsedimentary uplift zones may change the water depth, causing the rise of the coal generating swamp to the surface.

Such an instance is the axial zone of the Socu anticline in the northern part of the Jupînești area.

On the contrary, the more rapid sinking brings about changes in the depth regime which may lead to the superposition of a type of vegetal association upon another. Several vegetation types are superposed in the succession of a coal bed by repeated sinkings and uplifts, constituting a genetic series. At least four types of maceral associations can be identified in such a genetic series, corresponding to a certain type of vegetal association. In general two of these associations occupy over 50% of the thickness of the coal bed, a reason why they have been named main associations (Țicleanu et al., in press), the other two playing only a secondary role. The binary groups of associations may be dominated by one of them; this is why they are defined in the order of the percentage of various macerals indicative of the original phytocenoses. Based on these data the sketch of the humitogenic map has been drawn out at the level of bed V (Pl. IV).

An analysis of the humitogenic map shows that the binary *Glyptostrobus-Phragmites* group, which generated coal of the best quality, overlaps the Rovinari area, continuing towards the east with the Țicleni—Capul Dealului area (northern sector), then the Jupînești—Musculești area and the Căpeni—Hălăngești zone up to east of Tetoiu, where it passes to a low productive zone with *Phragmites* and aquatic plants.

Therefore it is found that the best quality group covers the internal flank of the foredeep, namely the zone of optimum sinking rates, as indicated by the thickness of the beds. The central zone of the foredeep is dominated by the *Phragmites-Glyptostrobus* group which is almost as important as the previous group. Farther south on the platform, in addition to the *Phragmites-Glyptostrobus* group, *Salix* is also present, a taxon which generally occurs in the final part of the evolution of a coal generating swamp.

3.2.2. *Coal Generating Area of the Platform*

This coal generating area is marked by small thicknesses of the coal complex (maximum 40 m), being frequently reduced to a single coal bed of 1—2 m in thickness.

Another characteristic of the thickness distribution of the coal complex in the platform area is the presence of some thickening zones. A frequent coincidence of maximum thickness of coal beds with the axes of depressions of the pre-Neogene relief is noticed. This fact appears from the superposition of the map of the pre-Neogene relief, drawn out by Osman et al. (1978) on the isopach map of the coal bed V. Thus the maximum thickness of the coal bed V (2.0—2.4 m) is found in the axis of the Bratovoiești couloir; the same bed reaches up to 1.5 m in thickness in the axis of the Caracal couloir and in the Cîmpul Părului Couloir. Concomitantly the coal bed V is more reduced in thickness (0.2—0.6) in the paleorelief more uplifted areas, as in the case of the Redea-Caracal promontory.

In our opinion this can be explained by the knowledge of the way in which the sinking of the coal generating swamps took place on the platform area.

It is admitted that the subsidence is of tabular type in the platform zone (Săndulescu, 1985), exhibiting approximately equal rate values throughout the zone.

In the depression areas of the pre-Neogene relief, prior to coarbogenessis, pelitic sequences have been generally deposited. Lithostatic pressure subsequently led to a more pronounced sinking of these deposits.

It follows that the general subsidence background of the platform along with the compaction rate gave rise to optimum sinking rates of the bottom of the coal generating swamps in some depression zones. The compaction rate depends mainly on the thickness of the pelites and implicitly on the areal development of the depression zone.

In addition to the paleogeographic and lithological factors several depression zones of the platform might be the result of the differential subsidence of some compartments delimited by faults.

3. 3. Bălcești Coal Complex

This coal complex, typically developed in the Bălcești zone, has been separated within the Cîndești Formation; it includes the coal beds XIV-XVIII, marked by a discontinuous areal development.

The thickness of the Bălcești complex may exceed 110 m in the maximum sinking zone of the foredeep (Fumureni borehole), gradually decreasing northwards and southwards. In the northern part of the foredeep the complex is surely developed in the Jiu-Gilort area. East of the Amaradia Valley, in the outcropping zone of Middle Romanian deposits, no coal beds have been identified.

As in the case of the Motru complex, in the platform area, the thickness of the Bălcești complex decreases, being often represented by a single coal intercalation of 0.05—0.15 m or may lack altogether.

The spatial position of the Bălcești complex suggests a southward migration of the coal generating facies in respect of the optimum development area of the Motru coal complex. We think that this migration was caused by the pronounced growth of the uplift rate of the source area, which gave rise to a large amount of coarse detrital material, determining the southward retreat of the shoreline.

Against the background of rapid warping of the circumbasinal zones there existed certain intrabasinal areas where the subsidence was propicious to the coal generating process. This is the case of the Bălcești and Vladimiru zones.

4. Conclusions

The analysis of the factors determining the spatial distribution of the coal deposits in Oltenia showed the existence of a close correlation between the thickness of the coal complexes and their structural position.

The greatest thickness of the Motru coal complex is found in the axial zone of the foredeep, the thickest coal beds being present on the flanks. Thus, on the inner flank the beds V—VII and X—XII show a remarkable development, while on the outer flank, beds V—VII are more developed, which points to a migration in time of the optimum accumulation zone of the phytomass.

A correlation between the maximal thicknesses of the coal bed V and the interval of 80—100 m of the Motru coal complex was noticed in the foredeep.

The zonal distribution of the thicknesses of the coal complex is due to the differential subsidence which controlled not only the amount but also the quality of the coal seams.

Finally, we consider that the results obtained in the study of the interdependence of the factors that participated in the Pliocene coal genesis constituite a basis for a more judicious guiding in the future prospection and exploitation works for coal in eastern Oltenia.

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OBSERVAȚII PRIVIND RELAȚIILE DINTRE DISTRIBUȚIA SPAȚIALĂ A COMPLEXELOR CĂRBUNOASE DIN SECTORUL OLT-JIU ȘI FACTORII STRUCTURAL-GENETICI

(Rezumat)

Succesiunea depozitelor dacian-romaniene din Oltenia, sectorul Olt-Jiu, cuprinde, după autorii lucrării, trei unități litostratigrafice :

— *formațiunea de Lazu*, de vîrstă getian-parscovian inferioară este predominant psamitică, devenind mai pelitică în partea superioară și conține complexul cărbunos de Valea Vișenilor alcătuit din stratele de cărbune AD și I—IV ;

— *formațiunea de Jiu-Motru*, principala formațiune productivă din Oltenia, este predominant pelitică și cuprinde complexul cărbunos de Motru constituit din stratele de cărbune V—XII ;

— *formațiunea de Cîndești*, de vîrstă romanian-medie — pleistocen inferioară, este inițial predominant detritic-grosieră, apoi în partea mediană pelitic-psamitică conține complexul cărbunos de Bălcești (stratele XIII—XVIII), iar partea superioară este predominant ruditică.

Din punct de vedere structural sectorul cercetat se încadrează în Avanfosa Carpatică și Platforma Moesică.

Complexul cărbunos de Valea Vișenilor este mai bine dezvoltat între Valea Jiului și Valea Gilortului, unde apar discontinuu, lenticular stratele de cărbune I—III, iar stratul IV prezintă grosimi variabile de 0,05—1,2 m. O altă zonă de apariție a acestui complex apare în estul sectorului, pe valea Aninoasa, unde au fost întîlnite stratele III și IV cu grosimi sub 0,5 m.

În ceea ce privește complexul cărbunos de Motru, acesta are o largă dezvoltare pe întreaga suprafață a sectorului Olt-Jiu. Analiza distribuției, pe orizontală și verticală, a complexului cărbunos de Motru a permis să se constate existența a două arii carbogeneratoare, diferite din punct de vedere structural-genetic, separate prin linia de flexură dintre cele două unități tectonice cărora le corespund.

Prima arie carbogeneratoare se suprapune Avanfosei Carpatice și reprezintă un bazin de tip depresiune premontană iar cea de a doua reprezintă un bazin de tip eroziv-tectonic de platformă.

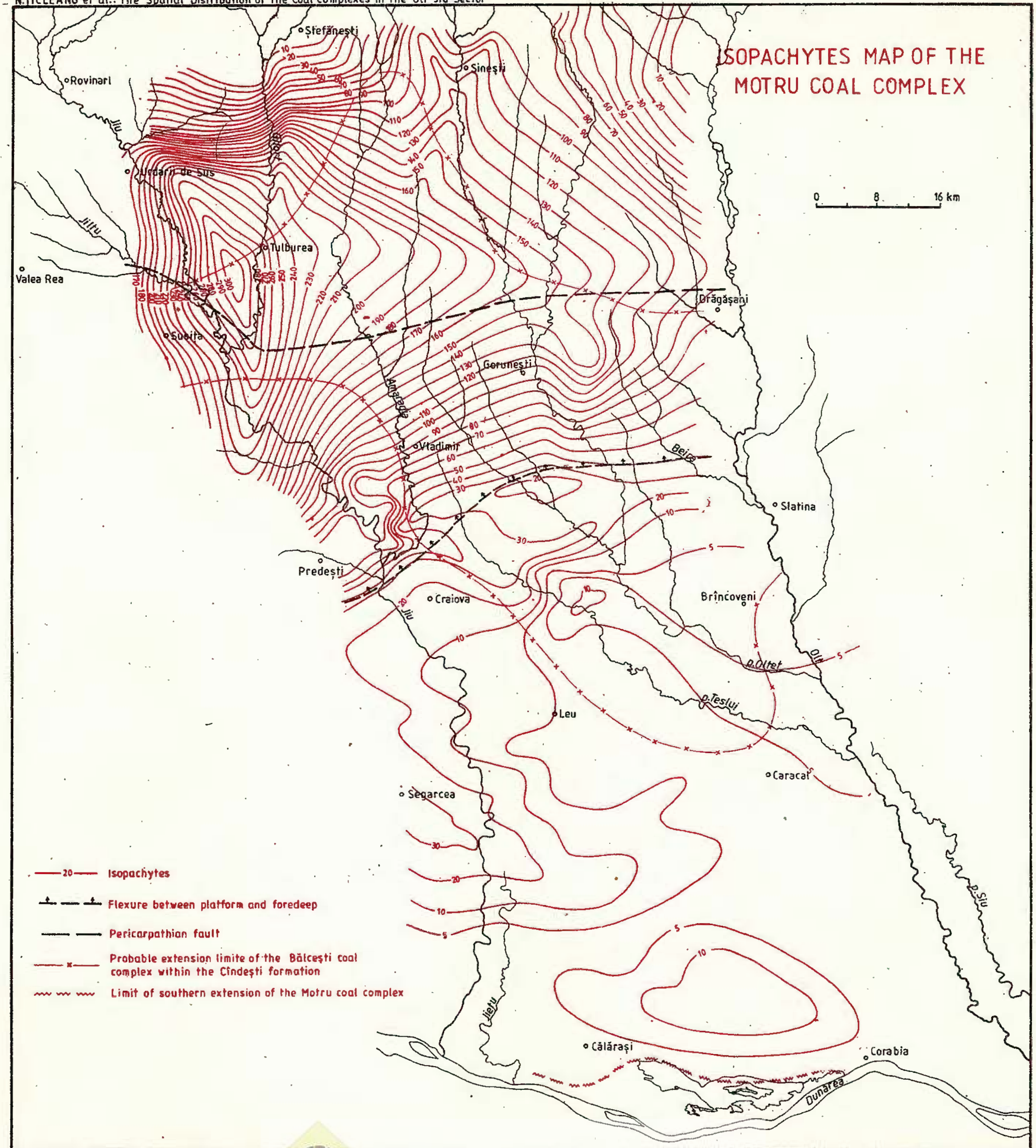
În aria carbogeneratoare a avanfosei s-a remarcat dispunerea grosimilor complexului cărbunos în funcție de poziția în cadrul acesteia, grosimile cele mai mari înregistrîndu-se în zona axială, unde are loc și digitarea stratelor. Grosimile optime ale complexului cărbunos se află pe flancurile avanfosei, intervalul de 80—100 m. grosime fiind optim pentru stratele de cărbuni cu grosimile mari, în special cele ale stratului V.

Factorul principal care determină distribuţia spaţială a grosimilor complexului cărbunos în aria avanfosei îl constituie subsidenţa diferenţială. Prin intermediul controlului pe care aceasta îl exercită asupra adîncimilor apei din mlaştina carbogeneratoare, ea determină tipul de asociaţie vegetală şi, implicit, calitatea cărbunilor.

În aria platformei grosimea complexului cărbunos se reduce, factorii care au determinat acumularea fitomasei sînt în primul rînd, paleogeografici şi litologici (tasare diferenţială) asociaţi însă şi cu o subsidenţă diferenţială, dar cu pondere scăzută.

Complexul cărbunos de Bălceşti are o dezvoltare tipică în zona axială a avanfosei, de unde trece şi pe platformă. Este redus ca grosime, cel mai frecvent fiind constituit doar dintr-un singur strat. În raport cu complexul cărbunos de Motru se constată migrarea spre sud a zonei de dezvoltare optimă a acestuia.

Stabilirea unor corelaţii între diferite aspecte calitative şi cantitative ale carbogenezei dacian-romaniene din Oltenia permite conturarea zonelor de perspectivă, ierarhizarea acestora în funcţie de importanţă şi orientarea lucrărilor de cercetare geologică.



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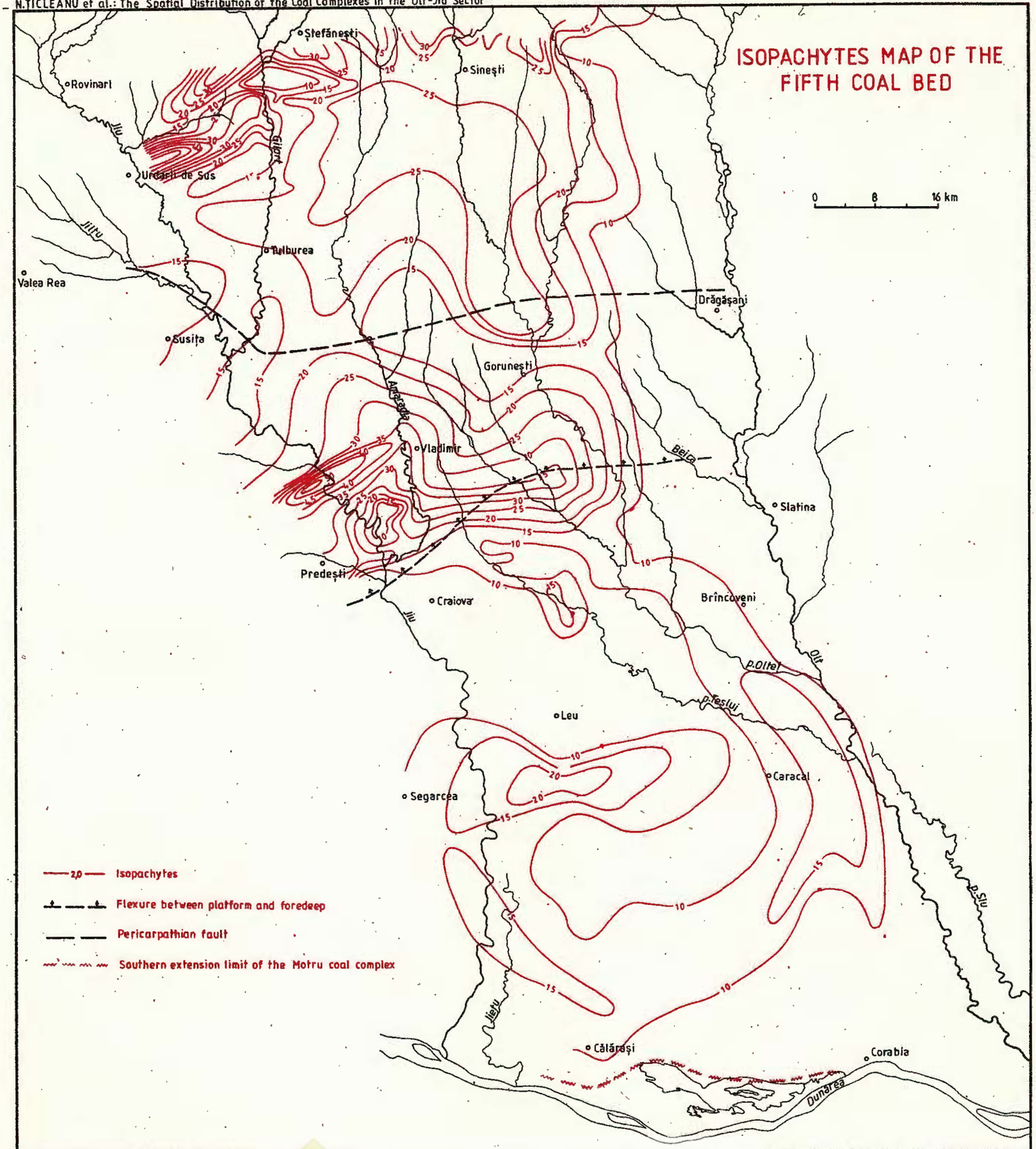

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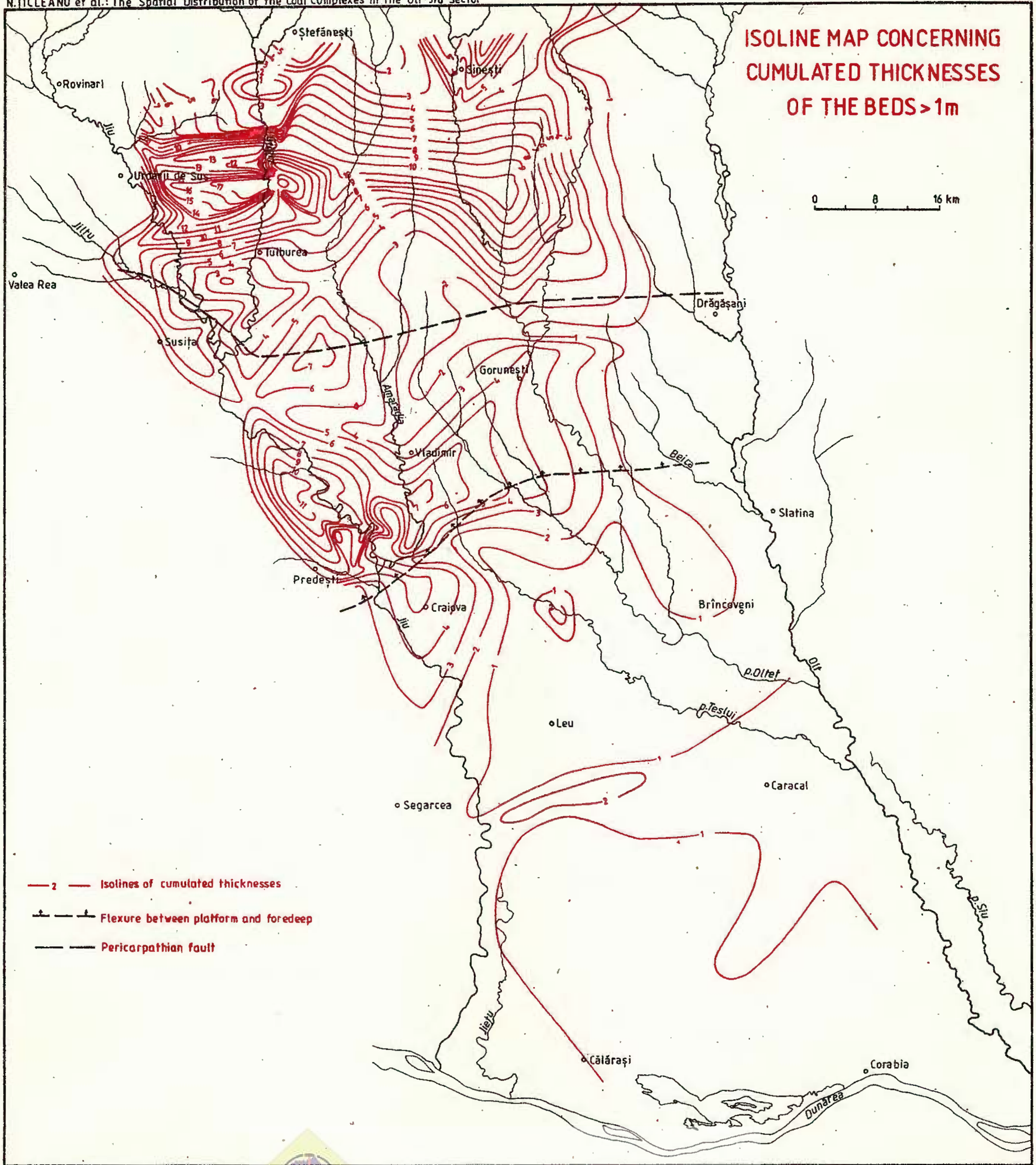

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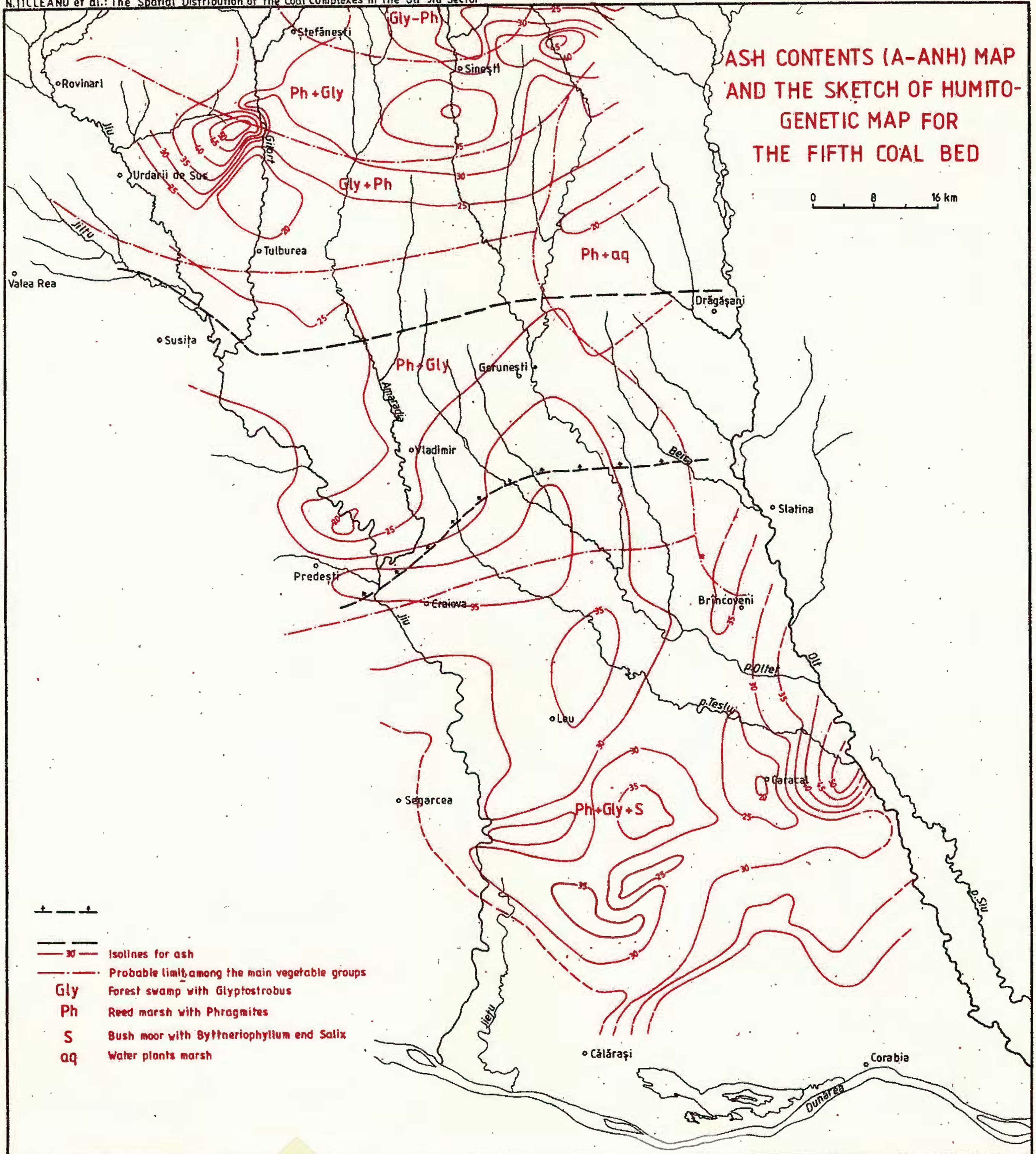
ASH CONTENTS (A-ANH) MAP AND THE SKETCH OF HUMITO-GENETIC MAP FOR THE FIFTH COAL BED
0 8 16 km
Gly-Ph
Ph+Gly
Gly+Ph
Ph+aq
Ph+Gly
Ph+Gly+S
Ştefăneşti
Sineşti
Rovinari
Urdarii de Sus
Tulburea
Valea Rea
Susiţa
Drăgăşani
Goruneşti
Vladimir
Slatina
Predeşti
Craiova
Brîncoveni
Leu
Caracal
Segarcea
Călăraşi
Corabia
Jiu
Jiltu
Gilort
Amaradia
Beica
Olt
P.Oltet
P.Tesluj
Jietu
P.Siu
Dunărea
Isolines for ash
Probable limit among the main vegetable groups
Gly Forest swamp with Glyptostrobus
Ph Reed marsh with Phragmites
S Bush moor with Byttneriophyllum and Salix
aq Water plants marsh

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2. ZĂCĂMINTE

CONSIDERATIONS ON THE DEVELOPMENT OF PLIOCENE COALY COMPLEXES IN THE JIU-MOTRU SECTOR (OLTENIA)[1]

BY

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Coal seams. Coal maps. Pliocene. Dacian. Romanian. Structural controls. Paleogeographic controls. Subsidence. Bălceşti Complex. South Carpathians — Southern Subcarpathian area — Subcarpathians between Jiu and Danube rivers. Getic Plateau — Strehaia Platform.

Abstract

The authors present the analytic result of the coaly complexes development inside the Dacian-Romanian deposits between the Jiu and Motru Valleys. The analysis was done by means of the contour maps drawn up on account of existing drilling data: average thickness of coaly complexes, average thickness of main beds and maximal thickness of component coal layers. It was also taken into consideration the structural aspect of the investigated area. Development of the Vişeni Valley coaly complex seems to have been conditioned first by paleogeographic factors and then by tectonic ones. The tectonics importance is pointed out by the maximal subsideuce area which overlies that of optimal subsidence. Within the Motru complex, it is noticed the zone of optimal subsidence constantly placed on the northern flank of the foredeep, while the maximal subsidence zone is situated in the axial zone of the foredeep. It was also remarked the existence of a direct relation between areas with high thicknesses of main coal beds and zones where coaly complexes have thicknesses between 80 and 140 m. Bălceşti coaly complex shows a reduction of coal-generating area as a result of the basin clogging.

Résumé

Considérations concernant le développement des complexes charbonneux pliocênes du secteur Jiu-Motru. Les auteurs présentent le résultat de l'analyse du mode de développement des complexes charbonneux des dépôts dacien-romaniens d'entre la vallée du Jiu et la vallée du Motru.

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On a utilisé les cartes de contour réalisées selon les données de forage existentes pour les éléments : épaisseur moyenne du complexe charbonneux, épaisseur moyenne des couches principales et l'épaisseur maximum des bancs qui entrent dans leur composition. L'aspect structural de la zone investiguée a constitué un élément principal pour l'interprétation.

Le développement du complexe charboneux de Valea Vișenilor paraît être influencé premièrement par des facteurs paléogéographiques suivis de ceux tectoniques. La tectonique est évidentiée par le chevauchement de l'aire de subsidence maximum sur celle de subsidence optimum.

Dans le complexe de Motru on constate la permanence de la zone de subsidence optimum sur le flanc septentrional de l'avant-fosse ; la zone de subsidence maximum est située dans la zone axiale de l'avant-fosse. On a constaté l'existence d'une relation directe entre les aires à épaisseurs grandes des couches principales de charbons et les zones où le complexe charbonneux présente des épaisseurs de 80 à 140 m.

Le complexe de Bălcești corresponde à la diminution de l'aire carbogénérateure conditionnée par le processus de colmatage du bassin.

1. Introduction

In Oltenia, Pliocene deposits, especially those on the internal flank of the foredeep, are characterized by the presence of numerous coal bed among which some are often more than 2 m thick, being interesting from economic point of view. Because most of these coal beds in the Jiu-Motru sector overlie the actual erosion base, they constitute the subject of some exploitations. This sector has been more and more known in comparison with other sectors of Oltenia, as a result of numerous geological investigations and mining works.

Starting with 1954 for the Jiu-Motru sector there have been elaborated numerous works, references with reserves estimations, geological reports and synthesis studies about different existing mining zones or referring to the whole sector : M. Chiriac (1954), V. Popovici (1956, 1959), Cârâc (1959), Liteanu, Feru (1964, 1967), Gh. Enache et al. (1968), Zberea et al. (1970), C. Enache (1974), Gologan (1974), Gologan et al. (1974), Teodorina Stănescu et al. (1974), Ghiuželi et al. (1975), Pană et al. (1981), Papaianopol et al. (1981, 1982), Pauliuc et al. (1981), Andreescu et al. (1985), and Țicleanu et al. (1985, 1986).

As a result of the investigations of Țicleanu et al. (1985, 1986), Andreescu et al. (1985) and Țicleanu (in print), there have been separated three coaly complexes [3] within the Dacian-Romanian deposits of Oltenia : Vișeni Valley complex, Motru complex and Bălcești complex. This paper proposes to analyse those three complexes development in the Jiu-Motru sector.

2. Stratigraphic background

According to Andreescu et al. (1985) and Țicleanu et al., (1985, 1986), the Dacian-Romanian deposits in Oltenia can be divided into three formations : Berbești formation, Jiu-Motru formation and Cîndești formation.

Berbeşti formation of Lower Dacian age is characterized by prevailing arenitic facies and includes six coal beds[4] (A,B and I—IV coal beds).

Initially, within the Vişeni Valley coaly complex, there were included only the I—IV coal beds. Subsequent analyses of the facies where occur coal beds in the Berbeşti formation and of their areal development determined us to include in the Vişeni Valley complex, the A and B coal beds as well; we should also consider that the IV coal bed has to be alloted to the Motru complex.

Jiu-Motru formation of Upper Dacian-Middle Romanian age is constituted of an alternance of pellito-psammitic deposits with ten coal beds (V—XIII coal beds).

In comparison with the initial content of the Motru complex (V——XII coal beds) and on account of recent data, it resulted the necessity to include also here the XIII coal beds, because beneath the IV coal bed begins the pellito-psammitic series which characterize the Jiu-Motru formation.

Cîndeşti formation of Middle Romanian-Lower Pleistocene age begins with prevailing psammo-psephitic facies which overlie the XIII coal bed; it contains in the middle part a pile of pellito-psammitic deposits with coal intercalations (XIV—XVIII coal beds) which represent the Bălceşti coaly complex.

3. Development of coaly complexes

For establishing the development way of coaly complexes, there have been drawn up contour maps of their average thickness and of main coal beds for maximal thickness of coal layers and average thickness of coal beds.

The contour maps have been drawn up dividing the area into geometrical figures, rectangles for choice, having maximal area of 12 km^2 and thinking at a more uniform distribution of observation points.

On account of existing data, for each geometrical figure, there have been determined average values, these values resulting from the arithmetical mean, relating them to the total number of information points (drillings) on a certain area. These values have been inscribed in geometrical centres of the delimited figures. Afterwards, there have been drawn the isolines for each coal bed and for maximal thickness of coal layers and average thickness of coal beds.

In order to distinguish the relation between structural arrangement and coaly complexes development, on the contour maps has been drawn the line of the Pericarpathian fault according to Stefănescu et al. (1986) interpretation.

3.1. *Vişeni Valley coaly complex*

Placed at the western end of the Dacic Basin where it crops out (Husnicioara-Livezile zone), Vişeni Valley complex has thicknesses ranging between 50 and 100 m (fig. 1) and includes only the I—IV coal beds.

The bed A was noticed only in a few drillings placed at western part and has thicknesses of 0.6 – 1.5 m.

Within the Jiu-Motru sector, Vișeni Valley complex develops on SW-NE direction and has maximal thickness (100 m) in axial zone of the foredeep between Florești and Horăști. In comparison with the axial zone, it is noticed that the complex has a smaller thickness both to NE and to

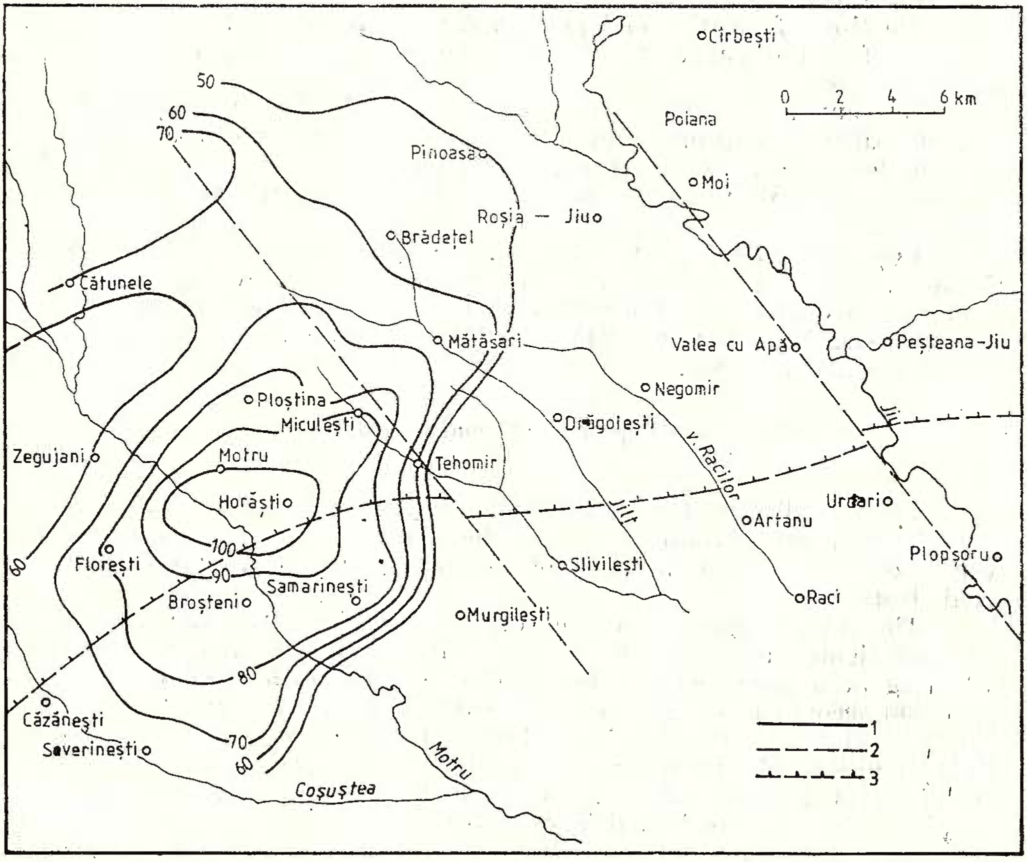

Fig. 1 — Contour map for average thicknesses of Vișeni Valley coaly complex; 1, isolines of average thickness; 2, fault; 3, Pericarpathian fault.

SW. South-eastwards, the thickness becomes smaller and smaller, so that starting with the Murgilești-Roșia de Jiu alignment, the complex contains only one coal bed (I bed) which has general thickness less than one meter.

Among those four coal beds (I – IV) which constitute the Vișeni Valley complex in the Jiu-Motru sector, the bed I is the most constant and is the thickest one, maximal value of average thickness (3.65 m) being noticed NE of Ploștina. Contour map for average thickness of the I coal bed (fig. 2) shows that the area inside the 3 m isoline is extended on SW-NE direction. Although the average thickness has small values (0.07 —0.6 m), the axis of the highest values zone is also SW-NE oriented.

In the investigated region, the III coal bed reveals an unequal development. Three areas having average thickness more than 1 m could be

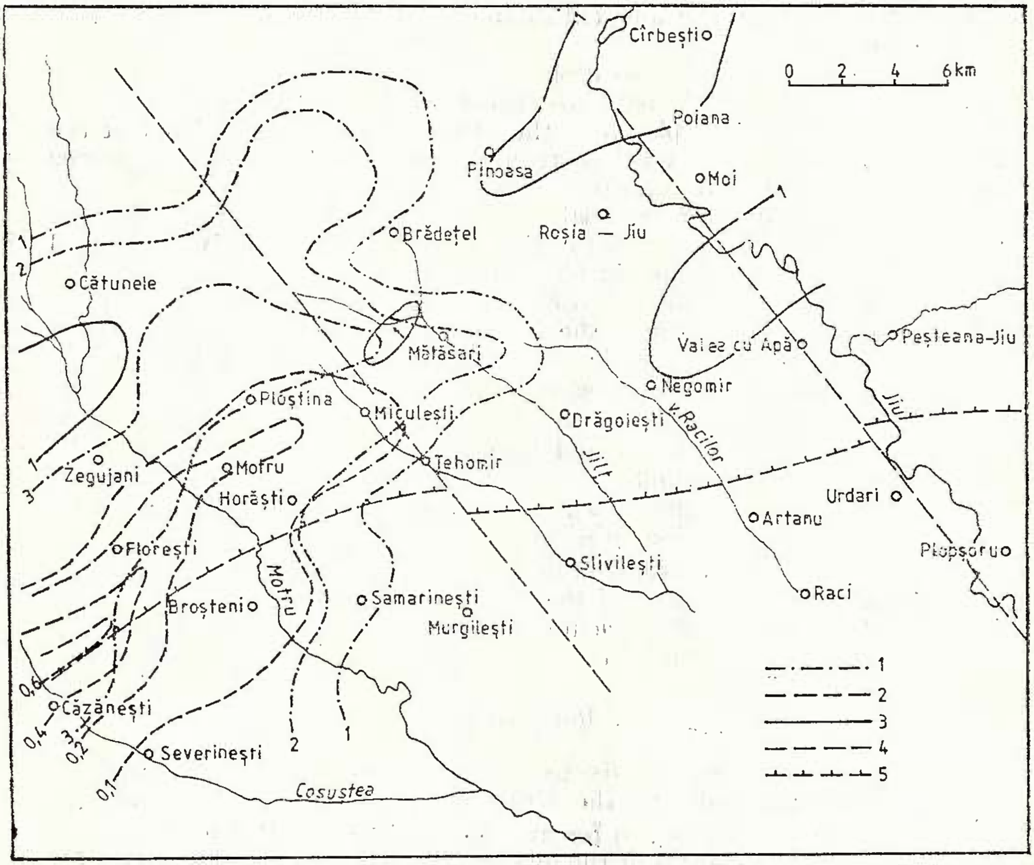

Fig. 2. — Contour map for average thicknesses of the I, II, III coal beds : 1, isolines of the I coal bed ; 2, isolines of the II coal bed ; 3, isolines of the III coal bed ; 4, fault ;5, Pericarpathian fault.

distinguished : the first area is located between Cătunele and Ploştina ; the second one and the most important in length and average thickness (up to 2.3 m) has the axis SW-NE oriented on the Miculeşti-Cîrbeşti alignment. The third area has the same direction and starts at Negomir continuing towards NE.

The three areas with maximal average thickness are placed inside a background of 0.25 to 0.8 m thickness, the most frequent one is 0.4 m. This statement and the fact that the axis of the second area with average thickness more than 1 m concides with the axis of the area showing thicknesses of more than 3 m in the I coal bed, led us suppose that in the Miculeşti-Cîrbeşti area, the I bed has been miscorrelated with the III coal bed.

The hypothesis on the miscorrelation of the I and III coal beds also agrees with the large development of the I coal bed in the whole western part of Oltenia.

Regarding the areas position with maximal values for average thickness of the I and II coal beds related to the Pericarpathian fault, it is noticed that they are placed in the north on the internal flank of the foredeep, where for this level there were the most favorable subsidence speeds during the coal genesis.

Sudden thinning of the coaly complex, SE of the Murgileşti-Roşia de Jiu alignment, beyond which, in our opinion, occurs only the I coal bed, the III bed having an insular development, seems to be related to the paleogeography of the territory, on which, coal-generating swamps developed, namely up to here the freshening has been felt owing to the western fluviatile waters. While the I coal bed deposition, fresh water occupied the largest area during the Lower Dacian.

Concerning the relation between maximal thickness of Vişeni Valley complex and average of the I and II coal beds, a superposition of these values could be inferred, indicating a coincidence of the zone of maximal subsidence of the coal-generating basin during the Lower Dacian with that of the most favorable subsidence.

Distribution of the average thickness of the IV coal bed (fig. 4) shows that the direction of the axis of the highest values area changed, the area inside the 2 m isoline being oriented about W-E has the axis on the Lupoaia-Brădăţel-Roşia alignment.

3.2. *Motru complex*

This complex corresponds to the widest development interval of coal-generating areas during the Upper Dacian and Middle Romanian.

The contour map (fig. 3) for average thickness of Motru coaly complex shows that the isolines of the average thickness are generally SW-NE oriented towards the Brădăţel-Dragoteşti-Raci alignment; then they are W-E oriented similarly to the Pericarpathian fault alignment and with that of the sedimentation basin. Modifications of the isolines trend seem to be caused by paleogeographic factor, reflecting predepositional morphologic configuration of coal-generating basin. The contour map shows important changes of the alignments Brădăţel-Dragoteşti-Raci and Tehomir-Horăşti. As concerns the first alignment, it is possible the tectonic factor should take part in these changes as well.

In relation with the position of the Pericarpathian fault, it is remarked a higher thickness of coaly complex towards SE, showing a migration in this direction of maximal subsidence zone in comparison with the Vişeni Valley complex.

In comparison with the development of the beds in the lower coaly complex, besides the changes of the direction of the area axis with the highest thickness, there is also an obvious width of the areas with average thickness of more than 1 m, representing a prelude of maximal extension of coal-generating basin at the level of the V coal bed.

The V coal bed knows a wide development in Oltenia and represent one of the most important coal beds from thickness and quality point of view. The area inside the 3 m isoline with maximal thickness of coal (given

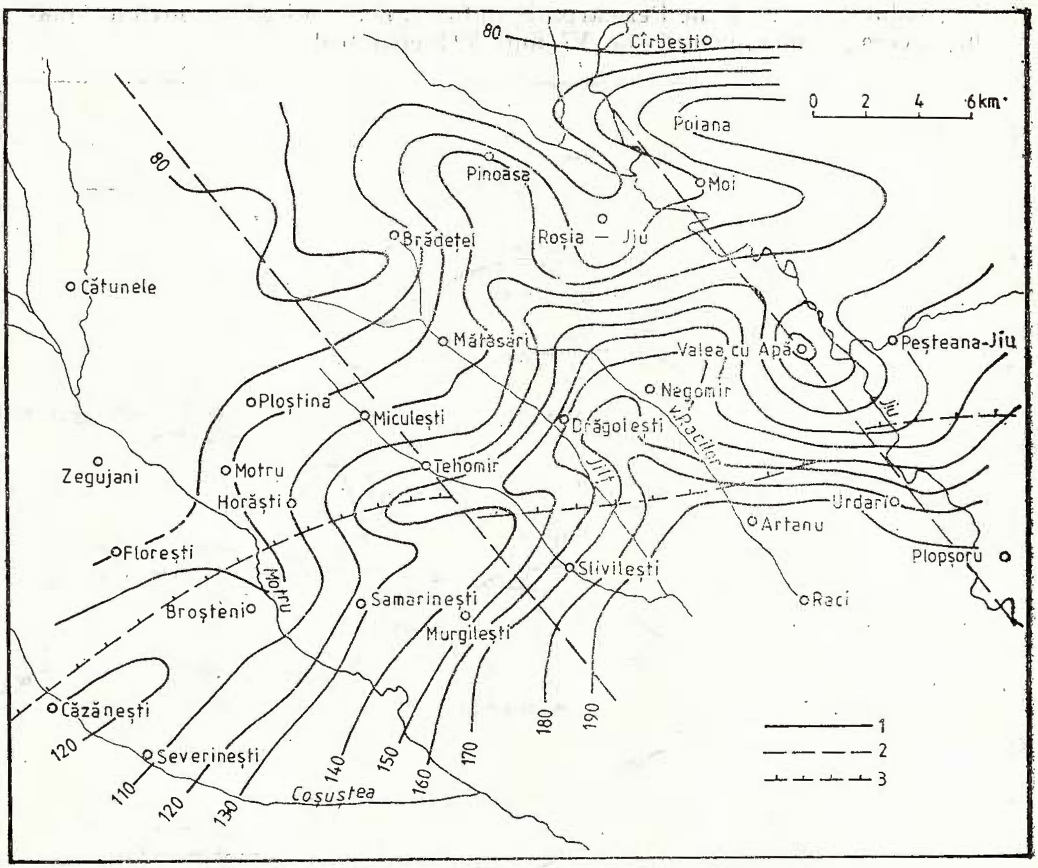

Fig. 3 — Contour map for maximal thickness of the IV coal bed : 1, isolines of maximal thickness; 2, fault; 3, Pericarpathian fault.

(fig. 5) covers almost the whole region of the investigated sector; it is WE oriented and is obviously developed towards E and SE.

Inside the 5 m isoline area, there are sometimes insular zones of more than 7 m and also other zones with less than 2.2 m thickness. This fact could be explained by involving the paleogeographic but also tectonic factors, related to the local uplifting and sinking synsedimentary zones.

The following two coal beds (VI and VII) have also a wide extension; the axis of their average thickness area with the highest values is placed north of the Pericarpathian fault suggesting the extension towards SE too in the Raci-Plopşoru zone. This accounts for the presence of the

VII and VI coal beds together with the V bed on the external flank of the foredeep in the Mihăiţa-Predeşti-Işalniţa zone and in the depressionary zone Băileşti-Terpeziţa-Capu Dealului, whose southern half overlies the Moesian Platform (Ţicleanu et al. 1986). In comparison with the V coal bed values, south of the Pericarpathian fault, it is noticed an obvious smaller average thickness of the VI and VII coal beds.

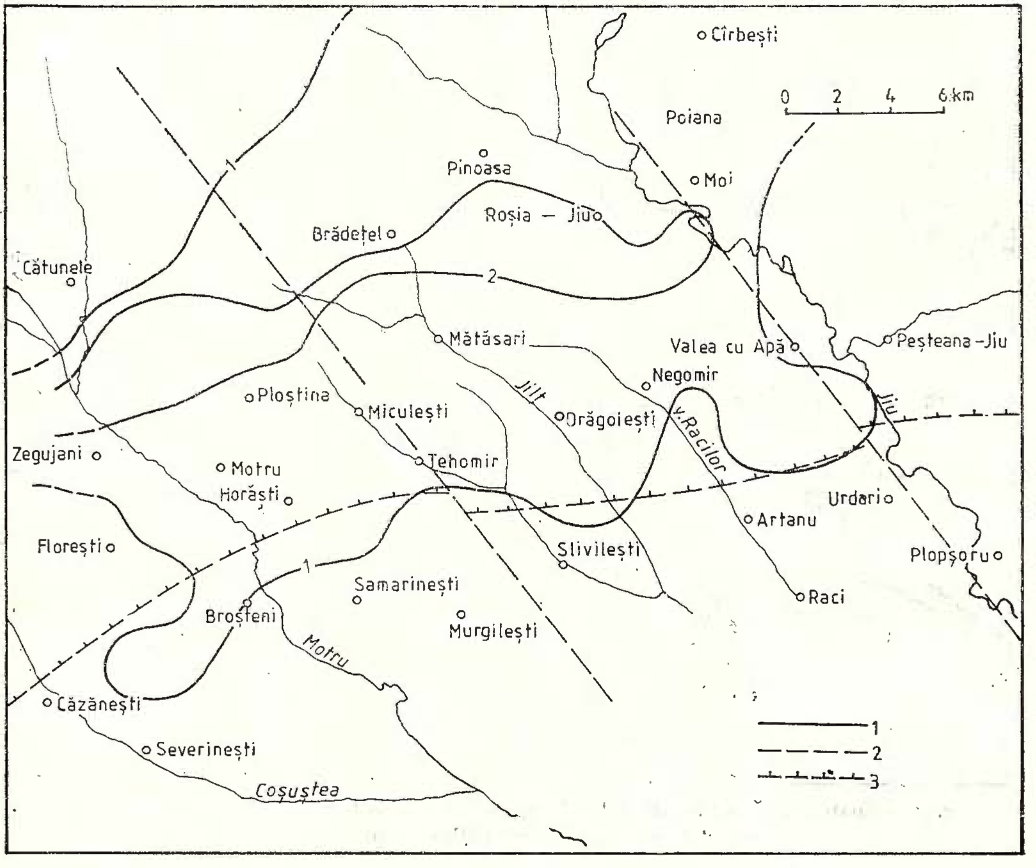

Fig. 4 — Contour map for average thicknesses of Motru coaly complex; 1, isolines of average thickness; 2, fault; 3, Pericarpathian fault.

The fact that during the V–VII coal beds accumulation, the coal-generating basin had a similar evolution, results from the existence of some zones where those three coal beds either joint (Tismana zone) or group, especially the VI and VII coal beds, as in the Pinoasa zone.

The VIII and IX coal beds have zones of maximal thickness on northern flank of the foredeep, but they are mining in a less degree in comparison with the V–VII coal beds. As a matter of fact, upper layer of the IX coal bed reaches the external flank of the foredeep having but very small thicknesses.

Another important coal-generating phase is placed at the level of the X coal bed (fig. 6) which has a large extension and high values of maximal thickness of coal layers, reaching up to 8.80 m in the Miculești-Mătăsari zone. The area inside the 4 m isoline is W-E oriented and is placed north of the Pericarpathian fault. The 2 m isoline is situated immediately

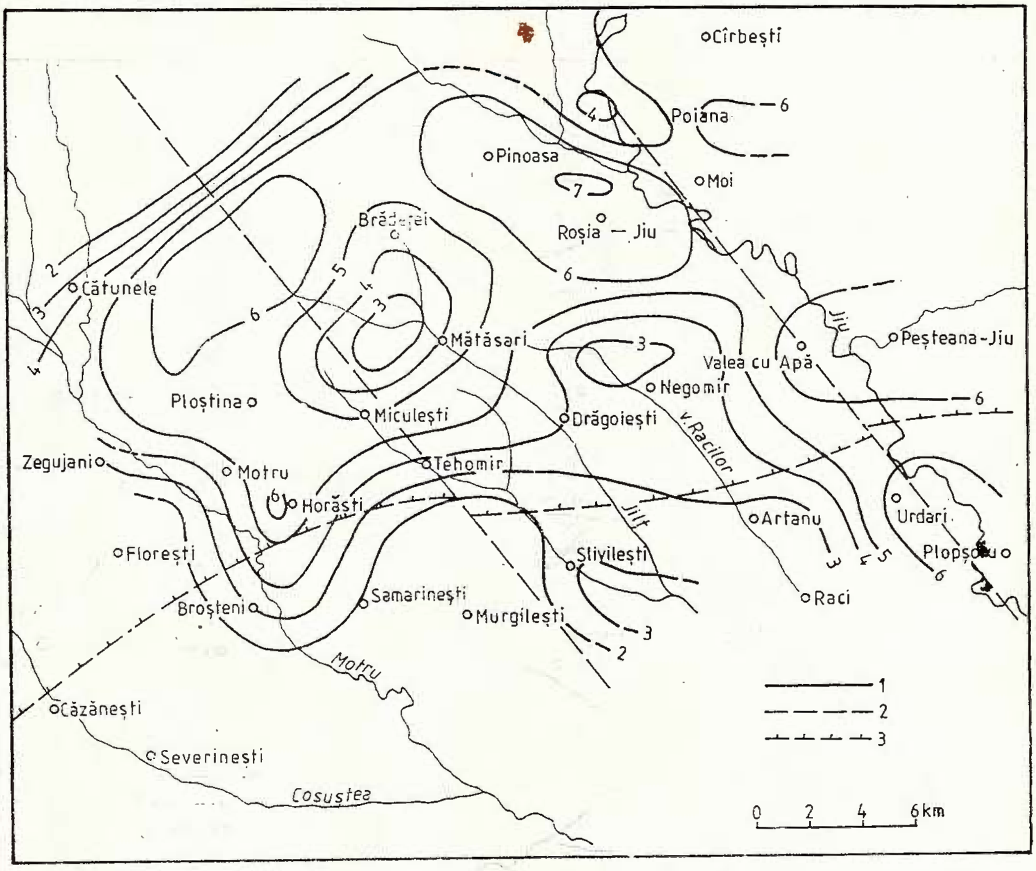

Fig. 5 — Contour map for maximal thickness of the V coal bed: 1, isolines of maximal thickness; 2, fault; 3, Pericarpathian fault.

south of the Pericarpathian fault on the Murgilești-Artanu-Plopșoru alignment.

Starting with the XI coal bed, an obvious reduction of the development areas of coal beds and of their thickness do occur. The XI coal bed shows three small areas where maximal thickness coal of layers is more than 2 m; Lupoaia-Ploștina, Horăști-Tehomir and Urdari-Plopșoru, then the values range between 0.1 m and 1.65 m.

The XII coal bed (fig. 7) exhibits more than 2 m maximal thickness of coal layers, only on the internal flank of the foredeep and the area inside the 3 m isoline has the axis on the alignment Ploştina-Mătăsari-Roşia de Jiu which is oriented SW–NE.

The last coal bed in the Motru coaly complex is the XIII bed and it is not so thick, seldom showing more than 1 m and being ununiformly developed.

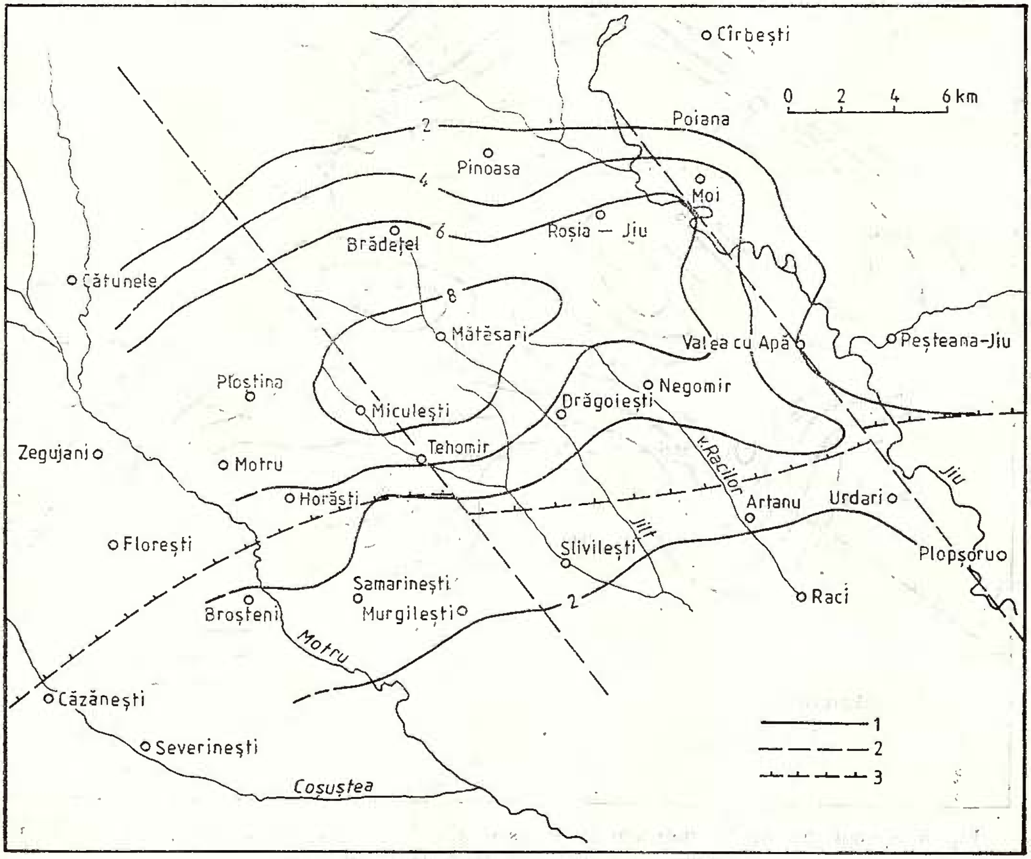

Fig. 6 — Contour map for maximal thickness of the X coal bed : 1, isolines of maximal thickness ; 2, fault ; 3, Pericarpathian fault.

Out of the aforesaid data, it results that during the formation of the Motru coaly complex, in the Upper Dacian-Middle Romanian time span, there were two more important coal-generating phases : the first one corresponds to the V–VII coal beds and the second one is placed at the level of the X coal bed. Although the temperature progressively lowered during the Dacian-Romanian, it is obvious that the main factor which determined small thickness of the VIII, IX, XI–XIII coal beds, was not caused by the climate. Decisive factors which led to the diminishing thickness of the VIII, IX, XI and XIII coal beds have been both tectonic and paleogeographic. During these beds formation took place the modification of subsidence regime proved by the reduction of optimal subsidence areas and of coal-generating swamps implicitly.

In the Jiu-Olt sector, N. Ţicleanu (in Ţicleanu et al. 1985) pointed out the existence of a connection between the thickness of Motru coaly complex and that of coal beds. This relation becomes obvious now in the

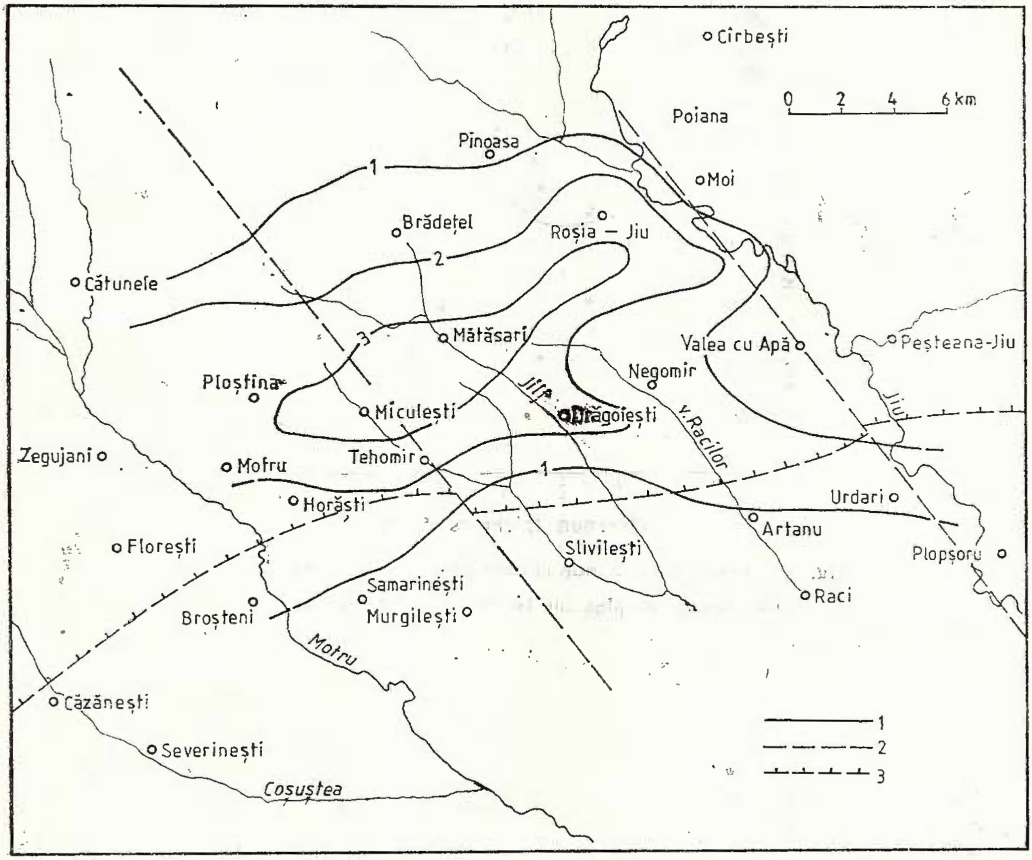

Fig. 7 — Contour map for maximal thickness of the XII coal bed; 1, isolines of maximal thickness; 2, fault; 3, Pericarpathian fault.

Jiu-Motru sector as well. Thus, the 3—7 m thicknesses of the V and X coal beds correspond to a thickness of the coaly complex ranging from 80 to 140 m and especially from 80 to 100 m. This fact is well illustrated by the dispersion diagram of the relation between the complex thicknesses and those of the V coal bed (fig. 8), and by the histograms of the same relation concerning the V and X coal beds (fig. 9). This relation is caused by optimal subsidence for the accumulations of coal-generating phytomass in the zones of coaly complex which are between 80 and 140 m thick, demonstrating once again the importance of tectonic factor.

Regarding the relation between the position of optimal subsidence zones and that of maximal subsidence (of maximal thickness zones in the coaly complex), it can be noticed that they do not overlie each other as in the case of the Vișeni Valley complex. Areas of optimal subsidence (fig. 10) are constantly placed north of the Pericarpathian fault, while the zone of maximal subsidence occurs in the south. Excepting the V —

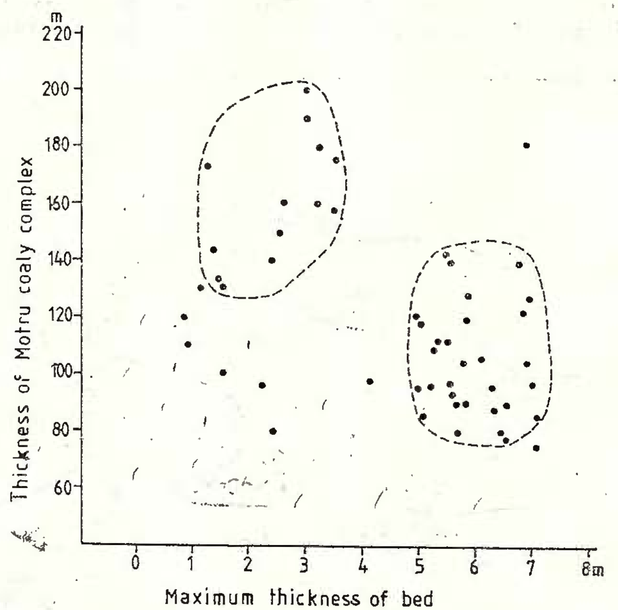

Fig. 8 — Dispersion diagram of the relation between the thickness of Motru coaly complex and the thickness of the V coal bed.

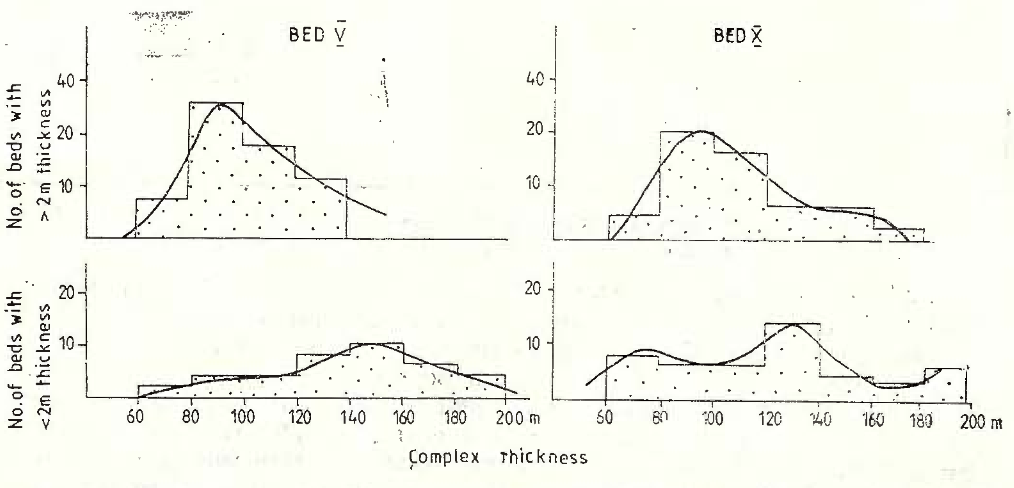

Fig. 9 — Histogram showing the relation between the thicknesses of the V and X coal bed and thickness of Motru coaly complex.

—VII coal beds, which include the most part of optimal subsidence areas north of the foredeep axial zone, some of them are placed on the external flank too, which shows they are very widely developed. In the zone of maximal subsidence, the coal beds contain several coal layers and their thicknesses become lower and lower.

3.3. *Bălcești coaly complex*

In the hill zone between Jiu and Motru, there were found the XIV—XVIII coal beds which belong to the Bălcești coaly complex (Țicleanu et al. 1985) being 10—40 m thick in the Horăști-Mătăsari-Samarinești zone and 20—80 m thick in the Dragotești-Valea cu Apă — Artanu zone.

For the presentation of the relations between the Motru complex and the Bălcești complex, there was drawn the contour map of average

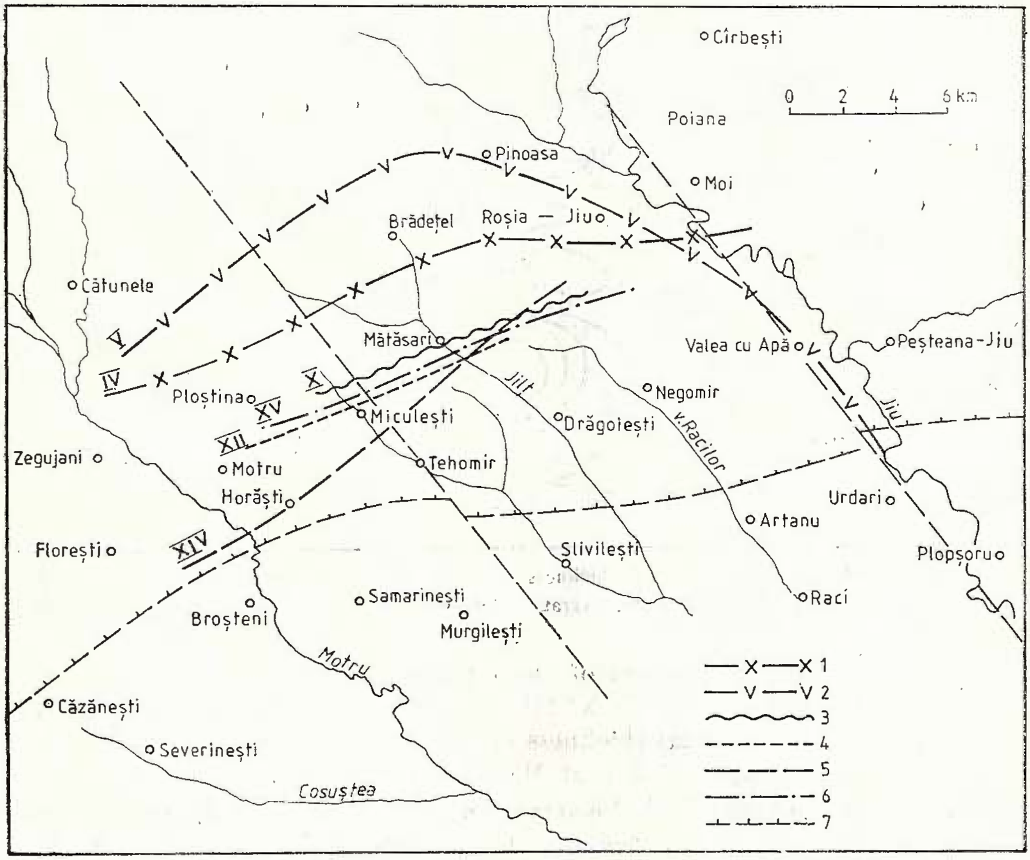

Fig. 10 — Distribution map of the axes of maximal thickness areas of the IV, V, X, XII' XIV and XV coal beds ; the axes of maximal thickness areas of the coal beds : 1, IV coal bed ; 2, V coal bed ; 3, X coal bed ; 4, XII coal bed ; 5, XIV coal bed ; 6, XV coal bed ; 7, Pericarpathian fault.

thicknesses between the XIII and XIV coal beds (fig. 11). Analysing the map, it is noticed that westwards and north-westwards, the thickness between Motru and Bălceşti coaly complexes reduces from 80 m in the Raci-Plopşoru zone to 20 m in the Motru-Pinoasa zone, showing the transgressive tendency of the Cîndeşti formation.

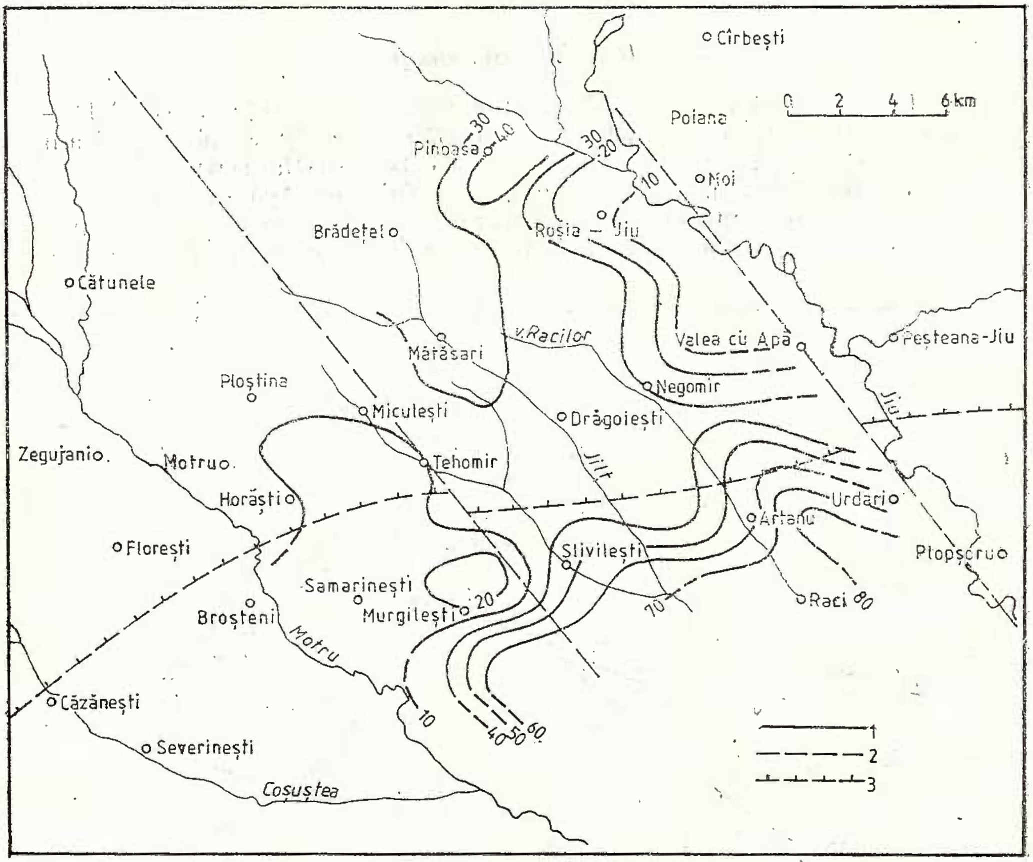

Fig. 11 — Contour map of averages thicknesses for the interval between the XIII and XIV coal beds ; 1, isolines for average thickness ; 2, fault ; 3, Pericarpathian fault.

The most important bed of the Bălceşti coaly complex are the XIV beds, the other three (XVI–XVIII) being only locally well developed. Contour map for maximal thickness of the XIV coal bed (fig. 12) indicates its thickening up to 4.0 m at Mătăsari and up to 3.0 m at Horăşti while the area of maximal thicknesses of more than 2 m appears to be more restricted, suggesting the diminution of the coal-generating environment to the end of the Romanian stage.

Similar state of affairs is shown by the XV coal bed, whose maximal thicknesses reach less than 4 m. Contour area for maximal thicknesses of coal layers with more than 2 m extends on ENE-SSW direction, between Negomir, Tehomir and Horăşti with a jonction to Miculeşti-Mătăsari.

The XVI – XVIII coal beds rarely occur, because either of the non-deposition, or of subsequent erosion and are seldom more than 1.5 m thick, most of the cases having less than 1 m.

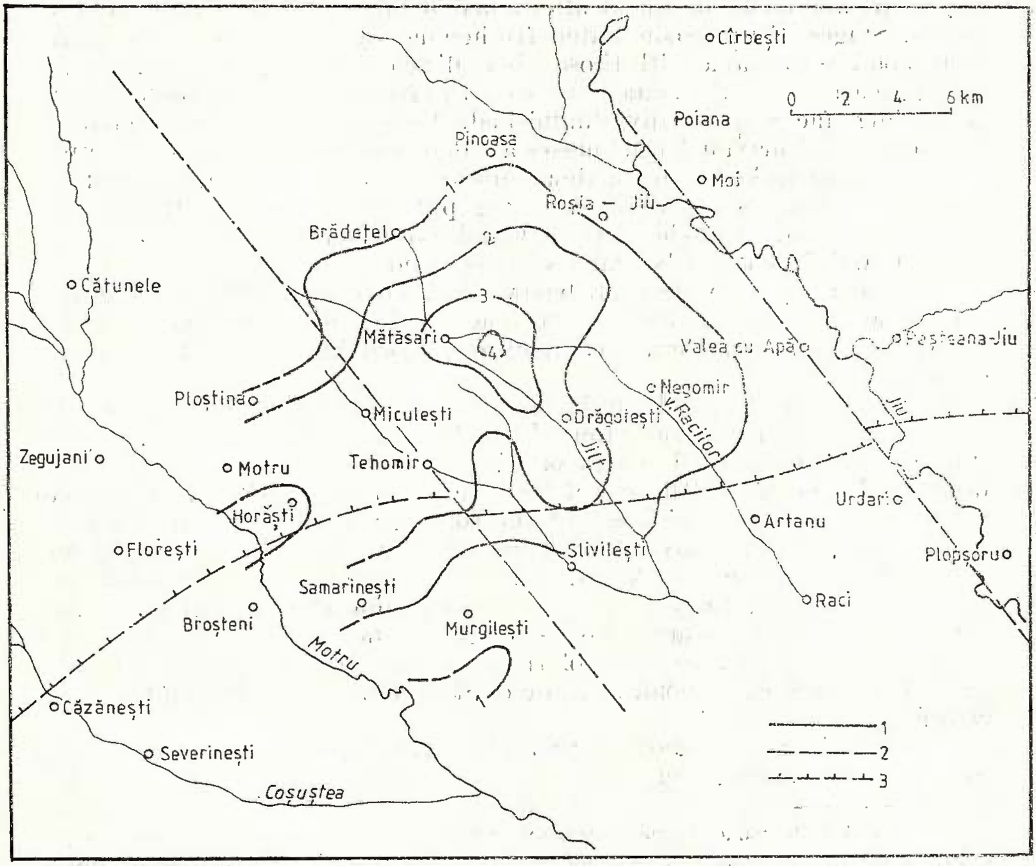

Fig. 12 — Contour map for maximal thickness of the XIV coal bed; 1, isolines for maximal thickness; 2, fault; 3, Pericarpathian fault.

If in the investigated area, maximal thicknesses areas of the Bălceşti coaly complex are placed north of the Pericarpathian fault, eastwards in the Bălceşti zone they are situated in the foredeep axis because of the clogging trend of the coal basin.

4. Conclusions

From the above mentioned data results the leading part played by both tectonic and paleogeographic factors, which acted in dissimilar ways in various regions during the Dacian-Romanian time interval.

The development of the Vișeni Valley complex seems to be first conditioned by paleogeographic factors (the presence of rivers rich in fresh waters and of a favorable predepositional relief). Its area extends towards the western extremity of the Dacic Basin, where on a background of paralic facies occurs an alternance of brackish fresh water environments. Stages of the basin waters freshening, by the rivers in the neighbourhood are the same with those where developed coal-generating vegetable associations. At the same time with the fresh water moving off, coal-generating facies gradually diminished. Tectonic factor is reflected by the position of maximal thicknesses areas of coal beds and coaly complexes ; it was remarked that maximal subsidence areas overlied those of optimal subsidence while coal-generating phytomass accumulation.

Motru coaly complex has maximal extension at the level of the V–VII and X coal beds and its areas trend is W-E.

Excepting the basic part, below the V coal bed, which is of paralic type, bearing a last brackish reccurrence in the Jiu-Motru sector, the other parts of the main coaly complex developed into a lacustrine-deltaic environment.

The area of optimal subsidence constantly maintained north of the Pericarpathian fault in the internal foredeep, while that of maximal subsidence migrated towards south of this fault or coincided with the foredeep axial zone. The influence of tectonic factor was noticed in the increase of coaly complex thickness of the foredeep axial zone concomitantly with the increase of coaly intercalations as a result of coal beds digitation and reduction of their thickness. North of the Pericarpathian fault, optimal subsidence led to coal beds thickening while the number of component coal layers is reduced. Consequently, in northern area of the foredeep the most favorable zones of the coal beds formation, having consistent thicknesses, correspond to those of 80 to 140 m thickness in the coaly complex.

Bălcești complex shows a reduction of coal-generating area as a result of the basin clogging.

[3] We give the name of „coaly complex" a gitological meaning, corresponding to a pile of coal beds which developed on a certain areal and having distinct structural-genetic characteristics.

[4] We use the notion of „coal bed" according to the Romanian geological literature which accepted the meaning of simple bed or composite bed which includes several layers separated by dirty intercalations.

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CONSIDERAȚII PRIVIND DEZVOLTAREA COMPLEXELOR CĂRBUNOASE PLIOCENE DIN SECTORUL JIU-MOTRU

(Rezumat)

Lucrarea prezintă rezultatul analizei modului de dezvoltare al complexelor cărbunoase cuprinse în depozitele dacian-romaniene dintre Valea Jiului și Valea Motrului. Analiza a fost efectuată pe hărțile de contur, întocmite pe baza datelor de foraj existente, pentru elementele: grosimea medie a complexelor cărbunoase, grosimea medie a principalelor strate de cărbune și grosimea maximă a bancurilor ce le compun. Dezvoltarea complexelor a fost raportată la poziția acestora în cadrul avanfosei, flancul intern sau cel extern, în funcție de falia pericarpatică.

În ceea ce privește complexul cărbunos de Valea Vișenilor (stratele A-B și I—IV), dezvoltarea acestuia pare să fie condiționată în primul rînd de factori paleogeografici ce au determinat existența unui aport important de apă dulce. În condițiile unui relief predepozițional favorabil, creat desigur prin acțiunea factorului tectonic, a fost posibilă formarea unor mlaștini de apă dulce în care s-au instalat asociații vegetale carbogeneratoare. Rolul factorului tectonic este evidențiat și de suprapunerea

ariilor de subsidenţă maximă, situate în jumătatea sudvestică a perimetrului, cu cele de subsidenţă optimă pentru acumularea fitomasei carbogeneratoare.

Complexul de Motru (stratele V—XIII) se caracterizează prin extinderea maximă la nivelul stratelor V—VII şi X şi modificarea aspectului ariei de dezvoltare care are o orientare generală est-vest.

Aria de subsidenţă optimă pentru formarea cărbunilor s-a menţinut constant la nord de falia pericarpatcă, în avanfosa internă, în timp ce zona de subsidenţă maximă a coincis cu traseul faliei pericarpatice, zona axială a avanfosei, sau a migrat spre sud de această falie. Controlul factorului tectonic s-a materializat prin creşterea grosimii complexului cărbunos în zona axială a avanfosei, concomitent cu creşterea numărului de intercalaţii cărbunoase ca rezultat al digitării stratelor cu scăderea corespunzătoare a grosimii stratelor şi bancurilor de cărbune şi dezvoltarea în grosime a intercalaţiilor de steril.

Pe flancul intern al avanfosei s-au realizat condiţii de subsidenţă optimă ceea ce a determinat formarea unor strate cu grosimi mari (peste 2 m), în special stratele V—VII şi X, care sînt constituite dintr-un număr redus de bancuri de cărbune, comparativ cu zona axială, datorită comasării intercalaţiilor cărbunoase. Tot pe flancul intern al avanfosei se constată o relaţie evidentă între intervalul de grosimi de 80—140 m pentru complexul cărbunos de Motru şi grosimea mai mare a stratelor de cărbune.

Complexul de Bălceşti (stratele XIV—XVIII) corespunde unei reduceri a ariei carbogeneratoare condiţionată de procesul de colmatare al bazinului. Zonele cu subsidenţă optimă sînt reduse ca suprafaţă şi situate de asemenea la nord de falia pericarpatică.

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2. ZĂCĂMINTE

DRAWING UP TWO TYPES OF HUMITO-GENETIC MAPS FOR NEOGENE COAL DEPOSITS IN THE BOROD BASIN (EAST OF ORADEA) AND IN THE MIHĂIȚA-PREDEȘTI ZONE (OLTENIA) [1]

BY

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Coal deposits maps. Neogene. Humito-genetic maps. Physicochemical features. Isopachyte maps. Xylite. Petrology — coal. Apuseni Mts — Neogene depression — Borod. Getic Plateau — Strehaia Platform.

Abstract

The authors present two types of humito-genetic maps, the first one being used for the study of the II seam of coal in the Sarmatian deposits of the Borod basin and the second one regards the V seam of coal within the Upper Dacian deposits from Mihăița–Predeşti (Oltenia). Starting from the fact already known of the connection between coal-generating vegetable groups and petrographical types of coals, which they determine, the authors noticed that on the vertical of a coal seam in a point of observation within the genetic series, there are always two prevailing petrographical types which reflect vegetable groups called according to the percentage participation, main and secondary groups. The humito-genetic map resulted from joining the points of observation with the same percentage values. The second type of map considers the fact that coal-generating vegetable groups contributed to a great extent to determine the main coal physico-chemical features: thickness, xylite content etc. It resulted through a successive superposition of the contour maps for each element.

Résumé

Elaboration de deux types de cartes humito-génétiques concernant les dépôts néogènes à charbons du bassin de Borod (E Oradea) et la zone de Mihăița—Predeşti (Oltenia). On présente deux types nouveaux de cartes humito-génétiques, le premier appliqué à l'étude de la couche II

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de charbon des dépôts sarmatiens du bassin de Borod, le deuxième concernant la couche V de charbon, trouvée dans les dépôts dacien-supérieurs de Mihăiţa—Predeşti (Oltenia).

Ayant comme point de départ la correspondence, déjà connue, entre les groupes végétaux carbogénérateurs et les types pétrographiques des charbons déterminés par ceux-ci, les auteurs ont constaté que sur la verticale d'une couche de charbon, dans un point d'observation, dans le cadre de la série génétique, il y a toujours deux types pétrographiques prédominants, reflétant les associations végétales, principale et secondaire, en rapport avec la participation quantitative. De l'union des points d'observation aux même valeurs quantitatives a résulté la carte humito-génétique.

Le deuxième type de carte est fondé sur le fait que les associations végétales carbogénérateures ont contribué en grande mesure à la détermination des caractéristiques principales physico-chimiques des charbons : épaisseur, teneur en xylite, Aanh, V^1, Q^1_i. Par la superposition successive des cartes de contour, pour chaque élément susmentionné a résulté le deuxième type de carte humito-génétique.

1. Introduction

In agreement with the ever increasing demands for power resources, the geological investigations keep on with establishing the development criteria for coal formations, owing to which it would be possible to outline some new prospect zones.

Concerning the distribution criteria of the coal deposits, one of the numerous objects of investigation is represented by their genesis.

In Romania, the genesis of Neogene coals has been lately studied. In the beginning, the problem of coal genesis constituted only an incidental concern being related to the petrographic study of coal. So there are some genetic remarks in the papers about the Pliocene coal petrography from Rovinari (Oltenia) (Cornelia Biţoianu and Smărăndiţa Ilie, 1967) and about the Sarmatian ones from the Comăneşti basin (Smărăndiţa Ilie and Cornelia Biţoianu, 1970). Presently, the coal genesis of Neogene deposits has also been studied from other points of view: paleobotany, lithology, sedimentology and tectonics. Concerning this, we mention the papers written by Givulescu (1974), Petrescu and Ferencz (1979), Preda et al. (1981), Pauliuc and Barus (1982), Ţicleanu et al. (1982, 1985), Petrescu and Kolovos (1983), Micu et al. (1984), Andreescu (1986), Ţicleanu (1986, a,b), Ţicleanu (in print).

Besides the published papers, Cornelia Biţoianu and N. Ţicleanu supplied data about the genesis of coal fields in various coal basins including them in several geological reports, namely: Marinescu et al. (1981), Papaianopol et al. (1981, 1982), Micu et al. (1982), Andreescu et al. (1984), Ţicleanu et al. (1984, 1985, 1986).

After studying the Borod basin, N. Ţicleanu and Cornelia Biţoianu have drawn up the first humito-genetic map for the second coal seam of the Volhynian deposits. Then the same authors drew up the humito-genetic sketch map for the V coal seam of Oltenia Dacian deposits (Ţicleanu et al. 1985, 1986). At the same time, they drew another humito-genetic map for the Mihăița-Predești zone (Oltenia), which gives us a better image about coal-generating swamps and also makes possible to establish the qualitative and quantitative development of the coal seams.

2. Humito-genetic map of the II coal seam in the Borod Basin (east of Oradea)

The Sarmatian deposits in the Borod basin constituted the object of numerous geological investigations, their results being presented in various geological reports, have been synthesized by Papaianopol (in Papaianopol et al., 1984). Considering the present subject, the authors do not want to treat in detail the lithology of Sarmatian deposits ; it is to mention that they are constituted of a great variety of rocks : clays, sandy clays, clayey silts, marly clays, marls, marly limestones, limestones, organogenous limestones, white vacuolar limestones, tuffites, tuffs, tuffaceous marls, diatomites, sands, gravels and coal intercalations. There are various facies types too, from typical brackish facies to typical freshwater facies.

The age of the presented deposits has been very much debated; we mention only that Papaianopol (in Papaianopol et al., 1984) considered it to be Volhynian.

Concerning the coal content of the Volhynian deposits in the Borod basin, there are two coal seams : I and II one which are numbered according to the stratigraphical sequence. The II seam is the most extended and the thickest one. In the Cornițel area, this seam is constituted of 3 –4 coal layers, 0.2 –1.4 m thick and in the Beznea-Valea Neagră area, it has two layers, 0.8 –2.3 m thick. Because of its development, this seam was considered when drawing up the humitogenetic map.

In the Borod basin, the Sarmatian deposits have a rich paleofloristic content studied by : Givulescu (1951), Istocescu and Givulescu (1977), Țicleanu (in Marinescu et al., 1980 and Papaianopol et al., 1984) and Givulescu and Țicleanu (in print).

From paleovegetation point of view, in the Volhynian coal-generating swamps existed at least 5 vegetable groups, namely : *Sequoia* forest swamp; *Myrica* bush moor, which can be partly replaced by deciduous forest swamp *(Acer tricuspidatum* and/or *Liquidambar europaeum)*; *Glyptostrobus* forest swamp which is important for the coal genesis; *Phragmites* swamp and water plants group, where its depth was more than 2 m. All these vegetable groups included one or several phytocenoses, the spatial distribution of which was controlled by the water depth, forming at a certain time more or less complete ecological series.

The microscopic analyses of coal point out that the II seam is constituted of macerals which belong to huminite, liptinite and inertinite groups. Among these, only huminitic macerals prevail, namely humotelinite (ulminite) and humodetrinite (densinite). Besides these, mineral components have been determined : clay, pyrite and others. The investigated seam is also constituted of gelinite, sclerotinite and cutinite.

The petrographical composition indicates an advanced gelification of the second seam, this fact being also confirmed by the abundant glossy coal rich in ulminite, gelinite and densinite.

As it is known (Stach et al., 1982), every coal-generating vegetable group determined a certain petrographical type of coal. On account of the lithotype percentage analysis, we may reconstitute the succession in time of various vegetable groups (genetic series) for a coal seam in a certain point of observation (drilling, mining, outcrop) and by joining several points of observation in zones with the same evolution features, one gets the humito-genetic map.

Petrographical analyses in 16 points of observation on the second seam in the Borod basin, show that each of them has four distinct petrographical types, which correspond to the vegetable groups : *Glyptostrobus* swamp, *Phragmites* marsh, *Myrica* moor and the water plants zone. The absence of the petrographical type characteristic of *Sequoia* moor shows its erosion and its minor importance to coal genesis.

In each point of observation, the four petrographical types are represented by various percentage contents. However, we notice that always two of them represent 68 – 88 %. These two types indicate the coal-generating vegetable groups, which we call main and secondary group, according to the percentage content.

By joining the observation with the same type of binary association of vegetable groups, we drew up the humito-genetic map. For the drillings with no petrographical analyses, besides the data we had from closer drillings, we also considered the thickness of coal seams, knowing that high thickness was caused by the *Glyptostrobus* swamp. For delimiting the area of the *Myrica* moor, the authors take into account the percentages for the petrographical type which characterize this association reported from the drillings. For the *Sequoia* forest, the paleofloristic data collected from drillings and outcrops are taking into consideration that the ecological series started with this vegetable group.

It is interesting to remark that the largest areas of interest are covered by three types of binary combinations of vegetable groups where *Glyptostrobus* is always present. At the same time, *Phragmites* occurs in three types of binary groups (Pl. I).

In our opinion, the way how binary combinations are placed east of Borod basin, namely *Glyptostrobus-Phragmites* group to the basin margin and *Phragmites-Glyptostrobus* to the center, constitutes an important argument to support the idea that this map is the real image of the Volhynian in the Borod basin.

By plotting probable and possible contours of development areas for various coal-generating vegetable groups, we see that this coal field may extend as far as the SW of this basin and the north of Aleșd as well.

3. Humito-genetic map for the Mihăița-Predești zone (Oltenia)

Mihăița-Predești zone is situated on the external flank of the Carpathian foredeep at about 20 km NW of Craiova town. The lithological composition of the Dacian-Romanian deposits consists of an alternance of clays, argillaceous silts, sandy clays, coal clays, sands, argillaceous sands and seldom gravel intercalations at upper side. Within this coal pile are known several coal seams which Țicleanu et al. (1986) correlated with the V – VIII seams in the Motru-Rovinari zone. The main seam occurs at the base and is often constituted of two coal layers ; sometimes the seam is more than 5 m thick. The upper seams are thinner, generally less than 1 m and have no economic importance. In order to draw up the humito-genetic map, we chose the V seam because of its uniform development and we had enough data regarding the physico-chemical features of coal.

Concerning the main vegetable groups which contributed to the Dacian coals formation, there are enough paleofloristic data which indicate the existence of the following coal-generating vegetable groups : *Glyptostrobus* forest swamp, *Phragmites* marsh, *Braunia* forest swamp, *Salix* bush moor and water plants zone. These vegetable groups contained interpenetration zones, a convincing example being the frequent association between *Glyptostrobus* and *Braunia* species.

The existence of coal-generating vegetable groups was confirmed by the petrographical analyses of coal because each of the main vegetable associations which contributed to the coal genesis, has a certain maceral group which is identified in the coals. For instance, huminite and inertinite groups came from the same woody material but under special conditions. The initial material belongs to big-sized trees bearing strong roots, represented by remains of bark, trunks, branches, all rich in lignin, cellulose and tannin. Most of them come from trees of *G. europaeus* type, which through diagenetic and later biochemical decomposition, under anaerobic, hydrogen rich conditions, gave rise to huminitic macerals, especially textinite and ulminite. The same remains changed into fusinitic macerals under aerobic oxygen rich conditions.

Besides the mentioned vegetable remains, coals also resulted from pallustrine monocotyledons (*Phragmites*, *Typha*, *Arundo* etc.), which generated huminitic macerals : attrinite and densinite.

Spores, resins, fats, waxes originating in fungi and ferns (spores) and *Glyptostrobus* respectively (resins, fats) gave rise to liptinitic macerals by biochemical processes.

The main vegetable groups which contributed to coal formation, were not uniformly distributed within the sedimentation basin, mainly in accordance with the water depth. Because, within the sedimentation basin, the water level had frequent oscillations caused by a lot of factors, the various groups of an ecological series presented modifications in their horizontal display while vertically various coal-generating vegetable groups come to overlie each other, forming a genetic series. These genetic series are confirmed by petrographical analyses which point to variable content of macerals in the coal seams investigated.

In comparison with the Borod basin, where we had the possibility to collect samples in order to determine coal petrographical features, in the Mihăiţa-Predeşti zone, because of advanced mining works, this was but partly possible. Here, we have numerous data regarding the main physico-chemical features of the V coal seam. By processing these data, we drew up the second type of humito-genetic map.

Starting from the fact that maceral associations reflect the vegetable associations of origin, we supposed that it has to be a connection between coal chemical composition and physical features, on one side, and vegetable associations of origin, on the other side.

In order to verify this hypothesis, we chose a zone with enough data regarding petrographical, physico-chemical, thickness and paleobotanic features. We considered Mihăița-Predești the best zone because here mining works were finished.

Owing to our data, we drew up contour maps for the variation of the following elements : A^{anh}, V^{i}, Q_{i}^{i3}, seam's thickness and quantity of wood mass (xylite + ulminite). Cumulating all these contour maps, a new type of humito-genetic map resulted.

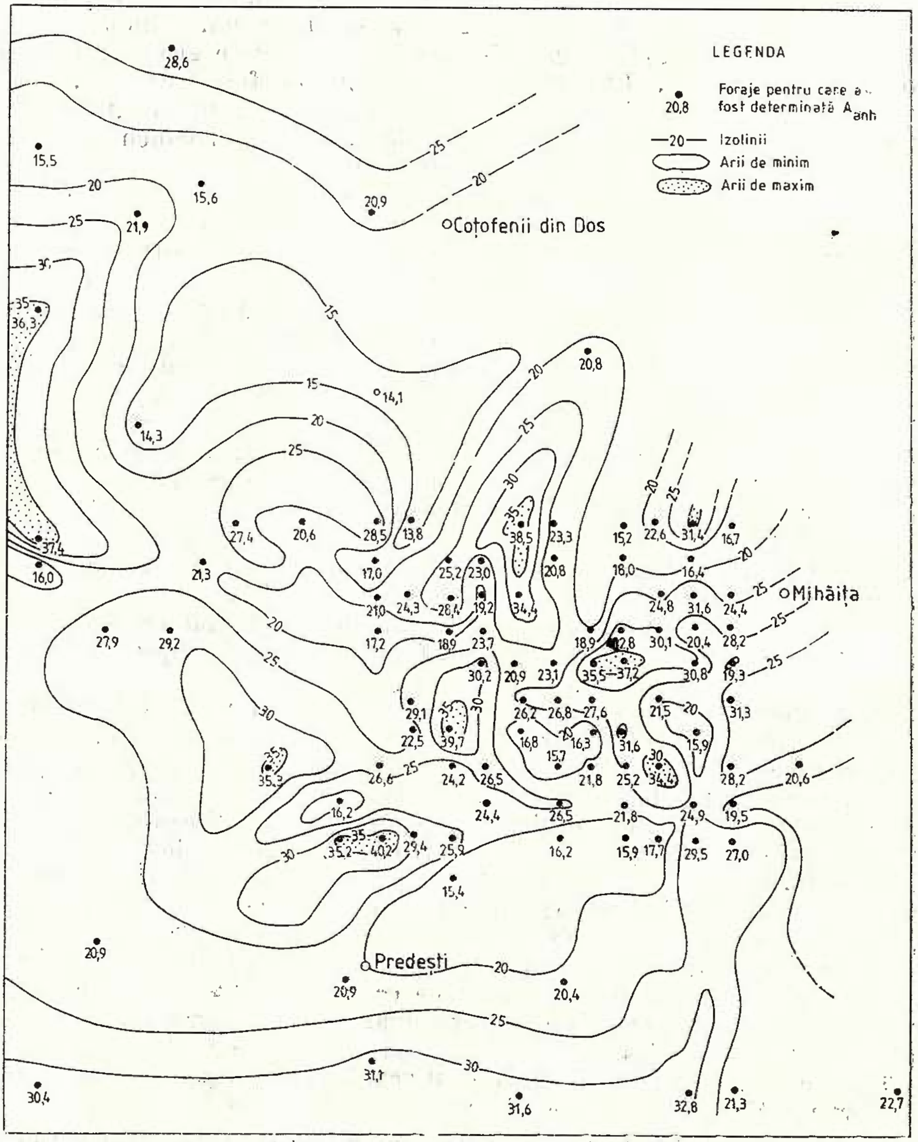

Fig. 1 — Contour map for A^{anh} of the fifth coal bed (lower coal pile) — Mihăița zone : 1, drilling for which A^{anh} (per cent) was determined ; 2, isolines ; 3, minimal areas ; 4, maximal areas.

Superposing the contour map for A^{anh} (Fig. 1) with that for V^{i} (volatile matter) (Fig. 2), it results that minimal ash zones are displayed on the zones with maximal volatile matter, in most cases. For instance, north of Predeşti, outlines a zone with $A^{anh} = 16.2\,\%$, which overlies a zone with $V^{i} = 30\,\%$, SW of Mihăiţa to 15.9 % ash and corresponds to 35 % volatile matter. We mention that ash varies from 13.8 to 39.7 % and volatile matter from 20.9 to 38.6 %. This situation is explained by the

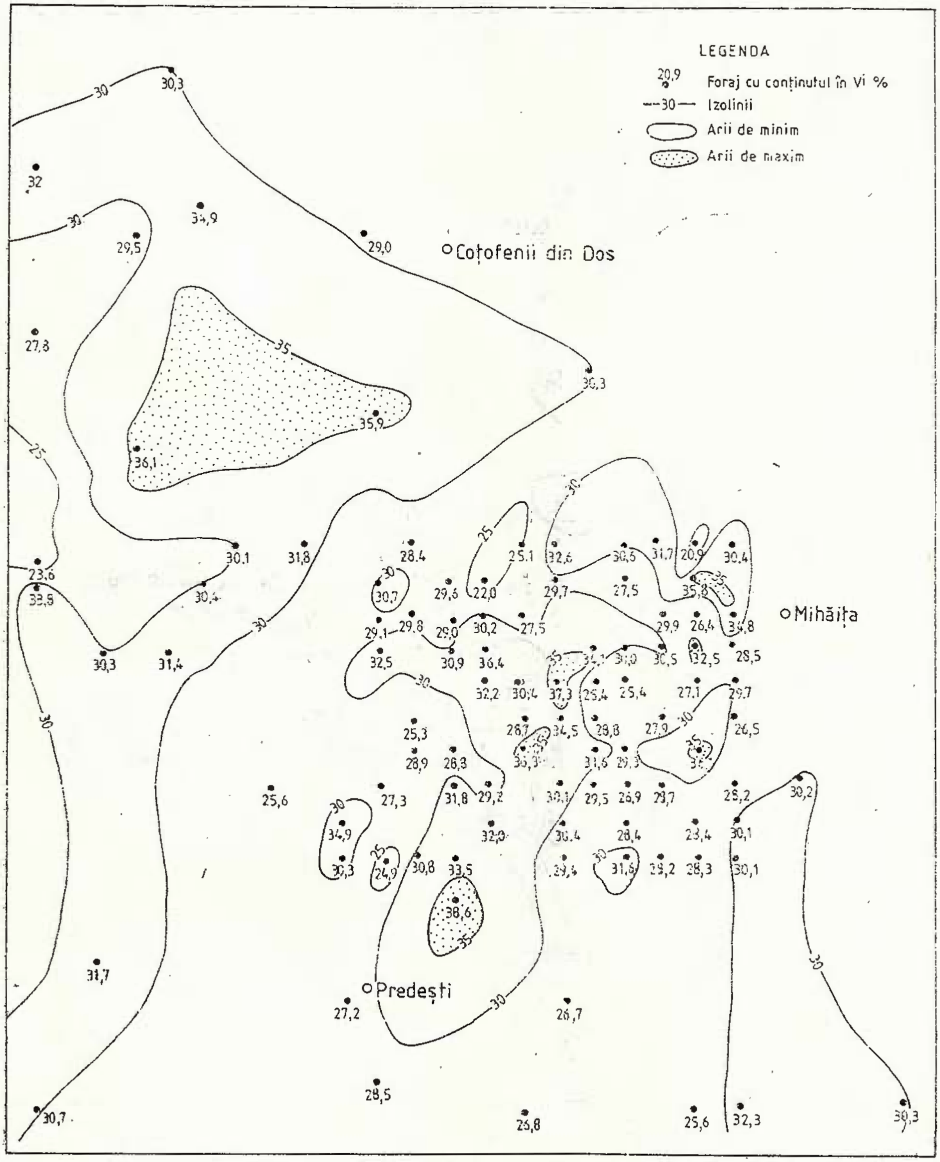

Fig. 2 — Contour map for V^{i} of the fifth coal bed — Mihăiţa zone : 1, drilling with V^{i} content (per cent) ; 2, isolines ; 3, minimal areas ; 4, maximal areas.

fact that the volatile matter comes from bituminous coal, being generated by resins, fats, waxes, cutine, sporine, these elements being frequent in the composition of *Glyptostrobus* association. Regarding the low ash content, it also occurs in the *Glyptostrobus*, association because in this swamp, mineral terrigene substances were stopped by marginal vegetable associations : *Salix* bush moor and *Phragmites* marsh. At the same time, low ash content is explained by a lot of vegetable biomass supplied by the respective association.

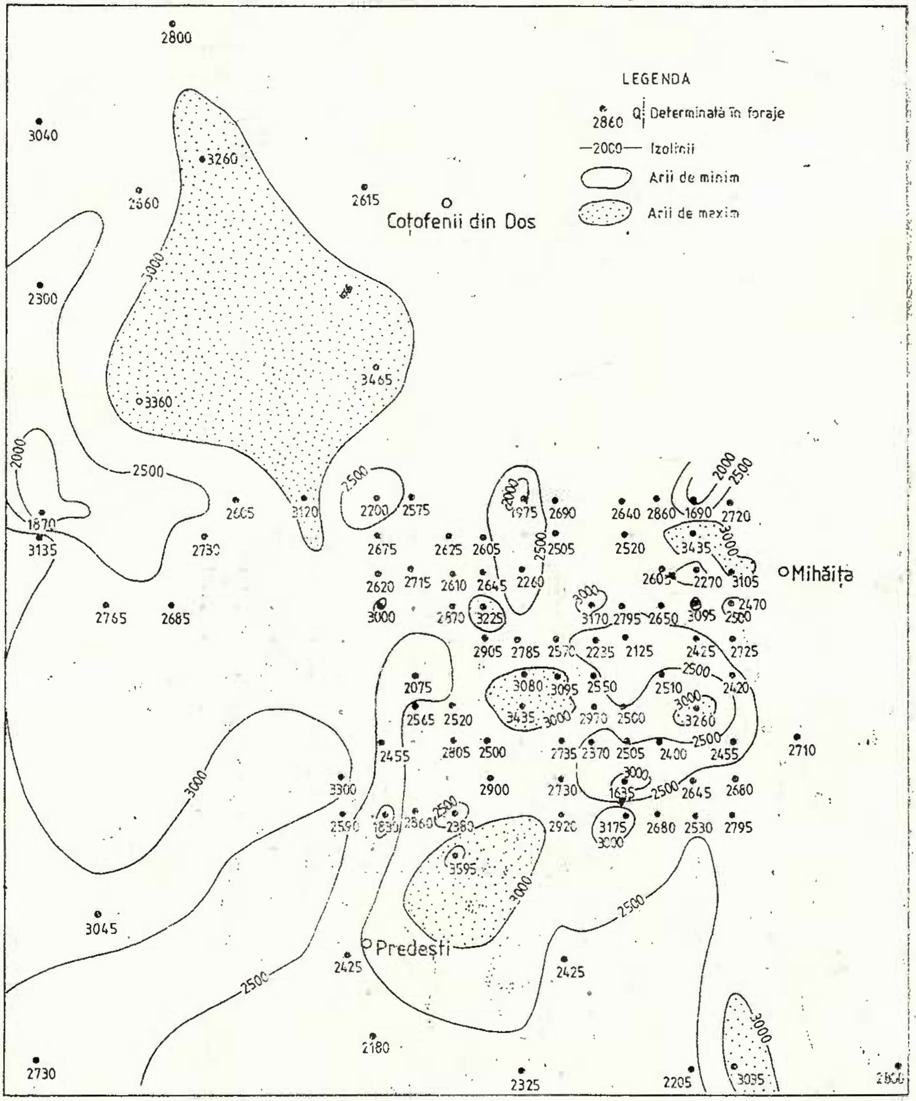

Fig. 3 — Contour map for Q_1^i of the fifth coal bed (lower coal pile) — Mihăiţa zone : 1, Q determined in dirilling ; 2, isolines ; 3, minimal areas ; 4, maximal areas.

The same situation is also noticed by superposing the contour map for Q_i^i (Fig. 3) and the map with A^{anh} (fig. 1), to a low ash content it corepond a high calorific value. Concerning this, we have examples in the zone NE of Predeşti where $Q_i^i = 3595$ Kcal/kg. Otherwise, the $A^{anh} - Q_i^i$ relation is known for a long time, presently existing nomograms to determine through ash the calorific value.

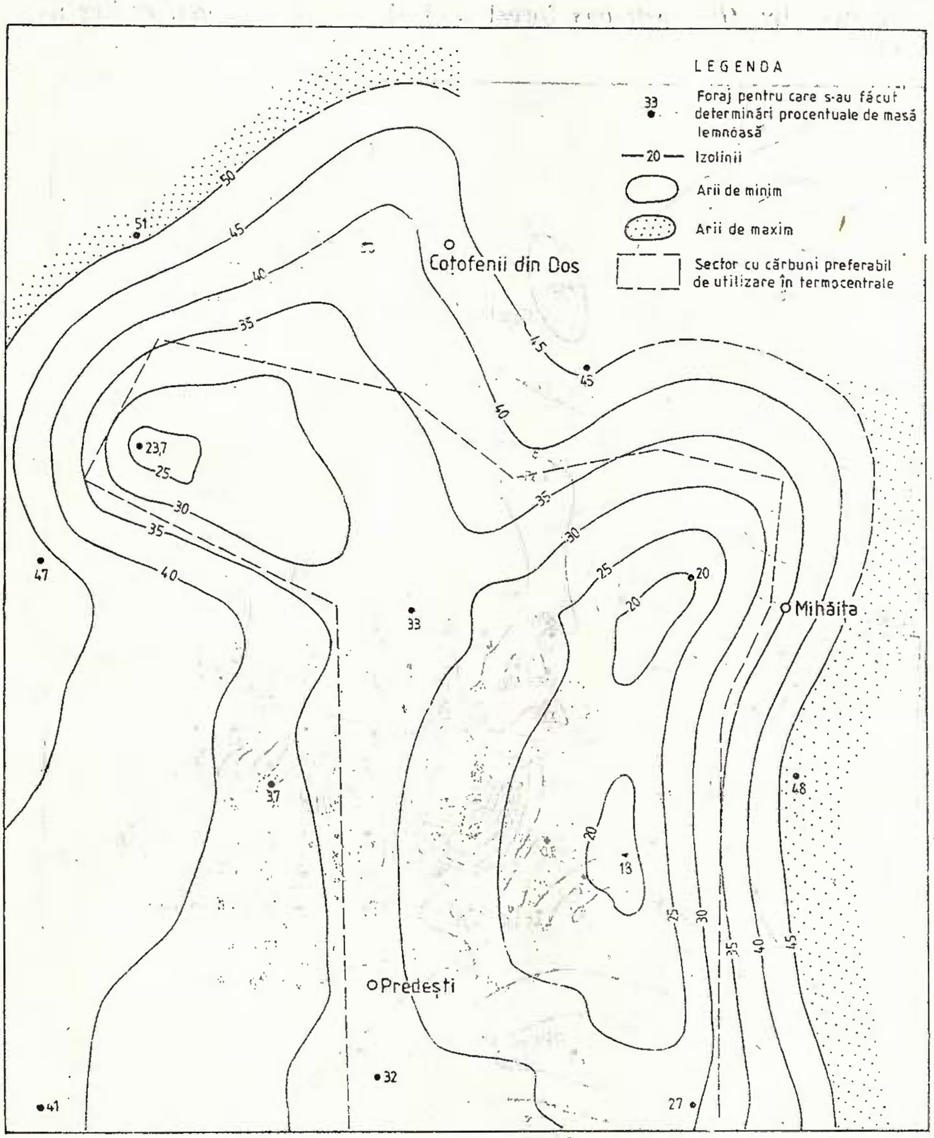

Fig. 4 — Contour map for xylite of the fifth coal bed (lower coal pile) Mihăiţa zone : 1, drilling for which xylite percentages were determined ; 2, isolines ; 3, minimal areas ; 4, maximal areas ; 5, coal sector used for the power-stations.

Because of few information about coal wood mass from Mihăiţa, the contour map for this element (Fig. 4) has an informative character. However, we can notice that xylite zones correspond a lot to those where ash is a little present and volatile matter often occurs. The explanation of this superposition results from the fact that the main xylite source is constituted by *Gluptostrobus* forest and the main coal-generating association.

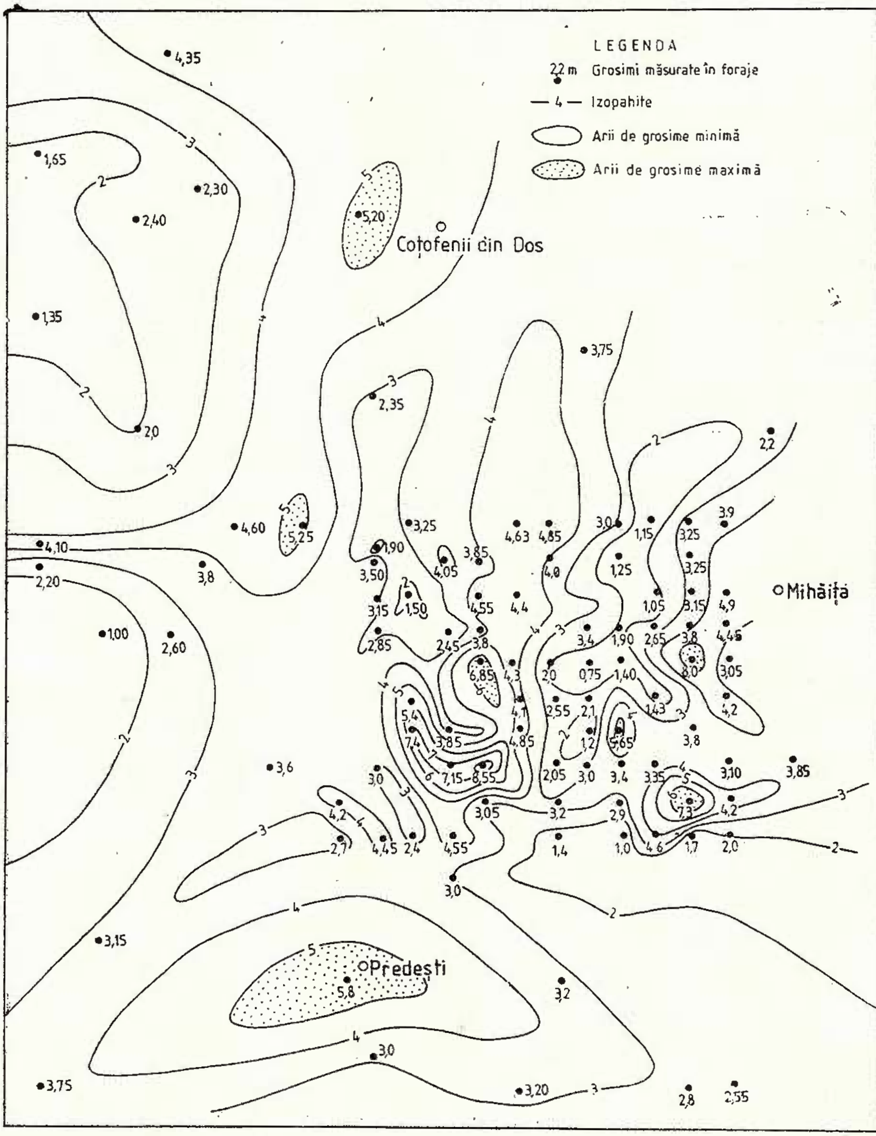

Fig. 5 — Map with the fifth bed isopachytes (lower coal-pile) — Mihăiţa zone : 1, thicknesses in the drilling ; 2, isopachytes ; 3, areas of minimal thickness ; 4, areas of maximal thickness.

Knowing that very thick coal seams have *Glyptostrobus* swamps, we drew up the map with isopachytes (fig. 5) for the lower layer of the V coal seam, noticing that very thick seams correspond to high ash contents in most cases. For instance, 5.8 m thick seam north of Predeşti has 20.9% ash and 8.55 m thick seam has 26.5% ash.

Superposing successively the five contour maps for the above analysed elements, we drew up the humito-genetic map for the Mihăiţa zone, where we separated areas with *Glyptostrobus*, *Phragmites* and water plants vegetable associations (fig. 6).

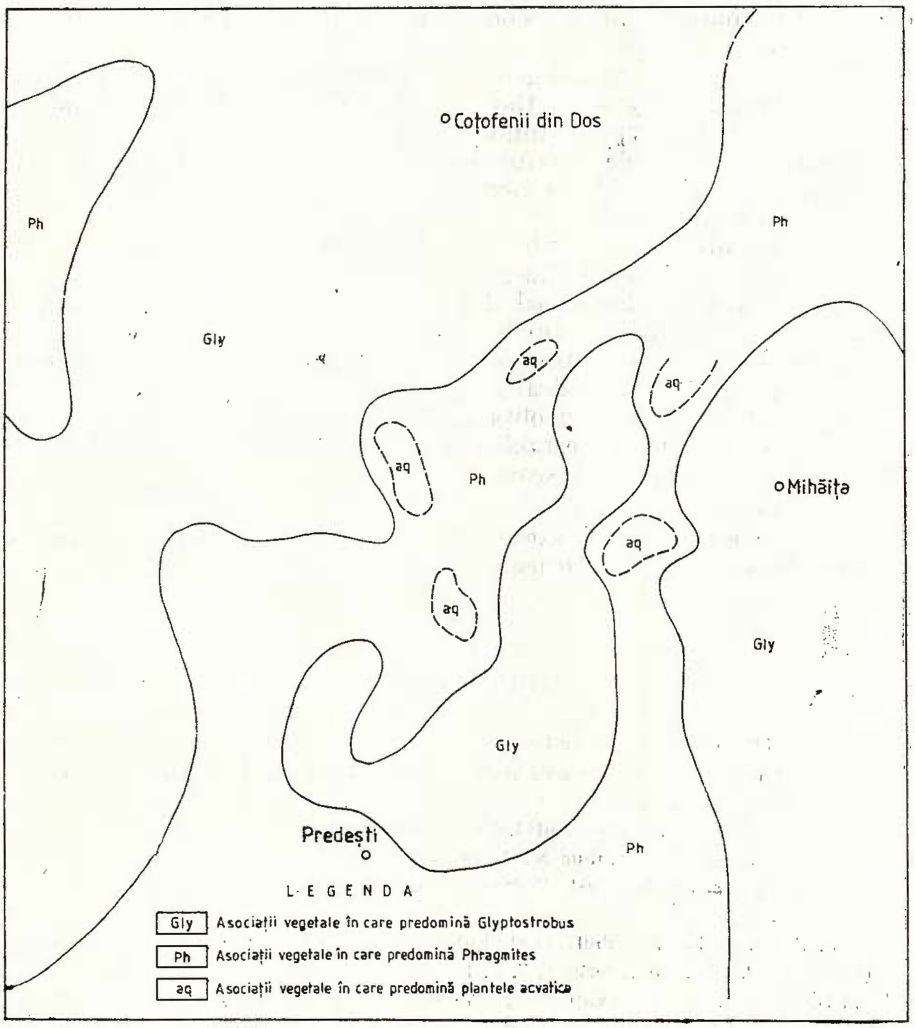

Fig. 6 — Humito-genetic map issued by correlating of the elements: A^{anh}., V^{1}, Q_s^{i}, thickness of bed and xylite percentages; 1, vegetable associations in which prevails *Glyptostrobus*; 2, vegetable associations in which prevails *Phragmites*; 3, vegetable associations in which prevail water plants.

4. Conclusions

Humito-genetic maps are drawn taking into consideration that the main vegetable groups from a coal-generating swamp determined a certain type of coal maceral and certain physico-chemical features and quantitative characteristics (thicknesses) as well. Starting from this fact, it is possible that through qualitative and quantitative petrographical analyses and correlating them with the results of paleofloristic investigations, to delimit on the maps the contours of vegetable groups which contributed to coal formation and to reconstitute the aspect of the swamp where the coal genesis took place.

The first type of humito-genetic map was drawn by comparing data about coal petrography with those about paleofloristic content of coal deposits. The second type of humito-genetic map considers the fact that coal-generating vegetable groups determined certain physico-chemical features of coals : ash, volatile matter, calorific value, xylite content and thickness of coal seams.

The successive superposition of contour maps for the elements mentioned above results in a humito-genetic map which can be used to investigate the Mihăiţa-Predeşti coal deposit.

Humito-genetic maps, which have been drawn up to now, represent only a stage liable to be improved by us, through coal petrographic, paleobotanic and physico-chemical analyses and computing as well. Using humito-genetic maps, we can obtain clearer images on coal formation in various basins and easily establish prospects zones on account of the tendencies to develop coal seams.

3. A^{anh} = ash at 105°C, V^{i} = content in volatile matter (%) related to initial test, Q_i^i = calorific value related to initial test.

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ELABORAREA A DOUĂ TIPURI DE HĂRŢI HUMITO-GENETICE PENTRU DEPOZITELE NEOGENE CU CĂRBUNI DIN BAZINUL BORODULUI (E ORADEA) ŞI ZONA MIHĂIŢA-PREDEŞTI (OLTENIA)

(Rezumat)

Lucrarea prezintă două tipuri noi de hărţi humito-genetice a căror esenţă constă în conturarea pe plan a principalelor grupări vegetale carbogeneratoare care s-au succedat în formarea unui strat de cărbune.

Primul tip de hartă humito-genetică a fost aplicat stratului II de cărbune cuprins în depozitele sarmaţiene din bazinul Borodului (NW-ul României). Elaborarea acestui tip de hartă a pornit de la constatarea, cunoscută deja, că fiecărei grupări vegetale din mlaştinile carbogeneratoare îi corespunde un anumit tip petrografic. Dispunerea, mai mult sau mai puţin concentrică, a grupărilor vegetale în cadrul mlaştinii, în primul rînd în funcţie de adîncimea apei, determină o serie ecologică. În timp, oscilaţiile nivelului apelor au condus la succesiunea mai multor grupări vegetale pe verticala stratului, determinînd o serie genetică.

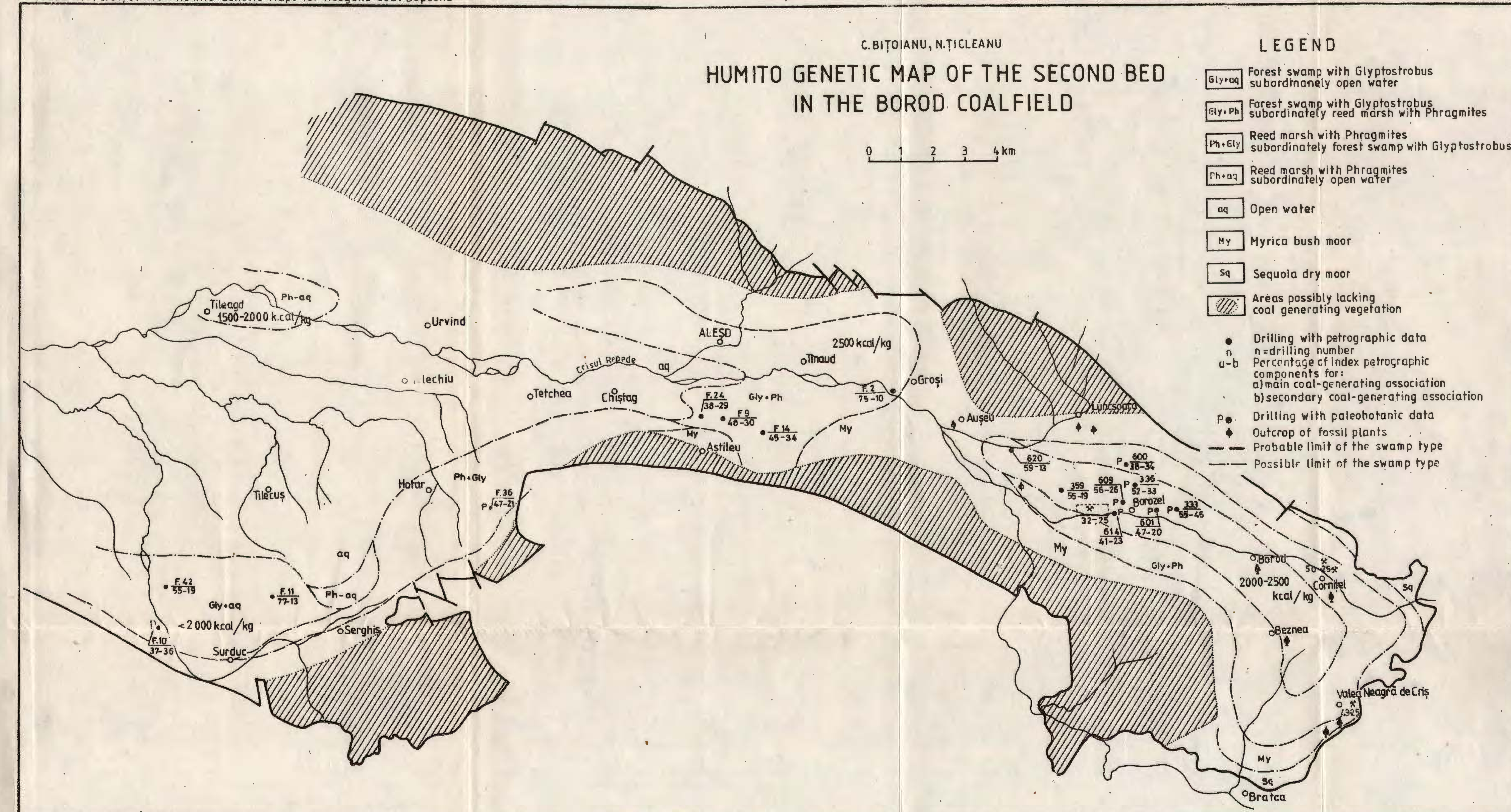
Prin analiza petrografică s-a constatat că la alcătuirea unei serii genetice participă 2—4 tipuri petrografice, reprezentînd tot atîtea grupări vegetale, din care două dețin întotdeauna mai mult de 60 %, motiv pentru care, în funcție de participarea procentuală au fost denumite : principală și respectiv secundară.

Din reprezentarea pe un plan a suprafețelor care au grupări vegetale cu valori procentuale asemănătoare rezultă harta humito-genetică. Uneori, acolo unde cea de a treia grupare vegetală se apropie procentual sau este egală, caz mai rar, cu gruparea secundară se pot contura și suprafețe cu trei grupări vegetale. Fiecare grupare vegetală este denumită după elementul predominant.

Cel de-al doilea tip de hartă humito-genetică, aplicat pentru studiul stratului V de cărbune din depozitele dacian-superioare de la Mihăița-Predești (Oltenia), a fost elaborat pornind de la același principiu ca și în cazul anterior : corespondența dintre tipurile petrografice de cărbuni și grupările vegetale din care provin, adăugînd constatarea că această corespondență se reflectă, în suficientă măsură pentru a fi sesizată și măsurată, și în unele proprietăți fizico-chimice : A^{anh} ; V^{i} ; Q_{i}^{i} ; conținutul în xylit și grosimea stratului de cărbune. Astfel, de pildă, gruparea vegetală a pădurii de *Glyptostrobus* este cea care a participat la formarea cărbunilor cu cea mai redusă cantitate de cenușă, cu substanțe volatile în cantitate mai mare, conținut mare în xylit și determină grosimile cele mai mari ale stratelor de cărbune. În contrast cu aceasta, gruparea vegetală a plantelor acvatice a produs cărbuni cu conținuturi mari în cenușă, cu xylit puțin și grosimi mici, fără importanță economică.

Pentru fiecare dintre proprietățile fizico-chimice luate în considerație au fost întocmite hărți de contur, din care prin suprapunere succesivă și ajustare a rezultat harta humito-genetică.

Cele două tipuri de hărți humito-genetice reprezintă evident un stadiu incipient, ele fiind susceptibile de îmbunătățiri ulterioare. Aceste hărți permit obținerea unei imagini mai clare asupra formării cărbunilor și facilitează stabilirea zonelor de perspectivă pe baza studiului tendințelor de dezvoltare, sub raport cantitativ și calitativ, ale stratelor de cărbuni.



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2. ZĂCĂMINTE

A SHEAR-ZONE RELATED Cu-Au ORE OCCURRENCE: VALEA LUI STAN, SOUTH CARPATHIANS[1]

BY

GHEORGHE UDUBAŞA[2], HORST PETER HANN[2]

Gold mineralization. Cu, Precambrian. Au, metamorphics. Shear zone. Structural control. Tectogene mineralization. Sulfur isotope analysis. South Carpathians — Getic and Supragetic crystalline domains — Lotru and Căpăţina Mts. Getic and Supragetic sedimentary domains — Valea lui Stan—Călineşti Zone.

Abstract

The Cu—Au mineralization from Valea lui Stan is considered to be genetically connected to an important shear zone in the Precambrian metamorphics. The arguments in favour of the tectogene origin are as follows: (1) the location of the quartz gold lenticular bodies exclusively within the shear zone; (2) the orientation of the ore lenses in the mylonitic foliation plane; (3) the relatively simple mineralogical association of the ore bodies (quartz, gold, pyrite, arsenopyrite, chalcopyrite $\pm$ sphalerite, galena, pyrrhotite); (4) the great dispersion of the $\delta^{34}S$ values within sulfides ($-5.09 \ldots +23.26^0/_{00}$); (5) the relatively high gold contents of the presumed gold protore, represented by the amphibolic rocks of the Sibişel Group; (6) the existence of some "geochemical bridges" between the rocks and the ore; (7) the lack of magmatic bodies in the vicinity of the mineralized structure as well as the lack of the hydrothermal type alterations in the host rocks of the ore bodies etc. The paper deals also with some general aspects of the genesis of the "tectogene mineralizations" connected to shear planes showing a critical dip.

Résumé

Minéralisations tectogènes de Cu—Au de Valea lui Stan, Carpathes Méridionales. Génétiquement, la minéralisation de Valea lui Stan est considérée liée à une importante zone de cisaillement dans des métamorphites précambriens. Les arguments en faveur de l'origine tectogène sont les suivants: (1) la localisation exclusive des corps lenticulaires de quartz aurifère dans la zone de cisaillement; (2) l'orientation des lentilles de minerai dans le plan de la foliation mylonitique; (3) l'association minéralogique relativement simple des corps de minerai

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(quartz, or, pyrite, arsénopyrite, chalcopyrite ± sphalérite, galène, pyrrhotine) ; la dispersion grande des valeurs $\delta^{34}S$ dans les sulfures (−5,09 ... +23,26$^0/_{00}$) (5) les téneurs assez élevées en or du protore aurifère représenté par les roches amphiboliques du groupe de Sibişel ; (6) la présence de quelques „ponts de liaison géochimique" entre les roches et le minerai ; (6) l'absence des magmatites dans la proximité de la structure minéralisée et des altérations de type hydrothermale dans les roches-hôte des corps de minerai etc. On met en discution aussi quelques aspects importants de la genèse des „minéralisations tectogènes" liées aux plans de cisaillement à une pendage critique.

The study of the gold mineralizations hosted by the crystalline schists was generally based on the epigenetic concept, these mineralizations being considered "old gold veins" and variously named. It was underlined that they occurred almost exclusively in older metamorphics. Only during the last decades the genetic concepts allowed other interpretations especially due to the lack of the associated magmatic bodies as well as of the hydrothermal alterations, their constant association with greenschist belts, in which there are iron ores of itabiritic type (or BIF) and their coexistence with shear planes.

The non-hydrothermal nature of the gold mineralizations from Valea lui Stan has been partly demonstrated since 1976 (Udubaşa et al., 1976); the present paper provides additional arguments in favour of this genetic hypothesis based on a better knowledge of the metamorphic formations involved in the mineralized structure.

Previous Researches

The presence of gold in the alluvial deposits from this zone was first pointed out in 1903 by Radu Pascu, but it was only in 1907 that the primary gold source was identified in the form of gold quartz lenses in the metamorphics from the left slope of the Stan Valley (Preotesiu et al., 1973). The old exploitation functioned with many breaks until 1950; the works were later resumed without notable results (Stavarache, 1960; Trifulescu, Dragomir, 1969; Preotesiu et al, 1973; Balabaş, 1976). The investigation of the zone pointed out an extended vein-like structure, with discontinuous mineralizations of hydrothermal post-magmatic nature, revealing also some effects of the deformations undergone by the ore minerals (Stavarache, 1960).

Petrulian (1936) underlines the peculiar character of these mineralizations, stating that "the deposit is not vein-like" and would be associated with pneumatolytic and hydrothermal phases of the eruptive cycle of the Cozia Gneiss. Ghika-Budeşti (1938) connects the formation of the mineralizations to the perimagmatic events subsequent to the appearance of the granitic Cumpăna "dyke" and the formation of the Cozia Gneisses, phenomena contemporary with the regional dynamic metamorphism. Trifulescu and Dragomir (1968) state that the mineralizations show a discordant injection character and are generally linked with the porphyric granites from the Ulii Valley; in their opinion, the ores are located in vein-like pegmatite as veins, impregnations or stockworks.

Geological Structure of the Valea lui Stan Zone

The recent data obtained by the investigation of a larger zone, extended along the Olt River (Balintoni et al., 1986; Hann, Balintoni, 1987), indicate an extremely complicated structure involving metamorphic and sedimentary formations of various age (Fig. 1). The most important lithostratigrpahic units involved in the formation of the mineralized structure are the following: Cumpăna Group, Sibişel Group, Călineşti Formation and Căpăţîna Group which belong, in the terminology used by Balintoni et al. (1986) to the Sebeş-Lotru multigroup (Cumpăna, Căpăţîna, Călineşti) and to the Negoi multigroup (Sibişel); the Sibişel Group is the most significant as it represents the equivalent of the greenstone belts from the zones with similar mineralizations in the world.

Căpăţîna Group

The petrographic background consists of biotite and muscovite paragneisses in which there are conformable intercalations of micaschists, amphibolites, migmatites and numerous unconformable bodies of pegmatites. The metamorphics of the Căpăţîna Group are of Proterozoic age; the metamorphism took place in the almandine amphibolite facies (Barrovian type). Hârtopanu (1982) demonstrated the polymetamorphic character of the whole Sebeş-Lotru Group, with a last retrograde phase, that resulted in the chloritization of biotite and garnets and deformations that gave rise to crenullation planes and microfolds.

The metamorphics of the Căpăţîna Group underwent an intense dynamic metamorphism close to the tectonic contact (overthrust plane) with the Sibişel Group (Fig. 2), whereby the rocks rich in phylosilicates got a phylonite-like aspect, while the quartz-feldspathic ones underwent cataclasations, which initially showed a breccified aspect and further a general mylonitic foliation. The effects of this metamorphism in pegmatites manifested by the cataclasation of the minerals and the boudinage of the rock bodies. The effects of the dynamic deformation decrease in intensity as the distance from the overthrust plane increases.

Sibişel Group

The metamorphics of this group are intensely compressed in the Valea lui Stan zone, where they form a narrow strip varying in thickness

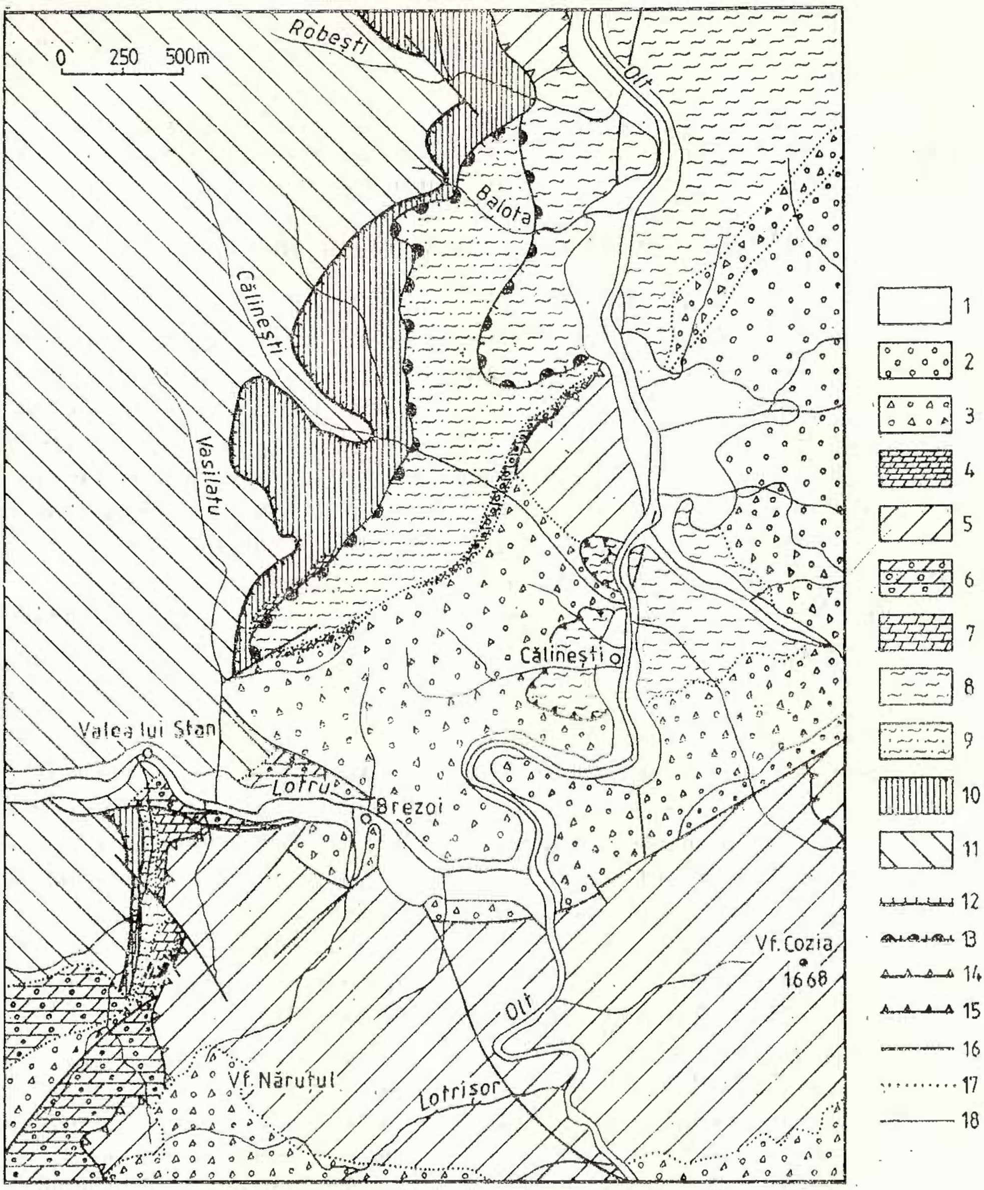

Fig. 1 — Structural Map of the Brezoi-Cîineni-Perișani Region (South Carpathians) : 1, alluvia (Holocene) ; 2, conglomerates (Neogene-Paleogene, Post-Late Laramian Cover) ; 3, breccias, conglomerates, marls (Lower Maastrichtian ,Post-Early Laramian Cover) ; 4, Rotalipora marls (Cenomanian-Post-Mesocretaceous Cover) ; 5, Cumpăna Group (Sebeș-Lotru Multigroup — Boia Nappe — Early Laramian, overthrust nappes) ; Lotru Nappe : 6, marls, conglomerates (Santonian-Coniacian, Vasilatu Formation — Lotru Nappe) ; 7, Valea lui Stan sedimentary Series (Triassic-Permian) Mesocretaceous tectonic units ; Cîineni Nappe with Călinești Scale ; 8, Cîineni Formation (Proterozoic Sebeș-Lotru Multigorup) ; 9, Călinești Formation(Proterozoic Sebeș-Lotru Multigroup) ; 10, Sibișel Group (Negoi Multigroup, Uria Nappe, Proterozoic) ; 11, Căpățîna Group (Proterozoic, Sebeș-Lotru Multigroup, Getic Nappe). Conventional signs : 12, Mesocretaceous overthrust ; 13, Mesocretaceous, presumed pre-Laramian tectonic plane ; 14, Early Laramian overthrust (overthrust plane of the Boia Nappe) ; 15, Late Laramian tectonic plane ; 16, fault ; 17, transgression ; 18, general geological boundary.

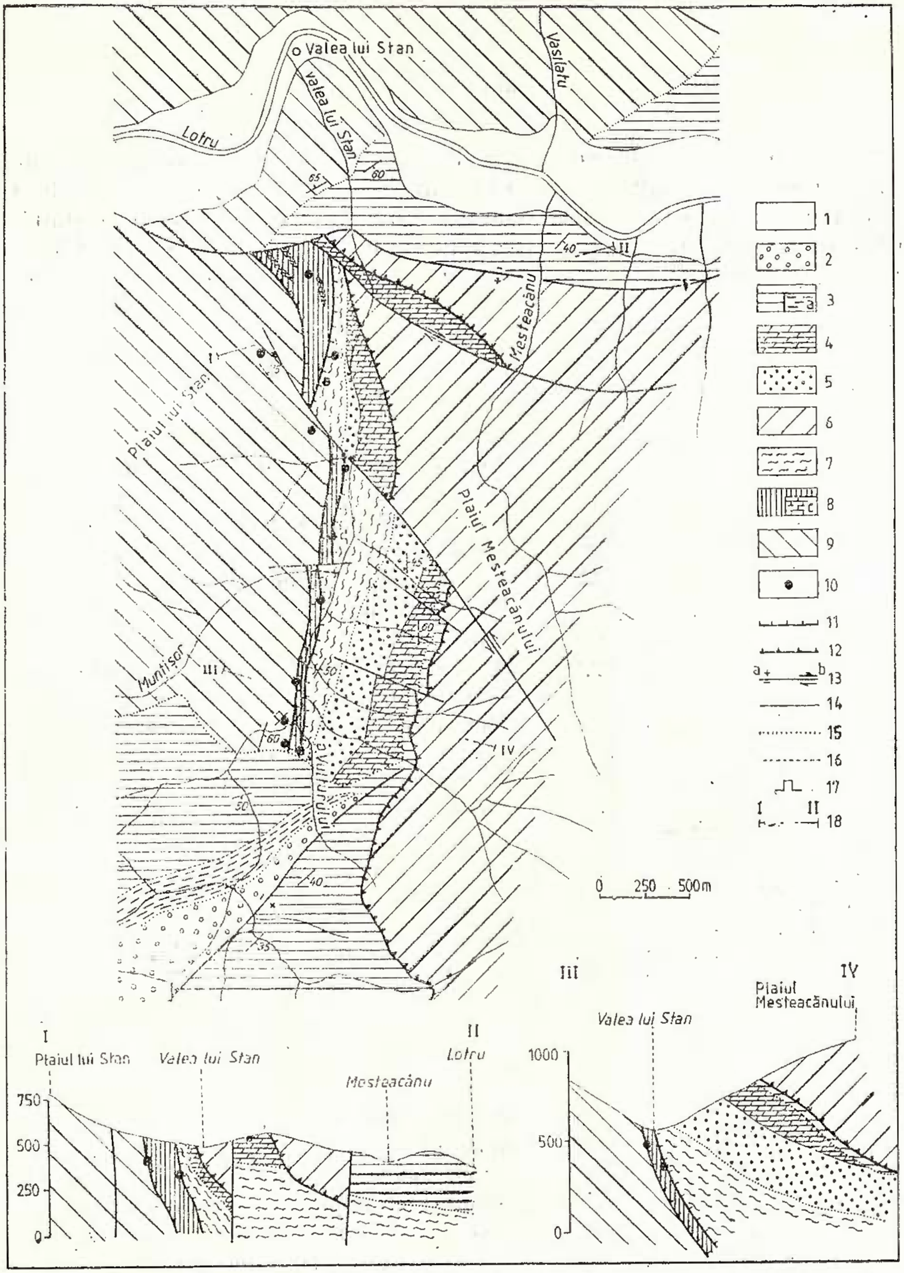

Fig. 2 — Geological Map of the Stan Valley Basin. Căpățîna Mountains — South Carpathians : 1, actual and subactual alluvia (Holocene) ; 2, polymictic conglomerates, massive sandstones, marls (Maastrichtian-Campanian) ; 3, polymictic conglomerates, marls, sandstones, organogenous gritty limestones, marly-sandy sandstones and clays (a), (Coniacian-Santonian) ; 4, organogenous marly limestones (Werfenian) ; 5, red-violaceous polymictic conglomerates (Werfenian-Permian) ; 6, Cozia augen-gneisses with paragneiss intercalations (Cumpăna Group, Sebeș-Lotru Multigroup ; 7, slightly regionally retromorphosed, partly intensely dynamically retromorphosed biotite and muscovite paragneisses with amphibolite levels (Călinești Formation, Sebeș-Lotru Multigroup) ; 8, paragneisses, amphibolites, intensely regionally and dynamically retromorphosed crystalline limestone (mylonites up to retromylonites), crystalline limestone boundines (c), (Sibișel Group, Negoi Multigroup) ; 9, intensely migmatized and pegmatized paragneisses, intensely mylonitized at the contact with the Sibișel Group (Căpățîna Group, Sebeș-Lotru Multigroup) ; 10, gold-sulfide mineralizations ; 11, Austrian overthrust nappe ; 12, Laramian overthrust nappe ; 13, vertical fault (a), wrench fault (b) ; 14, general geological boundary ; 15, transgression boundary ; 16, lithological boundary ; 17, gallery ; 18, position of geological sections.

between 30—50 m and 500 m (Fig. 3) and bounded by two tectonic planes, through which it contacts the Căpăţîna Group (to the west) and the Călineşti Formation (to the east). The metamorphics of this group were initially considered an independent series (the Valea lui Stan Series) of Cambrian age, in unconformable and transgressive position with respect to the

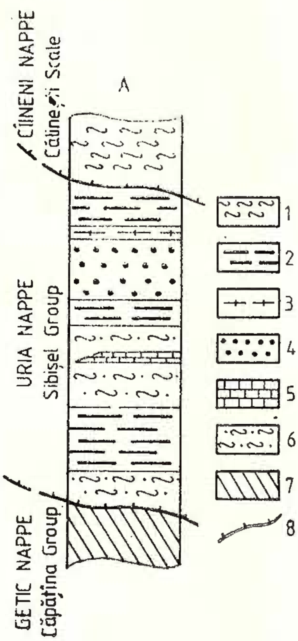

Fig. 3a — Sibişel Group — Uria Nappe : Synthetic Column (Uria Valley, Robeşti Valley, Călineşti Valley, Stan Valley). 1, Medium grade metamorphics of the Călineşti Formation ; 2—6, metamorphics of the Sibişel Group : (2, retrograde amphibolites ; 3, retrograde quartz-feldspathic white gneisses (quartz-feldspathic schists) 4, retrograde biotite paragneisses, amphibole and biotite bearing gneisses ; 5, metamorphic limestones, calcareous schists ; 6, retrograde paragneisses, micaschists, quartzitic paragneisses ; 7, medium grade metamorphics of the Căpăţîna Group (Sebeş-Lotru "Series") ; 8, overthrust plane.

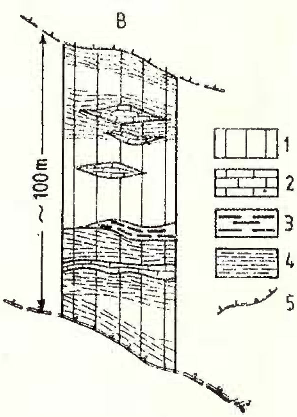

Fig. 3b — Sibişel Group in the tectonic zone from the Stan Valley 1, sericite-chlorite schists, sericite-chlorite quartzite schists (paragneisses with two micas, retromorphic quartzitic gneisses) ; 2, crystalline limestones, calcareous schists ; 3, laminated chlorite greenschists (retromorphic amphibolites) ; 4, mylonite and ultramylonite zones ; 5, overthrust plane.

Sebeş-Lotru Series (Savu et al., 1977 ; Gheuca, in Lupu et al., 1978). However, Hann and Szasz (1984) demonstrated that this series represents in fact the southward continuation of the retrograde Sibişel Series (group) that underwent an additional dynamic metamorphism along an overthrust plane, through which it thrustsover metamorphics of the Sebeş-Lotru Series (Căpăţîna Group), forming the Uria Nappe. The Sibişel Group consists of a leptyno-amphibolitic formation and a gneissic one (Hann, in Ştefănescu et al., 1982; Hann, Szasz, 1984). The repeated metamorphic deformations, accompanied by mineralogical reorganizations, led to the appearance of some aspects that at first sight suggest rocks of low grade metamorphism; however, this aspect is not uniform, old minerals and structures often coexisting with the new ones.

The Sibişel Group is marked by the amphiqolite + white quartz feldspathic gneisses + crystalline limestone association at the base and quartz and micaceous paragneisses at the top, which are generally subjected to retrograde transformations. The amphibole schists contain actinolite, chlorite, epidote, magnetite; the other rock types macroscopically resemble chlorite and sericite-quartz schists + relict garnet or sericite-chlorite schists, the greenschists locally prevailing. Actinolite with green hornblende nuclei, oligoclase with albite rims as well as the biotite chloritization indicate, along with the intense laminations, the effects of a retrograde regional metamorphism. This conclusion is also supported by the amphibole digestion by plagioclase, the appearance of magnetite as a new mineral through the retrograde deferrization of hornblende and biotite, the pseudoocelii from the quartz-feldspathic rocks which represent in fact porphyroclasts etc. The initial, probably Proterozoic metamorphism, achieved in the almandine amphibolite facies, was overlapped by a retrograde greenschists facies metamorphism, probably of Hercynian age. The local mylonitization and phylonitization of these rocks are likely of Alpine age.

The lithostratigraphic succession of the Sibişel Group is fragmentary in the Stan Valley basin, most of the petrographic entities being lenticular. The very strong and repeated laminations gave rise to blackish ultramylonites that macroscopicallay resemble the graphite schists, encountered as a rule in the zones where the compression on the whole sequence was the strongest.

Călineşti Formation

The petrographic constitution of this formation is represented by micaceous paragneisses, sometimes with albite-oligoclase porphyroblasts; there are massive amphibolites or amphibolitic gneisses, augen gneisses interbeds varying in thickness (Fig. 4). A slight retrograde metamorphism manifests in the rocks of this formation through the chloritization of biotite and garnets; mylonitization phenomena of varied intensity take place in the vicinity of the overthrust plane.

Cumpăna Group

The metamorphics of this group develop southwards, overthrusting the Coniacian-Santonian and Permo-Triassic sedimentary deposits. They are represented especially by ocular gneisses with microcline augen. The paleosoma of these ophtalmitic migmatites is represented by biotite paragneisses. The metamorphism grade corresponds to the almandine amphibolite facies. Contrary to the previous statements that the mineralized quartz lenses from Valea lui Stan are found exclusively in the augen (Cozia) Gneisses (Ghika-Budeşti, 1938), it is proved that the metamorphics of this

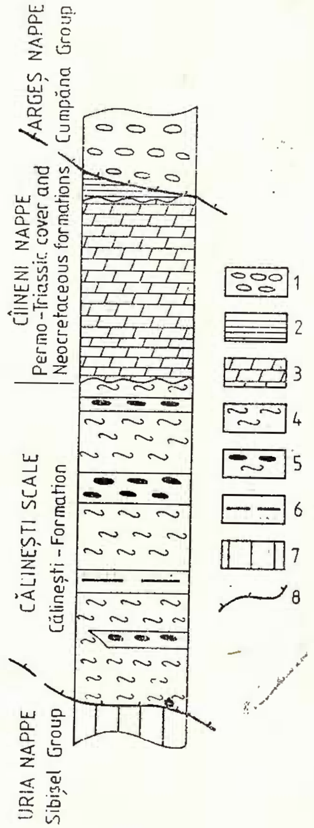

Fig. 4 — Călineşti Formation (Cîineni Nappe-Călineşti Scale). Synthetic column. Călineşti Valley-Stan Valley. 1, Cozia augen gneisses; 2, Coniacian-Santonian deposits in the Stan Valley; 3, Permian-Werfenian deposits in the Stan Valley; Călineşti Formation; 4, Paragneisses, micaceous paragneisses ± albite-oligoclase porphyroblasts; 5, augen gneisses and white, quartz-feldspathic gneisses; 6, amphibolites; 7, retrograde metamorphics of the Sibişel Group 8, overthrust plane.

group were the least involved in the formation of the mineralized structure and the mineralization indices within the Cozia Gneisses are on the whole extremely sparse.

Major Structural Elements

În the Olt Valley two regional overthrust nappes were identified, which were emplaced during the Early Laramian; they consist in turn of several Alpine, pre-Laramian (Mesocreataceous), tectonic units. The upper nappe, which thrusts over the Vasilatu Formation (Coniacian-Santonian) and is transgressively overlain by the Brezoi Formation (Campanian-Maastrichtian), is named the Boia Nappe. În the Valea lui Stan region the Boia Nappe includes only the Argeș Nappe, of lower grade, represented by the Cumpăna Group, forming east-westward trending structures. The lower nappe, named the Lotru Nappe, consists of the Getic, Uria and Cîineni (with the Călinești Scale) Mesocretaceous tectonic units. The Getic Nappe consists of the metamorphics of the Căpățîna Group, the Uria Nappe of the metamorphics of the Sibișel Group, and the Cîineni Nappe of the Călinești Formation. North of Valea lui Stan, under the overthrust plane of the Călinești Scale there are Middle-Upper Cenomanian sedimentary deposits. The same plane is overlain in the Stan Valley by Coniacian-Santonian sedimentary deposits, which indicates that the overthrust is post-Cenomanian and pre-Coniacian, i. e. Turonian in age.

The complicated geological structure from Valea lui Stan is transgressively and unconformably overlain by Coniacian-Santonian sedimentary deposits (southwards) and cut by the Brezoi Fault (to the north), the metamorphic formations and the Permo-Triassic sedimentary deposits involved in the overthrust structures contacting the mentioned Cretaceous deposits (Fig. 2).

Ore Occurrences

Several ore occurrences are known along the Stan Valley, situated especially on its left slope and hosted prevailingly by the metamorphics of the Sibișel Group, rarely by those of the Călinești Formation and of the Căpățîna Group (Figs. 2 and 5). There are numerous quartz bodies varying

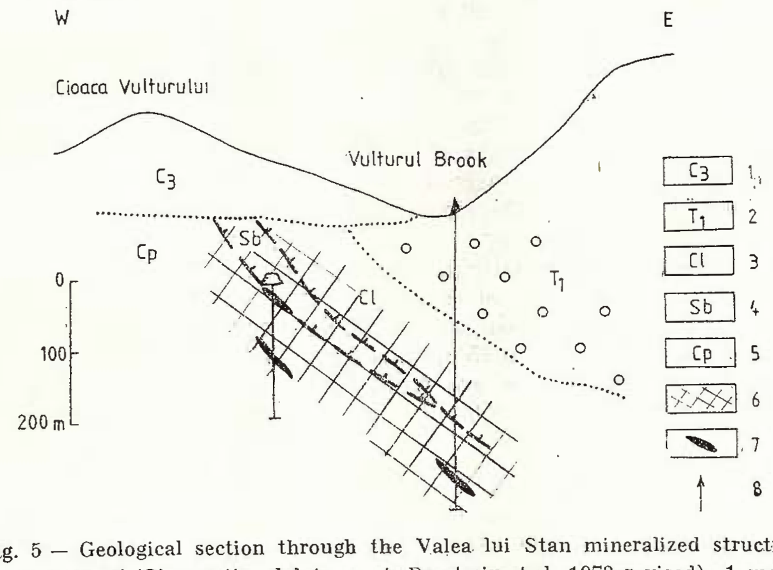

Fig. 5 — Geological section through the Valea lui Stan mineralized structure (southern part) (Observational data acc. to Preotesiu et al., 1973, revised)., 1, marls and conglomerates of the Vasilatu Formation (Santonian-Coniacian); 2, organogenous marly limestones, red-violaceous polymictic conglomerates of the Valea lui Stan sedimentary Series (Triassic-Permian); 3, Călinești Formation; 4, Sibișel Group; 5, Căpățîna Group; 6, cataclasation and mylonitization zone; 7, lens-shaped ore bodies; 8, boreholes.

in size; they lie either conformably or unconformably but always within strongly mylonitized metamorphics. The sulfide amount is of about 3–5% of the quartz lens volume. The identified ore minerals in the order of their frequency are as follows: pyrite, arsenopyrite, chalcopyrite, marcasite, sphalerite, galena; sporadically there occur pyrrhotite (as a rule included in arsenopyrite), gold (included in arsenopyrite and/or chalcopyrite) and secondary minerals (covellite, malachite, anglesite, cerussite, scorodite, hydrogoethite). Itabiritic, i.e. quartz rocks with magnetite and/or hematite were found in places, with which pyrite is sometimes associated.

The mentioned minerals show a relatively uniform distribution in the occurrences from Valea lui Stan; galena shows, however, a higher concentration towards the north, while an increase of the sulfide amount is recorded towards the south; as a matter of fact, the traces of the old exploitation can be seen at the confluence of the Stan Valley with the Vulturul Brook.

Pyrite and arsenopyrite are often fissured or broken and partly cemented with the other sulfides, a gradual transition from unfissured, euhedral grains to intensely broken, partly autocemented compact masses being noticed. Part of the pyrite probably represents an older, pre- or synmetamorphic "generation", forming almost monomineral bands; this pyrite is very poor in minor elements. Chalcopyrite is often associated with arsenopyrite; the most characteristic association mode is given by the cementation aspects of the fissured arsenopyrite through chalcopyrite, representing the preferential concentration loci of the gold; locally sphalerite can be also noticed in such fine intergrowth structures. The gold-chalcopyrite-sphalerite assemblage, hosted by arsenopyrite, represents a typical paragenesis for the Valea lui Stan ore. Sphalerite is in all the cases oversaturated with chalcopyrite exsolution-like bodies, which are sometimes replaced by covellite; this peculiarity of the sphalerite grains determines a false anisotropy; this is why sphalerite was mistaken for stannite (Petrulian, 1936). The microlaser analysis of such grains pointed out only the presence of Zn, Cu and Fe, tin being situated below the detection limit of the emission spectrography method (Udubaşa et al., 1976). Beside the above-mentioned characteristic assemblage gold also occurs as fine inclusions in chalcopyrite, in massive arsenopyrite, rarely in pyrite, accidentally in the goethite and hydrogoethite colomorphic masses, which sometimes contain also copper (0.25%) and zinc (0.40%). A few microscopic aspects characteristic of the ore from Valea lui Stan are presented in Plates I and II and in Figure 6.

Geochemical Data

The processing of the existing data for the amphibolitic rocks from Valea lui Stan zone shows that these are metamagmatites (Tatu in Udubaşa et al., 1985). The results of the chemical, spectrographic and neutron activation analyses carried out on rocks have been plotted on the diagrams from Figure 7, which show a positive correlation between Au and Fe_{total}, a negative correlation between Au and the alkaline elements, a positive one between Au and Cu, and a negative one between Au and Pb.

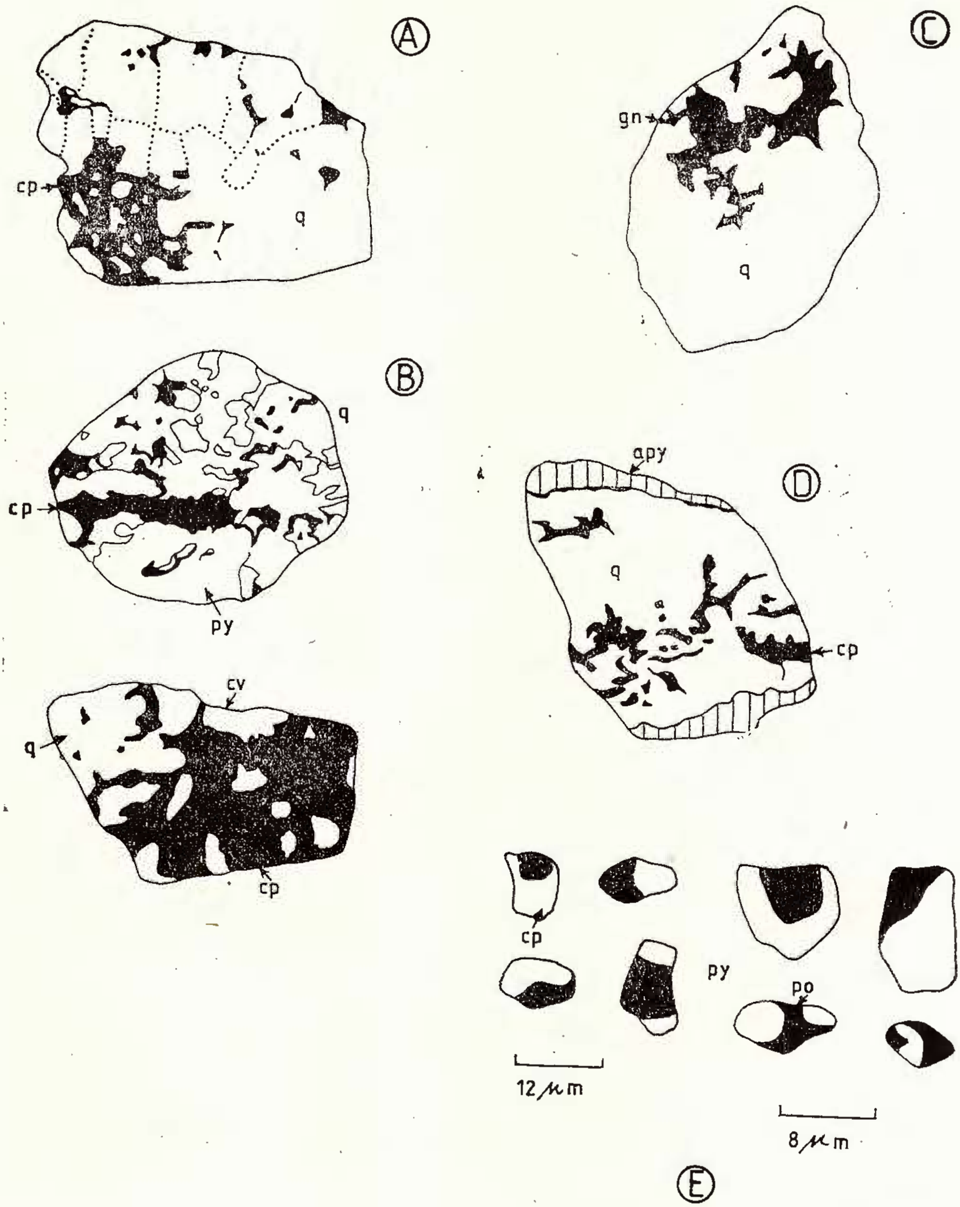

Fig. 6 — Mesoscopic (A—D) and microscopic (E) aspects of the ore. Abbreviations : po, pyrrhotite ; cp, chalcopyrite ; py, pyrite ; apy, arsenopyrite ; gn galena ; cv, covellite ; q, quartz.

Some significant chemical elements of the rocks and ores were plotted on the ternary diagrams from Fig. 8 ; the overlapping parts of the plotting fields of the rocks and ores may be interpreted as "geochemical bridges" from the rocks to the gold-copper ores.

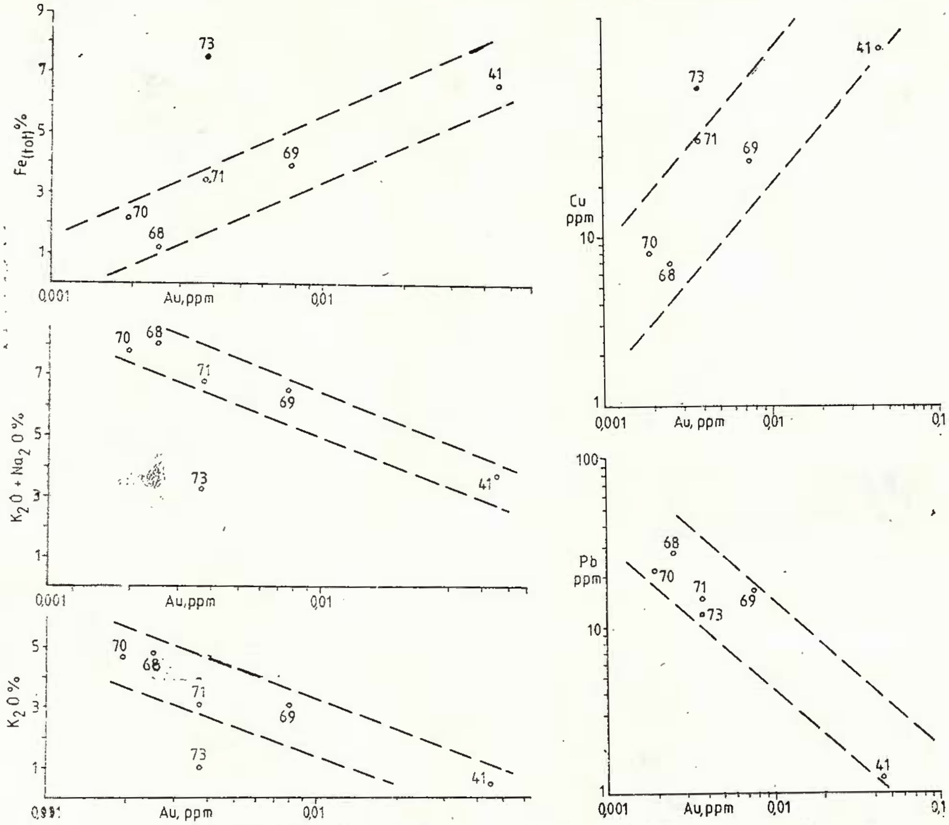

Fig. 7 — Correlation diagrams Au vs alkaline elements or Fe (a) and Au vs Cu and Pb (b). Numbers on the diagrams represent : 41, amphibolite (Sibişel Group) ;68 gneisses (Călineşti Formation) ; 69, micaceous paragneisses (CăpăţinaGroup) ; 70, idem ; 71, micaschists (Căpăţina Group) ; 73, mylonites formed at the expense of paragneisses (Sibişel Group).

The Co/Ni ratio in pyrite is supraunitary with a single exception, while the absolute values — especially those of Co — are relatively high, reaching 1.200 ppm. The As contents are high and very high due to the very fine pyrite and arsenopyrite intergrowths. The gold contents within pyrite decrease north-southwards in the direction of the increase of the total sulfide amount of the mineralized quartz. It is worth noting the occurrence of thallium within the pyrite present as veinlets in the crystalline limestones of the Sibişel Group, in a zone devoid of other ore minerals. The other spectrographically analysed elements indicate variable contents, partly due to the impurification with other sulfides (Table 1).

The data presented in Table 2 show that the mineralizations from Valea lui Stan are characterized by the Au—Cu—As association as well as by contrasting or subordinated Zn, Pb, Ag, Bi, Ni, Co values. The fine-grained pyrite (two samples) that occurs as nests or lenses in the cataclasation zone affecting the rocks of the Căpăţina Group in the Păscoaia Valley basin (north of Valea lui Stan), are generally poorer in minor elements, except Ti, for which a significant increase was recorded.

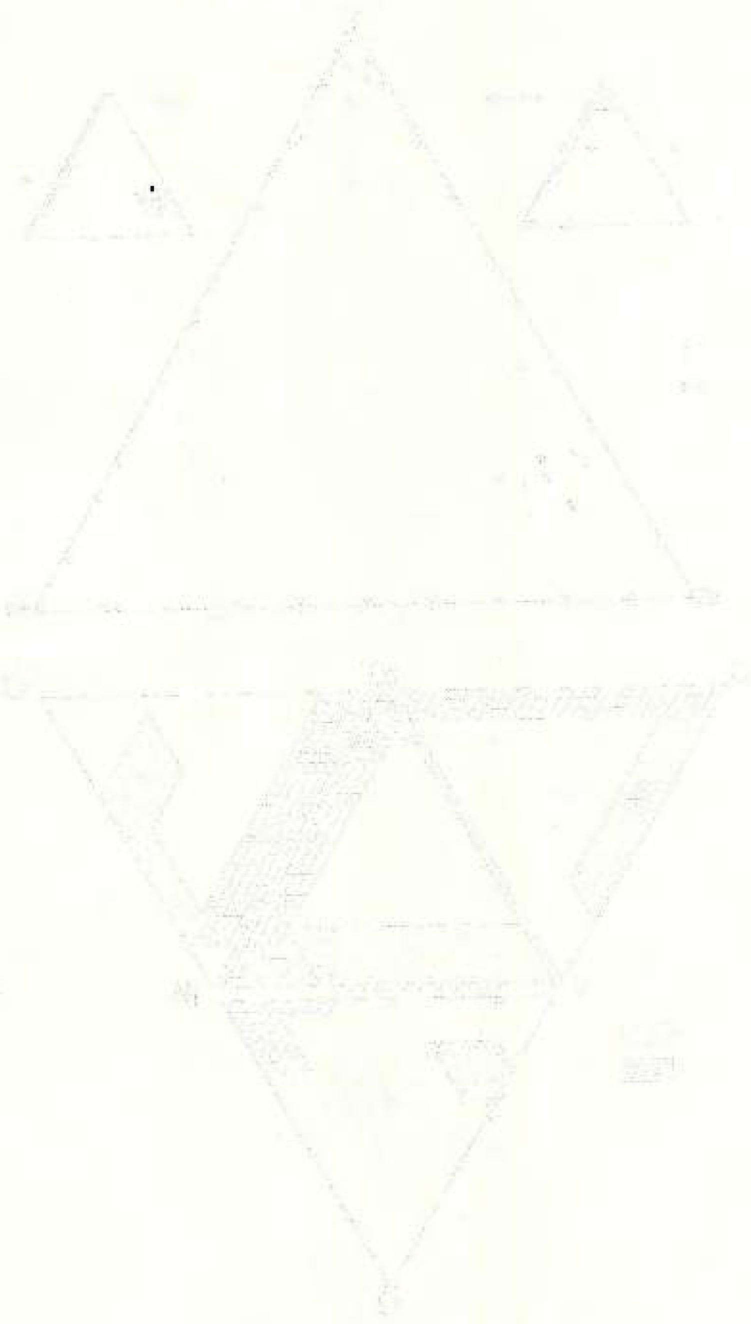

TABLE 1

Minor elements in sulfide monomineral samples (ppm)

No.	Mineral	Cu	Pb	Zn	Ag	Au	Tl	Bi	As	Mo	Mn	Ni	Co	Ti
1 (2)*	Pyrite	210	26	<100	75	65	<30	19	>3 %	<10	48	410	>3000	310
2 (11)**	Pyrite	18000	950	1300	79	60	>30	19	2600	<10	<10	30	15	<30
3 (9)	Pyrite	2500	135	1500	72	36	<10	105	3 %	<10	105	110	1500	<10
4 (8)	Chalco-pyirite	48	—	5200	280	< 3	<10	<10	2500	<10	67	< 3	< 3	<10
5 (13)	Pyrite	6500	16	360	30	<30	<30	<10	3500	16	18	200	260	<30
6 (14)	Pyrite	185	70	<100	33	<30	<30	13	<300	<10	450	140	1100	<30
7 (3)	Pyrite	90	200	<100	5	<30	70	10	300	<10	120	160	24	<30
8	Pyrite	7500	2400	>300	300	<30	<30	180	2800	60	13	70	190	13
9 (6)	Pyrite	800	44	>100	59	48	<30	11	1300	<10	<10	19	2400	<30
10	Pyrite	2100	1200	<100	29	<30	<30	22	24000	<10	<10	22	950	<30
11 (1)	Pyrite	33	<10	<100	< 1	<30	<30	<10	300	<10	<10	13	<10	140
12	Pyrite	530	550	<100	12	<30	<30	60	1400	<10	17	310	650	105
13 (5)***	Chalco-pyrite	—	5	780	300	—	—	—	2700	—	—	—	—	—
14****	Galena	—	—	—	850	—	—	<16	—	—	9	—	—	—

* The numbers in brackets correspond to those from Table 3.

** It contains 48 ppm Cd; the other samples: Cd < 30

*** It contains also 22 ppm Sn and 20 ppm In; bdl: Co, Ni, Mn, Ti, Bi, Tl

**** It contains also 1050 ppm Sb; bdl: As, Te.

TABLE 2

Results of the sulfur isotope analyses ($\delta^{34}S$ ‰)

No.	Analysed mineral	Location	$\delta^{34}S$
1	pyrite (py) [1]	Păscoaia Valley, cataclasation zone	—17.83
2	py	Vulturul Brook waste dump	— 2.81
3	py [2]	Podul Brook	— 2.43
4	sphalerite	Rudăriilor Hillock	— 0.51
5	chalcopyrite (cp)	Tomuş 13 dump	— 0.44
6	py	Tomuş Gallery	+ 2.26
7	cp	Stoianu Gallery waste dump	+ 4.01
8	cp	Stefan Gallery waste dump	+ 4.65
9	py	Stefan Gallery waste dump	+ 4.76
10	arsenopyrite [3]	Rudăriilor Hillock	+ 4.79
11	py	Stefan Gallery waste dump	+ 4.90
12	cp	Iancu zone	+ 9.17
13	py	Stoian Gallery waste dump	+10.16
14	py [4]	Stoian Gallery waste dump	+15.22
15	py [5]	Domide 15 dump	+23.26

[1] Fine-grained pyrite (centimetric lenses) in cataclasites (Căpăţîna Group)

[2] Nests and veinlets within limestones (Sibişel Group)

[3] Nests within black mylonites (Sibişel Group)

[4] Pyrite nests within magnetite amphibolic rocks (Sibişel Group)

[5] Fine impregnations within gneisses (Călinești Formation)

Sulfur Isotopes

The range of the $\delta^{34}S$ values for all the analysed sulfides (Table 2) is extremely wide, from $-17.83^0/_{00}$ to $+23.26^0/_{00}$. The two extremes are represented by samples collected from different environments; the negative maximum is found in the pyrite sample from the cataclasites on the Păscoaia Valley, while the positive one – in a sample in which pyrite appears as a fine impregnation in cataclased gneisses of the Călinești Formation; relatively high values, with a rather excessive amount of the heavy isotope (S^{34}), is recorded in some samples in which pyrite is associated with magnetite from rocks of (sub)itabiritic character (sample no. 14). The values of the other samples range within more restricted limits ($-5.09 \ldots +10.16^0/_{00}$), which are, however, wide enough for not expressing a unitary character of the isotopic abundances of the sulfides from the Valea lui Stan mineralized structure. Owing to the dispersion of sulfides in the samples examined, only in two cases analytical data for pairs of sulfides could be obtained (pyrite/chalcopyrite, samples 8/9 and 7/12 respectively). The differences between the $\delta^{34}S$ values are in both cases either too low or too high in respect of the normal isotopic fractionation. This suggests that the sulfides are not in isotopic equilibrium; as a matter of fact the microscopic observations indicate textural re-equilibration phenomena manifested by intense cataclasations, corrosion relationships among sulfides, local mobilization on mechanical discontinuity planes etc.. Such aspects are obviously induced by intense deformation processes. Thus it is not possible to use the isotopic geothermometer or to estimate the isotopic composition of the total (primary) sulfur. It might be admitted that the great dispersion of the $\delta^{34}S$ values is inherited from the pre-existing mineralizations, probably of different genesis.

Some Data Regarding the Gold Geochemistry

The primary gold source within the Earth Crust is represented by the mafic and ultramafic rocks, generally by the Precambrian greenstone belts, from which gold was subsequently remobilized (Anhaeusser et al., 1969). But not all the rocks of this type may be considered as gold protore, there existing significant regional geochemical differences (Saager et al., 1982). In addition, there are difficulties related to the optical identification of gold in such rocks due to either the very advanced dispersion and the very small dimensions. In such cases it is more correct to speak of "analytical gold", dosed through physico-chemical methods (atomic absorption, neutron activation etc.).

The gold contents in various rock types from the Valea lui Stan mineralized structure are presented in Table 3; relatively great differences are noticed between the gold contents from rocks of various petrography and belonging to various lithostratigraphic units. The relatively high contents within the amphibolic rocks are significant, their role as protore in the formation of the mineralization from this zone being confirmed.

TABLE 3

NAA of some samples from the Valea lui Stan zone

No.	Sample type	Au (ppm)	
		whole rock	magnetic concentrate
1	Amphibolite, Sibişel Group	0,0337	—
2	Garnet amphibolite, Căpăţîna Gr.	0,0446	—
3	Amphibole gneiss, Sibişel Gr.	0,0075	0,0081
4	Amphibolite, Sibişel Gr.	0,0035	0,0041
5	Mylonite, Sibişel Gr.	0,0037	—
6	Bedded gneiss, Călineşti Fm	0,0025	—
7	Biotite gneiss, Căpăţîna Gr.	0,0075	—
8	Migmatized gneiss, Căpăţîna Gr.	0,0019	—
9	Micaschist, Căpăţîna Gr.	0,0037	—
10	Alluvial material, V. lui Stan	0,0013	0,0374

Analyst: S. Anastase, Institute of Geology and Geophysics, Bucureşti

Interpretation of Data. Genetic Model of the Valea lui Stan Deposit

One of the authors of this paper (Udubaşa et al., 1976) has shown since 1976 that the mineralizations from the Valea lui Stan zone cannot be considered as postmagmatic hydrothermal veins, representing in fact a "non-hydrothermal" genetic type which may be defined now as "tectogenetic mineralizations". The arguments supporting this kind of genesis are as follows: (1) the prevailingly lenticular shape of the mineralized quartz bodies (a fact noticed by Petrulian (1936)), which are situated in the mylonitic plane foliation (a remark made by us now); (2) the lack of some eruptive massifs in the vicinity of the mineralized structure; the "Valea Ulii Granites" (Trifulescu, Dragomir, 1969) represent in fact granitic gneisses (Savu et al., 1977; Gheuca, in Lupu et al., 1978); (3) the restricted geochemical spectrum of the mineralization, qualitatively comparable with that of the host rocks; (4) the mineralogical variability of the main metallic elements (Au, Cu, Pb) in the mineralized exposures, often coinciding with a congruent variation of the same elements in the rocks prevailing close to the ore occurrences; (5) the negative correlation between Au and K within the ore, reversed in respect of the hydrothermal gold deposits, such as those in the Baia Mare mining region; (6) the lack of hydrothermal alterations in the surrounding rocks. The observed transformations are due in fact to the mylonitization processes (chloritization, carbonatation — on fissures, sericitization).

Instead of a supposed magmatic source, the gold source is to be found in the amphibolitic rocks, with which thin itabiritic beds are associated. There is a certain geochemical affinity between iron and gold, expressed by the appearance of some background contents of 0.1—0.01

ppm Au, with local concentrations up to 7 ppm Au in the itabiritic iron ores (Sawkins, Rye, 1974); the analytical data presented by Moiseenko et al. (1971) indicate a special affinity of gold for the magnetite within the rocks in respect of the other minerals.

The $\delta^{34}S$ values for the Homestake deposit from North Dakota show a relatively great distribution which supports the multiple sulfur source from this deposit for which Rye, Rye (1974) admit a similar, i.e. non-hydrothermal (in the classical sense) genesis. The occurrence of the mineralizations in the shearing zones is discussed by many authors: Ghosh et al. (1970) for the gold mineralizations from the Ramagiri mining field, Andhra Pradesh, India; Ghosh (1972) for the Cu and U deposits from the great Singhbum shear zone; Petrov (1974) for the gold mineralizations from the Yenissey River region. Rye, Rye (1974) shows that the Homestake gold deposit consists of "conformable substitution bodies in dilatating zones of the strongly deformed Homestake Precambrian formation". The metal source for the "metamorphogene-hydrothermal" deposits is considered to be represented by the volcanic green rocks or the coaly sedimentary ones (Buriak, 1983). Significantly, Bonnemaison (1986) considers "the gold quartz veins as a particular case of the gold shear zones".

The Cu—Au mineralizations from Valea lui Stan can be thus affiliated to a complex metallotect with two components: a passive component, represented by the high gold values of the amphibolic rocks from the Sibişel Group and the Călineşti Formation and an active component (the revealing metallotect, in Routier's sense, 1977), represented by the intense shearing of the rocks from the Sibişel Group and the Călineşti Formation in the double overthrust zone; this overthrust brought about a strong dynamic retromorphism, which determined the circulation of some fluids capable of concentrating the gold dispersed in the amphibolic rocks. The concentration of quartz and gold took place in the dilatation zones of the shearing system, which explains the lenticular shape of the mineralized quartz bodies as well as their disposition and orientation in the plane of the mylonitic foliation. The two components of the Valea lui Stan type metallotect overlapped in an extremely favourable way in the Valea lui Stan zone; the diagonal-directional position of the shear planes with respect to the gold protore led to the growth of the shear amplitude and of the volume of rocks affected by shearing and the dynamic retromorphism and to the formation conditions of the dilatation zones — traps for the silica and metal accumulations.

Silica is a "residual" component of the retrograde metamorphism processes, whereby a "basification" of the rocks is recorded, as a compensation of the silica elimination from the system (Iancu et al., 1980). Beside the metamorphic differentation, by which the formation of the quartz concentrations is generally accepted, Smith (1958) shows that the formation of the quartz concentrations may begin concomitantly with the metamorphism. If a sedimentary rock, which is relatively rich in quartz, is metamorphosed at 500°C and loses cca 2% of its weight in the form of aqueous solutions saturated in silica (the real loss of silica of the initial rock being of only 0.01%), a quartz body of cca 200.000 t may occur in 1 km^3 rock (Smith, 1958).

The Yellowknife gold deposit from Canada occurs in a shear zone affecting amphibolites and consists of lenticular quartz-carbonate bodies; the calculations made by Boyle (1959) indicate that the metals existing in the amphibolic rocks are in sufficient amount to lead, through the mobilization determined by mylonitization, to the formation of the gold ore. "Thus it seems very likely that the major constituents of the shear zones result from the rearrangement and introduction of the material from

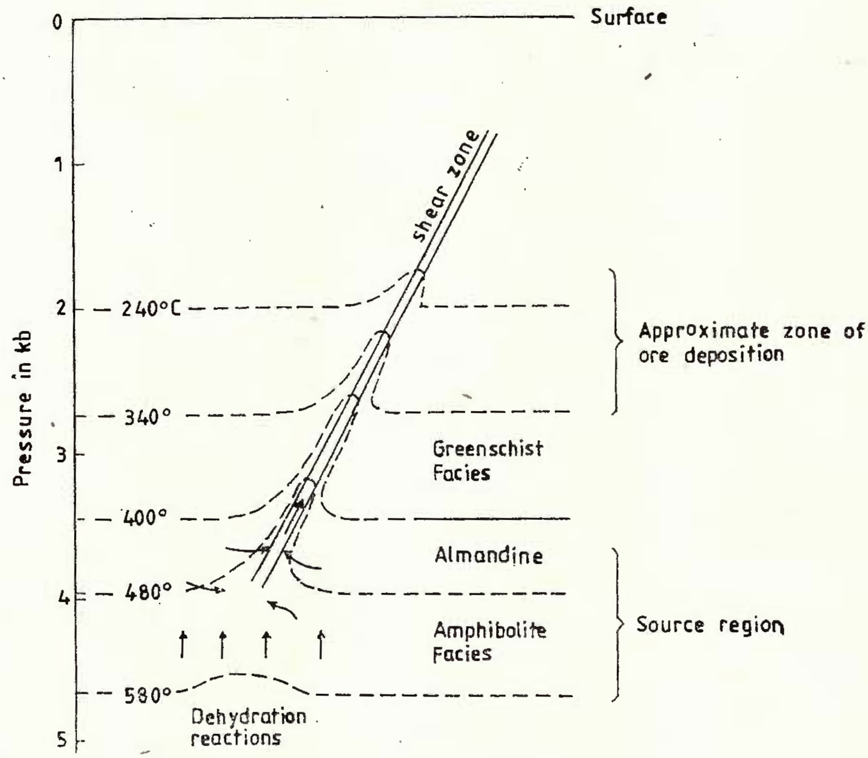

Fig. 9 — Diagram of a shearing zone with approximate position of the ore deposition zone (according to Fyfe and Henley, 1973). The arrows indicate the motion direction of the water originating from the dehydratation reactions. Compare Fig. 5 for location of shear and the associated ore occurrences.

the surrounding rocks" (Evans, 1984). Such a mode of occurrence of the gold concentrations is supported for the Morro Velho deposit in Brazil (Fyfe, Henley, 1973); these authors generalize the idea of the mineralizations connected to the shear zones, deducing by calculations also the probable ore deposition zone (Fig. 9). Helgeson and Garrels (1968) show which is the actual way in which some gold quartz accumulations with 15 g/t Au form, through the extraction of gold by acid solutions from the rocks with only 0.001 – 0.05 ppm Au; the leaching of some oxidic beds, in our case the itabiritic beds associated with the amphibolic rocks, leads to the growth of the oxygen fugacity in solutions, which become capable of extracting gold from the rocks and transporting it towards the dilatation zones of the shear systems at temperatures of about 300°C. The temperature increase on shear planes is supported among others by Oelsner (1960), who points out the possibility of the temperature increase by 100°C as function of the plane dipping, and by Seclăman, Hârtopanu (1985), who show that in extreme cases the temperature increase determined by the retromorphic reactions may be of about 500°C.

Quantitatively the calculations made by Fyfe, Henley (1973) for the Morro Velho deposit indicate an about 30 km³ volume of rocks capable of providing the gold and silica amount from this deposit, starting from a mean of 30 ppb Au in the initial rocks. Calculations made by Udubaşa et al. (1976) for the Valea lui Stan region indicate an about 1 km³ volume of amphibolic rocks necessary for the "tectogene processing" and the appearance of the known mineralizations, starting from an initial gold content in amphibolites of about 0.05 ppm Au.

Conclusions

The Cu–Au mineralizations from Valea lui Stan are considered to be of tectogene nature, having appeared as a consequence of the almost ideal overlapping of the two components of the Valea lui Stan type metallotect. The relatively high gold contents (as compared to the rest of the rocks) within the amphibolic rocks of the Sibişel Group and of the Călineşti Formation were activated by two shear planes superposed in diagonal-directional position on the amphibolitic gold protore. Gold quartz lenticular bodies formed in the new mylonitic plane of the shear system. The rocks were affected by an intense retrograde metamorphism; the gold concentration took place by its levigation from the rocks by the "retromorphic solutions" which are partly mixed with meteoric waters, through diffusion or even gravitational concentration. The mineralization grade of the shear zone is also connected to the intensity of the tectonic compression of the rocks; the mineralization enriches southwards as the compression grade of the Sibişel Group rocks increases; this Group shows the most reduced thickness in the southern part of the zone and of the mineralized structure as a whole.

The above statements show that there may occur mineralizations which are neither syngenetic in a classical sense, nor epigenetic in a postmagmatic sense. The mineralizing process is synretromorphic-synmylonitization, associated with an intense shear zone, probably of long evolution and repeated movement. The efficiency of such a mineralizing process is connected with the optimum superposition of the two components of the metallotect. Moreover, it should be noted that the shear planes do not represent an a priori metallotect. Their metallogenetic efficiency depends on the dip of the shear plane or planes; a too small dip prevents or makes difficult the circulation or movement of the substance, so the possibility of occurrence of dilatation zones being reduced; a too great dip (of the type of normal or reverse faults) leads to the formation of too large "free" spaces that make inefficient the transport mechanism of the substance (prevailingly diffusive in the case of the tectogene mineralizations) or it produces a too great dispersion of solutions, which leads sooner to the dispersion rather than concentration of the ore components. The "mineralizing flux" of the shear zones differs in respect of quantity from that of some hydrothermal systems, supplied by a magmatic source that ensures a "massive import" of components. Therefore the presence of the protore is as indispensable as the movement of the shear planes with a critical dip (probably optimum at 45°C); the directional position of the shear plane adds to the efficiency of the mineralizing process. In conclusion, the tectogene mineralizations do exist, but their formation conditions are quite restrictive.

The most typical, but not the only one, representative in Romania is the deposit from Valea lui Stan; the deposits or occurrences from Someşul Rece, Jidoştiţa and Văliug, the latter being probably magmatically regenerated by banatites i.e. Paleocene granodiorites), seem to be similar by their general structure, mineral assemblages and geochemical features.

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MINERALIZAŢIILE TECTOGENE DE Cu—Au DE LA VALEA LUI STAN, CARPAŢII MERIDIONALI

(Rezumat)

Mineralizaţiile de Cu—Au de la Valea lui Stan sînt considerate de natură tectogenă, apărute ca urmare a suprapunerii aproape ideale a celor două componente ale metalotectului tip Valea lui Stan; pe fondul unor conţinuturi relativ ridicate de aur (faţă de restul rocilor) din rocile amfibolice ale grupului Sibişel şi ale formaţiunii de Călineşti, s-au suprapus două plane de forfecare cu poziţie diagonală-direcţională pe protorul aurifer amfibolic. În sistemul de forfecare au luat naştere corpuri lenticulare de cuarţ aurifer, dispuse în planul milonitic nou creat. Rocile afectate au fost intens metamorfozate retrograd; concentrarea aurului s-a putut realiza prin levigarea acestuia din roci de către „soluţiile retromorfe", parţial amestecate cu ape meteorice, prin difuzie sau chiar prin concentrarea gravitaţională. Gradul de mineralizare al zonei de forfecare este legat şi de intensitatea procesului de comprimare tectonică a rocilor; mineralizaţia se îmbogăţeşte spre sud în paralel cu creşterea gradului de comprimare a rocilor grupului de Sibişel, care în partea sudică a zonei şi a structurii mineralizate în ansamblu are grosimea cea mai redusă.

Argumentele în favoarea originii tectogene sînt următoarele: (1) localizarea corpurilor lenticulare de cuarţ aurifer exclusiv în cuprinsul zonei de forfecare; (2) orientarea lentilelor de minereu în planul foliaţiei milonitice; (3) asociaţia mineralogică relativ simplă a corpurilor de minereu (cuarţ, aur, pirită, arsenopirită, calcopirită + sfalerit, galenă, pirotină); (4) dispersia mare a valorilor $\delta\ ^{34}S$ din sulfuri ($-5{,}09 \ldots +23{,}26^0/_{00}$), (5) conţinuturile de aur relativ ridicate din protorul aurifer reprezentat de rocile amfibolice ale grupului Sibişel; (6) existenţa unor „punţi de legătură geochimică" între roci şi minereu; (6) lipsa unor corpuri magmatice în apropierea structurii mineralizate şi a alteraţiilor de tip hidrotermal în rocile gazdă ale corpurilor de minereu etc.

Datele recente obţinute prin cercetarea unei zone mai extinse situate în lungul rîului Olt (Balintoni et al., 1984; Hann, Balintoni, 1985) arată o structură extrem de complicată, în care sînt implicate formaţiuni metamorfice şi sedimentare de diferite vîrste (Fig. 1). Mai importante pentru crearea structurii mineralizate sînt următoarele unităţi litostratigrafice: grupul Cumpăna, grupul Sibişel, formaţiunea de Călineşti şi grupul Căpăţîna, aparţinînd în terminologia utilizată de Balintoni et al. (1984) multi-grupului Sebeş—Lotru (Cumpăna, Căpăţîna, Călineşti) şi multi-grupului Negoi (Sibişel); grupul Sibişel are o semnificaţie deosebită, reprezentînd echivalentul centurilor verzi din zonele cu mineralizaţii similare din lume.

Grupul Sibişel, reprezentînd protorul aurifer — se caracterizează prin asociaţia amfibolite + gnaise albe cuarţo-feldspatice $\pm$ calcare cristaline, la partea inferioară, şi prin paragnaise cuarţitice şi micacee la partea superioară (Fig. 3), în general intens transformate retrograd. Peste metamorfismul iniţial, probabil proterozoic, realizat la nivelul faciesului amfibolitelor cu almandin, s-a suprapus un metamorfism retrograd, probabil

de vîrstă hercinică, la nivelul șisturilor verzi. Milonitizarea și filonitizarea locală a acestor roci este probabil de vîrstă alpină.

Succesiunea litostratigrafică a grupului Sibișel apare numai fragmentar în bazinul Văii lui Stan, majoritatea entităților petrografice avînd aspect lenticular. Datorită laminărilor extrem de puternice și repetate au luat naștere ultramilonite negricioase, care macroscopic seamănă cu șisturile grafitoase, întîlnite de regulă în zonele unde comprimarea întregii secvențe a fost cea mai puternică.

În lungul Văii lui Stan se cunosc mai multe ocurențe de minereu, concentrate în special în versantul stîng și localizate preponderent în metamorfitele grupului Sibișel, mai puțin în cele ale formațiunii de Călinești sau ale grupului Căpățîna (Fig. 5). În general este vorba de corpuri de cuarț, de dimensiuni extrem de variabile și cu poziție fie concordantă, fie discordantă, totdeauna localizate în metamorfite intens milonitizate. Cantitatea de sulfuri este de cca 3 –5 % din volumul lentilelor de cuarț. În ordinea frecvenței mineralele metalifere identificate sînt următoarele : pirita, arsenopirita, calcopirita, marcasita, sfaleritul, galena ; sporadic apar pirotina (de regulă inclusă în arsenopirită), aurul (inclus în arsenopirită și/sau calcopirită) și minerale secundare (covelină, malachit, anglezit, ceruzit, scorodit, hidrogoethit). Local au fost întîlnite roci cu caracter itabiritic, i.e. roci cuarțitice cu magnetit și/sau hematit, cu care se asociază uneori pirita.

Prelucrarea datelor chimice existente pentru rocile amfibolice din zona Valea lui Stan arată că este vorba de metamagmatite (Tatu, în Udubașa et al., 1985). Rezultatele analizelor chimice, spectrale și prin activare cu neutroni efectuate pe roci au fost proiectate în diagramele din Fig. 7, din care rezultă o corelație pozitivă între Au și Fe_{tot}, negativă între Au și elementele alcaline, pozitivă între Au și Cu și negativă între Au și Pb.

Selectînd cîteva elemente semnificative din analizele de roci și minereuri și proiectîndu-le în diagramele ternare reproduse în Fig. 8 se constată suprapuneri ale cîmpurilor de proiecție ale rocilor și minereului, suprapuneri care pot fi interpretate ca „punți geochimice" între rocile gazdă și minereul aurifer-cuprifer.

Analizele izotopice pentru sulf pun în evidență un interval larg de variație a valorilor $\delta^{34}S$, de la $-17{,}83‰$ la $+23{,}26‰$; rezultatele obținute arată lipsa echilibrului izotopic între perechile de sulfuri, indusă de puternica deformare a minereului ; reechilibrarea texturală a minereului este de altfel ușor de remarcat și prin analiza microscopică, fiind vorba de cataclazare intensă, relații de coroziune între sulfuri, mobilizarea locală pe plane de discontinuitate mecanică etc.

În locul unei surse magmatice presupuse, sursa de aur este de găsit în rocile amfibolice, cu care se asociază uneori nivele itabiritice subțiri. Între fier și aur există o anumită afinitate geochimică, exprimată prin apariția unor conținuturi de fond de 0,1 –0,01 ppm Au, cu concentrații locale pînă la 7 ppm Au în minereurile de fier itabiritice (Sawkins, Rye, 1974) ; din datele analitice prezentate de Moiseenko et al. (1971) rezultă o afinitate deosebită a aurului pentru magnetitul din roci în raport cu alte minerale.

Din cele expuse mai sus rezultă că în anumite condiții este posibil să apară mineralizații care nu sînt nici singenetice în sens clasic, nici epigenetice în sens postmagmatic. Mineralizarea este sin-retromorfă-sin-milonitizare, asociată unei zone de forfecare de intensitate mare, probabil cu evoluţie îndelungată şi cu mişcare repetată. Eficienţa unui asemenea proces de mineralizare este direct controlată de suprapunerea optimă a celor două componente ale metalotectului. În plus, trebuie subliniat un fapt la fel de important: planele de forfecare nu reprezintă *apriori* un metalotect. Pentru a avea această calitate este extrem de importantă înclinarea planului sau a planelor de forfecare; înclinarea prea mică elimină sau îngreunează circulaţia sau mişcarea substanţei şi reduce posibilitatea apariţiei zonelor dilatante; înclinarea prea mare (de tipul unor falii normale sau chiar inverse) creează spaţii „libere" prea mari, care fac ineficient mecanismul de transport al substanţei, în cazul mineralizaţiilor tectogene predominant difuziv, sau se realizează o dispersie prea mare a soluţiilor, ceea ce duce mai degrabă la dispersarea componenţilor utili decît la concentrarea lor. „Flŭxul mineralizant" al zonelor de forfecare este cantitativ deosebit faţă de cel al unor sisteme hidrotermale, alimentate de o sursă magmatică ce asigură un „import" masiv de componenţi.

EXPLANATION OF PLATES

Plate I

Fig. 1. — Subhedral arsenopyrite grains (white) associated with primary marcasite bands. Tomuş Gallery (median part of mineralized zone). Polished section (PS), N II, × 200.

Fig. 2. — Pyrite porphyroblast (?) in a chalcopyrite and fine-grained pyrite matrix. Stoian Gallery (median part of mineralized zone). PS, N II, × 200.

Fig. 3. — Gold (white, "porous"), associated with chalcopyrite (white-grey) in fissured arsenopyrite. Tomuş Gallery. PS, N II, oil immersion, × 500.

Fig. 4. — Euhedral arsenopyrite (white), fissured and cemented with chalcopyrite intergrown with sphalerite (white-grey, respectively grey). Waste dump of the Stefan Gallery (northern part of mineralized zone). PS, N II, × 200.

Plate II

Fig. 1. — Sphalerite (light grey) with numerous chalcopyrite inclusions, developed also as veinlets (white). On the margin of the photo — a pyrite grain (white) wrapped in sphalerite. Stoian Gallery, PS, N II, oil immersion, × 500.

Fig. 2. — Same image, N+ ; false anisotropy effects of sphalerite and twins of polysynthetic type are noticed.

Fig. 3. — Gold (white) included in sphalerite (grey), associated with chalcopyrite (grey white), all included in arsenopyrite. Waste dump of the Stefan Gallery. PS, N II, × 200.

Fig. 4. — Same image, with N+ ; in the position of not perfectly crossed nicols gold becomes evident, the effects of anisotropy of arsenopyrite being noticed, as well.

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2. ZĂCĂMINTE

THE METAMORPHOSED COPPER–NICKEL MINERALIZATIONS FROM THE VÎLSAN VALLEY, FĂGĂRAŞ MOUNTAINS [1]

BY

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ION GHEUCA [2], IOAN DINICĂ [2]

Cu, Ni, Precambrian. Metamorphics. Mineral assemblage. Lithostratigraphy. Gabbroic rocks. Pyrrhotite pyritization. Sulphur isotopes. Pentlandite. Violaritization. South Carpathians — Getic and Supragetic crystalline domains — Făgăraş Mts

Abstract

The Cu–Ni mineralization is hosted by Precambrian polymetamorphic rocks including a lenticular gabbroic rock sequence. The mineral assemblage is complex, comprising about 20 ore minerals, among which pyrrhotite, chalcopyrite and pentlandite prevail, while cobaltpentlandite, tochilinite and millerite are found in small amount. The transformations within the ore, on the whole correlable with the metamorphic deformations, are marked especially by the pyrrhotite pyritization and pentlandite violaritization. Graphite, zoned spinels, ilmenite and rutile are found both in the gabbroic rocks and within the ore. A last mineralization phase, represented by pyrite and calcite, differs from the regionally metamorphosed ore, by the morphological, geochemical and isotopic characteristics, being probably formed in connection with late solution circulations on fractures. The sulfur isotopes indicate a wide range of the $\delta^{34}S$ values (+2.09 ... +23.59 $^0/_{00}$) depending on the variable regime during the metamorphic deformations and on the stratigraphic location of the analysed samples.

Résumé

Les minéralisations de Cu–Ni metamorphisées de la valée Vîlsan, monts Făgăraş. La minéralisation de Cu–Ni est localisée en des roches polymétamorphiques précambriennes, comportant une séquence de roches gabbroiques à développement lenticulaire. L'aassociation des minéraux est complexe et comporte approximativement 20 minéraux métallifères, dont la pyrotine, la chalcopyrite et la pentlandite sont dominantes, tandis que la cobaltpentlandite, la

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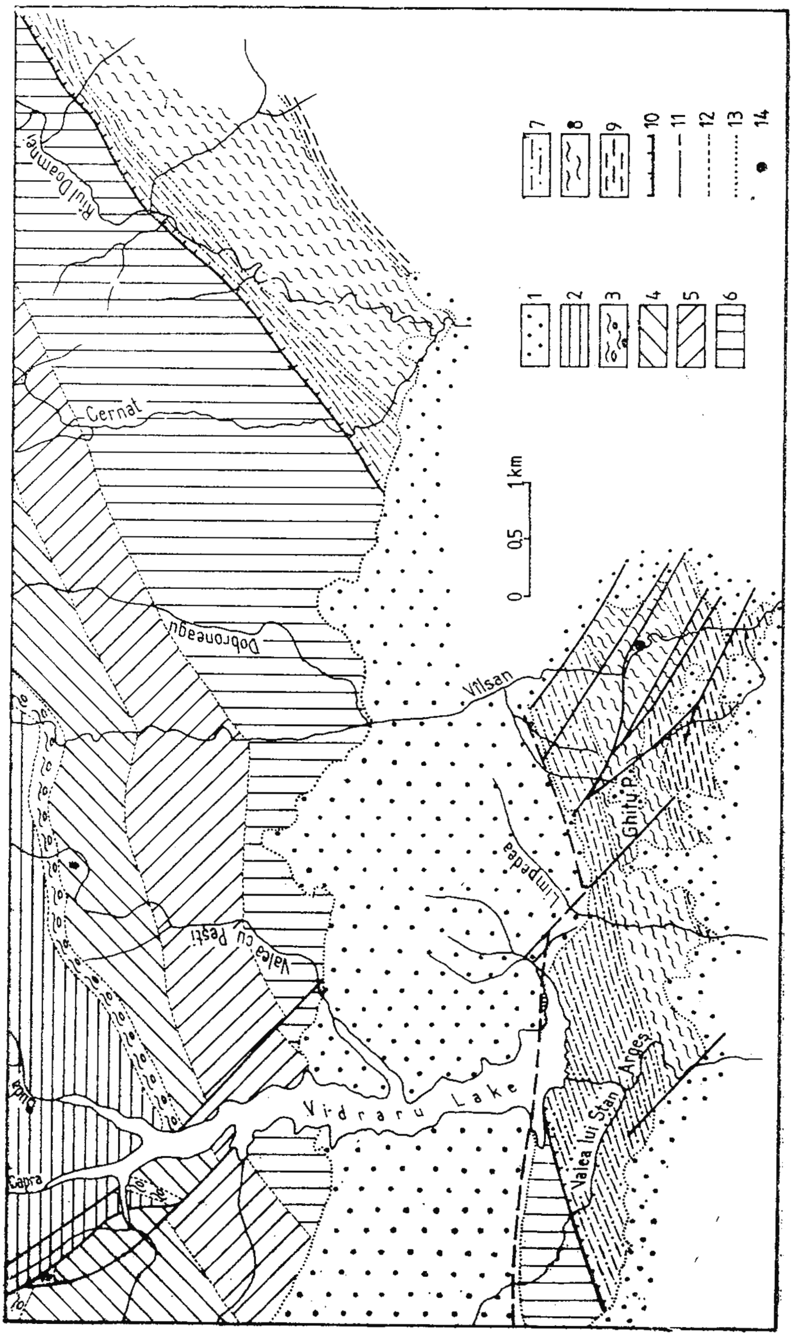
Rîul Doamnei
Cernat
Dobroneagu
Vîlsan
Valea cu Peşti
Limpedea
Ghitu P.
Argeş
Valea lui Stan
Vidraru Lake
Capra
Buda
0
0.5
1km
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Fig. 1

tocilinite et la millérite sont des minéraux très rares. Les transformations qui ont lieu dans le minerai, corrélables en grandes partie avec les déformations métamorphiques, se caractérisent spécialement par la pyritisation de la pyrotine et la violaritisation de la pentlandite. Le graphyte, les spinelles zonés, l'ilménite et le rutile apparaissent tant dans les roches gabbroïques que dans le minerai aussi. Une dernière phase de minéralisation, représentée par la pyrite et la calcite, s'individualise dans le minerai métamorphosé régionalement, étant engendrée probablement par les circulations tardives de solutions sur les fractures. Les isotopes du soufre indiquent une dispersion assez grande des valeurs $\delta^{34}S$ (+2,09 ... +23,59 $^0/_{00}$) par rapport au régime variable pendant les déformations métamorphiques et à la localisation stratigraphique différente des échantillons analysés.

There are few occurrences of nickel minerals in Romania, most of them being found in Precambrian, Paleozoic and Alpine ultramafic rocks (Southern Banat, Poiana Ruscă—Vadu Dobrii, Eastern Făgăraș Mountains, Ciungani etc.). They appear especially as disseminations, rarely nests or short veinlets. Nickel minerals occur also in the Leaota Mountains as part of some complex, pentametallic mineralizations, genetically differing from the above-mentioned ones. The only nickel occurrence identified so far in metamorphosed gabbroic rocks is the one from the Vîlsan Valley, which exhibits also the most complex mineral assemblage. These mineralizations will be dealt with in the present paper.

Previous Investigations

The mineralization from the Vîlsan Valley has been known since 1965 as pyrite occurrence in amphibolites, being very discontinuous and of limited development in the old mine. Its investigation was resumed after the identification by Pitulea, Arion (1966) of nickel pyrrhotite and frag ments of mineralized amphibolites in the Cheia Valley (Fig. 1). The work carried out by IPEG Argeș since 1984 have outlined the mineralizatio over several hundred meters, although over the first tens of meters only

Fig. 1. — Geological sketch of the southern slope of the Făgăraș Mountains between the Argeș Valley and Rîul Doamnei Valley (I. Gheucă, I. Dînică). 1, Sedimentary formations (Upper Cretaceous-Quaternary); 2—9, Precambrian metamorphic formations; 2—6, Cumpăna Group: 2, Topolog Formation (paragneisses, ocular gneisses, amphibolites, micaschists); 3—5, Cumpăna Formation: 3, Iedu Subformation: Lespezi gneisses; 4, Muntele Lăcșor Subformation; Bolovanu Valley amphibolites, paragneisses, ocular gneisses: 5, Colții Cremenii Subformation: linear gneisses; 6, Cozia Formation: ocular gneisses, paragneisses, amphibolites; 7—9, Leaota Group; 7, Iezer-Păpău Formation: micaceous paragneisses, micaschists; 8, Mioarele Formation: biotite paragneisses, ocular gneisses, amphibolites; 9, Vidraru Formation: white linear gneisses, amphibolites, paragneisses; 10, overthrust plane; 11, fault; 12, lithostratigraphic boundary; 13, transgression boundary; 14, ore occurrences.

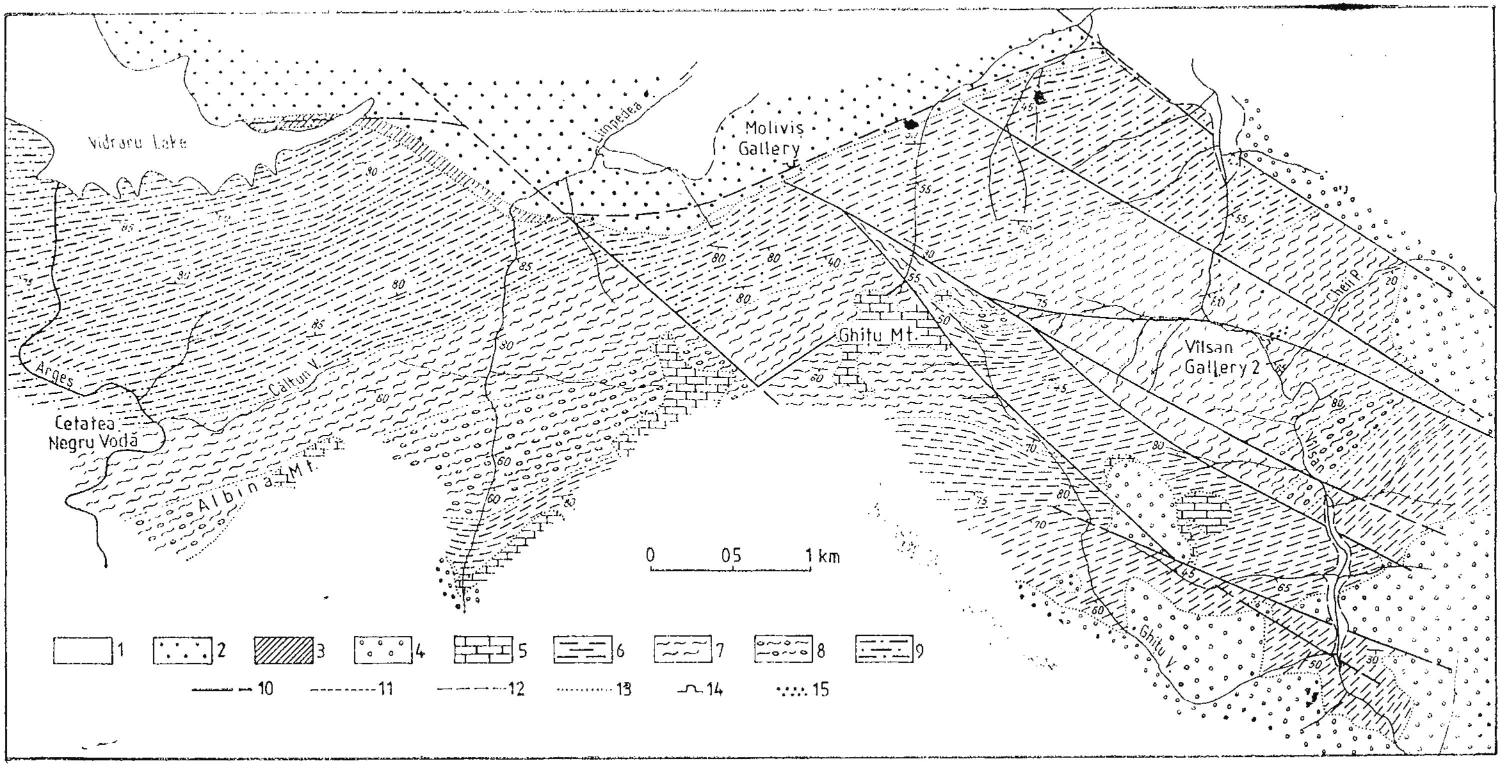
Vidraru Lake
Limpedea
Molivis Gallery
Vilsan Gallery 2
Vilsan
Cheii P.
Ghitu Mt.
Ghitu V.
Argeș
Cetatea Negru Vodă
Călțun V.
Albina Mt.
0 05 1 km
1
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Fig 2

the unmineralized and intensely tectonically fragmented host formation had been intercepted (Fig 2). The data on the exploration works provided by the geologists I. Popescu, I. Pascu, Constanța Caravețeanu and I. Sitaru — IPEG Argeș indicate that the mineralization is discontinuous, varying in thickness and metal contents. The mineral assemblages, which are very complex and in most cases non-paragenetic, formed during several stages that can be partly related to the main moments of metamorphic deformation; the studies made by the authors of the present paper are concerned with such aspects attempting at the same time to depict the premetamorphic features of the host rocks.

Structure and Lithostratigraphy of the Metamorphics in the Vîlsan Valley Zone

Lithostratigraphy

As regards the late (Neozoic) tectonics the metamorphics from the Ghițu massif belong to the Cozia horst. They have been so far assigned either to the "Cozia Crystalline" (Streckeisen, 1934) or, more recently, to the Cumpăna Series (group) (the last time in Balintoni et al., 1986 and in Dimitrescu et al., 1985, by H. Hann). Gheuca (unpublished data) attributes these metamorphics to the Leaota Group based on lithological and lithostratigraphical arguments and on structural considerations. The description of the formations will be made accordingly. Dimitrescu (1978 a, 1978 b) separates for the first time at the base of the Leaota Group the Mioarele paragneiss complex and the Iezer—Păpău micaschist complex. After the delimitation of the tectonic boundary between the Cumpăna and Leaota Groups in the Rîul Doamnei Valley (Balintoni, Hann, Gheuca in 1983) as well as west of the Argeș River (Gheuca, unpublished data), it has been pointed out that the leucocratic gneisses assigned by Dimitrescu (in Dimitrescu et al., 1978) to the Cumpăna gneiss complex, belong in fact to the Leaota Group, for which the name of Vidraru is proposed as lithostratigraphic unit. The relationships with the sedimentary deposits as well as the retromorphism manifested throughout this group lead us to the idea of a normal pile in which the lithostratigraphically lower metamorphics extend north-westwards (Figs. 1 and 2).

Fig. 2 — Geological map of the zone between the Argeș Valley and Vîlsan Valley (I. Dinică, I. Gheucă). 1, Quaternary (terrace deposits, alluvia); 2—3, Lower Miocene: 2, conglomerates, sands; 3, Sărata Gypsum (gypsum, marly clays, sandstones); 4, Ypresian-Paleocene: conglomerates; 5, Upper Senonian (limy sandstones); 6—9, Precambrian metamorphic formations (Leaota Group); 6, Iezer-Păpău Formation: micaschists, micaceous paragneisses; 7—8, Mioarele Formation: 7, biotite paragneisses, amphibolites (a), white gneisses; 8, ocular gneisses; 9, Vidraru Formation: linear gneisses, amphibolites (a), paragneisses, ocular gneisses; 10, fault; 11, lithostratigraphic boundary; 12, boundary of Quaternary formations; 13, transgression boundary 14, gallery; 15, ore occurrence.

Vidraru Formation. This formation, which is the deepest part of the Leaota Group, develops between the Vîlsan and Argeş Valleys on the northern slope of the Ghiţu massif. It comprises in its basal part (Lupu Brook dam) a band of ocular gneisses, followed by plane-parallel paragneisses and amphibolites. Next come granular or linear leucocrate gneisses, in places with smoaky bluish quartz, called in Dimitrescu et al. (1985) the Colţii Albinei gneisses. They make up a few hundred meters long band, which is frequently interbedded with amphibolites, amphibolic gneisses or biotite paragneisses. They develop in the Argeş Gorges between the confluence with the Stan Valley and the Poenari fortress (of Vlad Ţepeş) and extend eastwards displaying a few dextral slips up to the northern end of the Vîlsan Gorges. The assemblage of white (linear) banded gneisses, amphibolites and biotite paragneisses overlying the sedimentary deposits of the Loviştea Depression is found again in the Cernat Valley.

Mioarele Formation. There follows a plane-parallel sequence of paragneisses (plagiogneisses) with biotite (±) amphibole, with oriented minerals that give a characteristic linear aspect to the rock. Hann (in Dimitrescu et al., 1985) calls them Ghiţu paragneisses, attributing them to the Cumpăna Group. The amphibolite intercalations they contain are metric in size, so that only a very detailed mapping might provide information on their continuity. The mineralization from the 2 Vîlsan Gallery is associated with an amphibolite band whose continuity over a several hundred meters interval has been proved in this way. There follow small-sized white gneisses or augen gneisses that overlie these paragneisses (plagiogneisses). The whole sequence is only slightly (and irregularly) affected by retromorphism phenomena.

Iezer Păpău Formation. This formation has been separated also by Dimitrescu (1978), consisting of garnet micaschists with rare thin amphibolite interbeds. These micaschists often contain also albite porphyroblasts (pointed out by Manilici since 1955), which constitutes an additional argument in favour of their assignation to the Leaota Group.

We assign (with a degree of uncertainty) the micaceous paragneisses and micaschists cropping out in the southernmost part of the Vîlsan Gorges to this series. These rocks are generally blackish as a result of retromorphism and of an advanced chloritization respectively. They often contain plagioclase or garnet porphyroblasts, the latter being frequently chloritized. The rocks of this formation, especially the micaschists, exhibit a characteristic crenulation lineation. The amphibolite and gneiss intercalations are subordinated.

Tectonics

According to the new interpretation, the metamorphics from the Ghiţu massif form part of the Dîmbovicioara Nappe (Săndulescu, 1976; Balintoni et al., 1986). The metamorphics form an ENE—WSW trending monocline, highly inclined southwards. A fault system striking NW—SE affects both the metamorphics and the Upper Cretaceous—Paleogene sedimentary deposits. This fault system can be correlated over the Loviştea Depression with the Cumpeniţa—Scara Fault, figured in the Cumpăna Sheet (Dimitrescu et al., 1985) with a dextral slip of about 4 km.

On the northern slope of the Ghiţu massif Lower Miocene sedimentary deposits — Sărata gypsum, then conglomerates, overlie transgressively both strongly tectonized metamorphics and (immediately north of the Ghiţu Peak) Upper Cretaceous sedimentary deposits (limy sandstones) trending northwards. This situation may be interpreted admitting that the Cozia Fault (figured so far in the north of the Ghiţu massif) is Upper Paleogene in age and therefore overlain by Miocene sedimentary deposits.

Metamorphic Evolution of the Amphibolic Rocks in the Zone of the 2 Vîlsan Gallery

The amphibolic rock body on the Vîlsan Valley which hosts the copper-nickel mineralizations shows a remarkable continuity towards the east, being exposed directionally through the main gallery. The adjacent metamorphics are monotonous, showing a unitary lithology and having no index minerals.

The metamorphic rock sequence on the Vîlsan Valley represents a tectonite characterized by a well-marked foliation (through planes of mechanical discontinuity or planes of lithological banding) and another, more attenuated foliation, visible only in incompetent rocks that generates together with the former foliation an intersection lineation or, sometimes, crenulation folds. Some rock types (stromatito-ophtalmites) do not exhibit a visible S and even when this plane is evident it does not represent a mechanical discontinuity.

On a mesoscopic scale amphibolites show conformity relationships with the other formations, mechanically differing from them by the varied competence degree and implicitly the different penetrability of the S planes that formed during various deformation periods. When more micaceous, plagiogneisses preserve the textural record of two deformation stages : a principal S plane, which is quite visible, and the above-mentioned crenulation plane, whose position differs from that of the older plane.

Like the amphibolites, the ophtalmitic migmatites often exhibit a characteristic massiveness, that can be explained by the strong syn- and postkinematic blastesis of the potassium feldspar. The massiveness of the amphibolites is due to some more complex causes. First of all, it is due to the non-penetrability of the principal S planes which do not seem to have acted in such cases of competence degree ; secondly, it is due to a possible amphibole neoblastesis. The polyphase character of the evolution of the rocks in the zone is difficult to establish probably because of a strong adaptability of the component minerals and because of the long period of time in which the structural and mineralogical re-equilibration of the rocks involved could have taken place.

The mineralogical composition of the amphibolic rocks is rather constant, being represented by amphibole (green hornblende), chlorite, biotite, plagioclase ± quartz, zoisite ± carbonate ± garnet and accessory minerals such as sphene, apatite, ilmenite, rutile, zircon. Pyrrhotite and its associated sulfides may sometimes be prevailing minerals within the rock.

The texture is massive or foliated, the grain arrangement being often isotropic or nematoblastic.

Amphiboles appear as large crystals; they can rarely form a microcrystalline structure, displaying small-sized grains. In most cases the central zone of the amphibole crystals is full of inclusions, being bounded by a clear border. The inclusions show sometimes a regular, parallel disposition, marking a paleotexture (S_1) which is unconformable with respect to the foliation plane. There seems to be a succession relation between the central zones with inclusions and the marginal ones, as in some cases a difference in the position of the extinction angles (about 5°) may be noticed.

The relationships between amphibole and the other minerals within the rock are represented by equilibrium textures which, as a matter of fact, mask the succession relations existing among various minerals. However, amphibole corrosion by quartz can be easily observed. The relationships between amphibole and sulfides seem to be of synchronous formation, which might suggest synchronous recrystallization. As amphibole inclusions were noticed in the sulfide aggregates or sulfide inclusions in the amphibole aggregates, it may be assumed that one or the other of the two minerals formed previously.

Biotite appears as small crystals as compared to amphibole or chlorite, being associated with the latter. It contains orthite or other undeterminable fine-grained radioactive mineral inclusions that generate a pleochroic aureole and may include clinozoisite. The cleavage planes of biotite are often pointed out by the opaque minerals.

Chlorite usually appears as large crystals associated in bands or nodules, but may be also unassociated, coexisting with amphibole or biotite, joined to them or in an unconformable position with respect to the orientation of the crystals. It is uniaxial or biaxial with very small $+2V$, with a grey-olive first order birefringence colour. These optical characteristics are similar to those of the magnesian chlorites. The chlorite dimensions generally exceed those of biotite, its amount prevailing in most cases. Like biotite, chlorite includes very fine crystals of radioactive minerals with pleochroic aureoles, which might demonstrate its origin from the former minerals. Chlorite sometimes contains also sphene or zoisite. Chlorite shows much more rarely an anomalous (bluish) birefringence colour characteristic of penine.

Chlorite also occurs as veinlets generally penetrating the less compact or more incompetent rocks. A characteristic example is that of chlorite veinlets within carbonate, which would demonstrate the previous formation of the latter or more exactly the long period of chlorite growth. The laboratory experiments are in agreement with the field observation as to the existence of a large interval of chlorite-quartz compatibility, especially in the lower metamorphism grades.

Unlike the other minerals of amphibolic rocks, chlorite is the only one showing signs of deformation (except for quartz) in the form of kink folds. It is supposed either that chlorite is the only mineral which was affected by the deformation that determined the S crenulation or that it was autodeformed by the growth in an imposed environment.

Zoisite (clinozoisite) is present in the amphibolic rocks either as fine needles included in the newly formed minerals, or as large crystals close to amphibole in size. It may also appear as small conformable lenses associated with quartz. Sometimes a zoisite crystal group exceeds the present limits of a crystal including this group. This is the proof of a remarkable recrystallization of the rock in solid state, leading to the change of the former textures. It is the case of the formation of a quartz-feldspathic mosaic over a former crystal outline represented by an agglomeration of zoisite crystals. The mineralogical and structural neoformation of the rock may indicate the recurrence of metamorphic phases.

Carbonate is often found, but in small amounts, appearing as bands in the amphibole. Sometimes the banding is achieved by the alternation of the carbonate, chlorite and amphibole bands. Finally there are cases in which carbonate replaces zoisite or constitutes the border of the chlorite nodules.

Plagioclase of andesine composition is polysynthetically twinned or diffusely zoned. The zoning may contain either an acid term or a more basic term towards the margin of the crystal.

Garnet is quantitatively subordinated and it is not found in the massive amphibolites, but only in the marginal amphibolic plagiogneisses that might be considered an amphibolic term contaminated with the neighbouring crystalline. Implicitly garnet is exclusively metamorphic, being formed simultaneously with neoformation amphibole and chlorite.

Mineralization from the Vîlsan 2 Gallery and Adjacent Zones

This mineralization is hosted by the above described sequence of metamorphics (Fig. 3). It forms tabular or lenticular bodies varying in size. The concentration degree of the metalliferous minerals is extremely non-uniform. Macroscopically pyrrhotite and pyrite, sometimes chalcopyrite, were observed within the ore, the latter being visible especially when it appears as unconformable millimetric veinlets. The first two sulfides form both compact masses and dissemination zones, often found also in the gneissic rocks. The relatively homogeneous aspect of the mineralization, which is as a rule conformably disposed with respect to the S plane in the prevailingly amphibolic metamorphic rocks, is disturbed sometimes by the occurrence of some unconformable decimetric carbonate and pyrite bodies, in which cockade structures are often observed. As will be further shown, pyrite of these unconformable bodies differs from the pyrite of the stratiform ore both as regards the minor element content and the sulfur isotopic composition. The compact ore includes sometimes also some mm thick pyrite veinlets of limited extension which do not differ geochemically and isotopically from the pyrite in the ore bands parallel to the metamorphic S.

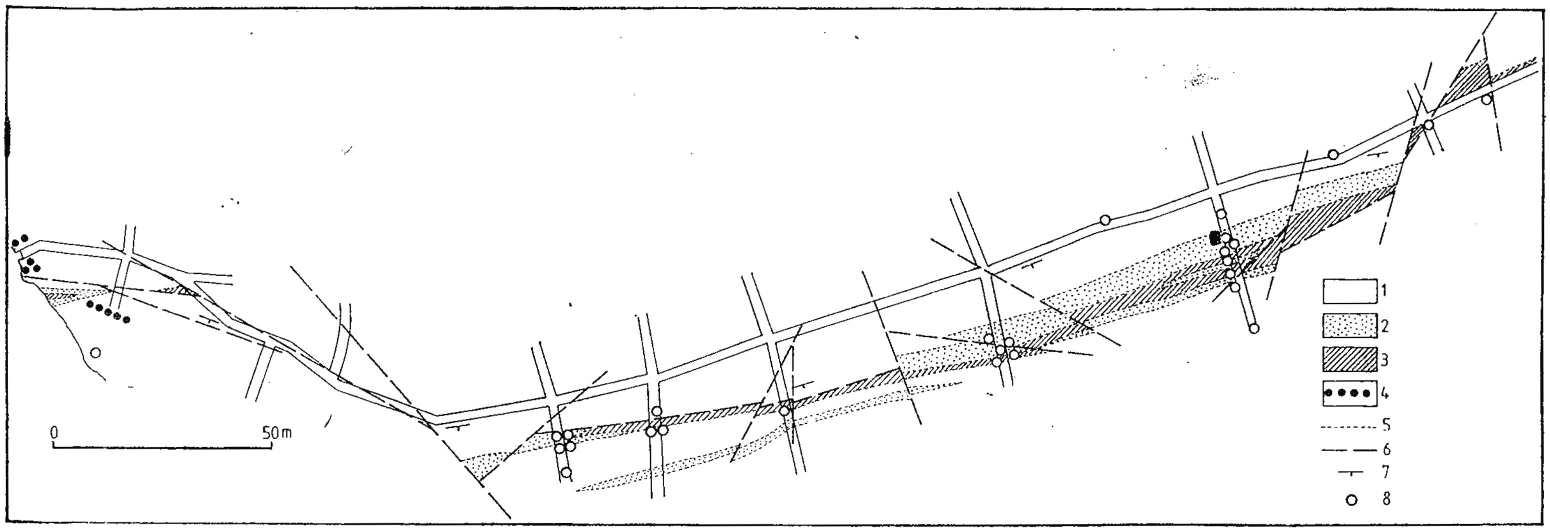


Fig. 3. — Sketch of the Vîlsan Valley gallery 2 (according to the data provided by the geological team ÎPEG Argeş), simplified. 1, Quartz-feldspathic gneisses; 2, amphibolites; 3, ore; 4, amphibolites and/or gneisses with disseminated mineralization; 5, geologic boundary; 6, fault; 7, foliation position; 8, analysed samples.

Mineralogical Composition of the Ore

The microscopic study of a great number of polished sections (about 100) proves that the mineralization is diverse, but the microscopic components are present in various amounts. On the whole the minerals may be grouped as seen in Table 1.

TABLE 1

Identified ore minerals

chalcopyrite pyrrhotite	major primary components
ilmenite rutile sphene	present both in the mineralized levels and at those devoid of sulfides
chrome-spinel pentlandite graphite	less frequent primary components
pyrite violarite millerite mackinawite bravoite marcasite magnetite	minerals formed at the expense of primary components by transformation or exsolution
cobaltpentlan-dite molybdenite gold tochilinite	rare, partly primary, minerals of uncertain position within the succession
mineral C goethite	secondary nickel-bearing minerals

Beside these, some other small-sized sporadic (only one grain) minerals were noticed, which could not be specifically identified; one of them seems to belong to the platinum group.

The distribution of the main minerals (pyrrhotite and pyrite) is non-uniform. The compact ore contains prevailingly pyrrhotite, while pyrite prevails in the dissemination zones. It should be noted that pyrite does not represent a primary component of the (initially magmatic) paragenesis, being formed at the expense of pyrrhotite, probably during metamorphism. The main argument is based on observation and consists in the presence of numerous pyrrhotite and magnetite relicts within pyrite (a general situation, except for pyrite within the mentioned carbonate and pyrite veins); in such mineralizations, formed at magmatic temperatures, pyrite cannot form directly, being unstable at temperatures exceeding 743°C — critical thermal point of pyrite — above which it disappears incongruently; the pressure growth leads to the increase by only a few degrees of the pyrite stability field.

Pyrrhotite forms compact aggregates consisting of lamellae which are sometimes twinned; as a rule it is associated with pentlandite; lamellar marcasite develops frequently on the pyrrhotite cleavage; ovoidal or euhedral pyrite grains form further on such aggregates. Within the massive ore pyrrhotite often contains pentlandite grains, more rarely cobalt-pentlandite grains (which differ from pentlandite by their higher reflectivity and less pronounced cleavage). The pyrrhotite : pentlandite ratio ranges round 8 :2, this value being also found in the grains included in the amphiboles from the weakly mineralized zones; this ratio may be thus considered to represent the composition of the initial monosulfide solid solution by the crystallization of which pyrrhotite and pentlandite formed.

Granular pentlandite rarely remains as such, being transformed into violarite quasi-simultaneously with the pyrrhotite marcasitization and pyritization; in such cases the exsolution pentlandite, present as flames in the pyrrhotite mass, remains unchanged; but it disappears when pyrrhotite changes into pyrite.

Spinels usually appear as euhedral, often zoned grains, dispersed in silicates or included in pyrrhotite; but their occurrence is not constant, being found especially in the zones with compact ore. The relationship with pyrrhotite is generally of juxtaposition : spinels are included in pyrrhotite, but may also contain pyrrhotite inclusions. Substitution effects can only be observed when spinels contact directly pyrite, which sometimes penetrates the fissures. Spinels seem to be more strongly zoned when they are associated with sulfides. Numerous spinel grains contain fine rutile inclusions (associated in a few cases with ilmenite) formed through exsolution from an initial titanium rich spinel. The optical properties (dark grey colour, lower reflectivity than that of magnetite, brown-reddish internal reflections) suggest that they belong to the chrome spinel group.

The titanium minerals (ilmenite, rutile, sphene) are very frequent in most samples examined, although they are non-uniformly distributed; ilmenite lamellae or grains, with or without sphene rims are as a rule found in the slightly mineralized barren rocks; the ilmenite frequency decreases close to or in the mineralized zones themselves, the ilmenite-sphene aggregates being replaced by sphene-rutile aggregates; the latter replace ilmenite within the sphene aggregates or grains. Pyrrhotite inclusions are sometimes observed within ilmenite, which remain sometimes also in the rutile mass. Besides granular aggregates of titanium minerals, especially rutile and sphene, acicular inclusions of the same minerals are almost frequent in the amphibole mass, suggesting their formation through exsolution from the initially rich-titanium silicates.

Graphite was noticed in most samples examined, both in rocks without sulfides, where they appear as fine lamellae showing normal optics, and in the mineralized zones, as almost isometric aggregates, in which the lamellae show sometimes a regular disposition imitating the cross extinction. From the morphological point of view such aggregates resemble the graphite paramorphoses after diamond described from the garnet pyroxenites (Slodkevich, 1982). The presence of graphite is in fact known in numerous mafic or ultrabasic magmatic complexes, being preferentially concentrated in the cummulates of the layered plutons (Bushveld, Stillwater, Osirabetsu; Boyd, Mathiesen, 1979). The graphite at Valea Vilsanului is closely associated with the sulfides, seemingly cemented by them; the graphite optics is generally slightly modified, especially in the last mentioned cases, when brown-reddish tinges and dark yellow anisotropy colours appear; considering the graphite chemical stability, it is possible that these slight anomalies be due to some submicroscopic impurities; it is also possible that some fine lamellae, showing an anomalous optics, should represent a mineral from the valeriite group (minerals with layered lattice), characterized by the alternation of the sulfide layers/subnetworks with the brucite type layers/subnetworks; in the present case the presence of haapalaite is presumed, a mineral having the formula of the type $Cu_nNi_mFe_p$ (Mg, Fe) $(OH)_2$.

Pyrite is a major component of the mineralization, being present in various amounts — in most analysed samples; pyrite distribution shows a compensatory character with respect to pyrrhotite, at the expense of which it forms. Pyrite contains as a rule pyrrhotite and/or magnetite inclusions, in most cases of microscopic size; locally the intermediate transformation pyrrhotite-pyrite product (the so-called Zwischenprodukt or intermediate product) was also noticed, through which pyrrhotite grades, by the increase of the sulfur fugacity and the setting of a slightly oxidizing environment, to the more stable compound under such conditions — pyrite; during this transformation magnetite may occur as intermediate reaction product, being as a rule intergrown with pyrite; it is a secondary magnetite, present in most ores containing pyrrhotite (Herja, Ţibleş, Rodna etc.). Pyrite within the unconformable veins contains also pyrrhotite relicts and secondary magnetite inclusions, thus suggesting that they formed through the local mobilization of pyrrhotite, which was subsequently pyritized through migration in solid state. The pyrite within the discordant carbonate+pyrite bodies is an exception to this rule, being characterized also by the scarcity of minor elements and especially by the sufur isotopic composition, clearly distinguished from the stratiform pyrite.

Violarite occurs frequently, its formation being connected with the pentlandite transformation, which is more frequent in the portions with poorer ore (of dissemination type) or in the zones in which pyrrhotite changes into marcasite and/or pyrite. The transformation takes place gradually, violaritization beginning from the periphery of the grains or from the cleavage planes of pentlandite. Violarite is brown-reddish with slightly violaceous shades, and the hardness is close to that of pyrrhotite. Violarite is sometimes associated with small millerite patches (light yellow, intensely anisotropic). Extremely fine mackinawite lamellae occur very rarely in the violaritized pentlandite mass (with strong bireflection and intense anisotropy effects), that formed by èxsolution from pentlandite. Violarite is generally inhomogeneous due to the subsequent transformations, manifested first of all by the occurrence of some pyrite grains or short lamellae, which sometimes form skeletal crystals, marking the formation of pyrite or bravoite; the matrix of these micrograins or lamellae gradually changes into a grey-brownish mass of amorphous appearance, probably representing a secondary nickel mineral (mineral C); this transformation stage is as a rule reached when the whole pyrrhotite mass is pyritized. The violarite identity was checked by the X-ray diffraction (Table 2).

TABLE 2

*X — ray powder data for violarite**

Diffractomer, CuKα radiation, Ni filter

Violarite		Pyrrhotite		Violarite		Bravoite		Pyrite	
Vîlsan Valley		ASTM 20—535		ASTM 11—95		ASTM 2—850		ASTM 6—0170	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
5.85	vw ?	—		—		—		—	
—		—		5.47	20	—		—	
4.70	vw ??	—		—		—		—	
3.90	vw ?	—		—		—		—	
3.36	w	—		3.35	30	—		—	
—		—		—		3.22	10	—	
—		—		—		—		3.12	35
—		—		—		3.09	10	—	
2.98	s	2.98	40	—		—		—	
2.86	w	—		2.85	100	—		—	
—		—		—		2.78	100	—	
2.71	w	—		—		—		2,71	85
2.64	ws	2.65	60	—		—		—	
—		—		—		2.49	50	—	
2.43	w	—		—		—		2.42	65
2.33	w	—		2.36	50	—		—	
—		—		—		2.27	25	—	
2.215	w	—		—		—		2.22	50
2.055	s	2.07	100	—		—		—	
—		—		—		1.97	25	—	
—		—		—		—		1.91	40
—		—		1.82	60	—		—	
1.74	w ?	—		—		—		—	
1.718	s	1.72	20	—		—		—	
1.670	w	—		1.674	80	1.68	75	—	
1.630	w	—		—		—		1.63	100

* The analysed material contains both pyrrhotite and violarite or violaritized pentlandite. However, no peaks typical of bravoite do occur.

? Peaks attributable to pentlandite

?? Peaks attributable to chrome spinel.

The identifiable bravoite has been noticed in association with pyrite, mostly with that from the discordant veinlets, in which there occur brown violaceous zones, parallel to the pyrite crystal faces. The presence of bravoite is assumed also in the fine-grained aggregates developed at the expense of violarite, but it is not identified with certainty due to its small dimensions.

Marcasite obviously occurs in two distinct stages of the ore evolution; the first stage is represented by the formation of the marcasite lamellae more or less directly at the expense of pyrrhotite; the second stage is characterized by the formation of marcasite at the expense of pyrite, in which lamellar marcasite occurs sometimes — often with polysynthetic twins — being irregularly disposed.

Magnetite is a minor component, forming exclusively as an intermediate reaction product in the process of transformation of pyrrhotite into pyrite; it was observed only as micronic inclusions in the pyrite mass, being associated or not with pyrrhotite relicts.

Cobaltpentlandite, molybdenite, native gold and tochilinite range among the rare minerals from the Vîlsan mineralization. The occurrence of these minerals is restricted to a few grains (cobalt-pentlandite) or small grains concentrated in a single polished section (gold) or to isolated occurrences of a single lamella (molybdenite and tochilinite).

Cobaltpentlandite occurs close to, but not associated with pentlandite as euhedral grains but usually it does not show transformation phenomena. Unlike pentlandite, the cobaltpentlandite is marked by higher reflectivity and the lack of cleavages.

Molybdenite was noticed in a single polished section; it is not associated with other metalliferous minerals. Within the same polished section tochilinite was also noticed, a mineral of the formula n. FeS(Mg,Fe) (OH_2) included in pyrite alongside with chalcopyrite as lamellae of 100×25 microns in size; it differs from the minerals of similar optics (valeriite, graphite etc.) by its optical properties: bireflection in grey-pink to grey-bluish tinges, with intense anisotropic effects in white-yellowish to dark grey-blackish nuances. Although rare, as is also cobaltpentlandite, tochilinite was recorded in similar formations, especially in the USSR, where it was described for the first time; molybdenite is also known from the Norilsk type mineralization, where it occurs as accessory mineral.

Gold was identified in a single polished section as micronic grains, disposed alongside with marcasite on the pyrrhotite cleavages or on the fissures between them.

Among the secondary minerals mineral C and goethite are worth mentioning; the former is relatively widespread, especially in the zones of advanced pyrrhotite pyritization. As in the case of violaritization, the initial pentlandite contours are preserved. In this transformation stage violarite is replaced by a grey-brownish matrix, isotropic in reflected light, in which micronic pyrite and/or bravoite grains can be distinguished. It is probably a secondary nickel mineral which could not be identified for the time being. Goethite was observed as veinlets cutting the ore; under the microscope it appears as fibrous aggregates, sometimes radially disposed, which penetrate and partially replace the violarite transformed in the mineral C. It is presumably a Ni variety of goethite.

The other two unidentified minerals, mineral A and mineral B, represent primary components. Mineral A occurs in an ore sample consisting of thin pyrite and chalcopyrite bands, as an isolated grain (100×50 microns) in the amphiboles. It polishes well, is white-cream coloured, isotropic, with slightly pronounced cleavages ; under great magnification irregular lamellae may be observed within the grain, which seem slightly anisotropic. Being the only grain encountered and not having any direct contacts with other sulfides, it can only be stated that mineral A has a high-mean reflectivity and probably belongs to the sulfospinel group.

Mineral B : a single grain, almost circular in section, 10 microns in diameter. It occurs as inclusion at the pyrrhotite/chalcopyrite boundary ; it has (very) high reflectivity, is yellow, anisotropic, has a higher hardness than that of pyrrhotite and chalcopyrite and may represent a mineral of the platinum group.

Geochemical Data

Chemical and Spectrographic Analyses of Rocks

In view of obtaining additional data supporting the initial nature of the rocks hosting the mineralizations 10 complete chemical analyses (Table 3), representing amphibolites (8 samples) and amphibolic gneisses

TABLE 3

Chemical analyses on the amphibolic rocks from the Vîlsan 2 Gallery

Oxides Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	H_2O	CO_2	S	Fes	Total
4099	46.60	0.70	20.80	1.71	6.23	0.13	8.68	7.47	0.58	3.02	0.14	0.98	2.41	0.57	0.50	100.52
4072	47.40	1.61	17.65	1.43	8.06	0.18	8.64	9.19	0.58	1.68	0.25	1.75	1.31	0.19	0.17	100.08
4080	64,60	0,76	16.93	1.23	2.38	0.05	2.20	5.12	0.54	3.60	0.32	0.60	1.05	0.44	0.38	100.20
4078	29.40	1.08	6.35	4.02	6.43	0.10	5.09	2.93	0.33	0.34	0.05			21.90	19.08	99.90
4069	49.25	0.64	21.07	1.35	4.98	0.11	7.70	7.37	0.79	3.30	0.14	1.95	1.32	0.15	0.13	100.25
4074	50.00	1.02	11.25	0.66	8.39	0.16	12.73	9.64	0.46	0.80	0.10	1.77	1.92	0.36	0.31	99.57
FV75	44.00	1.49	15.49	3.82	7.14	0.14	7.27	6.41	1.42	2.22	0.20	1.49	1.06	4.30	3.75	99.30
4125	55.30	1.24	18.30	1.70	6.04	0.16	3.35	6.13	0.78	3.82	0.52	0.40	[illegible].19	0.24	0.21	100.46
4122	50.40	1.38	20.38	0.33	6.54	0.12	6.07	8.46	0.53	3.13	0.16	0.99	1.49	0.19	0.17	100.34
4116	49.60	0.73	19.28	0.83	5.49	0.12	7.11	10.40	0.36	3.95	0.16	0.72	1.38	0.22	0.19	100.54

Analyst C. Vlad, Enterprise of Geological and Geophysical Prospections.

(samples 4122, 4116) as well as 13 quantitative spectrographic analyses (Table 4) were carried out. For lack of some isotopic data (Sr) or of analyses of rare earths, we used some classical diagrams in order to define the ortho- or paracharacter of those rocks (Figs. 4 —8). In most cases the analysed amphibolic rocks plot in the ortho-field, there existing a positive Cr/Ni and Co/Ni correlation, characteristic of the magmatic rocks. The chemistry and mineralogical composition of the rocks suggest the gabbroic character of the presumed magmatic rocks. Some deviations from this character may be connected to the metamorphic and postmetamorphic transformations, or to the sulfidization processes which may alter the relationships among the elements ; in such cases the iron mobilization takes place, being connected with its transfer from the silicates to the sulfide

TABLE 4

Minor elements in the amphibolic rocks from the Vîlsan 2 Gallery

Element Sample	Pb	Cu	Zn	Ga	Ni	Co	Cr	V	Sc	Y	La	Nb	Zr	Ba	Sr
FV75	9	1500	78	17	6200	280	3000	280	32	13	30	10	130	520	280
4069	8.5	6	48	14	210	30	450	110	20	8.5	30	10	115	290	570
4072	6	11	100	15	160	47	450	300	58	46	30	10	200	285	460
4074	2	4	100	11	220	38	1100	210	50	13	30	10	57	175	150
4078	2	1500	150	12	1.8%	1000	2800	120	10	5	30	10	42	120	38
4080	4.5	46	38	14	155	18	520	85	11	1.6	30	10	550	420	850
4099	4	110	75	14	1100	80	850	180	23	6.5	30	10	35	245	650
4093	2.5	2300	65	13	7000	460	3800	220	18	5	30	10	32	200	280
4094	13	6500	160	12	1.6%	800	6500	115	18	5	30	10	36	190	34
4104	3	620	46	11	38	3.5	160	22	3	5	30	10	125	330	220
4116	9.5	12	72	15	210	30	175	135	36	12	30	10	70	190	650
4122	2.5	35	80	14	115	22	130	160	28	13	30	10	55	270	670
4125	5	19	100	18	76	16	55	180	21	21	30	10	200	700	700

Sn < 2ppm in all the samples
Be < 1 ppm; in sample 4125 — 1,2 ppm
Yb < 3,2 ppm in all the samples

Analyst C. Udrescu, Institute of Geology and Geophysics

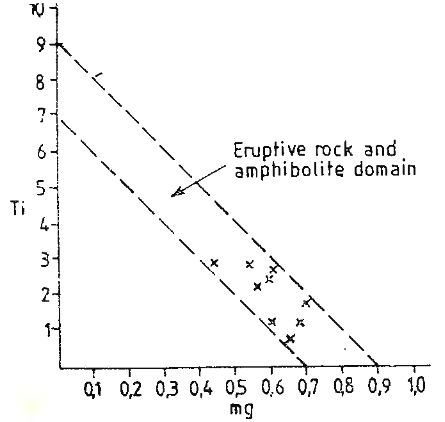
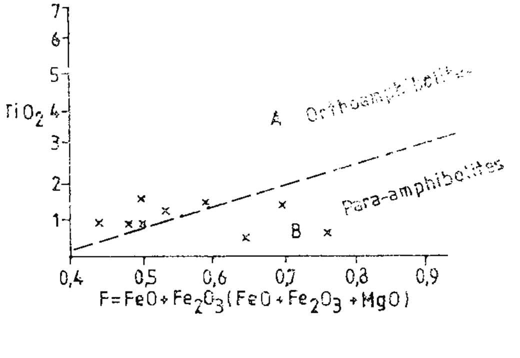
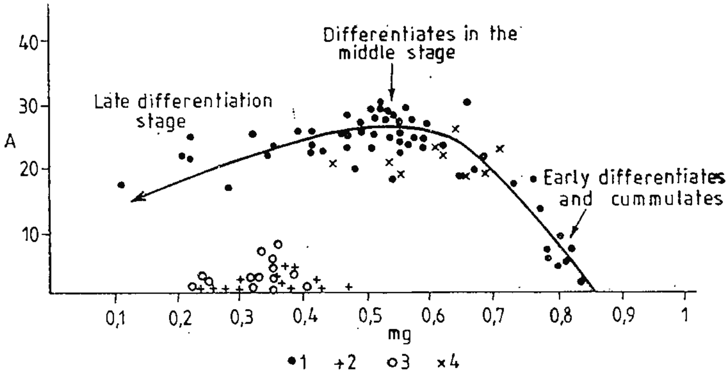


Fig. 4. — Fabries' diagram (1963) with the orthoamphibolite domain.

Fig. 5. — Misra's diagram (1971) with the separation of the ortho- (A) and para-amphibolite (B) domains.





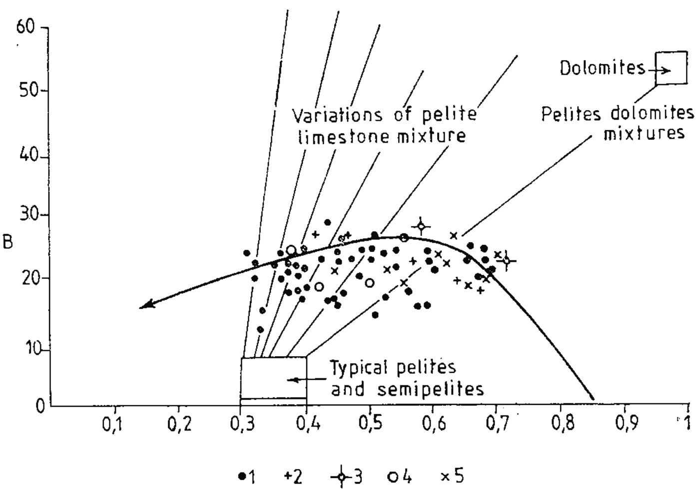


Fig. 6. — Differentiation tendency of the basic magmatic complexes (according to Leake, 1964). 1, Karroo dolerites ; 2, Littleton pelites ; 3, Connemara pelites ; 4, Vîlsan Valley amphibolites (in A) ; 1, Connemara amphibolites ; 2, Roan meta-dolerites ; 3, Roan orthoamphibolites ; 4, Langoy amphibolites ; 5, Vîlsan Valley amphibolites (in B).

structure. Another significant feature is the presence of euhedral spinels, in which the subsequent transformations manifested especially by the occurrence of an obvious zonality and/or the occurrence of some rutile, more rarely ilmenite exsolutions.

Minor Elements in Sulfides

As expected, the nickel and cobalt contents are relatively high, as a consequence of pentlandite, violarite, cobaltpentlandite, bravoite inclusions within pyrite and pyrrhotite (Table 5). The chrome contents are significant, especially for the samples in which spinels were identified under the microscope, which confirms their chromiferous character. The

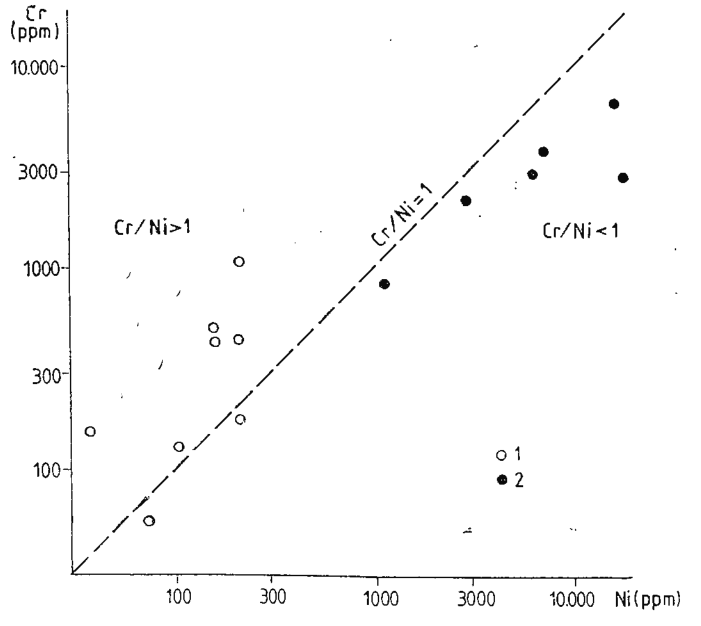


Fig. 7 — Cr/Ni correlation diagram in the rocks (1) and ore (2) from the Vîlsan Valley.

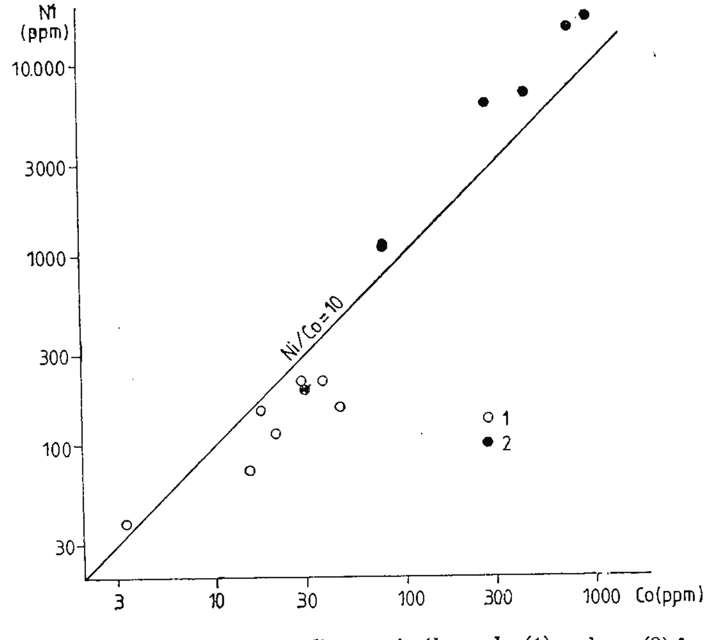


Fig. 8. — Ni/Co correlation diagram in the rocks (1) and ore (2) from the Vîlsan Valley.

TABLE 5

Quantitative spectrographic analyses on sulfide samples

	Analysed sulfide	Determined elements (ppm)									
		Cu	Pb	Zn	Ag	Ni	Co	Ti	Mn	V	Cr
1	pyrite (py)	780	15	100	2.2	>3000	1100	500	250	30	160
2	py*	1200	13	100	1.3	>3000	1400	800	450	36	210
3	py	3600	10	100	2.7	>3000	1100	300	220	13	85
4	py**	2200	17	100	1.8	>3000	700	2300	1000	85	480
5	py	420	380	110	1.4	>3000	700	90	80	10	65
6	py	620	10	130	1.3	>3000	1100	6000	1000	320	>3000
7	py	1100	28	100	1.9	>3000	1300	1000	560	65	800
8	pyrrhotite***	600	30	100	1	>3000	460	4200	900	220	2600
9	py****	1450	150	100	4.2	700	420	140	78	—	—
10	py	100	10	100	1	>3000	1050	10	175	—	—
11	py*****	10	10	130	1	90	9	10	11	10	30
12	py*****	10	10	100	1	9	3	10	60	10	30
13	py*****	10	10	300	1	120	15	95	300	10	30
14	pyrrhotite	90	10	70	3.1	>3000	1400	1600	420	90	>3000
15	py******	24	16	440	1	>3000	550	300	90	12	1100

Analyst: Alla Zămârcă, Institute of Geology and Geophysics, Bucharest

* The sample contains also 12.5 ppm Tl;

** Pyrite concentrate

*** Pyritized pyrrhotite concentrate;

**** The sample contains also 180 ppm Mo;

***** Pyrite from the discordant veins (see Figure 9);

****** Pyrite formed at the expense of pyrrhotite (sample 14), within which it appears as millimetric veinlets or lenses.

analysed sulfide samples generally show rather uniform minor element contents except for late pyrite in discordant veinlets in which cockade structures were noticed (Fig. 9). It is interesting that this pyrite also has a contrasting sulfur isotopic composition (samples FV 74 and FV-78 and B), which suggests once more that its genesis differed from that of the sulfides from the stratiform ore.

Sulfur Isotopic Composition

The results of some sulfur isotope analyses are presented in Table 6; the dispersion of the $\delta^{34}S$ is relatively high, but the high positive ones prevail, which are comparable to the $\delta^{34}S$ values obtained on sulfides from other regionally metamorphosed deposits of Romania (Table 7). The positive δ^{34} values range within wide limits, which might be explained by the different stratigraphic position of the samples; such variations are often recorded in stratiform deposits, being considered to be primary (Stanton, 1972). A different sulfur source may be assumed for pyrite within discordant veinlets (Fig. 9), for which $\delta^{34}S$ shows great negative values. The small number of available analyses does not allow an ampler discussion on the significance of these results which should be regarded as informative and the interpretation suggested as preliminary. The ore underwent intense mineralogical transformations, characterized especially by the primary pyrrhotite pyritization, a phenomenon which might have been accompanied by changes in the sulfur isotopic composition;

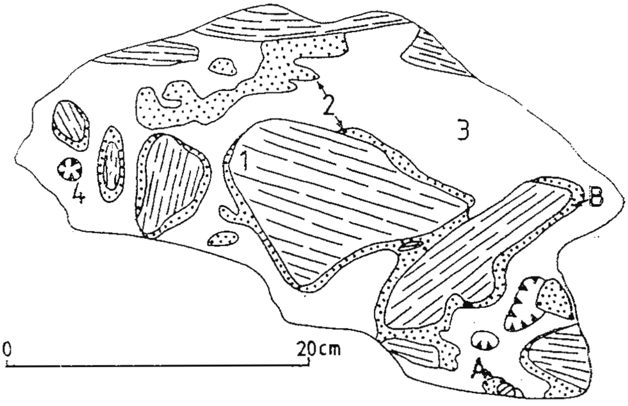


Fig. 9 — Pyrite-calcite association within the discordant bodies with respect to the metamorphics foliation, Vîlsan Valley gallery 2.
1, chloritized amphibolite fragments; 2, pyrite bands moulding the amphibolite fragments (cockarde structure); 3, calcite matrix; 4, geodes filled with calcite; A and B mark the location of the spectrographically and isotopically analysed pyrite samples.

TABLE 6

Istotopic composition of pyrite and pyrrhotite from the Vîlsan Valley deposit

Analysed mineral		$\delta^{34}S$ ($^0/_{00}$)
6*	pyritized pyrrhotite **	+23.59
1	pyrite	+20.80
3	pyrite	+18.00
7	pyrite	+12.65
2	pyrite	+ 2.18
5	pyrite	+ 2.09
12	pyrite***	− 9.03
11	pyrite***	−18.73
13	pyrite ***	−25.15

* The numbers correspond to those from Table 5

** ca 30—40 %

*** See Figure 9

Analyst: Filofteia Gaftoi, Institute of Geology and Geophysics, Bucharest.

TABLE 7

Isotopic composition of the sulfides from some metamorphosed syngenetic mineralizations from the Romanian Carpathians

Analysed mineral	$\delta^{34}S$ ($^0/_{00}$)	Deposit
pyrite *	+4.88...+21.74	Hărlăgia*
pyrite	+10.19	Boiţa-Haţeg**
pyrite	+15.51	Novicior*
chalcopyrite	+16.41	Bălan*
pyrite	+32.47	Sibişel**

* Metamorphosed syngenetic deposits from the Tulgheş Series (Lower Cambrian), East Carpathians.

** Metamorphosed syngenetic deposits from the Sebeş—Lotru Group, (Upper Precambrian), South Carpathians.

Analyst: Filofteia Gaftoi, Institute of Geology and Geophysics, Bucharest.

these changes seemingly manifested through an impoverishment of the heavy sulfur isotope, which may be correlated with the regressive character of the latest metamorphic phase that affected the host rocks of the ores.

Transformation Sequence within the Rocks and the Associated Mineralizations

The first event which can be followed back is the crystallization and recrystallization of the main minerals of the rocks and ores, i.e. the amphibole and pyrrhotite. These minerals are "compressible" within a wide PT interval preserving, however, the textural equilibrium. The recrystallization of pyrrhotite might have been accompanied by the migration in solid state, by simple gliding on the (0001) planes. The other primary minerals, pentlandite and chrome spinels, do not generally show deformation effects, suggesting that in this stage such migration processes were subordinated (Fig. 10).

An important phenomenon is that which accompanied the major deformation that determined the regional deformation; this led to the recrystallization and recovery of pyrrhotite, determining the appearance of the nematoblastic and plane-parallel textures; changes in the pyrrhotite composition may be assumed, however not demonstrated as yet. The pentlandite exsolution (as flames) from pyrrhotite took place prior to this deformation moment; locally, visible remobilization effects of pyrrhotite and chalcopyrite occur synchronously with deformations, often resulting in the appearance of variously oriented veinlets in the amphibolites; subsequently most of the pyrrhotite was pyritized, an effect possibly due to either an increase of the sulfur fugacity in the system or the settling of a slightly oxidizing regime.

In a next stage the chloritization of biotite and amphibole takes place, giving rise to the release of titanium and the formation of sphene

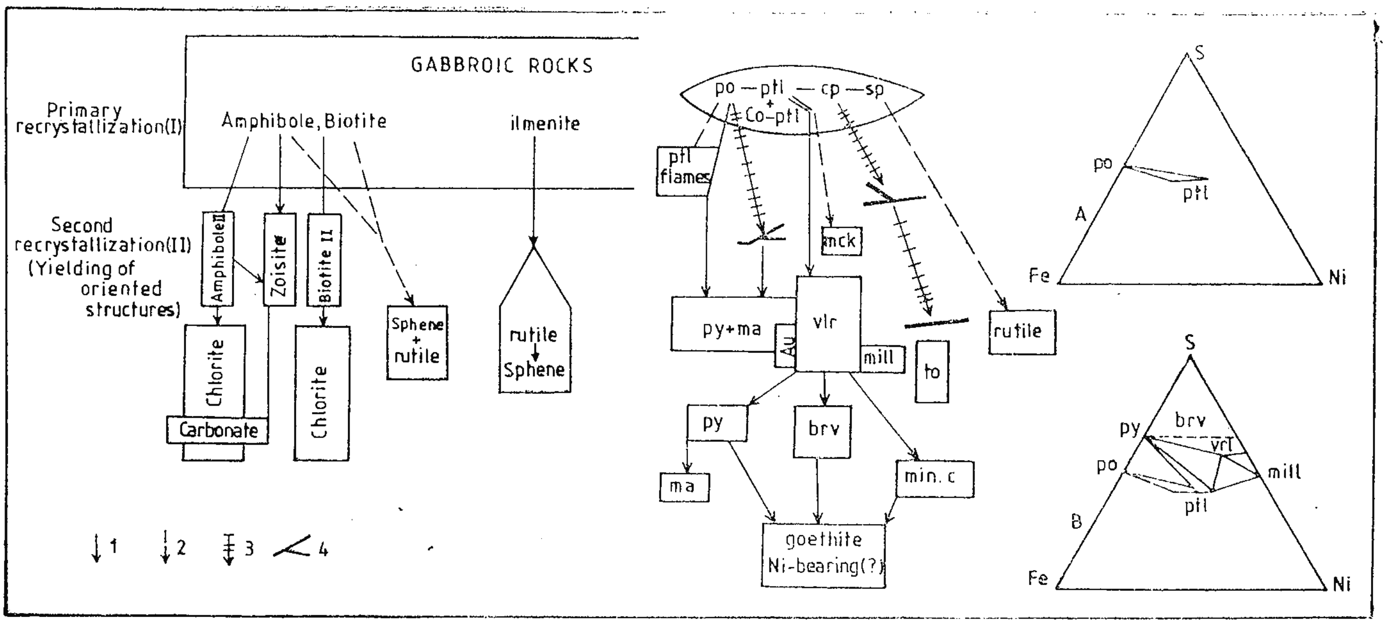


Fig. 10 — Evolution of transformations within the rocks and ore during metamorphism. Abbreviations: po, pyrrhotite; ptl, pentlandite; cp, chalcopyrite; sp, spinels; mck, mackinawite; py, pyrite; ma, marcasite; vlr, violarite, mill, millerite; brv, bravoite; to, tochilinite. 1, transformation; 2, exsolution; 3, solid state migration; 4, discordant veinlets with respect to the metamorphics foliation.

and rutile, which are often observed on the silicate cleavages; the exsolution phenomenon within the spinels (rutile±ilmenite) may have occurred also at that moment. The formation of zoisite at the expense of the calcium released through the amphibole decomposition also takes place; this would explain the constant association of chlorite with sphene and zoisite or even the inclusion of these two minerals within chlorite. The isolated grains within the amphibolic rocks, initially represented by ilmenite, gradually change into sphene, also at the expense of the calcium available through the transformation of amphibole — in which ilmenite often remains as nuclei; the process continues with the total replacement of ilmenite by rutile, which also occurs as islands in the sphene aggregates; the deferrization of the initial titanium mineral (ilmenite) is a manifestation of the sulfidization process, which has been relatively frequently observed in this mineralization type. The mackinawite exsolution from pentlandite may have also previously occurred, being a usual phenomenon which, from the chemical point of view, consists in the removal of a certain iron excess from pentlandite. The large scale transformation of pyrrhotite into pyrite, especially in the weakly mineralized zones is noticed; in the case of massive pyrrhotite instead, the marcasitization on cleavages or along fissures is observed; in such cases the marcasite associates sometimes with gold. The violaritization of granular pentlandite (pentlandite as flames from the pyrrhotite mass is preserved) seems to be contemporaneous with these transformations; millerite occurs alongside with violarite in the nickel-rich zones, probably depending on the initial composition of pentlandite. The tochilinite formation is difficult to specify, this mineral being observed only as isolated lamellae within pyrite; but it is likely that it formed quasi-concomitantly with the pyrrhotite pyritization.

The amphibole decomposition under near surface conditions entails the formation of carbonate which may substitute also zoisite. Chlorite continues forming either at the expense of garnet or at the expense of the other minerals within the rock or even by the reorganization of the old chlorite under absent stress (static) conditions or under conditions in which a fissuring of a brittle environment enables the chlorite remobilization in veinlike forms. The formation of the chlorite veinlets within carbonates can be explained in this way. The more or less simultaneous transformation of ore minerals consists in the substitution of the relatively homogeneous violarite by fine-grained aggregates of pyrite and/or bravoite displaying different colour shades; still more typical forms of bravoite may be observed also in the compact pyrite, the bravoite occurring as fine bands varying in colour, situated especially at the periphery of the pyrite grains. A last stage is characterized by the pyrite marcasitization; the transformation of the bravoitized or pyritized violarite into the mineral C takes place simultaneously or successively, the latter being likely to form directly upon violarite. Locally, in intense circulation zones, there occur goethite (probably nickel-bearing) veinlets that affect pyrite, bravoite or mineral C to the same extent.

A late stage in the ore mineral formation, represented by pyrite associated with carbonate (calcite) in the form of discordant bodies, should be related to remobilization or mineralization phenomena that occurred in zones affected by faults. As we have already shown, this pyrite has a peculiar geochemical character; it possesses low Cu, Pb, Ni, Co, V and Cr contents as compared with the rest of the monomineral samples; it shows an excessive enrichment in the light sulfur (S^{32}) isotope — which is difficult to explain only through the effect of the remobilization process.

Ore Genesis and Related Problems

The nickel occurrences from Romania include sporadic occurrences in the form of disseminations, nests or veinlets within ultramafic rocks associated with some Upper Precambrian, Paleozoic or Mesozoic rocks. The Precambrian occurrences are located in the South Carpathians and generally contain restricted mineral assemblages : pentlandite (ptl), pyrrhotite (po), chalcopyrite (cp) and mackinawite (the occurrences from the East Făgăraş Mountains, Venelu Brook, Bardaş Brook); ptl, po, cp and millerite (mil) (Dealu Negru and other smaller ultramafic bodies from the Sebeş Mountains), ptl, heazlewoodite and awaruite (Vadu Dobrii, Poiana Ruscă Mountains), po, ptl and mil (Păscoaia, Cibin Mountains). The mineral assemblage in the Paleozoic ultramafics from South Banat is richer, consisting of po, ptl, cp, millerite and heazlewoodite. The nests and veinlets consisting of po, ptl and bravoite are described by Petrulian (1943) and Socolescu (1944) in the Mesozoic peridotites at Ciungani, in the Metaliferi Mountains. The allochthonous Mesozoic ophiolites from the Rarău-Hăghimaş syncline contain also serpentinized ultramafic bodies with po, ptl, millerite, maucherite and hzw disseminations (Russo-Săndulescu et al., 1982). In contrast with these nickel-bearing occurrences, the mineralizations from the Vîlsan Valley are hosted by metamorphosed gabbroic rocks and show a much more complex mineralogical composition. The sequence including mineralizations of the Mioarele Formation from the Precambrian Leaota Group (Figs. 1, 2) contain, in addition to metagabbros (massive amphibolites), also biotite schistose amphibolites, amphibolic gneisses, micaceous gneisses etc. The mineralization is preferentially located in metagabbros; the other types of rocks host only sporadic sulfides, in which pyrrhotite prevails.

The initial aspect of the magmatic complex from the Vîlsan Valley, which is probably of ophiolitic type, was greatly changed during the prograde (possibly polyphasic, within the limits of the amphibolite facies) and retrograde (greenschist facies) metamorphism. Due to the long metamorphic history and recurrent deformations one may suppose that the ultramafic terms of the magmatic complex were removed from the succession as a consequence of their remarkable mobility. Most of the initial textures of the rocks and ore were obliterated due to the development of several sets of penetrative foliations accompanied by mineralogical reorganizations. The appearance of sulfides also in the gneissic rocks — characteristic of the non-magmatic cover of metabasites — may suggest either the existence of some independent mineralizations, therefore of a different genesis, or the secondary migration of the ore minerals during the deformation processes (Fig. 10). Both hypotheses would thus support the relatively high dispersion of the $\delta^{34}S$ values from the stratiform ore (+2.09 .... +23.59 ‰).

The genetic model may be only partly reconstructed, the existence of a liquid-magmatic (or synmagmatic) mineralization being admitted, whose initial composition consisted of pyrrhotite, pentlandite and chalcopyrite as well as ilmenite and chrome spinels. Graphite, noticed both within the rocks and ore, shows some optical anomalies in the latter case, which indicates the possible existence of some interbedded structures, possibly with minerals from the valeriite-haapalaite group. The chrome spinels occur only locally, but in relatively great amounts, suggesting the more complex nature (not mere gabbros) of the sequence of ore-bearing rocks. The post-prograde metamorphism transformations are complex, affecting the rocks and ore to the same extent. Due to the possible convergence phenomena and the lack of direct relations between the phases within the rocks and those from the ore (in many cases) the evolution of the processes is only assumed in the sketch on Figure 10, especially in respect of their simultaneity. Some phenomena which have been noticed, such as the exsolution ones, take place also in the unmetamorphosed ores, but, in our case, they may be correlated with some deformational moments.

As the tectonic regime of the Precambrian greenstone belts is not yet easy to establish, it is difficult to introduce the mineralizations from the Vîlsan Valley into the classification proposed by Naldrett and Cabri (1976); anyway their association with komatiitic suites is out of the question as these have a distribution restricted to the Archaic (at least so far). Based on the magnesium contents of the host rocks, the Ni:Cu ratio and the $\delta^{34}S$ value of sulfides, Godlevski and Lihacev (1979) divide the magmatic formations containing Cu-Ni sulfides in three groups (Table 8), the mineralized complex from the Vîlsan Valley belonging to the medium temperature group. The only inconsistency refers to the Ni:Cu ratio, which may be explained in two ways: (1) the selective migration of chalcopyrite during the deformational processes and, probably, the par-

TABLE 8

Classification of magmatic formations bearing Cu—Ni sulfide ores (Godlevski and Lihace 1979)

	MgO content of the host rocks (%)	Ni:Cu ratio in ores	$\delta^{34}S$ (‰)	Formation temperature of magmatic rocks	Examples
1	15—30	(2—30): 1	+ 1...+ 5	high	Kola, Canada Australia
2	10—15	1:(1—2,5)	+ 7...+10	medium	Norilsk
3	8—10	1:(3—4)	+12...+14	low	Kureisk (Siberia) Duluth (Minnesota)
	6—13	1:0,34	+ 2...+23	medium-low	Vîlsan V.

Note: The PGE content decreases from 1 to 3 (according tho the same authors).

tial removal of copper from the system and (2) the initial mixed (?), i.e. ultrabasic (type 1) and basic (type 3 from the table) character of the eruptive complex from the Vîlsan Valley, which was probably dismembered during deformations with the removal of the ultrabasic terms from the succession. Based on the existing data we cannot support one of these two alternatives which may have jointly contributed to the appearance of this intermediate situation.

The above-presented data constitute a first step in the study of the mineralizations from the Vîlsan Valley, which are the only ones of this type in Romania; isotopic analyses will be further carried out for obtaining a statistic stabilization of the variation intervals and observations on the extension of the Mioarele Formation in the adjacent zones will be also made. Microprobe analyses are being carried out for the knowledge of the sulfide composition, the checking of the existence of troilite (only assumed so far), the confirmation of the cobaltpentlandite existence, the identification of the minerals A, B and C, the explanation of the optical anomaly of the graphite within the ore etc..

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MINERALIZAŢIILE DE Cu-Ni, METAMORFOZATE, DIN VALEA VÎLSANULUI, MUNŢII FĂGĂRAŞ

(Rezumat)

Mineralizaţiile de Cu—Ni±Co, metamorfozate regional din Valea Vîlsanului sînt găzduite de roci gabbroice şi au o compoziţie mineralogică complexă. Secvenţa purtătoare de mineralizaţii, aparţinînd Formaţiunii de Mioarele din Grupul Precambrian Leaota (Fig. 1 şi 2) conţine alături de metagabbrouri (amfibolite masive) şi amfibolite şistoase cu biotit, gnaise amfibolice, gnaise micacee etc. Mineralizaţia este localizată preferenţial în metagabbrouri; în celelalte tipuri de roci există numai apariţii sporadice de sulfuri, în care predomină pirotina.

Aspectul iniţial al complexului magmatic din Valea Vîlsanului, probabil de tip ofiolitic, a fost puternic modificat în timpul metamorfismului regional prograd (posibil polifazic, în limitele faciesului amfibolitelor) şi retrograd (faciesul şisturilor verzi). Datorită istoriei metamorfe îndelungate şi deformărilor repetate este posibil, în primul rînd, de presupus că termenii ultrabazici ai complexului magmatic au putut fi îndepărtaţi din succesiune, ca urmare a mobilităţii lor deosebite. Structurile iniţiale ale rocilor şi minereului au fost în cea mai mare parte obliterate prin dezvoltarea mai multor seturi de foliaţii penetrative însoţite de reorganizări mineralogice. Apariţia sulfurilor şi în rocile cu caracter gnaisic —asimilabil învelişului nemagmatic al metabazitelor — ar putea sugera fie existenţa unor mineralizaţii independente, deci cu altă geneză, fie migrarea secundară a mineralelor metalifere în timpul deformărilor. Ambele ipoteze pot astfel argumenta dispersia relativ mare a valorilor $\delta^{34}S$ din minereul stratiform (+2,09.... +23,59$^0/_{00}$).

Modelul genetic poate fi doar parţial reconstituit, admiţîndu-se existenţa unei mineralizaţii lichid-magmatice (sau sinmagmatice), a cărei compoziţie iniţială a constat din pirotină, pentlandit şi calcopirită, la care se adaugă ilmenitul şi spinelii cromiferi. Grafitul, observat atît în roci cît şi în minereu, arată în ultimul caz unele anomalii optice, care lasă să se întrevadă posibilitatea existenţei unor structuri interstratificate, eventual cu minerale din grupul valleriit-haapalait. Spinelii cromiferi apar

doar local, dar atunci în cantitate relativ mare, sugerînd natura mai complexă (decît simple gabbrouri) a secvenței de roci purtătoare de minereu. Transformările postmetamorfism prograd sînt complexe și afectează în egală măsură rocile și minereul. Datorită posibilelor fenomene de convergență și lipsei relațiilor directe între fazele din roci și cele din minereu (în multe cazuri) evoluția proceselor este doar presupusă în schița din Fig. 10, în special în privința simultaneității lor. Unele fenomene observate, cum ar fi cele de exsoluție, se realizează și în minereuri nemetamorfozate, dar în cazul nostru este posibil ca ele să se coreleze și cu unele faze de deformare, cel puțin ca moment, nu neapărat și ca intercondiționare.

Întrucît regimul tectonic al centurilor de roci verzi precambriene nu este (încă) foarte lesne de stabilit, încadrarea mineralizațiilor din Valea Vîlsanului în clasificarea propusă de Naldrett și Cabri (1979) este dificilă, oricum excluzîndu-se asocierea lor cu suite komatiitice, care au (cel puțin pînă în prezent) o distribuție restrînsă în Arhaic. Luînd în considerație conținuturile de magneziu din rocile gazdă, raportul Ni :Cu din minereu și valoarea $\delta^{34}S$ din sulfuri, Godlevski și Lihacev (1979) împart formațiunile magmatice cu sulfuri de Cu-Ni în trei grupe (Tabelul 8), complexul mineralizat din Valea Vîlsanului fiind asimilabil grupei de temperatură medie. Singura neconcordanță se înregistrează la raportul Ni :Cu, care poate avea două cauze ; (1) migrarea selectivă a calcopiritei în timpul proceselor de deformare și, probabil, ieșirea parțială a cuprului din sistem (2) caracterul inițial mixt (?),i.e. ultrabazic (tipul 1) și bazic (tipul 3 din tabel) al complexului eruptiv din Valea Vîlsanului, dezmembrat probabil în timpul deformărilor, cu îndepărtarea termenilor ultrabazici din succesiune. Pe baza datelor existente nu se poate face o opțiune fermă pentru una din cele două alternative, care ar fi putut de fapt să și concure la apariția acestei situații cu caracter intermediar.

EXPLANATION OF PLATES

Plate I

Fig. 1. — Chalcopyrite and pyrrhotite veinlets (both : white) variously oriented in amphibolite. Polished section (PS), × 200.

Fig. 2. — Image similar to Figure 1, but the veinlets consist of pyrite (white), formed at the expense of primary pyrrhotite, coexisting as relicts within pyrite. PS, × 200.

Fig. 3. — Pyrrhotite (white) with pyrite and marcasite along fissures, giving the comb-like aspect. PS, × 200.

Plate II

Fig. 1. — Euhedral spinels (light-grey coloured, included in pyrrhotite (white) associated with violaritized pentlandite (shagreened aspect). At the top — pyrrhotite (white) in a concentric rutile texture (grey) and leucoxene (grey-blackish). PS, × 200.

Fig. 2. — Zoned spinel (various shades of grey) with a rutile inclusion (grey), included in partly marcasitized pyrrhotite (white). PS, × 200.

Fig. 3. — Pentlandite flames within pyrrhotite. PS, oil immersion, N+, × 450.

Fig. 4. — Partly violaritized, euhedral pentlandite (whitish) in pyrrhotite (white-greyish). The scratch on the left side points to the difference in hardness between pyrrhotite and pentlandite. PS, oil immersion, × 450.

Fig. 5. — Violaritized pentlandite (grey-whitish) in which bravoite is individualized (skeletal bands or crystals); everything is included in pyrrhotite (white). PS, oil immersion, × 450.

Plate III

Fig. 1. — Pyrite (white, high relief) partly included in an intergrowth of violarite + millerite. PS, oil immersion, × 450.

Fig. 2. — The same image with N+ ; the intense millerite anisotropy is noticed.

Fig. 3. — Molybdenite lamellae with kink type bands. PS, oil immersion, × 450.

Fig. 4. — Tochilinite lamellae (strong bireflexion) included in pyrite. PS, oil immersion, × 450

Plate IV

Fig. 1. — Graphite lamellae (with kink bands), associated with sphene, PS, oil immersion, × 450.

Fig. 2. — Graphite aggregate with hexagonal section (in which lamellae are radially disposed, included in grey violarite, shagreen surface), associated with pyrite (light grey). PS, oil immersion, N+, × 450.

Fig. 3. — Graphite aggregate (in which marginal zone consists of fine lamellae, perpendicularly, oriented on the aggregate margin), included in pyrrhotite (white). PS, oil immersion × 450.

Fig. 4. — Same image, with N+.

Plate V

Fig. 1. — Complete violarite pseudomorphosis after a euhedral pentlandite grain, associated with chalcopyrite (white). Round the "euhedral" violarite — fine intergrowth of "decomposed" violarite and geothite (blackish). PS, oil immersion, × 450.

Fig. 2. — Violarite alteration (grey-whitish) continues by the appearance of some goethite veinlets ; limonitization is pervasive at the periphery of the violarite aggregate (at the top). PS, × 200.

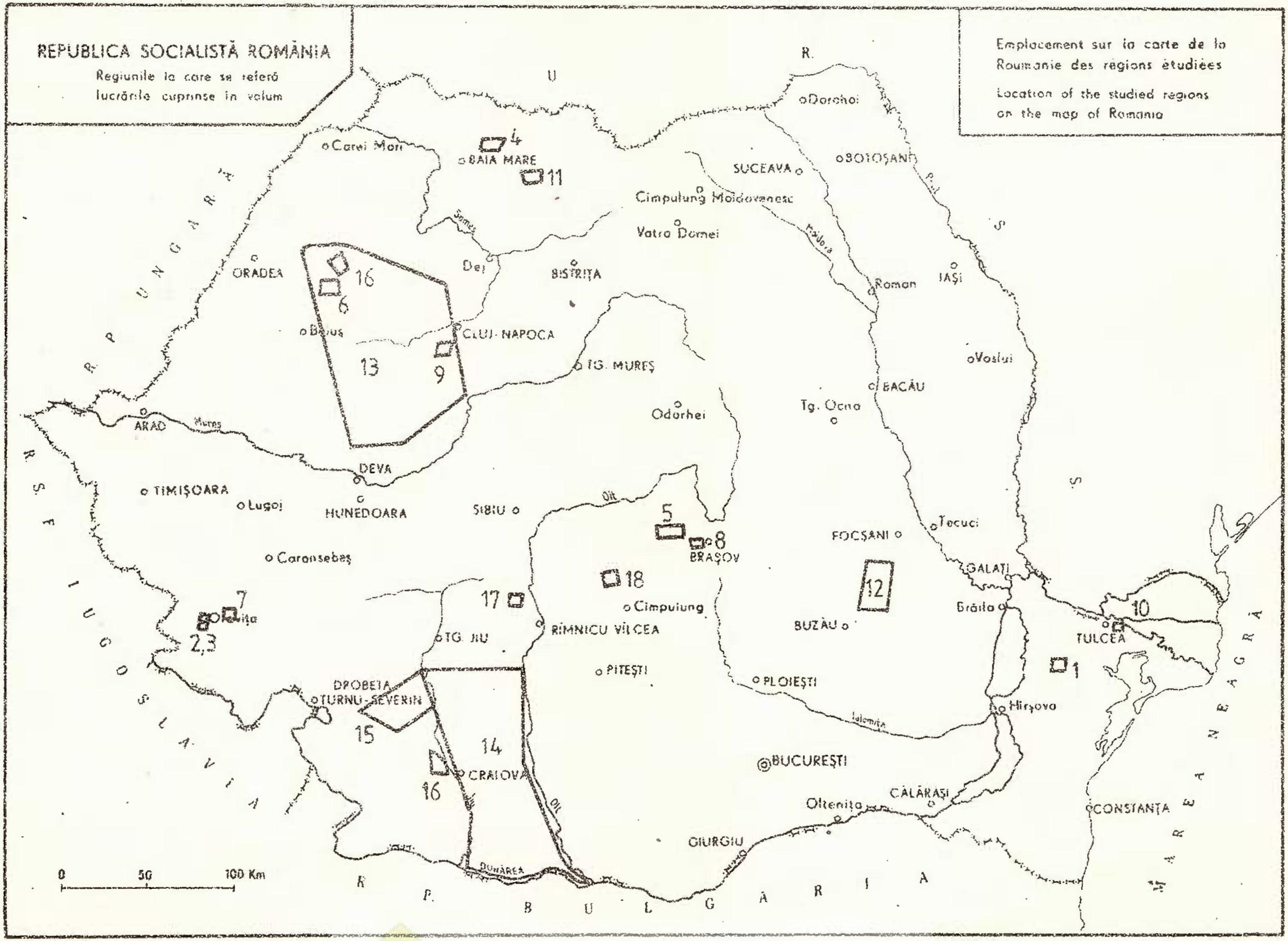
Fig. 3. — The complete alteration of violarite results in the appearance of the "mineral C". (see text), in which pyrite relicts are preserved. PS, oil immersion, × 450.

Plate VI

Fig. 1. — Violarite alteration results in some cellular aggregates consisting of pyrite and/or bravoite (whitish) with matrix of the "mineral C" (blackish). PS, oil immersion, × 450.

Fig. 2. — Gold (white) associated with marcasite formed at the expense of pyrrhotite (grey-whitish). PS, oil immersion, × 450.

Fig. 3. — Pyrrhotite (white) with pentlandite in the amphibolites from the right slope of th e Vilsan Valley, outside the mineralized zone. PS, oil immersion, × 450.



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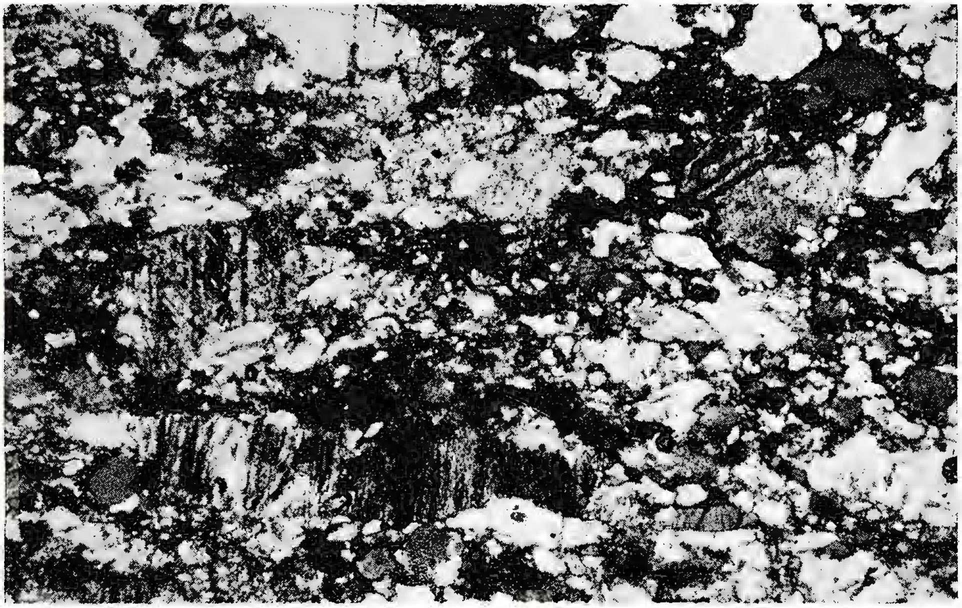

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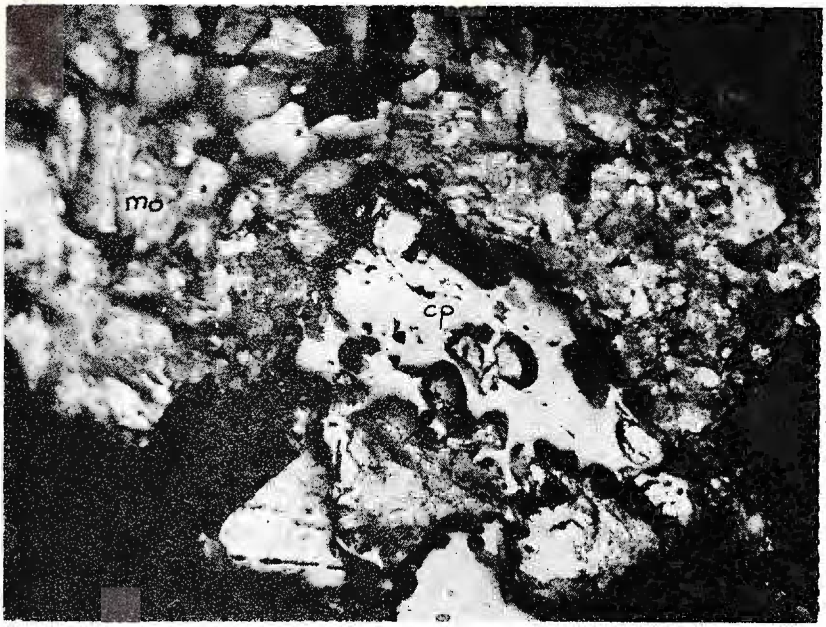

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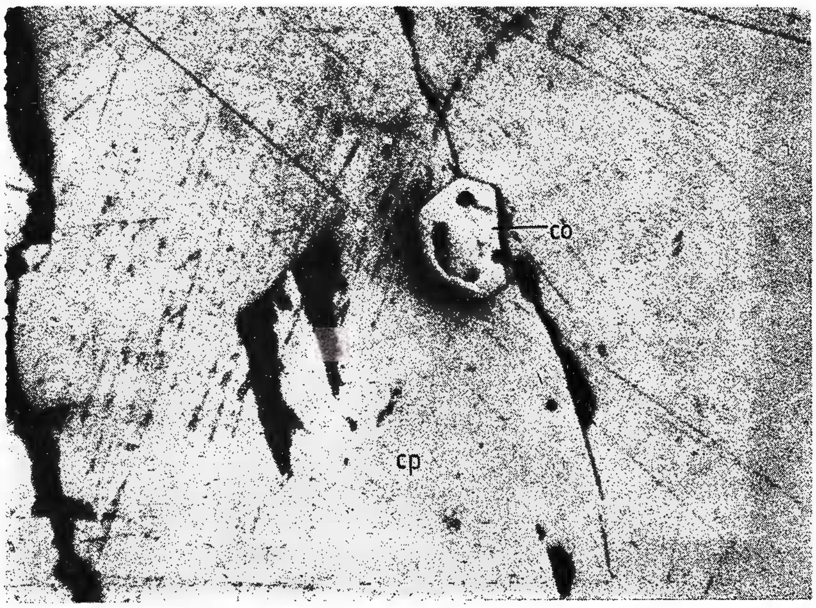

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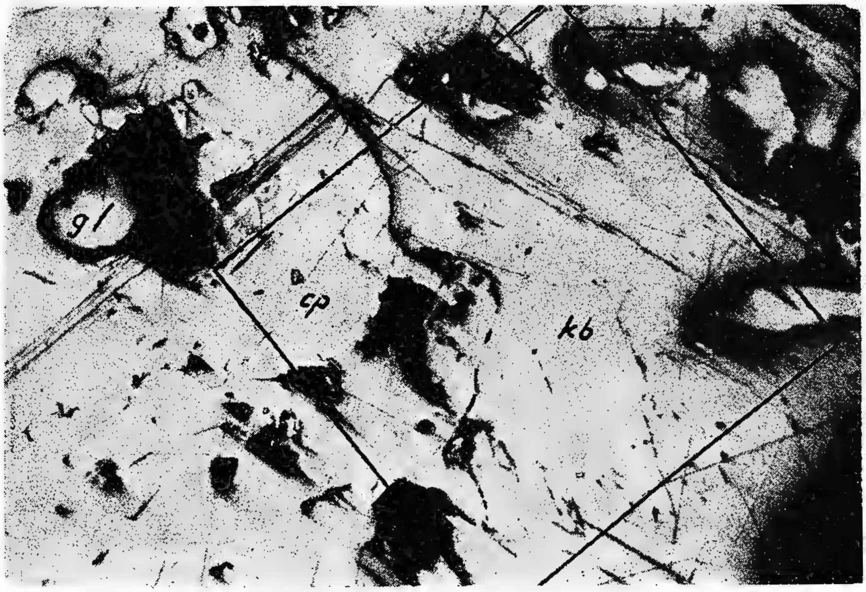
Pl. III



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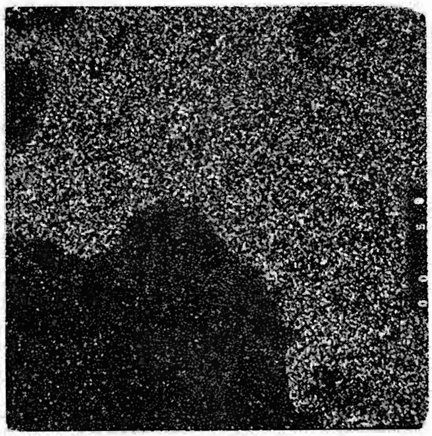

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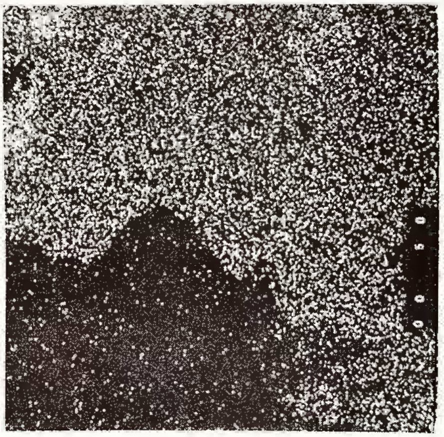

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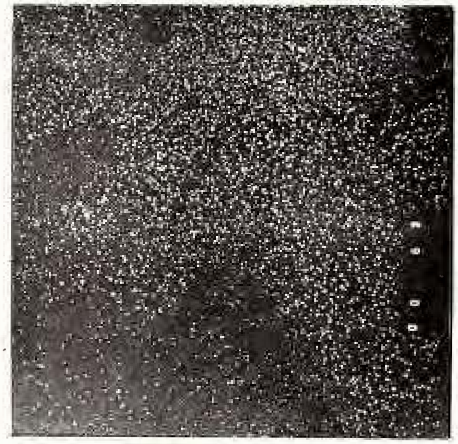

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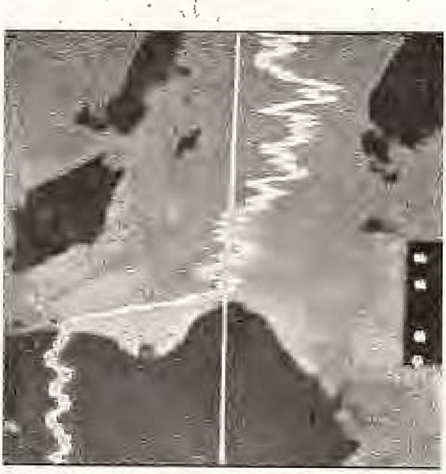

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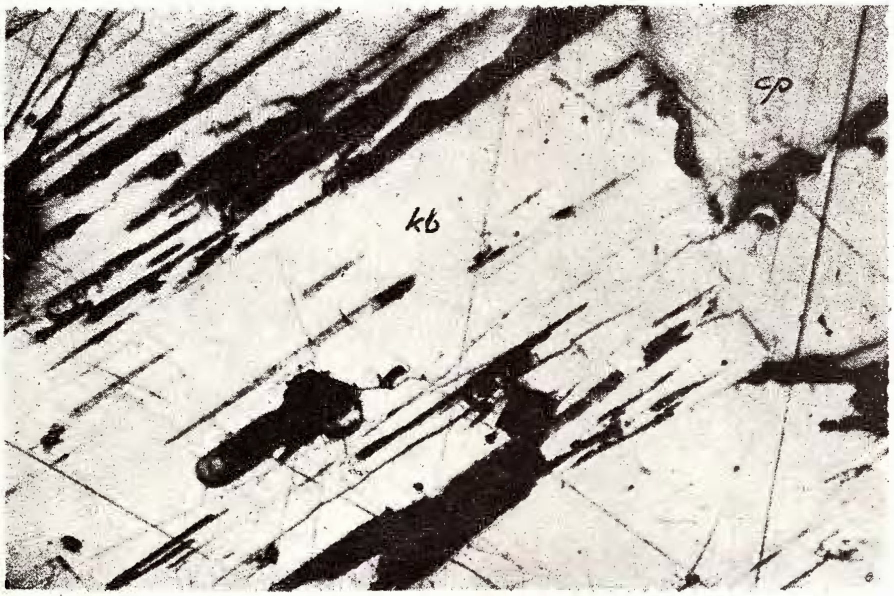

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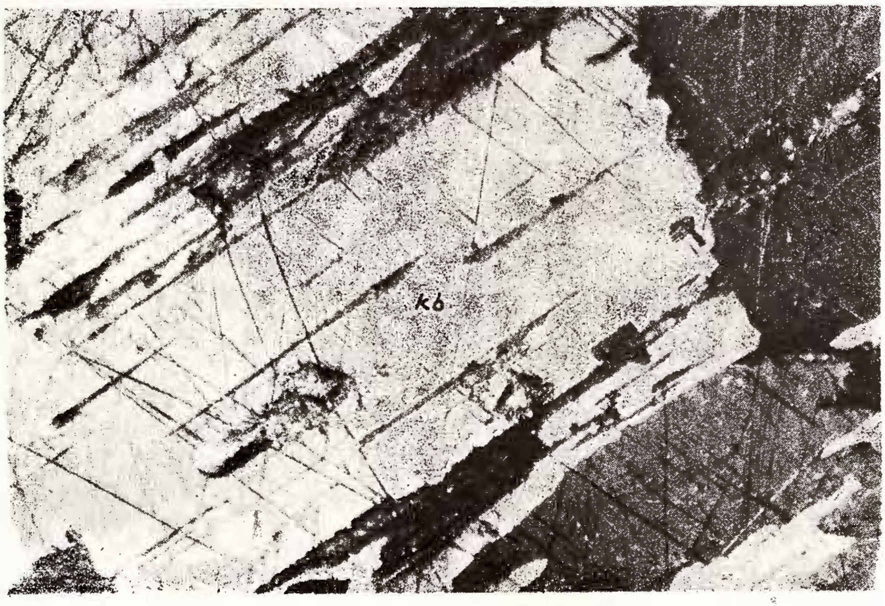

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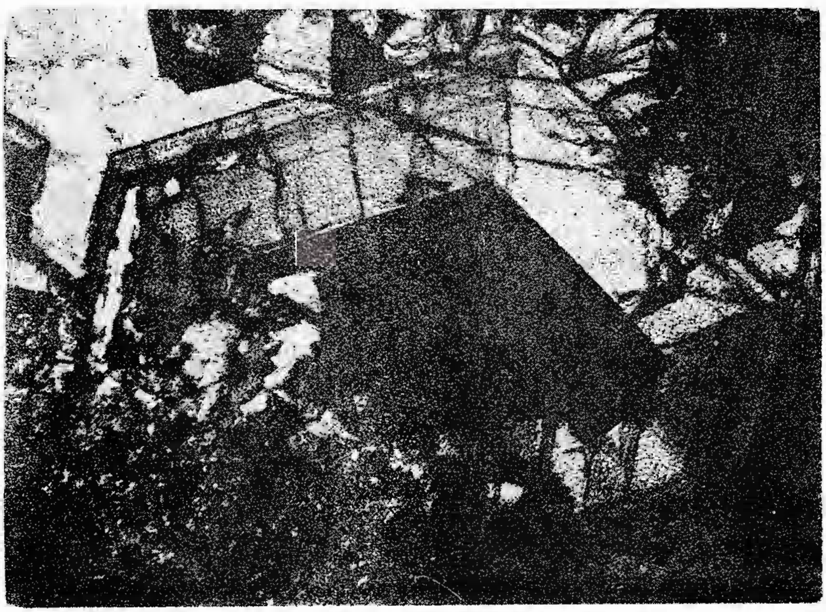

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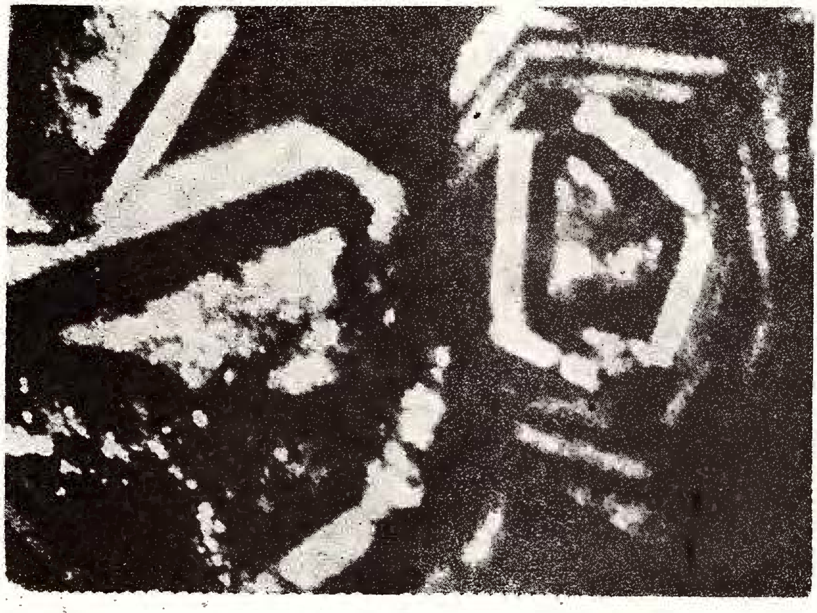

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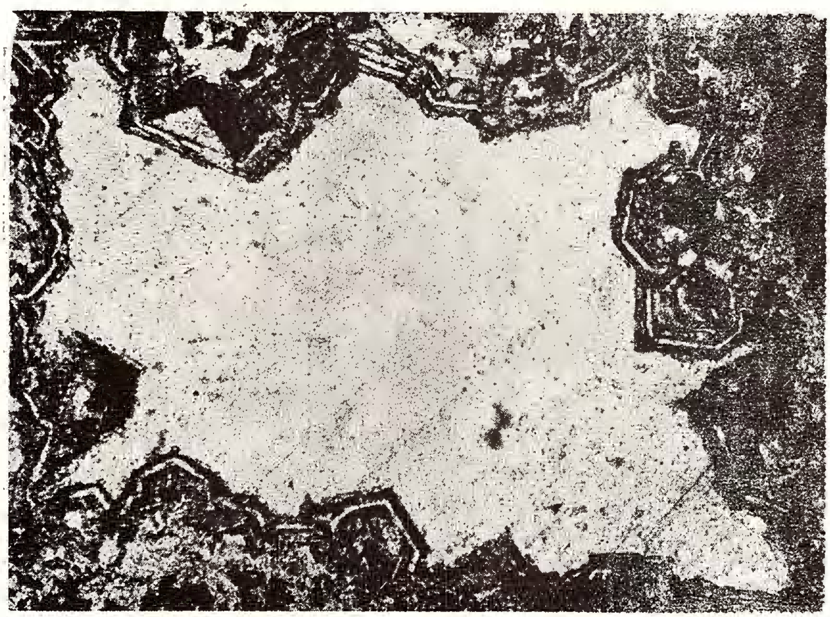

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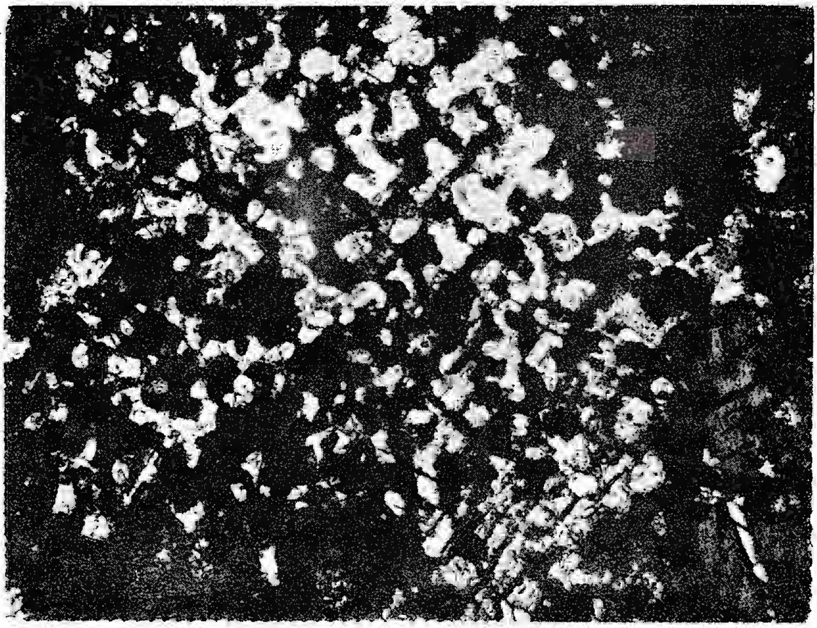

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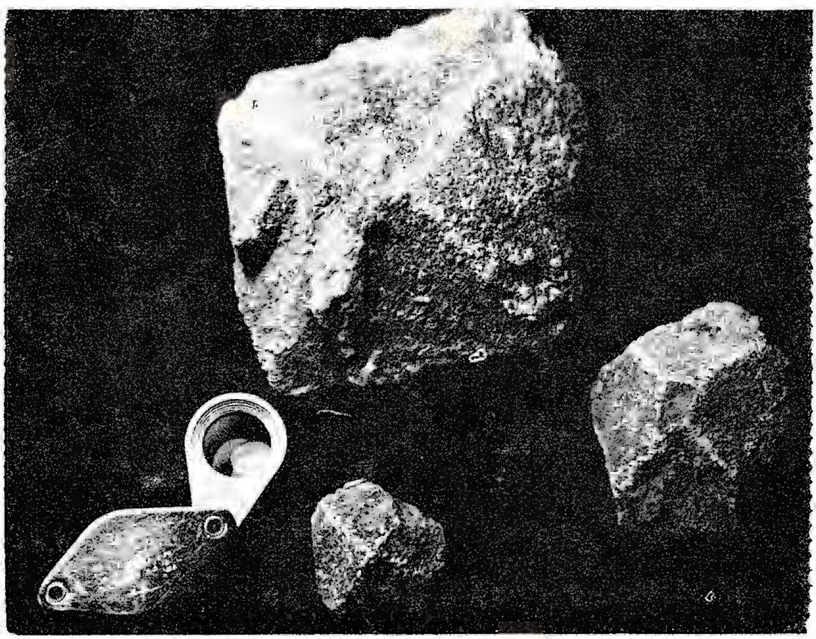

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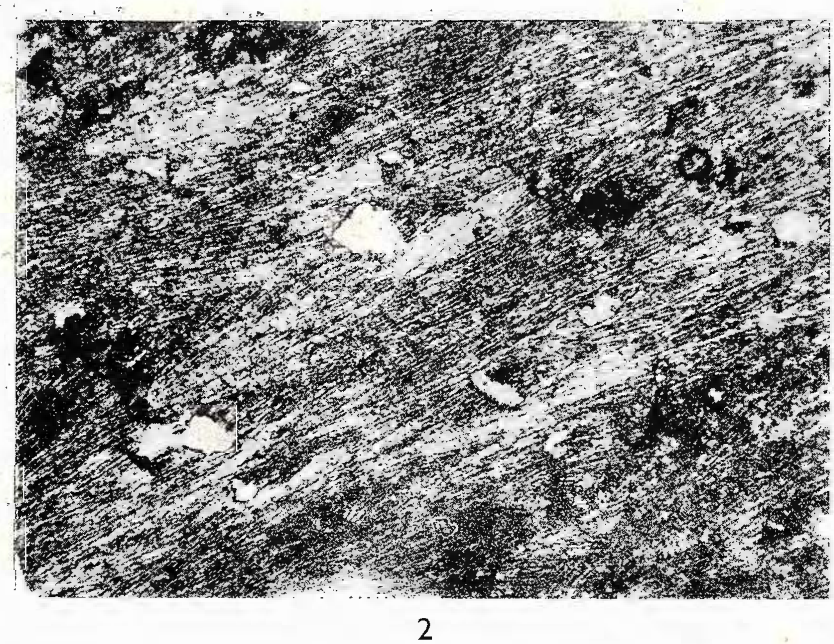

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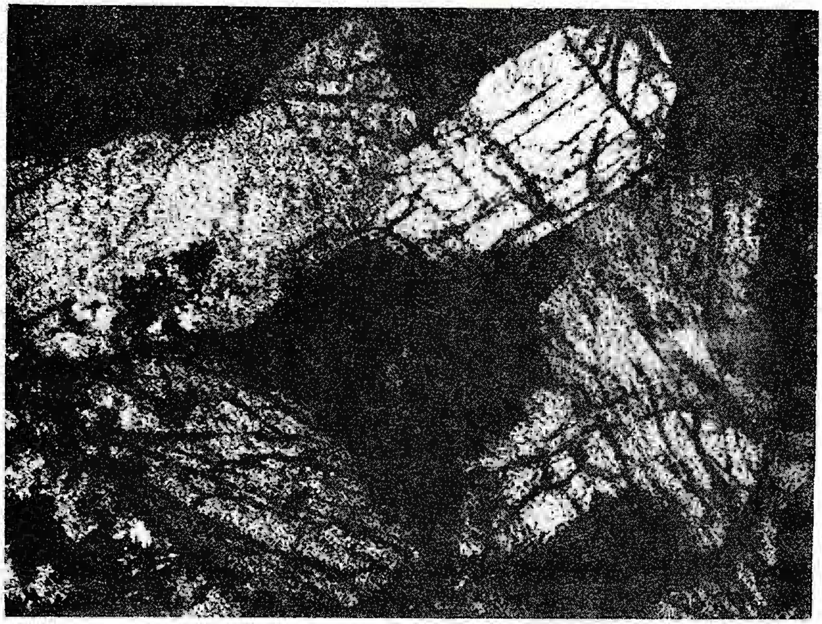

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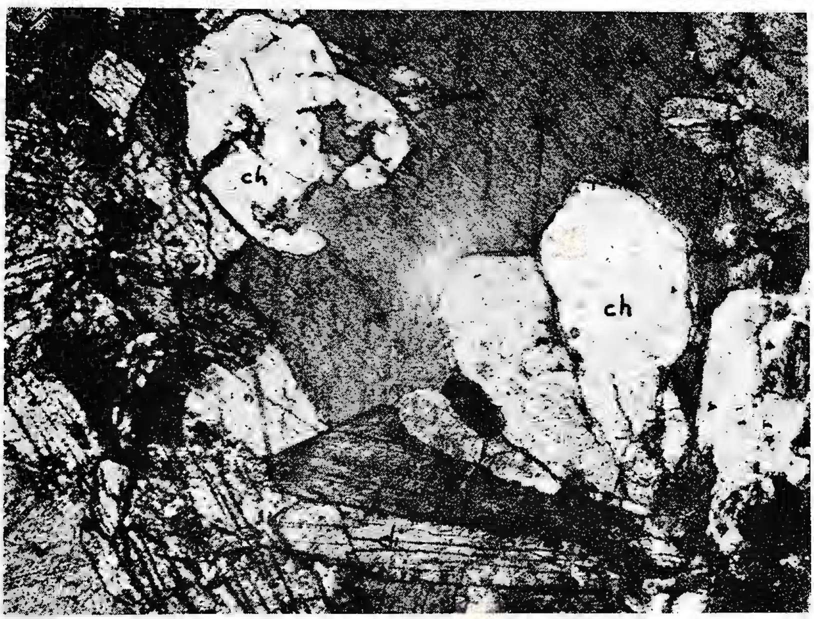

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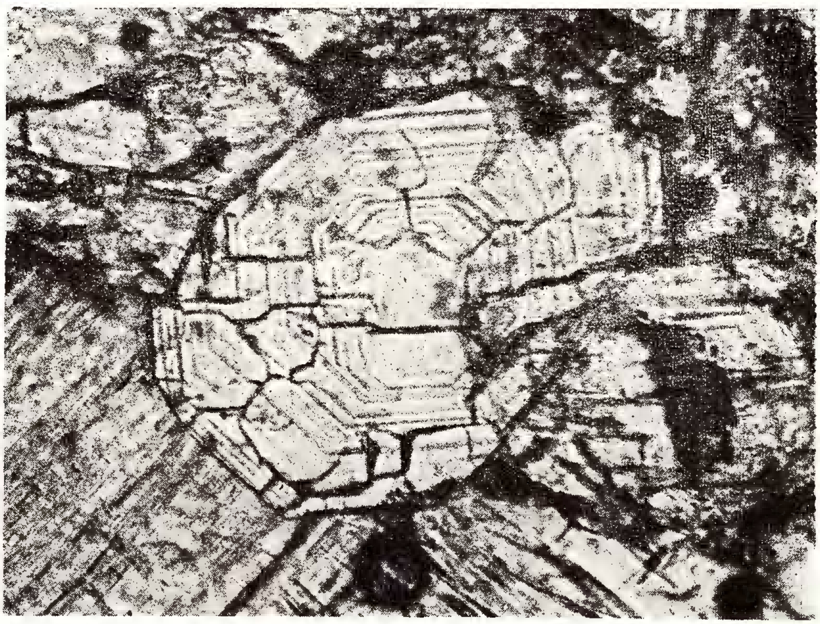

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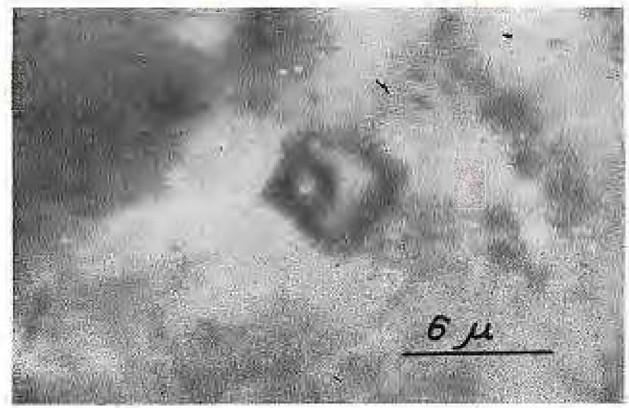

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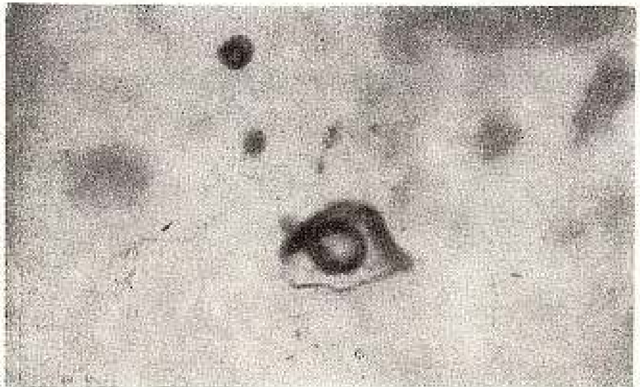

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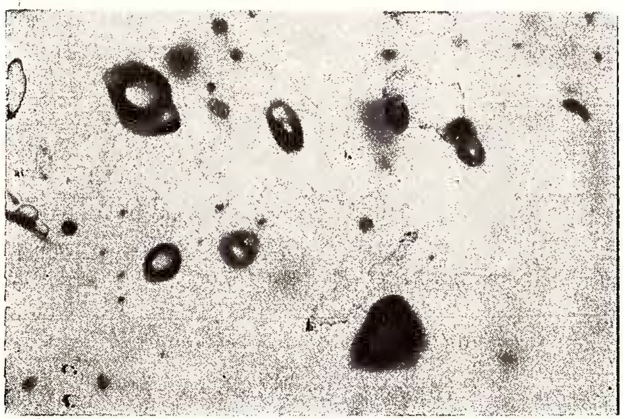

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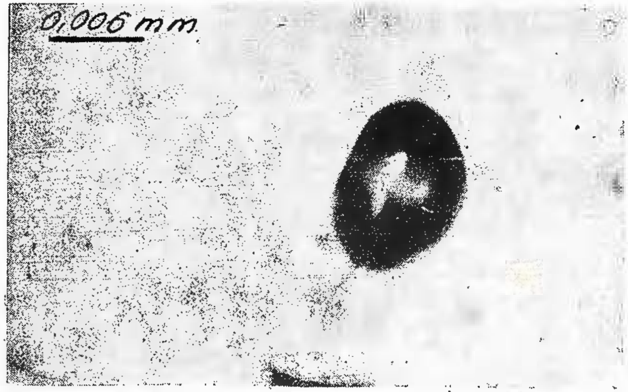

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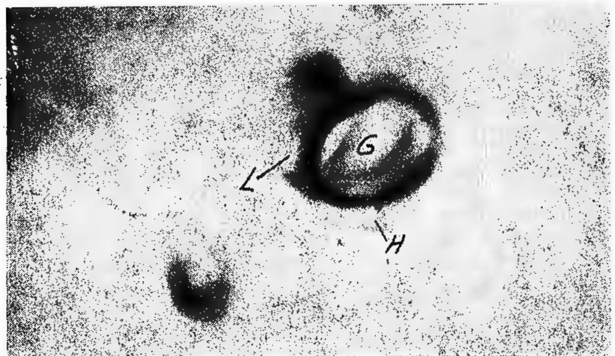

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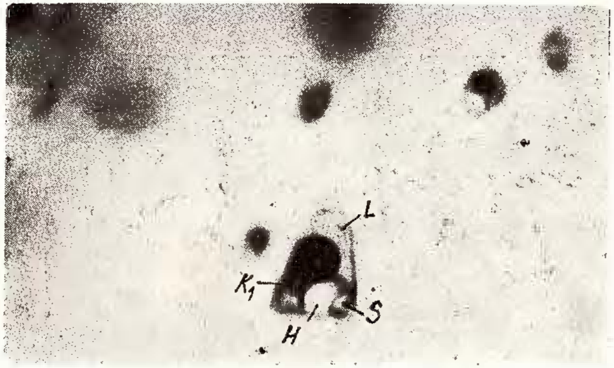

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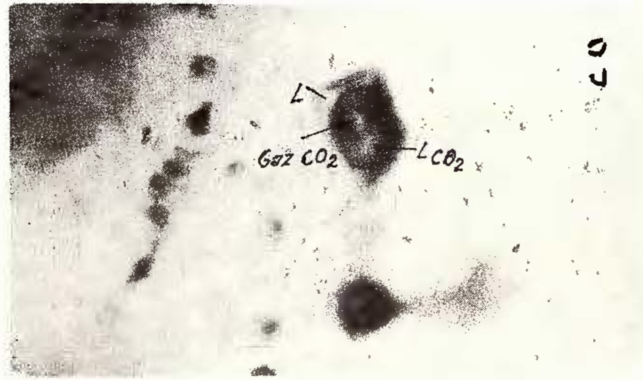

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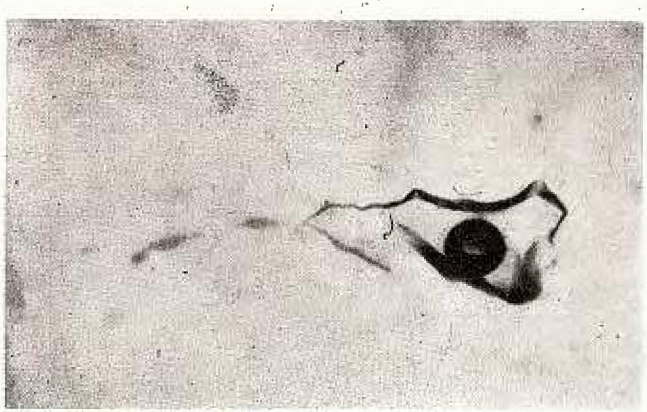

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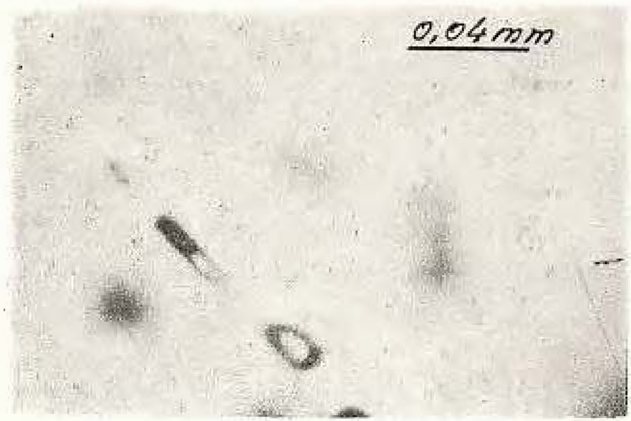

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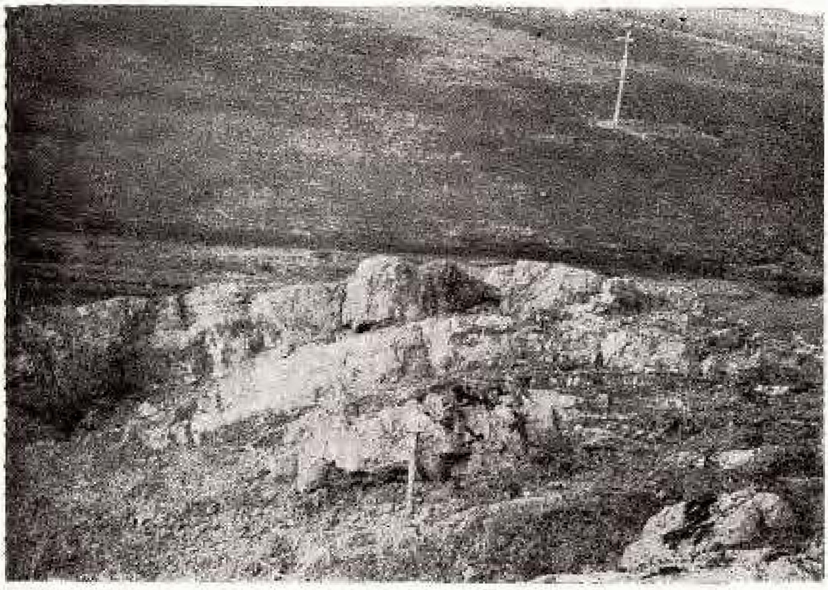

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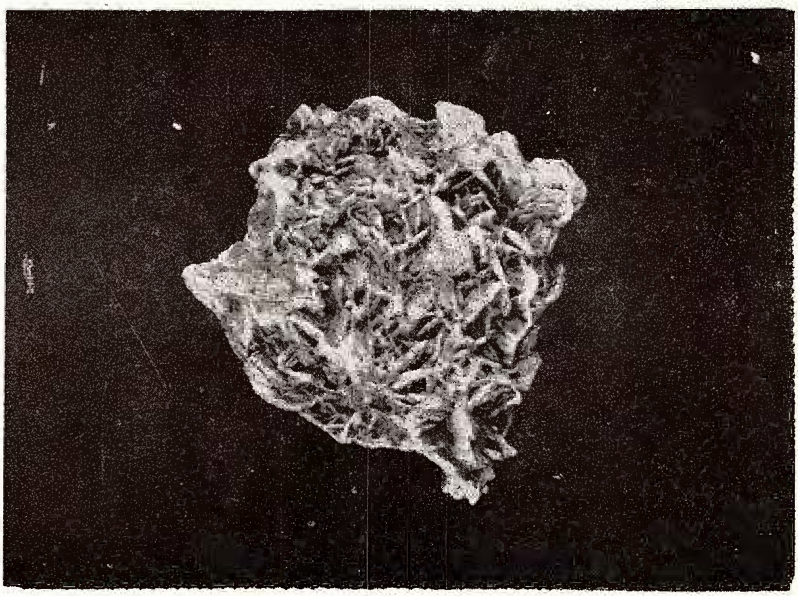

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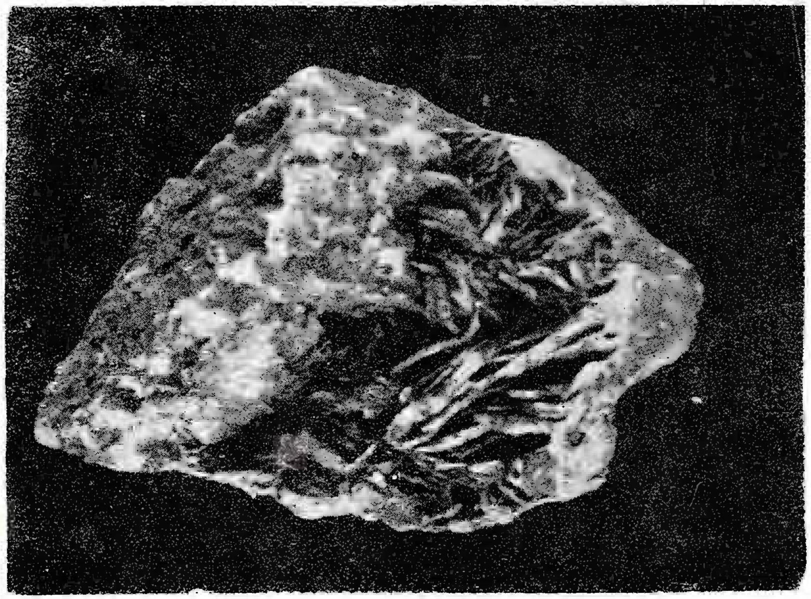

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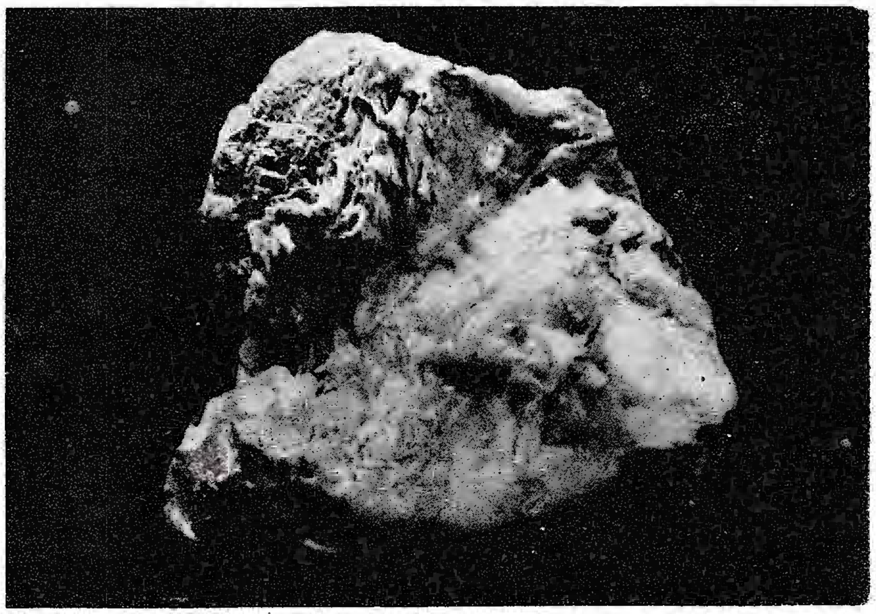

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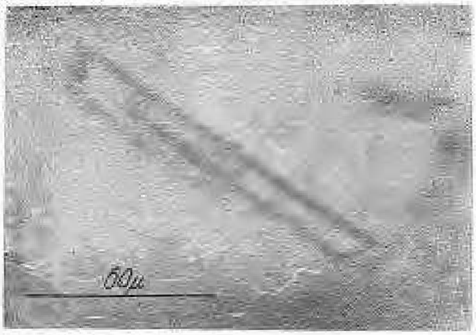

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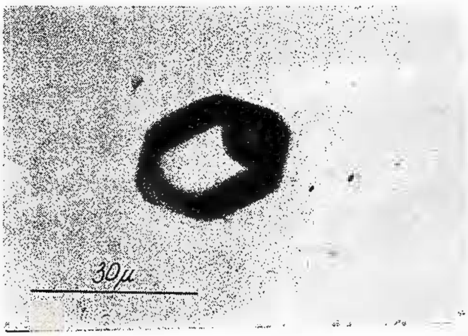

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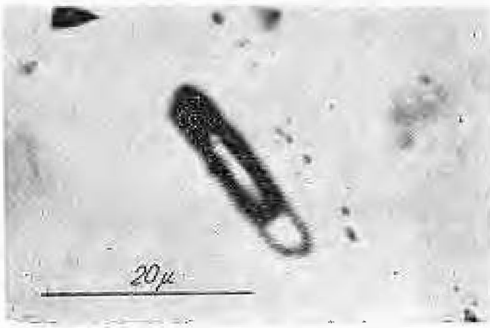

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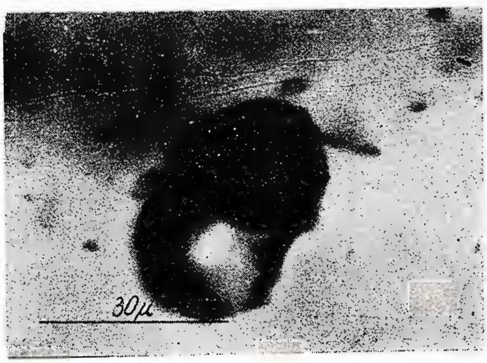

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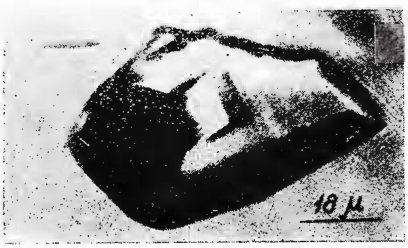

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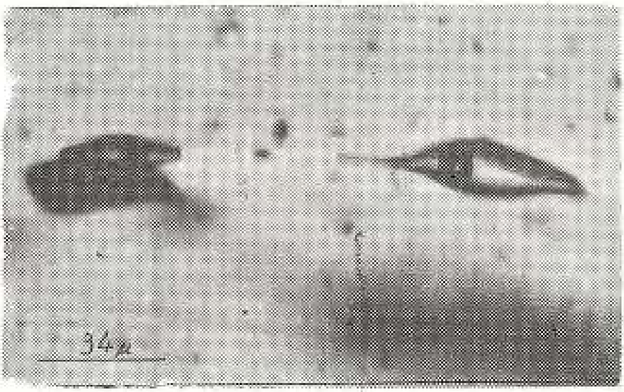

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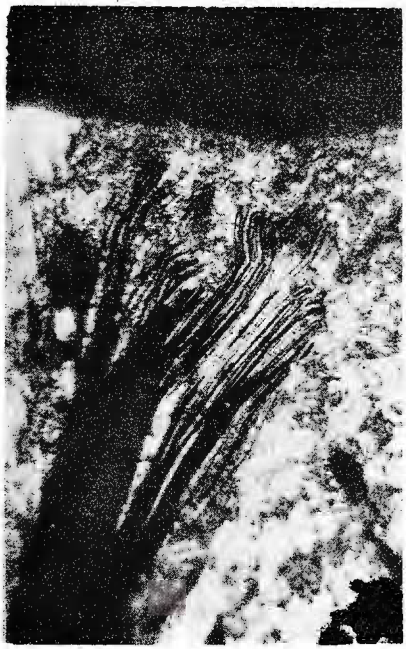

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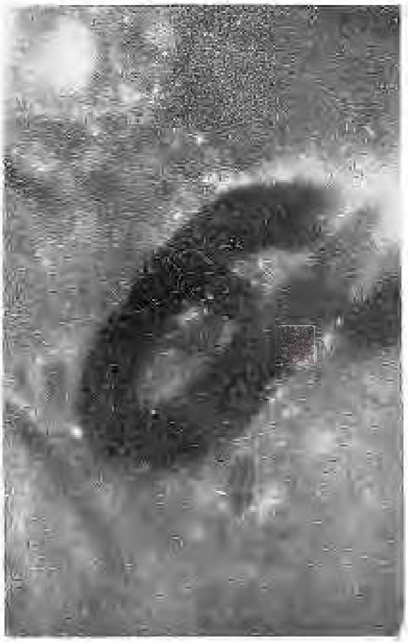

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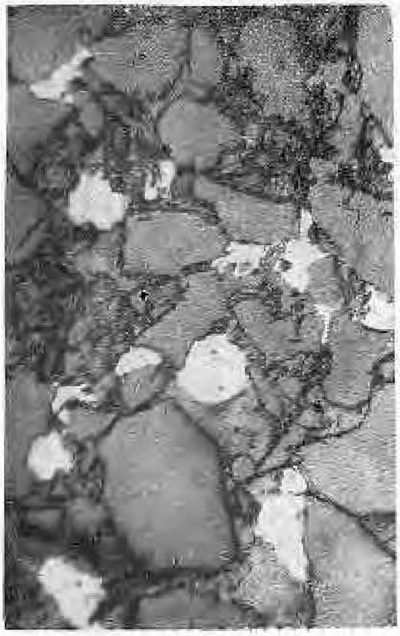

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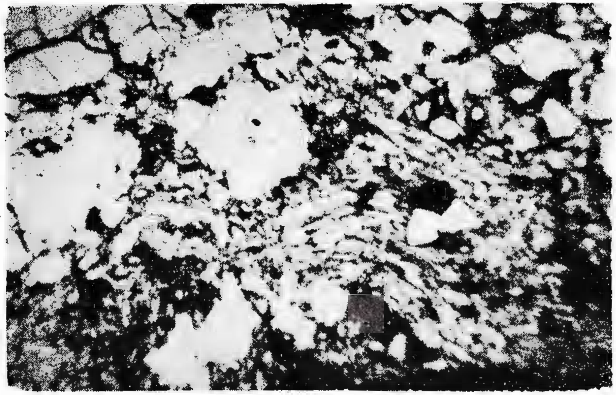

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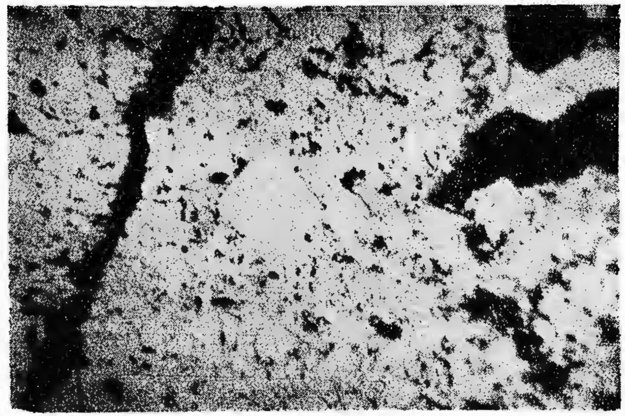

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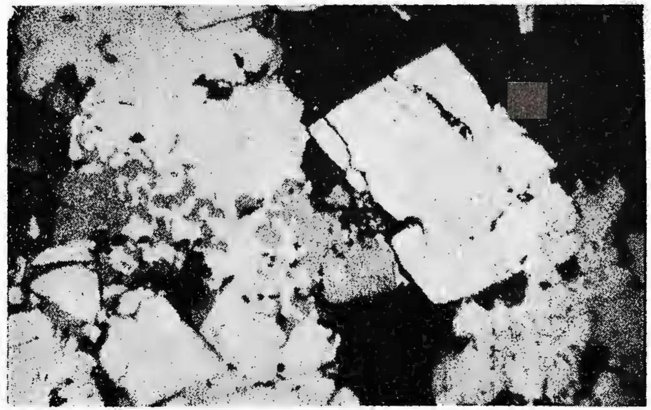

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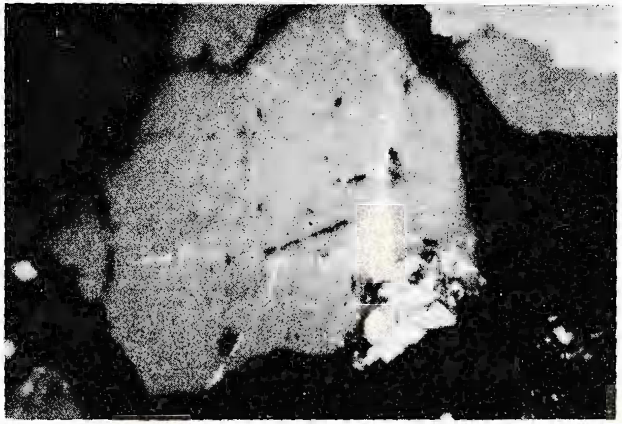

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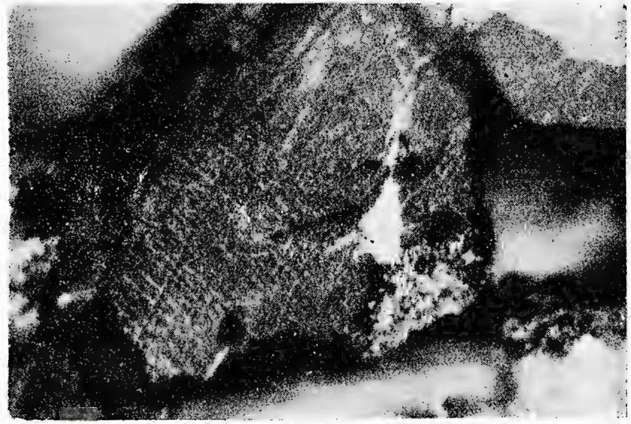

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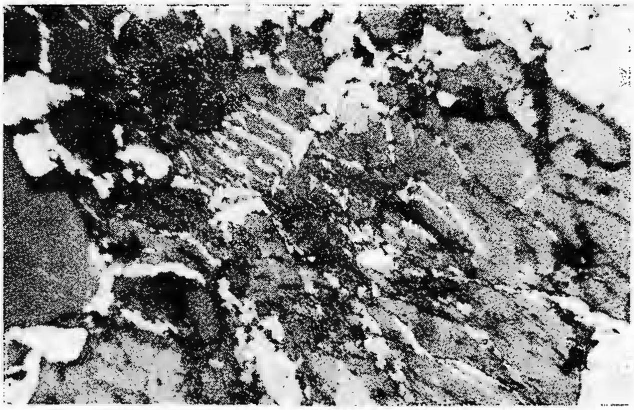

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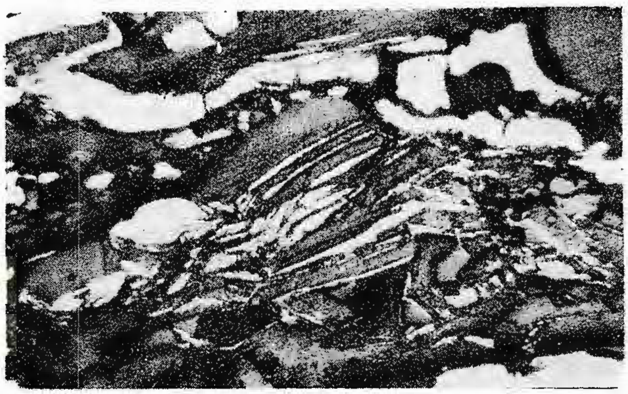

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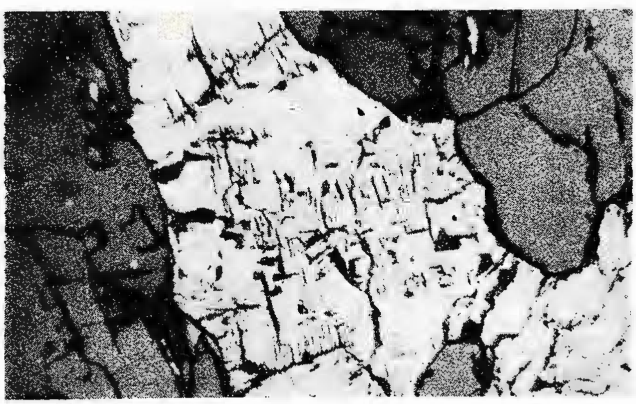

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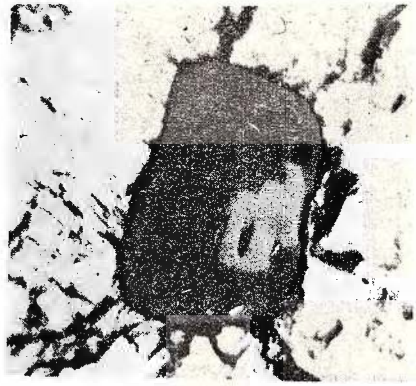

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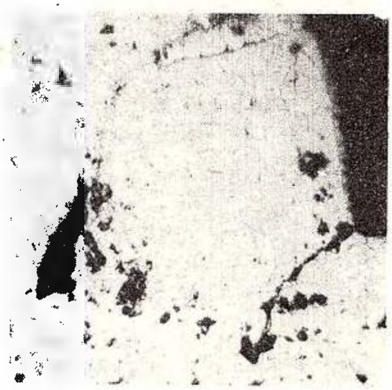

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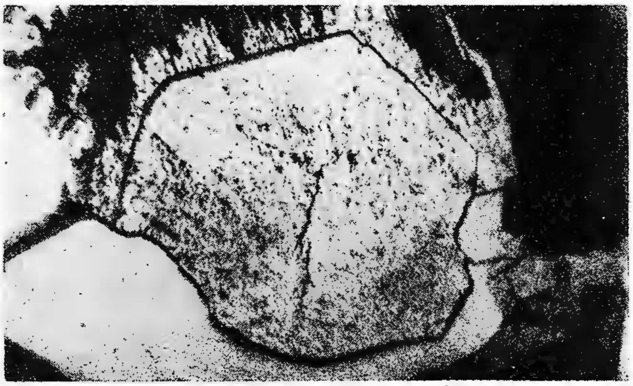

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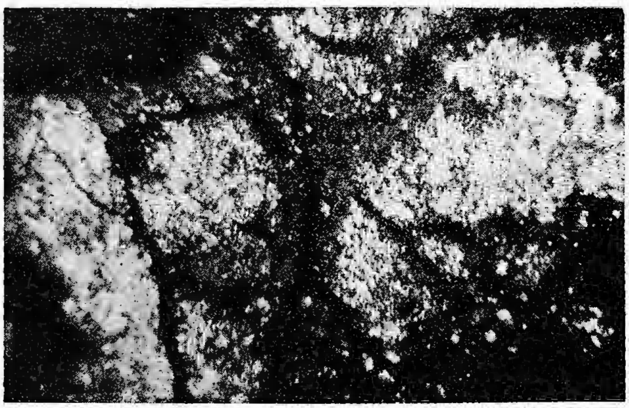

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Comitetul Geologic t. XXXVII-LII/1 (1953-1966)

Comitetul de Stat al Geologiei t. LII/2-LV/1 (1967-1969)

Institutul Geologic t. LV/2-LX (1970-1974)

Institutul de Geologie și Geofizică - à partir du tome LXI (1975)

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