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MINERALOGY DEPARTMENT
FACULTY OF GEOLOGY & GEOPHYSICS
UNIVERSITY OF BUCHAREST



THIRD NATIONAL SYMPOSIUM ON ECONOMIC GEOLOGY

**"Alpine Metallogenesis in Romanian
Carpathians and Adjoining Areas"**

Dedicated to Prof. dr. Doc. Gratiu Cioflica
(Honorary President of SGER)
on the occasion of the 75th Anniversary

1st-2nd November 2002, BUCHAREST



Institutul Geologic al Romaniei
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Third National Symposium on Economic Geology

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General informations

The scientific sessions will be held at the Mineralogy Dept. of the Faculty of Geology & Geophysics, located downtown Bucharest.

This Symposium is dedicated to **Prof. dr. doc. Gratiu Cioflica** (Honorary President of SGER) on the occasion of the 75th Anniversary.

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*dedicated to Prof. Dr. Doc. Gratiu Cioflica,
Honorary President of the Society of Economic Geology of Romania
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Foreword

The Symposia organized by the Society for Economic Geology of Romania and by the Department of Mineralogy at the University of Bucharest have reached their third edition. The Symposium we organize this year is dedicated to Prof. Dr. Doc. Grațian Cioflică – Honorary President of the Society for Economic Geology of Romania – on the occasion of his 75th anniversary and of more than 50 years of didactic activity and geological research.

The settlement of the Society for Economic Geology of Romania is linked to the name and activity of Prof. Cioflică, the first president of this society.

The Symposium entitled “Alpine Metallogenesis in the Romanian Carpathians and Adjoining Areas” and the papers we introduce here, represent a recognition of the special merits of Prof. Cioflică in the research of the metallogenesis belonging to the Alpine structures in our country, an activity reflected by tens of papers presented and published along the last decades.

His contributions focused especially on the Alpine ophiolitic formations in the Carpathians, whose petrology and metallogeny were treated with predilection. Prof. Cioflică also distinguished himself through his remarkable studies on skarns and the Iaramian metallogenesis in the Banatitic area.

In this anniversary year – 2002 – we also celebrate 75 years since the settlement, within the present the location, of the Department of Mineralogy, a veritable “High values producing institute”; until 1927, the Department had functioned in improper establishments with peripheral positions within the University. We dedicate this Symposium also to this event.

It is our pleasure to mention that a large number of Romanian research scientists – especially from the field of economic geology - have responded to the invitation to participate into the Symposium. Our satisfaction is even greater seeing that numerous scientists from Germany, Italy, Serbia, Norway, Israel, Iran, Jordany and USA, take part into this Symposium, each presenting valuable papers in the field of mineralogy, geochemistry and economic geology. In this context, the participation of Prof. Karamata from Serbia, and of Prof. Giovanni Ferraris from Italy, is to be dignified.

These constitute implicitly a recognition of the value of the scientific work of Prof. Cioflică, and it is our pleasure to relieve it.

We are convinced that also on this occasion, the Society for Economic Geology of Romania will offer a favorable framework for the exchange of useful ideas in the field of ore deposits research and exploitation, ideas that are especially necessary in this period of reassessing this domain of Geology in our country.

Prof. Gheorghe C. Popescu
President of the Society for Economic Geology of Romania

NEOGENE SILICEOUS DEPOSITS RELATED TO FOSSIL GEOTHERMAL SYSTEMS IN ROMANIA

CIOFLICA¹ Gratian, JUDE¹ Radu, PERRY² R.V., BERBELEAC³ Ion, SEGHEDI³ Ion, SZAKÁCS³ Alexandru, UDUBASA¹ Sorin Silviu

Introduction

In Romania, as in the other countries with active or fossil volcanic areas (Island, Russia, Japan, Taiwan, New Zealand, U.S.A., Chile etc) the surface and sub-surface deposits of geothermal system manifestations are very common. These manifestations can take the form of hot water seeps, hot springs, geysers, and hydrothermal acid alteration.

According to the temperature the geothermal systems are either hot water systems (HWS) or vapor dominated systems (>85% vapor, VDS). The surface manifestations of geothermal systems are represented by hot springs and geysers. Compositional varieties of surface deposits from hot springs and geysers include siliceous deposits, carbonatic deposits and ferruginous deposits. Siliceous deposits are mainly represented by silica sinter. Travertines are typical carbonatic sinters.

Sub-surface manifestations of geothermal systems include hydrothermal alterations of rock bodies through which the geothermal fluids (hot waters and vapors) circulate. They are most common in the central core-complex areas of volcanic edifices. There are variations of hydrothermalized rock bodies from veins, veinlets, lenses, breccia pipes up to diffuse pervasive alteration zones of various intensities. Acid leaching may result in formation of "secondary quartzites" by removal of most chemical components of the host rocks and local concentration of silica. Sometimes is difficult to distinguish such kind of silica bodies and surface deposited silica sinters.

The presence of these deposits in volcanic areas can stimulate exploration activities and must be taken in consideration when the geothermal potential is evaluated. In spite of their great varieties and extent, no modern investigations has been undertaken for these deposits in Romania, which probably covered much larger areas than today. Here we describe the siliceous deposits seen as products of fossil geothermal systems related to Neogene volcanism in Romania.

Some general features of surface manifestation of geothermal systems

The reservoirs of hot-springs and geysers are different and their characteristics are controlled by temperature, discharge rates, host rock type and structural factors. The surface manifestations of geothermal system are conditioned by the presence of permeable rocks and the system of fissures and faults which allow the fluid and gas circulations. Hydrothermal engine is driven by a deeper heat source represented by either magma chamber or cooling intrusive bodies. The surface hot spring discharges can directly overlie a heat source driven a geothermal system or they can be located laterally from it. The reservoir temperature of HWS can be low (<90°C), intermediate (90-150°C) and high (150-240°C). Note that this kind of hydrothermal system will not exceed the boiling temperature of water at the elevation of spring. The VDS occur in very high heat flow areas (e.g. California, New Zealand, Montana-Wyoming etc) and low water recharge. In the HWS, sub-surface gases from VDS, flow along the conduits, condense, form acid springs, and leach the rocks round the spring area. Bleached rocks, acid-sulfate springs, without chloride waters, mudpots, geysers and fumaroles are characteristic for these areas. A geyser can be defined as: 1) a hot spring that in time is hydrodynamically and thermodynamically unstable, while the common hot spring shows a continuous hot water flow; 2) a fountain (pool) of hot water from which, at some time intervals, blobs of superheated water suddenly rise to the surface and explosively flash, and 3) cones of siliceic sinter built up above subsurface conduits. The geyser eruption mechanisms show a cyclic behavior: 1) the

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conduits are filled with water that periodically flashes to steam, 2) emptying the conduits and 3) refilling (after some time) of the underground system.

Romanian Neogene siliceous occurrences

Romanian Neogene siliceous occurrences may represent fossil hot spring and geyser deposits or sub-surface hydrothermal alteration of host rocks. They are known in the East Carpathians calc-alkaline volcanic arc (between Badenian-Upper Pleistocene), a region with subduction-related mantle origin of the magmas and in the South Apuseni Mountains volcanic area with extension-related magmatism (14.8-1.6 Ma), (Fig. 1). In both regions, the andesite is the dominant rock type.

East Carpathians Neogene siliceous occurrences are known in northwest (Oas-Gutai Mts), in the northern part of Calimani-Gurghiu-Harghita volcanic chain and southern part of this chain.

In Oas Mts. the "siliceous formation" or "acid-sulphate alteration" has been recognized at Tarna-Turt area where opal, chalcedony $\pm$ quartz, pyrite and marcasite veins and veinlets or silicified breccia bodies related to advanced argillic alteration, are present. They usually appear as irregular

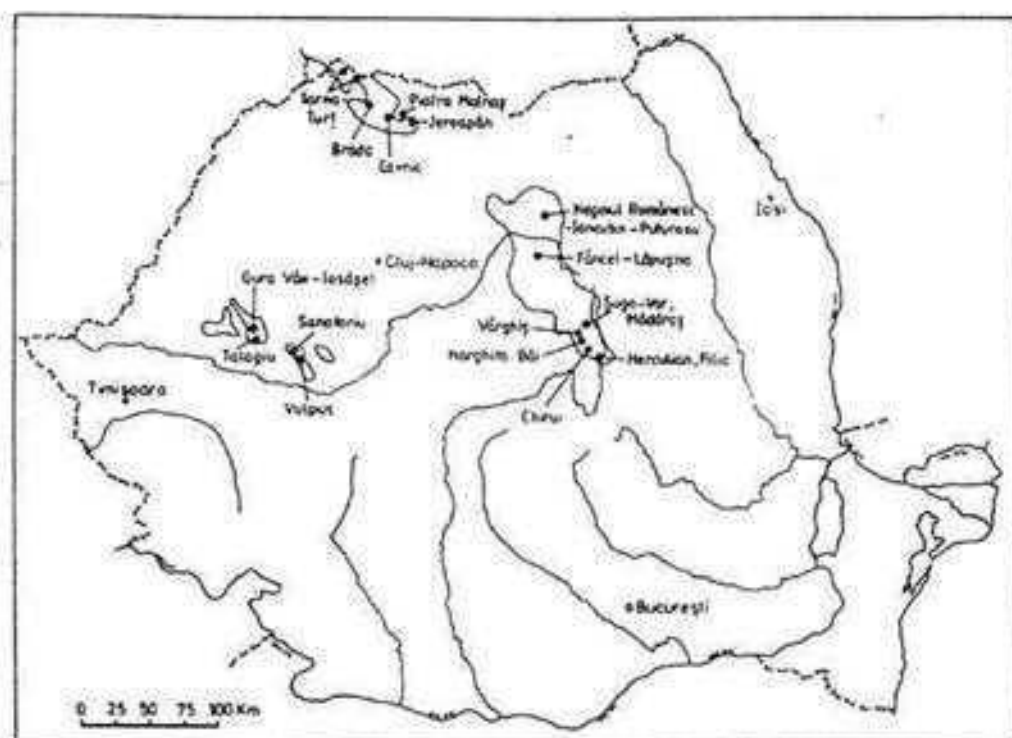


Fig.1 - Tertiary volcanic areas and main Neogene fossil siliceous deposits of geothermal systems in Romania.

elongated bodies on E-W fractures, range up to 1.5km long/ tens of meters wide and thick and are situated outwards or out of ore vein fields.

In Gutai Mts Sarmatian-Pannonian siliceous occurrences are preserved as white-yellow bedded silica sinters with plant casts (Piatra Malnas), breccia "pipe" (Cavnic Valley), veins and fissures filled with chalcedony and quartz. Breccified and limonitized porous rock ledges (crystalite, tridymite, opal, kaolinite, alunite, marcasite, melnicovite) within of a large (1-2Km/100-300m/tens meters thick) acid-sulfate advanced argillic alteration area are present at Jereapan-Varatec.

In Calimani caldera, at Negoiul Romanesc - Iancului Brook (up to 1 km²/80m thick) and at periphery of it, at Bradu Ciont - Puturosu Valley (up 0.5 km²/ 200m/tens m thick) a large silicic alteration area is present, previously known as "silicifications - gyserrites", "silicified pyroclastics" and "secondary quartzites". They are younger than the existing volcanic rocks (Pontian) and represent a white-yellow and brown-redish to dark brown siliceous deposit of an important solfatarian system. Close to actual surface were recognized lenses, beds, irregular veins and fissures with bedded, massive, compact or porous mass of opal, quartz, tridymite, sulphur, Fe hydroxides $\pm$ alunite,

barite, gypsum, jarosite, marcasite, melnicovite, etc. An inherited alternation of fine silica and Fe hydroxides lenses or beds are characteristic for Negoiul Romanesc siliceous deposit. Below mentioned deposit an advanced acid-sulfate alteration with native sulphur, marcasite, melnicovite, clay minerals assemblages, do occurs.

South of Calimani Mountains, as related to andesitic volcanics generated during Dacian-Romanian, the siliceous occurrences are products of "acid-sulfate alteration" in Fancel-Lapusna (Gurghiu Mts) and Varghis-Harghita Bai - Madaras area. Have also been described as "silicifications-gyserites" in Homorod Mic Valley "gyeiserites" with traces of plants and gasteropode casts north of Filia (limonite+opal) and Herculan areas (alternation of opal and siliceous limonite thin beds in pyroclastic rocks), "opalizations" in Chirui Valley and at Sugo-Var Valleys (Madaras) (cristobalit, alunite, kaolinite).

South Apuseni Neogene siliceous deposits are known as "jasperoids" at Vulpus Hill (Draica - Saliste Area) and "jaspers" at Sanatoriu Hill (Brad Area) in Metaliferi Mts, "sinters" in Cremeneasa Valley and products of "acid-sulfate alteration" in Talagiu Area (Zarand Mts). Jaspers and sinters were unanimously considered as geyser products.

At Vulpus connected to Upper Badenian andesite intrusion, along E-W roughly vertical contact between ophiolites and Upper Jurassic, gray-white, gray-blackish and yellow-brown irregular bodies, nets, veins and veinlets of quartz, tridymite, barite $\pm$ alunite, clay minerals, pyrite, marcasite, realgar etc, are present. Many sinters-like blocks can be seen on Draica Valley and its tributaries and toward south of Rea Valley.

Sanatorului Hill jaspers are undoubtedly the most characteristic Romanian sinter deposit. It includes multi-stages polychromatic chalcedony and opal sinter lenses (red, red-brownish, brown, yellow, white-yellow, ochre, white, blue-grey, black etc), hosted by Upper Sarmatian andesitic pyroclastics. The deposit lies at 5 km north from Brad Neogene volcanic-subvolcanic and metallogenetic area. Crisul Alb fault controlled lenses of sinter distribution which cover an area up to 0.01 Km², have 10-30m thick and represent terrace-like deposits with banded, massive, spongy and sometimes breccious mass. They preserve allothonus Badenian fauna, flora, fungi hiphae, bacteria and nannoplanton and poligenetic detrital fragments. Cristobalite-tridymite, opal-quartz and chalcedony-cristobalit-tridimit-quartz are the dominant mineral assemblages.

In Zarand Mts. silicic deposits are related with Sarmatian volcanic and metallogenetic activities at Talagiu and Gura Vail-Iosasel areas. At Talagiu within an advanced -argillic alteration siliceous, Fe hydroxides $\pm$ barite ("acide-sulphate") bodies and veins and veinlets of jasper (chalcedony and quartz, Bratosin Adit) are known. Here the thickness of acid-sulfate alteration usually does not exceed tens of meters, rarely 100-200m and it is superposed on propylitic, adular-sericite and feldspathic alteration or occur outward of this. At Gura Vail - Iosasel Area in upper part of Cremeneasa Valley many blocks of polychromatic chalcedony-quartz-opal sinters, some of them with water plant remainders and many gas globular voids, do appear. They cover up to 1km² area with advanced argillic alteration cross-cutted by numerous sub-surface veins and veinlets of jasper. In this area cinnabar occurrences are present.

Summary and genetic model

The Romanian Neogene siliceous deposits represent surface and sub-surface manifestations of hydrothermal system associated with Neogene-Pleistocene calc-alkaline volcanic activity. They can be considered the products of hot springs and geysers, as well as related to sub-surface hydrothermal alteration of host rocks. Hot springs and geyser type deposits have reliably been identified in a number of occurrences in the East Carpathians (Piatra Malnas, Chirui, Filia-Herculan) and in the South Apuseni Mountains (Sanatorului Hill, Gura Vail-Iosasel). They all display unequivocal evidence of surface deposition (preferentially occur at lateral locations with respect of central volcanic edifices, have terrestrial plant remainders, show layering and typical textural features of siliceous sinter deposits). Other occurrences can be assigned to sub-surface hydrothermal alteration processes (acid-sulfate alteration) related to central type volcanic structures or intrusive bodies. Sometimes they are related to epithermal mineralizations. Typical examples are: Tarna-Turt, Jereapan-Varatec, Calimani, Fancel-Lapusna, Vargis-Harghita Bai, Madaras from the Eastern

Carpathians and Talagiu and Gura Vail-Iosasel from the South Apuseni Mountains. A third category of occurrences include those siliceous deposits whose origin as surface or sub-surface deposition is uncertain according to the present level of knowledge.

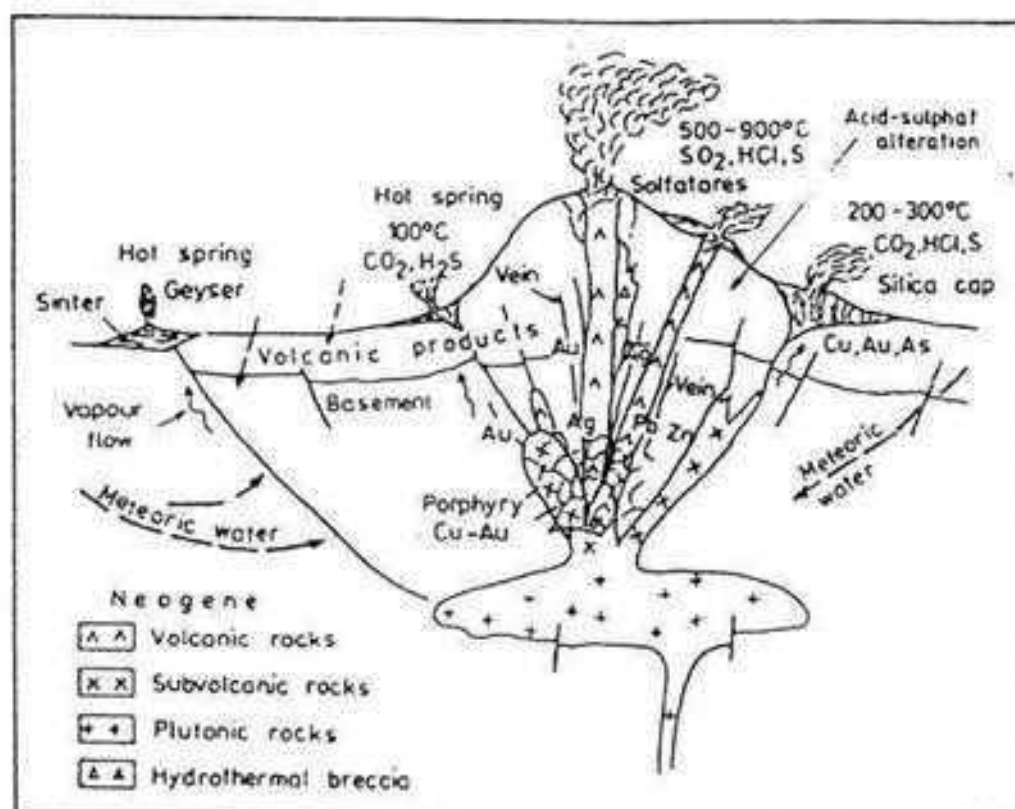


Fig.2 - Schematic cross-section showing environments for the formation of porphyry type, epithermal deposits and geothermal deposits (adapted from Henley (1985) and Hedenquist & Lowenstern, 1994, with modifications).

This is the case of Brada, Rachitele, Calimani and Sugo-Var from Eastern Carpathians. A schematic genetic model to explain the genesis of these deposits: siliceous deposits related to hot springs and geysers and siliceous deposits related with sub-surface acid-sulfate hydrothermal alteration is presented (Fig. 2).

Selected References:

- Henley R. W. (1985) *Reviews in Economic Deposits*, 2, p 298.
Hedenquist J. W., Lowenstern J. B. (1994) *Nature*, 370, p 519-527.

DISCOVERY OF ULTRAMAFIC-XENOLITHS LAYER IN THE TEPHRA SUCCESSIONS OF JABAL ARITAIN-S, JORDAN.

AL-MALABEH¹ Ahmad

Numerous occurrences of ultramafic-xenoliths outcrops have been described by the author in Harat Al-Jabban the Jordanian part of the large intercontinental alkali olivine basalt field of Harrat Al-Shaam that extends from northern Syria up to southern Saudi Arabia through Jordan. A 150 cm thick layer of of ultramafic-xenoliths has been discovered in the volcanic succession of the Strombolian volcanic cone of Jabal Aritain-S, Jordan. This layer is portray for the first time in this

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volcano and represents a distinguished worldwide record. These xenoliths are of oval to spherical in shape, and of 20-50 cm in long diameter.

Modal variation indicates that the studied xenoliths are mostly spinel lherzolite and spinel dunites. The xenoliths show protogranular and porphyroclastic textures. They formed of four anhydrous phases, olivine (60-75%), orthopyroxene (15-18%), clinopyroxene (9-15%) and spinel (~4%) and one hydrous phase of phlogopite (~6%).

The xenoliths are of Cr-diopside group and characterized by high content MgO (41-45 %) and Cr (1850-2443 ppm). Mineral chemistry shows that the xenoliths are of Mg-Cr-rich spinel and Mg-rich olivine.

The occurring of phlogopite represents as key indicators for mantle modal metasomatism related to the percolation alkaline melts. The absence of the other MARID hydrous mineral phases in the studied xenoliths indicating the limited degree of metasomatism.

Thermobarometry of the investigated xenoliths indicate temperatures: 980-1220°C and pressures: 14-16Kbar which represents a depth of about 45 km.

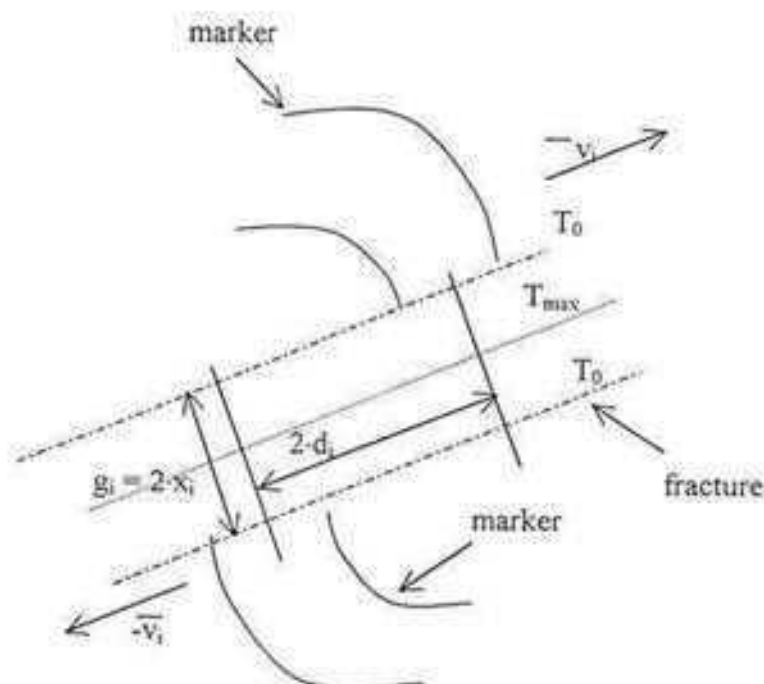
ATTEMPT TO CORRELATE THE "WIDTH" AND THE SHIFT OF A FAULT

BARBIR¹ Gabriel Dănuț

The tectonic and structural features represent the most important indication concerning the distribution and location of metallic ores (especially uranium) in metamorphic rocks. A very important practical problem is to determine the shift of the faulted ore bodies. In order to achieve this, it is imperiously necessary to assess the correlation between the "width" of the fractured zone (g_1) and the shift of the fracture ($2 \cdot d_1$). The example described, uses two real faults, with different positions, thickness and shifts:

- the incipient fault with $2 \cdot d_1 = 0.1\text{m}$ and $g_1 = 2 \cdot x_1$, macroscopically unobservable;
- the more evolved fault, within which the shear generated a shift of $2 \cdot d_2 = 1.0318\text{m}$ and $g_2 = 0.0668\text{m}$.

The problem to be solved out is whether there is any correlation between the width of the fracture and the associated shift.



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For the given starting data, the assumption has been made that the movement along the fracture determines an increase in the temperature which is directly proportional with the shift. According to the conservative non-stationary thermal conduction equation:

$$\frac{\partial T}{\partial t} - a_D \cdot \frac{\partial^2 T}{\partial x^2} = 0; a_D = 1.1 \cdot 10^{-6} \text{ m}^2/\text{s} \rightarrow \text{thermal diffusion coefficient};$$

one can deduce the time necessary to settle a transverse geothermal gradient across the fault, by taking a range of temperatures between 363.15 and 647.15 K. By solving the equation, we get:

$$\operatorname{erfc}\left(\frac{x_2}{2 \cdot \sqrt{a_D \cdot t_2}}\right) = \frac{T_0}{T_2} = \frac{363.15}{647.15} = 0.56 \Leftrightarrow$$

$$\operatorname{erfc}\left(\frac{0.0334}{2 \cdot \sqrt{1.1 \cdot 10^{-6} \cdot t_2}}\right) = 0.56 \Leftrightarrow$$

$$\frac{0.0334}{2 \cdot \sqrt{1.1 \cdot 10^{-6} \cdot t_2}} = 0.41 \Leftrightarrow$$

$$t_2 = 1508.25 \text{ s} \approx 25.14 \text{ min}$$

By knowing the time necessary for completing the shift and also, its value, as directly observed, one can deduce the initial speed (v_0), the final speed (v) and the acceleration in the final moment of fracturing. In order to solve this, we suggest the following equation:

$$v = v_0 \cdot \left(1 - e^{-\frac{a_D}{a \cdot d \cdot t}}\right) \Rightarrow$$

$$-a = \left(\frac{\partial v}{\partial t}\right)_d = \frac{v_0 \cdot a_D}{a \cdot d \cdot t^2} \cdot e^{-\frac{a_D}{a \cdot d \cdot t}};$$

$$\frac{1}{t} = \left(\frac{\partial v}{\partial d}\right)_t = \frac{v_0 \cdot a_D}{a \cdot t \cdot d^2} \cdot e^{-\frac{a_D}{a \cdot d \cdot t}} \Rightarrow$$

$$a = \frac{v_0 \cdot a_D}{d^2} \cdot e^{-\frac{a_D}{a \cdot d \cdot t}}; \Rightarrow a = -\frac{d}{t^2}; a_2 = -\frac{d_2}{t_2^2} = -\frac{0.5159}{1508.25} = -2.26 \cdot 10^{-7} \text{ m/s}^2$$

$$-a^2 = \frac{v_0 \cdot a_D}{a \cdot d \cdot t^2} \cdot e^{-\frac{a_D}{a \cdot d \cdot t}} \Rightarrow a = -\frac{d}{t^2}; a_2 = -\frac{d_2}{t_2^2} = -\frac{0.5159}{1508.25} = -2.26 \cdot 10^{-7} \text{ m/s}^2$$

$$|v_0| = \frac{a_2 \cdot d_2^2}{a_D \cdot e^{-\frac{a_D}{a_2 \cdot d_2 \cdot t_2}}} = \frac{-2.26 \cdot 10^{-7} \cdot 0.5159^2}{1.1 \cdot 10^{-6} \cdot e^{-\frac{1.1 \cdot 10^{-6}}{2.26 \cdot 10^{-7} \cdot 0.5159 \cdot 1508.25}}} = 5.52 \cdot 10^{-2} \text{ m/s}$$

$$v_2 = v_0 \cdot \left(1 - e^{-\frac{a_D}{a_2 \cdot d_2 \cdot t_2}}\right) = 5.52 \cdot 10^{-2} \cdot \left(1 - e^{-\frac{1.1 \cdot 10^{-6}}{2.26 \cdot 10^{-7} \cdot 0.5159 \cdot 1508.25}}\right) = 3.43 \cdot 10^{-4} \text{ m/s}$$

Assuming that the fracturing took place in adiabatic conditions, the speed for shifting the isotherms perpendicular to the shearing is approximately constant:

$$V_{\perp} = x_2/t_2 = 0.0334/1508.25 = 2.21 \cdot 10^{-5} \text{ m/s};$$

$$V_{\perp} = x_1/t_1 \Rightarrow x_1 = 2.21 \cdot 10^{-5} \cdot t_1$$

As an application, the case of a fracture with a shift equal to $2 \cdot d_1$ has been taken to deduce the acceleration $-a_1$, the fracture width $-g_1$, the time $-t_1$ and the temperature $-T_1$:

$$a_1 = -\frac{d_1}{t_1^2} = -\frac{0.05}{t_1^2} \quad (1); v_0 = -\frac{a_1 \cdot d_1^2}{a_D \cdot e^{\frac{a_D}{a_1 \cdot d_1}}} \quad (2) \Rightarrow e^{\frac{a_D}{a_1 \cdot d_1}} = \frac{d_1^3}{v_0 \cdot a_D} \Leftrightarrow$$

$$\Leftrightarrow t_1^2 \cdot e^{-0.00044 t_1} = 2058.03 \Rightarrow t_1 = 45.83 s \Rightarrow a_1 = -1.09 \cdot 10^{-3} m/s^2 \Rightarrow$$

$$\Rightarrow x_1 = 1.02 \cdot 10^{-3} m \Rightarrow g_1 = 2.03 \cdot 10^{-3} m$$

$$erfc\left(\frac{x_1}{2 \cdot \sqrt{a_D \cdot t_1}}\right) = \frac{T_0}{T_1} \Leftrightarrow erfc(0.071) = \frac{363.15}{T_1} \Leftrightarrow T_1 = \frac{363.15}{0.92} \Leftrightarrow$$

$$\Leftrightarrow T_1 = 394.94 K = 121.79^\circ C$$

This calculation approximates satisfactorily the parameters to be determined for shear faults with shifts of up to 1 m.

GRANITIC MASSIVE OF NORTHERN DOBROGEA – BUILDING MATERIAL DEPOSITS OR PROTECTION AREA?

CETEAN¹ Valentina, MARICA² Silvana

Introduction

The Macin Mountains are the oldest mountains in Romania, which have been transformed in a hundred thousand years of erosion and tectonic movements. Today they aren't mountains anymore, but is the mountain's root, representing the ruins of the original mountain of a hundred millions years ago. Their peaks have been eroded almost to their base by the winds and arid climate. The yellow dust covers irregularities in the ground. They stand above the Danube bed with about 300 – 400 metres. Macin Mountains have NW-SE direction, almost 500 square meters area and the maximum width is 24 kilometres.

They are composed of parallel summits, more numerous in the south-south-western side. The main summit of Macin Mountains (467 meters in Tutuiatu peak) go on - in the NW and SE - with the other parallel summits, what are constituted preponderantly of granitic rocks. The secondary summit, parallel with the main summit to, is constituted of more massifs with an island character. Morphological limit with the geotectonic eastern unit corresponds with an overlapping tectonic line. The Macin Mountains represent the most evidently local example of hercinic orogenesis from the end of Palaeozoic. They show a characteristic morphological structure, with a total concordance between the main lines of relief and geological composition. The morphological aspect of the Macin Mountains, being near the Danube and the existence of a unique flora and fauna contributed to the inclusion of this area into a reservation.

The Geology and the Genesis of Magmatic Rocks

The Macin Mountains originated into rifting cratonic area. The principal structure of these mountains finalized by orogenetic movements of hercinic (Upper Palaeozoic) period. Concomitant with these movements was formatted a large granitic volume. More of 80 percent of actual Macin area represent granitic rocks. Hercinic magmatic rocks are following deposit's shapes: batholith with many apophysiss and dykes, sills, laccolite.

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These granites were breaking Palaeozoic beds, what are metamorphosed at contact. In Northern part of these mountains exist a great laccolite - 6 km diameter. The most important types of rocks are representing by calc-alkaline and alkaline granites. Generally, these rocks are massive, but there is an alteration zone in the upper part of granitic area of 5-15 meters thickness. The magmatic source had an acid character, with distinct separations what formed similar mineralogical zones and different colours. The magmatic source had a strong acid character, with separations that determined the formation of granites, granodiorites, diorites, tonalities, gabbros and quartzitic porphyries. The calc-alkaline granites have a typical development in the Northern part of Macin Mountains and in the central part of mountains (Pricopan summit). In the Southwestern part, the granites have a light foliation and, sometimes, microgranulation character.

The Tectonic of Deposit

Such majority others granites deposits, Macin Mountains' granites have a primary fissuring due to the cooling of magmatic chamber and secondary, tensional fissuring due to two factors: involving granitic massif in tectonic movements and supergene alteration phenomena meet only in upper part of massif. Predominating fissures due to the cooling process of magmas have NW-SE or NNE-SSE direction and were recognized in deep, near to the limit of electrometer and drilling investigations. The representation of fissuring measurements achieved individual, for the predominant strikes (Fig. 1) and layer's inclinations (Fig. 2).

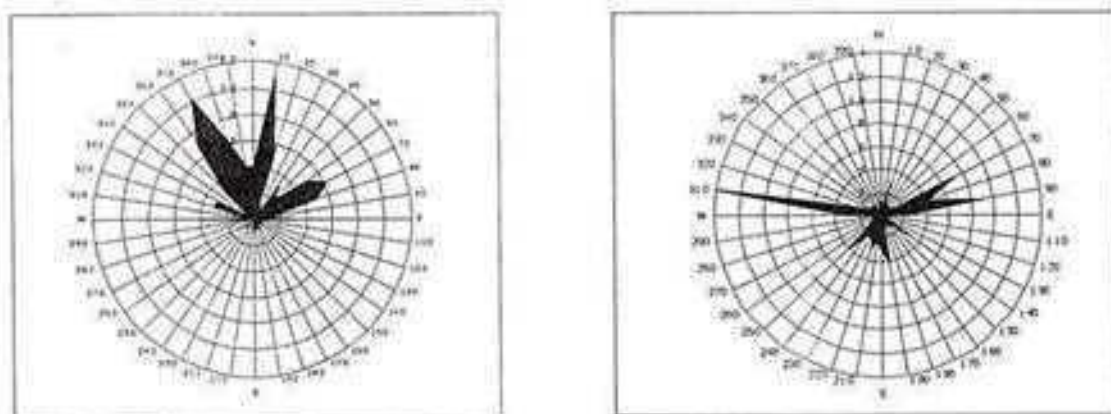


Fig. 1, 2 - Rose diagrams of predominant strikes and predominant layers' inclination in the Macin Mountains

Sharing fissures have a different orientation: NNE-SSW, NNW-SSE and NW-SE. These fissures determined turning and moving off of granitic blocks. The corneean rocks fill the most part of such fissures. They formed at contact between granitic magma and subsequent metamorphic rocks. The unloading fissures ("sheet structure") are, in principal, perpendicular on morphological surface (70° - 88° / 70° - 90°) and secondary almost horizontal on surface (40° - 75° / 2° - 20° , 90° - 95° / 10° - 30°). Tensional fissures associate with shearing phenomena and forms typical surfaces limits by 40-50 m² with chloritic minerals and fraction glasses. Tensional fissures appear sometimes associates with shearing fissures. All types of fissures limit useful blocks for ornamental tiles. Maximal volume of these blocks rich at 1.8 - 2.5 m³.

Mineralogy of Granites

The large part of the Macin's rocks is granite with biotite, what appearing in two varieties: rose and reddish granite, medium crystallized; grey - bluish granite, small crystallized. Percentage mineralogical compositions of Macin Mountains' granite are: Quartz 25-40%, Feldspar 50-72%, Ferromagnesian minerals 3-8%, Accessory minerals 3-8%, Opaque minerals 1-2%.

The both varieties have a variegated aspect due to elongated crystals of biotit. The granitic rocks have hypidiomorphic (subhedral) hollocrystalline structure and massive slowly orientate texture (Fig.3).

Oxidic compositions of granites

The values of the Niggli's parameters are indicating the Macin Mountains granites' affiliation at the chalcalkaline magmas originate at depths: engandinite-granite and type yosemite-granite. The chemical analyses on different samples demonstrated similar values of studied granites: Fe_2O_3 - 1.32-2.69, Al_2O_3 -12.85-13.22, TiO_2 - 0.18-0.28, CaO - 0.72-2.92, MgO - 0.35-0.84, Na_2O - 3.93-3.78, K_2O - 3.42-5.75, SiO_2 - 73.07-74.68.

Physical and mechanical characteristics

The granites have good physical and mechanical characteristics, reason they are able to use in the ornamental stone industry, for outside or inside plating (slabs). Also, the granite of Macin is good for roads, hydrotechnical works (crushed rocks) and for building industry (stone blocks, sett stones, buildings slabs, rubble stones, building's foundations). The characteristics are: density -2.709-2.720 Kg/dm^3 , apparent density -2.64 Kg/dm^3 , total porosity-2.35-3.19%, apparent porosity-0.22-0.25%, water absorption at normal pressure-0.08-0.14 %, water absorption through boiling -0.15-0.19%, coefficient of frostleftness - 0.03-0.04%, compression strength- 1254-1403 daN/cm^2 .

Considerations about granites exploitation in the Macin Mountains

In 2001 it was inventoried approximately 40 quarries for granites and granodiorites (Fig.4), but presently only 3 are in operation the production of crushed rocks blocks. For a good utilization of the Macin granite is necessary to adopt modern mining and processing methods what can reduce the big volume of sterile and the impact on landscape. Because the Macin are old mountains, they were suffering intense erosion. This reason and exploitation with explosives determined a big fissuring and alteration of rocks.

The cover of deposits varies between 5 and 15 metres and - sometimes, the recuperation of the blocks is only 5%. A thousands cubic meter remained in the waste-dumps, in each area where exploited the granites. The extraction of the Macin granite no affect the water level or people life, but easy access, little altitudes and the absence of big vegetation determined a irrational exploitation of these raw materials.

Building materials deposits or protection area?

The area of the Macin Mountains is one of the most important granite resources for ornamental building industry. The red and blue granites have a very beautiful aspect and good properties. Usual thickness of slabs is 1 centimetre and the edges are rights. On the Romanian ornamental stone market, Macin's granite has an important place. Besides, in the Eastern part of Romania (Dobrogea), the Macin Mountains are the only deposits for ornamental granites and they have a big economical importance.

Macin Mountains are a beautiful area for tourism, too (Fig.5). The typical flora and fauna (e.g. tortoises) and morphologic aspect so different, with megalithic forms (Fig.6), determined the inclusion of Macin Mountains into protected area. In present, the granite's exploitation carries out

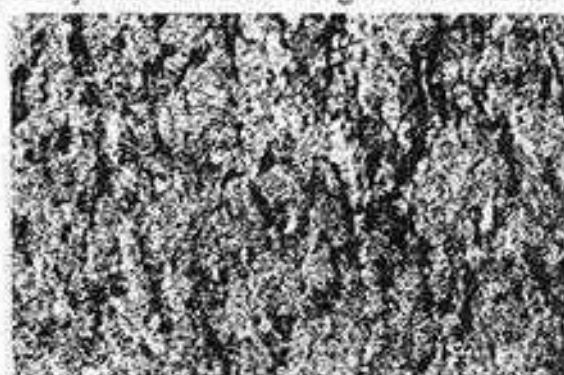


Fig. 3 - Petrographical type of the Macin Mountains' granite



Fig.4 - Abandoned quarry in the Macin Mountains

only the permit of Biosphere reservation Tulcea, the national organism what protect and The Danube Delta.



Fig 5 - Landscape in the protection area of the Macin Mountains



Fig 6 - Landscape in the Macin Mountains.
A witness over a 300 Mil. years

For geologists and for the nature lovers, the Macin Mountains remain an open book of geological and morphological history. A story, an invitation...

COMPARISON OF SPECIATION OF BI-SULPHOSALT ASSEMBLAGES IN UPPER CRETACEOUS 'BANATITIC' AND NEOGENE MINERALISATION IN ROMANIA

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Many of the foremost occurrences of Bi-sulphosalts (Bi-ss) worldwide are found in the Romanian segment of the Banatitic Magmatic and Metallogenetic Belt, BMMB (Ciobanu et al. 2002). A broad variety of Bi-sulphosalts have been reported from all skarns, except for the Fe-skarn at Băișoara; and lesser occurrences are known from porphyry deposits within the belt, e.g. Moldova Nouă. Sulphosalts have been described in many dozen publications over the past 125 years (e.g. Cioflica & Vlad 1979; Cioflica et al. 1990, 1995, 1997; Ilinca 1998; Mumme & Žák 1985; Žák et al. 1994; Ciobanu & Cook 2000, 2002). Indeed, the 'banatite' metallogenetic province has provided type localities for two new species, padëraite and makovickyite and both old and new samples from localities in the belt will surely continue to provide new insights for future ore mineralogists.

Minerals from each of the principal Bi-sulphosalt groups: bismuthinite derivatives (BD), pavonite, lillianite and junöite homologous series, cuprobismutite group etc., are present at Băița Bihor, Ocna de Fier and Oravița-Ciclova, as well as in many smaller occurrences, e.g. Tincova. A similar range of Bi-sulphosalts is known from vein and skarn deposits within the Bulgarian segment of the belt. In fact, the pronounced Bi-rich character, along with a pronounced enrichment in Au, Ag, Te, Se and Co is one of the characteristic features of the belt (Cook et al. 2002). Additional species and new occurrences have been described with some regularity in recent years, due to increased access to electron microprobe and single crystal diffraction techniques.

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In this presentation, we review a range of newly described occurrences and assemblages containing Bi-ss from both the Upper Cretaceous and Neogene mineralisation in Romania, the implications which these rare minerals have for understanding the processes of magmatic-hydrothermal mineralisation, and stressing the value of continued mineralogical studies from the perspectives of both systematic mineralogy and applied science.

A key feature of Bi-ss assemblages in the BMMB is that assemblages vary considerably from occurrence to occurrence and, significantly, within zones of individual deposits. The zoned skarn deposits formed at a broad range of moderate to high temperatures, a variety of environments in fS_2/fO_2 space, and not least, highly localised fluid evolution and cooling patterns, have caused great variation in assemblage and paragenesis within individual deposits, and indeed, within samples spaced just a few metres apart.

Assemblages within the Ocna de Fier-Dognecea skarn can be used to illustrate this point. Previously, we have described Bi-ss assemblages dominated by BDs with accessory lillianite homologues from the Fe-zone of the deposit (Ciobanu & Cook 2000), with emphasis on the intricate intergrowth patterns between coexisting minerals. Within the same zone, two further assemblages are identified: (i) complex intergrowths of cuprobismutite, padëraite and hodrushite at various scales within matrix BDs in the range gladiolite-bismuthinite (Cook & Ciobanu in press) and (ii) Bi-ss including lillianite-gustavite solid solution ($G_{20}-G_{75}$), feibertalite, a Bi-rich phase with a composition close to eclarite, and accessory tetradymite as inclusions within prograde pyrite, garnet and magnetite. Other assemblages containing Bi-ss are evident elsewhere in the system. We have recently investigated samples preserving relicts of a rich Bi-ss association in magnetite from distal skarn at Ocna de Fier and note that the entire prograde assemblage is crosscut by later μm -scale trails of one-, two- or three-component blebs with curvilinear boundaries between phases consisting of native-Au, -Bi, maldonite and Bi-tellurides/sulphotellurides with $\text{Me}/(\text{Te}+\text{Se}+\text{S}) > 1$ (hedleyite, Joséite-B) with tetradymite and bismuthinite. A further 'new' assemblage consists of matildite, the Ag-tellurosulphide cervellite, and a range of as-yet unidentified Bi-ss.

Similarly, in Băița Bihor, our investigations of bornite-rich ores currently under underground exploitation have revealed assemblages not recorded in either museum or dump material by other workers and which have, until now, formed the basis for most research identifying and characterisation of new species. Although prevailing wittichenite in the bornite ores appears to preclude formation of other Bi-ss, we note the widespread occurrence of berryite, associated with aikinite and galena within Pb-Zn ores in the same zone. In all investigated occurrences and associations, we note that Bi-ss commonly occur together with Ag- and Au-minerals, lending the assemblages an economic significance. Bi-ss (or associated Bi-tellurides and tellurosulphides) are a guide to Au-enriched parts of the ore.

In contrast to the abundance of Bi-ss throughout the BMMB, few have been previously reported from Neogene mineralisation in the Carpathian Arc. Indeed, with the exception of Bi-sulphosalts within the Băiș-Văratec and Toroiaga deposits of the the Baia Mare and Baia Borșa districts in northern Romania (Cook 1997, 1998), the only other known occurrence of Bi-sulphosalts in the Romanian Neogene is from the Larga hydrothermal system, South Apuseni Mts. Here, Bi-ss are found within veins and skarn-like bodies in the Larga hydrothermal system. Larga, with Fața Băii, Haneș, Breaza & Trîmpoie, constitutes a major orefield at the SE end of the Zlatna-Stanija volcanic zone. Exploitation of the Larga deposit concentrated on 3 lenses of high-grade gold-pyrite ore at the contact of Paleogene Fața Băii conglomerate and Badenian shale. Dense, NW-SE striking, <500 m long veins of the Fața Băii group occur in conglomerate at similar levels, 500 m to NW. Gold, both as native-Au and as Au- and Au-Ag-tellurides is abundant. Our sample material comes from ores accessible from the Horea exploration gallery, 250 m below exploited ores at Larga and Fața Băii and representing the median part of a 1km column of epithermal mineralisation consisting of massive sulphides and veins at upper levels, complemented by skarn-porphyry mineralisation at depth. Bi-sulphosalts are rare but persistent accessories of both vein and skarn ores outcropping on the Horea level (+516 m), where they occur as <100 μm inclusions within pyrite. Lillianite homologues are the dominant sulphosalts and all (lillianite, gustavite, heýrovskyite) display variable contents of Se

(Se/Se+S up to 0.22) and Sb (Sb/Sb+Bi up to 0.34) in many studied cases. In addition, an unusual occurrence of treasureite is noted, exsolved in hessite and intimately associated with tetradymite. BDs (aikinite, krupkaite, bismuthinite) are minor components and appear as inclusions within lillianite. Cosalite is a minor phase.

This occurrence, both in the dominance of lillianite homologues, typical occurrence within Au-enriched pyrite ($\pm$ arsenopyrite) ores, and variable but persistent substitution of Se and Sb shows sharp similarities with the Bi-sulphosalts described from the Baia Mare/Baia Borsa districts (Cook 1997, 1998). Their occurrence in the vein type deposits is controlled by the parameters of the pyrite-buffered environment. Co-existing tellurides and tellurosulphides (hessite, tetradymite, tsumoite) have $Me/Te(+Se+S) \leq 1$. Such assemblages indicate high fS_2 conditions are indicated, coupled with relatively high fTe_2 . The association between tetradymite and Bi-ss (aikinite-bismuthinite and lillianite series) is significant, since synthetic experiments show extensive solid solution in the Bi_2S_3 - Bi_2Te_3 system, e.g. 43-66 mol.% Bi_2Te_3 at 500°C (Yusa et al. 1979). The presence of minor Pb within the 'droplets' encapsulated in pyrite favours formation of Bi-ss and/or Bi-sulphotellurides since characteristic order-disorder (OD) mechanisms in these minerals can be accessed to accommodate non-stoichiometry (c.f. Bayliss 1991). Both Bi-sulphotellurides and sulphosalts are commonly non-stoichiometric, a fact that can be correlated with OD in both series. If tetradymite is absent, equilibrium formation of Bi-ss is normally precluded.

Discussion and conclusions

Bi-ss are highly sensitive to local environments of formation, highly localised domains of chemical equilibration, compositional factors and distinct cooling path histories, thus explaining the plethora of different assemblages, each of which points to a defined point on a petrogenetic grid. The high temperatures of formation (up to 650 °C) of some of the Romanian skarns allows phases to crystallise that may otherwise not form as stable minerals. In addition, the skarn environment is ideally suited for the development of intergrowths disordered on scales down to the unit cell, such as that between cuprobismutite, padérite and hodrushite from Ocna de Fier. The Romanian deposits offer excellent possibilities for the discovery of new minerals (for example, additional homologues in the pavonite, cuprobismutite and junotite homologous series). Also, as more assemblages are characterised, it is to be hoped that it will be possible to establish the external controls upon assemblages. The underlying reasons for the extraordinary enrichment in Bi require verification, as do the characteristics of the mineralising fluids that have so efficiently led to the variety of Bi-ss bearing assemblages within the BMMB. In contrast, the number of occurrences within Neogene mineralization will probably remain limited to volumetrically insignificant occurrences buffered by pyrite and controlled by local variance in fTe_2/fS_2 .

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Editor's Note :

The presence of Bi minerals in the Neogene ores of Romania is not limited to the occurrences presented by the authors of this paper. Simon and Alderton (1995) reported pilsenite and a Bi-rich "mineral A" in the ores of Sacaramb. Damian and Cook (1999) identified some members of the bismuthite - aikinite group, i.e. pekoite, gladite and krupkaite as well as cosalite in the ores at Nistru, Baia Mare area. Further on, Damian and Costin (1999) identified also vikingite at Varatec - Baiut.

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THE Bi-Te-Se-S SYSTEM: PROBLEMS, OPPORTUNITIES AND IMPLICATIONS

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Mineral compounds of bismuth with tellurium and/or selenium and/or sulphur are found in a wide range of magmatic, hydrothermal or metamorphogenic Au-, Cu-Au ores and base metal ores with by-product Au of all ages. These minerals can be sub-divided into seven sub-groups according to stoichiometry (Table 1). Despite more than 300 publications devoted to their nomenclature, compositions and occurrence over the past 100 years, systematic relationships remain obscure for some sub-groups, e.g. the 'simple' Bi-Te system. In particular, uncertainties exist about the extent of solid solution and/or isomorphism between members of individual sub-groups (e.g. Bi_4Te_3 - Bi_4Se_3 - Bi_4S_3 or Bi_2Te_3 - Bi_2Se_3 - Bi_2S_3), the crystal chemistry and compositional fields of some of the less well-characterised members of the group, e.g. 'protojoseite', and the extent of element ordering/disordering that can be structurally accommodated into minerals such as tsumoite, ingodite or nevskite. More complex still, are the further group of compounds within the five-component sub-system Bi-Pb-Te-Se-S, the natural occurrences of which remain very restricted in number.

There have also been very few attempts to characterise these mineral groups in terms of their paragenetic position within magmatic-hydrothermal systems, or to examine, subjectively and comparatively, phase relationships between co-existing minerals. This is despite the fact that this group of minerals occurs as accessory phases commonly intimately associated with native gold or Au-/Ag-Au-tellurides in, among others, Au skarns, porphyry Cu-Au deposits, epithermal massive sulphides, metamorphosed stratiform sulphides and in the Au-enriched parts of Fe- or Cu-deposits.

Problems

Although relatively abundant, these minerals rarely form grains of appreciable size, and most described occurrences are <100 µm. The complexity of some of the mineral groups is such that electron probe microanalyses may not be sufficient to characterise or identify the phase in question. For example, in the Bi-Te sub-system, where, tsumoite (BiTe) may be sufficiently disordered (i.e. variation in Bi:Te), such that the compositional range extends over that of other members of the class, e.g. hedleyite and pilsenite (Bayliss, 1991; Dobbe, 1993). A second example would be in the Bi_4Te_3 - Bi_4Se_3 - Bi_4S_3 sub-system, in which re-examination of type laitakarite (Ciobanu et al., 2002) reveals ambiguities regarding the possible existence of two minerals (dimorphs?) with the

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composition Bi_4Se_3 and $\text{Bi}_4(\text{Se}>\text{S})_3$, possibly analogous to guanajuatite/ paraganajuatite in the Bi_2Te_3 - Bi_2Se_3 - Bi_2S_3 sub-system. A third example is protojoseite, which although widely described, remains a non-approved species, without agreement on an accepted and without the structure having been defined.

The literature also contains reference to an appreciable number of species that are inadequately defined, generally because of small grain size. Because of the lack of sufficient X-ray data, the extent of solid solutions and the possible existence of dimorphic relationships are often poorly understood. Furthermore, experimental data, e.g. in the 'simple' Bi-Se system is commonly in conflict with observations of compositional variation in natural samples, and the natural analogues of numerous synthetic phases have not been identified.

Opportunities

Microanalytical and paragenetic data has been compiled from the literature and also from the natural occurrence of these minerals in a variety of mineral deposits particularly rich in these systems. These include the selenide-dominant deposits of Orijärvi and Ilijärvi (Finland; Ciobanu et al. 2002), Lega Dembi (Ethiopia; Cook et al., 2001), Maiskoe (Ukraine; Cook et al., 2002b) and Au-rich telluride-selenide suites from Glava (Sweden). Numerous

A. Bi tellurides (Bi-Te system)				D. Phases with $\text{Bi}:(\text{Te},\text{Se},\text{S})=1$, but with considerable non-stoichiometry.			
Hedleyite	Bi_7Te_3	trig.	R3m	Ingodite	$\text{Bi}(\text{Te},\text{S})$	hex.	P3m
(Pilsenite)	Bi_4Te_3	trig.	R3m	Nevskite	$\text{Bi}(\text{Se},\text{S})$	trig.	P3m1
Tsumoite	BiTe	trig.	P3m1	Telluronevskite	Bi_2TeSe_2		
Sulphotsumoite	Bi_2TeS_2	trig.	P3m1				
(Tellurobismuthite)	Bi_2Te_3	trig.	R3m				
B. Bi_2S_3-Bi_2Se_3-Bi_2Te_3 sub-system				E. Bi_3S_4-Bi_3Se_4-Bi_3Te_4 sub-system			
Tetradymite	$\text{Bi}_2\text{Te}_2\text{S}$	trig.	R3m	Rucklidgeite	$(\text{Bi},\text{Pb})_3\text{Te}_4$	trig.	R3m
Skippenite	$\text{Bi}_2\text{Se}_2\text{Te}$	trig.	R3m (?)	Poubaite	$(\text{Bi},\text{Pb})_3(\text{Se},\text{Te})_4$	trig.	R3m
Kawazulite	$\text{Bi}_2(\text{Te},\text{Se},\text{S})_3$	trig.	R3m (?)				
Tellurobismuthite	Bi_2Te_3	trig.	R3m	F. Other stoichiometries			
Paraganajuatite	$\text{Bi}_2(\text{Se},\text{S})_3$	trig.	R3m	Baksanite	$\text{Bi}_6\text{Te}_2\text{S}_3$ (*1996)	trig.	P3m1
Bismuthinite	Bi_2S_3	orth.	Pbnm	Vihorlatite	$\text{Bi}_{3+x}(\text{Se},\text{Te},\text{S})_{11-x}$	trig.	
Guanajuatite	Bi_2Se_3	orth.	Pnna	(not IMA-approved)			
C. Bi_4S_3-Bi_4Se_3-Bi_4Te_3 sub-system				G. Further minerals with variable stoichiometry and containing essential Pb			
Laitakarite	$\text{Bi}_4(\text{Se},\text{S})_3$	trig.	R3m	Babkinite	$\text{Pb}_2\text{Bi}_2(\text{S},\text{Se})_3$	trig.	P3m
Joséite-A	Bi_4TeS_2	trig.	R3m	Aleksite	$\text{PbBi}_2\text{Te}_2\text{S}_2$	hex.	(?)
Joséite-B	$\text{Bi}_4\text{Te}_2\text{S}$	trig.	R3m	Kochkarite	PbBi_4Te_7	trig.	P3m1
Ikonolite	$\text{Bi}_4(\text{S},\text{Se})_3$	trig.	R3m	Poubaite	$(\text{Bi},\text{Pb})_3(\text{Se},\text{Te})_4$	trig.	R3m
(Pilsenite)	Bi_4Te_3	trig.	R3m	Saddlebackite	$\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_3$	hex.	
Protojoseite	$\text{Bi}_3(\text{Te},\text{S})_4$	??					
	(not IMA-approved)						

Table 1. Principal named Bi-Te-Se-S system minerals, divided into sub-classes on a stoichiometric basis.

Romanian deposits are particularly well endowed with minerals of the Bi-Te-Se-S system (e.g. Cioflica et al., 1995). Here, our work is focussed on the telluride-dominant hydrothermal system at Larga, South Apuseni Mts., in which the speciation of Bi-tellurides and tellurosulphides over a depth of 1 km reflects changing physical-chemical conditions of ore formation (Cook et al., 2001). Investigation of the Upper Cretaceous skarn deposits, particularly Băița Bihor and Ocna de Fier (e.g. Cook & Ciobanu 2001), has also yielded an appreciable number of previously unreported assemblages and new information (Cook et al. 2002a). Microanalytical investigation of Bi-Te-Se-S minerals in natural occurrences representative of a broad spectrum of Au-bearing deposits allows criteria to be identified that govern their distributions (Ciobanu & Cook, 2002; Cook & Ciobanu,

2002). Comparison of assemblages in individual deposits allows for modelling of mineral paragenesis in terms of $f\text{Te}_2$, $f\text{Se}_2$, $f\text{S}_2$ and $f\text{O}_2$.

Implications

Natural compounds of Bi with Te and/or Se in particular, although rarely present in ores in major amounts, are recognised as valuable petrogenetic indicators in a range of Au-deposits. Mutual relationships are sensitive to temperatures of crystallisation, $f\text{Te}_2$, $f\text{S}_2$, $f\text{Se}_2$ and $f\text{O}_2$ and also other physico-chemical parameters and can therefore provide information on the sequence and evolution of mineralising events. Tellurides, selenides and related compounds are good tracers of $f\text{O}_2/f\text{S}_2$ buffered reactions during ore formation (e.g. magnetite-hematite, pyrrhotite-pyrite). Furthermore, comparison of assemblages containing Bi-Te-Se-S phases allows identification of trends across the magmatic-hydrothermal-metamorphic spectrum and correlation of disparate assemblages in terms of fluid evolution. Far from being random, the mineralogy of minerals in the Bi-Te-Se-S system in a given deposit can be broadly predicted from the prevailing $f\text{O}_2$ - $f\text{S}_2$ environment.

Associations of Bi-tellurides/selenides are thus highly relevant for Au deposition, and especially where Bi-sulphosalts are also present, can be highly determinative in a paragenetic sense. In the simple Bi-Te system, increasing $f\text{Te}_2$ controls the stability of Bi-telluride formation in the sequence: native-Bi $\rightarrow$ hedleyite $\rightarrow$ pilsenite $\rightarrow$ tsumoite $\rightarrow$ rucklidgeite $\rightarrow$ tellurobismuthite $\rightarrow$ native-Te, reflected by decreasing Bi/Te ratio. Although complicated by addition of $f\text{S}_2$ in the ternary Bi-Te-S system, Bi-sulphotelluride formation is configured in a similar way (joseite-A/joseite-B $\rightarrow$ ingodite/sulphotsumoite $\rightarrow$ tetradymite, with S-dominant minerals (joseite-A, sulphotsumoite) favoured at elevated $f\text{S}_2/f\text{Te}_2$. The buffering host assemblage and its position in $f\text{O}_2$ - $f\text{S}_2$ space constrains the assemblage of Bi-tellurides/sulphotellurides ($\pm$ selenides, seleno-sulphides) in each field. At higher $f\text{O}_2$ -($f\text{S}_2$) (hematite and pyrite stability, approaching the stability field of native-Te, Bi-tellurides/sulphotellurides with $\text{Bi}/(\text{Te}+\text{Se}+\text{S}) \leq 1$ will be stable (for example, the relatively widespread assemblage tellurobismuthite-tetradymite ($\pm$ kawazulite, if Se is available). In such systems with reduced $\text{Bi}/(\text{Te}+\text{Se}+\text{S})$, an affinity between tetradymite and various Bi-sulphosalts (aikinite-bismuthinite and lillianite series) is not uncommon and can be efficiently explained in terms of non-stoichiometry being readily incorporated into the sulphosalts phases because characteristic order-disorder (OD) mechanisms for these minerals can be accessed. Similarly, in systems with $\text{Me}/(\text{Te}+\text{Se}) \geq 1$, stability of Bi-sulphotellurides can be readily attained, as these phases (e.g. joseite-A, joseite-B, and especially, the poorly characterised 'protojoseite'), are commonly non-stoichiometric, a fact that can be easily correlated with OD, particularly if co-existing with Bi-sulphosalts. A parallel issue concerns the stabilities and petrogenetic significance of the Pb-bearing Bi-Te-Se-S minerals (aleksite, babkinite, etc.), including the occurrence of Pb-bearing tetradymite in some deposits and the unnamed phase, $\text{Pb}_2\text{BiTeS}_2$, identified in the Ilijärvi deposit, Finland (Ciobanu et al. 2002). Of relevance here are relationships between these minerals and coexisting galena ($\pm$ Bi-sulphosalts) in what appears restricted to Cu-deficient environments.

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THE NEOGENE METALLOGENESIS OF THE CENTRAL WESTERN AREA OF THE BAIJA MARE DISTRICT (GUTĂI MTS – EAST CARPATHIANS)

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The Neogene magmatic arc and the associated metallogenesis from the Eastern Carpathians is related to the final stage of evolution of the Tethys Ocean between Africa and Eurasia. Among the magmatic arc of the Eastern Carpathians, the metallogenetical district Oaş – Baia Mare is the most productive. It contains base metal ore deposits subordinately vein gold of epithermal type and rarely gold ore deposits. The location of the Neogene magmatites and of the metallogenesis is controlled by the Dragoș – Vodă crustal fracture (E-W), (Popescu C. Gh., 1986).

In the Baia Mare area the migration of the magmatism has been noticed from east to west. Thus, in the western part there are the oldest magmatic products, and in the east the younger ones. The subduction that generated this magmatism first occurred in stress conditions with comprehensive tendencies followed by extensional conditions, (Popescu C. Gh., 1994). The existence of a subduction at the beginning of the Miocene is believed to have led to the forming of a magma reservoir at the crustal level which afterwards has been activated through the collision of the intracarpethian microplate with the east-european one when they became intracrustal.

The central-western area of the southern part of the Gutăi Mts is characterized by an elevated Preneogene fundament in the central area (the Rising of the Southern Gutăi – R.S.G.). This rising can be observed from Chiuzbaia to Firiza (Roman Valley) – Ulmoasa – Nistru – Ilba (Mesteacăn Valley). This rising is characterized by the lack of the sedimentary formations from the lower Badenian, Sarmatian and lower Pannonian. The Preneogene formations belong to the transcarpathian flysch, (Săndulescu 1980). In the north and south of the R.S.G., the volcanic rocks increase their thickness and the succession of the sedimentary deposits from the lower Badenian to the upper Pannonian is complete. The limit between the transcarpathian flysch and the north – transilvanian subasment is situated in the southern part of the area (at south of R.S.G.) and it is affected by profound crustal fractures (Dragoș-Vodă) or North-Transilvanian and Bogdan-Vodă.

According to Giușcă et al., (1973) and Borcoș et al., (1973), the volcanic activity from the Gutăi Mts took place in three stages: the first stage in the Badenian – Buglovian with acide character and other two in the Sarmatian – Pontian and Pontian – Pliocene with intermediary character, (biostratigrafical dated). Based on the absolut data base (K-Ar) the volcanites are of a lower Sarmatian – upper Pannonian age, 13.4-9.0 Ma, (Edelstein et al., 1992). The volcanic activity has an initial acid character leading to a volcano-clastic complex of lower Badenian-Sarmatian age, largely developed between Racșa and Firiza Valley. Largely spread are the Sarmatian volcanic manifestations represented by the pyroxene andesites from Seini. The Panonian eruptive formations are represented by pyroxene andesites of Ilba, hyalodacites with pyroxenes of Șindileu, the quartz-andesites complex, the dacites from Dănești, the andesites with pyroxenes+hornblende from Dealul Crucii – Baia Sprie, the andesites with pyroxenes+hornblende from Firiza and Pietroasa. The complex of lava flows is accompanied by various intrusive bodies present in R.S.G. or in the sinked levels with thick lava and in volcanic structures.

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The intrusive magmatism has a subvolcanic and intravolcanic character. The spatial relationships suggest an ulterior emplacement of the intrusive bodies reported to the lava flows (especially the sarmatian ones). They are represented by microdiorites and quartz diorites, quartz monzonites, microgranodiorites, tonalites. Such intrusions appear in areas like Herja, Nistru, Ilba – Valea Mesteacănului, (Paulini et al., 1984). A lot of smaller intrusions were detected by drillings in Dealul Crucii, at Aurum, Sofia, Wilhelm, and Tyuzoşa. These intrusions have an essential role in the genesis of the ore deposits from the central-western part of the Gutâi Mts.

The mineralizations are distributed in an areal with a highly tectonitized Preneogene subasment which has spatial relationships with volcanic edifices and subvolcanic intrusions. In this areal we can distinguish more types of mineralizations, (Fig. 1).

A. The copper mineralizations (Cu+Py) appear in a small areas at Ilba and Nistru. The best example in this case is Mihai Nepomuc, (Jude R., Popescu R., 1987). The mineralization is disposed on a highly fractured area which is included in an intensely adularized and argillized zone. The Venera vein (Ilba) has a copper mineralization which becomes a predominantly gold one towards the upper parts. In the Nistru area, the Mihai Nepomuc, Domnişoara, Anton, 144 veins are copper veins associated with a monzodioritic intrusion. In the upper part they are rich in gold. An interesting paragenesis with chalcopyrite – native gold – Bi sulphosalts, (Damian F., 2000) occurs within these mineralizations (vein 144).

B. The base-metal mineralizations are the most frequent. These are represented by two different types, Cu+Pb+Zn and Pb+Zn, which, in the upper parts, become a gold mineralization developed on a restrained level. The Cu+Pb+Zn mineralizations are associated in depth with subvolcanic structures and they have formed during three stages of mineralization. The vertical zonality, also described in other areas of the Baia Mare metallogenetic district can be recognized at these mineralizations, (Giuşcă et al., 1973). In this type we can include the mineralizations from Sofia (Nistru – 9 Mai), Firizan, Valea Ardeleană, Creasta Faţa Mare, Făţutoaia – Speranţa from Ilba.

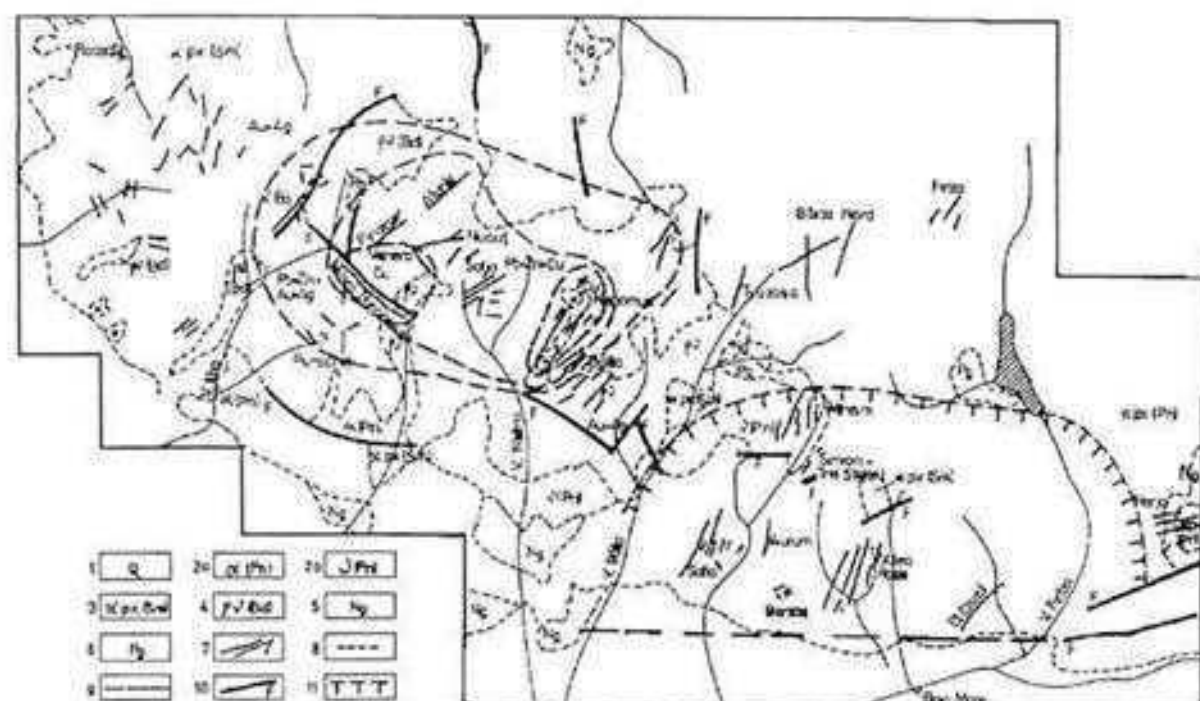


Fig. 1 - Geological sketch of the central-western part of the Baia Mare metallogenetic district

1. -Quaternary; 2a. -Pannonian andesite; 2b. - Pannonian dacite; 3. -Sarmatian pyroxene andesite; 4. -Badenian rhyodacite; 5. -Neogene sedimentary rocks; 6. -Paleogene sedimentary rocks; 7. -Vein group; 8. -Geological limit; 9. -Zoning mineralization; 10. -Fault; 11. -Caldera limit.

The Pb-Zn mineralizations are very numerous; they are characterized by high contents in Pb-Zn with a Au-Ag level in the upper part. Towards the lower parts they become a disperse pyrite

mineralization. Some mineralizations of this type develop on a high level as the ones at Herja and which are associated with intrusions. In this type are included the mineralizations from Colbului Valey, Aluniș, Cicârlău – Nucuș, Nistru (11 Iunie), Tyuzoș, Simion – Trei Stejari, Herja and Piatra Albă Gallery.

C. Base-metal mineralizations with gold and silver content. These are characterized by the Au-Ag level, highly developed at the surface, and which in depth is continued with a Pb+Zn mineralization. In this type are included the mineralizations from Purcăreț, Valea Băii Nord, Florian, Aurum, Dealul Crucii, Emerica, Firiza. In the lower parts, these mineralizations are associated with the apexes of the subvolcanic intrusions.

D. The Au-Ag mineralizations are typical for Săsar area. The mineralizations from Sofia, Valea Roșie, Adam Cremenea, Borzaș, Wilhelm, Valea Căpitanului are included here. These mineralizations are also frequent in the Nistru area: the vein group Lăpușna – Galbena, Mihai, Tarnița – Dubugău, Coroana de Aur – Laurențiu. In the Ilba area, such mineralizations appear at Valea Băilor from Racș, Valea Seinel, Valea Bradului from Săbiș.

In the Ilba – Nistru area the mineralizations are associated with two sinking zones and in the Săsar area the mineralizations are associated with caldera type structure, (Popescu C.Gh., 1986). In the sinking zones from Ilba – Nistru area the copper mineralizations are developing in connection with intrusions. The Cu+Pb+Zn+Au+Ag mineralizations are associated with these sinking zones. The Pb+Zn and Pb+Zn+Au+Ag mineralizations are distributed around these sinking zones, and typically epithermal Au+Ag mineralizations are disposed at the exterior around the sinking areas and at great distances away from the magmatic intrusions.

Most of the mineralizations from Săsar area are placed in a low area with thick volcanic deposits and which can be interpreted as a caldera type structure. Inside this structure Au+Ag mineralizations are developed on great height and from which some of them become typically Pb+Zn mineralizations towards the lower parts. In the marginal areas of the caldera there are the Pb+Zn mineralizations from Simion – Trei Stejari and Bartoș. At the north of the caldera Au+Ag mineralizations appear having a reduced development as the ones from Valea Căpitanului in Ulmoasa. In the eastern part of the caldera in R.S.G., the predominantly Pb+Zn mineralizations are developed at Herja, Piatra Albă Gallery, Firiza, Ludovica – Emerica and Tyuzoș.

The mineralizations from the central-western part of the Gutâi Mts have developed in three distinct stages. The first stage is represented by copper mineralizations, the second by base-metal mineralizations with Au and Ag and the final stage by Au-Ag epithermal type mineralizations. The metallogenetical unity of this area has been confirmed by the mineralogical and sulphur isotopes data. The genetic connection between the mineralizations from Dealul Crucii and Herja has been previously demonstrated, (Borcoș et al., 1973). All mineralizations have high contents in FeS in sphalerite, including the ones from Săsar area. The pyrrhotite and the ilvaite are present in the mineralizations from Herja, Ilba, Nistru. The presence of the sulphosalts: tetrahedrite, semseyite, bournonite, proustite – pyrargyrite has been noticed in all the mineralizations. The fineness of the native gold is low in all the mineralizations, including the ones from Herja. The mineralizations from Herja and Piatra Albă are completely different from the ones in Baia Sprie due to the content of FeS from the sphalerite (the low content for Baia Sprie and high content for Herja and Piatra Albă). The sulphur isotopes data (Damian et al., 1998) ($\delta^{34}\text{S} = -10 - +8$) demonstrates the metallogenetical unity of this area.

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THE WILDFLYSCH – OLISTOSTROMA – TECTONOSTROMA CONCEPT EVOLUTION IN THE SOUTH APUSENI MOUNTAINS SUTURE ZONE (ROMANIA)

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The South Apuseni Mountain (SAM), covering an area of about 3,300 km², are composed by J – K₁ N-type MORB sequences of ultramafic-mafic isotropic cumulates of gabbros and diorites / sheeted dykes / pillow lava forming an ophiolitic complex (Saccani et al., 2001) and volcanic island arc rocks (Savu, 1995; Savu et al., 1988; Savu et al., 1991; Savu et al., 1992a; Savu et al., 1992b; Savu et al., 1992c; Cioflica G. et al., 2001; Saccani et al., 2001) of J₂ and K₁ age. The geologic setting of SAM is completed by a variety of J – K sedimentary deposits which compose, together with the Mesozoic magmatic suites, the so considered *nappe structure*. Different interpretations of this *nappe structure* have been advanced, the most comprehensive belonging to Sandulescu (1984). Balintoni and Berza (2001) consider this *nappe system* of Laramian age. The present structure of SAM is accomplished by Laramian magmatics, by Miocene sedimentary deposits and Sarmatian-Quaternary calc-alkaline / alkaline volcanics. The arguments for a *nappe structure* are: stratigraphical discordances mapped in different outcropping locations, different composition of ophiolites (namely the presence of spilitic rocks in certain *nappe units* – Sandulescu, 1984), the presence of olistolithes and the prevalence of specific rocks like ophiolites and flysch-rocks (Sandulescu, 1984). A lot of unclear issues still persist on *nappe postulate* because:

- There is no detailed mapping to discriminate O, IAV the Mesozoic sedimentary deposits (generally covered with soil and vegetation);
- No detailed photogeological mapping was performed till now;
- Widespread ophiolitic tectonic breccias occurring within Capalnas-Techereu Nappe has been considered cartographically as "pyroclastics" (Borcos, M. et al., 1981)
- Breccias-type of the limestone olistolithes is entirely ignored;
- The olistolith elongation of few kilometers, despite the narrow width, of hundreds of meters, is also ignored;
- The obvious recurrence of some discordant stratigraphic successions (*Fenes area - Dambau*) are interpreted as successive faulting;
- The presence of crystalline rocks in the Capalnas-Techereu unit (mainly ophiolitic) still remains exotic, unaccountable in a unitary remnant of ocean floor crust.

The *nappe units* of SAM surround the North Apuseni Mountains (Internal Dacides) by their southern and eastern sides: Grosi unit, Cris u., Bucium u., Capalnas-Techereu u., Curechiu-Stanija u., Fenes u., Trascau (Bedeleu) u., Fundoia u., Boyes u., Cabesti u., Bejani u.

The *photogeological interpretation* reveals the development of some long, imbricate slides on the entire Transilvanides area. The slides are formed exclusively of Mesozoic rocks (fig. 2). Successive slides of ophiolites, limestone and flysch rocks, as well as successive ophiolitic and island arc volcanic rocks may develop. Only the thickness of the limestone slides may exceed 200-300 m. Within the ophiolitic slides, the typical succession of an ophiolitic complex (peridotite/gabbro/sheeted dikes/pillow lava) cannot be distinguished, though the specific ophiolitic types have been randomly described all over the Apusenide area. However, the basaltic pillow-lavas prevail, though frequently transformed into tectonic breccias. Both the carbonatic and the carbonatic - ophiolitic "olistolithes" develop linearly as continuous or discontinuous slides, being certainly the

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result of a tectonic process, not of the development of olistostrome or wildflysch. The slides design of the Mesozoic rocks is quite significant and it is slightly disturbed by the Banatitic volcanism (Laramian), the Neogen volcanism or by the Neogen sedimentary deposits. It subsequently develops along major E-W direction on the South segment of the Apusenides (the Capalna – Techereu area, the Ampoi basin) and along SW-NE direction in the eastern segment (Trascau Mountains), following the major suture line of the continental blocks of the Internal Dacides (ID)/ Median Dacides (MD).

Geophysical data: The magnetic and the gravity mass contrast between ophiolites and its lithological background, allow their regional outlining both to NE (beneath the Transilvanian basin) and to SW (beneath the Pannonian basin) to be defined (fig. 2). The NE extremity of the SAM (The Trascau Mountains) seems to represent a past subduction zone between an oceanic plane (which remnant generates the maximum aeromagnetic anomaly from the western part of the Transilvanian basin) and the continental plate of Internal Dacides. The stressed minimum gravimetric zone from Turda – Aiud – Alba Iulia area, NNE – SSW oriented, corresponds to a maximum thickness of Sennonian – Paleogene sedimentary deposits. In the south part of the SAM, the fractural directions and the major contacts between formations with different physical properties (the maximum horizontal derivative lines) are ENE – WSW (E – W) preferential oriented, parallel to the suture line between the two continental blocks (ID / MD), suggesting a NNW – SSE oriented collision. The western zone of the SAM, according to the gravimetric images, includes mainly ophiolites (and partially crystalline formations), advancing eastwards, the maximum gravimetric effect is maintained, but its intensity degrades, indicating probably a preponderance of island arc magmatics. Both the ophiolites and the island arc magmatites form a continuous belt of aeromagnetic maximum, that may be followed eastward and northward up to the Trascau Mts (fig. 1 and 3).

Within the alignments of regional maximum gravity, associated mainly to the ophiolitic piles, the subsequent detailed measurements (upon the Luncoiu – Valisoara area) have revealed a succession of gravity maximum and minimum relative parallel to the main direction (WSW – ENE) of the ophiolites. The relative gravity minimum may be associated either to the presence of island arc volcanics, or to sedimentary rocks. This alternation is better reflected by the horizontal gravity gradient (fig. 5), which suggests a possible suture structure.

Conclusions

The entire area between the ID and MD represents a suture mélange formed by slides of oceanic crust (equally composed by ophiolites and sedimentary rocks), which randomly solders to the continental margins at north and at south. The design of the majority of the *nappes* forehead, represented cartographically, may constitute a structural local reality, but the real nature of the *nappes*, as a whole, represents in fact, a recurrence in an uncountable number of such phases.

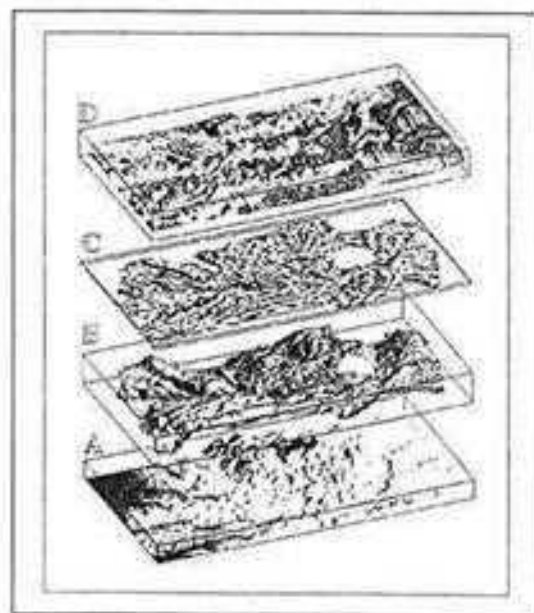


Fig. 1- The digital terrain model (A), the regional gravity (B), the first horizontal derivative of the gravity (C) and the aeromagnetic anomaly (D) 3-D images of the South Apuseni Mountains and the surrounding areas

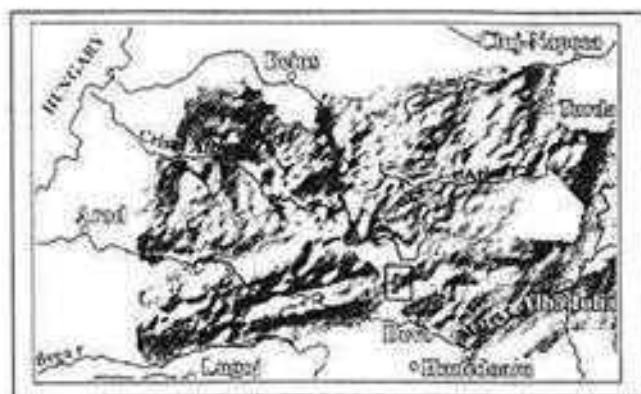


Fig. 2 - Regional gravity anomaly map (Lambertian reflection) of the South Apuseni Mountains



Fig. 3 - Aeromagnetic anomaly map (Lambertian reflection) of the South Apuseni Mountains



Fig. 4 - Photogeological map of Luncoiu-Valisoara area

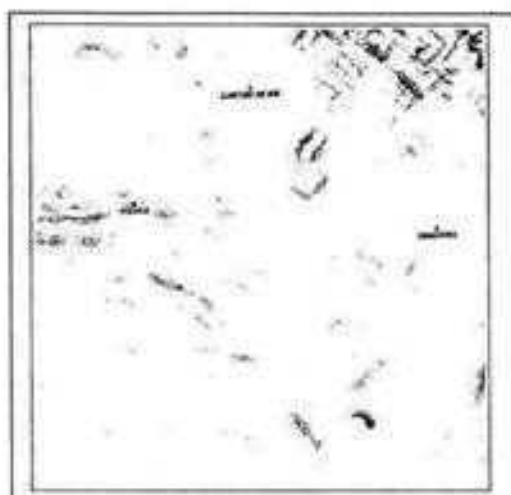


Fig. 5 - The first horizontal derivative map of the detailed gravity Luncoiu - Valisoara area

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APPLIED MINERALOGY IN USE OF INDUSTRIAL OFFALS AND MINING STERILES.

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In the synthesis of Di masses, we performed a series of experiments in the temperature range 980°C -1100°C. Five starting compositions were used to cover this fields (CaO~50%; Al₂O₃~10 %; MgO~10%; SiO₂~45 %).

The Di-glasses (CMAS system) contained a Cr₂O₃ as nucleating agent. The samples were drawn from each of melts by conventional glass working techniques and were allowed to cool rapidly in air. The melting was performed at temperature between 1400-1450°C.

The addition of Cr₂O₃ decreases the dimension of crystals and increases the samples mechanic resistance. In the system LMAS (Li₂O~44,8 %; MgO~5 %; Al₂O₃~15 %; SiO₂~65 %) the optimum crystallization temperature lie between 780°C-810°C.

The final glass-ceramics contained spodumen â (mainly), eucryptite, AT and "O silica". TiO₂ and ZrSiO₄ are nucleating agents.

MONITORING OF WHEATERING CAUSES OF BUILDING MATERIALS AT SOME HISTORICAL MONUMENTS OF TRANSYLVANIA

DUCA¹ Voicu, DUCA² Mihaela

There are related the principal types of extant deterioration in some monuments from Cluj, Brasov and present information will be completed with petroarchaeometrical analyses from German medieval monuments such as Sighisoara, Valea Viilor, Medias, Saschiz. Data are reported from a preliminary evaluation of damage forms through long-term exposure to natural, industrial and traffic pollution.

The paper presents the development of crusts, patinas and some weathering processes, as consequence of activity of salts transported by solution, SO₂ and NO₂ dissolved in rain, ash particles, etc.

The use of the Portland cement destroys the monuments because salts from cement are a very important source of alteration. In all cases of the southern walls appear large exfoliation and alveolisation, flaking, scaling and granular disintegration. Variations in decay processes demonstrate that mineralogical and textural heterogeneity is an important factor in rock weathering.

PETROARCHAEOMETRICAL RESEARCH OF SOME HISTORICAL MONUMENTS OF CLUJ-NAPOCA.

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In a first phase are analysed the sources of rocks used for building of some monuments from Cluj-Napoca.

One correlates the chemical weathering forms with damages that occur at Sf. Michael Cathedral, Reformed Church and 2-nd Defense Wall.

For all this monuments are examined the efflorescence, the black / white crusts, new formed minerals in exfoliation planes, etc. The analytical methods are optical microscopy, DTA, chemical analysis, RX.

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The crystallization of sulphate and alternation of the thaw-frost are producing the disintegration of building materials as a consequence of mechanical pressures up to 500 daN/cm².

The lichens are generating oxalate which make a layers with wavelite and weddelite,

The roots of plants are generating a pressure of 10-15 daN/cm² – all this factors affect the stability and integrity of the walls.

The paper analyses the results of some inadequate restoration works and suggests the recommendation for conservation and restoration activity.

LEOCOPHOSPHITE AND TARANAKITE IN THE BAT-GUANO DEPOSIT FROM LAZULUI CAVE (MEHEDINȚI MOUNTAINS)

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Two NH₄-substituted K- and Al-bearing hydrated phosphates, namely leucophosphate and taranakite, were identified during routine X-ray powder diffraction studies of the bat guano deposit in the Lazului Cave (Mehedinți Mountains). Both minerals occur in small quantities, as authigenic, early diagenetic, phases. Associated minerals include calcite, alpha (low) quartz, hydroxylapatite, brushite, ardealite, illite and interstratified kaolinite-illite. The present paper aims to give short descriptions of the two phosphate species, together with a brief report on other associated phosphates.

The Lazului Cave is located on the right slope of the Motru Sec Valley, at about 150-m downstream from its junction with the Săhodoarele Mici Valley. Geographically, the cave is situated in the northern part of the Mehedinți Plateau, near its limit with the Mehedinți Mountains. The cave is developed in Barremian-Aptian reef (micritic) limestones with rare calcarenite levels. The altitude of the entrance is 370 m. The cave is temporarily water-laden, being a part of a karst system of 4201 m in length (3201 according to Goran, 1982). The samples used for this study were collected from a guano-bearing room of about 30 x 20 x 8 m, located at about 100 m from the entrance and corresponding to a dry level of the cave.

Leucophosphate, ideally $KFe^{3+}_2(PO_4)_2(OH) \cdot 2H_2O$, is mentioned for a first time from a Romanian cave. Its presence, tentatively supposed after XRD and optical observations, is supported by wet-chemical data on impure material, which helped to discriminate between leucophosphate and sphegniscidite. The mineral occurs as cream-brown, earthy crusts located at the center of a guano mass admixed with clay material. The crusts are composed of very fine-grained (up to 25 μm in length and 10 μm in width) reddish-brown, platy crystals closely associated with illite and low (alpha) quartz. The mean unit-cell parameters, taken as average of the values obtained by least-squares refinements from two sets of X-ray powder data (81 and 87, respectively, reflections unequivocally attributable to leucophosphate) are $a = 9.760(9) \text{ \AA}$, $b = 9.651(3) \text{ \AA}$, $c = 9.742(1) \text{ \AA}$ and $\beta = 102.36(1)^\circ$.

A wet-chemical analysis was performed on a carefully handpicked, illite-exempted separate, in order to avoid the analytical interferences. This analysis, recalculated at 100 % after subtraction of admixed quartz (29.38 wt.%) gave (in wt.%): K₂O = 10.44, Na₂O = 0.31, (NH₄)₂O = 0.03, MnO = 0.08, MgO = 1.07, CaO = 0.64, FeO = 0.67, Al₂O₃ = 9.40, Fe₂O₃ = 25.14, P₂O₅ = 38.26, H₂O* (as calculated) = 2.17, H₂O* (obtained as difference between the total water measured by the Penfield method and the calculated H₂O*) = 9.93. This composition, normalized on the basis of 2 P and 9 (O,OH) in the anhydrous part of the compound, leads to the chemical-structural formula:

$[K_{0.822}Na_{0.037}(NH_4)_{0.004}Ca_{0.042}Mg_{0.098}Mn_{0.004}](Fe^{3+}_{1.168}Al_{0.684}Ti_{0.036}Fe^{2+}_{0.035})(PO_4)_{2.00}O_{0.121}(OH)_{0.879} \cdot 2.045H_2O$.

The chemical refractive energy (K_e) based on the formula given before and the Gladstone-Dale constants given by Mandarino (1981) is 0.24324. The calculated density for $Z = 4$ unit cells per formula (Dick & Zeiske, 1997) is $D_x = 2.772 \text{ g/cm}^3$, which agrees perfectly with the measured value,

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determined by sink-float in Clerici solution diluted with toluene [$D = 2.770(5) \text{ g/cm}^3$]. Taking into account the calculated density and the value of K_a , a mean index of refraction $\bar{n}_{G.D} = 1.674$ may be calculated. This value is lower than that deduced from the refraction indices given by Lehr et al. (1967) for the stoichiometric leucophosphate ($\bar{n} = 1.722$), which agrees perfectly with the chemical data. In fact, leucophosphate from Lazului is an intermediate member in the leucophosphate – tinsleyite solid solution series, containing 36.93 mol.% tinsleyite in solid solution; hence the lower refraction indices.

XRD reveals that leucophosphate is typically associated only with low (alpha) quartz [$a = 4.9150(5) \text{ \AA}$, $c = 5.4049(1) \text{ \AA}$ and $V = 113.07(2) \text{ \AA}^3$, as determined by least-squares refinement for a representative sample]. Some of the samples contain admixed illite (the 2 M_1 polytype) and interstratified kaolinite-illite. These assemblages correspond to a possible reaction in the natural guano – clay system upon decomposition of illite, as stated by Marinacea et al. (2002) for tinsleyite.

Taranakite, ideally $(K, NH_4)_3Al_3(HPO_4)_6(PO_4)_2 \cdot 18H_2O$, occurs as earthy white crusts of chalky appearance scattered locally on the *terra rossa* mass. The taranakite masses are soft, earthy-looking and porous.

A wet-chemical analysis of a representative sample (L 4) yielded (in wt.%): $K_2O = 8.29$, $Na_2O = 0.22$, $(NH_4)_2O = 0.80$, $MgO = 0.14$, $CaO = 0.24$, $Al_2O_3 = 18.51$, $Fe_2O_3 = 0.61$, $P_2O_5 = 42.10$, $H_2O = 29.32$, total 100.23. The resulting chemical-structural formula, calculated on the basis of basis of 8 P and 32 (O) in the anhydrous part of the compound, is:

$[K_{2.374}Na_{0.096}(NH_4)_{0.412}Ca_{0.058}Mg_{0.047}](Al_{4.897}Fe_{0.103})(PO_4)_2(PO_4)_{5.908} \cdot 18.172 H_2O$.

The unit cell parameters calculated by least-squares refinement from three sets of XRD powder data obtained from representative samples of taranakite are given in Table 1.

Table 1. Cell parameters of taranakite from Lazului

Sample	a (Å)	c (Å)	V (Å ³)	$a:c$	$n^{(1)}$	$N^{(2)}$
L 2 A	8.716(4)	96.12(13)	6324.1(82)	0.091:1	3	29
L 2 B	8.699(6)	96.45(22)	6320.4(93)	0.090:1	3	28
L 4	8.691(5)	95.82(13)	6267.6(88)	0.091:1	3	28

(1) number of least-squares refining cycles;

(2) number of reflections in the 2θ range $5 - 46^\circ$ used for refinement.

The average cell parameters obtained on the basis of the data in the table are $a = 8.702(13) \text{ \AA}$, $c = 96.13(32) \text{ \AA}$, $V = 6304.0(32) \text{ \AA}^3$. Even if a compares favorably, the c cell parameter is larger than those reported by Dick et al. (1998) for the synthetic $K_3Al_3(HPO_4)_6(PO_4)_2 \cdot 18H_2O$ [$a = 8.7025(11) \text{ \AA}$, $c = 95.05(1) \text{ \AA}$ as refined from X-ray powder data and $a = 8.6882(3) \text{ \AA}$, $c = 94.98(2) \text{ \AA}$ as refined from neutron-diffraction data], which accounts for an increased influence of the cations substituting for K in the ten-fold coordinated structural sites.

The density of Sample L 4, measured by the sink-float method, using a pycnometer and bromoform diluted with acetone as displacement fluid, is $2.12(1) \text{ g/cm}^3$. The measured value agrees favorably with the calculated value of 2.125 g/cm^3 , obtained on the basis of the chemical analysis and cell parameters in Table 1, for $Z = 6$ (Dick et al. 1998). Both values of density are smaller than that calculated by Dick et al. (1998) for the synthetic $K_3Al_3(HPO_4)_6(PO_4)_2 \cdot 18H_2O$ ($D_s = 2.145 \text{ g/cm}^3$), which essentially accounts for superior degrees of P protonation and sample hydration.

The Ca-bearing phosphates are more common in the bat-guano deposit from the Lazului Cave.

Ardealite occurs as irregular crusts composed by crystalline aggregates that generally overgrow hydroxylapatite, near the limit between the bat guano deposit and the moonmilk flows. The crusts are composed of very fine, acicular sprays of crystals of maximum $20 \text{ \mu m}$ in length and up to $1 \text{ \mu m}$ wide. The unit-cell parameters, calculated by least-squares refinement from 62 reflections taken off from the most representative diffraction pattern, are: $a = 5.722(2) \text{ \AA}$, $b = 31.012(12) \text{ \AA}$, $c = 6.252(2) \text{ \AA}$, $\beta = 117.25(1)^\circ$.

Brushite occurs as snow-white powdery coating on hydroxylapatite or as nodular earthy masses (several mm to 2 cm in diameter) in the bat guano groundmass, in the areas composed principally by hydroxylapatite. The cell parameters of a representative sample (L 7), calculated by least-squares refinement on the basis of 54 X-ray powder reflections, are $a = 5.811(1) \text{ \AA}$, $b = 15.194(3) \text{ \AA}$, $c = 6.247(1) \text{ \AA}$, $\beta = 116.41(1)^\circ$. They are close to those of synthetic brushite [$a = 5.812(2) \text{ \AA}$, $b = 15.180(3) \text{ \AA}$, $c = 6.239(2) \text{ \AA}$, $\beta = 116.43(3)^\circ$ according to Beevers, 1958 or Curry & Jones, 1971], indicating that the structural formula of the analyzed sample is reasonably close to the ideal composition.

Hydroxylapatite occurs as dull-cream to off-white crusts of few millimeters to 1 cm thick, disposed directly on the moonmilk flows or on the carbonatic subbasement. The samples show reasonable crystallinity. The cell parameters of a representative sample (L 7), as refined by least squares from 29 X-ray powder reflections, are $a = 9.430(3) \text{ \AA}$, $c = 6.860(3) \text{ \AA}$, $V = 528.3(3) \text{ \AA}^3$.

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DISCOVERING OF DIAMONDIFEROUS ASSOCIATION IN THE MAKHTESH RAMON AREA, NEGEV DESERT (SOUTHERN ISRAEL)

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Summary

Field geological and mineralogical investigations as well as geophysical data analysis have been recently applied in the western part of Makhtesh Ramon area (central Negev, Israel). The aim of this investigation was searching of proposed kimberlite pipes (diamondiferous associations) of the Cretaceous age. Interpretation of geophysical data and space image analysis allowed to identifying a few objects favorable for detailed investigation. Mineralogical analyses of selected samples and their

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electronic imaging permitted to classifying a lot of the most important indicator minerals of diamondiferous association and more than 400 microdiamonds.

Introduction

Effect of the Mid-Cretaceous tectonical-thermal activation (125 ± 80 Ma) is known in many regions of the world. In the context of the principles of rotational geodynamics it is an epoch of the maximum stretching the Earth's equatorial segment. Larson (1991) suggested a model of convective geodynamics (rising flows) named as "Mid-Cretaceous Superplume". Theoretical calculation conducted by Ringwood et al. (1992) and some other authors supported the hypothesis and later Larson (1995) put forward the main conclusion of the theory – extremely high development of diamond-bearing kimberlites during the Mid-Cretaceous period.

In Israel, the Cretaceous magmatic activity is well known in the central Negev. The first diamond in Israel was found in the Negev desert (Flexer et al., 1988) in the Maastrichtian below the K/T boundary. The mentioned authors associate its origin with an extraterrestrial event. However, a form, dimension as well as accessory minerals of the microdiamond (these peculiarities were described in detail in the above-mentioned works) allow to suggesting that the microdiamond was moved from the buried diamond-bearing placer.

Field investigations in the Makhtesh Ramon area

Makhtesh Ramon is the largest of three erosional valleys formed along anticlinal axes in the central Negev desert (southern Israel). The Ramon erosional depression is a major geomorphic feature in this region, forming a deep feather valley, 40 km long and up to 12 km wide, surrounded by steep cliffs up to 400 m high (Ben-David et al., 2002). The Makhtesh Ramon depression is, in some sense, a closed structural-geomorphologic system, in which the product of destruction of all volume of geological rocks available within the territory has been accumulated.

The field investigations were initiated, besides the common geological conclusions (Katz and Eppelbaum, 1998) by applying dowsing procedures and advanced analysis of magnetic data and space image processing (Eppelbaum et al., 2001, 2002). Favorable results obtained at these stages allowed recommending performing detailed geological and mineralogical investigations in the Makhtesh Ramon depression.

At this area about 80 kg of geological associations have been selected from the near-surface layer for subsequent mineralogical-geochemical analyses. The following minerals of the anticipating diamondiferous association were revealed in the selected samples: (*first group*) - chrome-diopside, orange garnet, bright-crimson pyrope, picroilmenite, moissanite, corundum, black spinel, olivine, anatase and tourmaline (including black samples). Chrome-diopside as an indicator mineral may be found only in the neighboring zone of basic pipe occurrence. Orange garnet, bright-crimson pyrope and tourmaline also are essential indicators of the presence of diamondiferous association in the studied district. Moissanite and corundum are the rarely occurring minerals indicating presence of buried kimberlite pipes. These minerals do not rolled and oxidized that is additional evidence of the neighboring occurrence of the indigenous rocks. Data of electronic microscopy show that the grains of (1) picroilmenite and (2) pyrope contain, respectively: (1) cobalt, chrome, magnesium and nickel and (2) chrome, magnesium and aluminum. These data indicate that both picroilmenite and pyrope have the hyper-abyssal origin that also is an indicator of the possible occurring of diamondiferous pipes. Besides above mentioned minerals, list of determined minerals in the samples (*second group*) includes: hexagonal quartz, feldspars, pyroxenes (black, green, dark-green, gray-green, brown-green), magnetite, hematite, ilmenite, galenite, pyrite, limonite, small magnetic spheres (quant. matter), mica, hydro-mica, chromite, leucosene, zircon, rutile, secondary minerals of cuprum (green and blue), calcite, etc. These minerals (by their considering with the first group) are also indicators of diamond-bearing of the studied area. It should be noted that the amount of these minerals is extremely high: in 80 kg of the investigated geological concentrate (selected from the loose deposits and conglomerate) till the present time altogether more than 8,000 grains of the proposed diamondiferous association have been detected.

Identification of small plates of Au and Ag as well as La, Ce, Th, Nb and Ta (rare earth elements) also maybe associated with the nearest kimberlite rock occurrence (Griffin and Ryan, 1995;

McDonald et al., 1995). The recent mineralogical analyses signify to discovering of quasi-kimberlite rock (meimechite). Finally, the total number of recognized diamonds (on June 25, 2002) is more than 400 units (size of the most large crystals exceeds 1 mm) (technological scheme of diamond recognition in geological concentrate is presented in Figure 1).

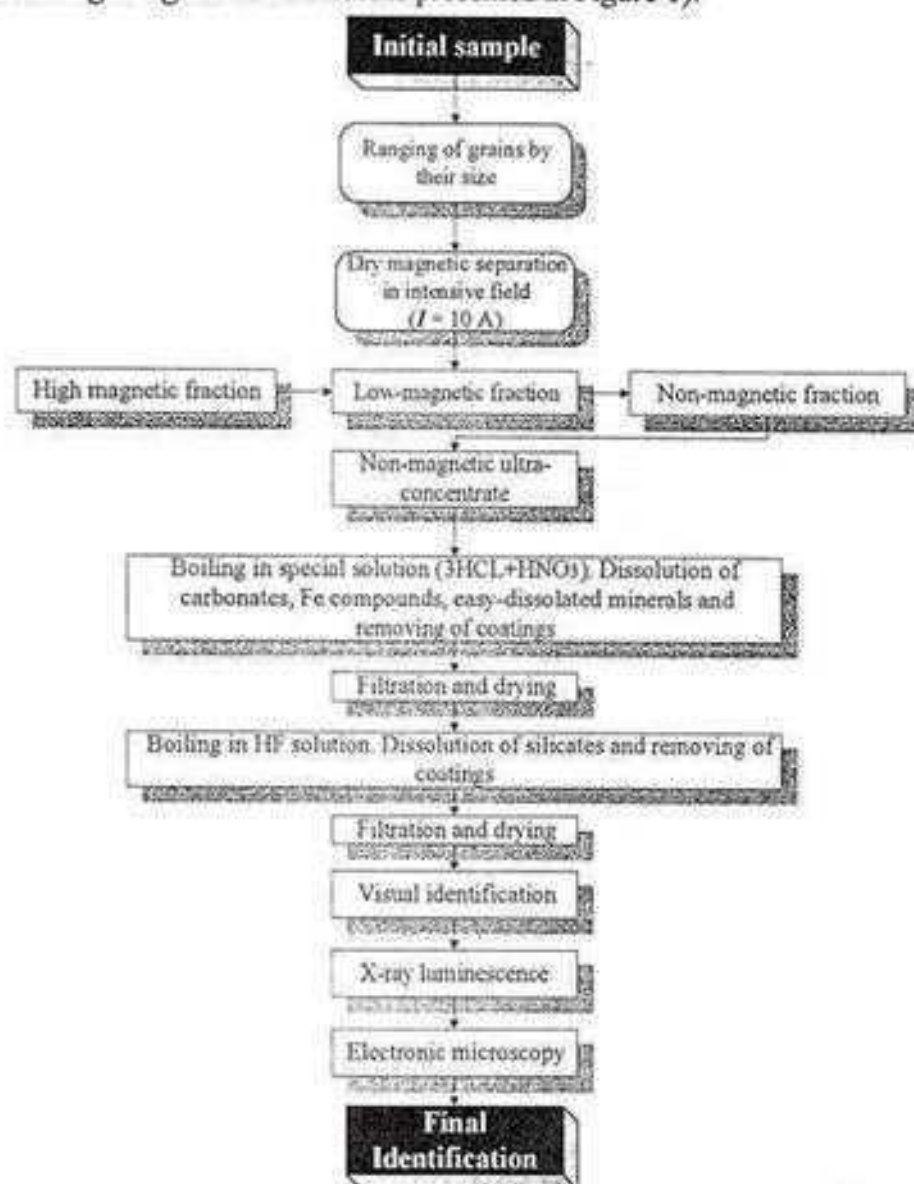


Fig.1. Fractionation of samples of titanomagnetite association: Technological scheme

The visual and qualitative analysis of the studied polymineral fraction has been performed using electronic scanning raster microscope CAMSCAN-4DV with energy-dispersion Roentgen micro-analyzer Link AN10000. Image of microdiamond No. 226 in back scattered electrons and its electrodispersion spectrum are presented in Figure 2a and 2b, respectively.

Conclusion

Integrated mineralogical (main), geological and geophysical analyses unambiguously indicate presence of diamondiferous associations within the Makhtesh Ramon erosional depression.

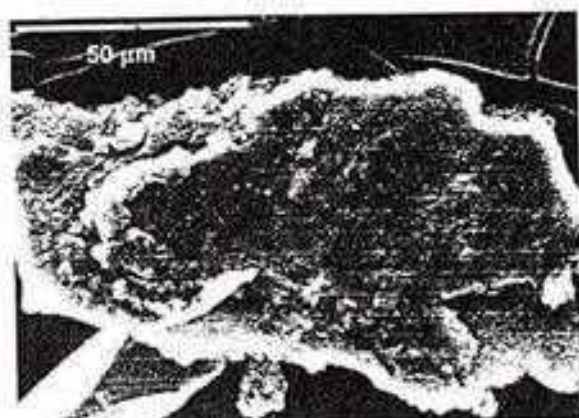


Figure 2a. Microdiamond 226. Back-scattered

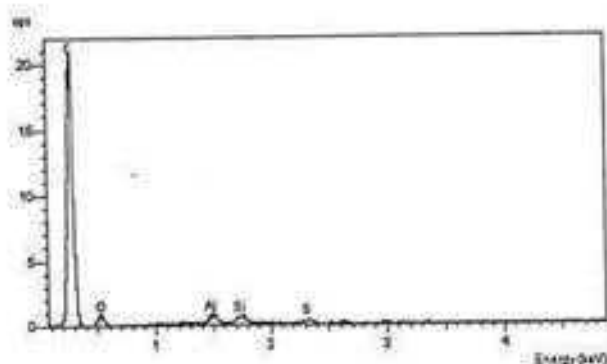


Figure 2b. Electrodispersion spectrum electron image of diamond 226.

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MICAS AND Al_2SiO_5 - POLYMORPHES IN SCHIST FROM BOBOLOS LOCALITY OF EASTERN SERBIA

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Abstract

In southern part of the Proterozoic crystalline complex of eastern Serbia (built mainly of gneisses, mica schist and amphibolites), near Bobolos locality occur kyanite - corundum schist which is exposed as a 5x4x3 m block, than andalusite schist and muscovite - paragonite schist as thin zones underlying kyanite-corundum schist.

Muscovites and paragonites from investigated mineral assemblages show clear differences in their chemistry and unit cell parameters. These differences are ascribed to different PT conditions during their genesis. Also unit cell parameters of kyanite from kyanite-corundum schist are higher than in kyanite from muscovite-paragonite schist. This difference is mostly expressed on axis c, and

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slight lower on axis a and axis b, what could be result of higher temperatures origin of kyanite-corundum schist.

The existence of both micas (determined in all mineral assemblages from locality Bobolos) enabled calculation of their equilibration temperature and gave following results: for kyanite-corundum schist $662 \pm 60^\circ\text{C}$, for andalusite schist $576 \pm 60^\circ\text{C}$ and for muscovite-paragonite schist $581 \pm 60^\circ\text{C}$.

GEOLOGICAL SETTING

This area is structurally related with the Gethian nappe that consists of different metamorphic rocks Proterozoic in age (gneisses, mica schists and amphibolites), as well as of granites, serpentinites, greenschists and sedimentary rocks of Middle and Upper Jurassic in age. According to Bogdanovic et al. (1980) this complex is thrust over the autochthonous Palaeozoic, Hercynian granites and Jurassic and Cretaceous sedimentary and volcanic rocks Thorthonian in age.

MINERAL ASSEMBLAGES

Kyanite-corundum schist (kyanite 75-80 vol%, corundum 15-20 vol%, rutile, paragonite, muscovite and chlorite - up to 5 vol%, as well as rare staurolite and tourmaline) is grey-bluish to dark-grey rock, displaying banding structure with alternating easily visible layers of corundum (0,5-1,3cm thick dark layers) and kyanite (gray-bluish layers up to 10cm in thickness).

Kyanite is a dominant mineral and form euhedral to subhedral grains while the corundum is present in unusual pseudolamellar grains. Small leafs of paragonite and muscovite are observed at the rim of both minerals, sometimes on the whole crystal. Rutile grains are irregular, up to 0,4mm in size and mainly are present as inclusions in kyanite, rarely in corundum grains.

Andalusite schist is grey-greenish, with megascopically visible prismatic pinkish crystals of andalusite, from 1 to 1,5cm in size. It is composed essentially of lath-like muscovite rarely developed in laths longer than $2 \times 0,6\text{mm}$. Andalusite crystals are idiomorphic and their basal sections exhibit two cleavages at an angle ranging from 90° to 102° . Along these cleavages small laths of muscovite are also noted while around some andalusite grains radial aggregates of chlorites were developed. The boundary between these minerals is sharp.

Muscovite-paragonite schist is grey-whitish in color with well-formed and easily visible needle- or pole-shaped kyanite porphyroblasts up to $1 \times 3\text{mm}$ in size, randomly distributed through the rock mass. Perfect cleavage could be often seen on prismatic crystals. Muscovite and paragonite, forming intergrowths of tiny micaceous plates of up to $1,5 \times 0,4\text{mm}$ in size, are optically indistinguishable. These two minerals are usually orientated along the schistosity direction of the rock. Average chemical composition (microprobe analysis) of Al_2SiO_5 polymorphes and micas from the three types of schists are given in table 1.

X-RAY ANALYSIS

Extremely low content of muscovite in kyanite-corundum schist and paragonite in andalusite schist (<1%) disabled determination of their unit cell parameters. According to data from ASTM - files (12-187) for paragonite, (6-263) for muscovite, (11-46) for kyanite and (39-376) for andalusite as initial values, their elementary unit cells were equaled using the programme LSUCRIPS (Garvey, 1986), and they are presented on the table 2.

Unit cell parameters of kyanite from kyanite-corundum schist are higher than in kyanite from muscovite-paragonite schist. This difference is mostly expressed on axis c ($5.573 > 5.554$), and slight lower on axis a ($7.106 > 7.092$), and axis b ($7.845 > 7.834$), what could be result of higher temperatures of kyanite-corundum schist origin.

EQUILIBRATION TEMPERATURE FORMATION OF MICAS

Data on the Na-K compositions of both micas (Pg and Ms) were used for determination of final equilibration temperature (T_f), in seventeen of the Pg-Ms pairs from all investigated minerals assemblages. This was attained with paragonite-muscovite solvus thermometry (PMST), on the basis of equations 9-11 (Blencoe et al., 1994), that conform to the following guidelines:

Table 1. Average microprobe analyses of kyanite, muscovite, paragonite and andalusite

rock:	kyanite-corundum schist			andalusite schist			muscovite-paragonite schist		
mineral number of analysis	kyanite (n=20)	muscovite (n=4)	paragonite (n=7)	andalusite (n=8)	muscovite (n=7)	paragonite (n=4)	kyanite (n=15)	muscovite (n=5)	paragonite (n=2)
SiO ₂	38.29	45.89	46.18	38.11	47.17	45.82	38.22	46.75	47.10
TiO ₂	0.02	0.31	0.18	0.11	0.64	0.21	0.04	0.55	0.15
Al ₂ O ₃	61.52	37.47	39.55	60.64	35.92	40.06	61.43	35.54	38.33
FeO	0.06	0.61	0.23	0.59	0.59	0.27	0.14	0.51	0.26
MnO	0.04	0.03	0.01	0.04	0.03	0.01	0.03	0.03	0.00
MgO	-	0.51	0.04	0.24	0.44	0.21	-	0.34	0.00
CaO	0.01	0.02	0.47	0.01	0.02	0.26	0.01	0.01	0.35
Na ₂ O	-	2.43	6.13	0.03	1.72	6.94	-	1.96	6.27
K ₂ O	0.01	7.54	1.58	0.02	8.22	2.03	0.01	7.83	0.71
Total:	99.95	94.99	94.37	99.79	94.75	95.81	99.88	93.52	93.17
Cations calculated on the basis of 20 oxygens for kyanite and andalusite and 22 oxygens for micas									
Si	4.133	6.041	5.960	4.131	6.215	5.858	4.126	6.232	6.119
Ti	0.002	0.042	0.018	0.009	0.063	0.021	0.003	0.055	0.015
Al	7.812	5.808	6.013	7.746	5.576	6.199	7.816	5.580	5.866
Fe	0.003	0.067	0.025	0.054	0.065	0.028	0.013	0.056	0.028
Mn	0.004	0.004	0.001	0.004	0.004	0.001	0.003	0.003	0.000
Mg	-	0.100	0.008	0.039	0.087	0.035	-	0.068	0.000
Ca	0.001	0.002	0.072	0.001	0.003	0.037	0.001	0.001	0.049
Na	-	0.620	1.535	0.005	0.441	1.732	-	0.507	1.580
K	0.002	1.266	0.259	0.003	1.382	0.333	0.001	1.332	0.118

Table 2. Unit cells parameters of investigated Al₂SiO₅ polymorphes and micas

mineral / rock	a (Å)	b (Å)	c (Å)	α	β	γ	V (Å ³)
kyanite / kyanite-corundum schist	7.106(4)	7.845(4)	5.573(3)	90.07(3)	101.09(3)	105.93(1)	292.7(3)
paragonite / kyanite-corundum schist	5.138(4)	8.92(3)	19.44(3)	-	94.31(4)	-	888.1(6)
andalusite / andalusite schist	7.781(5)	7.902(5)	5.558(4)	-	-	-	341.8(4)
muscovite / andalusite schist	5.188(4)	9.006(5)	19.962(4)	-	95.68(3)	-	928.1(6)
kyanite / muscovite-paragonite schist	7.092(3)	7.834(4)	5.554(2)	89.97(3)	100.09(2)	106.01(2)	290.8(5)
paragonite / muscovite-paragonite schist	5.120(4)	8.909(4)	19.36(2)	-	94.88(4)	-	881.0(6)
muscovite / muscovite-paragonite schist	5.171(5)	8.995(5)	19.94(2)	-	95.79(2)	-	922.9(3)

1) The mol% of margarite (Mrg) in Pg is less than 5%. Higher concentrations of Mrg have a marked effect on Pg-Ms solvus relations.

2) $\Sigma(\text{Mg}+\text{Fe}^{2+}+\text{Fe}^{3+})$ (=Fm content) in Ms is low, as indicated by Si/formula unit =6.2 and/or $\Sigma(\text{Mg}+\text{Fe})=0.35$ /formula unit (22 oxygens, anhydrous basis). These values are typical for the degree of phengite substitution in muscovites for Al-saturated rocks that equilibrated at p=8kbar (Guidotti, 1984, Guidotti et al., 1992).

Average equilibration temperatures:

Kyanite-corundum schist- $T_r^{\text{Pg}} = 662 \pm 60^\circ\text{C}$; $T_r^{\text{Ms}} = 657 \pm 50^\circ\text{C}$; $T_r^{\text{width}} = 668 \pm 60^\circ\text{C}$;

Andalusite schist- $T_r^{\text{Pg}} = 511 \pm 60^\circ\text{C}$; $T_r^{\text{Ms}} = 585 \pm 50^\circ\text{C}$; $T_r^{\text{width}} = 567 \pm 60^\circ\text{C}$;

Muscovite-paragonite schist- $T_r^{\text{Pg}} = 372 \pm 60^\circ\text{C}$; $T_r^{\text{Ms}} = 604 \pm 50^\circ\text{C}$; $T_r^{\text{width}} = 559 \pm 60^\circ\text{C}$;

Practical applications of Pg-Ms solvus thermometry are restricted to quasibinary Pg-Ms pairs that equilibrated at pressures between approximately 2 and 8 kbar (for investigated minerals assemblage p=4-7kbar, Eric, 1998).

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ROCKS WITH POZZOLANIC PROPERTIES USABLE IN THE CEMENT INDUSTRY

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General

During the last years, due to the increasing energy crisis, several programs have been drawn up and put into practice in the cement industry (cement, lime, plaster) in various countries regarding the rational use of existing raw materials and minimising the use of high-energy-consuming materials, such as cement clinker. In this context, an efficient way tackled by researchers and cement manufacturers has been the use in cement manufacture of a kind of rocks which due to their pozzolanic properties can substitute clinker in certain proportions in cement.

Pozzolanic properties signify the aptitude of a finely ground raw material to bind the calcium oxide in the presence of water, at normal temperature, with formation of compounds with hydraulic properties. According to SR 3832-10, pozzolanic materials, either natural or artificial, consist essentially of reactive SiO_2 and reactive Al_2O_3 . Reactive SiO_2 is that part of silica dioxide that becomes after treatment with HCl soluble in KOH brought to a boil.

Natural pozzolana cement is standardised in all countries with well-developed cement industries. In most cases, the maximum admissible ratio of natural pozzolana material is of 40%, although there are countries where higher proportions are allowed. Thus, China produces cement with 50% pozzolana; the USA and Yugoslavia, with 85% pozzolana; and Italy—the pozzolana homeland—produces a wide range of cement sorts with pozzolana materials.

In Romania, the pozzolanicity of a natural or artificial material is established in conformity with standard SR 3832/1998 and taking into account the physicochemical characteristics shown in Table 1.

In 1996, a significant result was the drawing up and taking effect of the standard SR 1500, which stipulates production of Portland cement with a single addition of natural pozzolana in ratios of 6–20% (type II/A–P) and 21–35% (type II/B–P), as well as composite Portland cement (type II/A–M and II/B–M), pozzolana cement (type IV/A), and the composite cement (type V/A), where natural pozzolana materials concur beside other active additions (granulated blast furnace slag, thermal power station fly ash) and/or limestone.

Table 1

SR 3832/1998 Characteristics	Requirements (%)
SiO_2 content	
- total	≥ 50
- reactive	≥ 25
Physical activity index (I)	≥ 85
Chemical activity index expressed by the insoluble residue (RI)	≤ 35

As is well known, the activity of natural or industrial pozzolana materials is determined in principal by their content in vitreous phase whose free energy is higher than the crystalline phase and gives a pregnant instability to the system. The vitreous phase may have a silica, alumino-silica or ferrite-aluminate-silica nature.

Natural pozzolana materials can be uncrystallised volcanic rocks (vitrophyre, retinite, obsidian, perlite, and pumice stone) consisting of volcanic glass, as well as pyroclastic rocks containing in part a vitreous phase of volcanic origin. Among sedimentary rocks, pozzolanic materials are silicolite and diatomite rocks containing amorphous silica of chemical precipitation or organic origin, respectively. Besides volcanic and

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sedimentary rocks containing uncrystallised phases, also as natural pozzolana materials are recognised a number of sedimentary rocks of special mineralogical composition. These kinds of rock contain in significant proportion minerals with high absorption capability and high level of ion exchangeability, such as zeolite and montmorillonite.

Experimental investigations

During the last years, the National Institute of Cement has carried out extensive investigations to characterise from the pozzolanicity point of view a large number of rocks to be employed as raw materials in the cement industry.

The investigations have focused on more than 50 varieties of rock originating from perimeters as close as possible to cement plants, such as vitroclastic tuff (Slanic-Piatra Verde quarry, Mirsid quarry, Paglisa Cetate-Deva quarry), vitrocristaloclastic tuff (Borsa-Apahida, Hadareni, Cleja-Bacau), ignimbrite (Pojoga, Baija-Barbura), coarse pyroclasts (Baita-Craciunesti, tuff (Ciugud-Alba Iulia), bentonite (Gurasada and Mihaesti-Dobra), diatomite (Urluia-Adamclisi, Patarlagele-Buzau), radiolarite (Paulis-Deva), porcelanite (Pinoasa-Targu Jiu and Berbesti lignite quarries), etc.

Chemical and mineralogical analyses and pozzolanicity tests of essential importance in determining the activity of the rocks under investigation have been carried out according to SR 3832. Pozzolana rocks corresponding to the requirements in SR 3832 were used in obtaining laboratory cement sorts according to SR 1500. The cements obtained were tested as to their chemical, physical and physicommechanical characteristics. At the same time, the grindability of cements with natural pozzolana has been determined as compared to the cements containing granulated blast furnace slag addition.

Results and interpretation

Table 2 shows the results of chemical analyses on several kinds of pozzolanic rocks.

Table 2

Type of rocks/Location	Chemical characteristics, (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Zeolitic vitroclastic tuff Slanic-Piatra Verde quarry	67,49	11,44	1,60	4,48	0,20	2,68	0,86
Zeolitic vitroclastic tuff Dej-Mirsid quarry	67,95	12,31	1,04	3,35	0,39	2,81	0,53
Vitrocristaloclastic tuff Borsa-Apahida	67,68	13,04	1,60	5,56	0,58	2,76	0,32
Ignimbrite Pojoga	69,67	13,53	1,20	1,39	0,00	2,61	1,34
Diatomite Urluia-Adamclisi quarry	78,66	5,32	1,91	0,90	1,09	0,82	0,40
Bentonite Gurasada quarry	74,02	12,62	1,55	1,90	1,45	2,96	0,86

Table 3 shows the results of the chemical analyses and pozzolanicity determinations as compared to the requirements in SR 3832/1998.

Table 3

Type of rocks/Location	SiO ₂ total (%)	Reactive SiO ₂ (%)	Chemical activity index (insoluble residue) (%)	Physical activity index (%)
Requirements SR 3832	min. 50%	min. 25%	max. 35%	min. 85%
Zeolitic vitroclastic tuff Slanic-Piatra Verde quarry	67,49	63,46	8,20	127,90
Zeolitic vitroclastic tuff Dej-Mirsid quarry	67,95	63,69	7,35	133,02
Vitrocristaloclastic tuff Borsa-Apahida	67,68	39,48	18,80	88,58
Ignimbrite Pojoga	69,67	57,35	28,75	82,77
Diatomite Urluia-Adamclisi quarry	78,66	56,02	14,58	93,62
Bentonite Gurasada quarry	74,02	45,25	23,71	81,04

The results show that the investigated pozzolana rocks correspond to the requirements in SR 3832 regarding the pozzolanicity tests.

Cements type II/A-P obtained using investigated pozzolana rocks in ratios of up to 15–20% correspond to the requirements in the standard and classify into the resistance class 32,5. Also, satisfactory results have been obtained on cements type II/B-P with 25–30% tuff addition from Slanic-Piatra Verde and Mirsid. With a 35% tuff addition from Slanic, cements resistant to aggressive mediums have been obtained.

In terms of grindability, for a fineness of $R_{900} = 10\%$, the cement with natural pozzolana addition required a lower specific power consumption than in the case of a blast furnace slag addition, as shown in Table 4.

Table 4

Clinker	Cement with addition of		Specific power consumption in kWh/t at a fineness of
	Slanic tuff	Galati slag	$R_{900} = 10\%$
Fieni	-	-	43,07
	-	-	45,50
	-	-	42,30
	-	18 %	
	20%	-	

Allowing for the obtained results, natural pozzolana complying with the requirements in SR 3832/1998 can be used to obtain cements II/A-P and II/B-P as per SR 1500/1996. Cements type II/A-P and II/B-P may be employed both as masonry mortar and rendering plaster as well as for works in aggressive mediums.

Conclusions

Diversification of the range of natural pozzolana materials recommended for manufacturing cements with natural pozzolana addition has led to involving in the economic cycle of natural resources less utilised at the moment and to an increasing incentive for companies in the binder industry field concerned with reducing of production costs.

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TITANOSILICATES: FROM A CHALLENGE IN MINERALOGY TO AN OPPORTUNITY IN MATERIALS SCIENCE

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Several achievements of the modern technology have their roots in the observation and understanding of natural phenomena and materials. In particular, some key products for materials science are either minerals or have been synthesised starting having minerals as model. Zeolites represent a well known example; because of their microporous properties, these aluminosilicates play crucial roles in very different fields such catalysis, agronomy and horticulture (controlled release of fertilizers and water) and animal nutrition (e.g., regulation of digestion fermentation). Other groups of minerals possess channels and cavities and potentially can act as porous material: labuntsovites (Chukanov *et al.* 2002), eudialytes (Johnsen & Grice, 1999) and tobermorites (Merlino *et al.* 1999) are some examples. The presence of cations like Ti and acidic OH groups increases the catalytic possibilities of microporous materials. In this context the titanosilicates have attracted the attention of materials scientists and some compounds of technological interest have been synthesised having natural structures as model (see Rocha & Anderson, 2000; Saxton, 1999). The technological interest of these microporous materials is enhanced by the possibility of incorporating heteroatoms into the framework thus allowing a fine-tuning of physical and chemical properties in the fields of optoelectronics, non-linear optics, batteries, magnetic materials and sensors.

(Hyper)agpaitic rocks occurring in famous complexes like those of Kola Peninsula (Russia; Khomyakov, 1995; Pekov, 2000), Ilmaussaq (Petersen & Secher, 1993), Mont Saint-Hilaire (Horváth & Gault, 1990) are a major source of complex titanosilicates (Sørensen, 1997). These rocks are not common but the presence of rare elements (Li, Be, Rb, Ga, REE, Nb, Ta, Hf, Zn, Sn, U, Th) and the high contents of Na, Zr, Cl and F have favoured the formation of a huge amount (more than 500 species; some 150 new species) of minerals. Some of these minerals show complex and characteristic crystalline structures that offer a wide pattern of opportunities to materials scientists. The structural variability depends also on a similar crystal-chemical role of Si-tetrahedra and Ti-octahedra. This role is based both on dimensional (O...O distances) and bonding aspects. In fact a (TiO₆) octahedron bears a formal negative charge 8-, 4- or 2- according it is isolated, shares 4 or 2 corners. Thus, in the order, an octahedron can supply the same bonds as 2(SiO₄)⁴⁻, (SiO₄)⁴⁻ or a (SiO₃)²⁻ group in a pyroxene-like chain. In particular, the introduction of Ti-octahedra in a silicate structure can lead to a framework structure as illustrated in some examples given below. As a matter of fact, more than 1/3 of the new mineral species reported from the mentioned localities are represented by titanosilicates.

The characterisation of several titanosilicates occurring in the agpaitic rocks is a challenge even for the modern analytical methods mainly because of their defect crystallinity. The morphology is often fibrous and single-crystals suitable for classical X-ray structural analysis are missing. Transmission Electron Microscopy (TEM) and structural modelling based on the concepts of modular crystallography (Merlino, 1997), like polysomatism and OD theory, are sometimes the only way to obtain key information for the characterisation of these minerals. But even when an X-ray crystal structure determination is possible, a wide possibility of isomorphous substitutions together with the presence of partially occupied sites and widespread disorder require a skilled structural and crystal-chemical analysis in order to properly describe the phase. Typical examples are the labuntsovites and eudialytes, two groups of minerals known since long time and which are now rapidly expanding after that subtle features of their structures have been recently unravelled.

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Some examples shall be shown and discussed particularly for layer titanates [heterophyllosilicates polysomatic series (Ferraris *et al.* 1996); bafertisite mero-plesiotype series (Ferraris *et al.* 1997; Ferraris *et al.* 2001a, 2001b)]. Further examples are eudialytes (Gula *et al.* 2001; Johnsen & Grice 1999), labuntsovites (Chukanov *et al.* 2002; Khomyakov *et al.* 2001) and seidite-(Ce) (Khomyakov *et al.* 1998).

The heterophyllosilicates have formula $A_{2+n}Y_{4+3n}[Ti_2(O')_{2+p}Si_{14-4n}O_{14+10n}](O'')_{2+2n}$ where A = interlayer cations; Y = octahedral cations; O' (bonded to Ti) and O'' (belonging to the octahedral O sheet) can be oxygen, OH, F or H_2O , the $14+10n$ oxygen atoms are bonded to Si. The value of p (0, 1, 2) depends on the coordination number and edge/corner sharing of the Ti coordination polyhedron. The structure is based on three different types of HOH layers; H (hetero) is a sheet which may be derived from the tetrahedral sheet T of the phyllosilicates by inserting 6- or 5-coordinated Ti (or other vicariant cations like Nb and Zr); O is an octahedral sheet like those occurring in the phyllosilicates.

Labuntsovites have general formula $A_4B_4C_{4+2n}[D_4(H_2O,OH)_{2n}]M_4(O,OH)_4[Si_4O_{12}]_n nH_2O$ and their crystal structure is built up by a three-dimensional framework of $M(= Ti^{4+}, Nb^{5+})$ -octahedra and Si-tetrahedra where A , B , C and D cavities host various alkaline, earth-alkaline, other bivalent extra-framework cations and water molecules.

A general formula $[N(1)N(2)N(3)N(4)N(5)]_2[M(1a)M(1b)]_2M(2)_2M(3)_2M(4)_2Z_2[Si_4O_{12}]_nO'_4X_2$ holds for eudialytes; N = Na, K, Sr, REE; $M(1a)$ & $M(1b)$ = Ca, Mn, REE; $M(2)$ = Fe, Mn; $M(3)$ = Nb, Ti, W; $M(4)$ = Si; Z = Zr, Ti; O' , X = O, OH, H_2O , Cl, F, CO_3 . The structure may usefully be seen as a three-dimensional framework where channels and cavities host different cations in the sites N , O' and X .

The structure of seidite-(Ce), $Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4 \cdot 5H_2O$, has been obtained for comparison with miserite, $KCa_3(Si_2O_7)(Si_6O_{15})(OH)F$. Since both these minerals show zeolite-like exchange properties, partially successful attempts of synthesis have already been attempted by some research groups (e.g. by M. S. Dadachov, K. Okamoto & X.D. Zou, Structural Chemistry Department, Stockholm University, private communication) after the publication of seidite-(Ce) as a new species.

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SOME CONSIDERATIONS REGARDING INTEGRATED STRATEGIC ANALYSIS IN METALLOGENY

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The aim of the paper is to propose the usage of Integrated Strategic Analysis (ISA) in the domain of metallic mineral resources using quantitative and qualitative methods. The purpose is to make some considerations applying ISA in metallogeny, as an influencing factor for local, regional and global sustainable development.

The type of natural mineral resources (NMR) taken into account in ISA is:

- Solid / fluid as they appear in nature,
- Energetic / non-energetic, fuel / non-fuel as they are used.

Metallogeny, by definition, is the science studying the formation, distribution and classification of NMR, being characterized by descriptive, qualitative and quantitative parameters. The approach of metallogeny can be interactive, in a modular system. The metallogenetic operating elements are determined by the metallogenetic factors: magmatic, tectonic, geochemical, petrographical, etc.

The term "management" used in almost all disciplines is referred to as both a science and the process of applying it in real world. Actually, it has a three-fold meaning: process (practical application), decision factor (individual or team) and science (as research subject).

In the above-mentioned area, strategic management (SM) defines the "Mission of the Mineral Resource", medium and long term objectives as well as the ways to achieve them, taking the effects and costs (economic, environmental, social) into account.

The key elements of SM are the **Institutional phase** – the making of an infrastructure able to develop a management program in the three main directions: social, economic and environment – where one must involve all the decision factors, and an **evaluation and monitoring system** both qualitative and quantitative.

Institutionally, we distinguish three main levels (Pop and Bolchis, 2002):

Strategic level – which has the role of defining the strategy plan for the developing the potential metallogenetic area. It is the main decision factor and must be in permanent contact with all involved factors, both vertically – tactic level and operational level and horizontally – the stakeholders

Tactic level – auditing – task accomplished by the tactical analysis division of the management. It is characterized by the three synergetic domains (economic, social, environmental), the output being the audit which contains the evaluations, estimations, forecastings and threats that the NMR generates by its exploitation.

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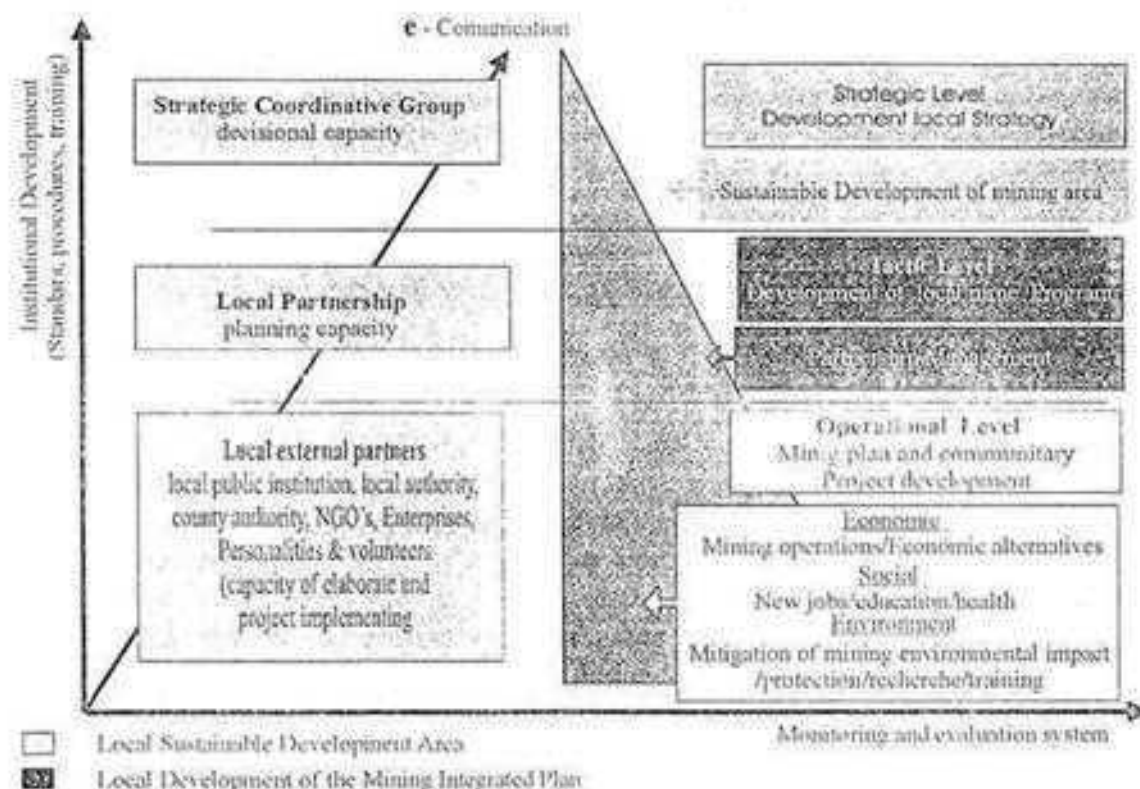
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Operational level – characterized by working groups specialized in various areas and able to develop and implement the projects by objectives, objectives needed to achieve the integrated development of the metallogenetic area.

The metallogenetic domain is one with huge development potential both economically and socially. The potential becomes manifest when exploitation is granted. Exploitation must follow the Integrated Development guidelines, in order to achieve sustainability. Alternative economic solutions must be taken into account as well as social and environmental aspects.

Diagram of integrated relationship between the Mining Area/metallogenetic zone and Local Sustainable Development



In accordance with Robertson (2001), the World Bank procedures (2002) and Pop (1999), in the decision process, the mining development plan (opening, operating and closing a mining area) should follow some principles in order to achieve sustainability:

1. A global approach is needed when planning a sustainable exploitation of resources. This implies a healthy management policy at local, regional and national level. This implies conservation strategies and the 3 R's.
2. Exploitation uses the area only temporary. This gives a high value both at the beginning and during the exploitation being able to bring development and wealth locally and regionally. This development and its benefits can fertilise and incite the development of the area even after the mining area is closed. This is one aspect that must be stimulated in order to insure sustainable development.
3. Mining is invasive and brings changes hard to envision. This can be physical, chemical and biological. Determining this impact and minimizing its effects is one of the responsibilities of administration.
4. Mining activity is temporary. There can be several mining operators and thus the careful planning of terrain usage during and after mining operation is compulsory.
5. The mine is placed in space and time as well as in an ecological, social and economical environment. Everybody involved in the process of exploiting the area must be consulted and

made responsible for the decisions taken. Commitment is needed in order to insure a sustainable development

6. The various types of impacts (social, economic, environm.) are measurable. The different stakeholders have different views and outputs regarding the effects of their activity, depending of the measurables taken into account. A consensus to be achieved, one must provide a platform for exchanging different types of information between involved operators. This consensus ensures also a unitary understanding of working procedures

In conclusion, we consider that metallogenetic forecasting has a determinant role in the development of an area at local, regional and global level. We consider that ISM must follow the guidelines mentioned above in order to ensure the sustainable development of the potential metallogenetic area.

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GEOMETRY OF 15.4 MA RHYOLITIC IGNIMBRITES FROM GUTAI MTS., EASTERN CARPATHIANS, ROMANIA

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Gutai Mts. are part of the northern segment of Romanian Eastern Carpathians. They belong to the Neogene volcanic chain of Carpathians, edified during complex subduction processes (Seghedi et al, 1998).

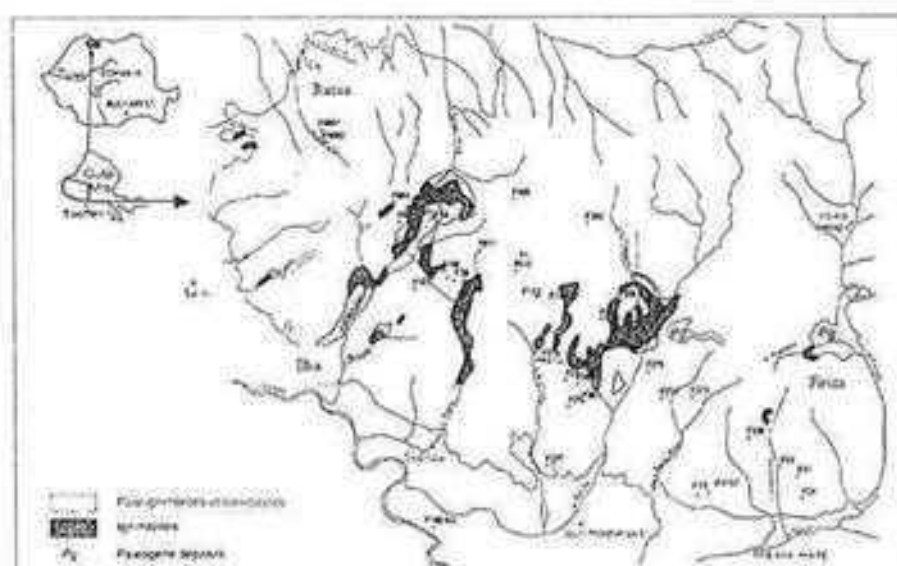


Fig. 1 – Areal distribution of ignimbrites and drilling works on the south-western part of Gutai Mts.

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Gutai Mts. have been built up during Miocene. Volcanic processes developed during 15.4-7.0 Ma (Pecskay et al, 1995; Fulop, 2001), resulting a wide range of igneous rocks. Sedimentation developed contemporaneously with the volcanism.

- dilute, maintained density stratified suspension currents, as parental flows of ignimbrites;
- compatibility with "boiling over" eruption style and caldera collapse;
- location of the source within the area of Gutai Mts (Fulop, in press).

Volcanic activity began 15.4 Ma ago, on the Paleogene island - the actual sedimentary basement of the massif. The ignimbrites overlay the flysch deposits, spreading on the south-western part of the mountains (Fig. 1). Studies in outcrops and under microscope emphasized the lithological features and the sedimentary structures of the ignimbrites (Fulop, 2000).

The lithology of ignimbrites shows fine grained deposits, lapilli tuffs of rhyolitic composition, locally covered by co-ignimbrite ash fall deposits.

The sedimentary structures reflect the mechanisms of transport and emplacement, useful to evaluate the style of eruption (Freundt 1998, 1999). Their study suggests:

Geometry of ignimbrites

The geometry of deposits is a valuable element in reconstructing the source location and the subsequent evolution of the area.

The geometry of ignimbrites have been modelled using 51 drilling works located on the south-western part of the mountains (Fig. 1). The estimated area covered by ignimbrites is around 200 km² and the volume, calculated on the basis of boreholes, is about 34 km³.

Ignimbrites show an actual blanket morphology, elongated on W – E direction, with irregular lower and upper surfaces (Fig. 2, 3). The thickness decreases from W towards E, from 350 m in Ilba and Racsa areas, to estimated 30 m in Firiza area (Fig. 1).

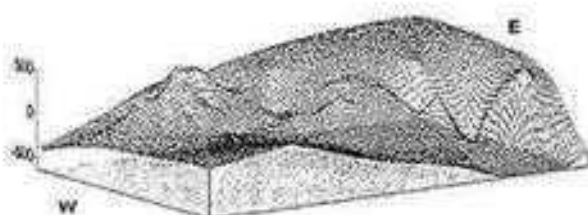


Fig. 2 Lower surface of ignimbrites

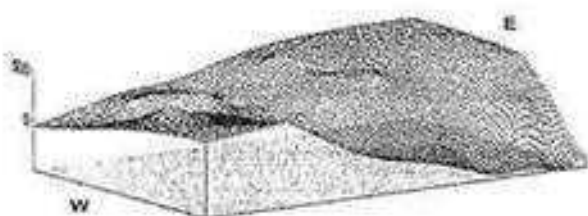


Fig. 3 Upper surface of ignimbrites

In order to model the original geometry, certain features may be inferred from the rheology of parental flows. The maintained subcritical flow regime of parental flows corresponds to ignimbrites emplacement on a flattened or slightly undulating surface. The incorporated alluvial debris suggests channelized flows; those channels have been overwhelmed by the large volume of ignimbrites, which filled and flattened the area. Both the lower and upper surfaces were flat, dipping from W towards E.

The supposed original morphology, correlated with the actual thickness variation, suggests that deposits from western area had a constant, at least 350 m thickness and eastern area showed an exponential decrease to several tens of meters.

The actual geometry of ignimbrites reflects the original geometry modified by the combined action of subsequent tectonical and erosional processes. A comparative study of the inferred original geometry and actual geometry emphasizes the tectonical processes involved in the evolution of south – western part of Gutai Mts., after ignimbrites emplacement. Two different areas have been separated.

- the western area, comprising the whole south – western corner of Gutai Mts., accumulated the thickest, flat topped ignimbrites; they underwent a subsequent uplift related to the Paleogene ridge uprising, which was combined with active erosional processes, leading to the actual, very irregular morphology; ignimbrites have been washed out partly, being preserved only in N, Racsa area and S, Ilba area;
- the eastern area, from Ilba towards E, Firiza lake, shows an exponential decrease of ignimbrites thickness, modified also by the subsequent Paleogene uplift and erosion.

These features are very important in reconstructing the source location: the thickest, western deposits suggest intracaldera ignimbrites and the exponential decrease of thickness corresponds to eastward ignimbrites outflow.

Conclusions

A series of studies related to the 15.4 rhyolitic ignimbrites from Gutai Mts. presented their lithology, sedimentary structures, geometry and which are the genetical implications of these descriptive features (Fulop, 2000, 2001, in press). The next elements have been inferred from the previous studies:

- magmatic explosions of an acidic, rhyolitic magma are responsible for ignimbrites genesis;
- ignimbrites have a fine-grained texture;
- ignimbrite deposits are overlain by co – ignimbrite ash fall deposits;
- expected underlain Plinian fallout deposits are lacking.

A major step has been done evaluating the parental flow rheology (Fulop, in press), essential in the assumed “boiling over” style of eruption followed by caldera collapse and location of the source within the area of Gutai Mts.

The study of the geometry of ignimbrites emphasized the actual morphology. The original morphology resulted from flow rheology. A comparative study between the two morphologies has been carried out concluding about subsequent tectonical and erosional processes. The thickness variation in accordance with the original morphology separated two areas of different evolution:

- western area with constant, thickest deposits;
- eastern area with exponential thickness decrease;

They are valuable indicators of intracaldera ignimbrites and ignimbrites outflow respectively, accepting the already created scenario, inferred from all the other descriptive features.

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MIOCENE CALC-ALKALINE VOLCANISM IN BAIA SPRIE-CAVNIC AREA (GUTAI MTS., EASTERN CARPATHIANS)

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Gutai Mts. belong to the Neogene-Quaternary volcanic chain of Romanian Eastern Carpathians. The subduction of the European Plate beneath Alcapa and Tisza-Dacia microplates and the hinterland extensional reply in the Pannonian Basin (Csontos, 1995) are responsible for the volcanic activity of Gutai Mts. Two types of volcanism had developed during Miocene (15.4-7.0 Ma, Pecskey et al, 1994) in Gutai Mts.: an acidic calc-alkaline extensional type and an intermediate calc-alkaline arc-type (Kovacs, Fulop, 2001). Baia Sprie-Cavnic area, very complex from the volcanological point of view, is situated in the south-eastern part of Gutai Mts. (Fig. 1), close to the southern border of the volcanic zone. It has a Neogene sedimentary cover composed of Badenian-Pannonian syn- and postvolcanic deposits. Oligocene-Early Miocene deposits, Paleogene flysch-type deposits belonging to the Pienides (as overthrust nappes), represent the predominant pre-Neogene basement.

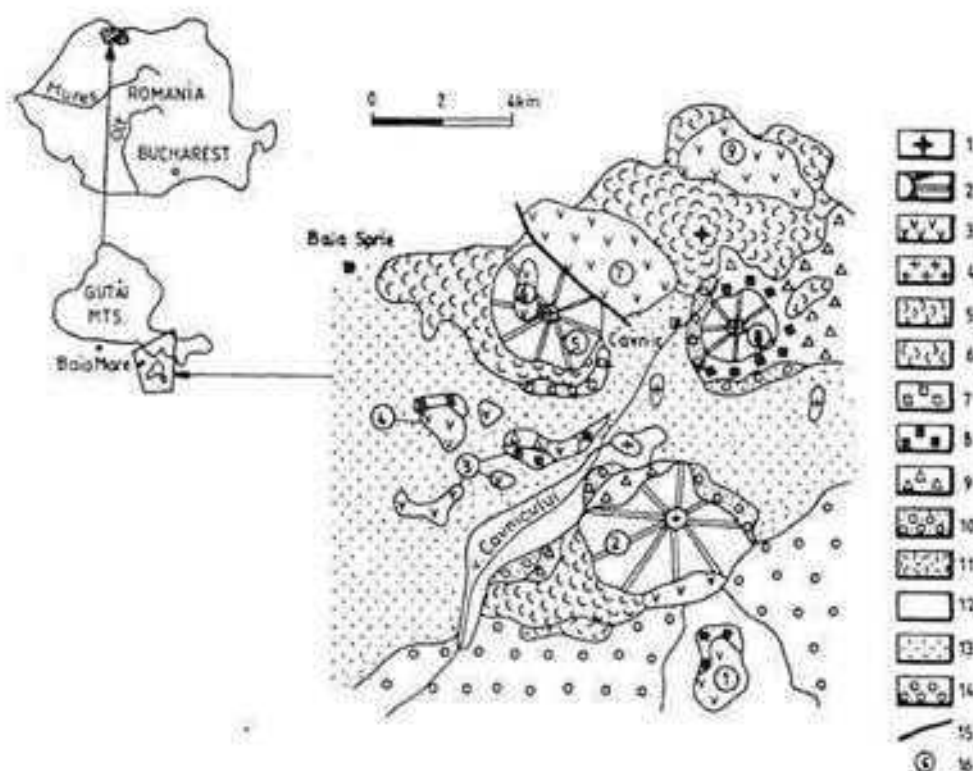


Fig. 1. Volcanological map of Baia Sprie-Cavnic area (SE Gutai Mts.). 1. Eruption centre; 2. Effusive cones; 3. Extrusive domes; 4. Intrusions; 5. Lava flows; 6. Lava flows with unknown centre; 7. Autoclastic rocks; 8. Hyaloclastic rocks; 9. Coarse volcaniclastics; 10. Fine volcaniclastics; 11. Tuffs; 12. Quaternary; 13. Syn- and postvolcanic Neogene sedimentary cover; 14. Prevolcanic sedimentary deposits; 15. Fault; 16. Volcanic structures.

1-Satra (pyroxene dacites, 13.2 Ma); 2-Rochitele (pyroxene andesites, 13.4-13.3 Ma); 3-Piatra Rosie Cetatele (pyroxene ± amphibole dacites); 4-Danesti (biotite dacites/rhyolites, 11.6 Ma); 5-Mogosa (pyroxene basaltic andesites, 11.4-9.5 Ma); 6-Valea Morii (pyroxene ± amphibole dacites, 10.1 Ma); 7-Poiana Cremenii (quartz andesites, 11.3 Ma); 8-Higea (pyroxene ± amphibole andesites, 10.1 Ma); 9-Gutai (biotite andesites, 9.3-9.0 Ma).

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Volcanological and petrological data

Volcanics (primary and reworked tuffs) belonging to the acidic calc-alkaline volcanism outcrop in some limited areas and have been intercepted in a few boreholes (pumice-rich pyroclastic flows and associated volcanogenic epiclastic deposits).

The intermediate calc-alkaline volcanism is very well represented in the entire area by a great variety of rocks belonging to different volcanic structures (Fig. 1). It had started in Early Sarmatian, in the southern part of the area and had a subaqueous character (Rachitele and Satra volcanic structures). Volcanic activity had continued during Pannonian and two subaqueously extruded domes were emplaced: Piatra Rosie-Cetatele and Danesti. The paroxysm of the volcanic activity was reached in Pannonian, in the central and northern part of Baia Sprie-Cavnic area; it had started subaqueously (e.g. Higea volcanic structure) and continued subaerially. Gutai extrusive dome is the youngest structure from Gutai Mts. (9.0 Ma, according to Pecskey et al, 1994), which ceased the volcanism.

Lava flows related to both effusive cones and extrusive domes are predominant. They are associated with a series of volcanoclastics proving the subaqueous eruption and emplacement of lavas: quench fragmentation products (in situ and resedimented hyaloclastites) as well as phreatomagmatic products (primary and reworked pyroclastics) have been identified. Most of them have been resedimented by mass flows and encapsulated by mudstones in submarine environment (Fulop, Kovacs, 1996).

Intravolcanic shallow level and subvolcanic intrusions of different sizes and morphologies are associated to volcanics, especially from the central and northern part of the area.

Volcanic rocks consist of basaltic andesites, andesites, dacites and rhyolites (Fig. 2). Pyroxene basaltic andesites and andesites are predominant. Complex petrogenetical processes are suggested by mineralogical and petrographical peculiarities of most of the volcanics: acidic rocks having an exclusive pyroxene character (Satra dacites) or containing scarce amphibole (Piatra Rosie-Cetatele and Valea Morii dacites), mineralogically differentiated rocks containing large amounts of biotite, amphibole and magmatic quartz (Danesti dacites/rhyolites), volcanics having abundant cognate xenoliths (Valea Morii dacites), quartz crystals with pyroxene corona (Gutai biotite andesite), plagioclase xenocrystals (Danesti dacites/rhyolites).

Intrusive rocks consist of a large variety of textural and compositional types. Porphyritic textures of pyroxene andesites and microdiorites are predominant. (Micro)gabbros, quartzdiorites, tonalites and microgranodiorites form well-developed intrusions in Cavnic mine and adjacent areas (intercepted in boreholes).

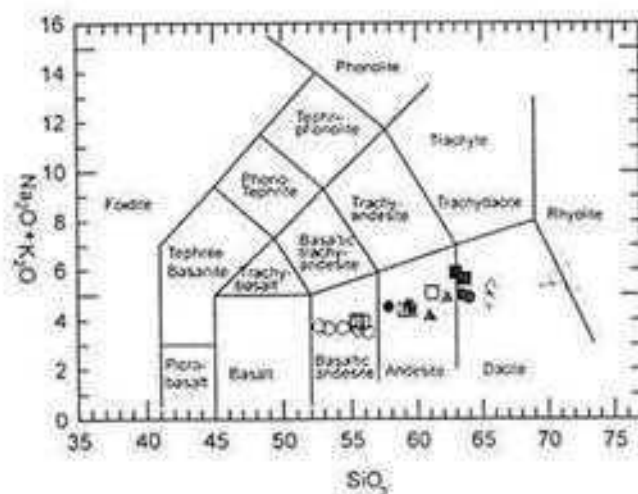


Fig. 2. TAS diagram for the volcanic rocks of Baia Sprie-Cavnic area.

* - Rachitele andesites; Δ - Danesti dacites/rhyolites; $\diamond$ - Piatra Rosie-Cetatele dacites; $\triangle$ - Sutor (Poiana Cremerii) quartz andesites; $\square$ - Cavnic-Sutor (Higea) andesites; $\circ$ - Mogosa basaltic andesites; $\odot$ - Valea Morii dacites; $\blacksquare$ - Gutai andesites.

Major and trace elements geochemistry points out some features of the intermediate volcanism from Baia Sprie-Cavnic area (resembling to the bulk of volcanics from Gutai Mts., Kovacs, 2001).

- the predominant medium-K character (emphasized by K_2O-SiO_2 diagram), excepting Gutai dome biotite andesite which has a high-K character;
- the calc-alkaline character (Fig. 3 A), with tholeiitic trends of magmas responsible for Piatra Rosie and partly Mogosa structures;
- the arc-type (subduction related) character, emphasized by REE contents and patterns in chondrite-normalized REE diagrams (LREE enrichments, negative Eu anomaly) and by strong enrichments of LILE and LREE and depletions of HFSE in the NMORB normalized incompatible trace elements diagram (Fig. 3 B).

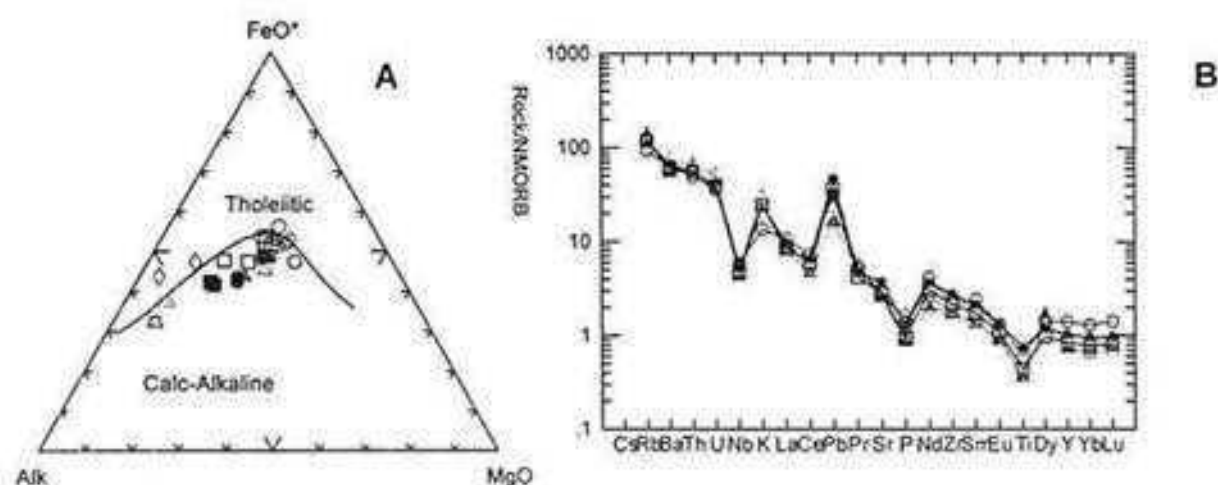


Fig. 3 – AFM diagram (A) and NMORB normalized diagram (B) for the volcanics of Baia Sprie – Cavnic area

Conclusions

A complex calc-alkaline (subduction-related) volcanism had developed in Middle Miocene (13.4-9.0 Ma) in Baia Sprie-Cavnic area. Lava flows and lava domes associated with primary and resedimented volcanoclastics evolved predominantly in submarine conditions. The mineralogical and geochemical peculiarities of the intermediate volcanics assert complex petrogenetic processes (fractional crystallization, crustal assimilation, mixing and mingling of magmas). They are related to the evolution of parental magmas in crustal reservoirs of different compositions, emplaced at different depths.

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GEOLOGICAL AND TECHNOLOGICAL CHARACTERISTICS OF CLAY DEPOSITS FROM THE WEST OF ROMANIA USED IN TRADITIONAL CERAMICS

MARICA¹ Silvana, CETEAN² Valentina, KOVACS³ Gavril

Introduction

The west region of Romania, by its position as to Western commercial borders, by its millenary tradition of processing clayey raw materials and by its specific cosmopolitanism, represents one of the most developed areas in Romania from an economic and industrial point of view, where were set up the first factories with industrial productions of ceramic materials, at Jimbolia in 1864. Geological team from PROCEMA, studied in the west areas of Romania 13 units used for the manufacture of coarse and fine ceramic products (Table 1)

Table 1

No	Deposit	County	Illite (%)	Kaolinite (%)	Montmorillonite (%)	Geological age
1	Zalau	Salaj	30	15	20	Pannonian Quaternary
2	Beius	Bihor	5	5	20	Upper Pliocene
3	Calea Clujului	Bihor	5	8	20	Quaternary
4	Bihor Episcopy	Bihor	50	-	-	Quaternary
5	Michael Valley	Bihor	11	4,9	7,7	Quaternary
6	Suncuius	Bihor	15-24	50-65	4-5	Upper Jurassic
7	Belu	Arad	35	25	7	Upper Neogene
8	Halmagiu	Arad	13	25	15	Upper Neogene
9	Santana	Arad	30	30	20	Quaternary
10	Jimbolia	Timis	15	-	20	Quaternary
11	Cărpiniș	Timis	-	-	-	Quaternary
12	Lugoj	Timis				Pannoniene
13	Botesti	Timis	13	57	20	Upper Pliocene

Methods and experiments

Present paper represents a synthesis of geological and ceramic researches on clay deposits from the west part of Romania. Each deposit was studied by mapping, drilling and sampling. Then raw materials were studied by petrographical, mineralogical, oxidic and physical-ceramic investigations. Final documents contained an evaluation of quantity of useful resource, feasibility studies and experiments on products obtained by each sample.

Qualitative characteristics of clay deposits

Most of clay deposits in the west area belong to the Superior Pliocene Quaternary, excepting one refractory clay deposits (Suncuius from Bihor county) that belong to the Jurassic period. As a whole, the structure of most of the clayey deposits in this area consists of three geological horizons: *a yellow clay horizon*, generally sandy clays, 3-10 m thick at the upper part (Beius, Calea Clujului, Jimbolia), *a yellow-coffee colored clay median horizon* with ferruginous or kaolinous intercalations (Botesti, Suncuius), 3-12 m thick, *a bluish-grey - grey clay horizon*, with a marly character on certain parts, 5-12 m in thickness.

The large majority of the clays from the west area clays with an illite-kaolinite composition (Fig.1).

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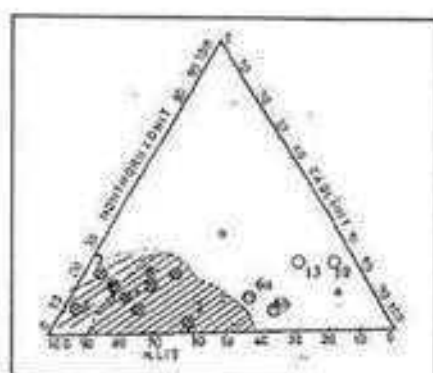


Fig.1 – Inclusion in the ternary diagram of the mineralogic content of the clays in the west of Romania

- ⊗ Illit-Kaolinitic Clays
- ⊙ Kaolinitic Clays

The type of the clayey material, especially the present kaolinite one show the faster rhythm and intensity of the kaolinisation processes that took place in the sedimentation basin of mudding origin, more especially that in the north of the Pannonic depression (the Bihor county).

The montmorillonite comes from the volcanic rocks that were the basis of sediment, suffered alteration processes and led to the present oxidic composition.

Depending on the chemical contents, the clay in the west area placed in the Augustinic diagram are included for direct or with proportions of sand used in the all fields of ceramic (Fig. 2).

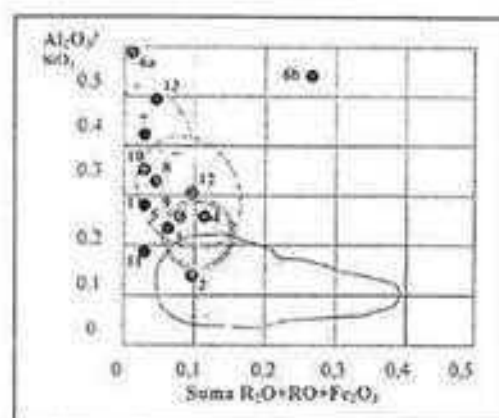


Fig.2 - The Augustinic diagram of the fields of use of the clay deposits from the west of Romania

- Fine and refractory ceramics
- Floor tiles, pipes and acid-proof floor tiles
- ===== Wall tiles and pottery
- Roof tiles
- Clinkerized materials
- ===== Bricks

From the physical-ceramic data it was found that, in general, the clays from this area are sensitive to drying, have significant plasticity (between 30 and 58%) and relatively high shrinkage (with values between 6 and 21%), have good and very good capability, average water absorption (9-16%) and good and very good mechanical resistance (compressions between 325 and 355 daN/ cmp) and bending between 90 and 460 daN/cmp (Fig.3,4)

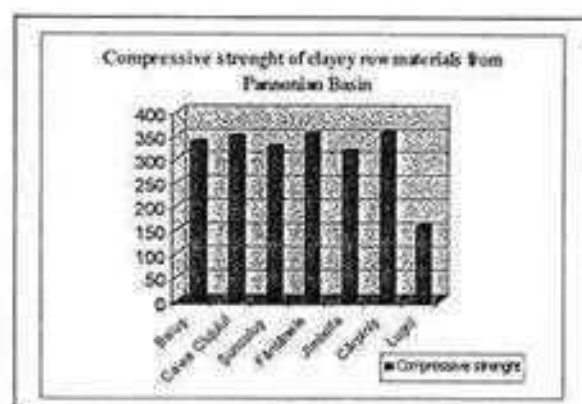
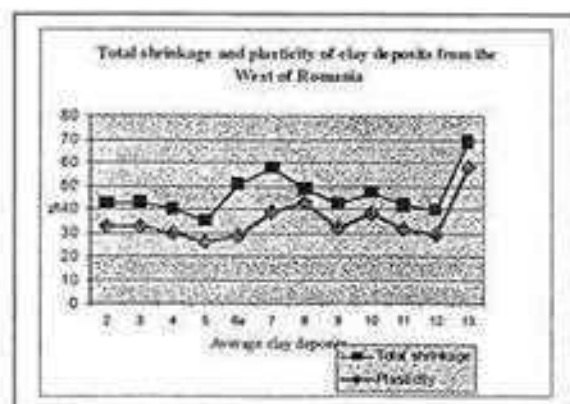


Fig.3,4 - Comparative diagrams of physico-mechanical characteristics of clayey deposits from the West of Romania

The clay processing require maceration processes subsequent to the quarry extractions (Fig.5), homogenization of the extracted row materials and degreasing of the clayey materials, carried out with sands present more often than not as intercalation in the mass of the deposits or with coal bearing sludge from adjacent areas. Although the clays in these areas are generally uniform as far as granulometry is concerned, the technological processes by roller crushing.

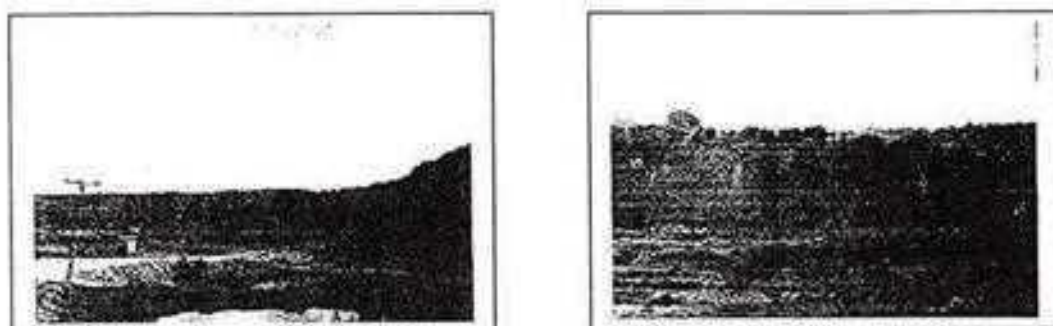


Fig.5 – Images of clay quarries from Suncuș (Bihor county) and Zalău (Salaj County)

The ceramic products currently obtained are included in the traditional pottery, majolica, building coarse ceramics, roof tiles, ceramic floor tiles, semi-vitrified and vitrified products (floor tiles, ornamental and household ware), fine ceramic products. These products have superior functional characteristics: accurate sound, pleasant colors, durability and functional versatility and the engobes and glazes used to cover the fine ceramic products have various decorative colors and very resistance to wear (Fig.6)

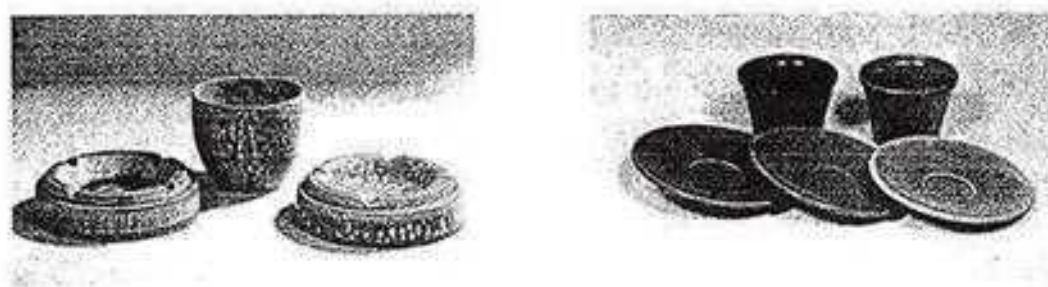


Fig.6 - Pottery products covered with with varied coloured glazes

Conclusions

In the west of Romania there are a great number of clayey deposits that can be used in the traditional building ceramics. From the synthesis study about these deposits results few important conclusions:

- The clays are classified according to the their geological age in Jurassic clays, Miocene-Pliocene clays and Quaternary-Pleistocene clays.
- From a mineralogical point of view, they are included in the category of clays with illite-kaolinite composition (illite 5-35%, kaolinite 15-65%).
- The chemical composition includes them in the fields of fine and coarse ceramics of refractory materials of ceramic floor tiles of pipes and roof tiles.
- These clays are generally sensitive to drying, have high plasticity, relatively high shrinkage, good shape-ability, average water absorption and good and very good mechanical resistances.
- The products obtained have superior properties: accurate sound, pleasant colors, durability and functional versatility.
- The engobes and the glazed have varied decorative colors and good resistance to wear.

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MINERAL RESOURCES FOR DIMENSION STONE FROM ROMANIA - GEOLOGICAL ECONOMIC ASPECTS, CHARACTERIZATION, STRATEGIES

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Trend on world market of mineral resources of building dimension stone

At present, the term of *dimension stones* means all those natural stones that may be cut or shaped to specific sized, in view of using them at constructions or in decorative applications. The term includes a wide range of types of rocks. Due to their special qualities as to long working life and beauty of colors, the mineral resources for dimension stone have been used for a very long time in various civil and artistic structures.

The industrial utilizations of composite materials consisting did not prove a viable and long term solution as such materials failed the test time. The natural stone has acquired, owing to its characteristics and the implementation of the new production and processing technologies, a worldwide new dimension, coming back in fashion especially by the hard, granite rocks, attractive on a long-term basis and of high functional versatility.

The dimension stone processing industry is at present one of the most dynamic industrial sectors, being the most efficient building material with a continuously ascending trend and with a market tendency of increase in the whole world in the next years.

In the years 1999-2000 there were more than 20 great producing countries of natural stone products both as far as export and import are concerned. The world supremacy Italy had in the field of stone was replaced in the years 2000 by China that dominates the world market by 19%. According to the petrographic type of the rocks and of products on the market, the world market is dominated at present by the granite products both for import and export (Fig. 1,2)

Recent important buildings are concrete examples of these tendencies the IBM building in New York, wholly dressed in gray granite or Crocker Citizens Bank in Los Angeles. The most in demand on the Romanian market is the red granite of Macin in the Tulcea county, to be found in several places in the Pricopan massif from Northern Dobrudja.

Romanian dimension stone resources, characteristics and geological - economic aspects

The oldest building stone quarries in Romania were the Roman ones in the Southern Dobrudja, near the towns of Deleni and Adamclisi, and more recently those for ornamental coverings opened up more than 125 years ago at Ruschita from Poiana Rusca Massif.

The highest peak of the Romanian dimension stone production was achieved in 1989, in the conditions generally known and was estimated at ca. 110 thousand tons being generated by the carrying out of the finishing works for the Palace of Parliament, where the highest share was

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practically represented by two quarries – Ruschita and Podeni. At that time, 8 quarries were permanently worked off, with productions around 1,35-4,5 thousand tons a year.

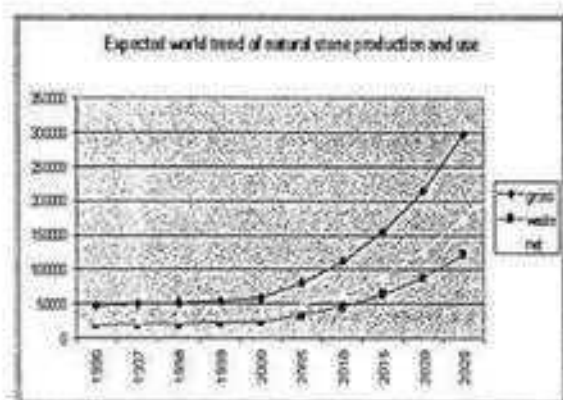


Fig. 1. Expected world trend of natural stone production and use

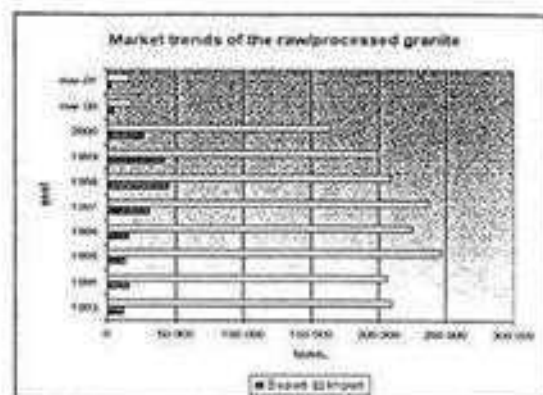


Fig. 2. Market trends of the raw/processed granite
Source: World Stone Industry

At present, the number of the Romanian operators on the domestic and foreign dimension stone market is over 200, and that of the deposits in operation, possessing a quarrying permit is 61. Most of the dimension stone rock deposits under quarrying in Romania are of a metamorphic nature (marbles) from the Southern Apuseni Mountains (*Moneasa and Sohodol marble*), the Preluca massif (*Buteasa marble*), Rodna Massif (*Anies marble*), Poiana Rusca Massif (*Ruschita and Alun Marble*) and the northern side of the Fagaras Mountains (*Porumbacu marbl*).

The ornamental limestones with opened up quarries belong to the Jurassic period either in the Apuseni Mountains (*Pojoga, Caprioara marble*) or in the Mehedinti plateau (*Gura Vail –Varanic marbl*). At present Romania has no large quarry of ornamental granite, although many deposits have homologated with reserves for at last 50 years.

After the 90's, geologists from PROCEMA Bucharest has revealed at least 10 perimeters with granites that may be processed as dimension stone. Among these are the *Caprarie and Piatra Imbulzita granites* located in the Pricopan massif and some granite perimeters situated in the tardikinematic *granitoidic masses of Tismana, Pocruia, Meri, Novaci*. Such granites can compete with brands that are well-known on the world market.

All granites under research have very good quarrying and exploitation technical economic conditions and very good aptitudes of processing into thin cladding and favorable cutting and polishing indicators. They also present a wide range of petrographic and color varieties among which is the orbicular granite of Tismana.

The distribution of the dimension stone deposits by counties is non-uniform: at present three counties monopolize the concentration of these resources, due to favoring geological- economic conditions. The county with the most perimeters of dimension stones- rocks that are being quarried is the county of Bihor with 16 deposits followed by the counties of Maramures with 12 deposits and of Tulcea with 10. (Fig 3)

The immediate potential of dimension stone quarrying and production Romania can be developed in the following 5 years up to a rate of 500-600 thousand a year.

At present there is another important demand in our country, namely for crystalline limestones of the white variety, a series of small producers, carrying out a limited quarrying of the perimeters with dimension stones. The best known and most in demand, for their statues are the *marbles of Alun, Bucova or Buteasa* and the limestone of Caprioara and Varanic- Gura Vail.

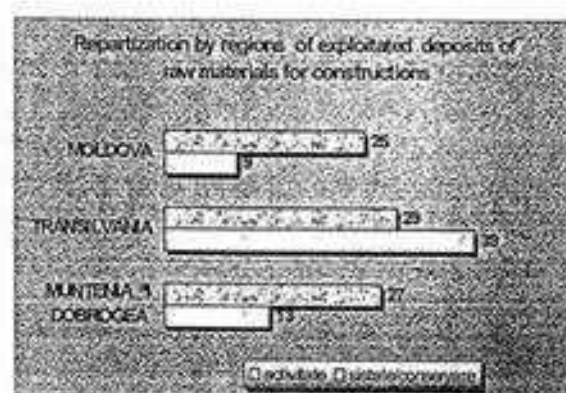


Fig. 3. Distribution by counties and provinces of the Romanian dimension stone deposits

Technical characteristics of the dimension stone products

According to the latest European norms, the main dimension stone products are as follows: dimension blocks, raw plates, finished plates and wall and floor coverings.

The *thin slabs* is a piece of natural stone of standard dimensions, obtained by cutting or splitting and which has a rated thickness between 8 and 12 mm, to be set on a structure with mortars or adhesives. The thin slabs, cut to 1 and 1,5 cm are currently most in demand on the market and are used both in public, but more especially in private buildings.

It can be thus found the best Romanian marble is still the one in Ruschita with values close to the Arabesco - Corchia brand, an Italian marble near Carrara. With the Pietroasa, Macin and Meri granites, the values of the compression strengths are also very good, even though they do not reach the values of the Taivassalo granite.

One of the most important requirements for Romania refers to being accepted on the world markets, especially on the European Union market, at least with a few brands, among which Ruschita and Macin varieties of products.

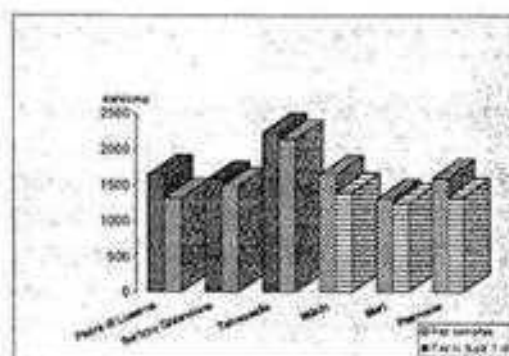


Fig.4 & 5 - Comparative compression strength for marbles and granites from Romania and varieties intensely use in world market

Pollution and waste exploitation in dimension stone quarries

In most Romanian dimension stone quarries the mining activity is carried out underground, in open strip mining, generally in mountains areas with steep slopes. Natural stone extraction in quarries consist in freeing the blocks by using the natural fissuring and a wide range of techniques that are classified from some coplanar hole perforation and detaching by explosive to using a jet of water or a diamond string.

An important problem one may be confronted with in this field, too, is represented by the resulting wasted and be confronted with in this field, too, is represented by the resulting wasted and by the deterioration of the environment. The large quarries that are being worked produce profound

wounds to the landscape and the natural habitat and greater or smaller quantities of blocks that get out of classification. Cutting and primary processing also produce an unsorted, inert mud (slime), besides other fragments of various dimensions.

The average recovery into blocks in all these quarries from Romania does not exceed 30% and only exceptionally, in the Ruschita quarry, it reaches ca. 50-60%. The result is this great volume of industrial sterile of which more than 75% pieces out of the normal dimensions or a dust of various dimensions, processing and extraction also bringing about destructive effects on the environment by placing extraction wastes in refuse heaps.

There are some negative ecological effects brought about by these quarries: the loss of some natural areas and the landscape degradation; a lack of balance in the slopes; the increase of the discharge coefficient and the decrease of evaporation – exudation in the area; temporary diminishing of the value of the land affecting of the flora and some species of animals.

There results the importance of the exploitation of such chemically inert wastes, that can be used for a wide range of building products (lime, decorative plastering, mosaic) as well as the environment protection by new solutions for diminishing the destructive effects and for integration into the habitat of the quarrying effects.

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WOLLASTONITE 2M IN THE OUTER ZONE OF THE HIGH-TEMPERATURE SKARN FROM CERBOAIA VALLEY (METALIFERI MASSIF, APUSENI MOUNTAINS, ROMANIA)

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The occurrence of high-temperature, gehlenite-bearing skarns in the Upper Cerboia Valley (Măgurea Vaței area), associated with the Upper Cretaceous-Paleocene magmatism in the Metaliferi Massif, Apuseni Mountains (Romania), has been known for over two decades (Ștefan et al. 1978). Previously, Cioflică (1960) has first described the contact phenomena in the area, insisting on the hornfels and low-temperature skarns.

The skarn on the Upper Cerboia Valley occur at the very contact of a monzodiorite body of Paleocene - Ypresian age (Ștefan et al., 1988), with micritic reef limestones with elastic intralayers of probable Tithonic age.

Systematic distribution of different minerals across the skarn area outlines a pronounced metasomatic zoning. As described by Ștefan et al. (1978) this zoning is, from the inner to the outer part of the metasomatic area: monzodiorite / gehlenite + vesuvianite + garnet (A) / wollastonite + garnet + gehlenite (B) / wollastonite + garnet (C) / calcite (marble). More recently, Pascal et al. (2001) described this zoning in greater detail and introduced sequences that subdivide the A zone into A1 (wollastonite, grossular, sodian diopside), A2 (wollastonite, grossular, diopside), A3 (gehlenite, wollastonite, grossular, titanian andradite) and introduces another separation, namely the vein-like subzone BV, defined as an insight of the B paragenesis into the C zone, at its very contact. It results

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that gehlenite is conspicuous in the outer endoskarn zone, whereas the rock in the outer exoskarn zone is characterized by the extensive development of wollastonite.

The aim of this work is to investigate the crystallography and the crystal chemistry of the wollastonite from Cerboia, in order to offer a first characterization of the mineral. Taking into account the development of the industrial use of wollastonite (as ceramic charge but also as reinforcing mineral fibers to replace chrysotile in plasters), this first investigation of the Cerboia deposit may be of real interest for the potential users.

The C zone, of about 10-m thick, is largely composed by wollastonite (90 - 95 vol.%), but Ti-bearing andradite, vesuvianite and grossular also occurs. Even this is the sole zone of high purity and, hence, of economic importance, our analysis also refers to wollastonite to the other zones. Note that, at about 1 km west - northwest from the classical outcrop in the Cerboia Valley, on a forest road that crosscuts the Crămuț Valley, a wollastonite-bearing skarn similar to that described by Pascal et al. (2001) from the A 2 zone was found at the contact between a microdioritic dike and the marble.

Wollastonite from the C zone occurs as large crystals, of up to 10 cm long and 1.5 cm thick, aggregated as parallel and subparallel bunches. In the A zone, the crystals are smaller (up to 1 cm in length), slender prismatic, and generally grouped in fan-like or radial aggregates. Crystals in the B zone are rod-shaped, of up to 1.5 cm in length, and grouped in bunches that do not differ in morphology, but in dimensions from the crystals in the C zone.

The density of a selected sample of wollastonite from the C zone (2292), measured by suspension in methylene iodide diluted with toluene, is of 2.90(1) g/cm³, which agrees well with the calculated density of 2.915 g/cm³, based on the average chemistry in Table 1 and on the cell volume in Table 2. The indices of refraction measured for the same sample are $\alpha = 1.619(2)$, $\beta = 1.632(2)$ and $\gamma = 1.635(3)$. The mineral is optically negative, with $2V$ (measured) = 60°, which perfectly matches with the calculated value ($2V_{calc} = 50.99^\circ$).

Electron-microprobe analyses of a few representative samples are given in Table 1, together with the number of ions calculated on the basis of 18 oxygen atoms.

As can be observed in Table 1, the analyzed samples show a narrow compositional range. The chemistry conforms closely the stoichiometric one, since very low Mn, Mg, Fe, Al, Na and K contents characterize the mineral. No significant compositional variation is observed within single crystals. All the compositions are in the range recorded for wollastonite from skarns and silicate-bearing marbles by Abrecht (1980; see also references therein). The mean crystal-chemical formula of wollastonite from the C zone is:

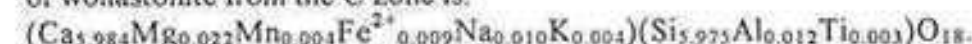


Table 1. Representative electron-microprobe analyses of wollastonite from Măgureanu Vatei*

Sample	P 25 ⁽³⁾	P 34 ⁽³⁾	2297	P 8	P 5	2292	P 6	PV 2
N ⁽¹⁾	3	3	8	4	3	11	4	3
Zone	A 2	A 2	A 3	B	BV	C	C	C
SiO ₂	51.31	51.57	51.39	51.40	51.8	51.57	51.28	51.37
TiO ₂	0.02	0.07	0.00	0.07	0.03	0.00	0.04	0.08
Al ₂ O ₃	0.03	0.14	0.09	0.11	0.09	0.07	0.09	0.10
FeO ⁽²⁾	1.10	0.09	0.09	0.10	0.15	0.11	0.14	0.03
MgO	0.21	0.10	0.11	0.15	0.25	0.14	0.12	0.12
MnO	0.09	0.00	0.07	0.05	0.00	0.06	0.05	0.01
CaO	47.23	47.97	47.72	48.01	47.64	47.84	48.26	48.05
Na ₂ O	0.01	0.01	0.01	0.05	0.02	0.01	0.02	0.10
K ₂ O	0.00	0.02	0.00	0.03	0.00	0.00	0.00	0.09
Total	100.00	99.97	99.48	99.97	99.98	99.80	100.00	99.95

Number of cations on the basis of 18 (O)

Si	5.973	5.984	5.992	5.971	6.001	5.993	5.961	5.970
Ti	0.002	0.006	0.000	0.006	0.003	0.000	0.003	0.007
Al	0.004	0.019	0.012	0.015	0.012	0.010	0.012	0.014
Fe ²⁺	0.107	0.009	0.009	0.010	0.015	0.011	0.014	0.003
Mg	0.036	0.017	0.019	0.026	0.043	0.024	0.021	0.021
Mn	0.009	0.000	0.007	0.005	0.000	0.006	0.005	0.001
Ca	5.891	5.963	5.961	5.975	5.914	5.957	6.011	5.983
Na	0.002	0.002	0.002	0.011	0.004	0.002	0.005	0.023
K	0.000	0.003	0.000	0.004	0.000	0.000	0.000	0.013

* results expressed in wt.%; (1) number of point analyses; (2) total iron as FeO; (3) samples from Crămuș Valley.

Despite the variety of occurrences (*i.e.*, position *versus* contact) the chemistry is remarkably uniform, with Mn < 0.009 *apfu*, Fe²⁺ < 0.014 *apfu* and Mg < 0.043 *apfu*.

The cell parameters of many wollastonite samples, as refined by least-squares analysis of the X-ray powder data (XRD), are given in Table 2. Since the identification of the polytype is of vital importance to the optimal industrial use of monomineralic masses, an attempt to indexing the XRD patterns in both the triclinic (1*T* and 3*T*) and monoclinic (2*M*) versions of symmetry was carried out. The best fitting between the calculated and the observed *d* spacings was recorded in all cases for the 2*M* indexing. We concluded, then, that the 2*M* polytype ("parawollastonite" according to Taylor, 1997) is the sole or dominates in the analyzed high-temperature skarn areas. This conclusion perfectly agrees with the statement of Henmi *et al.* (1983) according to that "the 2*M* polytype may be regarded as characteristic for higher temperatures", as well as with the experiments of Taylor (1997) in the SiO₂-CaO system.

Table 2. Cell parameters of selected samples of wollastonite from Măgurea Vajei

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	<i>n</i> ⁽¹⁾	<i>N</i> ⁽²⁾
P 5	15.426(2)	7.328(1)	7.069(1)	95.33(1)	795.7(1)	9	81
P 6	15.412(5)	7.321(3)	7.075(2)	95.34(2)	794.8(4)	6	81
1517	15.415(2)	7.317(1)	7.064(1)	95.36(1)	793.2(1)	10	85
2158*	15.416(2)	7.314(1)	7.064(1)	95.37(1)	793.0(2)	10	66
2159*	15.416(1)	7.315(1)	7.064(1)	95.36(1)	793.0(8)	10	77
2292	15.414(6)	7.318(3)	7.069(4)	95.37(2)	793.8(4)	6	57
2299	15.411(4)	7.322(2)	7.065(2)	95.37(2)	793.7(3)	5	72
2336	15.406(4)	7.318(2)	7.057(2)	95.37(2)	792.2(2)	8	61

* samples from Crămuș Valley; (1) number of refining cycles; (2) number of reflections in the 2θ range between 10 and 80° used for refinement.

Three generations of garnet closely associate with wollastonite in the analyzed skarns and may be recognized on the basis of textural relationships. (1) A first generation consists in Ti-poor grossular, in fact a solid solution of grossular (54.22 - 80.49 mol.% Grs), andradite (17.01 - 44.78 mol.% Adr), and minor "pyralspite" (0.78 - 3.06 mol.% Psp). This garnet generation, which was considered by Pascal *et al.* (2001) to be in equilibrium with gehlenite, occurs in all the three zones. (2) A second generation that occurs generally in the B zone, is a Ti-rich grossular, containing 50.44 - 55.39 mol.% Grs, 27.33 - 38.47 mol.% Adr and 4.64 - 19.40 mol.% morimotoite (Mor). (3) The third generation is a Ti-rich andradite, frequently associated with the wollastonite in the C zone. In terms of the garnet end-members, the compositional field of this garnet generation ranges from 37.12 to 41.47 mol.% Adr, with significant Grs (31.89 - 44.84 mol.%) and from 14.64 to 28.39 mol.% Mor.

Beside garnet and wollastonite, vesuvianite is the sole mineral occurring in all the skarn zones. It was found as product of both primary and late-stage metasomatism, when this mineral partially replaces gehlenite, and is very scarce in the C zone, which is of interest for this study.

As concerning the alteration products, secondary, residual or recrystallized calcite occurs frequently on the fissures affecting the wollastonite mass and is interstitial to or penetrates on an extremely fine scale along the cleavages and crystal boundaries of the wollastonite crystals.

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NONTRONITE FROM LECHINȚA, SATU MARE COUNTY

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Abstract

Our paper reports the first important occurrence of nontronite from Romania. Nontronite is deposited as a network of milimetric to centimetric ore-fillings, and resulted from the alteration of a porphyry monzodiorite (Neogene). Beidellite, opal and goethite (diagenetic) are associated to nontronite which is the main mineral (cca 95%). Moessbauer spectroscopy showed exclusively the presence of Fe^{3+} occupying two different distorted octahedral positions.

Keywords: Nontronite, porphyry monzodiorite transformation to nontronite, Lechința (Oaș), Satu Mare county.

Location

The nontronite occurrence is situated in the northwest of Romania, on the territory of Lechința village (north of Călinești - Oaș), Satu Mare county. Summary mentions on this occurrence can be found in Mărza and Ghergari (1993) and Mărza (1999).

Geologically the region is included in the volcanic chain of the Eastern Carpathians, in their northwestern extremity.

Methods of analysis

The mineralogical investigation of the nontronite occurrence is based on the following methods:

- transmission polarizing optical microscopy, using a Jenapol instrument;
- transmission electron microscopy (TEM) with a B650 microscope;
- X-ray diffractometry (DRON3);
- Thermal analyzes (MOM derivatograph);
- Moessbauer spectroscopy (Moessbauer spectrometer in transmission configuration). The gamma radiation source (14,4keV): ^{57}Co in Rh matrix; Doppler velocity field for the source: $V=\pm 4,5\text{mm/s}$; accumulation of resonance spectra on 400 channels.

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Petrography of the host rock

The host rock of the epithermal nontronite is a yellowish-grey porphyry monzodiorite. The limit between the fresh rock and the fillings is sinuous, marked by color variations. During rock alteration, hydrothermal solutions entered unequally the rock mass through the joint system.

The porphyry monzodiorite has a porphyric structure with a holocrystalline groundmass consisting of prismatic plagioclase feldspars (oligoclase) with various orientations, but with a slight tendency of parallel distribution, giving the rock a quasi-oriented texture. Other minerals that appear in the groundmass are orthoclase (12%), biotite (2%) and quartz (4%). Phenocrysts (15-20%) consist of plagioclase feldspars and pyroxenes, and the accessory minerals (3%) are magnetite, ilmenite and apatite. Plagioclase feldspars are prismatic, zoned and twinned, and contain inclusions of microlitic apatite. Some plagioclases contain volcanic glass inclusions in the central areas and sometimes on the microfissures crossing the minerals. Pyroxene is hard to identify due to partial argillizations.

Mineralogy of nontronite

Nontronite results by the advanced alteration of the rock and appears as a soft, fine mass with greasy aspect, canary yellow to green in color. Microscopic studies evidenced fine lamellar aggregates with reniform, radial or vermicular disposition, with pleochroism from green (Ng) to yellowish green (Np), parallel extinction, positive elongation and strong birefringence $\Delta=0,025$. In the nontronitic mass appear colomorphous aggregates of $\text{Fe}(\text{OH})_3$, while the open voids are filled with silica (opal) with numerous dehydration fissures.

The crystal morphology (TEM, Fig. 1a, b, c, d) indicates the association of nontronite with small amounts of beidellite. Nontronite (N) forms elongated lamellas with irregular edges; the transparency at the electron beam is low and inhomogeneous; thin darker discontinuous bands appear along the lamellae and are normal to the elongation. Unlike nontronite, beidellite (B) forms unequally thick isometric semitransparent lamellas, with dimmed edges and unequal torsions.

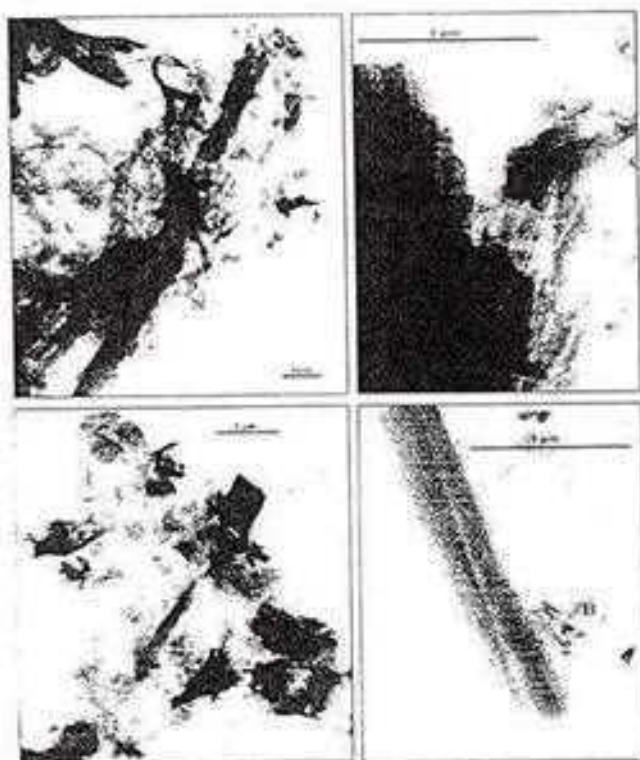


Fig.1 TEM images of nontronite. N – nontronite; B – beidellite.

X-ray diffraction spectra were obtained on oriented samples from the clay fraction ($<0.002\text{mm}$ diameter), both natural and treated with ethylene glycol (Fig. 2). The small number of peaks is due to low crystallinity. The 00l – type lines appear as follows: (001) at $15,33\text{\AA}$, (004) at $4,59\text{\AA}$ and (005) at

3,05 Å, respectively (020) at 4,59 Å. After treatment with ethylene glycol, the basal line (001) appears at 16,97 Å and lines (002) at 8,40 Å, (005) at 3,34 Å and (020) at 4,56 Å.

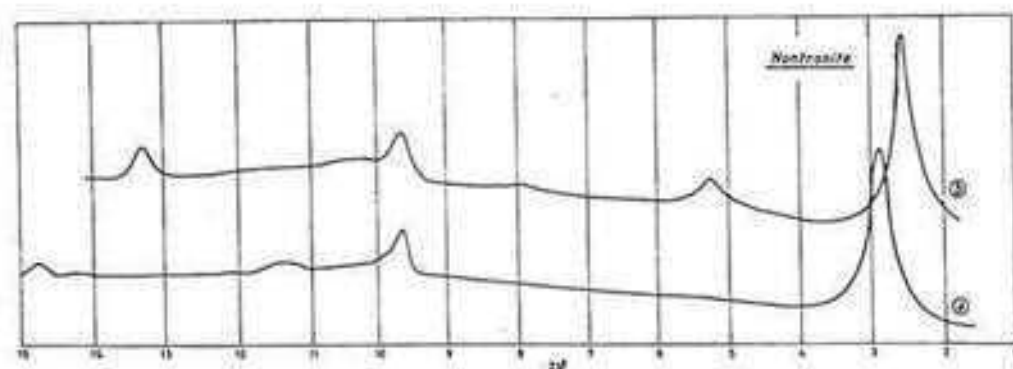


Fig. 2. XRD for natural nontronite: a – untreated; b – treated with ethylene glycol.

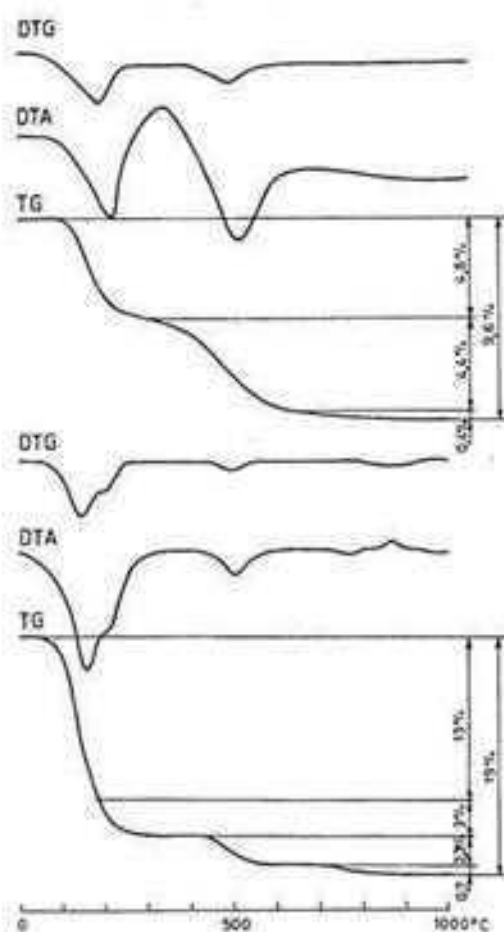


Fig. 3 Thermal analysis.

The thermal analyses were performed on two samples (Fig. 3). The DTA graph obtained on the first sample shows two endothermic effects: the first is wider and occurs between 50 and 260°C, with a single minimum at 220°C and a loss of 4,8%, while the second occurs between 350 and 600°C, with a minimum at 515°C and a loss of 4,4%, somewhat larger than for usual nontronite. The second sample has for the first interval a two-peak effect (160°C, 210°C) with an important loss (13%), followed by an endothermic effect at 505°C with a loss of 0,7%, probably due to beidellite, and finally a small exothermal effect at 865°C, corresponding to lattice restructuration. The first endothermic effect with a minimum at a temperature higher than 200°C for the first sample, and the two endothermic effects of the second sample, indicate that nontronite, respectively beidellite from the mixture are saturated with calcium, which has a high hydration energy.

The Moessbauer spectrum (Fig. 4) shows exclusively the presence of the trivalent iron ion. The computer-assisted data treatment (table 1) shows that Fe^{3+} occupies two different positions in the structure. The spectrum is formed by the superposition of two quadrupolar doublets, signalling the presence of two iron species in the sample.

The values of the hyperfine parameters δ and ΔE_Q show that both iron species correspond to Fe^{3+} ions in distorted octahedral vicinities.

The distortion of the octahedral vicinity of species 2 (indicated by $\Delta E_Q=0,56$) is larger than that of species 1 ($\Delta E_Q=0,2$), which in turn is smaller than the one normally occurring in silicates. The spectral width $\Gamma=0,4$ corresponding to species 2 shows that Fe^{3+} ions belonging to this species do not have the same distortion of their octahedral vicinity, thus there is a crystallographic inequivalence of Fe^{3+} ions from species 2; the value of $\Delta E_Q=0,56$ represents an average. Species 2 has a stronger signal ($A=0,63$) than species 1, therefore a higher concentration. The concentration ratio is $A_2/A_1=1,72$.

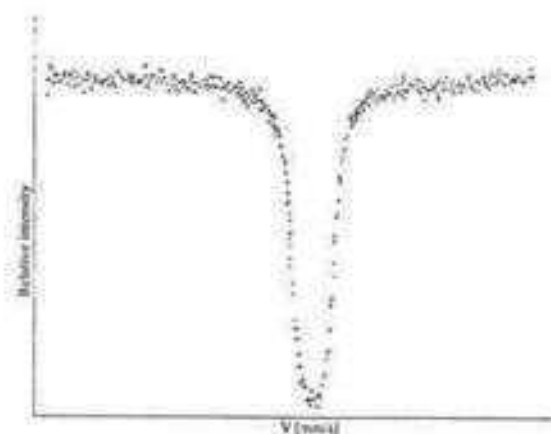


Fig. 4 Mössbauer spectra

Table 1
Mössbauer spectrum parameters for nontronite at TC

Species	δ_{Fe}	ΔE_Q	Γ	A	FIT parameters
	mm/s	mm/s	mm/s	-	
1	0.43	0.18	0.32	0.37	$\chi^2=1.2316$; MISFIT=0.0446
2	0.42	0.56	0.63	0.63	
Error	± 0.01	± 0.02	± 0.02	± 0.05	

Where: δ_{Fe} – isomer shift with respect to Fe;
 ΔE_Q – quadrupole splitting,
 Γ – width of spectral resonance at mid-height,
A – normalized spectral area.

Conclusions

- The argilization of the porphyry monzodiorite from Lechița (Oaș) caused by epithermal solutions circulating on a fissure system, had as consequence the formation of filonian nontronite and associated minerals (beidellite, opal).

- Nontronitization affected both the rocks in the vicinity of the fissures and the rock fragments caught as a tectonic detritus in their mass; the first minerals to transform were probably the mafic ones, judging from their advanced degree of transformation into nontronite; melanocrates contributed to the iron input necessary for transformation in bentonite of the leucocratic minerals from the zones circulated by fluids.

- Mössbauer spectroscopy showed the exclusive existence of Fe^{3+} , which however occupies two octahedral positions differently distorted.

- The nontronite occurrence from Lechița (Oaș) represents the richest concentration of this mineral reported from Romania.

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SEDIMENTOLOGICAL CHARACTERISTICS OF PRIABONIAN GYPSUM ROCKS, STANA ZALAUŁUI - TREZNEA - BUCIUMI AREA, N-W TRANSYLVANIAN BASIN

MOMEA¹ Gheorghe, FRUNZESCU² Dumitru, CEHLAROV³ Aura, MOMEA⁴ Lucia

The Stăna Zalăului - Treznea - Buciumi area discussed in this paper lies on the northwestern part of the Transylvanian Basin, in the proximity of the crystalline mountains of Meșes.

The study of the field relations, mineralogy, petrography and chemistry of the Priabonian Upper Gypsum Formation has lead to a reconstruction of the environment of deposition.

Upper Gypsum Formation, represented by secondary gypsum or alabaster - gypsum in outcrops, is characterized by:

- a clear facies distribution of depocentral laminated lithofacies and debris - flow deposits and local selenitic shoal,
- the lithofacies which hosts gypsum is argillaceous finely laminated (Turbata Formation);
- a diagenetic evolution of primary intratidale anhydrite to gypsum / alabaster gypsum, followed by its final re-anhydritization,
- sedimentation in the gypsum unit reflects cyclicity in the depocentre, cycles were controlled by evaporation and gravitational instability based on the presence of rounded clasts in the intraformational gipsrudites and displays a shallowing upward trend;
- during late diagenesis celestite and barite were formed.

Acknowledgements:

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A BRIEF OVERVIEW OF SINTER DEPOSITS OF YELLOWSTONE PARK, USA

PERRY⁵ R. V.

Introduction

Hot spring regions such as Yellowstone Park are the surface manifestations of often deep - circulating hydrothermal systems. Trace to significant amounts of volatile elements (As, Hg, Sb, Tl $\pm$ Au, Ag) in sinter deposits are considered positive indicators for an underlying sequence of vertically zoned ore minerals such as Au, Ag, Cu, Pb, and Zn. In some systems these precious metals may be precipitating hundreds or even thousands of meters below the surface. There is however, as demonstrated at the McLaughlin Mine in Central California, that economic quantities of gold may be present at the surface in areas of presently active hot springs and high levels of mercury. Thus, the extensive thermal regions of Yellowstone Park represent a valuable natural laboratory in which to study the relationships between fossil hot springs, associated hydrothermal alteration and their dispersed trace elements.

With more than 10,000 geysers, hot springs, and thermal features, the Yellowstone thermal / volcanic region is the world's largest and most active thermal site (Fig. 1). The region is so clearly unique and wondrous that it was designated as the world's first National Park in 1872. It covers

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898,349 ha and includes the still-recognizable 70/48 km crater of its 630 ka caldera eruption. Even the large size of the park is not adequate to cover the entire rim of Yellowstone's 2 Ma caldera. This first (largest eruption) / the subsequent major eruptions (1.3, 0.630 Ma) ejected 2500 km³ / 1275 km³ of ash and lava. Yellowstone is the present site of the Yellowstone mantle hot spot; mantle plume has an unusually deep root, estimated to have a vertical extent of 200 km. Beginning with 16.5 Ma, the hot spot initiated a major caldera center on the Nevada-Idaho border. Since then the North American plate has been moving southeastward at about 2.5 cm/yr. over the hot spot resulting in at least seven major caldera centers in its 575 km path from Nevada to Yellowstone (Smith and Siegel, 2000). Yellowstone remains very active and recent measurements show the caldera has been inflating with 19 mm/yr. between 1976-1984 and deflating with 35 mm/yr. in 1984-1985 then began deflating at rates as high as (Fournier, et al., 1984). The magnitude 7.5 Hebgen Lake earthquake in 1959 is only the most recent manifestation of the dynamic magma chamber underlying Yellowstone.

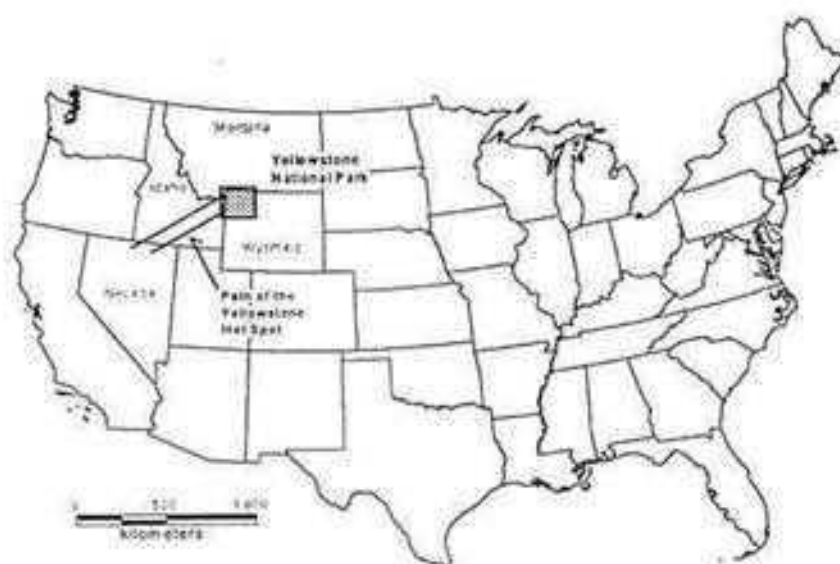


Fig.1: Yellowstone National Park, Wyoming, USA. The Yellowstone Hot Spot has migrated 575 km from Nevada to Yellowstone Park

Yellowstone was covered by extensive ice sheets up to 500 m thick during the Pinedale Glaciation, which lasted from roughly 50,000 to 15,000 years ago. Virtually all of the thermal features, including the exposed sinter deposits in Yellowstone, have developed since the retreat of the Pinedale ice sheets. Indeed, Norris Basin Pinedale glaciation may have removed 10 m of surficial material (White et al., 1988). The lithostatic load of this thick ice cover also explains near-surface fluid inclusion filling temperatures in drill core as high as 280°C (Fournier et al., 1984).

Sinter Deposits

Sinter deposits provide a thin veneer to most of the active thermal basins in Yellowstone Park. Hot water with high concentrations of dissolved SiO₂ cools as it ascends and the solubility of SiO₂ decreases to develop a supersaturated condition and resulting precipitation of amorphous opaline sinter. Chalcedonic sinter is believed to form from neutral to alkaline waters. Initially, the silica deposits as subaerial amorphous opal or silica gel, which with burial and elevated but non-boiling temperatures undergoes crystallization to cristobalite, then chalcedony, and finally quartz (White et al., 1988). In Yellowstone, the one notable exception to silica-rich flows is Mammoth Hot Springs, where magnificent white travertine terraces mark the thermal vents. Most exposed sinter in the Park

is spongy to thinly laminated and will dry out and crumble in a matter of 10's of years if it is left exposed (Fig. 2). Bacterial mats and organic materials influence and serve the deposition, layering and rapid precipitation of the sinter and appear to be an integral factor in the deposition of sinter (Fournier et al., 1984, White et al., 1988).

Norris Geyser Basin is one of the largest and most impressive thermal basins in Yellowstone. Post-Pinedale sinter deposits are typically no more than 1m thick and confined to selected springs with high flow rates, high temperature, neutral to alkaline pH, and high silica content. Much of the basin shows very little sinter cover in spite of high discharge rates of silica-rich waters. These areas have 2-3.5 pH values. Brock (1978) reports that bacterial oxidation of sulfur in the rocks or H_2S in spring water releases sulfuric acid and is responsible for the low pH of these springs and many others. The principal area of hot spring activity and alteration in Norris Basin covers 277 ha, but sinter deposit is mapped over 28.4 ha (10%) of the central part of the basin (White et al., 1988). This relatively small percentage coverage by sinter, even in an active basin, is one indication of how quickly the thin layers of sinter disappear when relatively short-lived springs cease to flow.

Geochemistry

Drummond and Ohmoto (1985) describe a process of flash boiling and preferential partitioning of H_2S into the vapor phase. This forces precipitation of gold dissolved in the now destabilized gold bisulfide complexes. Fournier et al., (1994) add that boiling, cooling, and dilution by mixing with descending groundwater all serve to lower the concentration of H_2S and thus force precipitation of gold in ascending hydrothermal fluids. They believe that some or all of the gold that comes out of solution when gold bisulfide complexes break down may be carried to the surface as colloidal particles in the up-flowing water and steam. This gold then becomes attached to colloidal silica and deposited along with the silica. There is no correlation between Au and concentration of H_2S in associated hot spring waters. A comparison of gold and trace metal contents in sinters from Yellowstone and Steamboat Nevada, an active gold-bearing hot spring system shown that gold and trace-metal content of Yellowstone waters, altered rocks, and sinters are typically much lower than Steamboat Springs, Nevada, due to the high recharge of dilute surface water in Yellowstone (White et al., 1992). Detectable gold ($\geq$ to 0.1g/t), as analyzed by short-wavelength-radiation emission-spectrographic methods (SWR), is present in just 9 of 119 samples collected in hot-spring related alteration in Yellowstone (White et al., 1992). The same samples using neutron activation (NA) have been analyzed. Though the results of analysis are dramatically different gold-bearing sinters still seem to cluster in the same three general areas of the western portion of the caldera. Trace metals are a weak and inconsistent indicator of gold in Yellowstone sinter deposits; As, B, Hg, Sb, Tl, and Zn shown are very poorly correlated with gold. Indeed, some of the highest values of Hg and As are from samples with no detectable gold. The very limited drill data available (Y-12, Norris Geyser Basin and Y-13, Lower Geyser Basin) shows no evidence of gold content increasing with depth. This, in spite of the fact that, in the other parts of Norris Geyser Basin, the gold is present in surface sinter as high as 2 g/t (Fig. 2). However, White et al., (1992) emphasize that Y-13 was not drilled in the immediate area of the gold-bearing sinter deposits. A crude plot of the nine gold-bearing samples analyzed by NA (White et al., 1992, Tab. 1) shown them to occur along a well-defined north-south line traversing the western half of the 0.630 Ma caldera rim (Fig. 2).

Additionally, gold content of these samples, based on NA analyses, increases strongly in order from south to north: 0.00X g/t range in upper geyser basin, 0.0X g/t range in the Gibbon Geyser area to a value of 9.X g/t in Norris Geyser Basin, a distance of 40 km. However, in contrast to White et al., (1992) data, Fournier et al., (1994) report lower gold values in Norris Basin than in Gibbon Canyon and Sylvan Springs. These differences may be explained by the differing analytical methodologies, the small sample suite, and relatively low gold values of the Yellowstone sinters in general. Fournier et al., (1994) note that there is no distinction between gold content of sinters within or outside of the caldera rim.

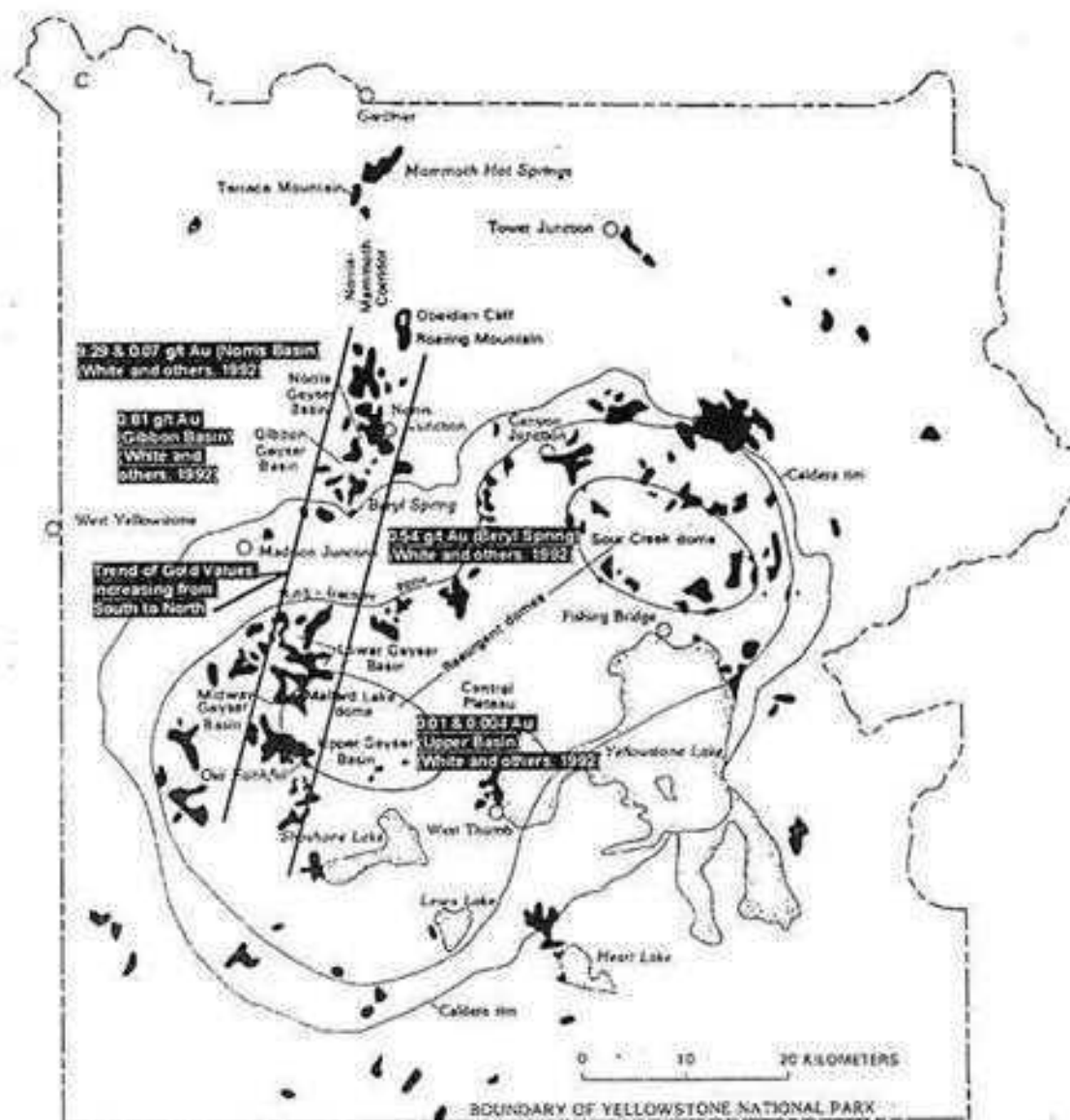


Fig. 2. Significant thermal features of Yellowstone Park including gold-bearing springs (White et al., 1992). Note the narrow alignment of gold-bearing springs along a 40 km north-south trend.

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THE SIGNIFICANCE OF FLUID INCLUSIONS FOR PETROGENESIS

POMĂRLEANU¹ Vasile

Out of a multitude of problems concerning petrogenesis and fluid inclusions, this paper treats the contribution of two magmas to the formation of the volcanic rocks in Gilău and Călimani Mts.

1. The dacites from Păniceni (Gilău)

The dacites of the banatitic complex of Păniceni (Gilău) are formed of plagioclases, quartz, green hornblende, biotite and pyroxenes (augite and hyperstene).

There are abundant fluid inclusions in quartz, plagioclase feldspars and hyperstene. The fluid inclusions consisting of silicate melt have a primary character, are biphasic: glass + glass globe, glass + gas globe. The secondary fluid inclusions are deposited along fissures, and they display a biphasic character of the liquid-gas type.

The presence of glassy inclusions with glassy globes in a glassy matrix, under the form of a negative crystal (Fig. 1), shows that two types of magmatic fluids contributed to the consolidation of rocks: one of acid-alkaline composition and another, with pyroxenic composition, represented by internal glassy globes (Pomârleanu, 2002).

2. The andesites of Călimani

Among the various igneous rocks in the South and North Călimani Mts., biotite + quartz andesites (e.g. those at Drăgușul and Petricelu) occupy large areas. The andesites belong to effusive domains and represent the last manifestation of the Neogene volcanism in the region.

The rock is constituted by feldspars, biotite, hornblende, pyroxenes, olivine and subordinately, by quartz xenolithes.

The plagioclase of Drăgușul and Petricelu andesites contain biphasic, primary glassy inclusions (glass + glass globe and glass + gas), as well as secondary inclusions (liquid + gas, and sometimes, daughter minerals).

The fluid inclusions of glass + gas type show that the gas bleb was formed as a consequence of lava cooling somewhere close to the surface (Fig. 2). Similar inclusions of smaller dimensions have been found also in other minerals as quartz, augite and hyperstene.

Within the same section, and even within the same visual microscopic field, fluid inclusions with two immiscible phases have been found: one occurring as blebs, and another forming the matrix (Fig. 2). These inclusions have crystallized early from the magma and raise in their turn several problems of petrogenesis mainly concerning the stage of crystallization, the degree of fractioning when miscibility occurred, and whether their exsolution took place in a stable or unstable manner (Phillipots, 1981).

The immiscible blebs in the glassy inclusions were formed through the coalescence of smaller blebs in the initial melt. The composition of the two glassy phases in the fluid inclusions of the plagioclases is different: the globular glass is characterized by a pyroxenic composition, poor in silica but rich in cations of the Ti, Fe, Mn type; the rhyolitic matrix is rich in SiO₂, Na, K and Al (Krasov, Clocchiatti, 1979; Phillipots, 1981).

As concerns the origin of the Petricelu andesite, there have been several hypotheses, of which, the most probable is that stating its formation from a mixture of magmas: one acid and another one basic (Nichita, 1934). On the basis of this idea, and of mineralogical studies, Nitoi (1987) brought new arguments to the idea of a parental hybrid magma.

A decisive proof pleading for the formation of Petricelu and Drăgușul andesites from a hybrid magma, is the presence within the plagioclase of fluid inclusions with two glassy phases: one rhyolitic, and another one pyroxenic.

The extension of similar studies on the basalt-andesites from Deluț and of other rocks in the region may raise and solve new problems of petrogenesis.

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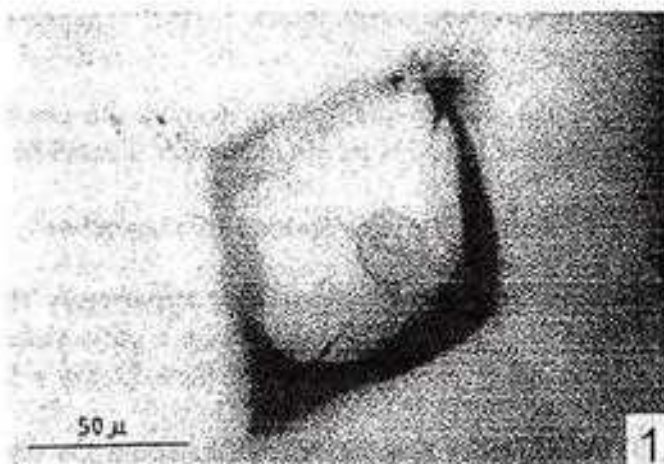


Fig. 1

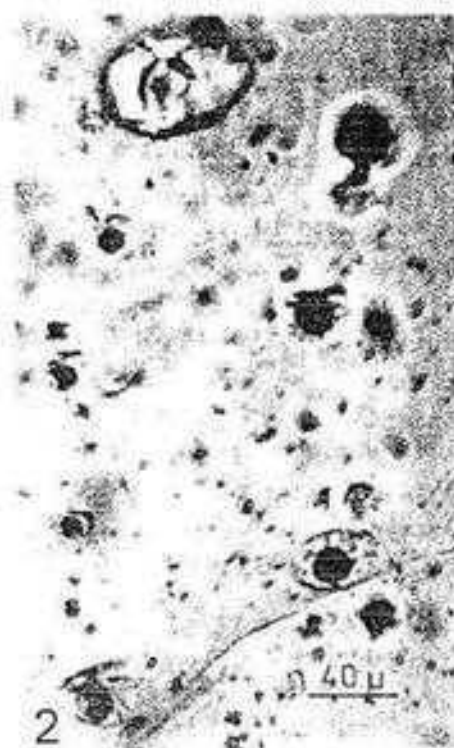


Fig. 2

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THE PHILOSOPHY OF ORE EXPLORATION

POPESCU¹ C. Gheorghe

Until the XIX-th century, autodidactic and encyclopedic prospectors could meet the demands of new ores only for semi-industrial production of metals. However, during the industrial revolution, the empirical approach of ore exploration was no longer adequate. In the beginning, the quest for metals and ores has been under the influence of the idea that "*Ore deposits are to be found where they occur*". The empirical research that followed up, used a step-by-step strategy, a "centrifugal" principle stating that "*Ore deposits are to be found near other ore deposits*". One has to admit that up to this stage, geology had very little influence. After that however, the analysis of geological similitude was to be the basis for the discovery of new ore deposits. This principle of analogy had no chance other than being founded on scientific knowledge.

Geology has become a science relatively late. In the beginning, it was basically a field science. The mineral, rock and fossil collector could not achieve much – the most he could do was to

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wonder in front of a multitude of odd things produced by Earth. The miner, on the other hand, was so preoccupied by the ore, by all the indications that signaled its existence and by its association with the host rocks, that he could not explain – and neither had the curiosity do so – the ore genesis and history, and even less, the Earth's structure and history. However, along with a growing interest for nature, an ever increasing number of XVIII-th century scientists started to study rocks and fossils. They were thus able to state that shells found in the mountains proved that those areas had been ocean floors – confirming an idea first stated by Leonardo da Vinci. From this point on, up to speculating upon an origin of life lost in immemorial times, was only a short distance. The travels and the amazing stories about volcanoes and earth-quakes from various parts of the world have stimulated a new conception about Earth, stating that its crust underwent continuous cataclysms during which it cracked and/or folded, due to an internal fire. This started a sterile polemic between the “neptunists” – whose exponent was the famous professor Werner from the Freiberg Mining Academy – and the “plutonists” – illustriously represented by the Scotsman Hutton. In his famous work *„The theory of the Earth”* – Hutton exposed a revolutionary theory – the *uniformism* – which stated that the processes we see operating to form and shape the Earth today have always operated in the past. For this, Hutton is considered the father of geology. As his successor – the Englishman Lyell – later demonstrated: *“the Present is the key to explain the Past”*. Lyell amended the uniformism and renamed it as the *principle of actualism*. Beside the principle of superposition of rock strata formulated two hundred years earlier by Nicolaus Steno, this principle constitutes the foundation of geology. Without these principles, geology would not have any sense and could not be conceived. How these principles helped to discover ore deposits will be a matter discussed in the following paragraphs.

A. von Humboldt, was the first to observe the links between metallic concentrations and igneous rocks. This idea has been perfected and scientifically substantiated by Ellie de Beaumont, in his theory regarding volcanic and metallic emanations. In fact, this theory is an expression of two fundamental principles governing the contemporary metallogeny – the principle of actualism (as long as today we observe deposition of metals – especially sulfides – in volcanic fields, the old ore deposits should have formed in the same way), and the principle of similarity (the rocks and ores have formed by the same geological processes). These principles agreed with the seen reality of today's ore deposits distributed mainly in volcanic areas. The concentrated expression of the above is in the saying: *“if you want to discover ore deposits then go in the mountains”*. This kind of thought had a practical and guiding meaning and reflected in the “centrifugal” principle of prospecting new ore deposits in the vicinity of known ones.

As to the application of the principle of analogy in discovering ore deposits, the case of the Siberian diamonds is well known. In the early '50s of the XX-th century, Prof. Semenco has drawn the attention upon the geological similarities between Siberia and South Africa. On this basis he suggested an extensive diamond search campaign in the Yakutian area. As the country needed diamonds and had plenty of geologists (over 10,000), a fever of Siberian diamonds broke out. After few years, first diamonds were discovered in the frozen alluvia of Yakutia, and next, their primary source areas – the kimberlitic chimneys.

One should not overlook the fact that due to the progress achieved in the research of extraterrestrial space, geology has overcome its initial object from which it actually received its name: Geia = Earth, and added a new branch: the Planetology. Thus, geology could benefit from a new space technology – the remote sensing. By investigating the interaction between electromagnetic waves and terrestrial environments, some extraordinary images of the geological structures, including those rich in mineral resources could be obtained. Thus, one could obtain cartographic - geologic images of territories still unseen by man – in deserts or under the ice covers. Through analogy with lands well known for their mineral resources, it has been possible to predict their existence even in such remote, still unknown areas. This has brought back an old concept that had been abandoned for a long time – the *liniamentarism*. The re-actualization of this concept has been made possible only by the remote sensing, and has helped in the discovery of several gold

deposits in old terrains such as those from South Africa, Namibia, South Australia, and in our case, in the South Carpathians.

At the end of the second millenium, geology brought a revolutionary and profound concept, with implications that exceeded by far its object: the Global Tectonics. It was called "global" not because it referred to the Earth's Globe, but for its general and comprehensive approach to all fundamental problems of geology especially to those having a high impact on human knowledge: the formation of mountain chains, of oceans and seas, the transformation of continents – their movements and evolution.

Perhaps only the XIX-th century's concept of evolutionism had such a dramatic influence on natural sciences. The concept of global tectonics emerged gradually from the initial core of the continental drift – developed in the last fifties and the sixties, together with the newly achieved knowledge on the morphology and content of the ocean floor. It eventually evolved into two theories: the ocean floor spreading and the plate tectonics.

The global tectonics has been dominating the human knowledge about Earth and nature, for more than 30 years. Obviously, the concepts and the practice of ore-deposits discovery could not escape its influence. The global tectonics placed the formation of ore-deposits and of related rocks in the areas of strongest interaction between the lithospheric plates, thus yielding an unprecedented strategy for the exploration of ore deposits. Never a scientific theory has been applied so rapidly and so successfully as the plate tectonics.

Starting from a deterministic relationship between subduction areas and calc-alkaline (andesitic) magmas associated with large accumulation of copper, molybdenum and gold – the porphyry copper type, a veritable copper and gold rush broke out in the actual and pre-quaternary subduction areas.

The results have arisen very quickly. New ore deposits have been found in areas that had been previously well known for their mineralized structures, and also in areas where nobody had had a clue about any ore deposits: it was the case of some accumulations in Peru, Bolivia, Iran, Indonesia, the Philippines, Polynesia and not the least, in our country. It is equally true that geophysics contributed a lot to this success. The magnetometry proved to be a very efficient method to spot porphyry structures, especially due to the high magnetite contents of these deposits.

In the end, we will give two examples to illustrate the above considerations. The first example comes from the Indonesian Irian, Papua-New Guinea island. The Ertsberg (The Ore Mountain) ore deposit, discovered by an Dutch expedition, in dense forest, at over 4300 meters in altitude, as early as 1936, has remained inaccessible for a long time. During the '60s, the American mining company Freeport – McMoran, decided to invest about 1 billion USD in this project. The helicopters began to fly over the jungle, modern roads began to advance slowly (4-6 m/day) in rough terrains with inclines exceeding 70 %. Huge efforts were made, but eventually everything was worthy, as an immense profit expected the explorers: a "capture" of 40 billion USD. In 1988, the Freeport geologists discovered another ore-deposit: Grasberg, lying at an even higher altitude – 4600 m. Its exploitation meant an even more extensive use of helicopters and giant bulldozers, working in an extremely rugged terrain, with cascades of over 600 m. The ore deposit was estimated at 60 billion USD, and represented the biggest and richest gold deposit in the world. Its daily ore production is of 160,000 tons, and it is expected to grow in the near future, to 300,000 tons. These, and other similar ore deposits could not possibly be exploited unless modern extracting and ore-processing technologies were involved. It is an example of convergence of science and technology, where a revolutionary idea – the plate tectonics – is well served by a break-through heavy engineering.

Such convergence is also well illustrated in the case of our country. The gold fields in Brad-Săcărâmb and Roșia-Bucium districts, have been extensively explored and mined in the '50s and '60s. The geology of these areas, was re-examined in the new context of the plate tectonics. Thus, several structures with disseminated copper – much poorer in comparison with their vein counterparts – could pass the productivity exam, of course, by using technology adapted to intensive large scale exploitation, by excavating and by moving mining masses of previously unimaginable volumes, and

in favorable economic circumstances. In just few years, so many copper and gold deposits have been discovered, that they exceeded in volume all that had been discovered in the previous decades.

We can conclude that the relation between geology and mining is one of unity – tight and mutually determined. The progress of geology gives mining unlimited fronts of action, and the progress of them both, serves the human civilization, by yielding what we now so commonly call “mineral raw materials” – without which the progress of humankind was not, it is not and will never be possible.

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REE GEOCHEMISTRY AND GENETIC ASPECTS OF PEGMATITES FROM ROMANIA

RADASANU¹ Smaranda, MURARIU¹ Titus, KASPER² Haino Uwe

Introduction

In agreement with Mârza (1980) pegmatites within metamorphic series of Romanian Carpathians form the Romanian Pegmatite Province (RPP). It consists of four subprovinces as follows: Preluca Pegmatite Subprovince (PPS), Rodna Pegmatite Subprovince (RPS), Getic Pegmatite Subprovince (GPS) and Gilău -Muntele Mare Pegmatite Subprovince (G-MMPS). The pegmatites are hosted within Precambrian metamorphic rocks, typical of amphibolite facies (paragneisses, micaschists, amphibolites, marbles, usually associated with migmatites), as part of the metamorphic series of: Rebra, Baia de Arieș, Someș, Sebeș-Lotru. Generally the pegmatites show a customary mineralogical composition. Quartz, plagioclases, K-feldspar and muscovite represent the rock-forming minerals, while biotite, tourmaline, garnets, apatite are accessory minerals. Spodumene, beryl, columbite + tantalite, montebrasite, rutil, purpurite, cassiterite, ilmenite, kyanite, sillimanite were found only in pegmatites from GPS. As preliminary results two of the authors (T.Murariu and H.U. Kasper in collaboration with T.Schoenbeck) have found for the first time in Romania the phosphate minerals Sicklerite etc by electron microprobe analysis (EMPA) (in prep.).

The pegmatites occur as discordant and/or concordant lenses and veins, nests and dykes. Considering the closed association of pegmatites to metamorphic rocks and the lack of any connection with granitic bodies some authors suggested a metamorphic origin for these pegmatites (Murariu, 2001). Based on mineralogical and geochemical features, the pegmatites from RPP belong to the following classes: (1) ceramic pegmatites; (2) muscovite pegmatites and (3) rare-element pegmatites, which include two types: (3a) beryl type and (3b) albite-spodumene type (Solodov, 1971; Černý, 1992; Murariu, 2001).

This study presents the REE behaviour during pegmatitic evolution as well as some new genetic considerations.

Analytical methods

REE analyses were performed by inductively coupled plasma quadrupole mass-spectrometry (ICP-MS, Perkin Elmer/Sciex Elan 6000). Samples (100 mg) were analysed on dry basis (105°C)

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after microwave digestion (Multivawe Sample Preparation System, Perkin Elmer/Paar Physica) with HF and HClO₄ at high pressure (50-60 bar) and temperature (210°C). After evaporation of HClO₄ and a twice evaporation with HCl the sample cakes were dissolved in HNO₃ and filled up to 50 ml (finally 2 % HNO₃) and stored in polyethylene bottles. The sample dilution factor ranges from 500-5000 depending on element concentration. Results were checked with CRM's Mica-Fe (Biotite) and Mica-Mg (Phlogopite), both from CRPG (France).

Results and Discussions

REE content of pegmatites vary relative to their mineralogy, bulk composition and sample position within pegmatite body, respectively. The highest REE content is typical of ceramic pegmatite (Na₂O > K₂O) located in the border zone (Table 1).

Table 1. REE content of pegmatites from Romanian Pegmatite Province

(μg/g)	Ceramic pegmatite				Muscovite pegmatite		Albite-Spodumene pegmatite
	*I10.2 ¹	III 1.3	*IV.1 ¹	IIg L	*I.13.1 ¹	*IV.1.3 ²	
	PPS			GPS	PPS		
LREE	48,455	6,585	18,000	3,796	7,645	13,607	0,482
HREE	4,461	0,426	2,700	0,552	5,379	4,827	0,106
ΣREE	52,916	7,011	20,7	4,348	13,024	18,434	0,588

* samples from the same pegmatite body: ⁽¹⁾ border zone, ⁽²⁾ first intermediate zone.

Within the muscovite pegmatites (K₂O > Na₂O) from the first intermediate zone the REE content decreases (Table 1). In spite of this general trend, there is a difference between LREE and HREE behavior during pegmatite crystallization. Thus, LREE reach the maximum concentration level in ceramic pegmatites, while HREE are concentrated in muscovite pegmatites. The lowest REE content was found in albite-spodumene pegmatites, which is from the geochemical point of view typical for more evolved pegmatites (Černý, 1992).

The pattern of chondrite-normalized REE reveals certain geochemical particularities. The ceramic pegmatites (Fig. 1a) from border zone show a positive Eu anomaly and sometimes a negative Ce anomaly. The Eu anomaly denotes reducing conditions during crystallization of ceramic pegmatites. The presence of Ce anomaly may be generated either by the behaviour of accessory minerals (e.g. apatite; Wolf and London, 1995) in the source-rock during partial melting which give rise to pegmatitic melt or by post-crystallization alteration processes (Rollinson, 1993). In muscovite pegmatites, two negative anomalies were found (Fig. 1b). These two anomalies result from Eu and Nd accommodation in high concentration into plagioclases crystallized in the border zone (fig. 2).

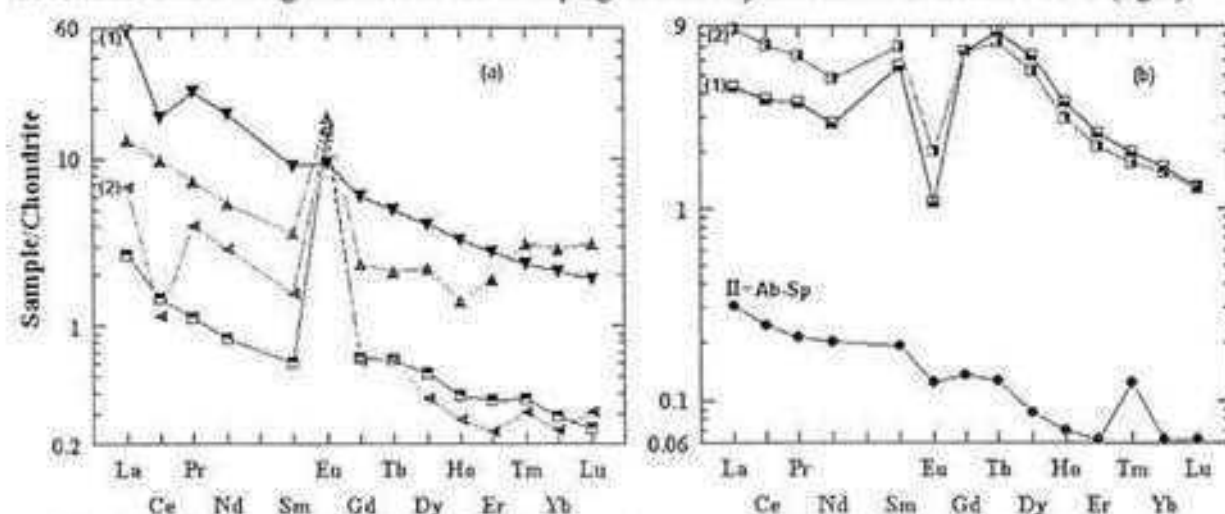


Fig. 1. Chondrite-normalized pattern for: (a) ceramic pegmatites; (b) muscovite and albite-spodumene pegmatite

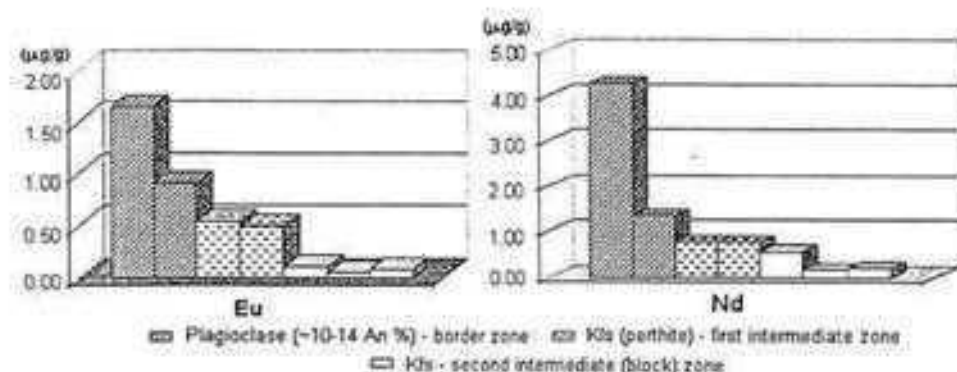


Fig.2. Eu and Nd contents in feldspars from pegmatite (PPS).

The REE abundance within pegmatite composition depends mainly on the change of feldspar composition among successive generations. Thus, Plg from border zone (~10-14% An) are enriched in REE, while the contents gradually decrease to Kfs from intermediate zone and then to Kfs from block zone (Table 2). The REE content of feldspars is the result of the following substitutions: EuCa_{-1} , REENaCa_2 , REE_2Ca_3 și $\text{REEAl}(\text{CaSi})_1$.

Table 2. REE content in plagioclase (Plg), potassium feldspar (Kfs), garnet (Grt) and apatite (Ap) from pegmatites

(µg/g)	*Plg ⁽¹⁾	*Kfs ⁽²⁾	*Kfs ⁽³⁾	*Grt. X ⁽²⁾	*Gr. X bis ⁽²⁾	*Ap X ⁽²⁾
LREE	16,11	4,11	2,52	6,87	7,96	1442,30
HREE	1,05	0,38	0,86	164,89	273,78	1155,07
ΣREE	17,16	4,49	3,39	171,76	281,75	2597,37

⁽¹⁾ border zone, ⁽²⁾ first intermediate zone, ⁽³⁾ second intermediate zone (block); *pegmatite minerals from PPS

Considering the patterns of chondrite-normalized REE of plagioclase (border zone) and potassium feldspar (intermediate and block zone) collected from the same pegmatite body, we observe almost the same fractionation trends for REE, like those displayed by pegmatites. At the same time, HREE from feldspars tend to concentrate into the block K-fs representing the last generation of these minerals.

In muscovite and biotite from PPS and G-MMSP, the REE contents are low (0,60-5,46 µg/g – Ms; 0,87-5,15 µg/g – Bt). The concentration of REE in muscovite from RPS (1,36-101,305 µg/g) and GPS (5,14-59,31 µg/g) range in a wider interval compared to the previous two subprovinces. Generally, when muscovite and biotite coexist, REE tend to be accommodated preferentially in the biotite structure. The highest content in REE is found in muscovite formed in the quartz core in association with tourmaline.

The garnets show a typical high content in REE (Table 2) being controlled by the Mn content of these minerals. Substitutions such as $(\text{Y,REE})\text{AlMn}_1\text{Si}_1$ enhance the REE concentration in garnets. As expected, the garnets are enriched in HREE relative to LREE.

The apatite shows the maximum content in REE (table 2). Due to its composition, apatite allows the accommodation of an important amount of REE by substitutions like TRNaCa_2 and $\text{TRSiCa}_1\text{P}_1$ (Hughes et al., 1991).

Among the analysed pegmatite minerals, feldspars, biotite and muscovite tend to accommodate mainly LREE, while HREE enter the garnets. The apatite concentrates both LREE and HREE as well.

Conclusions :

– The maximum concentration level of REE is typical of ceramic pegmatites, due to feldspar abundance;

* structural vacancies

- The low REE content in albite-spodumene pegmatites emphasizes their evolved geochemical feature;
- The degree of REE enrichment in pegmatite minerals is as follows: Apatite > Garnet > Biotite > Muscovite;
- The high HREE content in garnet is due to the high spessartine component in the garnet solid solution;
- The positive Eu anomaly for ceramic and graphic pegmatites turns to a negative Eu anomaly in muscovite pegmatites. This change points out at least two different stages during crystallization of pegmatites.
- The ability to form complex compounds with F and Cl denotes increased mobility of HREE. Pegmatitic minerals with more enriched HREE formed during latest crystallization stages suggest the formation of analyzed pegmatites from a fluid phase (melt) enriched in volatiles.

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THE ORIGIN AND GEOCHEMISTRY OF ANGOORAN Pb-Zn DEPOSIT, NW, IRAN

SADEGHI BOJD¹ Mahmood, MOORE Farid

Abstract

Angooran Pb-Zn deposit is located in Zanjan province, northwest of Iran (47°20'N, 36°40'E), 90 Km west of Zanjan city. The deposit is the largest of its kind in Iran, and contains the highest ore grade in Middle East.

Angooran Lead-Zinc mine occurs in metamorphic rocks and younger strata of Mesozoic and Tertiary age. The host rocks include schist and crystalline limestone. The ore body seems to form discontinuous lenses and layers between the two rock types. There are two major faults trending E-W and N-S respectively. These faults resulted in extensive brecciation and alteration of the ore.

The ore body is divided into two distinct zones namely the Oxidation or Zinc carbonate zone, and zinc sulfide zone. Sphalerite, Galena, Smithsonite, Cerussite, Pyrite, Arsenopyrite, Ilmenite, Mimeteite, Hemimorphite, Boudantite and Skocordite are identified under reflected light.

Electron probe microanalysis of oxide and sulfide ores shows that Sphalerite contains 2.63% Fe and 0.26% Cd. Minor amounts of Ni, Co, Sb and Sc are also detected in Smithsonite. The Arsenopyrite has 4.3% Ni, and 1.5% Co. The Zinc content does not vary in the two main zones of the mine. However, The Pb content in the carbonate zone is higher than that of the sulfide zone. It is thought that elements such as As, Mn and Ni were added to the sulfide zone during alteration. Copper and Silica content is similar in both zones. It seems likely that the second generation Pb, formed by alteration, is responsible for the observed variation in Pb content of the carbonate zone.

$\delta^{34}\text{S}$ value of Angooran deposit is similar to Cyprus and Kuroko type deposits showing that the origin of the sulfur is probably sea water. The $\delta^{13}\text{C}$ varies between 0-4‰ indicating that, the origin of the CO_2 is the sedimentary carbonate, The bicarbonatation of which is the reason for the observed increased $\delta^{13}\text{C}$. The $\delta^{18}\text{O}$ is 20 ‰, which is less than that of meteoric water, Probably because of the reaction between supergen fluid and ore forming Systems.

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The geology, geochemistry, ore microscopy and isotope study indicate that Angooran deposit is a VMS type Zn-Pb deposit formed in three stages:

- 1- Formation of an explosive diatrem;
- 2- Ascent of a geothermal system;
- 3- Bicarbonatation and dissolution of the hanging wall, followed by development of a hydrothermal system.

PHYSICO-CHEMICAL CHARACTERISTICS OF ZINC MINERALS IN ANGOORAN MINE, IRAN. FIRST REPORT ON OTAVITE AND FRAIPONTITE

SADEGHI BOJD¹ Mahmood, MOORE Farid

Abstract

Angooran Zinc-Lead mine is located at NW of Iran, and is the largest of its kind in Iran, and contains the highest ore grade in Middle East. Regarding the importance of mineralogy of the mine, particularly Zinc minerals, Otavite and feripontite are diagnosed in this mine for the first time via studying thin and polished sections, and prob quantitative analysis. Smithsonite with varying quantities as the major component of the mine is evaluated within all samples. Smithsonite exhibits vast variations in physical feature and genesis and varies from free granules and fine aggregates to complex intergrown with other phases. Proper release of every fine intergrown is just applicable for very fine granules. Hemimorphite is usually a depend mineral and relative frequency of this phase is mainly consistent with the smithsonite quantity, but it is a major source of silica contamination in Zinc concentrates due to the accompanying of SiO₂. Analysis of Sphalerite reveals that this mineral basically lacks elements like Cobalt and Nickel. Hence, this is hypothesized that sphalerite is replaced by smithsonite by alteration and Nickel is present in the matrix of carbonate zone as a trace element in addition to the existence in the structure of smithsonite. Definitely, source of nickel is not related to sphalerite and sulfide ore, and its increment is related to the later alteration of the ore deposit.

Introduction

Angooran Pb-Zn deposit is located in Zanjan province, northwest of Iran (47° 20'N, 36° 40'E), 90 Km west of Zanjan city. The deposit is the largest of its kind in Iran, and contains the highest ore grade in Middle East.

Angooran Lead-Zinc mine occurs in metamorphic rocks and younger strata of Mesozoic and Tertiary age. The host rocks include schist and crystalline limestone. The ore body seems to form discontinuous lenses and layers between the two rock types. There are two major faults trending E-W and N-S respectively. These faults resulted in extensive brecciation and alteration of the ore.

Goal of this study is evaluating of the existing minerals from aspect of size, shape, way of mineral interlocation and amount of useful and extra elements in every ore. This is of importance in the view of economics and is regarded in various processes of ore dressing, extraction and recovery.

The ore body is divided into two distinct zones namely the: Oxidation or Zinc carbonate zone, and zinc sulfide zone. Sphalerite, Galena, Smithsonite, Cerussite, Pyrite, Arsenopyrite, Ilmenite, Mimetite, Hemimorphite, Boudantite and Skordite are identified under reflected light.

Electron probe microanalysis of oxide and sulfide ores shows that, Sphalerite contains 2.63% Fe and 0.26% Cd. Minor amounts of Ni, Co, Sb and Sc are also detected in Smithsonite. The Arsenopyrite has 4.3% Ni, and 1.5% Co. The Zinc content does not vary in the two main zones of the mine. However, the Pb content in the carbonate zone is higher than that of the sulfide zone. It is thought that elements such as As, Mn and Ni were added to the sulfide zone during alteration. Copper and Silica content is similar in both zones. It seems likely that the second generation Pb, formed by alteration, is responsible for the observed variation in Pb content of the carbonate zone.

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Macroscopic features of the ore

The ore sample suite is highly variable in nature and consists of materials that range from very soft, earthy type through slightly harder, but nevertheless friable and pulverescent types to moderately hard and more coherent varieties. The bulk of the ore samples in the current sample suite comprise materials that belong to the first two categories (very soft to slightly harder). Moderately hard and coherent samples are far less common. Individual samples may consist almost entirely of ore minerals, but in other cases they contain variable proportions of highly altered schistose rock that may, itself, show evidence of fracturing, brecciation and other forms of deformation. The mineralogical composition of individual samples is therefore highly variable and this is also reflected in difference in color that is evident on all scales. The majority of samples tend to exhibit slightly brownish-cream color tones, but variations to ward-white gray, reddish brown, red and purple shades are also observed. Small black specks and dendrites of secondary manganese minerals may also be developed locally within certain samples.

The more coherent samples tend to consist largely of Zn and, to a lesser extent, Pb-bearing ore mineral that are often intimately intergrown on various scales. The samples are usually heterogeneous in nature and exhibit variable mineralogical composition, but they most commonly consist of moderately porous, fine-grained aggregates of smithsonite that may contain patches of intergrown mimetite and cerussite. These samples are also often vuggy in nature and contain numerous open spaces that have been filled in to varying degrees by finely crystalline smithsonite and hemimorphite. Smaller, but variable amounts of finely crystalline mimetite, manganese oxides and a variety of other minor secondary minerals may also be present in minor to trace amounts.

Description of individual Zinc Minerals

Introduction

The majority of hand specimens that were examined is moderately to well mineralized and is generally Zn-rich with the most common ore mineral being smithsonite. Subordinate amount of hemimorphite is, however, invariably present and may show complex intergrowths with the smithsonite. A number of other Zn-bearing phases are also present and may exhibit complex relationships. These phases are, however, only of localized importance and are not of great significance in terms of the overall Zn mineralogy of the ores. Limited attention was therefore given to the characterization of these phases. The more important of these phases include relatively small amounts of a Zn-Al-Silicate mineral and various Zn- and Pb-bearing secondary manganese minerals. Traces of sphalerite also survive locally, both as inclusions within quartz and as discrete grains.

Smithsonite

This represents the most common Zn-bearing ore mineral in both the samples and various Zn-rich plant products. Qualitative electron microprobe analyses of this phase as well as wavelength dispersive spectrometer traces indicate that it is very close to the theoretical ZnCO_3 (equivalent to 52.1% Zn) composition and that all other elements are below the limits of detection (250-500 ppm). Smithsonite characteristically forms complex intergrowths with all ore mineral phases in the sample suite and these may be developed on all scale ranging from the micrometer-size up to the millimeter scale.

The grain size of the smithsonite is highly variable ($<1\mu\text{m}$ to $>5\text{mm}$) and the smithsonite-rich aggregates are commonly highly porous. In many cases the porous and fine grained nature of the smithsonite suggests that it may represent the leached and carbonate residue of former Zn-bearing sulfides (presumably sphalerite). In other cases, however, the smithsonite has clearly been precipitated from solution and forms well defined crystals that line the margins of vuggy cavities and other open space or form coarsely crystalline fillings of former open fractures. These crystalline varieties tend to show the development of rhombohedron crystal faces that may be gently curved. The bulk of the smithsonite, however, does not generally show the development of crystal faces and the crystal may be locally zoned with the zones being defined by the presence of numerous inclusions or zones of intergrown hemimorphite.

The bulk of many samples consist of fairly monotonous areas of fine grained smithsonite that generally ranges in color between light cream and a very light reddish brown. Subordinate amounts of

smithsonite may show colors that range between white and grey with a small proportion of colorless crystals also being present. Very fine, pulverescent varieties of smithsonite are also present. The great bulk of the smithsonite is very well crystalline and yields very sharp, well-defined x-ray power diffraction patterns irrespective of the size, color or physical nature of the material. This is in marked contrast to many of the order constituents of the ores that are commonly poorly crystalline.

One of the most common forms of intergrowth consists of fine-grained aggregates of smithsonite and mimetite in which the mimetite exhibits a similar grain size to the smithsonite. These intergrowths may have formed either by the co-precipitation of both phases or by the filling in of open spaces within the porous smithsonite aggregate by mimetite. In otherwise the smithsonite may surround small quartz crystals or fragments. This quartz may represent a primary constituent of the original unaltered ore or, less probably, may have actually grown in situ during the alteration process. Mimetite, and less commonly cerussite, may also be present in such intergrowths.

The smithsonite aggregate may also contain fine-grained porous aggregates of various complex secondary Mn minerals. These Mn minerals commonly show the development of characteristic botryoidal and concretionary textures that are indicative of precipitation from solution on exposed surfaces. These may be developed on the outer margins of smithsonite grains and aggregates, but they are commonly completely enclosed within smithsonite aggregates which strongly suggests that the bulk of the smithsonite is secondary in nature and was precipitated after the formation of the Mn-bearing phases. In certain cases, the botryoidal Mn-phases may also be intergrown with other phases (e.g. mimetite) that appear to be present as inclusions within the mass of smithsonite.

Hemimorphite

Hemimorphite is widely distributed within the various specimens and plant products examined during the course of this study, but is generally very subordinate to smithsonite in terms of abundance. Hemimorphite is a Zn-silicate mineral with an idealized formula that may be written in the form of $(\text{ZnOH})_2\text{SiO}_3$ or, in terms of oxides, as $2\text{ZnO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$. The mineral consists largely of ZnO (67.5%), with subordinate SiO_2 (25.0%) and lesser H_2O (7.5%). The metallic Zn content is equivalent to 54.2% Zn and similar to that of smithsonite (52.1%).

Smithsonite is most readily recognized in situations where it developed characteristic well formed crystal that lines the margins of vugs and other open space within the ores, particularly in smithsonite-rich samples. The crystals are commonly transparent or white in color and form closely packed scale-like aggregates in which individual crystals may range in size between a lower limit of approximately 25 μm and an upper limit exceeding several millimeters. In other cases former open spaces may be completely filled with medium to coarse-grained hemimorphite thus forming discrete veinlets.

In many cases, the darker colored varieties of hemimorphite appear to be associated with very finely divided secondary Mn-bearing phases, which might, in part, be responsible for the color. Hemimorphite also shows the development of more complex intergrowth, largely with smithsonite, but also to a lesser extent with virtually all of the minerals that are present in the ores. The spaces between hemimorphite crystals in both well formed crystalline intergrowths and less regular, granular aggregates are commonly filled to a certain extent by smithsonite and, to a lesser extent, by other phases such as mimetite, and cerussite. Other rare phases such as *otavite* (CdCO_3) may also be present in similar associations. Alternating zonal growth between smithsonite and hemimorphite are relatively common and reflect the alternating precipitation of these two phase from solutions under differing conditions.

Sphalerite

Sphalerite-rich ores are reported to be present in certain areas of the open pit, but those are not currently mined. A single samples of this was subjected to cursory examination and found to consist predominantly of very fine grained polygonal sphalerite grains that show partial alteration and replacement by smithsonite. It is possible that a significant amount of the smithsonite and hemimorphite in the ore may represent the alteration products of former Zn-sulfide ores, but the investigation of this aspect was beyond the scope of the current project.

Very minor amounts of sphalerite are present in the secondary ores, largely in the form of tiny inclusions that are encapsulated within quartz and have therefore survived the widespread and pervasive alteration of the ore. These sphalerite inclusions are commonly rounded and rarely exceed 20µm in maximum dimension. Inclusion of this nature is generally single-phase in nature, but in certain cases they may be composite and consist of intergrowths with one or more other phases. Composite sphalerite-galena inclusions are the most common, but other minerals including acantite may be present. A small number of these inclusions were examined by SEM for the sake of completeness, but they contribute very little to the overall ore composition and were not studied in detail. These phases presumably represent components of the primary ore mineral assemblage and their detailed study would provide a considerable amount of information on the original nature and possible origin of the ore.

Other Zn-Bearing Phases

The most common of these Zn-Silicate minerals consists essentially of Zn, Al and Si and may represent the mineral *fraipontite* the composition of which may be expressed as $8\text{ZnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 11\text{H}_2\text{O}$. This mineral is present in trace amount in the Zn concentrates and is generally found intergrown with smithsonite. The presence of Si, Al and Zn within this phase is illustrated by the portion of a wavelength dispersive spectrometer trace shown in Fig. that reproduces part of the characteristic X-ray spectrum produced by this mineral. The relative abundance of this mineral could not be established, but it appears to represent a very minor component of the ore.

Scanning of the whole rock polished sections under the electron microprobe also shows the presence of small amounts of Zn in areas that can not generally be resolved and it is not immediately apparent whether the Zn is present in the form of extremely fine grained smithsonite or might possibly be adsorbed on to the surface of clay minerals. Similar relationships hold with various secondary Mn-bearing minerals that are present in the ores. These commonly show the presence in the form of sub-micrometer sized smithsonite intergrowths. A number of secondary Zn-bearing Mn minerals are known (e.g. heterolite, chalcophanite and zincdibraunite) and it is also possible that one or more of these phases are also present. The characterization of these minerals would require a very detailed study that is beyond the scope of the current investigation.

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AN EXPERIMENTAL ELECTROGRAPHIC STUDY: THE ANALYSIS OF RELATIONSHIPS BETWEEN THE LIMESTONE AND WATER

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1. Introduction

Different methods have been used along the time to observe the electro luminescence of the bodies. The non-conventional photographic process currently referred to as "Kirlian photography" has been in existence since the late 1890. In 1898, Yakov Narkevici Todks demonstrated "electrographic photos obtained with the help of quiet electrical discharges". These discharges appear in the form of a bluish flame. Interestingly, the NASA picture on the cover of a 1970 "Life" magazine

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issue devoted to the Apollo 12 Moon landing shows astronaut Pete Conrad on the Moon, with a bluish glow around him. Apparently this glow is generated by the various items of voltage producing equipment contained in his baggage.

This study present basic data regarding the problems of interpreting the images of electrical structures by electrographic technique obtained for the limestone in relationship with water.

2. Analytical technique for registration of electrographic images

The working device of this electrographic technique consists in putting a film AZOIX-RXR-2, blue sensitive, on a dielectric surface (glass) in direct contact with under bottom of the sample and placing in electrical circuit of device.

The apparatus - Petroelectrograph II is the monoimpulses electric generator - value of the tension between 8 and 55 kW, 2500 Hz (the reference frequency) and 0.2 ms duration of the obtained impulse. The mono-impulses is applied on a capacitor, created between the sample and the electrode. The electrode can have a positive or negative charge. The luminescent aura of the samples (anodic or cathodic images obtained by anodic or cathodic electric discharges) expresses the characteristics of rocks-water relationship. The electro-luminescence (the samples aura) is produced only when the rock being in a more or less saturate state with fluids (any natural rock represents a complex system: solid-water solutions-air).

3. Application of electrographic technique in analysis of porosity and the fluids infiltration velocity in limestone

Porosity analysis is one of those specialized areas of geological science that is perhaps not as widely known or understood as it should be. Electrography has been successfully applied in this study to the investigate of limestone permeability, moisture content or macro porosity of the rock-water system, small scale heterogeneities and local microstructure.

In all experiments, mechanically polished form (40x40x5mm) of limestone was studied (Table1).

Typology of samples

Table 1

Deleni I:	- medium-grained shelly limestone - continuous matrix of intergranular cement; the grains are not complete creating pore space; - mineral assemblage: calcite (95-97%)+ quartz (1-2%)+ argillaceous minerals + iron hydroxide; - porosity 14-16%
Deleni II:	-large grained shelly limestone; -nonecontinuous matrix of intergranular cement; oolites; radial arrangement of calcite in the oolites; concentric layers of crystalline calcium carbonate; -mineral assemblage : calcite (94-96 %) + quartz (1-2 %) + argillaceous minerals (1-2 %) + iron hydroxide; - porosity 20-22 %.

Laboratory conditions were: atmospheric temperature $25^{\circ}\pm 2^{\circ}$ C; temperature of solutions $8^{\circ}\pm 2^{\circ}$ C; atmospheric pressure 760 mm Hg, relative humidity 60 %, absolute humidity 9.1 g/m³.

4. Results

The images obtained by anodic/cathodic discharge express the characteristics of the pore morphology and the mineral/rock-fluid relationship in connection with a very fine chemical peculiarity and volume of the fluids. The electrographic image of electric signals recorded on the bodies surface reveals a nimbus branched out radial, cathodic and anodic streamers (streamers - bright effect of an avalanche of electric charges in one electric discharge). (Fig.1)

The existence of some types of streamers form having ramifications and certain space layout indicates that the space surrounding the samples is uneven, discontinuous and compartmented electromagnetic.

Deleni I



A (-)



B-a (-)



B-b (-)

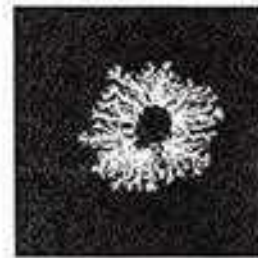


B-c (-)

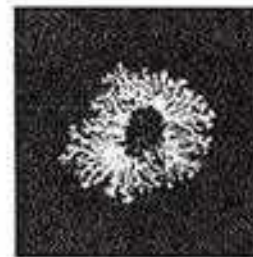
Deleni II



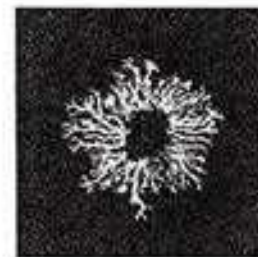
A (-)



B-a (-)



B-b (-)



B-c (-)

Fig. 1. *Electrographic images, convergent electric field (-). Shelly limestone in the natural state (A). Shelly limestone treated with de-ionized water (pH= 7) (B): (a) initial state, with 0.1 ml water (the time 0); (b) after 10 minutes, with 0.2ml water; (c) after 20 minutes, with 0.3 ml water. Configuration of the draining area, maximum penetration zone of water in the shelly limestone sample in the center of images.*

5. Conclusions

Our applications present here only the domain of porous-permeable rocks characterized by an ionic conduction. The studies for physical proprieties of rocks permit to characterize the degree of moisturizing for rocks pores and image to water penetration in rocks.

In the time, limestone and shelly limestone was used for the many buildings and monuments (in especially cathedrals) constructions.

The properties of the limestone used for features in the interior differ from those of the exterior. There was for less concern about susceptibility to weathering and for more emphasis on suitability for carving. For restoration work, the electrography is a new method to estimate more rapidly the stage of weathered over time. water absorption is high and unforeseeable in weathered

rocks. After studying many electrographic images of the rocks (shelly limestone in this study) with various moisture stages, future contributions of research data will have not excuse for such deficiencies: the motivation is standardization in technique and possible adequate appreciation of errors.

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MINERALOGICAL STUDY AND ORE PROCESSING: CASE STUDY ROȘIA MONTANĂ, APUSENI MOUNTAINS, ROMANIA

TĂMAȘ¹ Călin Gabriel, COSTIN² Dan Florin

The Roșia Montană ore deposit is a typical low sulfidation system. Based on the morphology of the ore deposit, gangue and ore mineralogy, alteration assemblages, zonality of alteration assemblages and geochemical associations, Mârza et al. (1997) assigned the Roșia Montană ore deposit to the low sulfidation (adularia-sericite) type. Further on, Tămaș and Bailly (1998, 1999b), Pinteș (1999) provided additional fluid inclusion evidences to support this opinion.

The Roșia Montană area is pervasively mineralised. It is quite difficult to find a piece of totally barren rock in this mining field. Beside the widespread impregnations, higher ore grades are given by vein systems, stockworks, and mineralised breccias, as well as placers and paleoplacers.

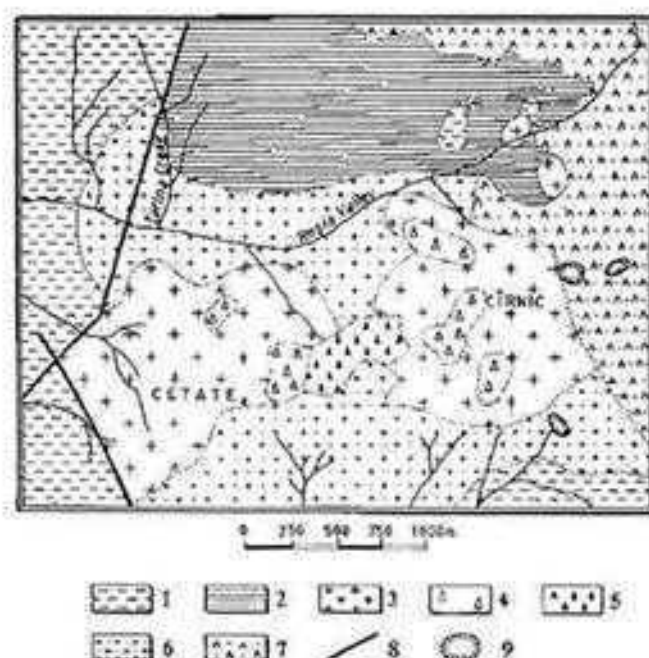


Fig. 1 Geological map of the Roșia Montană area (Tămaș, 2002):

- 1 - Cretaceous flysch; 2 - Neogene sedimentary rocks (Sarmatian); 3 - Cetate dacite; 4 - Phreatomagmatic breccia pipes; 5 - Fluidization channel of the Cetate breccia pipe (Glam Formation); 6 - Base surge deposits; 7 - Andesite pyroclastic deposits; 8 - Faults; 9 - Lakes.

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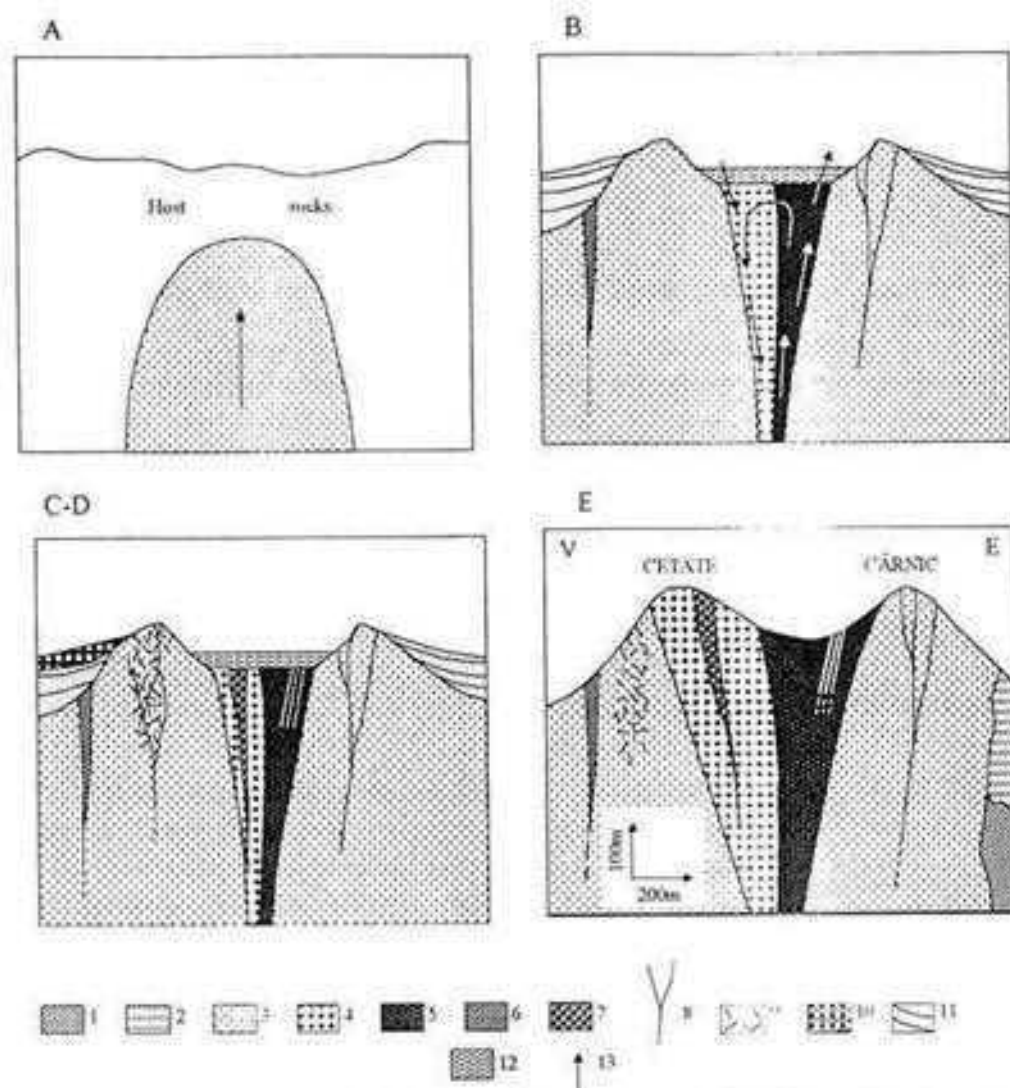


Fig. 2 – Petro-metallogenetic model of the Cetate – Cărnă structure (Roșia Montană ore deposit) centred on the Cetate phreatomagmatic breccia pipe (Tămaș, 2002). **A** – Rise of the Cetate dacite; **B** – The genesis of the proto-phreatomagmatic Cetate breccia pipe and related base surge deposits. The fluidization cell is well developed (Glauconitic Formation and Cetate Breccia – in its old meaning); **C** – **D** – Au – Ag mineralizations (impregnations, phreatic breccias, tectonic breccias, veins, vugs, stockworks, placers etc.); **E** – The present day Cetate – Cărnă structure from Roșia Montană. 1-2 – Host rocks (1-Cretaceous, 2-Neogene); 3 – Cetate dacite; 4 – Cetate Breccia (in its old meaning); 5 – Glauconitic fluidization channel; 6 – Tectonic breccias; 7 – Phreatic breccias (superposed onto the phreatomagmatic breccia pipe body); 8 – Veins; 9 – Stockworks; 10 – Gold placers; 11 – Base surge deposits; 12 – Alluvial sediments; 13 – Direction of transport.

The hydrothermal alterations are extremely well developed. Potassium silicate (adularia I, adularia II) and phyllic (illite, interlayered illite/montmorillonite) alterations are widespread all over the area. It is obvious that intense silicification delineate the high-grade ore bodies (in breccias, stockworks and veins). There are also intermediate (kaolinite, halloysite, montmorillonite) and advanced argillic (kaolinite, pyrophyllite) overprints. Carbonates (calcite, rhodocrosite) as well as rhodonite often occur within the veins, stockworks and breccias.

Breccia pipe structures are very abundant in the Roșia Montană area. The most representative one is the so-called Cetate Breccia, located between the Cetate and Cărnă hills (Fig. 1). This breccia body is probably the largest of its kind in Romania and is cited by many Romanian as well as foreign authors (Sillitoe, 1985; Laznicka, 1988).

Roșia Montană is a mega breccia pipe centred low sulfidation ore deposit. The Cetate phreatomagmatic breccia pipe controlled the development of the hydrothermal system during and after the phreatomagmatic eruptions. Additional styles of brecciation (phreatic, tectonic) as well as fluidization, hydraulic fracturing, injection breccias are to be taken into account (Fig. 2).

Mineralogical investigations (thin and polished sections, X ray, TEM, SEM, microprobe) were carried out for different types of ore bodies: breccias, veins, and stockworks.

Cetate breccia. Mineralized rock fragments, matrix and superimposed later mineralized structures (vugs infillings, veins, etc.) altogether rise the ore grade of Cetate breccia pipe. There is also a clear spatial variation of the ore grades laterally and vertically within breccia body. The upper parts of the structure are anomalously rich. The Au-Ag content gradually decreases with depth.

There is lateral variation, too. The western part of the breccia is richer as compared to the eastern part (Glamm Formation). Extremely high precious metal contents were delineated, randomly distributed within the open pit and underground workings. The spectacular rise of the ore grade is given by the metal input of phreatic breccias superimposed on the Cetate phreatomagmatic structure. These overprinting breccia structures – the result of a vigorous hydrothermal activity – represent the richest ore zone of the whole Cetate breccia body. Perhaps even the famous “Romans Courts” – ancient open pits from the Cetate Massif – exploited several phreatic breccia chimneys that crosscutted the main Cetate Breccia.

The following types of mineralizations from the Cetate breccia pipe body have been studied: impregnations, stockwork veining, veins - veinlets and former open spaces filled with amethyst gangue, veins with common sulfides and quartz, veins with Mn-rich gangue minerals from the Glamm Formation, phreatic breccias superimposed on Cetate Breccia, clast supported (dacite) breccias, stockworks within dacite confined rock. Different chemical compositions of the gold (electrum), and several gold mineral associations were identified (Table 1).

Genetic type	Mineralogical association
Fissures and open spaces with amethyst	Pyrite - Au
	Quartz amethyst - Au
Veins with rhodochrosite-rhodonite	Rhodochrosite - Au
Phreatic breccias	Galena - Au
Clast supported breccias	Sphalerite - Au
Host rocks	Pyrite - Au
	Sphalerite - Au

Table 1 Mineralogic peculiarities of Au-Ag mineralizations within the Cetate Breccia

Cărnic II breccia. Besides the Cărnic II Breccia, the Cărnic II mining field also hosts several veins (both shallow and steeply dipping). Within Cărnic II breccia there are two main styles of mineralization. In phreatomagmatic breccias there are very common impregnations and superposed veins (contact and crosscutting veins). The eastern part of the phreatomagmatic Cărnic II breccia shows a spectacular phreatic reworking of the former breccia body. This part of the Cărnic II breccia body revealed high ore grades (over 220 g/t Ag and over 10 g/t Au). In this part of the structure the clasts (angular fragments of dacite and breccias) are rimmed by ore minerals (Ag-rich minerals, electrum, common sulfides) held together by hydrothermal cement (cryptocrystalline quartz, crustiform overgrowths, extremely fine grained hydrothermal mud - “chinga”). Within the open spaces well developed feebly amethystized quartz crystals are still preserved.

The mineralogy of the ore is very complex. Polished section study, electron microscopy (SEM) and microprobe analyses throw some light on the ore composition. The spectra obtained (SEM) suggest the occurrence of argyrodite-canfieldite, proustite-pyrrargyrite (?), pearceite-polybasite, stephanite, miargirite (?). The microprobe results confirmed the presence of polybasite-pearceite, tethraedrite, stephanite, acanthite, native Ag, and also of several unidentified Ag-rich minerals (or mixings). Common sulfides (chalcopyrite, galena, and sphalerite) as well as two types of electrum were also identified. The grains of electrum are included in pyrite, quartz and silver minerals. Silver is a very common minor element in galena and sphalerite.

From geochemical point of view the ore from Roşia Montana ore deposit is a typical Au-Ag one without any other by-products (Cu, Pb, Zn, etc.). Gold occurs as free gold and electrum. Silver

occurs as native silver, and it is also hosted in tetrahedrite (freibergite), argyrodite-canfieldite, proustite-pyrrargyrite, pearceite-polybasite, stephanite, miargirite, acanthite, galena, sphalerite (up to 6 % Ag). Microscopic studies (polished sections) revealed that the gold grains' dimensions range between 150 – 5 microns, with about 60-70% of them exceeding 20 microns. Very minor quantities of chalcopyrite associated with Ag sulphides and sulphosalts were also identified. Microprobe analyses revealed the ubiquitous presence of As in pyrite (up to 1 %).

Taking into account the mineralogical peculiarities of the Au-Ag ore from Roşia Montană ore deposit, the following ore recovering techniques may be used: cyanide leaching, gravity concentration, and flotation.

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GEOLOGIC, MINERALOGIC AND FLUID INCLUSION STUDIES OF THE MINERALIZED BRECCIA PIPE AT ROTUNDA-KELEMEN (GUTII MOUNTAINS, ROMANIA)

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The Rotunda-Kelemen mineralized breccia pipe is located on the eastern part of Gutii Mountains, between Cavnic and Baiut, epithermal vein ore deposits. It is atypical form of deposit for this area, but not a unique one, since ore deposits of this type were found at Socea (Oas Mountain), on the East Carpathians (Udubasa et al., 1982), and on Apuseni Mountains (Ghitulescu et al., 1979, Udubasa et al., 1982).

On the eastern part of Gutii Mountains the Neogene magmatic activity developed on a metamorphic and Paleogene basement divided in blocks with a complicated tectonics in overthrust sheets (Fig.1)

The spatial, temporal and genetical relationships between the magmatic intrusive activity of intermediate composition and the metallogenetic activity are obvious.

The mineralized breccia pipe is associated to the Magura Ciorii intrusive structure. The breccia-pipe has an ellipsoidal shape in the horizontal section, with a ESE-WNW orientation. It has a sub-vertical position. It has been studied on 370 m deep (from the surface +850 m to the +480 m level). In the upper part, dimension of pipe is 45x85 m, and it is 135x45-50 m at 200 m depth below the surface. Below that level, the breccia body is much elongated (150x20-30 m approximately, with a ESE-WNW orientation).

The breccia column penetrates the Paleogene sedimentary formations and the intrusive body. The igneous-intrusive process was also active after the formation of breccia body and mineralizations. Some small intrusive apophyses partially penetrate the mineralized breccia pipe.

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The contact of breccia pipe with the surrounding rocks is very sharp. The contact zone frequently contains sheet fractures. Composition of breccia is heterogeneous: hydrothermally altered clasts consist of Paleogene marls and sandstones, Badenian sandstones and limestones, Sarmatian marls, sandstones and tuffs, Pannonian sandstones and igneous rocks (microdiorite, andesite). The breccia is matrix supported especially in the marginal areas where the breccia magnitude is higher and the maximum base metal content occurs.

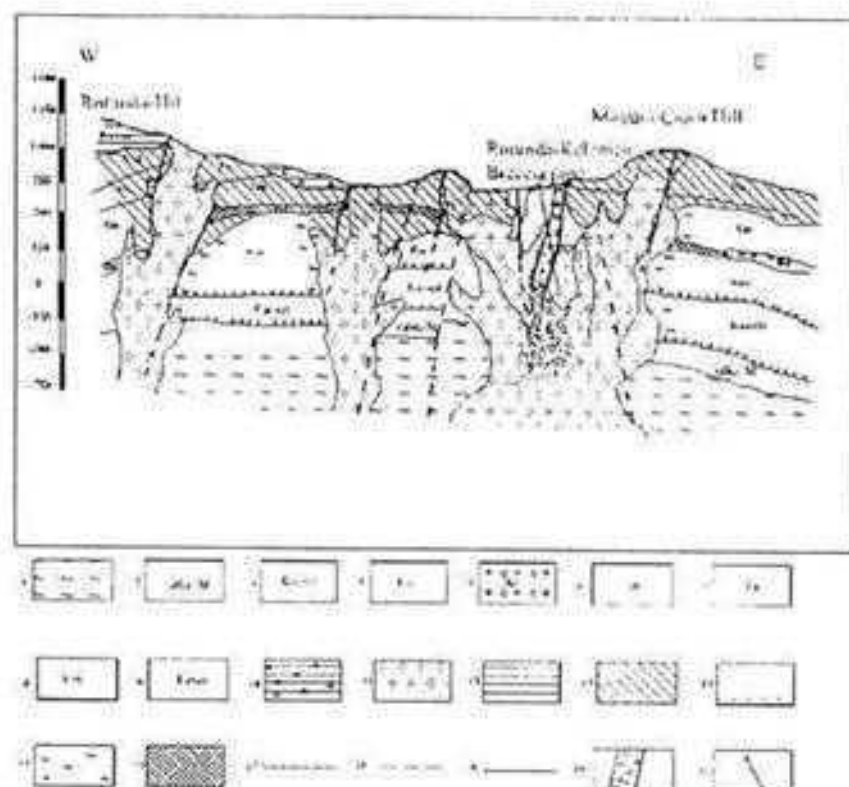


Fig.1. Geological section through Rotunda-Kelemen zone

1. Crystalline basement; Paleogene basement; 2. Autochthon (Oligocene-Miocene); 3. Wildtitsch nappe (Eocene-Oligocene); 4. Botiza nappe (Eocene); Neogene rocks; 5. Badenian; 6. Sarmatian; 7. Pannonian; 8. Volcano-sedimentary rocks; 9. Lava flows; 10. Volcanoclastics; 11. Intrusions; Hydrothermal alterations: 12. Advanced argillic alteration; 13. Intermediate argillic alteration; 14. Sericitic alteration; 15. Magmatic contact metamorphism; 16. Metasomatic contact metamorphism; 17. Overthrust nappes; 18. Faults; 19. Veins; 20. Rotunda-Kelemen breccia pipe; 21. Drillings

Illitic-sericite hydrothermal alterations with evident zonation characterize the breccia pipe and its contact zones. Around the breccia body an 5-10 m envelope of kaolinite-illite ($\pm$ montmorillonite) alteration occurs. The frequency of the illite alteration is major in the contact area and the breccia clasts. Chloritization is stronger at approximately 60-100 m far from the ore deposit and they are less frequent surrounding the breccia. At 60-100 m far from the breccia body, kaolinite and illite appear in smaller amounts. Silification is less developed compared with the previous alterations. Adularization surrounds the veins associated with the breccia body both in magmatic rocks and Paleogene sandstones.

The richest polymetallic type (Zn, Pb, Cu $\pm$ Au, Ag) mineralization deposited in the second stage of an prolonged hydrothermal activity with four major stages. Brecciation occurred at the beginning of each stages.

The first stage of mineralization is characterized by assemblages of magnetite, hematite and sulphide minerals (pyrite, sphalerite, pyrrhotite, chalcopyrite) associated with quartz. Based on the study of fluid inclusions, the temperature of the hydrothermal processes was between 270-340 °C.

The second stage of mineralization with abundant base metal sulphide minerals (pyrite, sphalerite, pyrrhotite, chalcopyrite, galena, marcasite, arsenopyrite, cubanite, bornite) formed during cooling of fluids from about 270 °C to about 220-250 °C.

The mineral association of the third stage is also dominated by the base metal sulphides, and in addition sulphosalts also appear. The gangue consists of quartz, carbonates (calcite, siderite, dolomite) and clay minerals.

The brecciation moments were associated with pressure release in the hydrothermal system thus boiling and gas loss of fluids may have occurred. Following the breccification moments, the hydrothermal system became more and more opened, thus dilute and cold meteoric water penetrated deeper and deeper and therefore its mixing with the deep hydrothermal fluids became more and more intense. Boiling with gas loss and fluid mixing processes are reflected by fluid inclusion data (Fig. 2). This environment allowed the formation of mineralogical associations of low temperatures, where the percentage of sulphosalts and concentrations of Au, Ag increased.

The fourth stage consists of a polymetallic epithermal vein-type mineralization ($\pm$ Au, Ag) that mostly occurs around the breccia body, but some veins also cut the breccia, supporting that this ore type formed after the main mineralization stages. Fracture systems hosting this late ore opened in several pulses. The gold-silver mineralizations in some veins, overlapped the polymetallic ores.

Based on the geochemical data and the morphological study of pyrite (Nedelcu L. et.al.1984), the major part of Au in mineralization is connected to the pyrite.

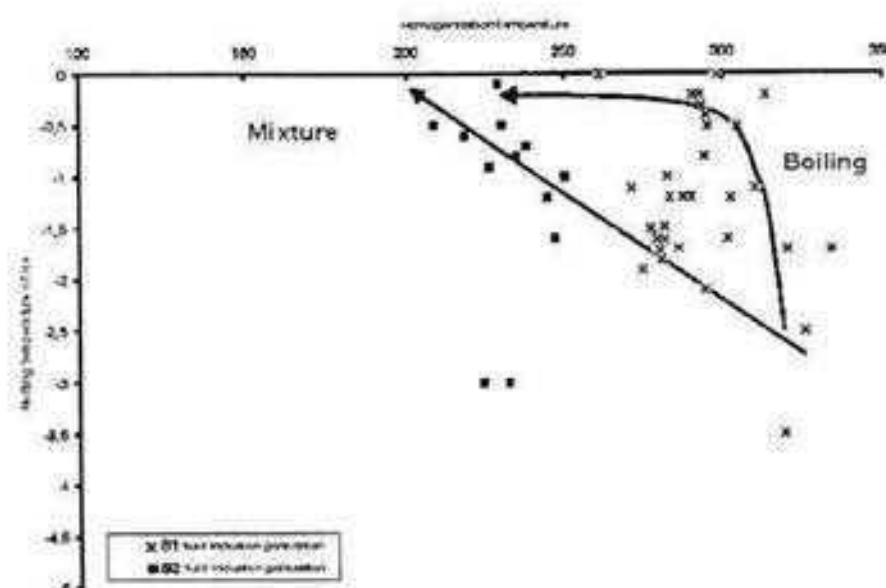


Fig.2. Distribution of concentration values of fluid inclusions as a function of homogenization temperature in Rotunda - Kelemen breccia type ore deposit.

According to the results of fluid inclusion studies the hydrothermal processes took place between 200 °C and 340 °C. The composition of fluids can be modelled by the NaCl-H₂O-system. The total salinity of hydrothermal solutions varied between 0.5-3 wt % NaCl equiv.

The hydrothermal processes developed in two temperatures ranges. From 270 °C up to 340 °C the generation of high temperature inclusions were formed (S₁), and from 200 °C up to 270 °C the generation of lower temperature inclusions were formed (S₂).

On the basis of the distribution of concentration values of fluid inclusions as a function of homogenization temperature one can suppose that the generation of high temperature inclusions was formed by boiling of hydrothermal solutions, and the generation of lower temperature inclusions was formed by cooling and mixing of hydrothermal fluids with different temperature and salinity (Fig.2). A decrease of the solutions grade with the decreasing of the temperature can be noticed. The association of thermobarometer minerals (exsolution of chalcopyrite and pyrrhotite in sphalerite, exsolution of pyrrhotite in chalcopyrite, exsolution of sphalerite in chalcopyrite etc.) indicates 350-400 °C (after Mizuta T. and Scott S. D., 1997; Kojima S. and Sugaki A., 1985) to about 150 °C temperature range for hydrothermal activity.

The $\delta^{34}\text{S}$ values measured in various sulphide phases indicate predominant magmatic origin of sulfur in the form of H_2S ; however, the influence of sulfur from the sedimentary units of the host rocks can also be noticed. (Fig.3)

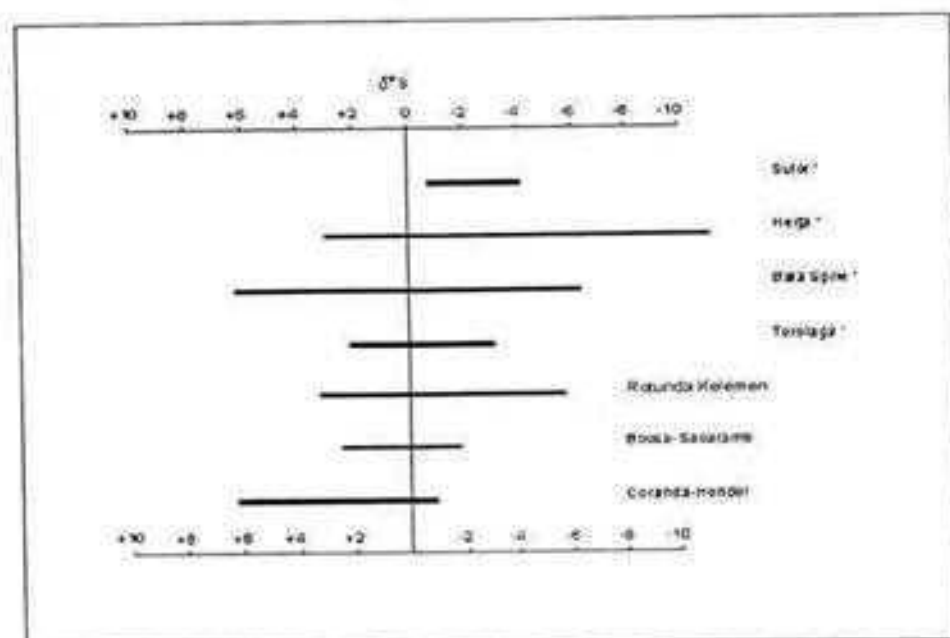


Fig.3. Diagram of the isotopic composition of sulphur ($\delta^{34}\text{S}$) in individual vein and breccia pipe deposits from East Carpathians and Apuseni Mts. (Romania).

* vein deposits

The isotopic values of Pb, measured in the Rotunda-Kelemen breccia pipe galena are similar to the ones measured in the galena of the ore deposits and the Pannonian igneous rocks in the surrounding areas.

Ore deposits / rocks	$^{206}\text{Pb} / ^{204}\text{Pb}$	$^{207}\text{Pb} / ^{204}\text{Pb}$	$^{208}\text{Pb} / ^{204}\text{Pb}$
Suior*	18.820	15.677	38.917
Baia -Spiru*	18.861	15.669	38.914
Cavnic*	18.855	15.667	38.911
Rotunda-Kelemen	18.930	15.720	39.020
Pannonian igneous rocks*	18.766	15.695	38.790

* after Marias Z. (1996)

That indicates a genetic relationship between the mineralizations and the igneous host rocks

On the basis of the genetic conceptual model for Rotunda-Kelemen mineralized breccia pipe, in the early stages of evolution, the ore deposit was a magmatic-hydrothermal breccia. The phreato-magmatic processes were more intense in the following stages of the evolution.

THE RELATION BETWEEN GEOTHERMAL FIELD AND HYDROCARBON MATURATION IN THE GEODYNAMIC POLYGON CĂLDĂRUȘANI – TULNICI

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A comprehensive study of hydrocarbon source-rock area requires the location of potential hydrocarbon source rocks, the knowledge of organic matter quantity per rock volume as well as the estimation of organic matter maturation degree.

The customary approach used for the evaluation of these data is based on geochemical analyses accomplished on a pre-selected number of samples and cuttings drawn from boreholes.

Nevertheless, without any extra cost, the same objectives can be approached using the continuous measurements of well logs customarily recorded in each well from ground surface to the bottom hole.

The use of well logs for source rock evaluation and hydrocarbon migration avenues knowledge, started in the Geodynamic Institute, several years ago. Reliable results have been acquired in connection with hydrocarbon generation and migration concepts, some of them being presented in this paper.

According to our concepts, the objectives and performances of well logging measurements (Gamma Ray, Neutron, Density, Sonic, Induction and Laterolog) meant to establish the source rock – hydrocarbon generation conditions are the following:

1. Identification and correlation of potential source rock beds as well as the outlining of organic facies-areal distribution
2. Determination of bulk source rock-beds parameters:
 - total organic carbon (TOC)
 - S₂ value, corresponding to the particular (S₂) peak of Rock-Eval pyrolysis
 - thickness and if it is possible, the volume of source rock-beds.
3. Calculation of source rock beds parameters related to the organic matter thermal evolution
 - temperature values on definite locations of thermal field
 - time-temperature index (TTI)
 - vitrinite reflectance (R_o)
 - level of organic metamorphism (LOM)
 - thermal alteration index (TAI)
4. Evaluation of source rock evolution stages (diagenesis, catagenesis, metagenesis).
 - set out of present oil generative window thresholds (the onset, the peak oil and the end of oil generation)
 - set out of oil window position during the geologic time (oil window dynamics).
5. Outlining of maturation organic facies areal distribution and the generation timing of each organic facies

The field applications of this paper are coming from the deep Oligocene of the so-called "Mio-Pliocene zone" located in the western part of the Căldărușani-Tulnici Geodynamic Polygon.

The stratigraphical and tectonical data of this areal show that Paleogene sedimentary sequences are made up of clays, marls, sandstones, conglomerates and evaporites. The source rock beds belong to the Oligocene Kliwa facies and include pelitic intercalations of black shales, dysodiles and some bituminous calcareous marls.

Many deep wells have been drilled in this zone and temperature maps at 5 km and 6 km deep have been carried out in our institute. The deepest well drilled in Romania at 7025 m is also located in this zone.

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Our analysis of the wire line operations has enabled to determine the following physical characteristics of the hydrocarbon generation process and organic matter thermal evolution at 7 km deep.

1. The steady-state well temperature reached 145°C at 6 km deep and 170°C at 7 km deep.
2. The formation pressure gradient of the over-pressured source rock beds located between 6 km and 7 km is 19.7 kPa/m and the bottom hole formation pressure at the total depth is 138 MPa.
3. The Oligocene formation-burial rate during the subsidence period was 207.5 m/mill. yrs.
4. The heating rate of the main source rock – sequence reached 5.17°C/mill. yrs.

These data established during the first processing pass have further enabled to continue the processing calculations and interpretations substantiating the following final conclusions:

1. The Upper Oligocene source rock beds reached the stage of the start of oil generation 5 million years ago at 4.4 km. deep (onset of oil generation).
2. The maximum oil generation (oil peak) was reached 3 million years ago when the Oligocene top was located at 4.72 km deep.

3. Nowadays, the oil window is situated in the Lower Miocene, in the depth interval 4.4 km – 5.6 km.

4. The main stages of organic matter thermal evolution are situated as follows:

– Diagenesis:	0 – 4.4 km
– Catagenesis:	4.4 km – 6.2 km
– The onset of condensate and wet gas:	5.6 km
– Metagenesis:	under 6.2 km.

5. In the above-mentioned area, the Oligocene formations crossed by very deep wells belong to the Upper Kliwa and Podul Morii sedimentary sequences. The petroligenous potential of the investigated Oligocene sequence is fairly good. Organic carbon amounts surpass the value of 0.5% generally accepted as a low limit for the existence of a source rock bed. Several thick layers with TOC values higher than 4% supplied in the past, large quantities of oil and they probably are responsible for the high gas background recorded by the chromatographic analysers during the borehole-drilling period.

6. A large number of layers with good petrophysical characteristics (porosity, fissure-fracture index, etc.) suitable to be good reservoirs and carrier beds are identified on well logs. Unfortunately, in many places, the actual formation overpressure conditions are less favorable to primary and even to secondary migration.

In our paper two examples showing the good correlation of source rock beds belonging to four organic facies-intervals are given and illustrated. The TOC values determined at each 0.5 m have been inferred from well logs and the accompanying exemplifications are coming from 3 wells situated on the same alignment 2 km and respectively 15 km apart.

The last part of our work is devoted to the presentation of some synthetical graphs connected with Oligocene organic matter - thermal evolution in the depth interval 5–7 km. One of these graphs relates burial rate, vitrinite reflectance, oil window dynamics and organic matter – thermal evolution stage just under the Miocene / Oligocene stratigraphical boundary.

To conclude we have to say that the possibility to determine distinct physical properties of source rock-beds on the basis of well logging measurements represents an useful method to evaluate organic matter-maturation degree and hydrocarbon generation conditions. The high quantity of data existing at each well logging-data bank may be used without any extra charge, to attain such targets in other geological provinces of our country.

USING WELL LOGS FOR SOURCE ROCK-BEDS. APPLICATIONS IN THE NORTH AFRICA SEDIMENTARY BASINS

ZUGRĂVESCU¹ Dorel, POLONIC² Gabriela, NEGOITĂ¹ Victor

This paper tries to present an overview of hydrocarbon source rock systems of North African countries bordering the Mediterranean Sea (Morocco, Algeria, Tunisia, Libya and Egypt) as well as the acquired results using well logging techniques discussed in the previous paper.

This part of the African continent forming a geographically contiguous unit shows a common geological history making part of a single geological plate during the Phanerozoic history.

Source rock-beds deposition, timing of maturity and hydrocarbon generation in this area are related to two main extensional tectonic cycles which ended in the compressional and destructive events of the Hercynian and Alpine orogenies.

Although, in the above-mentioned area, the hydrocarbon reservoirs as well as the significant oil and gas fields are very scattered, the source rock-beds are restricted to a very limited number of stratigraphical levels.

More than 4/5 of the recovered oil and gas and the future reserves are attributed to two main source rock intervals belonging to Early Silurian – Late Devonian and Late Cretaceous – Eocene.

The most important source rock interval, distinguishable on well log recordings, possible to be correlated over wide areas of North-Africa is represented by the radioactive black shale of the Lower Silurian, whose thickness is larger than 50 m. Total organic carbon (TOC) values are not too high, source potential index (SPI) is about 3.5 and as a peculiarity it is worth to emphasize that Silurian source rocks at similar stratigraphical levels have been found on the Russian and Amazon platforms as well as in the USA interior basins. They seem to be related to a widespread global sea level rise, which flooded a series of sag basins overlying the earlier Cambrian-Ordovician rifts and as a consequence a lot of restricted anoxic areas came into being.

Late Cretaceous source rock are also already extensive but the source rock intervals and levels are not fully time correlative over the region brought into discussion. Some of the most productive thick source rock-beds are noticed in the following formations: the shales of the Cenomanian Sirte basin, Santonian Limestones of Suez, Tarfaya immature Turonian black shales, Turonian shales from Tunisia etc. In most of the cases they are associated with transgressions and sea level rises during the Late Cretaceous as well as to oceanic anoxia and tectonically controlled marine restrictions.

About 1/10 from North Africa oil and gas reserves are attributed to Eocene source rock-beds occurring generally along a similar-trend to the Late Cretaceous source rock development. The most prolific source rock intervals are located in the Pelagian onshore and offshore, in the Suez and Sirte basins, etc., their productivity being related to the interval thickness, TOC and SPI values.

Other source rock-beds dated as Triassic, Middle Jurassic and Early Cretaceous have been locally documented as being regionally correlated. They are localized in the Essaouira and Tarfaya basins (Morocco), Atlas and Triassic basins (Algeria), Northern Tunisia and Western Desert (Egypt). Source rock-bed thickness, TOC and SPI low values, frequently organic matter over-maturations and other circumstances have conditioned their poor source rock potential.

Till now, the geochemical literature documented that hydrocarbons are formed from disseminated organic matter within sedimentary source rocks by a complex reactions of overall first-order governed by the Arrhenius equation. The rate of these reactions are primarily dependent on

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temperature and heating duration, both variables being neither more nor less, related to the heating rate through the geothermal gradient and burial rate.

The heating rate effects begin early as the sediments of source rocks are exposed to the earth geothermal gradient. They start very slowly, but their rate generally doubles as the exposure time doubles, or the temperature rises by 10°C. This exponential growth in oil products with depth, ultimately results in a period of a rapid generation – in time and depth – called "oil window". The formation of commercial quantities of oil and their expulsion from the source rocks do not occur until the main phase of oil window called "peak oil generation" is reached.

Several organic and mineral thermal indicators of the source rock maturation degree are routinely used in the geochemical laboratories to ascertain the oil window position in time and depth.

But the same indicators may be determined by means of well logging measurements. The general concept that the electric resistivity changes are related to the start of oil generation and the replacement of more or less electric conducting water – filling the source rock pore space – with the thermally generated oil has been asserted in the literature by several authors.

Consequently, a proper processing and interpretation methodology has been carried out to establish the source rock-oil window position in the ground subsurface, including its three boundaries: the onset, the peak oil and the end of oil generation, as well as the limit between catagenesis and metagenesis stages.

Applications, on the basis of well logging measurements, have been achieved on Essaouira, Illizzi – Murzuk and Western Desert basins, whose results are presented. Some specific well logging recordings coming from different source rock intervals are also shown.

Vitrinite reflectance (R_0) values obtained from common laboratory methods were related to time-temperature index (TTI) values determined on the basis of geothermal gradients and a documented geological history. For the Murzuk basin we adopted a linear function and finally obtained with a correlation coefficient of 0.94 the following least square fit:

$$\text{Log TTI} = 4.87 \text{ Log } R_0 + 2.26$$

This equation, linearly relating TTI and R_0 , as well as the commonly used Waples, Issler and Goff equations are graphically presented and discussed in the case of Murzuk and Ghadames basins (Libya).

QUARTZ-SANDY FORMATIONS FROM CARPATHIANS AND AFFERENT AREAS – ON PROPERTIES AS APPLICATIONS IN THE OIL INDUSTRY

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The aim of the study was the identification and the research works about quartz-sandy formations from Romania as the utility in drilling operations for hydrocarbon wells, in conformity with national and international standards. In this order, we have selected 285 sandy occurrences from all geological units of Romania: the East Carpathians, the South Carpathians, the Apuseni Mountains, Transylvania Basin, Pannonic Basin, Moldavia Basin, Getic Basin, Romanian Plain, and Dobrogea. Inside of this units, the distribution of the quartz-sandy occurrences is very non-uniform, and their qualities high variable. The stratigraphic interval where quartz-sandy occurrences are, is from Eocene to Quaternary. The oldest formations are weak-consolidated, or affected by strongly decemented processes in their diagenetic evolution (as in the case of Kliwa Oligocene "sand"), and the youngest formations (Pliocene and Quaternary) include unconsolidated deposits, as mobile, so easy to exploration works.

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The total thickness of sandy formations for each occurrence are between 0.50 – 10.15 meters, and the quality of sand, generally, is not very close to most of the requirements for drilling operations in the hydrocarbon wells. In the class grain-size intervals, the quartz content is 50 – 95 %, the sphericity index 0.2 – 0.8, and the roundness index 0.2 – 0.8.

In spite of the great number of the identified occurrences, only 35 of them have sandy formations with more than 90% quartz content, and also, the properties are close to requirements in the standards. The quartz-sandy occurrences selected by us in order to carry out detailed evaluations to reveal their properties for drilling operations in hydrocarbon wells are placed in the East Carpathians, the Apuseni Mountains, Pannonic Basin, Transilvania Basin, and the Moldavia Platform areas.

The analysis – grain-size, shape, mineralogical, chemical, and technological (leaching analysis, acid solubility, crush-resistance) – was carried out on 40 samples, and was revealed textural parameters C, Md, M, So, Ro, Sf, mineralogical composition, also their technological quality of sand (in compliance with reference standards API 56/1986 and 58/1986).

By lithological point of view, the examined occurrences are siliciclastic deposits with different stages of consolidation, as following:

- strong-cemented sandstones – as occurrences from Patarlagele area (Valea Sibiciului, Colti, Alunis), and Suceava area (Plesa, Manastirea Humor);
- decemented sandstones – as occurrences from Valeni area (Gura Vitioarei, Copaceni), Patarlagele area (Valea Sibiciului, Crivineni, Valea Rea), Suceava area (Paltinoasa);
- weak cemented sand – as occurrences from Botosani (Hudesti, Miorcani), Faget area (Faget Scaune si Jupanesti), Aghires area, and Fagetul Ierii area.

The age of this sandy deposits is Eocene for Fagetul Ierii sands (the Apuseni Mountains), Oligocene for Teleajen Valley sands (Valeni area), Buzau Valley sands (Patarlagele area), Humor Valley sands (Humor area), Nadasu Valley (Aghires Quarry), Miocene for Moldavia Platform sands, and Pliocene for Pannonic Basin sands.

In all cases, the petro-types correspond to quartz-rocks (i.e. rocks with more than 90% quartz). In sequences, at outcrop scale, these types of rocks are associated, as interbedded, with fine grain-size rocks (i.e. siltites, shales and slates, marls), and even carbonate rocks (as in the case of the Manastirea Humor area). Arenite vs. other grain-size fractions ratio is variable between 9/1 – the maximum values (~75%) in cases of Humor area (Plesa, Paltinoasa), Patarlagele area, and Valeni area (Copaceni, Gura Vitioarei) – to 6/4 – the minimum values in the case of Faget Timisoara area (Faget Scaune Quarry).

The qualities of the sand from the selected and analysed occurrences are as following:

The **grain-size analysis** was shown, for occurrences in exploration technological processes, a high percent of very fine arenites (under 0.125 mm class), fine arenite (0.1 – 0.2 mm), and medium arenite (0.2 – 0.4 mm, and 0.3 – 0.6 mm). Coarse arenites occur in Paltinoasa-Iliesti area, but in this case the deposits are cemented. Often, arenitic class (named “usefully”) is associated with silto-lutitic class and/or carbonatic (“poor” class). In the analysed samples “u” vs. “p” ratio is 78.98 – 98.97 %, generally 88 – 92%. The maximum content of “u” (over 90%) is registered by samples from Aghiresti, Hudesti, and Miorcani areas. For each selected sort (e.g. preferred grain-size class) the obtaining efficiency is 30.82 – 90.39%, but generally 62 – 73% (for 0.1 – 0.2 mm sort), and 39 – 69 % (for 0.2 – 0.4 mm, and 0.3 – 0.6 mm sorts). The maximum efficiency is for samples collected from Hudesti, Miorcani, Aghires, Fagetul Ierii areas, and in part for samples collected from Valeni, and Plesa areas.

The grain-size classes and sorts required by API standards are:

0.6 – 1.8 for 16/30 sort, 0.4 – 0.8 for 20/40 sort, 0.3 – 0.6 for 30/50 sort.

From our analysed samples, the most close are which are collected from Aghires, Miorcani, Faget Scaune, Hudesti, Paltinoasa areas.

Morphometrical analysis, evaluation of roundness index – Ro, and sphericity index – Sf (Krumbein & Sloss, 1956), for global sample and for different sorts, was shown a large variation. For this reason, for all samples analysed by this study, indexes Ro = 0.1 – 1, and Sf = 0.1 – 1, so, the

whole interval. A direct proportional relationship was detected on increase of Ro (Sf) as increase grain-size class of quartz grains. The grains with more than 0.6 Ro index are variable between 30 – 60 % per sample, and maximum values was determined on samples from Hudesti, Miorcani areas, and in part from Valeni (Gura Vitioarei), Patarlagele (Valea Rea), and Aghires areas.

The API required values for morphological parameters are

- Ro = min. 0.6 for 16/30, 20/40, and 30/50 sorts,
- Sf = min. 0.6 for 16/30, 20/40, and 30/50 sorts.

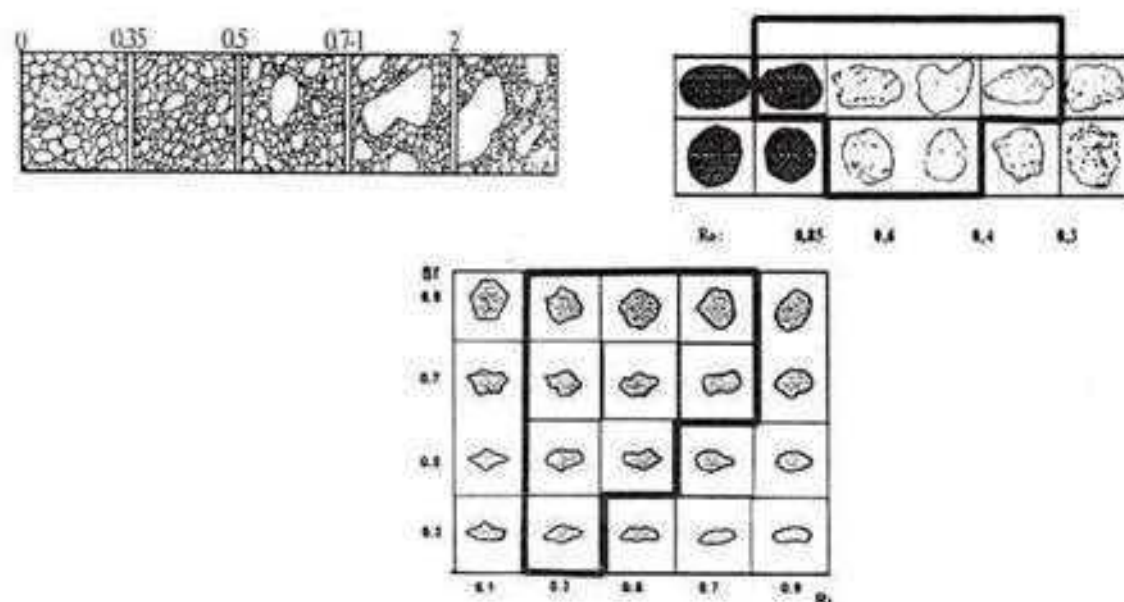
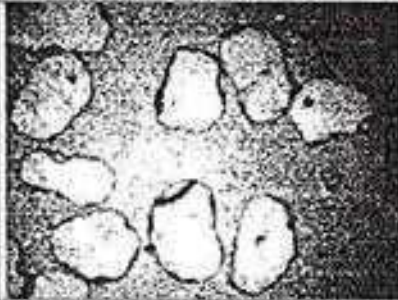
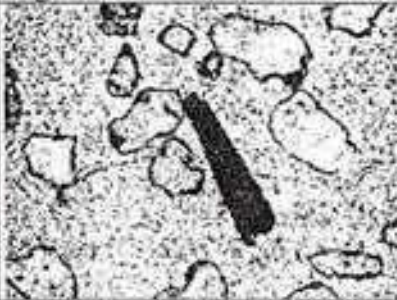
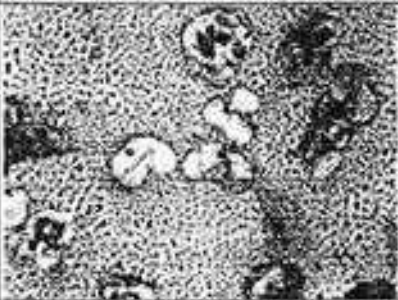


Fig. 1 Standard drawing showing the variability of morphological parameters: sorting, roundness and sphericity. The area marked with grey fill represent parameters qualities of Hulliburton sand and black line contour represent the morphological parameters of Pleasa sand, prepared in Romania.

The closest samples analysed are collected from Hudesti, Miorcani, Faget Scaune, Gura Vitioarei, Aghires areas.

The mineralogical and petrographical analyses put in evidence mineralogical assemblages dominated by quartz (over 90 %), feldspars, micas (biotite and muscovite), glaucony, heavy minerals, calcite, also bioclast and lithic fragments. Quartz grains are both mono-, and polycrystalline, with or without straight extinction, showing many inclusions (frequently solid, but some time as fluid state), oriented (corresponding systems) or unoriented microjoints, corroded surfaces, overgrowths (in Kliwa-type sandstones)

Hulliburton	Aghires	Miorcani
		
Quartz 94-98%	Quartz 90% Feldspar 2-3 % Micas 1-3 %	Opal, calcedony

The requirements by standards for quartz content are: min. 90% (API 56/1986), and min. 96% (API 58/1986). In our case, the closest samples are collected from Valeni, Patarlagele, Hudesti, Miorcani, Faget-Scaune, Jupanesti, Aghires areas, and in part from Humor area (Paltinoasa, and Plesa perimeters).

Our study shows that from all the identified quartz-sandy occurrences, both in exploration technological processes as well as in outcrop state, the closest samples, in respect to API standards requirements (as international reference system – Hulliburton sorts), are only the following occurrences:

- in the East Carpathians – Valeni (Gura Vitioarei, Copaceni), and Patarlagele (Valea Rea) areas,
- Pannonic Basin – Faget Scaune area,
- Transylvanian Basin – Aghires quarry.

Concluding, only by technological processes, as secondary, the API standard requirements could be realizable.

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INFLUENCE OF THE FLUID PHASE COMPOSITION ON THE MINERAL TRANSFORMATIONS IN Mn-METAMORPHOSED ORE FROM BISTRITA MTS, EAST CARPATHIANS.

HÎRTOPANU¹ Paulina

Bistrita Mountains form part of the Crystalline Mesozoic Zone of the East Carpathians which consists of superposed Variscan and Alpine Nappes, over thrusting eastwards over the Flysch Zone. The manganese ore is contained in Tulghes Group (Tg2 level), of the Variscan Putna Nappe, situated over Pietrosu Bistritei Nappe and supporting the thrusting of Rebra Nappe. All these Variscan nappes constitute in their turn, the Alpine Sub-Bucovinian Nappe, localised between Alpine Infrabucovinian Nappe in the East and the Alpine Bucovinian in the West.

The Tg2 level displays a varied lithology dominated by quartz-muscovite-graphite-chlorite-albite-calcite schists with some relics of biotite, almandine, hornblende, ilmenite and others. It is a polymetamorphic retrograde series, its evolution being marked by three successive metamorphic events (Caledonian, Variscan and Alpine) and complex thrustings and deformations. The very complicated tectonic setting enabled the opening of many pathways that permitted a good circulation of the metamorphic fluid, the compositions of which varied in time. Ionic mobility accompanied deformation episodes and hydrous infusion was high. The Tg2 level was initially an amphibolite rock, subjected to several repeated retromorph metamorphisms. The biotite, hornblende, garnet and plagioclase were altered by CO₂ fluids to carbonates. The carbonation is the first and the main retrograde metamorphic process that disturbs the Tg2 level, transforming the primary amphibolite into unhydrated rock, composed of carbonates, albite, quartz (M₂ event). Under the microscope one can see the relics of biotite, amphibole and garnet in the carbonates of different compositions; in many places the relics totally disappeared and only carbonates remained. The carbonation process was a dehydrated one. We suppose that the amphibolite facies of Tg2 level was initially in equilibrium with a fluid phase, any decrease of H₂O content of the fluid resulted in the partially destroyed of

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amphibole constituents by transfer and change reactions. The modal abundance of amphiboles was decreasing, because CO_2 was introduced into fluid. The big CO_2 source was the decarbonation reactions, which in the present case, involved rhodochrosite and Mn-silicates from Mn-ores. The decarbonation reactions of rhodochrosites from Mn-deposits secured big CO_2 volumes which are petrologically important. We suppose that the mobility of fluid was great and the fluids were predominantly CO_2 - H_2O solutions. The replacement of H_2O by CO_2 was realised by a volume to volume mechanism. One can say that small rhodochrosite bands present in Cambrian deposits, were potentially enough to dehydrate the initially amphibolite facies of Tg2 level, determining the appearance of different carbonates, albite, quartz - that is an anhydrous assemblage. In the M_1 event there were formed the muscovite and epidote, because the metamorphic fluid became rich in H_2O . In the M_2 event there were formed different chlorites and carbonates, imprinting to the Tg2 level rock the actual petrographic character. The Mn ores have a predominantly carbonate over silicate mineralogical composition, that means a great CO_2 fluid control in the carbonation and dehydration processes along the many stage of the whole history of the ore and the Tg2 level. But, substantial volume of CO_2 can be released through such discontinuous reactions if the silica volume in Mn-sediments was sufficient to allow most of the rhodochrosites to be consumed. The strong influence of the composition ($\text{CO}_2/\text{H}_2\text{O}$ ratio) of the fluid phase on the equilibrium temperature can be nicely demonstrated for the tephroite assemblages in Mn ore from Bistrita Mts. In an H_2O rich fluid the tephroite can form directly from rhodochrosite and quartz, such reactions occur in Swiss Alps. This mineral assemblage includes tephroite and quartz. The experimental data gives $T=420^\circ\text{C}\pm 10$ at $P=2000\text{b}$. In the Mn deposits from Bistrita Mts the tephroite-rhodochrosite assemblage is undersaturated and there is no quartz present. It is an anhydrous assemblage (no hydrous phases like manganese amphiboles have been detected), which experimentally forms at 581°C , in the presence of pure CO_2 . Because the P_{total} was much higher in the tephroite ore than in the experiment, it means that the formation reaction of tephroite from Bistrita Mts must be occurred at a T higher than 581°C . The rhodochrosite-tephroite assemblage is crucial for amphibolite facies of manganese deposits and the assemblages tephroite-quartz is crucial for the greenschists facies one. The mineral reactions were of decarbonation type, their temperatures were strongly influenced by composition of metamorphic fluid, that is, the decarbonation reactions took place at low temperature and high $X_{\text{H}_2\text{O}}$ -greenschists facies and at high temperature and high X_{CO_2} -amphibolite facies.

The Bistrita Mn-humites coexist with tephroite, rhodochrosite and rhodonite. Humites are more undersaturated than olivines because they have $R^{2+}/\text{Si} > 2$, but substitution of the excess R^{2+} is paired to $\text{OH}+\text{F}+\text{Cl}$. Leucophoenicite and Mn-humite family members are characterized by the absence of F, and significant F contents, respectively. The Mg humite have no leucophoenicite family equivalents and invariably contain substantial F substituting for OH. Variations in $\text{CO}_2/\text{H}_2\text{O}$ alone may explain the presence of the all known Mn-humite terms in the Mn-ores. The water rich conditions are required for manganese humites, and local variations in $X_{\text{H}_2\text{O}}/(\text{H}_2\text{O}+\text{CO}_2)$ and a_{CO_2} explain their various assemblages found in the Bistrita ores.

Stability of pyroxmangite is considerably extended under high $X_{\text{H}_2\text{O}}$ (>0.5) in the fluid phase and is rather insensitive to X_{CO_2} at high temperature ($>500^\circ\text{C}$) and low pressure (2Kb), this is consistent with the experimental data. Low and unbuffered X_{CO_2} in the fluid phase during amphibolite facies metamorphism (event M_1) and high $X_{\text{H}_2\text{O}}$ have inhibited the development of pyroxenes and determined instead the appearance of amphiboles. Frequent, the Bistrita pyroxmangite assemblages contains no carbonates, evidently suggesting a very low X_{CO_2} , the pyroxmangite being specific to the saturated assemblages. In the Borea deposit the pyroxmangite inverted to rhodonite via the well-known polymorphic transformation. Experimentally pyroxmangite recrystallizes to rhodonite at temperatures between 610°C and 640°C . Both pyroxmangite and rhodonite are preserved since with the entry of Ca in rhodonite, the inversion is no longer univariant but divariant. The replacement of pyroxmangite by mangangrunerite occurred at temperature of cca 550 - 600°C and P ca 5 - 6Kb and under an elevated $X_{\text{H}_2\text{O}}$, and at a constant and low f_{O_2} as no secondary magnetite was produced.

The evolution of calderite (?) to pyroxmangite-magnetite, the spessartine to spessartine-calderite and the spessartine to spessartine-grossularite requests beside a great P variation, a variation

of P_{CO_2} as well. The natural spessartine enriched in grossular component, that occur frequently in M_1 event, is specific to blueschists facies. Garnet resorption adjacent to homogeneous rims on zoned crossite indicates that such amphiboles grew at the expense of spessartine during hydration episode.

Johannsenite is altered to rhodonite and xonotlite by increasing $P_{\text{H}_2\text{O}}$. Pyroxene compositions are sensitive mainly to P and f_{O_2} , being strongly affected by metasomatic exchange, particularly when the reduction of Fe and Mn is involved. The freedom for Fe^{2+} and Fe^{3+} solid solution offered by the sodic amphiboles makes them potentially sensitive indicators of the local oxidation state that is itself, through its distribution within the minerals controlling the local f_{O_2} . The zonation and overgrowth often observed in pyroxenes and amphiboles are a record of changing metamorphic conditions, including and metamorphic fluid. The nonalkali amphiboles were replaced by sodic amphibole and the aegirine-augite were replaced by ferriwinchite. These relationships are explained in terms of model hydration reactions consuming cummingtonite, and components of aegirine-augite and producing sodic and calcic amphiboles.

The presence of manganiferous phyllosilicate assemblages (manganpyrosmalite, friedelite, schallerite, carvopilit, etc grown at the expense of anhydrous silicates) is a function of the fluid composition, i. e., the availability of chlorine and arsenic (in a very H_2O -rich fluid). The presence of CO_2 in these fluids is indicated by the retrograde formation of Mn-carbonates. The two additional fluid components Cl and As affect the stability relations between the hydrous phases and control the appearance of either friedelite group minerals or serpentine like minerals.

The stability field of stilpnomelane is reduced by increasing X_{CO_2} and X_{Mg} and is also a function of $a_{\text{K}}/a_{\text{H}}$ in the metamorphic fluid. If this value is smaller, stilpnomelane decomposes to chlorite, but if larger, it is replaced by biotite, and at very high value zussmanite forms (Miyano & Klein). The stability of K-bearing minerals are a function of the activity of potassium in metamorphic fluid. In Bistruta Mts stilpnomelane decomposed to a mixture of minnesotaite+chlorite (at lower K values in fluid) and to minnesotaite+biotite (at higher K value in fluid). The stability limit of stilpnomelane is a function of CO_2 in the metamorphic fluid. The addition of CO_2 as a component can be accomplished by the addition of a solid phase, siderite, to the equilibria. With increasing CO_2 the stability of stilpnomelane shifts to low temperatures. The stilpnomelane and chlorite are the two rival low grade sheet minerals.

The common occurrence of rhodochrosite with hausmannite and its rare association with manganosite are natural expressions of the f_{O_2} , f_{CO_2} and temperature dependence of the rhodochrosite stability field. Rhodochrosite is stable at high temperature only at low f_{O_2} . Metamorphic manganese oxide lens from BM have high inherited f_{O_2} values due to internal buffering, which causes gradients between them and Tg2 country rock containing iron oxides or graphite. Some of the manganese Bistruta ore were metamorphosed at f_{O_2} considerable higher than their enclosing rocks- it means that oxygen behaves as an inert component during metamorphism and considerable f_{O_2} gradients exist between adjacent layers.

The stability field of a manganiferous carbonate is a function of f_{O_2} , in addition to T , P and f_{CO_2} . Beneath the graphite surface CO_2 is reduced to graphite. The rare association graphite-rhodochrosite may justify this reduction reaction in Bistruta ore. At different but high values of P_{CO_2} rhodochrosite reacts to forms hausmannite, bixbyite, pyroluzite. The jacobsonite was formed by decarbonation-oxidation reactions from a carbonate precursor under unbuffered X_{CO_2} situation. By prograde oxidation the jacobsonite transforms to hausmannite. Pyrophanite was formed at lower values of f_{O_2} and with dominance of Mn^{2+} , whereas at high values of f_{O_2} and high T , where the Mn^{3+} dominantes, the spinel structure formed. The hausmannite and magnetite fields are of comparable size, but the hausmannite field is displaced toward more oxidizing conditions.

The occurrence of alabandite require a relatively reduced and sulfidizing environment, restricting $\log f_{\text{O}_2}$ and $\log f_{\text{S}_2}$ between 10^{-19} - 10^{-4} and 10^{-18} and 10^0 . These conditions were probably buffered throughout metamorphism by reaction of a sulphur-rich, carbonate-rich and oxygen-poor protolith, at quite different levels within the manganese deposit, at M_1 event.

Closely associated assemblages of diverse mineralogy from Bistruta Mn-ore suggest that the X_{Mg} and $X_{\text{H}_2\text{O}}$ rather than physical conditions of metamorphism are the decisive factors in forming

the observed phase diversity. The Bistrita metamorphosed Mn-rich mineral assemblages evolved under a variety of constraints. These include the diversity in the character of the sedimentary protolith and the nature of buffering of the fluid phase during metamorphism. The presence or absence of carbonates in the metamorphosed products do not indicate per cent the carbonate or noncarbonate character of the primary sediments. Carbonation of primary Mn-oxide/hydroxide sediments can take place during early or late diagenesis and complete decarbonation under unbuffered X_{CO_2} situation during metamorphism may yield carbonate-free assemblages. The absence of carbonate in these assemblages does not necessarily imply a noncarbonate precursor. Textural evidence from Mn-carbonate-oxide ores shows that during prograde metamorphism from a carbonate precursor progressively oxidized phases will appear via decarbonation-oxidation reaction, and that progressively reduced phases will appear from an oxide precursor with increasing temperature via deoxidation reactions.

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MINERAL RESOURCES OF ROMANIA – A SHORT QUANTITATIVE OVERVIEW

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INTRODUCTION

In this paper, only the identified mineral resources of Romania are presented. The term "identified mineral resources" has the same sense as the one used for classification of resources according to the degree of knowledge, elaborated and used by the Bureau of Mines. According to the actual UNO classification, officially used in Romania as well, the analyzed resources refer to the identified resources (from which prognosis resources are missing), valuable resources and exploitable reserves.

1. ENERGETIC MINERAL RESOURCES

In Romania both non-fuel and fuel mineral resources totalize around $2,24 \times 10^{10}$ tons conventional fuel (tef).

The non-fuel resources are represented by nuclear resources (uranium) and heat resources from hydrogeothermal systems (geothermal water).

The resources of radioactive ore are exhaustible and contain around 26 000 tons uranium, which represent the equivalent of $3,7 \times 10^8$ tef.

Geothermal water, a non-exhaustible resource, contains a much higher energy, estimated as equivalent to around 1×10^{10} tef, representing over 96% from the non-fuel resources of Romania.

The fuel resources are equivalent, as magnitude order, with the non-fuel ones, being estimated as around $1,2 \times 10^{10}$ tef.

The solid fuel resources (coals, coal shales, bituminous shales and sands) totalize $1,8 \times 10^{10}$ tons that is 9×10^9 tef. The most important amount (89%) is given by the coal resources (lignite, brown coal, pitcoal, peat, anthracite).

The fluid fuel resources (oil and natural gas) are more difficult to estimate because the available data are older, uncertain and sometimes contradictory. However, they are appreciated to represent the equivalent of $3,5 \times 10^9$ tef, which would be around 28% of the identified fuel resources and 17% of the identified energetic resources of the country. The amount of each type of resource within the energetic resources of Romania is shown in Fig. 1.

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2. NON-ENERGETIC MINERAL RESOURCES

The identified resources of non-energetic mineral substances, resulted following an approximate calculation are of the order 1.2×10^{11} tons. As liquid mineral substances resources (different types of water), gaseous (mofettic carbon dioxide) or even some of the solid ones (therapeutic muds and peats, ornamental rocks, sand and gravel) are expressed in cubic meters, it was necessary to approximate the equivalent in tons for each of them.

2.1 METAL RESOURCES

The metal resources are estimated as around 8.8×10^9 tons, representing only approximately 7% from the non-energetic mineral resources of Romania. They are usually classified in ferrous and non-ferrous resources.

The ferrous ore resources (iron ore, manganese ore, iron and manganese ore, iron ore with low content) reach almost 1.2×10^9 tons, representing only 14% of the total metal ore resources of Romania.

The non-ferrous ore resources constitute the wider part of the metal resources of Romania and involve most of the types: polymetal ores, copper-bearing ores (copper ore, copper-bearing pyrite, copper ore with low content), aluminium ores (bauxite, pyrophilitic shales, nephelinic sienites), gold and silver-bearing ores, sands with heavy minerals, as well as other ores of rare and disperse metals (molybdenum, bismuth, tungsten, mercury, lithium, berilium, boron, niobium and tantalum, titanium). They reach 7.6×10^9 tons.

Quantitatively speaking, among the non-ferrous ores resources, the most important are: sands with heavy minerals (3.5 billion tons), copper-bearing ores (2.7 billion tons) and aluminium ores (0.5 billion tons).

2.2 NON-METAL RESOURCES

The identified non-metal resources of Romania are obviously the most numerous and in the highest quantity from all the identified mineral substances resources. They reach 1.1×10^{11} tons and represent 93% of the non-energetic resources.

Waters, rocks, non-metal ores and industrial minerals, mofettic carbon dioxide, therapeutic peats and muds are considered as non-metal resources.

The water resources of Romania, both surface water and groundwater, reach over 4.9×10^{10} m³/year, with a non-uniform geographical distribution, on types and geological structures.

The **surface water resources** (rivers, lakes, River Danube) or the hydrologic potential (the multiannual average volume) is around 3.6×10^{10} m³/year, from which natural lakes totalize only 1×10^9 m³/year. Even if this quantity seems big enough, if it reported to the whole population of the country (around 23 million inhabitants), we come to 1565 m³/year/inhabitant, which represents only approximately one third of the average in the European countries.

The **groundwater resources** include industrial water, drinking water (including the bottled non-carbonated water) and water used for irrigations, as well as mineral waters (drinking, balneo-therapeutic, thermo mineral - therapeutic waters). Groundwater resources (speaking only of exploitable resources) reach 1.3×10^{10} m³/year, representing almost one third from the surface water resources. Taking into account the dynamic reserves, we would reach a much higher value that is 3.2×10^{11} m³/year.

The raw material resources used in constructions (as aggregates for concrete, road stones and railroad ballasting, ornamental rocks) are around 1.5×10^{10} tons, representing almost 24% from the solid non-metal substances resources. These resources have been identified and calculated only in the zones where there are consumers and taking into account the demand over a reasonable period of time.

The following mineral substances are classified as raw materials: ornamental and industrial alabaster, ornamental aragonite, basalt and basaltic scoria, diabase, ornamental, industrial and construction andesites, industrial construction dacite, porphyry, ornamental and construction granite, ornamental and construction granodiorite, diorite, amphibolite, serpentinite, green shales, mica-schist, gneiss, quartzite, marble, ornamental and industrial limestones, travertine, ornamental silicolite, sandstones, sand for construction materials, sand and gravel.

The most important identified resources are: industrial limestone (7,8 billion tons), sand and gravel (3,6 billion tons), industrial and construction andesite (0,7 billion tons), diabase (0,4 billion tons) and construction granite (0,3 billion tons).

Non-metal ores and industrial minerals resources (halite, potassium salts, graphite rock, sulphur rock, gypsum, anhydrite, celestine, barite, calcite, rocks with kyanite, wollastonite, mica, pegmatite, feldspar pegmatite, rocks with talc, rocks with asbestos, quartz, perlite, nepheline, nepheline, serpentine, chalk, dolomite, marl, loess, ordinary clay, refractory clay, kaolinized rocks, kaolinized clay, kaolinized sandy clay, kaolinized sand, siliceous sand, industrial tuffs, bentonite, diatomite, phosphatic rocks, silex balls, coloured earths) of Romania are estimated as around $4,6 \times 10^{10}$ tons. They represent approximately 76% of the solid non-metal resources of the country.

The most important identified resources are: halite (39 billion tons), siliceous sand (2,2 billion tons), dolomite (1,8 billion tons), ordinary clay (1,3 billion tons), marl (0,8 billion tons) and gypsum (0,4 billion tons).

Other non-metal substances, which constitute resources, identified following geologic research, are mofettic carbon dioxide (11,4 million m^3 /year) and therapeutic peat and muds (22,1 million m^3). Their amount in the total non-metal resources is neglectable (0,03 %).

Figure 2 shows the distribution of non-metal resources on the main groups of mineral substances.

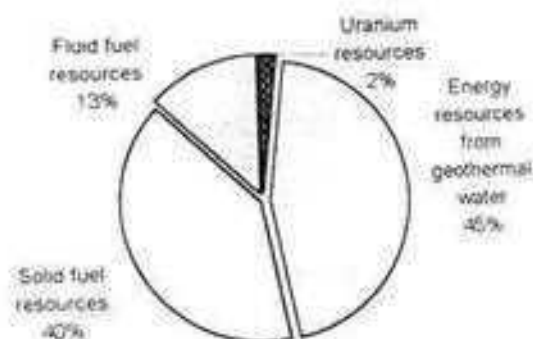


Figure 1 - The percentage of resources groups within the total energetic resources of Romania

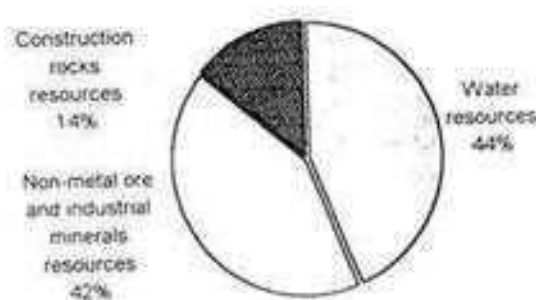


Figure 2 - Distribution of non-metal resources on the main groups of mineral substances

3. CONCLUSIONS

In Romania there have been identified, estimated, renewable resources of water (drinking, industrial, irrigation, non-carbonated), mineral water (drinking, balneo - therapeutic and thermomineral - therapeutic), thermic energy from geothermal water, sand, sand and gravel, mofettic carbon dioxide, therapeutic mud and peat.

The identified, estimated and renewable resources are numerous. Some of them like salt (39 billion tons), lignite (16 billion tons), construction rocks (15 billion tons), oil and gas are in the order of tens of billion tons. The undiscovered resources for many rocks are, practically, un-exhaustable. Other resources (sand with heavy minerals, copper-bearing ores, siliceous sand, dolomites, ordinary clay, iron ore) exceed one billion tons. Most of these resources are between 1 million and 1 billion tons, while some of them (celestine, wollastonite, asbestos, coloured earths, silex balls) are in low quantities (less than 1 million tons).

MINÉRALISATIONS MÉTAMORPHISÉES DU GROUPE TULGHEȘ (ORDOVICIEN INFÉRIEUR) DANS LA PARTIE MÉRIDIONALE DE LA ZONE CRISTALLINO-MESOZOÏQUE DES CARPATES ORIENTALES

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Dans la Zone cristallino-mésozoïque (ZCM), le Groupe Tulgheș - Tg (Ordovicien inférieur, métamorphisme régional à la fin de celui-là - Mureșan, 2000 - déroule dans le faciès des schistes verts, de type barrovien - Kräutner et al., 1975) est divisé en quatre formations lithostratigraphiques - Tg 1, Tg 2, Tg 3, Tg 4 (Bercia et al., 1976; Vodă, 1980; Kräutner et al., 1992, Arch. I.G.R.). Le Tg est logé dans les socles métamorphiques des Nappes subbucovinienne et bucovinienne - alpines (définies comme des unités autrichiennes par Săndulescu, 1967, 1975, 1976). On a démontré (Krautner, Bindea, 1996; Mureșan, 1996, 2002) que dans le socle cristallin de la dernière unité il y a une pile tectonique de nappes de charriage qui englobent exclusivement des successions partielles du Tg. Conformément à notre modèle, il s'agit de cinq nappes de charriages - Groupe des Nappes de Giurgeu (GNG), présentées au-dessous. Nous mentionnons que les épimétamorphites du Tg et les minéralisations concordantes (syngénétiques), associées, ont des pendages générales vers le NE.

1) MINÉRALISATIONS MÉTAMORPHISÉES (MM) DE LA NAPPE DE CAPU CORBULUI (NCC). La NCC (l'unité inférieure du GNG) englobe la Succession de type Capu Corbului (plus de 100 m d'épaisseur), formée par la Tg 1 (des quartzites) et la Tg 2 (des quartzites noirs et des schistes sériciteux à graphite). Dans le secteur Corbu-Capu Corbului et au sud de Tulgheș (dans le forage 1 Hagota - l'interv. 939-994 m), il y a des petites lentilles concordantes de minéralisations hydrothermal-sédimentaires manganésifères métamorphisées (principalement, rodonite - Ro, rodocrosite - Rds, dannemorite), associées aux quartzites noirs de la Tg 2 (comme les autres minéralisations manganésifères de la Tg 2 - Ciocănești, Iacobenii, Dealul Rusului etc - connues dans la partie centrale de la ZCM).

2. MM DE LA NAPPE DE ȘUMULEU (NSu). La NSu inclut la Succession de type Șumuleu - SSu (plus de 1000 m d'épaisseur), représentée par la Tg 4 (schistes sériciteux à chlorite, schistes sériciteux-chloriteux à graphite, roches blastodétritiques, quartzites noirs, schistes verts). Les MM sont représentées par quelques couches lentilliformes de minéralisations hydrothermal-sédimentaires de sulfures - de type Kuroko (MHSSK), riches en pyrite - Py (à la quelle s'ajoutent, en petites quantités, quartz - Qu, calcopyrrite - Cpy, sphalérite - Sph et galénite - Ga), rencontrées dans quelques forages (au S de Tulgheș): 5 Vallée Putna (434,37-437,00 m - minéral massif) et 10 Pârâul Bălaj (573,00-581,50 m - surtout minéral disséminé).

3. MM DE LA NAPPE DE SADOCT (NSa). La NSa est constituée par la Succession de type Sadocut (SSa), représentée par la Tg 3, des métavolcanites rhyolitiques (métatufs et coulées de laves), roches blastodétritiques, schistes sériciteux à chlorite, quartzites etc. La Tg 3 est bien connue dans les nombreux forages, effectués dans la région Tulgheș-Vallée Putna (la partie SE de la Demi-fenêtre tectonique Tulgheș). Les MM de la SSa sont représentées seulement par des MHSSK. Nous mentionnons que, plus au nord (dans la partie centrale de la ZCM), la SSa, de la NSa, devient plus large lithostratigraphiquement et loge (Mureșan, 2002) les gisements de sulfures (de type Kuroko) d'Isipoaia, de Leșul Ursului, de Crucea, de Fundul Moldovei etc. **a) La région Tulgheș-Vallée Putna.** Là, la SSa (plus de 400 m d'épaisseur) abrite une importante MHSSK, (connue dans quelques affleurements - par exemple, Pârâul Filler et Pârâul Darvaș - et dans les forages 7, 9, 10, 24, 28, 29, 47, 79, 80, effectués par "GEOLEX" S.A. (Airinei, 1988-1997, Arch. GEOLEX, Miercurea Ciuc; Mureșan, Mureșan, 1988-1991, Arch. I.G.R.; Mureșan, 1992-1997, Arch. I.G.R.). Là, dans un mince paquet terrigène (surtout des schistes chloriteux à séricite quartzeux), intercalé dans l'horizon inférieur (riche en métavolcanites rhyolitiques) de la SSa, est logé le Niveau à sulfures Baratu Mare - NSBM (nom donné par Kräutner & Bindea, 1996) - type Kuroko, stratiforme (1-4 m d'épaisseur, connu en profondeur dans les forages dans un aéra de quelques kilomètres carrés), parfois

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accompagné, en proximité, par quelques minces intercalations de MHSSK. Les principaux minéraux métallifères sont représentés par Py (dominante), Cpy, Sph, Ga, mispikel - Mis, tétrahédrite - Tet, il y a aussi des minéraux non-métallifères surtout Qu (formant, fréquemment, des masses mosaïquées - des gels siliceux métamorphisés), chlorite - Cl (fréquemment délessite - Del), séricite - Se, carbonates ferifères (ankérite?), calcite - Ca et, rarement, albite - Ab. Le minerai massif, plus répandu (le minerai disséminé est rencontré surtout dans les MHSSK satellites), a fréquemment une structure porphyrique (des individus millimétriques de Py, logés dans une masse de sulfures finement grainulaire - principalement pyriteuse), la texture est surtout rubannée (paleostratifiée), due aux alternances de minces couches (millimétriques ou centimétriques) riches en sulfures avec celles riches en Qu ou riches en Cl et Se. Les relations actuelles entre les sulfures reflètent le comportement du minerai primaire au cours de la recristallisation métamorphique, c'est-à-dire entre le minéral «dur» dominant (Py) et les minéraux «mous» (Sph, Ga, Cpy, Tet), qui occupent les espaces irréguliers entre les granules de Py, ainsi que dans leurs fissures (les termes «dur» et «mou», sensu Ramberg, 1960). Parfois, autour de la Py, il y a des «ombres de pression» («pressure shadows»), formées, habituellement, par les individus allongés de Qu. Nous avons récemment argumenté (Mureșan, 2002) que le NSBM a la même position lithostratigraphique que celle de l'Horizon à sulfures Leșul Ursului (les Zones I et II Leșul Ursului), du Membre Leșul Ursului, séparé dans la Tg 3 des Monts Bistrița (Kräutner et al., 1992, Arch. I.G.R.).

b) Dans le versant gauche de la Rivière Bicaz (environ 2 km au SE de Bicaz Chei, il y a une petite apparition de MHSSK, de minerai massif (Py, Sph, Ga, Cpy, aux quelles s'ajoutent bornite, pyrrotine, Tet, Mis, tennantite, Qu, carbonates - Vodă, 1976, 1977, Arch. I.G.R.), qui, dans notre opinion, appartient à la SSa, englobée dans la NSa, (serree tectoniquement en ce point entre les roches de la Tg 4 de la SBe).

c) Près de Prisecani (environ de 4 km au ENE de Tulgheș), il y a quelques petites couches lentilliformes concordantes de MHSSK, logées soit dans les métatufs rhyolitiques à intercalations des épiclastites (Pârâul Argintăria), soit dans les schistes quartzeux sériciteux à chlorite (Pârâul Popii). Le minerai disséminé et le minerai massif (moins répandu) sont constitués principalement par la Py, à la quelle s'ajoutent Cpy, Mis (dont la fréquence, est caractéristique pour ces MHSSK), Sph, Ga, Tet et, aussi, des minéraux nonmétallifères: Qu (surtout), Cl (fréquemment Del), Se, Ca, Ab et, très rarement, fluorine (Pârâul Popii). Ces MHSSK sont logées dans la Tg 3, de la NSa.

4) MM DE LA NAPPE DE BELCINA - NBe. La NBe est constituée par la **Succession de type Belcina SBe** (plus de 1500 m d'épaisseur), représentée par la **Tg 4** - qui a une composition pétrographique similaire à celle de la SSu, mais les schistes verts (SV) sont plus répandus. Dans la SBe, sont logés des corps intrusifs de métagabbros et de metarhyolites (Porphyroïdes de Mândra - PMd). Les MM sont représentées (Mureșan et al., 1972) par des minéralisations hydrothermales-sédimentaire ferifères et/ou manganésifères (MHSFe/Mn) et par des minéralisations hydrothermales de sulfures métamorphisées (MHSuM).

A) Les MHSFe/Mn sont fréquemment associées à des SV (ce qui montre une connexion génétique vis-à-vis de l'activité magmatique basique synchrone avec la déposition primaire de la Tg 4), développées surtout dans le Membre Pârâul Crucii (dans les Horizons Șipoș et Vârșăraia), de la Tg 4 (de la Sbe).

a) Près de Secu (Pârâul lui Ignat), il y a des petites apparitions manganésifères, lentilliformes (associées à des SV), constituées (Jakab, 1990, Arch. GEOL. EX., Miercurea Ciuc), principalement, par Ro, Rds, spessartine - Spe).

b) Nous mentionnons les petites lentilles manganésifères associées à des quartzites noirs de la Tg 4 (de la Sbe) par exemple, à l'est de **Piatra Serisă** (environ 4 km au NO de Bălan) et dans la **partie moyenne de la Vallée Huruba** (affluent gauche supérieur de la Rivière Bistrițioara) - là, mises en évidence par Mureșan & Mureșan (1977 a). A la surface, les deux apparitions sont transformées en oxydes de Fe et de Mn.

c) Dans Dealul Ghermanului (environ 1 km au NO de Bicaz Chei), il y quelques lentilles (plus de 1000 m de longueur, quelques m d'épaisseur) ferifères, faiblement manganésifères (mises en évidence par Rîșă et al., 1965, Arch. I.G.R.), logées dans les SV et représentées par des roches quartzéuses hématitiques à magnétite - Mt et Spe, ces minéralisations sont attribuées par nous au type Lahn-Dill.

d) A l'O du Sommet Piatra Roșie (5 km au N de Tulgheș), il y a des petites lentilles de quartzites hématitiques (de type Lahn-Dill), logées dans les SV.

e) Au N de Valea Frumoașă (auparavant, la localité "Sângerăasa"), dans Pârâul Hujan et Ighabul lui Milui (des petits affluents

gauches de la Rivière Bistricioara), il y a des petites lentilles concordantes ferrières (Chelărescu, 1938), riches en Mt, à la quelle s'ajoutent carbonate ferrière, hématite - Hem et Qu, il y a aussi de petites quantités de Py, Cpy, thuringite, Del, pénnine, clinocllore et stilpnomélane. Nous attribuons cette MM (aussi associées à des SV) au type Lahn-Dill. **D) Près de Săndominic** (environ de 20 km au SSE de Gheorgheni), dans les SV du Horizon Sipoș, il y a de petites lentilles de quartzites à Hem et Mt de type Lahn-Dill (Krautner et al., 1992, Arch. I.G.R.). **B) Les MHSuM**, zinco-plombifères (argentifères subordonnées) constituent des filons (jusqu'à 1 m d'épaisseur, longueur et profondeur connues - quelques décimètres), des réseaux filoniens et des impregnations (surtout pyriteuses), logées dans les corps intrusifs des PMd et, rarement, dans les métamorphites terrigènes avoisinantes. Parmi ces MHSuM de la région Tulgheș, nous mentionnons celle de Paltin (la plus importante), celles du bassin de la Vallée Barasău (Pârâul cu Linia, Pârâul Argintăriei, Pârâul Păvăloanei, Pârâul Alunului), Pârâul Săngeroasa, Pârâul Tisaș, Pârâul Borviz, Pârâul Băii Mici (là, dans la MHSuM, logée aussi dans les PMd, à côté de Py, Sph, Ga, Qu, Cl, s'ajoute là chloritoïde) et les apparitions de Valea Muncelul (affluent gauche de Bistricioara - au ONO de Tulgheș). Le minerai des MHSuM, de la région Tulgheș, est constitué (Chelărescu, 1937, 1953, Arch. I.G.R., București, Mureșan, Mureșan, 1977 b), de manière prédominante, par Sph et Ga, auxquelles s'ajoutent, secondairement, Py, Cpy, Tet, proustite - Prs, pyrargirite, associées à Ca, dolomite et Qu (une partie du Qu et du feldspath proviennent de PMd). Le minerai des ces MHSuM montre le métamorphisme régional subbi (en même temps avec celui du Tg) la présence de la chloritoïde (Pârâul Băii Mici), l'existence de la schistosité (surtout dans les variétés galenitifères), parfois microplissée, les déformations subies par le Ca (ses clivages sont fréquemment courbés) et par le Qu (extinction ondulatoire), la structure porphyrique dans le minerai pyriteux, la bréchification fréquente de la Py (parfois, de la Sph), l'absence des géodes primaires, l'ordre de la grandeur de l'âge du minerai (570-610 m. a. - données obtenues par la méthode Pb/Pb Houtermans - Vâjdea, Anastase, 1971) vis-à-vis de l'âge ordovicien inférieur du Tg. Les MHSuM "de type Paltin" (notion proposée par Mureșan & Mureșan, 1977 b) sont liées par l'activité hydrothermale du volcanisme rhyolitiques qui a engendré les PMd. Plus au S, il y a une concentration similaire plombo-zincifère, dans le secteur Gherpotocul Mic (affluent gauche de la Vallée Belcina), logée aussi dans les PMd (là, il y a aussi une minéralisation hydrothermale, post-métamorphique - génétiquement liée au Massif alcalin Ditrău - Jakab, Popescu, 1982, Jakab, 1982, 1998).

5) MM DE LA NAPPE BĂLAN - NBa. La NBa englobe la Succession de Bălan - SBa (la NBa et la SBa selon Krautner & Bindea - 1996, les données géologiques selon Krautner et al., 1970 & 1972, Arch. I.G.R.), constituée par la Tg 3 (schistes sériciteux à chlorite quartzeux, quartzites, metavolcanites rhyolitiques et des importants MHSSK - les gisements de Bălan, Fagul Cetății et Mediaș, formés par des lentilles stratiformes de minerai massif et disséminé. Parmi les minéraux constitutifs, il y a: Py (prédominante), Cpy, Sph, Ga, Tet, bournonite, Mis, jamesonite, Mt, Hem, cassitérite, Qu, Cl, Se, carbonate ferrière, stilpnomélane, Ab, baryte) et la Tg 4 (des roches terrigènes à intercalations de SV et de metabasites et une faible MHSSK d'Arama Oltului - surtout pyriteuse). Dans la partie supérieure de la Vallée Hărlăgia (environ à 30 km, au NO de Tulgheș), affleure une couche (presque 3 m d'épaisseur, 4 m, longueur visible) de MHSSK (Mureșan, Mureșan, 1977 a), pyriteuse, zinco-plombifère, secondairement cuivrière et argentifère (principalement, ayant les mêmes caractéristiques que le minerai massif du NSBM), logée dans un paquet de schistes chloriteux à séricite et calcite. Cette MHSSK est située dans la partie inférieure connue de la SBa (au-dessus du plan de charriage inférieur de la NBa - situation démontrée par les forages et les travaux miniers d'exploration), qui, là, constitue un petit lambeau de charriage (selon la Carte 1 : 200.000 de la ZCM, rédigée par Krautner & Bindea, 2000, Arch. I.G.R.). Les minéraux métallifères sont représentés par: Py 32-77 %, Sph 1,5-20 %, Ga 1-9 %, Cpy 0,40-2,60 %, sporadiquement pyrrhotine, Tet, Prs, marcassite. Il s'ajoute Qu (surtout), Cl (surtout Del), rarement Ab.

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LA NAPPE ALPINE DE RARĂU (STRUCTURE INTERNE; MINÉRALISATIONS) DANS LA ZONE CRISTALLINO-MÉSOZOÏQUE DES CARPATES ORIENTALES

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La Nappe de Rarău (NRa), dont la partie inférieure est constituée de mesométamorphites, se développe classiquement dans le **Compartiment Tisa-Ciuc (CTC)**, le segment le plus septentrional et le plus étendu de la **Zone cristallino-mésozoïque (ZCM)**. Là, la NRa constitue quelques lambeaux de charriage dont les plus importants sont, au sud, le **Lambeau Hâghimaş (LHg)** et, au nord, le **Lambeau Rarău (LRa)**. La NRa est charriée sur les épimetamorphites ordoviciennes du Groupe Tulgheş (Tg).

A) Aperçu historique. La NRa (qui a reçu plusieurs noms, dont on utilise aujourd'hui celui de « **Nappe de Rarău** »), mise en évidence par Popescu-Voiteşti (1929, 1942), a été acceptée par Streckeisen (1934), Krautner (1938), Băncilă (1941, 1958), Dessila-Codarcea (1967), Mureşan (1967, 1968, 1976, 1984), Săndulescu (1967, 1968, 1974, 1975), Pitulea (1967), Popescu-Voiteşti et Mureşan, qui ont affirmé l'âge alpin de cette nappe, lui ont attaché, outre les mesométamorphites, la couverture mésozoïque transgressive sur celles-ci. Tous les autres auteurs ont soutenu la formation anté-alpine (hercynienne) de cette unité, affirmant qu'elle est constituée uniquement de mesométamorphites. Săndulescu a toujours renfermée la NRa, comme unité hercynienne, dans la partie supérieure du socle métamorphique de la **Nappe bucovinienne (NBu)** - autrichienne. Dans ce socle, sous la NRa, il y a une pile de **Nappes de charriages plus anciennes que le Massif alcalin Ditrău - NAMAD** (Balintoni, 1981, 1997, Balintoni et al., 1983, Mureşan, 1981, 1983, 1996) : **Nappe de Rodna** (Groupe Rebra - précambrien), **Nappe de Negrişoara** (Groupe Negrişoara - précambrien), **Nappe de Porphiroides de Pietrosul** (précambriennes ?) et les **Nappes du Tg**. La NRa a pris naissance par cisaillement post-métamorphique (Săndulescu, 1967, 1975, 1976, 1984, Mureşan, 1967, 1976, 1984).

B) Principaux arguments pour l'âge alpin de la NRa. 1) Les dépôts mésozoïques autochtones des régions Rarău et Hâghimaş couvrent transgressivement les mesométamorphites précambriennes de la NRa. En quelques endroits, les dépôts mésozoïques (surtout triasiques) reposent d'une manière apparemment normale sur les épimetamorphites du Tg, mais, dans les cas étudiés par nous (dans la « **Crête de Dâmuc** », située immédiatement à l'ouest du LHg), ces dépôts sont soit situés transgressivement au-dessus des minces plaques de mesométamorphites, soit reposent directement sur le Tg, en ce cas leur base étant brechiifiée. Ces deux aspects indiquent la présence de petits lambeaux de la NRa. A notre avis, la dernière situation est rencontrée aussi dans la partie orientale du LRa. La, par exemple, dans le secteur Est Breaza-Sud Lefele, Mutihac (1966) et Săndulescu (1973, 1976) ont représenté une bande allongée NO-SE (plus que 6 km en longueur), faite en épimetamorphites du Tg (à la base) qui supportent directement soit les dépôts détritiques verfeiens, soit les dolomites anisiennes, soit les Couches à jaspes (Ladinien inférieur), pour nous, ça signifie que le contact directionnel entre les dépôts triasiques et le Tg est de nature tectonique - le plan

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de charriage de la NRA. 2) Dans le secteur de la Cime Obcina-Fagul Inalt, la NRA est charriée sur l'aurole de contact (cornéennes), de la partie NE du Massif alcalin Ditrău - MAD (anté-autrichien, parce que les processus endogènes liés à la mise en place du MAD se sont achevés pendant l'Aptien – cf. Kräutner & Bindea, 1998, bases sur les données géochronologiques. 3) Selon Podoleanu et al. (1989, 1990, 1992 – Arch. I.G.R.), les contenus en U et Th des roches mésométamorphiques (de la NRA), tout près du MAD, se situent à un niveau normal; en revanche, dans les épimétamorphites du Tg. proches du MAD, les mêmes éléments présentent des valeurs très élevées, montrant l'influence géochimique de ce massif alcalin. **En conclusion**, la NRA est alpine, ne pouvant pas être plus ancienne que l'Aptien (les points 2 et 3), ça signifie que les dépôts triasiques, jurassiques et néocomiens (transgressifs sur les mesométamorphites de la NRA) reviennent sûrement à la NRA.

C) Éléments constitutifs de la NRA. Selon notre conception, la NRA englobe un échafaudage de plusieurs entités. 1) **Les mésométamorphites du Groupe Bretila (Br)** – précambriennes, représentées de micaschistes, amphibolites, gneiss leptiniques quartzo-feldspathiques, gneiss ocellés blancs. Dans la partie inférieure de la NRA, les roches du Br sont intensivement laminées et diaphorisées (**BrLam**) qui accompagnent le plan de charriage de cette unité (Mureșan, 1967, 1976). Puis, les BrLam ont été regroupées soit dans la Nappe de Chiril - NCh (dans le cas du L.Ra - Nedelcu, 1980), soit dans la Nappe de Bălaj - NBj (dans le cas du L.Hg - Bindea et al., 1995, Kräutner, Bindea, 1996), charriées sur le Tg et développées sous la NRA. Săndulescu (1984) et Vodă & Balintoni (1994) ont souligné que les roches des ces unités proviennent du Br. Mureșan (1998), basé sur la transition graduelle entre les BrLam et les mésométamorphites non-laminées, a soutenu que les BrLam, renfermées dans la NCh et dans la NBj, appartiennent en réalité à la NRA. 2) **La Formation de Dâmuc** – ordovicienne – constitue de petites apparitions (dans la Crête de Dâmuc) formées de schistes muscoviteux-graphiteux à grenat (Mureșan et al., 1974), transgressifs sur les roches du Br. 3) **La Nappe des Granitoïdes de Hăghimaș (NGHg)** – pré-triasique (Mureșan, 1998), charriée sur le Br, englobe des granitoïdes précambriennes, mésométamorphisées et gneissifiées simultanément (pendant le Précambrien) avec la pile du Br (Mureșan et al., 1975, Kräutner et al., 1976, Mureșan, Mureșan, 1980). 4) **La couverture du Permien supérieur** (la Formation des Breches de Hăghimaș - Mureșan, 1970) et **du Mésozoïque bucovinien** – triasique-jurassique-néocomien (en dehors de Wilflysch – voir D), transgressive sur les mesométamorphites.

D) La Nappe du Wildflysch de Perșani-Hăghimaș (NWfyPelHg) (autrichienne) se dispose au-dessus de la couverture mésozoïque de la NRA et est constituée de 1) **Le Wildflysch - Wfy** (barremien-albien – Săndulescu, 1975), auquel s'associent les nappes transylvaines (NT) suivantes (de bas en haut). 2) **La Nappe d'Olt (NOt)** – intra-aptienne, bien représentée, dans le L.Ra, par les roches ultrabasiques de Breaza, qui reposent sur le Wfy (Săndulescu, Săndulescu-Russo, 1981, Săndulescu, 1973, 1984). 3) **La Nappe de Perșani s.s. (NPe s.s.)** – intra-aptienne, constituée, dans le Synclinal Rarău (Săndulescu, 1976, 1984), quelques petits lambeaux de recouvrement, faites en dépôts triasiques. 4) **La Nappe de Hăghimaș (NHg)** – intra-albienne, renferme (Săndulescu (1967, 1968, 1969, 1975, 1984) des dépôts du Jurassique supérieur et du Crétacé inférieur. 5) Dans les Monts Perșani, il y a encore une unité transylvaine: **la Nappe des dépôts calcaires et du Flysch à orbitolines** » (les deux entités du l'Aptien supérieur), charriée sur le Wfy (cette alternative tectonique a été discutée par Săndulescu – 1984 et Balintoni – 1997, mais sans être adoptée finalement par les deux auteurs).

E) Arguments pour le charriage du Wildflysch. Auparavant, Preda (1940) a montré que "la Série noire" (en fait, le Wfy d'aujourd'hui) est charriée sur les métamorphites et les dépôts mésozoïques autochtones des Synclinaux Hăghimaș et Rarău. Le charriage du Wfy des Monts Perșani a été soutenue par Popescu (voir les Feuilles géologiques, à l'échelle 1:50.000, Perșani – Popescu, 1970) et Racoș - Popescu et al., 1976) et Vodă & Vodă (1985). Balintoni (1997) a présenté une argumentation en faveur de cette conception, en même temps, soutenant que, pendant son charriage, le Wfy a transporté solidairement les NT. Voici quelques arguments de cet auteur qui montrent qu'à la base actuelle du Wfy il y a un plan de charriage. 1) Directionnellement, à petites distances, on peut constater que la partie basale du Wfy est représentée par différents termes lithologiques, transversalement, il y a une asymétrie lithofaciale évidente entre la partie inférieure orientale et celle

occidentale du Wfy (les deux situations sont décrites dans le Synclinal Hăghimaş par Săndulescu, 1975). 2) Assez fréquemment, dans la partie inférieure du Wfy, il y a des brèches tectoniques, qui renferment tant des éléments métamorphiques du Br et du Tg, que de la couverture mésozoïque bucovinienne (situation observée tant dans la région Hăghimaş – Săndulescu, 1975, que dans les Monts Perşani – Vodă & Vodă, 1985) 3) La matrice argileuse du Wfy présente une foliation, montrant les déformations tectoniques subies pendant le charriage de celui-ci. Nous précisons que, en dépit de ses arguments, Balintoni n'a pas représenté la Nappe du Wfy sur la Carte tectonique des Carpates Orientales, annexée à son ouvrage de 1997. Compte tenu tant de tous les arguments exposés ci-dessus, que la situation du Wfy des Monts Perşani, nous sommes totalement d'accord avec le charriage du Wfy par rapport à la couverture mésozoïque bucovinienne. Ainsi, la partie basale primaire du Wfy n'est pas connue. Puisque les NT sont étroitement liées à la déposition du Wfy (celui-ci a des clippes sédimentaires provenant des formations constitutives de ces nappes – Săndulescu, 1975, 1984), il faut admettre que la NWfyPeHg englobe aussi les NT, étant, donc, une unité transylvaine composite. Par conséquent, le Wfy ne peut pas être renfermé dans la Série mésozoïque bucovinienne, parce qu'entre les deux entités il y a un plan de charriage. La NWfyPeHg appartient à la Nappe bucovinienne, parce qu'elle a été transportée pendant le charriage alpin de la dernière unité (voir F II 3).

F) Étapes principales de la formation de la NRa. Les mésométamorphites du Br ont été reconnues aussi bien dans la Nappe subbucovinienne (NSBu) que dans les Nappes infrabucoviniennes (NIBu). Là, on a considéré (Balintoni, 1981, Balintoni dans Săndulescu et al., 1981, Balintoni et al., 1983) que ces roches représentent la NRa, englobée comme unité pré-alpine dans les socles métamorphiques des nappes mésochrétacées mentionnées ci-dessus. 1) Dans la NSBu, les roches du Br sont charriées sur le même échafaudage des NAMAD (voir A) existantes dans le socle de la Nbu et supportent une couverture triasique-jurassique en faciès subbucovinien (Săndulescu, 1972, 1975, 1984). 2) Dans quelques NIBu, sur le Br se disposent transgressivement des épimétamorphites siluriennes, dévoniennes et du Carbonifère inférieur (Ilieşcu, Kräutner, 1975, 1978, Ilieşcu et al., 1976), en ces cas, on ne connaît pas des dépôts mésozoïques. Très rarement, sous le Br sont connues les métamorphites des NAMAD (par exemple, dans le socle la Nappe infrabucovinienne de Iacobi – Balintoni et al., 1982; Vodă et al., 1999). Les dépôts mésozoïques sont de type infrabucovinien (Săndulescu, 1972, 1975, 1984) et englobent surtout des termes du Trias et du Jurassique, ceux du Crétacé inférieur étant très rarement connus. Fréquemment, sous le Mésozoïque, il y a des formations permienues. 3) La NWfyPeHg manque dans les NIBu et la NSBu.

I. Pour expliquer la présence de la NRa (comme unité autrichienne) dans toutes les nappes du système bucovinien, il est besoin d'une reconstitution rétrotectonique, déroulée en deux étapes, dans l'hypothèse que ces nappes ont leurs origines quelque part à l'ouest de ZCM. 1) Ainsi, dans la première étape, la Nbu devient l'unité autrichienne la plus occidentale, à l'est, suivent la NSBu et (plus à l'est) les différentes unités infrabucoviniennes. 2) La deuxième étape, ainsi que d'autres données nous révèlent que a) à l'origine, le Wfy s'est formé plus à l'ouest, dans le domaine de l'Océan téthysien transylvain (origine soutenue par Balintoni, 1997), là, après le début de la sédimentation du Wfy, a commencé (en différentes étapes) le mouvement (vers l'est) des ensembles mésozoïques transylvains (sédimentaires et ophiolitiques – formes aussi dans le domaine téthysien – Săndulescu, 1984) sur le Wfy, ensembles qui deviendront les actuelles NT, englobées dans la NWfyPeHg, b) plus à l'est, c'était un domaine marin formé sur une croûte continentale faite en mésométamorphites du Br et de la NGHg, au-dessus de celles-ci se sont formés des dépôts mésozoïques (triasiques, jurassiques et néocomiens), constituant les Séries bucovinienne (à l'ouest), subbucovinienne (dans les parties centrales) et infrabucovinienne (vers l'est), entre lesquelles il y a des différences faciales, dans chaque série il y a des discontinuités stratigraphiques (Săndulescu, 1973, 1975, 1975, 1984), c) plus à l'est, existait une terre exondée et constituée par les métamorphites des NAMAD.

II. Principaux événements mésochrétacés: 1) L'ensemble formé par les mésométamorphites et les dépôts mésozoïques transgressifs a constitué la NRa, à la suite du charriage (vers l'est) sur la pile des NAMAD. 2) Ulterieurement, s'est formée la NWfyPeHg (et les

NT englobées) à la suite du charriage (obduction) sur les parties occidentales de la NRa, c'est-à-dire sur la couverture mésozoïque de type bucovinien. 3) Plus tard, cet échafaudage complexe a été cisailé successivement de l'est à l'ouest (en angle aigu vis-à-vis des plans de charriage, formés antérieurement), donnant ainsi naissance aux nappes mésocretacées du système bucovinien (conformément à l'ordre chronologique établi par Săndulescu – 1984): les NIBu (les plus anciennes), puis la NSBu et, enfin, la NBu (qui a transporté solidairement la NWfyPeHg), toutes charriées sur la Zone du Flysch (ZF), leur ensemble constituant la ZCM. 4) Pendant les charriages des nappes mésocretacées, ont pris naissance des éléments structuraux (aussi mésocretacés), parmi lesquels les **digitations frontales de la NBu - DFNBu** (Săndulescu, 1973, 1981, 1984, Ștefănescu, Ștefănescu, 1981, Kräutner, Kräutner, 1988; Kräutner, 2000; Vodă, Vodă, 1989, Vodă, Munteanu, 1997, Vodă, 2000), qui affectent les parties orientales de la NRa et du Tg. Les DFNBu englobent: des métamorphites (du Br de la NRa et du Tg), des dépôts du Mésozoïque bucovinien et de la NWfyPeHg. Pour nous, l'implication de la dernière entité (par exemple, dans les deux DFNBu de Sădova), c'est une épreuve que ces digitations sont mésocretacées, formées pendant le charriage de la NBu sur la ZF.

III. Les nappes mésocretacées supportent les dépôts transgressifs du Crétacé supérieur (par exemple, les Conglomerats de Bărnadu, cenomaniens - Săndulescu, 1975) et du Paléogène.

G) Les minéralisations logées dans la NRa. 1) Dans les mésométamorphites du Br de la Nappe infrabucovinienne de Iacobeni, il y a (dans les Vallées Ciotina et Haj) dans les amphibolites, des concentrations ferifères (magnétite, hématite, spessartine, pyrite), de type Lahn-Dill (Kräutner, 1967). 2) Dans la fenêtre tectonique Rusaia, les roches calcaires de la base du Groupe Rusaia - silurien (transgressif sur le Br) loge une minéralisation syngénétique ferifère (magnétite, hématite, sidérite, ankerite, pyrite - Kräutner, 1967). 3) Dans le Groupe Repedea (silurien), transgressif sur le Br (de la Nappe infrabucovinienne de Stiol - Monts Rodna) il y a (dans Izvoarele Cepei) une minéralisation hydrothermal-sédimentaire pyriteuse (Kräutner, 1967).

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LA METHODE DE ROCK-EVAL ET SON AVANTAGE EN EXPLORATION PÉTROLIÈRE

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Avant-propos

L'objectif essentiel de la géochimie organique, en exploration pétrolière, consiste à caractériser la matière organique (MO) contenue dans les roches, qu'il s'agisse de roche mères, de drains ou de réservoirs et d'en tirer parti, ensuite, dans la recherche des prospects. L'extrait organique permet bien d'accéder à la caractérisation des roches, des huiles et des indices, ainsi qu'à leurs corrélatifs et si l'examen de la fraction kérogène conduit bien à une appréciation de la nature de la

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MO et de ses états de maturation, ces différents examens ne conduisent jamais à l'expression quantitative du potentiel pétrolier des roches mères, non plus qu'à l'expression quantitative des états de maturation de leur MO (la méthode de pyrolyse Rock-Eval est largement utilisée en exploration pétrolière).

1. Principe

Les fondements de la méthode ont été décrits par ailleurs (Espitalié et al., 1973, 1977). Rappelons brièvement qu'ils sont basés sur l'étude physico-chimique des kérogènes isolés de leur roche (Durand et al., 1973; Espitalié et al., 1973) et sur les travaux concernant leur pyrolyse (Souron et al., 1975).

La méthode consiste à chauffer et programmer de température (à la raison de 25° C/ min en moyenne), sous atmosphère inerte (hélium) un petit échantillon de roche (100 mg environ) afin de déterminer quantitativement et de façon sélective:

- les hydrocarbures libres sous forme de gaz et d'huile contenus dans l'échantillon de roche;
- les composés hydrocarbonés et oxygénés (CO₂) qui sont expulsés lors du craquage de la matière organique non extractible de la roche (kérogène).

Dans les dernières versions d'appareil (Rock-Eval II- c'est qui nous l'avons), le carbone organique total (COT) de l'échantillon peut être déterminé automatiquement grâce à l'oxydation sous air de la matière organique demeurée dans l'échantillon après pyrolyse (carbone organique résiduel).

2. Les appareils

La première génération d'appareils, dénommée 'Rock-Eval I', a été commercialisée en 1977. Il s'agissait d'un appareil semi-automatique équipé d'un système électronique classique (Espitalié et al., 1977). Il fallait lui adjoindre un intégrateur et l'enregistrement des signaux d'analyse, le calcul des paramètres étant effectué manuellement.

Dès 1979 des autres versions du Rock-Eval étaient proposées: - celle du Rock-Eval II qui peut être équipée, en option, d'un module d'analyse du carbone organique résiduel permettant de doser le COT; - celle du Rock-Eval III appelée encore Oil Show Analyser (OSA), dérivée de la précédente et qui permet d'analyser séparément le gaz et l'huile contenus dans les échantillons de déblais ou de carottes fraîchement remontés du forage.

3. Cycles d'analyse et choix des températures

Dans les appareils équipés d'un module de carbone, les phases de pyrolyse et d'oxydation se produisent simultanément, l'oxydation se faisant sur l'échantillon pyrolysé au cours du cycle précédent.

La phase de pyrolyse

Schéma de principe du cycle d'analyse du Rock-Eval II- PYROLYSE:

- la purge du four et de l'échantillon pendant 5 min dès que ce dernier est mis en place au sommet du piston par le passeur automatique (sous balayage d'hélium). Pendant cette étape la température du four s'élève de 300° C à 450° C, ce qui permet d'éliminer l'oxygène introduit pendant l'ouverture du four. En fin de purge, la température du four revient à 300° C.

- la volatilisation des hydrocarbures libres (pic S1) s'effectue ensuite dès la montée du piston dans le four maintenu en isotherme à 300° C. Cette étape dure 3 min.

- au terme des 3 min commence la phase de pyrolyse proprement dite. Le four est alors amené, selon une programmation dite. Le four est alors amené, selon une programmation de température de 25° C/min, jusqu'à 600° C. C'est la phase de volatilisation des composés hydrocarbonés très lourds (>C₄₀) ainsi que celle du craquage des résines, des asphaltènes et, surtout, du kérogène (pic S2). Le piège est réchauffé et la détection du CO₂ (pic S3) effectuée au cours du refroidissement du four de pyrolyse.

La phase d'oxydation

Schéma de principe du cycle d'analyse du Rock-Eval II- OXYDATION:

Elle commence avec le début de la pyrolyse proprement dite. L'échantillon pyrolysé au cours du cycle précédent est introduit dans le second four. Au cours de l'oxydation la nacelle est poussée

contre la partie supérieure du four obligeant ainsi l'air ou l'oxygène à traverser l'échantillon. La matière organique résiduelle est brûlée à 600° C pendant 7 min, ces conditions de durée et de température étant optimales dans la cas de la détermination du COT d'une roche totale. Le stade de la combustion est suivi de la purge du piège à CO₂ par le détecteur correspondant (TCD)- également localisé dans ce module – le pic de CO₂ obtenu (pic S4 est intégré par le microprocesseur du module).

4. Les paramètres obtenus

Le Rock-Eval II muni d'un "Module de Carbone ", les paramètres fondamentaux obtenus par pyrolyse d'un échantillon de roche sont (tableau I)

-la quantité d'HC libres (gaz et huile) qui se sont volatilisés à 300° C pendant 3 min: elle correspond au pic S1 de l'enregistrement

-la quantité de composés hydrocarbonés provenant du craquage, entre 300°C- 600°C, du kérogène et des composés extractibles lourds comme les résines et les asphaltènes: elle correspond au pic S2 de l'enregistrement.

-la quantité du CO₂ piégé séparément lors du craquage du kérogène (pic S3) à des températures plus faibles, entre 300°C et 390° C. (exprimés de CO₂ par gramme de roche)

-la température, en degrés celsius, atteinte au sommet du pic S2 et dite " Tmax".

-la teneur en carbone organique résiduel (% pondéral) de l'échantillon précédemment pyrolysé, obtenue par combustion de ce dernier sous air à 600° C. Le CO₂ issu de cette combustion correspond au pic S4.

-la teneur en carbone organique total (COT, en % pondéral) de l'échantillon , comme étant la somme du carbone organique résiduel et du carbone organique pyrolysé.

-l'Index d'Hydrogène (IH) et l' Index d'Oxygène (IO) comme étant les valeurs de S2 et S3.

-l'Index de Production (IP) comme étant le rapport S1/(S1+S2).

Tab. I: Paramètres obtenus à l'aide du Rock-Eval II muni d'un "module de carbone " et le principale application à l'exploration pétrolière.

Paramètres	Quantités d'huile et de gaz et potentiel pétrolier	Détermination du COT	Types de matière organique	Indices d'huile et de gaz	Degré d'évolution
Gas	Quantité de gaz (mg HC/g roche)	Carbone Organique Pyrolysé	Index d'Hydrogène: (mg HC/g CO ₂)	Index de Production du Gaz (PG=S0(S0-S1-S2))	
Huile	Quantité d'huile (mg HC/g roche)			Index de Production De l'Huile (PH=S1(S0-S1-S2))	
Gas+Huile	Quantité huile-gaz (mg HC/g roche)			Index de Production De l'Huile + Gaz (PT=S0-S1(S0-S1-S2))	
Composés hydrocarbonés issus du craquage du kérogène	Potentiel pétrolier résiduel (mg HC/g roche)				
CO ₂ issu du craquage du kérogène		Carbone résiduel	Index d'Oxygène: (mg CO ₂ /CO ₂)		
CO ₂ issu de l'oxydation du carbone organique résiduel					
Température du sommet du pic S2			Tmax (°C)		Tmax (°C)

5. Interprétation des paramètres

Le pic S1-HC libres

S1 est la quantité de gaz et d'huile déjà formés dans les roches et obtenus par thermovaporisation. S1 dépend de la

→ quantité et du type de la MO

→ du degré de maturation

→ de l'intensité des phénomènes de migration

Le pic S2-HC potentiel

S2 est la quantité d'hydrocarbures qu'une roche mère peut encore générer par craquage thermique (dans les conditions géologique ou par pyrolyse). S2 dépend de la quantité et du type de la MO pour une roche immature. Type I>II>III (S2 représente 80% 50% 30%) du TOC; dépend du

degré de maturation : $\leftrightarrow$ roche immature ($T_{max} < 435^{\circ}\text{C}$) S_2 = potentiel pétrolier initial; $\leftrightarrow$ roche mature S_2 = potentiel pétrolier résiduel

T_{max} au sommet du pic S_2 (paramètre standardisé)

T_{max} est marqué le maturation 435°C $T_{max} < 435^{\circ}\text{C}$ MO immature

$T_{max} < 470^{\circ}\text{C}$ MO zone à huile

$T_{max} > 470^{\circ}\text{C}$ MO zone à gaz, dépend du type de la

MO (largeur de la fenêtre) bon marqueur Type III et Type II, mauvais marqueur Type I

Index d'Hydrogène IH (rapport S_2/TOC)

HI s'est corrélié avec le rapport atomique H/C des kérogènes et aussi dépend du type de la MO à maturité donnée,

	Type I	Type II	Type III
MO immature	850 mg/gC	650 mg/gC	300 mg/gC
Pic zone huile	450 mg/gC	400 mg/gC	200 mg/gC
Début zone gaz	100 mg/gC	100 mg/gC	100 mg/gC

et aussi marqueur de maturation pour un type donné,

Index d'Oxydation (rapport S_3/TOC) ;

IO marqueur d'oxydation (ou alteration) de la MO, dépend du type pour une MO immature type I < type II < type III, corrélié avec le rapport atomique O/C des kérogènes

$\text{COT} = \text{PC} + \text{RC}$

Le COT (Carbone Organique Total) ; pour COT modéré le S_2 est modéré, HI = 0/0, pour une MO mature, S_2 est min, T_{max} est modéré.

Nature et évolution des MO vus par les paramètres Rock-Eval

- corrélation R_v/T_{max}

- le diagramme IH/ T_{max} , permet un classement par lignées et maturité

- le diagramme IH/IO, obtenu directement sur les roches, équivalent au diagramme H/C vs O/C des kérogènes, permet un classement par lignées de MO avec suivi des alterations.

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BIOGEOCHEMICAL AND MICROBIOLOGICAL CONDITIONS OF INORGANIC AND ORGANIC CHANGES IN THE SOIL - THE MAIN FACTOR REGARDING THE GENESIS OF HYDROCARBONS AND ESSENTIAL ECONOMICAL MICRO COMPONENTS

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The soil is different from its original mineral and organic material, the differences being made mainly by the qualitative features as for example fertility and composition. Therefore soil must be considered as a result of bioaccumulative synthesis on the lithosphere surface, today and during the geological time.

Distinguish from the lithosphere rocks, which are the bases of its origin, the soil also constitute the reasons of everlasting transformation processes. Biological and geochemical data implies that soil it's not only a condition and a consequence of life but it is as well its source.

From its features as a natural laboratory, the soil becomes a condition of formation and development of organic material on the continental area as well as in the marine and oceanic domain. He is also the main factor concerning the hydrocarbon genesis.

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Generally, the soil genesis is the result of diverse activity of dead and alive organisms operating on the original source-rock. In many continental and marine environments the great diversity of chemical substances, their complexity, their macromolecular nature and all the processes of transformation regarding the organic substances from soils are insufficient known.

The soil is the result of the interaction between living organisms and rocks. It is an organic system where the transformations of mineral and organic material are continuously developing, suitably for each geological formation.

Thus, organic material is reanimated and then passes through into physical – chemical phases. Now the lipids support minor structural modification forming molecules named “geochemical fossils”; the amino acids and simple glucoses forms, during the multicondensation processes, humic and folic acids like those already existing in soil. This form the marine humus – a complex product, alike with the one of the soil, hardly to be affected by dispersed microorganisms and which, because of sedimentation, reaches a depth of ten to hundred meters. As a result of continuous multicondensation processes, the transformation of organic sediment into kerosene (the main source of petrol, gases and bituminous schists), is carried out.

The greasy acids obtained following the saponification are transformed in acetone, liberating CO_2 and H_2O and then through pass into hydrocarbons.

The sedimentation process go on in geological time and the medium temperature gradient of about 30°C/Km cause thermal degradation of kerosene, the consequences being the disappearance of functional groups (acid, ester, cetone). This process is associated with several chemical modifications, which finally direct all over again to the elimination of CO_2 , H_2O with less iodine and oxygen products that chemical composition is different from those of oil. The oil is generated at last and he contains oxygen, sulfur and nitrogen compounds as well as some different mineral and organic substances especially those with complex structure (named asphaltenes).

Regardless the geological time or rocks, the soil is influenced by organisms’ activities. The exchange processes between organisms and their environment are an important bound between organism and rocks, later soil, forming a generator system. Every each organism during its life cycle takes over substances and then returns to the environment the dissimilation compounds, and so establishing the petroleum and organic water chemical composition.

A special feature of the organic matter is the permanent accumulation and transformation. Thus, the fundamental elements are involved into a permanent close circuit, resulting in an endless generating character. Because of the synthesis and decomposition complex activity of microorganisms, the organic matter is forming and transforming in the same time until the equilibrium of chemical elements.

The role of microorganisms concerning the transformation of organic matter and hydrocarbons formation.

The activity of microorganisms, in connection with its own nutrition, is possible with the assistance of cells produced enzymes. One part of those enzymes (coenzymes) is secreted in the cell proximity with hydrolytic disintegration reactions of hydrocarbons and albumins. All that’s leads to the soluble combination, which penetrate then by osmoses into the microorganism cell. Here, the disintegration and oxidation is going on, but now the reactions are conducted by typical intracellular endoenzymes. This process liberates energy, which in part is accessible for endothermic reaction that generates the cell material, the rest being emitted as heat reaction. In this process, the enzymes have got only the role of decomposition agent. In the same time, the enzymes are biocatalysts in the synthesis process of lignin decomposition products, carbon hydrates, proteins and aromatic chain condensation. So, the humus is a product of two phases biochemical process, where the microorganisms have a dominant role. This humus represents the marine humus from marine domain, which is considered as a complex colloidal produce.

The microorganisms also produce other kind of reactions, they further transform the mineral products proceeding from organic material decomposition. For example the biochemical oxidation and reduction processes.

In certain geological conditions, such as increase pressure, the decay or non-decay organic matter (especially the vegetable matter), tends to be surrounded by layers of mineral material, where the microorganism doesn't have the properly condition for living. In this case the organic matter is submitted to slow chemical transformation (the bio-chemically transformation are very reduced). The result of these transformations is the carbonification of organic matter, producing different categories of coals. In good condition for the development of aerobe and anaerobe microorganisms the vegetable organic matter is transformed in humus. The organic sediment is then transformed in kerosene, which will further generate the hydrocarbons.

In conclusion the soil represents a determinative factor in processing organical material, where an important role it's given by organical substances (from dead vegetable or animal organisms), but in the same time from microorganisms, too; from a long periods they are put out of biological system, and then by means of ourselves storage in fossils combustible, in the principal way like kerosene and coal. The petroleum kerosene is a complex mixture of gas, solid and liquid hydrocarbons. To all these, many carbon and hydrogen compounds with O, N, S, and P are added.

The composition of petroleum is different from exploitation to another depending on the physical (especially viscosity) and chemical properties. The average range for principal elements is: C = 82,2-87,1 %, H = 11,7-14,7 %, S = 0,1-5,5 %, N = 0,1-1,5 %, O = 0,1-4,5 %, mineral salts -0,1-1,2 %. Depending on its origin, the kerosene could contain especially aliphatic compounds (e.g. paraffines), naphthenic compounds (from benzene series), or fatty acids compounds, phenols, asphaltenes, sulphanes, organic sulfides, sulphanic acids, sulfur oxides etc. Until the present time, neither one of the theories regarding the genesis of kerosene was able to point out the chemical reactions from which this extremely complex mixture was generated. From this reason, some oldest theories such as: *the theory of inorganic origin - Berthelot, 1866*, *the theory of cosmic origin - Sokoloff, 1890* are not out of the question, and have just historical acknowledgements.

In present time there is a generally agreement regarding the petroleum and coals formation, from organic matter generated in soil in special environment conditions. The transformation of organic matter and hydrocarbons generation is an old and continuous process although still to be discovered.

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EVALUAREA HIDROGEOCHIMICĂ A COMPONENTILOR, MICROCOMPONENTILOR ȘI INDICATORILOR POSIBIL DE PETROL ȘI GAZE DIN PLATFORMA MOESICĂ, ZONA GLIGANU, BUCUREȘTI, VIDELE, -PALEOZOIC, TRIASIC, JURASIC-

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Abstract

Platforma Moesică se înscrie, în ordinea perspectivelor pentru hidrocarburi imediat după depresiunea Precarpatică. Deși până în prezent s-au descoperit zăcămintele de hidrocarburi în Triasic, Jurassic, Cretacic, Miocen, indicații de hidrocarburi s-au înregistrat în mai toate formațiunile începând din Paleozoic și până în Romanian.

Condiții geologice cu totul specifice ale acestei mari unități, pun într-o lumină deosebit de favorabilă perspectivele sale de petrol și gaze și chiar încurajatoare în zona Gliganu-București-Videle. Se impune în primul rând prospectarea prioritară a microcomponentelor direcți și specifici hidrocarburilor, cu o atenție sporită pentru relieful fundamentului cristalin, a grosimii și a variațiilor de facies în formațiunile sedimentare și a grosimilor lor precum și și parametrii hidrogeochimici de perspectivă și de identificare a hidrocarburilor după microcomponente și indici de genă și de metamortizare a fluidelor de zăcămant din zona generatoare, pe traieul migrator și până în zona propriu-zisă de acumulare.

În mod deosebit s-a avut în vedere pentru evaluarea hidrogeochimică a hidrocarburilor, microcomponente specifice precum iodul după concentrație, insistând asupra legăturii indisolubile ce există între compoziția chimică a petrolului și a gazelor și apele de zăcămant asociate și neasociate hidrocarburilor, roci, soluri, materia organică animată și reanimată în vederea individualizării zonelor cu microcomponente și chiar componente specifice de petrol și indici hidrogeochimici de închidere hidrogeologică propice zăcămintelor de hidrocarburi. Astfel că zona de anteciză și zonele periferice ale sinclinalelor adiacente, s-au dovedit a fi sectoare de primă importanță cunoscute astăzi ale platformei. Ele s-au individualizat hidrogeochimic purtătoare de microcomponente direcți de acizi naftenici, fenoli, microcomponente specifice organici de iod și amoniu și reziduali de brom și bor în zona de Căzănești-Deleni-Constantinești-Mogășești-Optași, Mozăceni-Vultureanca, Călugăreni-Mihai Bravu etc., și reprezintă sectoare de primă importanță cunoscute astăzi ale Platformei Moesice.

În cuprinsul lor, pot fi purtătoare de hidrocarburi și fluide de zăcămant unele roci granulare, fisurate sau vacuolare, aparținând întregii serii mezozoice (în special triasice) și pe alocuri paleozoice. Alte elemente noi hidrogeochimice, geochimice, tectonice sau stratigrafice, care vor rezulta de pe urma activității viitoare de prospecțiune și foraj, vor mări perspectivele de petrol și gaze în perimetrul considerat Gliganu-București-Videle.

Condiții de genă, acumulare și conservare a fluidelor de zăcămant din zona de studiu.

Fluidele de zăcămant acumulate în Paleozoic, Permo-Triasic, seria carbonatică triasică și seria terigenă jurasică, reprezintă exemplificarea tipică a rolului pe care îl are mediul de acumulare a materiei organice, natura și originea apelor bazinelor de sedimentare în care s-a petrecut și perfectat procesul de bituminizare.

Apele acestor bazine de sedimentare ar fi fost izolate în trecutul geologic și sustrate circulației pe măsura umplerii lor cu depozite sedimentare și păstrate ca "ape fosile" (veterice) în depozite acvicide de genă și acumulare dintr-un complex acvifer limitat în spațiul fiecărui bazin.

Raportat hidrogeologic și în special hidrogeochimic, acviferele au caracter închis hidrogeologic, potrivit valorilor coeficienților NaCl subunitare, de acumulare și de conservare geologică potrivit coeficienților CaMg și Cl-NaMg cu valori supraunitare și mult crescute, a fluidelor de zăcămant. În aceste condiții hidrogeochimice au generat fluidele de zăcămant, cu

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precădere apele de orogine organică, cu microcomponenți asociați petrolului și gazelor naturale de Sacizi naftenici și fenoli, iod amoniu, brom și bor.

Faza finală a procesului de geneză constă într-o deplasare a produselor bituminoase de care este legată apa organică (produsul descompunerii materiei organice – faza biologică și faza fizico-chimică) dintr-un mediu marin cu roci cu o structură fină, într-una cu structură mai grosieră, crăpături și fisuri, colectoare. Împreună, apoi, formează un complex unitar de geneză, de colectare și conservare.

Astfel, pentru seria roșie inferioară, ape asociate hidrocarburilor cu microcomponenți direcți de acizi naftenici și fenol și specifici de iod, se întâlnesc în zona Piatra Olt-Barza-Videle, ape de tip Ca-Cl și cu mineralizații cuprinse între 20 și 40 g/l, specifice zonelor generatoare de hidrocarburi. De asemenea și zonele Drăgănești-Opărelu-Spineni cu ape de zăcământ cu sulfați scăzuți cauzate de reducerea lor din ape de către hidrocarburi și bacteriile desulfurante.

Pentru seria carbonatică triasică, sunt specifice apele asociate hidrocarburilor cu acizi naftenici în zona Străești-Priseaca și toată zona la vest de meridianul Corbu.

În seria terigenă jurasică, se întâlnesc ape asociate, atât specifice zonelor generatoare cu acizi naftenici, fenoli și benzen, și iod peste 100 mg/l, cât și pentru zone de cercetare cu H₂S prezent efectiv apelor din zone colectoare, rezultat din procesul de reducere a sulfaților de către hidrocarburi. Astfel de zone iau contur în zona Văleni-Ciurești-Mozoceni, Poiana-Tufeni-Ciurești-Petrești și Cărligăți-Carțojeni-Periș.

Se constată, că în configurația compoziției chimice a fluidelor de zăcământ un rol important l-a jucat evoluția geologică a Platformei Moesice, unde seria depozitelor mezozoice de pe platformă, discordanțele unghiulare existente în Paleozoic nu au mai fost constatate deși anumite lacune stratigrafice au putut fi bănuite sau chiar semnalate. Astfel, raporturi de discontinuitate pot fi bănuite la limita superioară a Muscelkalk-ului, unde mineralizațiile apelor sunt de 2-17 g/l, tipul Na₂SO₄ și Mg-Cl (ape cu caracter vados și mixte), iar coeficienții hidrochimici de geneză Na-Cl au valori atât sub cât și peste o unitate, fiind de 0,01 și 1,11. Astfel că ele au devenit ulterior ecrane hidrodinamice de închidere hidrogeologică a acviferelor pentru conservarea fluidelor de zăcământ.

În acest caz un rol important l-a jucat și sedimentul mineral de catalizator, de accelerare sau încetinire a reacțiilor chimice și rol de reținere și conservare a substanțelor bituminoase formate în bazinele de sedimentare a formațiunilor din perimetrul studiat și implicit microcomponenții direcți și specifici din apele de zăcământ imprimând apelor caracter de ape asociate hidrocarburilor din zonele enumerate.

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GOLD SOURCES AND RESOURCES IN ROMANIA

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The "mineral triad", i.e. gold, salt and oil, is a characteristic feature of the Romanian mining during the last centuries. The exploitation of gold, salt and oil dates back to very old and old periods of time. Gold and salt from Romania were used already during the Roman (probably pre-Roman as well), whereas the oil has a different priority: it was the first European industrial production of oil, (1877, barrels), obtained 1861 at Mosoare, near Bacau.

There are many papers and books dealing with the gold deposits, production and perspectives in Romania. Every mineral deposit books published in the last 100 years contains data about the Transylvanian gold deposits. The "gold spot" in the Metaliferi Mts., called also "the Golden Quadrangle" (GQ) is now quite well known and the new results of intensive exploration at Rosia Montana seem to put this deposit at the top of gold deposits in Europa.

To the historical hydrothermal gold veins and stockworks within the GQ a new feature was added in the last decades, i.e. the close relationship of the hydrothermal (now called epithermal) deposits to the porphyry copper systems. Overlapping of porphyry type mineralizations by veins containing mostly gold (but also base metal ores, such as at the Bolcana-Troita) is now doubled (by a supplementary feature, i.e. the existence of several porphyry copper-gold deposits (e.g. Voia, Bolcana-Troita, Bucium-Tarnita etc). Some data might suggest that the true protore of the epithermal gold deposits (EGD) are the porphyries themselves, in which the gold was seemingly caught by the primary rock-forming minerals and reconcentrated in veins (or stockworks) by a nearly continuous magmatic-hydrothermal metallogenic process. Still unsolved problems are related (1) to the source of tellurium (and of manganese as well) as many EGD contain a typical geochemical triad Au-Te-Mn (Udubasa et al., 2001), (2) the contribution of the adakite tendency of some volcanic rocks in the Metaliferi Mts (Rosu et al., 2001) in the establishing the unique position of the GQ within the whole Carpathian Neogene magmatic-metallogenetic belt, even if we consider a comparison of the Metaliferi Mts with the quite similar Baia Mare area, where gold is subordinated and Pb-Zn-Cu-Sb ores prevail!

Two additional gold sources are known in Romania:

- (1) the shear zone related mineralizations (SZRM) in the polyphase metamorphics in the South Carpathians, with the locus typicus at Valea lui Stan, and in the Apuseni Mts, at Someșul Rece. The genesis, perspectives and many other aspects of the SZRM were largely discussed in the last years however by using different approaches: Udubasa, Hann (1988), Udubasa et al. (1998), Popescu, Lupulescu (1996), Popescu, Tamas-Badescu (1998), Marza (1990), etc.
- (2) alluvial gold (partly placer gold such as the Pliocene gold accumulation at Vartop, near Rosia Montana), which is also quite well known (see Barlea, Barlea, 1963; Borcos et al., 1998, Berbeleac et al., 1998, and the references herein), although the source of gold is not always satisfactorily defined.

Therefore it may be concluded that the gold deposits (sources) in Romania belong to the following genetic types:

1. Porphyry copper-gold deposits (Metaliferi Mts)
2. Hydrothermal gold (Neogene volcanic belt)
 - a) satellite gold veins and stockworks of porphyry systems (Metaliferi Mts)
 - b) independent gold veins and stockworks in complex volcanic and subvolcanic structures, e.g. Sasar, Borzas etc. in the Baia Mare area, as well as gold-silver telluride deposits such as Sacaramb in the Metaliferi Mts, not obviously related to porphyry systems

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- c) Gold as by-product of Pb-Zn-Cu ore processing (practically all the Neogene deposits in the Metaliferi Mts., Baia Mare area as well as in the Calimani-Gurghiu-Harghita (e.g. Stanceni).
3. VHMS either of Mesozoic age (e.g. Vorta, Kuroko-like) or of Lower Paleozoic age, metamorphosed deposits in the East Carpathians ore belt, where gold is present in subordinate amounts (e.g. Baia Borsa district, especially, where a value-added influence of the Toroiaga subvolcano cannot be excluded).
4. Shear zone related gold mineralizations in metamorphics of the South Carpathians (Valea lui Stan, Costesti-Horezu, Jidosita, Valiug) and the Apuseni Mts. (Somesul Rece).
5. Alluvial gold (placers included) derived either from magmatic gold ores in the Metaliferi Mts or from the SZRM in the South Carpathians (especially Pianu, Lotru, Strei Valleys).

That is indeed all about the gold resources in Romania? The answer is: no.

6. Taking into account a worldwide relationship between BIF (banded iron formations) and gold (enriched in the silica rich bands within the BIF), a reliable assumption has been made by Udubasa (1998) that the BIF-like deposits in Romania might contain gold as well. This would be the case (1) of Palazu Mare deposit in Dobrogea located in Precambrian or even Archaic medium grade metamorphics. They consist of magnetite-bearing quartzites and amphibolites (Giusca et al., 1976; Ianovici et al., 1966) and of the iron deposits in Poiana Rusca Mts., namely Iazuri, Tomesti, Cerbal, etc. located in Paleozoic low grade metamorphics, consisting of itabirites with spessartine, magnetite-and hematite-bearing quartzites etc (Krautner, 1964). No direct proofs are available yet but the similarity of these deposits to other gold-containing BIF in the world is worth of mention. This could represent a new start in future exploration or re-evaluation programs for the two areas.
7. (?) Speculations have been also made concerning the possibility to find Carlin-type gold ores in Romania. North Dobrogea and Banat were two zones envisaged to potentially contain such ores. However, no convincing arguments were presented in order to sustain such challenging assumptions. Curiously enough, the idea was put forward several times by persons not having direct scientific relationship to such a complicated gold-bearing setting. At least for North Dobrogea, fulfilling one of the three conditions to carry Carlin-type gold, i.e. the distensional regime (Ilchik and Barton, 1997) the absence of gold (even alluvial) in the area is noteworthy and hampers any ideas thereupon. It is important to remind that in the Carlin zone, Nevada the gold was first obtained from alluvia!

8.

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ROMANIA's "MINERAL TRIAD"

Gold-Salt-Oil

Ore resources		Gold	Other resources
CZ	Alluvial gold	○	Heavy minerals
	Au-Te-Mn veins	○	SALT
	Au-Ag veins	○	OIL & gas
	Au-Ag-base metals veins	○	Coal
	Porphyry Cu-Au, Mo		
MZ	Skarn related complex ores (Banat, Apuseni Mts)		
	Kuroko-like ores (Vorta)	○	OIL Coal
	Veins & stockworks Mo, REE (Ditrau)		
PZ	Stratabound iron ores (BIF-like) (P. Rusca)	⊙	Pegmatites
	Stratabound base metal ores (EC)	○	Graphite
PE	Stratabound ZnPb ores in marbles (Rodna, Fagaras Mts)		Pegmatites
	Stratabound iron ores (BIF) (Palazu Mare)	⊙	

Carlin?

SHEAR GOLD

ENVIRONMENTAL IMPACTS OF METAL MINING IN ROMANIA: PROBLEMS, ISSUES AND OPTIONS

VELICU¹ Șerban, UDUBAȘA² Gheorghe

Romania is world-wide known by the "mineral triad" gold-salt rock-oil, each of them forming world-class deposits or fields and contributing to the economic development of the country in the last centuries. Nevertheless, the exploitation yielded also many long-time lasting negative effects on the environment. By far the "hard minerals" are more dangerous and the ores (gold ores included) are at the top.

There are many ore genetic types in Romania but few are economically important: (1) strata bound pyrite-Pb-Zn-Cu ores in the metamorphics of the East Carpathians, forming a belt some 200 km long, (2) skarn ores (Fe, Cu, Bi, W, Mo, Pb, Zn) in the Western Romania, (3) hydrothermal gold ores (mostly veins) in the Metaliferi Mts (the celebrated "Golden Quadrangle" of the "siebenburgisches Erzgebirge"), (4) hydrothermal base metal ore veins, gold as by-product and some gold deposits (both veins and stockworks) in the Northern Romania (Baia Mare County).

This presentation tries to highlight one of the most important issues related to metal mining in Romania: the wastes. Historically, or even just a few decades ago, environmental awareness, legislation and management practise did not adequately consider the long-term safety and environmental risks involved in the metallic mining waste management. Major reasons for the slow progress in dealing with mining wastes include the fact that no institution can be identified to take legal responsibility and further, the legal, financial and technical instruments being used to address the problem have often been borrowed from other programmes, and are not necessarily well suited to the problem. Issues that need addressing include the costs of rehabilitation and the setting of criteria and standards of rehabilitation.

Romania having a total surface of 237,500 sq. km and a population of 22,670,000 inhabitants, its metalliferous geological reserves are assessed as: 40 millions tons of Au+Ag ores, 90 millions tons of poly-metallic ores, 900 millions tons of Cu ores. The metallic ore deposits are characterised by small to medium dimensions, complex geological and mining conditions, difficult mechanical and metallurgical processing, complex tectonics, high exploitation depth, thin ore veins, low content of metals, difficult hydrogeological conditions. Annual production capacities for metallic mining have a total of 21 millions tons/year (13.8 for Cu, 2.2 Au+Ag, 3.6 polymetallic, 0.8 Fe+Mn, 0.6 radioactive).

The activities of capitalisation of the natural metallic mineral resources through geological exploration, extraction operations, mining metallurgy etc. represent only some of the main fields that lead to the degradation of the environment. Large surfaces for access routs, building sites, waste storage areas resulted from uncover process or the processing plants are affected adversely by pollution. Results of pollution may occur directly or indirectly and may have immediate or long-term character. Due to underground and surface excavations also the neighbouring areas suffer adverse influences such as changes in the flow of underground waters, modification of geochemical nature of the elements, erosion etc. The largest porphyry copper deposit located in the Apuseni Mts., Western Romania ("Rosia Poieni" ore deposit) is an active acid-rock drainage (ARD-producing site). Chemical analyses show that the stream waters from the region contain significant amounts of heavy metals that are potentially dangerous to the environment.

The impact of mining activities as prospecting, exploration, mining and concentration of useful mineral substances ("dressing minerals") imply the carrying out of different assessments of the environment from the following standpoints: mine wastes, residual waters - polluted waters as a

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result of mining and processing of ores, physical stability of the areas where underground or surface mining voids are present as a result of mining activities, visual impact as degradation of the landscape.

The mine wastes resulted after the mining and concentration process of useful mineral substances are discussed being separated into two categories according to their granulometry:

(1) large sized products: fragments of rocks and ore with a low content of useful elements as a result of exploration and mining of deposits. They form heaps of mine wastes or waste dumps. Only in the Western Romania a number of 179 waste dumps resulted from metal mining, exhibiting a total volume of 107 million m³ and being spread on 418 ha.

(2) fine-type material as a result of concentration process. They form the decanting or tailings ponds. The metallic mining in Romania uses a total of 64 major tailings ponds (29 active, 26 inactive, 9 as backup). These cover a total surface of 1,351 ha and contain 128 million tons of useless rock.

The inventory forms the standardised information basis for the environmental impact assessment using tools of geological and geochemical site assessment, environmental and spatial modelling. The scientific objectives of the study are the definition and demonstration of methods:

- to conceptualise and demonstrate a standardised regional inventory of waste sites from mineral mining in Romania in relation to catchment areas, making it possible to develop a concept for impact assessment allowing to link the site/source related indicators with spatial information at catchment scale;
- to compare the legal criteria for the assessment and remediation of contaminated areas with regulations adopted by Romania and with the existing EU legislative framework in the area of waste management;
- to contribute to the assessment of the consequences of mining accidents such as the Baia Mare/Baia Borsa (Romania) events.

The two accidents of Baia Mare (January 2000) and Baia Borsa (March 2000) in NW Romania, are presented, their causes, aftermath, and transboundary implications. Baia Mare accident released over 100,000 m³ of process wastewater with cyanide compounds and heavy metals such as Cu and Zn but also Fe, Cd, Mn, and had a marked impact on the Someş/Tisza/Danube catchment. Baia Borsa accident spilled over 20,000 m³ of heavy metals loaded slurry into the Tisza catchment throughout NW Romania, Ukraine and NE Hungary.

The implementation of today's "best practice" for cyanide management completely eliminates the risk of a cyanide spill similar to Baia Mare. Indirect effects that have been identified as a consequence of the accidents are also discussed.

Given the widespread nature of mining waste, it is attached a particular importance to prioritisation in this area to facilitate the environmental approximation process and to consider appropriately the situation in the new Romanian legislation.

FRAMEWORK CLASSIFICATION FOR RESERVES/RESOURCES (UNCF). THE HARMONIZATION OF THE ENERGY RESERVES/RESOURCES TERMINOLOGY.

BOGATU¹ Laurențiu

By the enforcement of Mining Law (No 61/1998) in the 13th of June and the publishing in the Romania's Official Gazette (No 330 bis from 1st of September 1998) of the Technical Instructions (No 85-08/1998), there have been established the classification and estimation principles for the mineral resources and for the reserves of solid utile mineral substances and mineral commodities, that will be used in the process of their capitalization. In the petroleum sector, in 1995 a new Petroleum

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law entered into force, based on the modern principles with regard to the reserves/resources classification.

The new proposed classification system corresponds to the terms and codification used in the International Classification of the Reserves/Resources (Decision ECOSOC/1997/226 of the Economic and Social Council of the United Nations at 1997 July's session and that of Committee for Sustainable Energy (ECE/ENERGY/32 paragraph 9), both recommending the testing implementation of the reserves/resources classification worldwide

The new classification and estimation of the mineral reserves in Romania is experimentally proposed till the end of 2002. In the same time it will be also used the old system of reserves classification.

The main feature of the national frame of solid reserves / resources classification are

- harmonizes and equates the new classification with the terms of the old one and with the UN International framework for reserves / resources classification, so that they could be comparable and compatible;
- creates the connection of the market economy and transition and centralized economy criteria in the field of solid mineral reserves / resources estimation;
- helps the annual statistic reporting concerning the Romania's reserves / resources record of changes, without causing any malfunctions;
- eases the communication at national and international level.

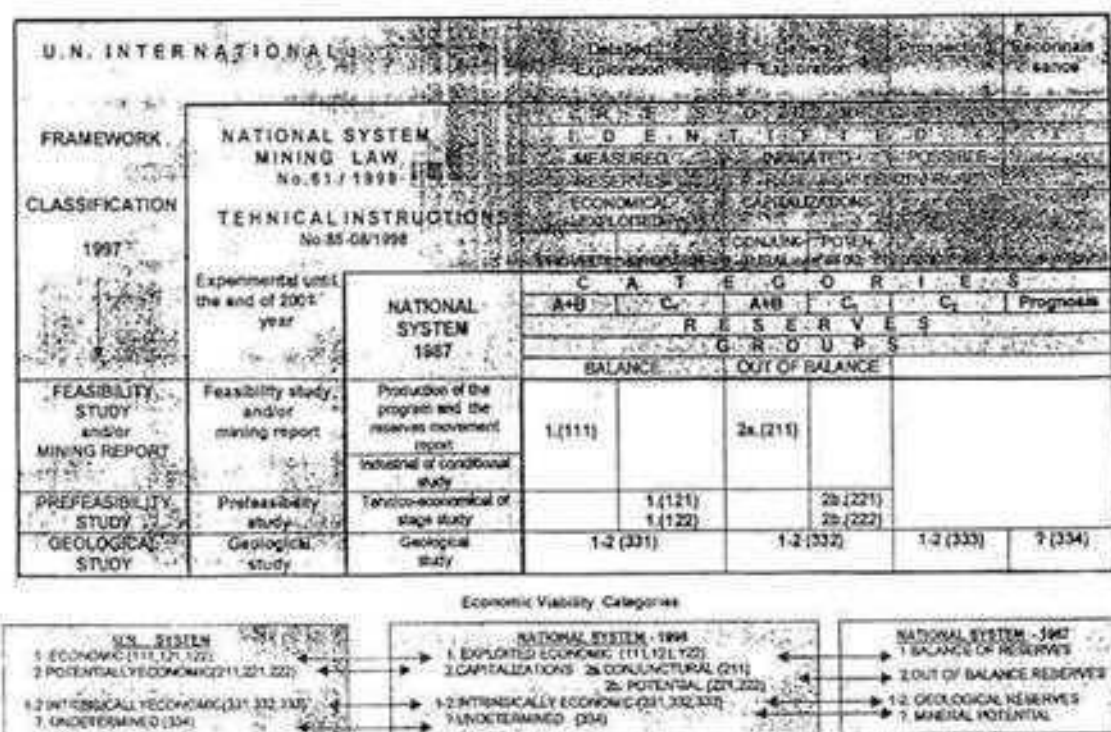
In Annex I there are presented the integration of the national system into the United Nations Framework classification for reserves / resources of solid fuels, mineral commodities, annex from which results that the category of resources potentially economic equates the category of capitalizing resources which includes two categories: 2.a conjunctural / code (211) and 2.b. potential / code (221) and (222).

In Annex II is shown the classification system for oil & gas reserves/resources used in Romania in harmonization with the International classification system proposed by SPE and WPC.

Annexes III, IV, V and VI present the harmonization of the reserves/resources terms used in the Romanian National Classification System with the UN Classification System for Coal, Oil & Gas and Uranium.

Annex I

INTEGRATION OF THE TWO NATIONAL ROMANIAN SYSTEM OF CLASSIFICATION FOR RESERVES/RESOURCES INTO THE U.N. INTERNATIONAL FRAMEWORK CLASSIFICATION FOR RESERVES/RESOURCES



Harmonization of the Petroleum Resource/Reserve Terms used in the Romanian Classification System with the International Classification System (SPE and WPC)

International Classification System (SPE & WPC)	Economically recoverable, assessed in detail Recoverable Reserves		Economically recoverable, preliminary assessment Unproved Reserves		Continental Resources	
	developed	undeveloped	Probable	Possible	Low estimate, Possibly economically recoverable in future (potentially economic), assessed in detail	Best estimate High estimate Possibly economically recoverable in future (potentially economic), preliminary assessment
Romanian Classification System According to Petroleum Law No. 34/99 and Governmental Order No. 103/2001	Economically recoverable, assessed in detail Proved Reserves		Economically recoverable in the future, insufficient estimated and preliminary economically assessed	Economically recoverable in the future, insufficient estimated and informally assessed	Resources Different estimation levels, unclassified, economically unrecoverable, in detail or preliminary assessed	
	developed	undeveloped	Probable Reserves	Possible Reserves		

Harmonization of Coal Reserve/Resource Terms in the National Romanian Classification System and UN Classification System

Codification	Coal		Comments
	(CMM/UN)	ROMANIA	
111	Proved Mineral Reserves	Economical Exploited Reserves - Proved Mineral Reserves	
121 + 122	Probable Mineral Reserves	- Probable Mineral Reserves	
211	Feasibility Mineral Resource	Conjunctural Capitalized Resource	
221 + 222	Prefeasibility Mineral Resource	Potentially Capitalized Resource	
331	Measured Mineral Resource	Measured Mineral Resource	
332	Indicated Mineral Resource	Indicated Mineral Resource	
333	Inferred Mineral Resource	Inferred Mineral Resource	
334	Reconnaissance Resource	Prognosis Resource	

Harmonization of Oil & Gas Reserve/Resource Terms in the National Romanian Classification System and UN Classification System

Codification	CMM/JUN	Oil & Gas		Comments
		(SPE/WPC)	ROMANIA	
111	Proved Mineral Reserves	Proved Reserves - developed - undeveloped	Proved Reserves - developed - undeveloped	Economically recoverable, assessed in detail
121 + 122	Probable Mineral Reserves	Unproved reserves - Probable Reserves - Possible Reserves	Probable Reserves Possible Reserves	Economically recoverable in the future, partially estimated and preliminary economically assessed Economically recoverable in the future, insufficient estimated and informally economically assessed
211	Feasibility Mineral Resource	Contingent Resources estimate Low	Resources	Different estimation levels, unclassified, economically unrecoverable, in detail or preliminary assessed
221 + 222	Prefeasibility Mineral Resource	Contingent Resources Best estimate High estimate		
331	Measured Mineral Resource	Not applicable	Not applicable	
332	Indicated Mineral Resource	Not applicable	Not applicable	
333	Inferred Mineral Resource	Not applicable	Not applicable	
334	Reconnaissance Resource	Prospective Resource	Not applicable	

Harmonization of Uranium Reserve/Resource Terms in the National Romanian Classification System and UN Classification System

Codification	CMM/JUN	Uranium		Comments
		(NEAMA/EA)	ROMANIA	
111	Proved Mineral Reserves	Reasonably Assured Resources at prevailing market price (Reserves)	Economical Exploited Reserves - Proved Mineral Reserves	
121 + 122	Probable Mineral Reserves	Estimated Additional Resources I at prevailing market price (Reserves)	- Probable Mineral Reserves	
211	Feasibility Mineral Resource	Reasonably Assured Resources above prevailing market price	Conjunctural Capitalized Resource	
221 + 222	Prefeasibility Mineral Resource	Estimated Additional Resources I above prevailing market price	Potentially Capitalized Resource	
331	Measured Mineral Resource	Reasonably Assured Resources in-situ	Measured Mineral Resource	
332	Indicated Mineral Resource	Estimated Additional Resources I in-situ	Indicated Mineral Resource	
333	Inferred Mineral Resource	Estimated Additional Resources II in-situ	Inferred Mineral Resource	
334	Reconnaissance Resource	Speculative Resources	Prognosis Resource	

Harmonization of Coal, Uranium and Oil & Gas Reserves/Resources Terms used in Romania with the UN Classification System

Codification	CMMUN	ROMANIA	
		Coal & Uranium	Oil & Gas
111	Proved Mineral Reserves	Economical Exploited Reserves	Proved Mineral Reserves
121 + 122	Probable Mineral Reserves	Probable Mineral Reserves	Proved Reserves - developed - undeveloped
			Probable Reserves
			Possible Reserves
211	Feasibility Mineral Resource	Conjunctural Capitalized Resource	Resources
221 + 222	Prefeasibility Mineral Resource	Potentially Capitalized Resource	
331	Measured Mineral Resource	Measured Mineral Resource	Not applicable
332	Indicated Mineral Resource	Indicated Mineral Resource	Not applicable
333	Inferred Mineral Resource	Inferred Mineral Resource	Not applicable
334	Reconnaissance Resource	Prognosis Resource	Not applicable

POLUAREA SALINA NATURALA A RETELEI HIDROGRAFICE A AREALULUI EXTRACARPATIC SI POSIBILITATILE DE LIMITARE A ACESTUI FENOMEN

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Zona externa a flisului si Unitatea pericarpatica sunt caracterizate, incepand de la valea Sucevei si pana la valea Cernei (in Oltenia), de prezenta unui numar foarte mare de izvoare si paraie sarate, fapt ce duce la cresterea salinitatii (a concentratiei in clorura de sodiu) unor rauri importante, fenomen cunoscut sub numele, poate impropriu, de "poluare salina naturala a raurilor". Prezenta clorurii de sodiu in solutie se datoreaza dizolvării masivelor de sare (de varsta miocen inferioara sau medie) de catre apele de precipitatie, de infiltratie sau direct de catre apa raurilor si paraielor, deci solubilizarii naturale a corpurilor de sare aflate in aflorimente sau la diferite adancimi.

Izvoarele sarate au debite foarte variate si concentratii foarte diferite, dar pot fi identificate si paraie sarate a caror sursa de alimentare cu clorura de sodiu nu este certa. In mod obisnuit aceste izvoare, bine cunoscute de localnici, sunt adesea sumar amenajate fiind frecvent utilizate pentru uz casnic incepand cu cele aflate in apropiere de Gura Putnei si la Cacica, si sfarsind cu izvoarele sarate legate de versantul drept al vaili Cerna, in zona anticlinalului faliat Magura Slatioarei (Oltenia).

Salinitatea neobisnuita a unor importante segmente ale retelei hidrografice din arealul extracarpatic este tradata si de numeroasele toponime (hidronime) precum Tazlaul Sarat, Ramnicul Sarat, Sarata, Cricovul Sarat etc, carora li se adauga raurile cu numele "Slanic" si toponimele de genul "Slatina", "Slatioara", precum si apelativul "saramura", cu varianta vranceana "salamura" (proprie bazinului hidrografic al vaili Putnei). Acestora li se adauga si numeroasele localitati ce reflecta direct preocuparea locuitorilor pentru exploatarea masivelor de sare (gen Sarari, Sarulesti, Sari - Sarile, Targu Ocna, Ocnele Mari, Ocnita etc).

Prezenta in cantitati mari a clorurii de sodiu in apa unor rauri mai importante are ca urmare restrangerea in anumite zone a surselor de apa potabila, iar pe de alta parte aceasta conduce la aparitia

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unor importante zone cu saraturi, lipsite de vegetatie sau cu vegetatie saraca, xerofila, catre zonele de varsare in Dunare a acestor rauri. Astfel, o importanta arie de saraturi poate fi delimitata incepand de pe cursul inferior al raului Siret si pana in zona de sud a bratului Borcea, si de la Campia Saratei (la NV de Urziceni) si pana la Insuratei (pe Calmatui), zona ce cuprinde si locuri cu salinitate neobisnuita (Amara, Lacul Sarat – langa Braila etc). Catre aceasta arie cu saraturi se indreapta Siretul (aducand apele raurilor Suceava, Moldova, Bistrita si Trotus ce traverseaza zona subcarpatica bogata in zacaminte de sare), Putna, Ramnicul Sarat, Buzaul (cu afluentul sau Slanicul de Buzau) si Ialomita, dar si Dunarea ce aduce aici si apele Oltului, dar si pe ale raurilor ce spala masivele de sare badeniene din Transilvania (Mures, Somes).

Pentru diminuarea efectelor nedorite ale acestui fenomen natural usor de evidenciat se impune imaginarea (crearea) unui sistem complex de statii de desalinizare a apei raurilor si paraielor sarate, plasate pe marginea exterioara a ariei cu zacaminte de sare ale arealului extracarpatic. Pentru stabilirea amplasamentului optim al acestor statii de desalinizare sunt inesa necesare studii hidrogeologice, respectiv geochimice, de mare detaliu, mai ales in bazinele hidrografice ale Tazlului Sarat, Putnei, Ramnicului Sarat, Slanicului de Buzau, Cricovului Sarat, Saratei etc.

In acelasi timp, existenta unui sistem de statii pentru desalinizare a apelor sarate ale raurilor amintite ar putea conduce practic si la obtinerea unei importante productii de sare, in conditiile in care exploatarea masivelor de sare prin solubilizare subterana cu ajutorul sondelor pare sa se contureze ca o metoda ce poate pune in pericol stabilitatea si securitatea zonelor invecinate acestora. In plus, pe aceasta cale s-ar imbunatati simtitor si calitatea apelor folosite in alimentatie in toate zonele situate in aval de un astfel de sistem de statii de desalinizare, fapt ce ar permite de asemenea si efectuarea, fara riscuri de salinizare secundara a solurilor, a unor irigatii care in prezent sunt supuse pe plan local unui asemenea risc.

CORRELATING BADENIAN RHYOLITIC PYROCLASTICS OF THE WESTERN GUTAI MTS. WITH THE DEJ TUFF COMPLEX

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Introduction

The "Dej Tuff" is the most prominent and widespread Neogene volcanic tuff complex in Romania, mostly occurring in the Transylvanian Basin. However, numerous tuff occurrences of similar stratigraphic age are present in areas outside the basin. No correlation attempts have been substantiated by comparative geochronological and petrochemical studies so far. This paper aims at correlating chemical and mineralogical features, along with geochronological data, of the felsic Lower Badenian volcanoclastic rocks occurring in the south-western Gutai Mts. and those of the Dej Tuff Complex in order to test whether these two felsic volcanoclastic sequences might belong to a common volcanic source.

Occurrence and general features

The Lower Badenian Dej Tuff Complex represents the oldest Neogene volcanic activity in Romania. It is widespread in the Transylvanian Basin where is largely exposed along the north-western and northern margin of the basin ("Dej Tuff") as well as along its south-eastern margin ("Persani Tuff"). The Dej Tuff Complex displaying variable thickness, from meters up to 116 m (Marza et al., 1991a), consists of a number of 4-5 sequences of coarse reworked rhyolitic sediments (sandstones and microconglomerates), zeolitized fine to medium tuffs and alternating thin tuffs and

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marls. They have been secondarily emplaced by submarine debris flows and high to low density volcanoclastic turbidite currents (Szakács, 2000). In a single case primary pyroclastics, represented by slightly welded pumice-and-ash-flow tuffs, have been identified at Magura Ciceu east of Dej. (Marza & Mirea, 1991, Seghedi & Szakács, 1991), emplaced by a lobe of pyroclastic flow across the sea-shore (Szakács, 2000). The "Persani Tuff", the "Slanic Tuff" and the "Govora Tuff" are all fine reworked distal equivalents of the "Dej Tuff" (Szakács, 2000). Although all these rocks were long known as typical "dacitic tuffs", recent studies have revealed their rhyolitic composition (Szakács, 2000).

Lower Badenian volcanoclastics of felsic composition in the Oas-Gutai volcanic range, occur in a ca. 20 km long and 10 km wide area along the south-western margin of the Gutai Mts. They have recently been recognized, in both outcrops and numerous drill-cores, as moderately to strongly welded rhyolitic ignimbrites of decreasing thickness from the west (350m) to the east (30m), overlain by a thick sequence of reworked epiclastics encapsulated by mudstones (Fulöp, 2001).

Given their similar age and composition, one may question whether the Dej Tuff Complex and the rhyolitic ignimbrites and epiclastics of the south-western Gutai Mts. can be correlated to each other. The overall north-west coarsening of the volcanoclastic rocks of the Dej Tuff Complex and its distal equivalents, demonstrated recently (Szakács, 2000) lends additional credit to such a hypothesis.

Age

The stratigraphic ages of the Gutai Mts. felsic volcanoclastics (GFV hereafter) and of the Dej Tuff Complex (DTC hereafter) are compatible. The DTC has long been dated on faunal and microfaunal basis as belonging to the Tortonian (Koch, 1900), later on to the Badenian (Meszaros et al., 1977). The presence of numerous interbeds of terrigenous sediments (especially marls) within the DTC sequences allowed a quite precise microfaunal dating – at the level of the nannoplankton zone NN5 (Meszaros et al., 1977, Marunteanu, personal communication, 2000). The stratigraphic age of GFV is more difficult to be determined: few determinations on scarce microfauna from the thick mudstones emplaced above the ignimbrites suggest a larger time interval, from Lower Badenian to Lower Sarmatian. Attempts of radiometric dating of the DTC used various methods. K-Ar and Ar-Ar dating were used on biotite separates. Since the biotites are more or less altered, with marked K loss, 4 datings resulted in minimum age estimations in the range 11.5-12.8 Ma (with their respective analytical error). One sample, with the biotite fraction chemically treated (in order to remove alteration products) yielded 14.7 ± 0.6 Ma, which is much more precise than the previous ones obtained on the DTC. The Ar-Ar method has been used on the biotite fraction of the apparently most suitable sample (slightly welded ignimbrite from Magura Ciceu with the highest K content). No plateau age has been found, but a minimum age estimate of 13.7 Ma could be inferred. Fission track dating has been undertaken on zircon crystals separated from 7 samples (15-30 zircon grains in each sample). Average ages obtained range between 13.98-16.05 Ma, with an overall average of 14.93 Ma. Taking into account all these data, a radiometric age at about 15 Ma can be accepted as the best approximation of the geological age of the DTC.

The biotite fraction of one sample from the GFV (Valea Romana) has also been dated by the K-Ar method, yielding an analytically reliable age of 15.4 ± 0.6 Ma. This age is consistent, within the analytical error, with the inferred radiometric age of the DTC.

Petrography

Primary magmatic minerals in DTC include, in the form of crystalclasts, quartz, plagioclase and biotite as ubiquitous principal components, K-feldspar, amphibole and pyroxene in accessory amounts in part of the occurrences or tuff levels, and Fe-Ti oxides, allanite, zircon and apatite as a ubiquitous accessory minerals. Monazite and xenotime have been identified sporadically by microprobe analysis. The frequency order of the main rock-forming minerals is: plagioclase, quartz, biotite.

The principal mineral components of the GFV include plagioclase, followed by quartz and biotite, as principal components; pyroxene and Fe-Ti oxides, subordinately.

Vitroclasts of the DTC include glass shards, pumice and obsidian fragments. Obsidian is always an "accessory" vitric component while, the relative amount of glass-shards and pumice is variable according to grain-size and genetic type of the rock. At comparable grain-size, the vitroclast population may either be dominated by glass shards or by pumice at the same location, according to the level in the sequence, as is the case at Cepari. Vitroclasts from GFV are represented by pumice, glass shards and scarce obsidian. Plastically deformed pumice clasts (fiamme and microfiamme) are prevalent in the welded ignimbrites, while typical cusped glass shards prevail in the non-welded distal facies. Resedimented pyroclastics show pumice clasts with spheroidal to ovoidal and tubular vesicles and cusped, Y and X-shaped shards, and microvesicular pumice shards. Pumice is more abundant in the generally coarser-grained GFV ignimbrites than in most DTC rocks, so that shard/pumice ratio cannot be used for correlation purposes.

Although detailed correlation of the DTC and the GFV cannot be undertaken on compositional basis, because the dominantly primary pyroclastic nature of the GFV in contrast with the mostly reworked and redeposited DTC rocks, the general mineralogical and compositional features of the two rock sequences are compatible to each other and are consistent with a possible common volcanic source.

Major element composition

Determining chemical composition of tuffs and, especially, of reworked volcanoclastics, is very complicated because contamination of the original magmatic composition is difficult to be avoided. However, carefully selected samples may minimize such contamination problems. Therefore, we preferred to analyze a small number of very rigorously selected samples instead of a statistically representative sample population in order to characterize the magmatic composition of the two tuff complexes.

The comparison of the major element compositions is based on two selected whole-rock analyses of rhyolitic ignimbrites belonging to the GFV (XRF method) and a couple of whole-rock analyses of selected samples of the DTC (both XRF and classical "wet" methods). It is obvious that the GFV samples plot within the field of the DTC samples in the alkali vs. silica diagram. Older published analyses, recalculated on volatile-free basis, on samples of the DTC (Marza et al., 1991b) or on samples of Lower Badenian tuffs from the Borod Basin (Muresan et al., 1986) and from the Simleu Basin (Muresan et al., 1975) have also been plotted. All of these analyses clearly show the common rhyolitic composition of the Lower Badenian tuffs of the north-eastern Transylvanian Basin, of the nearby marginal sub-basins of the Pannonian Basin in Romania, as well as the ignimbrites of GFV. This strongly suggests that all these tuffs might belong to a common source. From the viewpoint of major element composition, GFV ignimbrites are not different from the DTC volcanoclastics.

Trace element distribution

Trace element distribution in spider diagrams, displays similar, almost identical patterns in rocks from GFV and DTC. The MORB-normalized diagram of Pearce, 1983 is identical for the two groups of rocks, while the chondrite-normalized Thompson diagram and the N-MORB-normalized Sun & McDonough diagrams show some differences only of Sr content for some of the DTC samples as compared to GFV ignimbrites. Sr is higher in two DTC samples likely because its covariance with higher CaO due to the presence of cryptic calcite in the reworked tuffs deposited in a submarine environment. It is noteworthy to mention that the DTC sample which perfectly fits the trace element distribution pattern of the GFV ignimbrites is the Magura Ciceu ignimbrite, the only primary pyroclastic rock in the DTC encountered so far.

The REE distribution pattern of the two GFV and the three DTC samples is practically identical. The trace element – including REE – distribution patterns represent a strong evidence in favor of their origin from a single volcanic source area.

Mineral chemistry

The main rock-forming minerals plagioclase and biotite from both DTC rocks and GFV ignimbrites have been analyzed by microprobe technique. However, compositional representativity is different due the uneven number of analyses performed (much more in the DTC).

The compositional range of plagioclase in the GFV ignimbrites (An=30-46.1%) is entirely included within the much broader compositional field of the DTC plagioclase. Although no relevant statistical analysis of the GFV plagioclase compositions can be undertaken, it is apparent that their average value (38.4%An) coincides with one of the two compositional maxima (at 30-40%) of the DTC An distribution histogram, the other DTC plagioclase An% distribution maximum is at lower values (20-25%) (Szakács, 2000). Thus, plagioclase compositions of the two rock series is consistent with the hypothesis of their common volcanic source.

Biotite compositions are, in contrast, dissimilar. Besides the fact that the analytical representativity of the GFV group is even much scarcer than for plagioclase, Fe oxides in biotite display different distributions: while all iron is in form of FeO in the GFV ignimbrites, most DTC rocks display various degrees of oxidation represented by the variable ferrous/ferric oxide ratios. For this reason, the structural formulas of the two biotite populations are hardly comparable. What, however, the two biotite populations have in common is their similar Ti contents (4.3% for DTC, 4.6% for GFV). Too, both biotite populations plot in the C (calc-alkaline) field of the Abdel-Rahman diagrams (1994) which discriminate granite tectonic settings according to biotite composition. Therefore, primary biotite compositions of DTC and GFV rocks seem to be similar to each other.

Discussion and conclusions

According to their radiometric ages, the Badenian rhyolitic volcanics of the southwestern Gutai Mts. and the Dej Tuff Complex can be correlated. Their major element and trace element compositions are very similar, while their REE distribution patterns are identical. The mineral chemistry of the main rock-forming minerals plagioclase and biotite are also compatible, although the representativity of the measured sample populations is quite different. Other similarities include petrographic features such as crystalclast composition and vitriclast types, as well as overall textural features, especially of the reworked volcanics (representing the common lithology of the two sequences). The characteristic presence of unsorted or slightly sorted pumice-rich volcanics strongly suggest the provenance from pyroclastic flows of a part of the volcanic material in both volcanoclastic sequences. Hence, eruptive mechanisms should be similar as well. Major differences are lithological and they are mainly related to the different depositional environments - prevailingly subaerial for GFV and submarine for DTC - as well as to different proximity to the source.

The overall picture including field observation, analytical data and genetic/volcanologic interpretation of the two volcanoclastic complexes strongly suggests their correlability. Moreover, lithological and grain-size characteristics of the volcanoclastic deposits belonging to GFV suggesting a proximal location with respect eruptive centers (Fülöp, 2001) fit well with the regional grain-size distribution pattern of the DTC showing a general trend of coarsening towards NW and inferred volcanic source location in the same direction (Szakács, 2000). Thus, it is very likely that the two sequences are not only correlable in time, providing a regional lithological marker horizon in the eastern part of the intra-Carpathian area, but they were probably originated from the same volcanic source area (a caldera or a caldera complex). A discussion on the nature and location of the volcanic source(s) is beyond the scopes of this contribution.

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AMBER - ECONOMICAL REFERENCES

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In modern times amber has remained a valuable substance as ornamentation techniques have become more complicated and the creations of countries which lack artists more expensive. Ironically, amber deposits tend to be located in the modern technology and qualified labor for adding value to the raw form.

The mining and processing of amber harms the local ecology, an example being the Baltic Sea, which has been deteriorated for the last 50 years due to rapid development of mining and industrialization.

Amber is a fossil resin with specific properties, which have been known since prehistorical times. There are many amber varieties all over the world, but only a few fossil resins are well-studied: succinite, rumanite, Sicilian amber (simetite), Burmese amber (burmite), Mexican amber from Chiapas, Canadian amber (cedarite), Ecuadorian amber (guayaquillite), Dominican amber and Lebanese amber.

Succinite is an Eocene-Miocene amber variety, which could develop not only in the Baltic countries, but also at any point on the Globe where the paleobotanical, paleogeographical and geochemical conditions necessary for its development are present (Savkevich, 1981). This is proved by the existence of geological sources of succinite more than 1000 Km from the Baltic, in Belarus, the Ukraine, near the Caspian Sea, on the island of Sakhalin, in NE Yakuty, Sweden, Denmark, and Great Britain; deposits of succinite have not so far been detected geologically by the south of the Alps. It must be noted that Langenheim (1969) and Broughton (1974) have found ambers with similar spectra to Baltic amber, in North America and Greenland, while Savkevich would extend this to Asia (Fraquet, 1987). Succinite is commonly used to describe Tertiary Baltic amber which has been generally noted to contain more succinic acid (>8%).

In Romania fossil resins have been sporadically recorded at the level of Cretaceous and Eocene formations, but the most frequent outcrops occur in the Oligocene flysch deposits of the Eastern Carpathians, from Bucovina to the Ialomița Valley. In interior of the Carpathians, yellow amber is found at Sibiu and Alba. In 1891, Otto Helm published an article referring to many varieties of Romanian amber, where he noticed that rumanite is amber from Buzău. So, various kinds of Romanian fossil resins were mentioned: schraufit (Schrokinger, 1875) from Vama (Bucovina), almaschit (Murgoci, 1902) from Piatra Neamț, muntenit (Istrati & Mihailescu, 1923) from Olanesti (Vilcea district) and telegdite (Zechmeister & Vrabely, 1927) from Săsciori (Alba district), last being probably an inferior fossil resin named retinite.

It was during the Bronze Age that the famous amber trade routes were established. These were accepted "Highways", trade routes across the whole Europe and extending into the far east.

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(fig. 1). These routes have been established by amber finds found in archaeological sites around and along these ancient courses.



Fig. 1. Amber trade routes (www.gplatt.demon.co.uk)

Phoenicians went to great lengths to hide the source of their golden bounty and ancient literature tells stories (www.gplatt.demon.co.uk) of Phoenician ships captains wrecking their own boats when being shadowed and followed by rival traders trying to ascertain the source of amber (the first case of industrial espionage?).

Amber began to make something of a comeback in the medieval period. The Teutonic Knights in 1283 became absolute rulers of Prussia and also created a monopoly on amber production within the Samland Peninsula (www.gplatt.demon.co.uk). The major product became Paternoster beads. In fact, the makers of this particular religious article even had their own job title: *Paternostermachers*.

The Teutonic Knights ruled the amber industry with an iron hand, to the extent that they forbade the collection of amber from the Baltic beach on pain of death. "The Beach Master" or "Amber Lords" enforced this law and there are many accounts of unfortunates who picked up amber and were hanged for it. In the ensuing years, licenses and agreements were granted to different personages and retrieved over the following 500 years. Paternoster remained the staple amber product.

By the end of the 14th century, the sale of amber as well as the gathering was completely encompassed and controlled by the Order, to such an extent that within the city of Königsberg a mining site, it was forbidden for anyone to own or possess any unworked pieces of amber.

The Teutonic monopoly was transformed over this period into a series of monopolistic Guilds. In 1480 the Danzig Amber Guild was formed. The Guild consisted of amber lathe turners who wanted to become another centre for amber working. The Teutonic grip still existed but was answerable to the king of Poland.

One of the principles of control, which was maintained throughout this time, was the separation of the gathering of the amber from the working of the amber. This was applied with some rigor and artists wishing to work with amber outside one of the guild's centers had to apply for a license to do so. It was as late as 1641 before this protocol was breached and Königsberg was officially granted a guild for working amber, the first where amber was both extracted and worked in the same place.

In the 17th century the Baltic amber trade drew closer to becoming an industry. But the oppressive rule continued, the fisherman of the Baltic coast had to swear an oath to the state that they would turn in to the authorities anyone they knew guilty of illegally gathering amber.

In ancient times, exploitation methods were similar in all places: primitive box-like mines were commonly used. The method consisted of digging shallow, several-meters pits. Only sometimes, their depth exceeded 20 meters. In some places, miners built timber linings into the pits, which not only made the work less dangerous but also allowed them to dig deeper (Kosmowska-Ceranowicz et al., 1984).

A different method of exploitation where lateral galleries were dug along with shafts was known in Sambian Peninsula, Lithuania. The lateral galleries usually had outlets to let in the air. Started from 1867 following geological research, mechanized mines were opened. The shaft system was expensive and dangerous. Ceilings had to be disposed off regularly (Kosmowska-Ceranowicz, 1984). For these reasons, the method was gradually phased out, and starting from 1914 it was replaced by opencast mining, applied till the present day.

The extraction process had undergone complete mechanization by 1930 at Palmnicken amber mine. There was established in 1875 the first open pit amber mine and a million pound mark was reached in 1895. Conveyers dump earth-containing amber into waiting freight cars, which then transport the earth to spray houses. Next, high-pressure hoses separate the "blue earth", the name that Germans gave the amber-containing soil, from amber. Experts estimate that more than 180000 tons remain in the Yantarny mine (the ex-Palmnicken mine), enough for another three centuries of extraction at the current rate.

Since strip mining started over a century ago, the Yantarny plant into the Baltic has discharged more than 100 million tons of waste. The mining and processing of amber produces matter which the Baltic's brackish water cannot dissolve. Since the Baltic is largely cut off from the Atlantic Ocean, it cannot easily refresh itself.

Another consequence is a Wild West atmosphere which reigns at the Yantarny mine. The mine management is accused from mafia connections, according to a 1996 estimate, annual losses due to illegal extraction are amount \$ 1 billion. As a result of the legislation, from 1996 amber will have to be guarded in foreign currency like other precious stones (www.gplatt.demon.co.uk).

About 70% of the amber artifacts produced in 1996 worldwide originated in Poland, and of those 805 in Gdansk. The number of amber factories increased in the region of Gdansk from 600 to 3000 between 1989 and 1996, the number of artists and workers from 700 to 8500, and the amount of raw amber used in the artifact production from 40 to 193 metric tones during that time. Most of the amber manufactured is imported from Samland Peninsula (today's Kaliningrad).



Fig.2 The map of amber mines from Baltic Sea (www.gplatt.demon.co.uk)

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