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Foreword

The symposia organized by the Society for Economic Geology of Romania (SGER) have reached their 7th edition. For the present one, the meeting will locate in Baia Mare.

Baia Mare is a famous mining city, with an important development thanks to the extraction and processing activities of the non-ferrous and gold ores.

The mining centers Baia Sprie, Dealul Crucii and Cavnic were known in the Middle Ages, also like type localities for some new minerals – sulphosalts especially: andorite, semseyite, dietrichite, felsöbanyaite, klebelsbergite, szmikite, fizéelite, parajamesonite, fülöppite.

The ore deposits in Baia Mare are famous not only for the new minerals, but also for the new established metallogenetical principles in this district. I am referring to the metallogenetical vertical zonality in Baia Sprie, a hot spot one (Ghițulescu, 1935, Helke, 1938), the correlation between the adularization process and gold metallogenesis (Giușcă, 1961), some aspects of the metallogenetic regeneration process in a regional (Socolescu, 1961) or a local area, i.e. Cavnic (Popescu, 1978) and a vertical extended depth of hydrothermal mineralization (Maldarescu, Popescu, 1981).

Although a decrease of geologic and mining activities is a fact during last years in Romania, the Baia Mare district, rich in mining and related industries, is of key economic importance to Romania. Therefore, a higher education and research institution has developed – the North University. Baia Mare is the place of research and utilization of minerals activities and also of environmental protection in connection with extraction and processing activities. In the same time, in the 90 , a gold production activity began in the district, by processing some tailing dams, which are, in fact, recyclable ore deposits. Unfortunately, same unfavorable circumstances create serious environmental problems and the image of all mining industry in Baia Mare has greatly affected. The longer-term economic implications of the spill and other polluting activities recorded in 2000 on January 30, are of great importance: geological and economical projects which could decisively contribute to the progress of Romania have compromised (see the Roșia Montană Project). In a same context I should mention the activity of the Romaltin Company in order to process gold of the older tailing dams.

The topics of the present meeting cover a large number of topics including entire segment of the Carpathians. It is an opportunity and a challenge for people that have an optimistic vision

looking economic geology in Romania. I am happy because experts and companies have responded to our invitations. Most of them promoted important projects, like porphyry copper-Au mineralizations, i.e. Rovina, Metaliferi Mts. A special mention is due to geologists of Carpathian Gold and SAMAX, Baia Mare.

Both scientific parts of the Symposium will include papers regarding economic geology (20), ranging from general theoretic issues (Popescu et al., Jude, Mârza et al., Munteanu et al.) to applicative approaches (Halga et al., Andrei, Mureşan, Berbeleac et al., Drăgănoaia, Ilie et al.). Source for basic materials, mining of mineral aggregate deposits, an intensive activity of the present-days, is the object of two papers (Costea et al., Marinescu, Stanciu).

Like others joint meetings, I am happy to meet authors from abroad. I would like to thank to Professor Bilal, an old friend of the Romanian geochemists and ‘ environmentalists ’. Mr. Professor will present us his scientific results in cooperation with Brazilian geologists, referring to phosphogypsum, a mineral of great interest in our country too (see papers about phosphogypsum in Turnu Măgurele).

The environmental problems are of interest too, papers to be presented regarding acid drainage (Lefticariu), recyclation of mineral residual deposits (Fechet et al., Ghiţă et al.) or phytoremediation of dams (Udubaşa et al.).

I would also mention papers about fluid inclusions (Pintea) or those regarding geochemistry of gold and associated elements (Cioacă et al., Popescu et al.).

There are also papers about uncommon problems related to mineralogical and geochemical study of gold (Cristea et al) and bronze (Macovei), both with implications in archaeology, another about dust mineralogy and geochemistry (Curcă) and, finally, about heavy metals from snow (Balint).

In the end I wish to emphasize the wide variety of research, confirming the affiliation of the economic geology at the large spectrum of geology. Geology is today a complex science, with many valences, exceeding its conventional limits.

Prof. Dr. Gheorghe C. Popescu

President of the Society for Economic Geology of Romania

PLENARY LECTURES

METALLOGENY OF EAST CARPATHIANS WITH A SPECIAL VIEW TO THE METALLOGENETIC DISTRICT OF BAIA MARE

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There exists a close correlation between the metallogeny of an area – i.e. the specific way in which various metallogenic facts evolved and interacted – and their geological evolution. From this point of view, the metallogeny of Romania offers a convincing example of metallogenic consequences due to crustal and superimposed local processes.

In agreement with the geological diversity of the Romanian territory, its metallogeny is different in content and organization, both in the Carpathian area and in its vorland. This fact has lead to the individualization of metallogenic units that are specific to the two areas. (Fig.1)

The metallogeny of the Carpathian area displays a large variety of manifestations and it is quantitatively much more significant; it s defining and has a much more significant participation; its defining characters are given Alpine mineralizations and pre-Alpine, tectonically regenerated accumulations. Thus, especially in the South and East Carpathians, the tectonically regenerated crystalline formations contain manganese, iron and polymetallic mineralizations of certain pre-Alpine origin; certain concentrations of iron, various sulfides and barite, formed during the convergence that built and finished the continental structure of the Carpathian area.

The repartition and structure of the metallogenic units on the Romanian territory denote the action of a series of crustal factors (geodynamic processes) that constituted the background of specific metallogenic processes. Among the consequences of these processes are the metal concentrations that can be regarded both as local manifestations and as logical groupings determined by geodynamic and petrogenetic causes.

By following the development in time and space of the geodynamic processes in the Romanian territory, we are allowed on one hand to reveal their role in the formation of various geological entities and on the other hand, to stress their metallogenic significance. The establishing a relation between the metallogenic factors and metallogenic units implies a hierarchy that complies with their own systematic and that materializes a cause-effect relation. All the authors concerned with the classification of metallogenic units agreed that beside the fundamental unit – the ore deposit – there are two more units of superior rank – the district and the metallogenic province - representing natural groupings of fundamental units.

However, there is no general agreement on the classification and the definition of the metallogenic units. This situation is determined by the fact that the criteria used for separating these units were either economic or purely dimensional. A typical example in this respect is the way in which the metallogenic province is defined. Thus, several authors define the metallogenic provinces as being regions with extended ore deposits, of at least 1000 km in one direction (Petraschek 1965, Park, McDiamird 1970), whereas others consider them as areas that can span from the size of a mining field to hundreds of even thousands of kilometers. Other groups of authors consider the metallogenic province as an area that is strongly mineralized or contains the same type of ore deposits or has unitary genetic characters (Turneure 1955).

In the case of metallogenic units we have such a classification – even though there is no general consensus upon it. However, the systematic of metallogenic factors is very recent and has only a draft character.

Classic researchers considered that the concept of metallogenic province is strongly related to that of metallogenic epoch, both notions defining metallogenic maxima, in a spatial and temporal sense, respectively (De Launay 1913, Fynlayson 1910, Lindgren 1933). Roughly, the same sense of the notion is transparent in the metallogenic maps made for the Romanian territory (Ianovici et al. 1966, Rădulescu et al. 1969) where the definition of the metallogenic units is made both on

temporal and petrological criteria. Thus, in most cases, metallogenic provinces coincide spatially and temporally with petrological units.

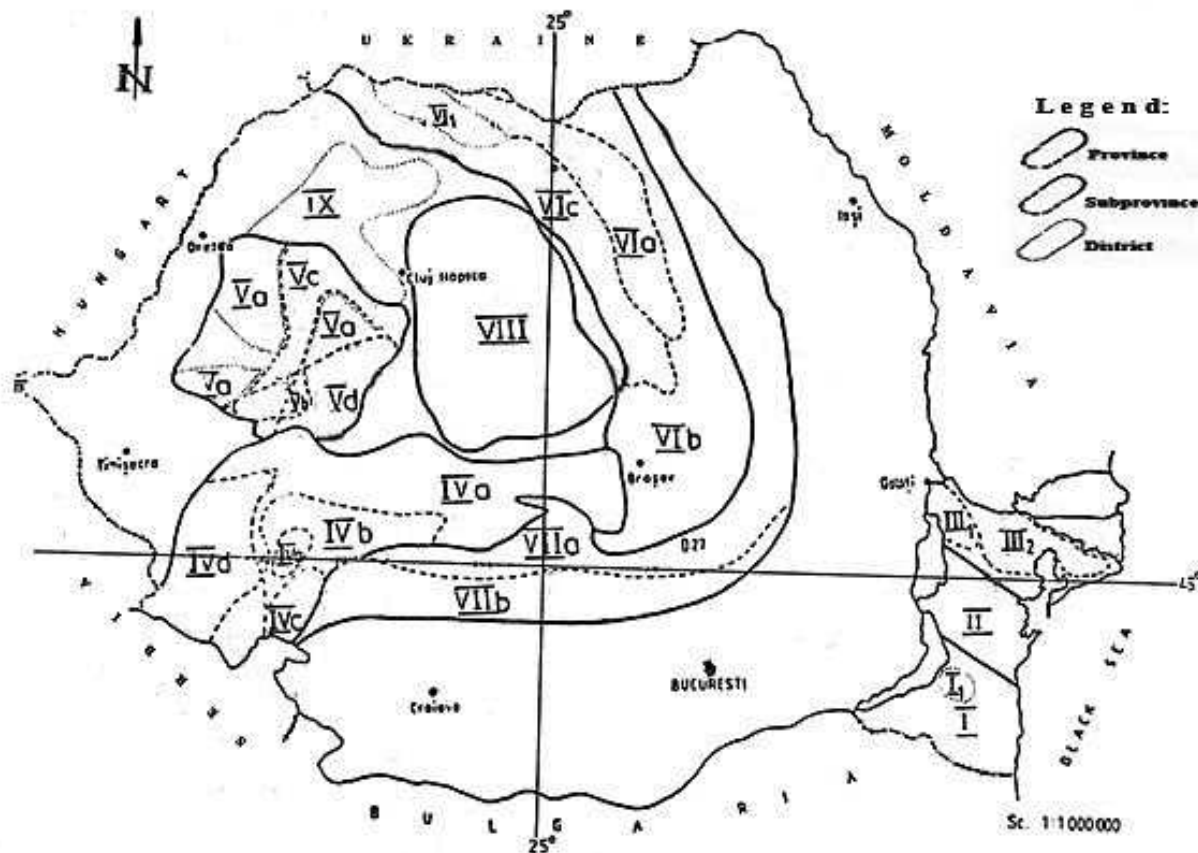


Fig. 1: Metallogenic units of Romania.(Popescu, 1986).

Vorland domain: I. South Dobrudja province, I.1. District with phosphorites and glauconite, II. Central Dobrudja province, III. North Dobrudja province, III.1. Măcin district, III.2. Tulcea district, Carpathians Realm, IV. South Carpatians province, IV.a. Getic subprovince, IV.b. Danubian subprovince, IV.c. Mehedinți subprovince, IV.d. Subprovince associated of banatites, V. Apuseni Mountains province, V.a. North Apuseni province, V.b. Subprovince associated of mesozoic magmatism, V.c. Subprovince associated of banatite, V.d. Subprovince associated of Neogene volcanos, VI. East Carpatians province, VI.a. Crystalline-Mesozoic subprovince, VI.b. Flysch subprovince, VI.c. Subprovince associated to Neogene magmatism, VI.d. District of Maramureș basin, VII. Pre-Carpatians through province, VII.a. Subprovince with evaporates, VII.b. Subprovince with Ti-Zr placers, VIII. Transilvania basin province, IX: Gilău Mezeș-Preluca district

Other authors (Magakian 1959, 1973, Janković 1974) consider that the metallogenic provinces one should be delimited on structural criteria, on the metallogenic content of the structural units. As a result, the provinces are clearly defined in space, and confined to their respective structural units. This point of view is in principle different from those discussed above and introduces a natural, geological and objective criterion in the definition of the metallogenic units. Some recent approaches of the definition of the metallogenic units based on the plate tectonics concept (Guild 1974, Mârza 1982) are basically in the same spirit. For example, Guild grouped the metallogenic units (provinces, districts, ore deposits) into two main classes (types), located at or close to the lithospheric plate margins and in the interior of these plates.

In connection to the issues discussed above it is useful to point out the following facts:

- Regardless of their rank, the metallogenic units are geological entities and therefore geological criteria must be used for their definition and delimitation.
- The terms used for defining metallogenic units would preferably have no correspondents in other fields of geology. Thus, terms such as metallogenic zone or ore deposit should be abandoned. The notion of zone for instance is used in tectonics (e.g. the crystalline-

Mesozoic zone of the East Carpathians) in petrology (e.g. metamorphism zone), as well as in the geology of ore deposits (e.g. Emmons zone or Andine subduction related zones). The term ore deposit has both an economic and utilitarian meaning, and thus should be replaced in metallogeny by the notion of mineralization body to signify the fundamental unit in metallogeny.

As a consequence an hierarchy of the metallogenic units that can be applied to Andine systems would be the as follows: metallogenic belt; metallogenic province; metallogenic subprovince; metallogenic district; metallogenic sector; metallogenic field; mineralization body. The underlined terms are the essential (mandatory) ones, whereas the others may sometimes be unnecessary to distinguish or to mention on metallogenic maps.

It is self understood that in a descriptive or cartographic language, other terms may be used: e.g., zone (but only in the sense given by Emmons), metalliferous node – for defining maximum local concentration of mineralization bodies, alignments etc. The term of metallogenic sector that may be used as a subdivision of certain metallogenic districts defines a certain metallogenic specialization directly related to a particularity of the genetic factors (e.g., the gold mineralization sector of the Baia Mare metallogenic district).

A hierarchy of the metallogenic factors has been suggested relative recently (Popescu 1981, Popescu, Lupulescu 1983, Laznicka 1985, Popescu 1986) and it has been made possible only by applying the concept of plate tectonics to metallogeny and by revealing the dependency of petrogenesis upon tectogenesis, and of metallogeny upon tectogenesis. This fundamental idea, this methodological principle, makes possible to classify the metallogenic factors and to establish their differential role in the formation of metal concentrations. Thus, one can define crustal factors that determine the qualitative differentiation of the Earth's crust from both petrographical and metallogenic point of view, resulting in the formation of macro metallogenic units (belts and provinces), as well as other, local factors, among which a prime role is held by the petrographic ones which determine both the differentiations among the macro metallogenic units and the formation of inferior rank units such as districts and fields.

The first type of factors act both in the marginal portions of the lithospheric units, during divergence (extension) processes and convergence (compression) processes, and within the tectonic plates, along crustal faults, proto-rifts and intra-continental rifts. The second type of factors are mostly of petrogenetic character and result in the formation of continuous (metallogenic body) or discontinuous (metallogenic field) micro units.

Thus it becomes obvious that the large metallogenic units are the consequences of crustal factors that are active mainly at the level of lithospheric units. Thus it becomes obvious that the large metallogenic units are the consequences of crustal factors that are active mainly at the level of lithospheric units.

The metallogenic province of the East Carpathians includes important deposits of economic interest, with an obvious relic character. There has been already mentioned that some sulfide deposits in the East Carpathians show similarities with extra Carpathian deposits, suggesting that they were parts of a much ampler metallogenic unit, may be even a belt such as the Caledonides. (Fig. 2)

Subduction related metallogeny from the Eastern Carpatians had as result a specific subprovince containing the consequences of the differentiated stress regime both in space and time. Along the subduction there are three igneous districts with different morphologies and associated metallogeny also formed. The district situated to the north of Dragoș Vodă fault has been generated under the conditions of a tensional stress and contains andesite and dominantly base-metals and subordinately Au-Ag metallogenesis. The central district situated between Dragoș Vodă and Someșului faults has been formed under the conditions of a compressive stress and has some base-metals with cupriferous trend metallogenesis and a southern sector, characterized by less intense stress, ample volcanic activity, but less extended metallogenesis, generally with a polymetallic character with subordinate Au-Ag, Hg, S, Fe (siderite). Indications of a porphyry copper metallogenesis have recently been pointed out in Gurghiu Mts. (Fig.3).

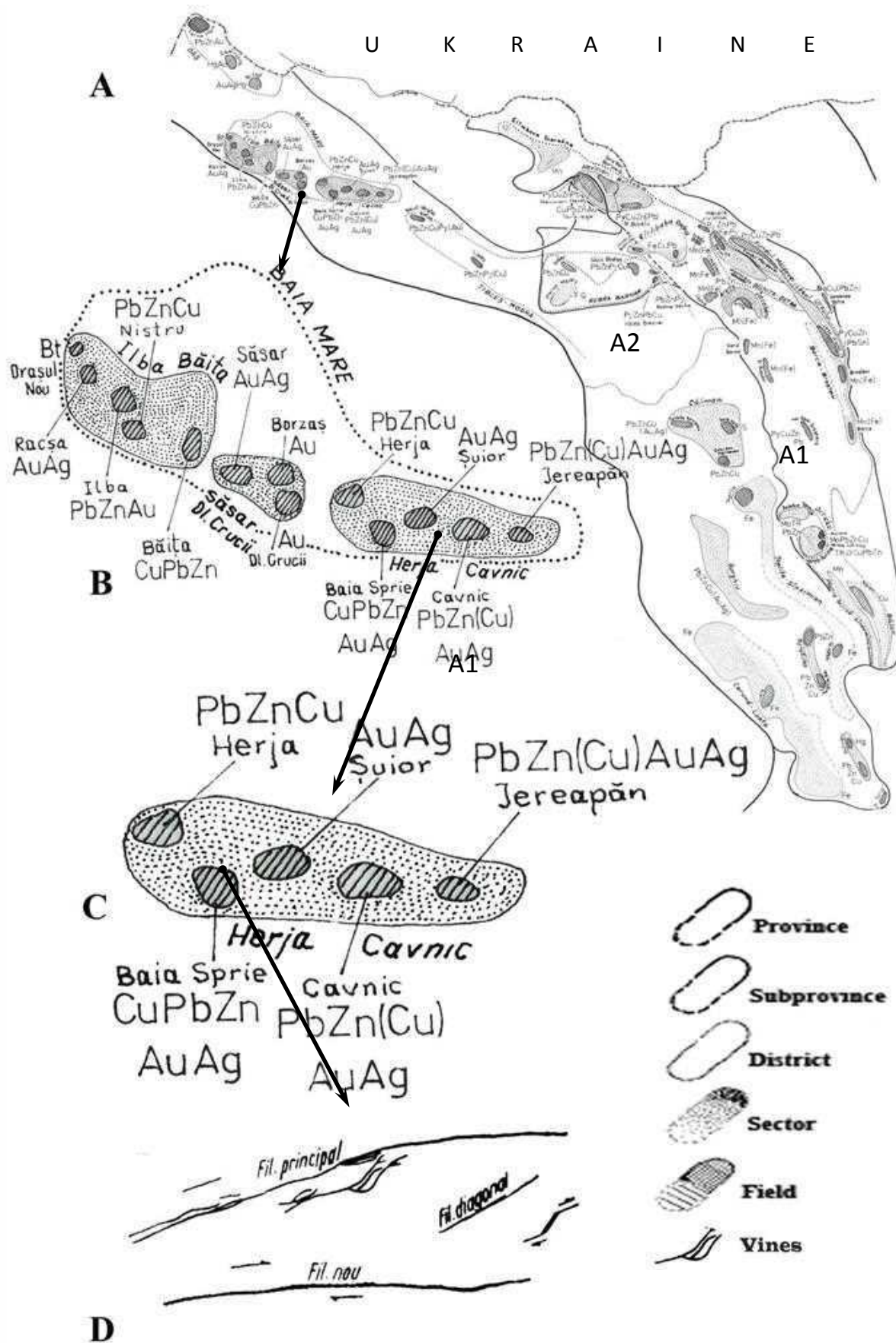


Fig. 2: Hierarchy and terminology of metallogenetic units, illustrated by examples from Easter Carpathians. A. Eastern Carpathian s Metallogenic province A1. Christalino-mezozoic subprovince, A2. Metallogenetic subprovince associated with the neogene magmatisme, B. Metallogenetic District of Baia Mare, C. Metallogenetic Sector Herja-Cavnic, D. Metallogenetic Field of Baia Sprie, E. Legend of maps.

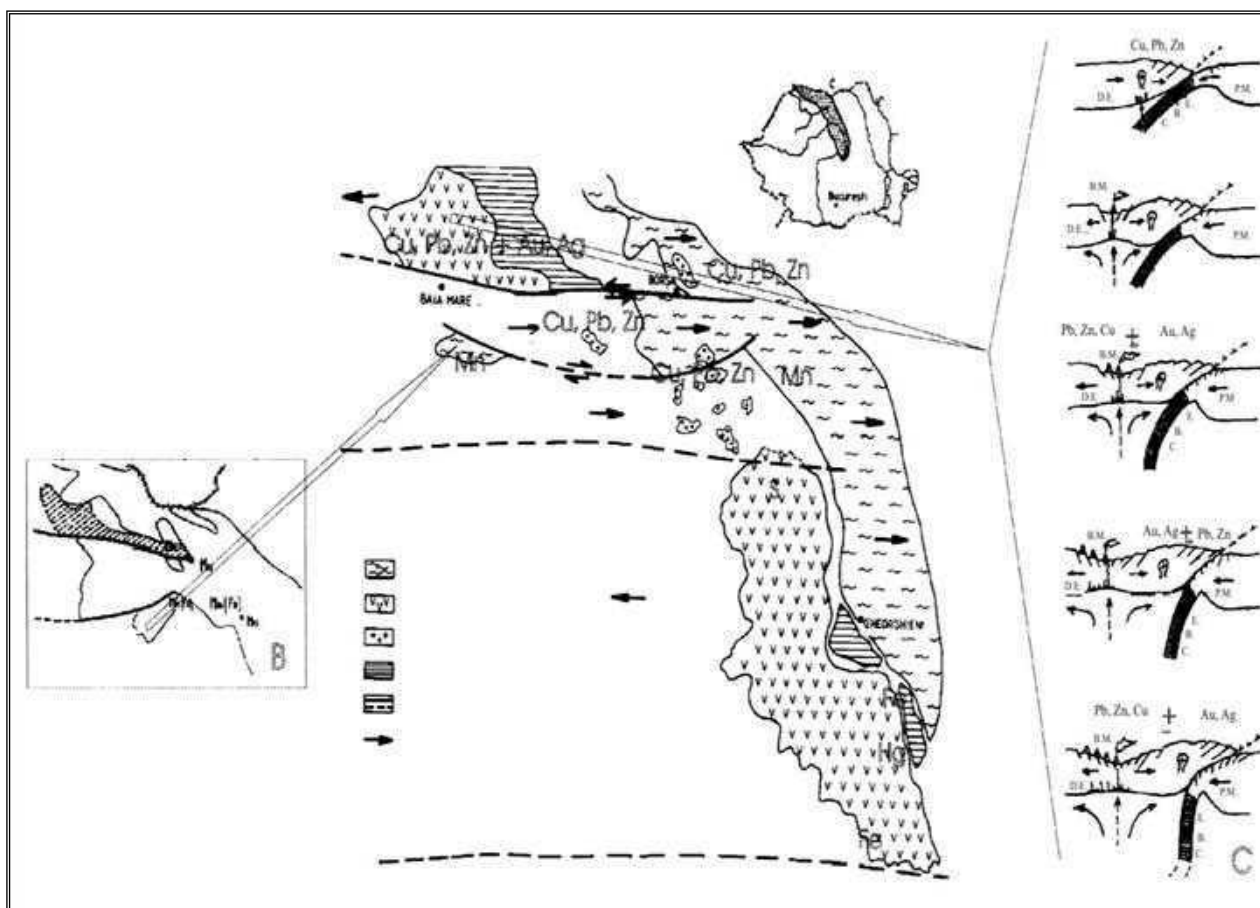


Fig. 3: The subduction arch s components of the East Carpathians and the relationships between stress regime and metallogenesis. A: Metamorphic accretionary prism, Neogene volcanites intrusions and crustal fractures influencing them. B: Distribution of manganese deposits and occurrences in the northern segment of East Carpathians and Preluca Masif at the end of Cretaceous. C: The subduction process stage in the northern segment of the East Carpathians and its correlation with magmatism and metallogenesis. (D.E.- Eastern Dacite, P.M.- Moldavian Platform, C.B.E. - Oceanic crust, B.M.- Maramures basin.

The stress regime had a variable character in time especially, shown by the northern part of the Eastern Carpathians. In this segment of East Carpathians, there are five stages of subduction (Fig. 3A, B, C).

The first stage had compressive character of the stress field and favoured an intrusive calc-alkaline magmatism - Toroiaga Massif, associated with base-metals with copper.

The second stage had a tensional stress regime and favoured the first volcanic manifestation, expressed by acidic-rhyolite and dacite.

The third stage was a typical tensional regime of stress and favoured volcanic andesitic manifestation and associated base-metals metallogenesis.

The fourth stage is represented by eruptions of dacites quartz-andesite and has a Au-Ag metallogenesis.

The last stage represented by the andesite with pyroxene and amphibole has an important base-metals and partially Au-Ag metallogenesis.

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THE ROVINA VALLEY PROJECT, APUSENI MTS., ROMANIA: GOLD-COPPER PORPHYRY DISCOVERIES IN A HISTORIC MINING DISTRICT

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The Rovina Valley Project (RVP) in west-central Romania lies within the historic gold-mining district known as the 'Golden Quadrilateral (GQ)' with estimated +55 Moz of gold produced well before the Roman period (more than 2000 yrs ago). The bulk of this historic production has come from volcanic-hosted low-to-intermediate sulphidation epithermal veins. Since opening-up to western exploration companies, a further 20 Moz gold resources have been defined associated with these systems. The GQ is also host to copper-porphyry deposits of similar age which can occur in proximity to the epithermal gold mineralization. This paper presents recent discoveries of gold-rich porphyry systems in the GQ.

Carpathian Gold Inc. through its Romanian subsidiary, SAMAX Romania SRL was awarded the Rovina Exploration License in late 2005. Carpathian geologists recognized the potential of this terrain for multiple gold-rich porphyry deposits and concurrent with detailed generative exploration, diamond drilling was initiated in 2006 with 71,375 metres drilled to date. Drilling in 2006 and 2007 discovered the Au-rich Colnic porphyry and defined a significant gold component in the previously-recognized Rovina-Remetea porphyry. Colnic is located 2.5 km south of Rovina-Remetea with both containing isolated outcrop occurrences of Au-Cu stockwork mineralization. Drilling in 2008 discovered the 'blind' Ciresata –V. Garzii Au-rich porphyry 4.5 km south of Colnic where mineralization starts 50-150 metres below the surface.

The Rovina-Remetea Cu-Au Porphyry Deposit is hosted in a feldspar-amphibole diorite porphyry complex with the bulk of mineralisation hosted in the earlier Porphyry C and the later axial core Porphyry B both intruding a pre-mineralisation Intrusive Magmatic Breccia. Porphyry C has higher Cu grades than Porphyry B while the latter is enriched in gold. A post-mineral phreatic-magmatic Glamm Breccia cuts part of the mineralised porphyries. The main alteration types associated with the mineralization at Rovina-Remetea are: early potassic alteration (biotite – magnetite – quartz – K feldspar) and an overprinting Mace alteration (magnetite – chlorite – epidote ± K feldspar ± quartz ± anhydrite ± carbonates). The mineralization is represented by a quartz-magnetite-pyrite-chalcopyrite stockwork and disseminated pyrite-chalcopyrite outcropping in a stream-bed exposure in the Baroc Valley and extending to about 450-550m below the surface. The deposit measures ~350m in the NW-SE direction and ~600m in the NE-SW direction. Typical grades range between 0.1-1.0 g/t Au and 0.05-0.70% Cu with a central higher grade core associated with Porphyry B (0.4-0.6 g/t Au and 0.4-0.6% Cu) that extends ~400m below the surface.

The Colnic Au-Cu Porphyry Deposit is exposed along the Bucuresti-Rovina road and extends to 200-350m below surface. The deposit measures ~600m in the NW-SE direction and ~400m in the NE-SW direction. The mineralization is hosted in an intensely developed quartz-pyrite±chalcopyrite stockwork within a feldspar-amphibole diorite porphyry complex. The most intense mineralisation is hosted in the Colnic Porphyry interpreted to have two stages, with lower-grade mineralisation hosted in the later F2 Porphyry. Both porphyries intrude an earlier unmineralised wallrock Porphyry. Post-mineral barren dykes are also present. The earlier alteration associated with the mineralization at Colnic is potassic alteration (biotite – quartz ± K feldspar with pyrite > pyrrhotite > magnetite >> molybdenite). Multiple-phase mineralizing events created at Colnic a series of overlapping events: Mace alteration (quartz – magnetite – chlorite ± epidote – carbonates – pyrite – chalcopyrite) overlaps the potassic alteration and both Mace and Potassic Alterations are overprinted by a later quartz-sericite alteration (sericite – quartz – pyrite ± clay minerals) associated with the intense developed stockwork in the upper part of the Colnic Porphyry. Typical grades range between 0.3-1.3 g/t Au and 0.05-0.18% Cu with a central higher grade core (0.8-1.2 g/t Au and 0.1-0.2% Cu) that develops from surface to -200m.

The blind Ciresata-V.Garzii Au-Cu Porphyry Deposit has been discovered by a combination of ground-magnetic survey, geochemical soil sampling and detailed surface alteration mapping. The deposit, as it is known today, measures ~350m in the NW-SE direction and ~400m in the NE-SW direction. Drilling indicates mineralisation starts 50 to 150m below surface and extends vertically at least 800m below surface. The mineralization is hosted in both feldspar-amphibole diorite porphyry (Early Mineral Porphyry) and in the adjacent hornfelsed siliciclastic Cretaceous Sediments. Sub-vertical Late-Mineral Porphyry dykes, less than 40m in width, hosting low-grade mineralization, represent the last intrusive event. The gold-copper mineralisation occurs in intensely developed quartz-magnetite-pyrite-chalcopyrite stockwork that locally comprises +80% of rock volume. This mineralisation occurs within magnetite-potassic alteration (magnetite - biotite – quartz $\pm$ K feldspar, pyrite, chalcopyrite). The alteration occurs both in the Early Mineral Porphyry and the hornfelsed sediments. Typical grades range between 0.3-5.0 g/t Au and 0.05-0.4% Cu with a central higher grade core (0.8-2.0 g/t Au and 0.15-0.3% Cu). These exceptionally high gold grades, make the Ciresata-V.Garzii deposit the richest Au-porphyry occurrence known to date in Romania. The deposit is still open towards the south-west, south and east directions as well as at depth. Exploration drilling is ongoing to delineate the size of this deposit.

Gold in the RVP deposits occurs mainly as liberated grains at the contact with pyrite and locked in chalcopyrite +/- magnetite. Locked cycle flotation testing has demonstrated that a simple flotation flow sheet with moderate grinds and low reagent additions is able to generate saleable copper concentrates averaging 18 to 22% copper and 50 to 60 g/t Au concentrate.

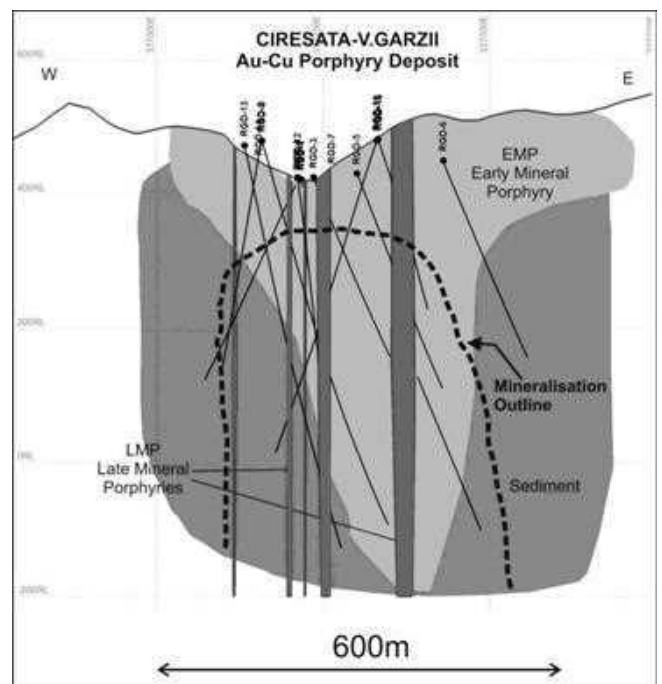
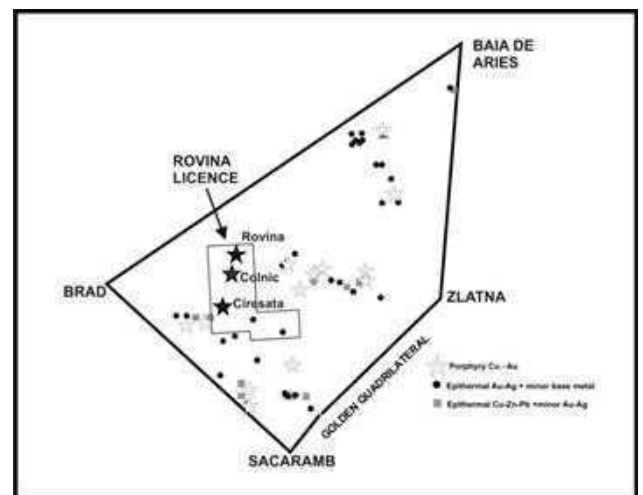
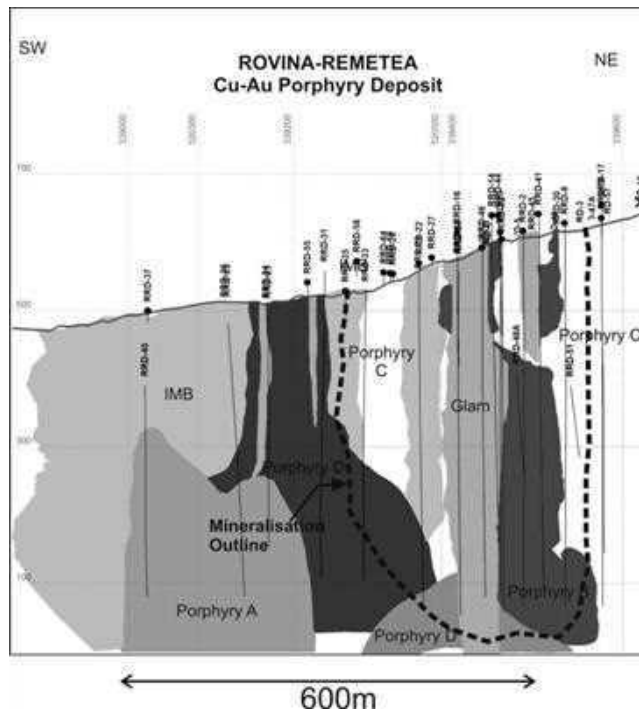
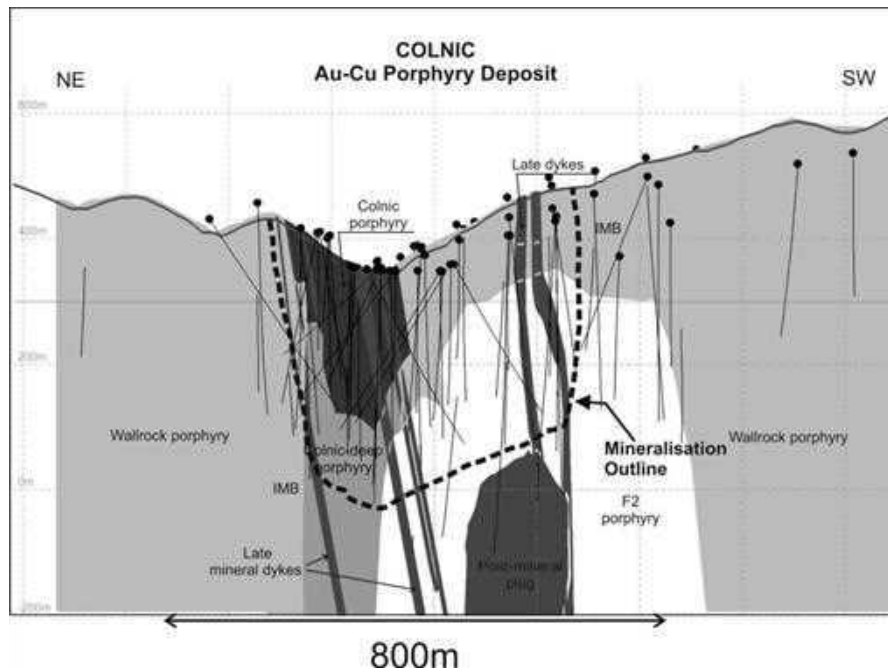
The Rovina-Remetea, Colnic, and Ciresata-V. Garzii porphyry deposits comprise the RVP, for which a 43-101 compliant Resource Estimate was completed in November 2008 as summarized in the table below:

Resource Category	Tonnage (Mt)	Au (g/t)	Cu (%)	Au-eq* (g/t)	Gold (Moz)	Copper (Mlbs)	Au-eq* (Moz)
Measured+ Indicated	193.1	0.49	0.18	0.82	3.07	759.1	5.09
Inferred	177.7	0.68	0.17	0.99	3.89	663.1	5.66

- *Au-eq. uses US\$675/oz-Au; US\$1.80/lb.-Cu
- Base case cut-offs: Colnic 0.45 g/t Au-eq.; Ciresata 0.70 g/t Au-eq.; Rovina 0.30% Cu-eq.
- Note, tonnes are rounded

In March 2010 a group of independent engineering companies finalised a Preliminary Economic Assessment (PEA) over the Rovina Valley Project deposits. The PEA returned positive results, focusing on mining the higher grade core contained in each deposit. Highlights of the PEA Study include:

- Mine Type: Open Pit (Rovina-Remetea and Colnic) & Underground (Ciresata-V.Garzii)
- Ore Processing Rate: 20,000 tpd Open Pit; 20,000 tpd Underground; Total 14.4 Million tpa
- Tonnes Produced: 265 Million tonnes of 0.66 g/t Au & 0.18% Cu
- Recovery (flotation process): 68% Au & 91% Cu
- Concentrate Production (wet metric tonnes) 122,000 tpa
- Concentrate Grade (dry) 50 – 60 g Au/t; 18% - 22% Cu
- Annual Production: 196,000 oz Au; 49.4 Million lb Cu
- Mine Life: 19 years
- Total Recoverable Production Life Of Mine: 3.72 MM oz Au & 938 Million lbs Cu
- Operating Cost: US\$8.49/t ore Open Pit; US\$11.51/t ore Underground
- Total Cash Cost (net of Cu credits): US\$379/oz Au
- Initial Capital Cost: US\$509 Million
- Total Capital Cost, including sustaining capital: US\$786.4 Million



FLUID AND MELT INCLUSIONS EVIDENCES FOR AUTOMETASOMATISM AND REMELTING IN THE ALPINE PORPHYRY COPPER GENESIS FROM ROMANIA

Motto: ...*"unlike silicate melts, polymetallic sulfide melts never quench to a glass."*- Frost et al., 2002

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Introduction

The Alpine porphyry copper deposits from South Banat, Metaliferi Mountains and East Carpathians show multiple and intimate autometasomatic (endomorphic magmatic-hydrothermal) features mainly within the potassic and phyllic assemblages known as protolith. These generated sulphide, silicate, brine, aqueous and vapour phases preserved now as fluid and melt inclusions assemblages trapped mainly in quartz grains from the characteristic stockwork zone.

Magmatic aqueous liquid - rich inclusions

These are monophase (L), biphasic (L+V) or had including silica globule, halite, sulphide/oxide as daughter-? minerals (Fig. 1); they are trapped in quartz grains and seem to be representative for a high density magmatic H₂O-rich liquid (quench vapour ?). They are firstly mentioned now, inspired from literature data presented in others subvolcanic environments by Naumov et al., 2002, and Davidson et al., 2005. The mentioned authors argued about pure magmatic origin of these high density magmatic water-rich fluids, deep seated at high pressure conditions. Our preliminary observations were based upon the fluid appearance as gray-silver colour in transmitted light and form unique assemblages in the quartz grains microtexture (Fig. 1). These fluids were successively flushed in the endocinetic fissure system of the crystallizing shallow body and partly digested the surrounding minerals including quartz already present in the vein from any earlier stage. For comparison the excellent data presented by Rusk et al., 2004 and Landtwing et al., 2005 were used. In addition it should be emphasized that the saccharoidal microtexture of the quartz veinlets from the stockwork reminded the textural features of high pressure rocks in subduction zones (Mibe, 2001) and so, if the θ dihedral angle between two solid quartz grains is $<60^\circ$ this would facilitate the silicate rich liquid to flow upwards by percolation. As temperature drops, the silica globules solidify (crystallize?) on the spot and trap consistent aqueous liquid inclusion assemblage (Fig.2). No microthermometry is available at this moment on this kind of fluid inclusions, the work is in progress.

Glass and silicate melt inclusions

The study of silicate melt inclusions is still problematic in porphyry copper system (Student & Bodnar, 2003) and in this revised paper it is shown that silicate melt inclusions assemblages in Carpathians has been generated as internal growth zones left behind in the silica matrix (now quartz), clusters or trails. In such circumstances the dimension of the crystallized silicate melt inclusions ranged frequently between 1 and 10 micrometers, so the microthermometry become difficult to use. Nevertheless there are many data reported on silicate melt inclusions, especially on glass inclusions from quartz in Alpine Carpathian s porphyry copper deposits showing a trapping temperature between 800°C and more than 1100° C (Pintea, 1993; 1995; 1997; 2009); such high temperature data were also reported elsewhere by Wilson et al., 1980 and Campos et al., 2002.

Recently it was emphasized the role of hydrosilicate liquid in quartz formation by in situ segregation of residual SiO₂ and H₂O-rich liquid during magmatic – hydrothermal transition (Vasyukova et al., 2008). Our microtextural observations shown that the magmatic fluids digested progressively the earlier minerals of the solidifying country rocks in potassic and phyllic zones and produced aqueous fluids, silicate, carbonate and sulphate rich fluids together with globules of sulfide and oxide minerals. Frequently new and old minerals phantoms are revealed by the presence

of characteristic assemblages of fluid, brine and silicate melt inclusions, and restitic (partially digested) silicate, sulphide, oxide or carbonate minerals.

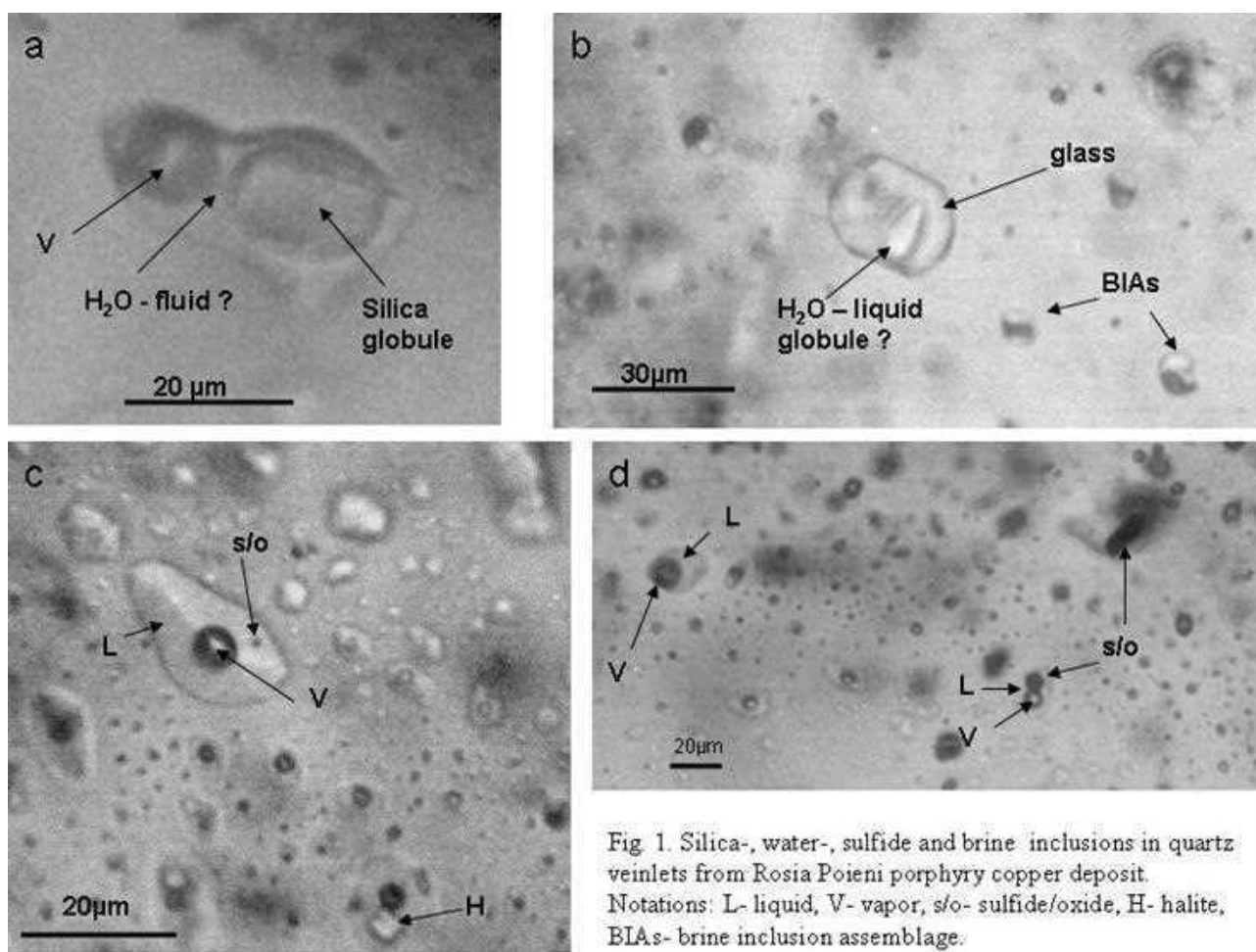


Fig. 1. Silica-, water-, sulfide and brine inclusions in quartz veinlets from Rosia Poieni porphyry copper deposit. Notations: L- liquid, V- vapor, s/o- sulfide/oxide, H- halite, BIAs- brine inclusion assemblage.

Globular remelted sulphide/oxide inclusions

Some features about the presence of globular sulphide/oxide melt inclusions in Carpathian s porphyry copper deposits were presented some time ago (Pintea, 2002) and was shown that these opaque globular phases are ubiquitous in quartz from veinlets and in the surrounding rocks in felsic and mafic silicate minerals. It was shown elsewhere that they could have been generated repeatedly by successive transformation of mafic minerals such as amphiboles, biotite and chlorite and also feldspar in porphyry copper system (Shahabpour, 2000). They could be recognized by their rounded, elliptic or lobate shape. Spreads flakes of sulphide are also characteristic. Frequently they are partially digested showing around haloes formed by globular sulphide inclusions as clusters and separate grains. These features are ubiquitous in Alpine porphyry copper deposits from Romania (Fig. 2).

Brine inclusions assemblages (BIAs)

Strong microtextural evidences shown that many of BIAs form successively by magmatic fluids (H_2O + volatiles) interaction with solidifying magmatic host rocks during formation of the potassic and phyllic zones. They are complex in composition with salinity up to 70 wt % NaCl eq. and immiscible in silicate phases, often trapped as boiling assemblages and shown a large temperature interval of homogenization from ca 450° up to 1300°C (Pintea, 1996). The pressure of the fluid at the moment of trapping ranges between several ten of bars up to 12kb in a specific

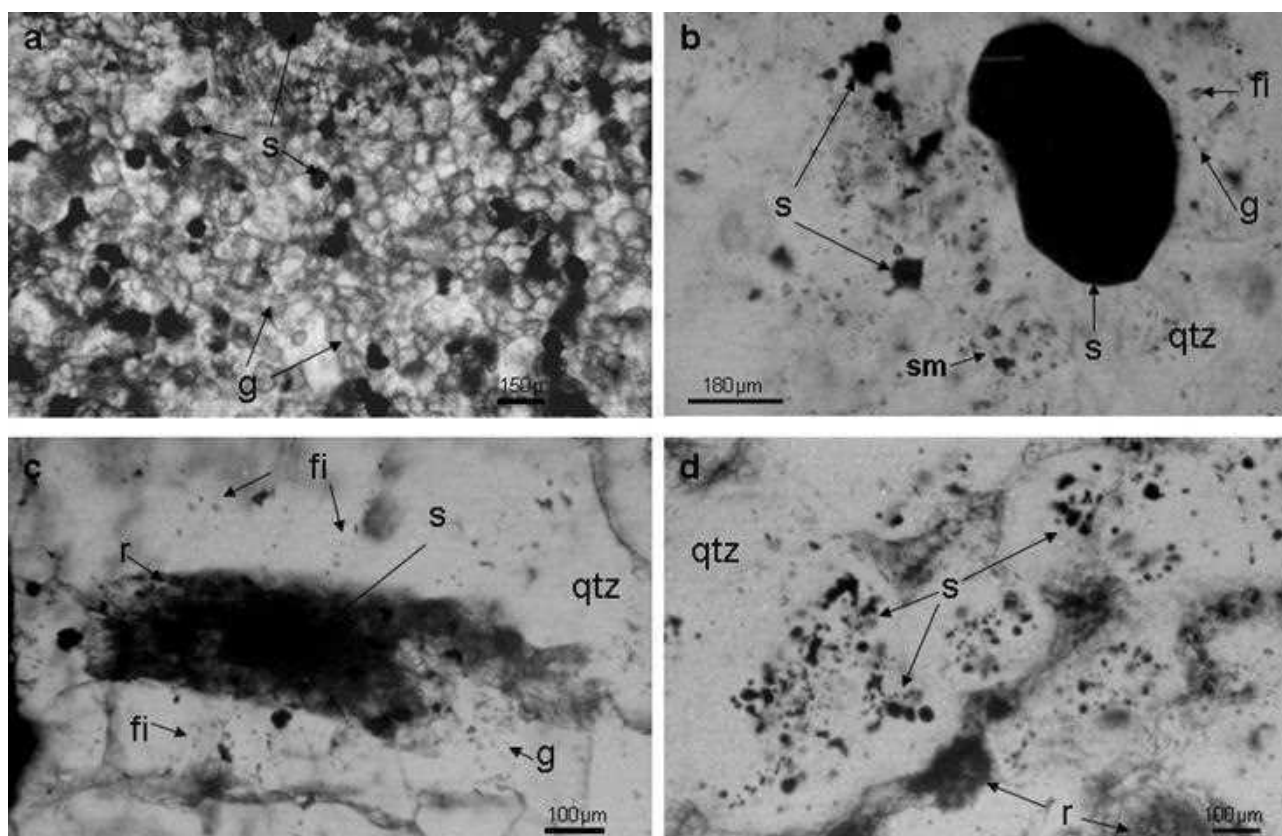


Fig.2. Autometasomatic and partial melting produced glass (g), sulphide globule (s) and fluid inclusions (fi) including silicate melt inclusions, brine, liquid and vapour in quartz veinlets from alpine porphyry copper deposits altered in the potassic-phyllitic facies.

a. Probably feldspar, biotite and chlorite transformed into glass and sulphide globules (the picture also contains quartz, K-feldspar and other unidentified minerals. Some microscopic areas shown a ghost matrix of the feldspar under the microscope; mirmekite microtexture is also frequent (not shown), - samples from monzogranodiorite in the Magura – Neagra zone (Tibles Mts). It should be noted the microtextural similarities of this genuine microtexture with some features obtained in experimental run products (e.g. Antignano & Manning, 2008). **b.** Partly digested sulphide in hydrosilicate melt, now quartz (qtz), surrounded by globules and flakes of sulphide together with silicate melt inclusions (sm), glass inclusions (g), brine and fluid inclusions (fi); andradite is also present elsewhere in this sample and contain silicate- carbonate glass inclusions, brine and aqueous rich inclusions, - sample from Moldova Noua porphyry copper deposit (upper Cretaceous). **c.** Restite mineral phase partially melted in situ and produced glass, sulphide globule, silicate melt inclusions, brine inclusions, vapour and aqueous rich fluid inclusions all trapped in quartz grains, - sample from Talagiu porphyry copper deposit. **d.** Sulphide globules trapped as clusters in quartz grains. There are some restite (r) phases between the quartz grains (former silica globule); silicate melt, glass, brine and aqueous rich inclusions were also trapped, - sample from Valea Morii porphyry copper deposit.

geodynamic evolution (Cloos, 2001; Richards, 2003; Pintea, 2009). This suggest that quartz in some veins come from different level and magma batches, but the mechanism of fluid inclusions production remains the same. They shown the same features as silicate melt inclusions and forms specific growth zones, clusters and trails in the silica matrix, now magmatic - hydrothermal quartz.

Brine including vapour phases are considered the main mineralizing fluid phases in porphyry copper genesis (Harris et al., 2003; Heinrich et al., 2005) but it should be emphasized based upon the microtextural evidences presented in this paper that the fluid and melt inclusions assemblages were formed as the result of the subtle autometasomatic processes and probably these fluids are not necessary the main cause of the ore grade in the protolith stage.

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EXTENDED ABSTRACTS

CONSIDERATIONS REGARDING THE POTENTIAL FOR GOLD-BEARING EPITHERMAL MINERALIZATIONS ASSOCIATED WITH THE NEOGENE SUBVOLCANIC STRUCTURE OF PORPHYRY COPPER TYPE FROM TĂLAGIU (ZARAND MOUNTAINS, ROMANIA) DEDUCED FROM THE CORRELATION OF GEOPHYSICAL AND GEOLOGIC DATA. A POSSIBLE RETURN TO THE CLASSIC- STYLE MINING

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In the central-western sector of the Talagiu complex intrusive-effusive subvolcanic structure (Arad County), a subvolcanic complex buried at depths greater than 200 m was evidenced by drill holes. This is made up of hornblende + pyroxenes andesite-microdiorite, which includes a porphyry copper-type mineralization. The inner zone of the porphyry copper system is characterized by alteration-mineralization products of potassic type, with dissemination of magnetite, pyrite, chalcopyrite, with low Cu contents, but with significant Au/Cu ratio (Berbeleac and Andrei, 1989). In the uppermost part of the outer zone of the porphyry system, the andesitic volcanics, represented by lavas and pyroclastite of pyroxene andesites and hornblende + pyroxenes andesite of Volhinian age (Roşu et al, 1997), are intensely affected by argillaceous ± phyllic transformations. The metallic minerals are represented almost exclusively by iron sulfides. The significant contrast of the magnetic susceptibility between the inner and outer zones of the porphyry system (Fig.1), allowed the delimitation at depth of the subvolcanic body, based on the ground magnetic measurements (Fig.2). The dimensions of the subvolcanic bodies are approximately 1800-600m (Andrei et al, 1988, unpublished data, IGR archive). Subsequent to the porphyry copper-Au system and in spatial correlation with the subvolcanic, epithermal, especially vein-type, were identified in drill holes but rarely at the surface. These contain iron sulfides ± Cu ± Pb ± Zn ± Au, Ag, in a gangue of quartz, anhydrite (or gypsum) and carbonates (Berbeleac et al, 1995).

Although the Au-Cu porphyry mineralization associated with the Talagiu subvolcano has no economic value (Cu=0.17%, Au=0.6 g/t, buried at depths in excess of 200 m), any volcano of similar size and with such a complex metallogenetic evolution, has certain potential for the epithermal mineralization. This is overwhelmingly proven by the subvolcanoes from the Metaliferi Mountains at Musariu and Valea Morii, which evolved from the Au-Cu porphyry type to the richest Au-Ag vein-type epithermal mineralization from the golden Quadrilateral. The similarity between the metallogenesis associated with the Musariu and Valea Morii subvolcanoes and Tălagiu, is striking, with the mention that the latter is located deeper, buried at ca. 300 m.

The geophysical investigation of the epithermal Au-Ag mineralization is a classic objective of the geoelectric prospecting (induced polarization and resistivity). The IP maxima reflect the pyritization aureoles surrounding the vein fractures and the breccia bodies. The resistivity maxima indicate the presence of silicification and carbonation. At Tălagiu the gold is associated with marked silicification and carbonation, as well.

To obtain new information on the epithermal metallogenesis, in 1978 we performed six major profiles orientated VSV-ENE, approximately perpendicular on the subvolcanic body, from Valea Tomii to Valea Peştelui. On these profiles, with stations at the equidistance of 20 m, we performed magnetic measurements ΔT and we collected soil samples, on which we performed dosing of Cu, Pb, Zn, Ag and mercurimetric measurements by pyrolysis in the laboratory.

The most spectacular result of these informative profiles was the mercurimetric maximum (900mV) from the brook Secărişte (right-hand tributary of the Tălagiu valley), closely associated with an aureole of secondary dispersion of Ag (5ppm). The location of this anomalous couple on the eastern flank of the subvolcano, as well as its association with a band of IP maxima ca. 900 m long, accompanied by resistivity maximum (Fig. 2) made me support in front of the group of authors the project of drilling an 650 m deep exploration borehole (F8). The results were quite

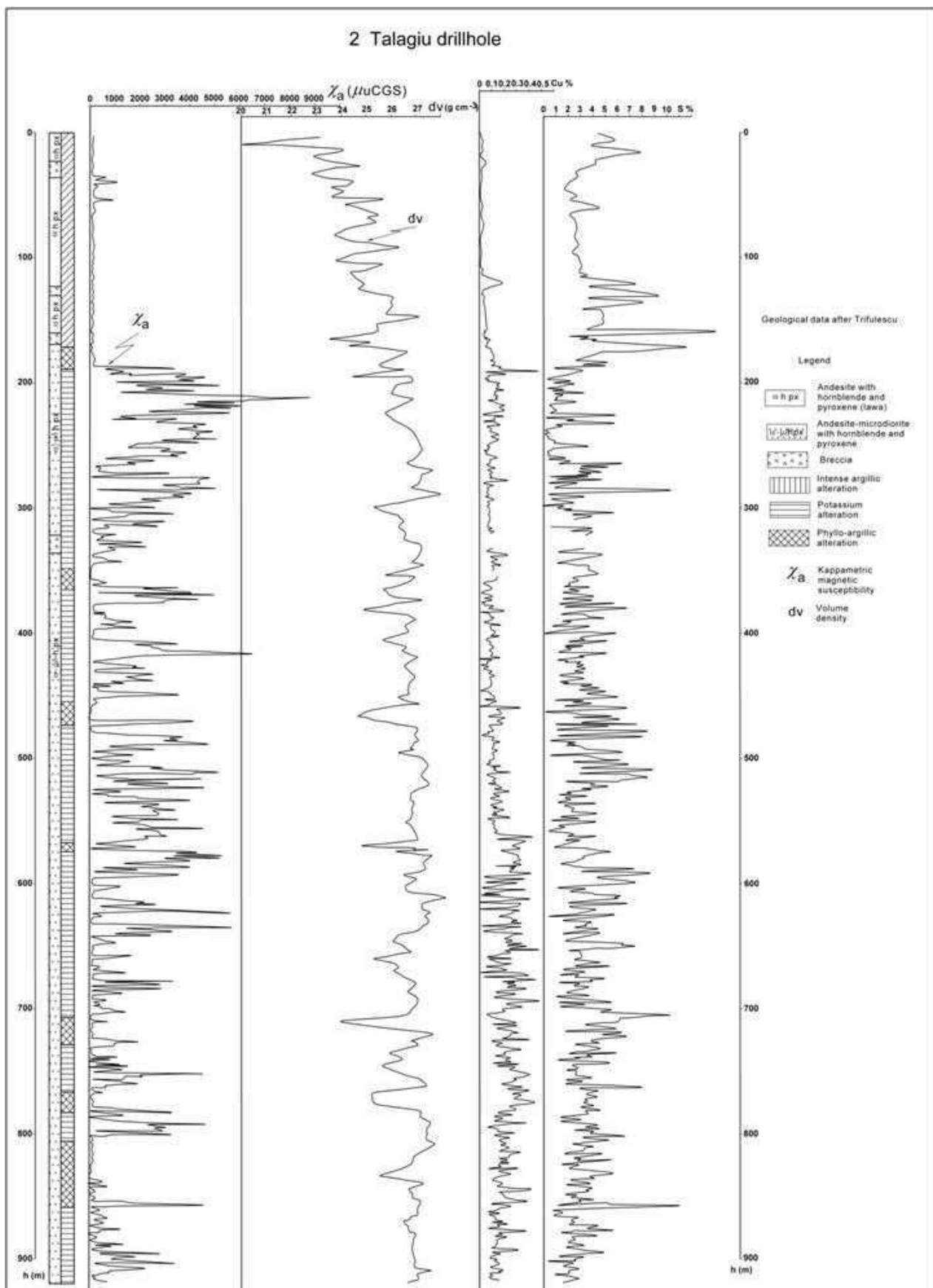


Fig. 1: Magnetic kappametric susceptibility on samples from F2 drill Talagiu: volume density and copper and sulfur grades

spectacular. At a depth of 595m a vein with an apparent thickness of 1m was intercepted. It contained pyrite and chalcopyrite in gangue of quartz, anhydrite and carbonates, and the Au content was 5.5 g/t. At a depth of 616 m a macroscopically identical mineralization was intercepted, but with an average Au content of 25 g/t (15, 25, and 35g/t), (Andrei, 2000).

The facts and considerations exposed above suggest the high potential of the epithermal Au-Ag + polymetallic mineralization, associated with the Tălagiu subvolcano. We do not have certain data regarding the upper topographic limit of the rich vein-type mineralization, but the logic suggests the likely position at the apex of the subvolcano (200-300 m). The distribution of the bands of IP maxima, associated sometimes with resistivimetric maximum, denotes that the most important epithermal mineralization with Au-Ag are located on the eastern flank of the subvolcano (especially south of the Secăriște brook) and in the central part of the intrusion, in the western slope of the Peștelui valley (Fig.2).

The economic value of the Au-Ag epithermal mineralization in the exposed parts seems to be submediocre (probably the horse tails of the veins). On this ground we consider that the attempts of mining in microquarries of the Au-Ag disseminations, associated with the dispersion towards the surface of the deep veins, do not have much potential.

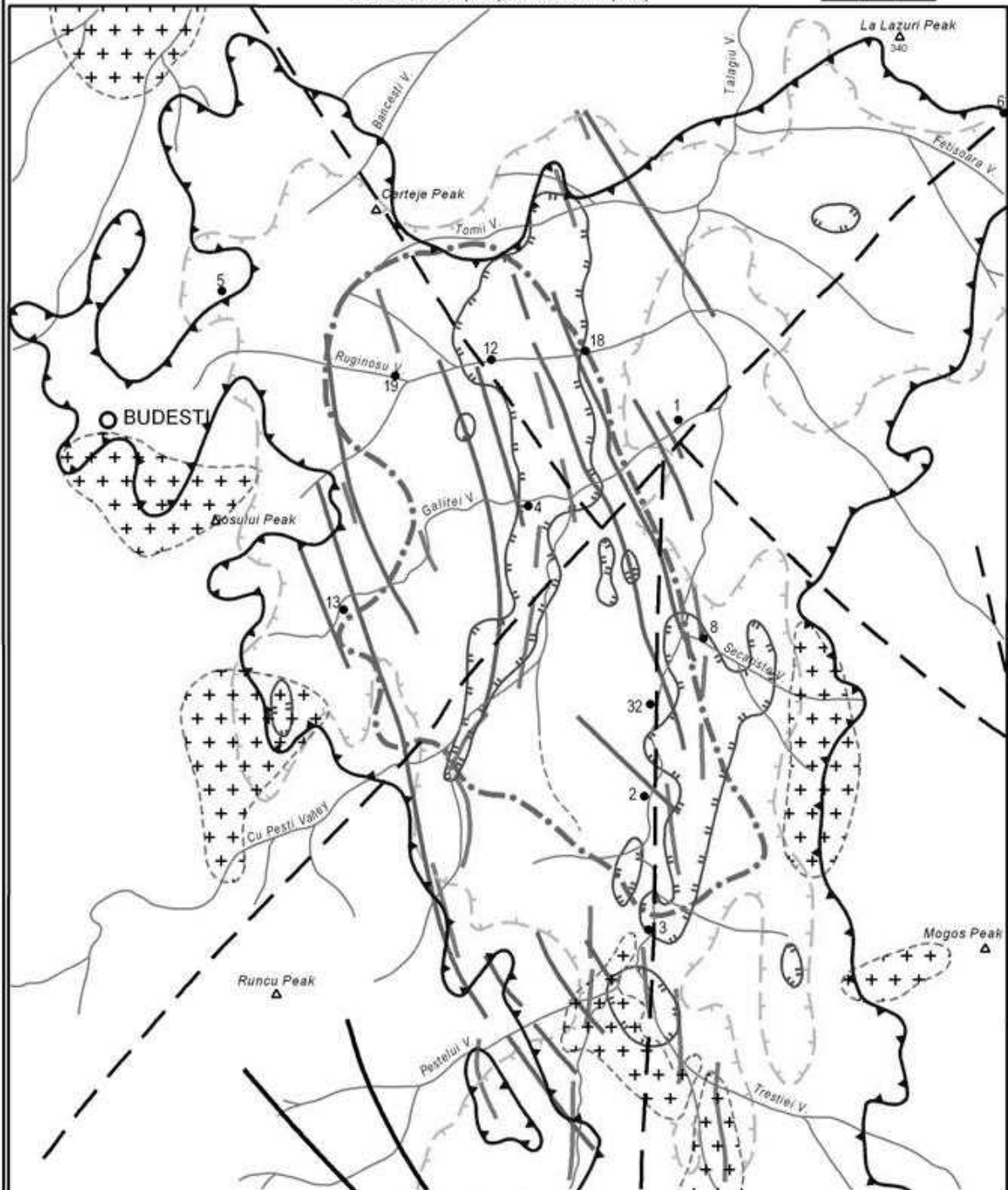
Considering the potentially high grade of the epithermal Au-Ag mineralizations associated with the Tălagiu subvolcano, we recommend the detailed mercurimetric-pedogeochemical prospecting of the entire structure, followed by the exploration with drill holes and mining works. As the mercurimetric-pedogeochemical prospecting mentioned above is a strategic objective, it must be funded by the state or by a public-private joint venture.

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TALAGIU AREA - ZARAND MOUNTAINS
STRUCTURAL - METALOGENETIC SKETCH AS INFERRED
FROM GEOLOGICAL AND GEOPHYSICAL DATA
 Geological simplified sketch according to
 Berbelec, Andrei (1989), Berbelec et al. (1995)

0 100 200 300m



L E G E N D

- Hornblende and pyroxene bearing andesites; a. volcanics and volcanoclastics; b. intrusive bodies (after Berbelec)
- Fracture and ore vein (after Berbelec)
- Major fracture according to gravity data
- Subvolcanic andesite - microdiorite body and porphyry copper ore body according to magnetic data (depth contour)
- Drillhole

- Intense argillic alteration according to magnetic data
- Fe - sulphide dissemination according to IP data; a. intense; b. moderate
- Strong silicified zone deduced from resistivity measurements

Fig. 2

**STRUCTURAL - MAGMATIC AND METALLOGENETIC PROGNoses
(ESPECIALLY FOR GOLD) INFERRED FROM GEOLOGICAL AND GEOPHYSICAL
DATA IN THE BUNESTI – ALMASU DE MIJLOC – ARDEU – ROSIA AREA (THE
METALLIFEROUS MOUNTAINS).
POSSIBLY A RETURN TO THE CLASIC STYLE MINING**

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1. Introduction

Metallogenetic prognoses based only on geological data now belong to the past. For further geological knowledge, the basis of any metallogenetic prognosis, we need to relate it to a space with at the least three dimensions, an operation impossible to complete without a sound understanding of geophysical anomalies. In our case, this understanding was possible due to previous study of the physical properties that govern Gravimetry and Magnetometry (density, magnetic susceptibility and the intensity of remanent natural magnetization).

The considerations I am presenting are part of a series of preoccupation of the author in the last six years aiming to identifying hidden intrusive magmatic structures, Neogene or older, able to contain gold and silver mineralization similar in economic importance with those that, for the last two millennia, have made famous the gold quadrangle in Metalliferous Mountains.

The metallogenetic prognoses for mineralization previously elaborated for the area specified in the title have not been optimistic. In my opinion, the negative conclusion of these prognoses had the following causes:

- they were actually based only on geological data;
- they couldn't take into account certain recent geological data;
- they started from a wrong concept, i.e. they considered that the metallogenetic activity in this area was governed only by the Neogene magmatism.

Taking into account all existing geological data, as well as a structural–metallogenetic image that includes information derived from the reinterpretation of gravimetric and magnetometric data, I will try to present in this paper a new prognosis concept, less pessimistic, regarding the perspectives for gold mineralization.

2. Structural – magmatic aspects

The major gravimetric peak Voia – Valisoara – Almasu de Mijloc (8 / 2-3 km), oriented WSW – ENE, reflects a quartz-dioritic plutonic body (Andrei, 1961, unpublished data, Archive of Prospectiuni S.A.). On the surface, this pluton presents a series of apophyses identified on Porcului Valley, at Bunesti etc. Until two decades ago, this pluton was attributed to the banatitic magmatogenesis (Ghitulescu, Socolescu, 1941, Berbeleac, 1975, Borcos et al., 1981 etc.). Following the resemblance with the situation at Savarsin, where the age of former banatites was identified through radiometric determinations as being 128,6 ± 1 Ma old (Savu et al., 1986), I suggest a similar age for the Voia – Almasu de Mijloc pluton. A Lower Cretaceous age also results from the ratio of sedimentary deposits and the pluton's apophyses or hydrothermal products. The top of the pluton consists of basic tholeiite magmatites, and especially calco-alkaline, Jurassic (lava, pyroclastite, rarely basic and ultrabasic intrusions).

In the Voia – Balsa and Almasu de Mijloc – Gold sectors, a series of gravimetric peaks with sub-kilometric dimensions and generally isometric form seem to reflect Lower Cretaceous andesitic bodies (partly identified at ground level). In relation with the pluton mentioned above, the andesitic bodies would constitute a satellite system. It is only in the Balsa sector that the Lower Cretaceous andesitic bodies seem to have been put in place under the control of the major fracture Galbena - Balsa – Ardeu – Bacaia, reflected in terrestrial gravimetric and magnetometric images, but emphasized long ago through geological mapping (Ghitulescu, Socolescu, 1941). The gravimetric images (Andrei, 1961, Andrei, 1962, unpublished data, Archive of Prospectiuni S. A.) suggest that this fracture of Laramic age, or reactivated in the Laramic phase, continues

westward in the direction of Barbura – Salistioara – Furcsoara – south of Vorta. Between Trestia and Voia, this fracture is masked by Neogene andesitic eruptions in the Brad – Sacaramb area.

In the southern slope of the Rosia Valley, between Rosia and the Dosul Hill, 1 – 1.5 km south of the major fault mentioned above, a gravimetric minimum appears, combined with a low intensity magnetic peak ΔZ . This abnormal couple defines a perturbing body oriented WSW – ENE, and its dimensions are 3.6 / 0.8 km. The magnetic anomaly has a main apex east of the Talposel Hill, centered on Barremian – early Aptian marl limestone. The gravimetric peak probably reflects an acid intrusive body. Indeed, only a rhyolite-microgranitic body could determine a gravimetric minimum in relation with the pile of pyroclastite and adjacent Jurassic andesitic and basaltic lavas, with densities of approximately 2.65 g/cm³. Considering that this sector the afore-mentioned Jurassic calco-alkaline volcanites are intensely transformed hydrothermally in a clayey facies, the presence of the ΔZ magnetic anomaly closely associated with the gravimetric minimum, especially of the apexes on the Urgonoian marly limestone, it seems strange at first sight. This dilemma is solved by the presence within limestone of this type in the left slope of the Rosia Valley of breccia cemented with carbonates, quartz, muscovite and ferrous oxides (Berbeleac, 1968, unpublished data Archive of Prospectiuni S.A.). We inferred from this that the ΔZ magnetic anomaly, closely associated to the Rosia – D. Talpsel – D. Dosul gravimetric minimum, is determined by the hornfeling the lutitic fraction of the Urgonian marl limestone. Geophysical data suggest that the acid intrusion is located at depth of approximately 150 m.

The age of afore-mentioned acid intrusion is post – early Aptian and ante – Maastrichtian (the Almasu Mare formation covers to a large extent the anomalous area, without being affected by the respective body). Having in mind a few other geological facts, it is possible for the rhyolite-microgranites in Rosia to be synchronous with the Lower Cretaceous riolit-microgranites of the Baita – Craciunesti type.

3. *Mettalogenetic aspects*

The distribution of the aureoles of hydrothermal metasomatism of the known mineralization, as well as that of the presence of gold in alluvia (see figure 1) in parallel with the position of magmatic structures inferred geophysically and analyzed in chapter 2, allow a delineation of metallogenetic prognoses.

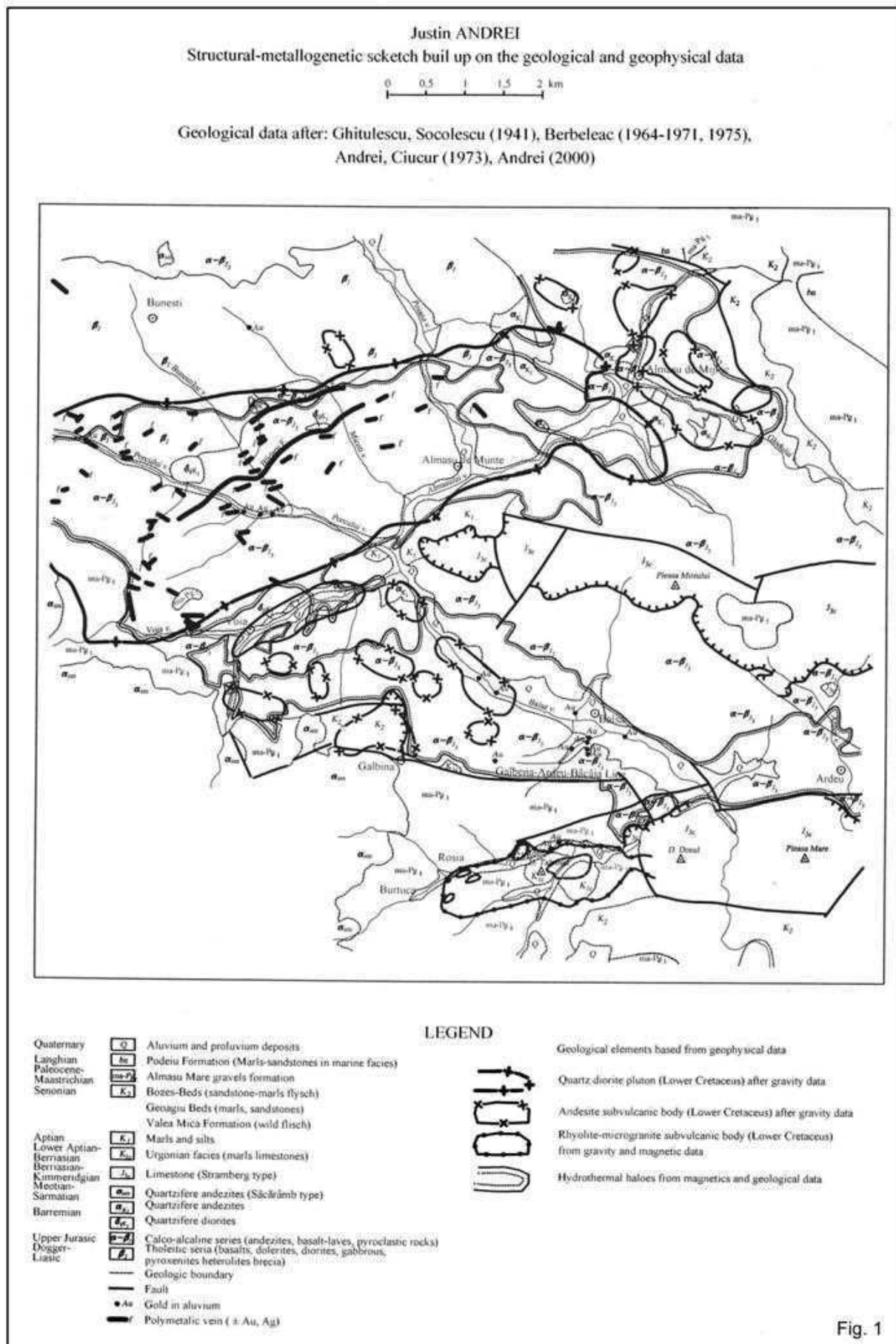
The Voia – Almasu de Mijloc pluton seems hydrothermal, polymetallic, vein mineralisations with a modest content of gold and silver. The satellite andesitic bodies in the Almasu de Mijloc – Glod and Voia sectors don't seem to underline remarkable metallogenetic perspective.

The western segment of the major fracture Galbena – south of Balsa – Ardeu – Bacaia seems to be playing an important role. Indeed, figure 1 shows a high frequency of occurrence of alluvium gold in the respective sector. Besides, westwards, the respective fracture north of the Stogu Peak – Barbura – Salistioara – Furcsoara – south of Vorta) seems specialized for Lower Cretaceous gold and silver mineralization. Indeed, gold and silver mineralization, sometimes extremely important, appears at Baita – Craciunesti and the Speranta adit (south of Dealu Mare).

The rhyolitic-microgranitic subvolcanic body Rosia – Dosul Hill was also put in place in the vicinity of the major fracture mentioned above. We don't have direct information on its metallogenetic potential for the time being. We do know instead that both intrusive body and the adjacent basic formations are intensely hydrothermalised, that there are some indices regarding both age and lithology to the Baita – Craciunesti rhyolitic-microgranitic structure. The latter constituted one of the richest subvolcanic structures, carrier of precious metals in the gold quadrant, intensely exploited as early as the Roman period.

The fact that an eventual gold and silver mineralization has not been identified in the Rosia – Dosul Hill structure is due to the advanced degree of coverage with deposits subsequent to its being put in place (the Maastrichtian – Paleocene Almasu Mare gravel). In order to check the underlined perspectives step by step, it is mandatory, as a first emergency, to have an electrometric

survey, using the induced polarity method, for the entire area of the intrusive structure and its northern extension, up to Balsa.



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THE SEDIMENT OF FORMOSO RIVER, MINAS GERAIS STATE, BRAZIL

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1. Introduction

The research area is inserted in Rio San Francisco hydrographic basin, upper to middle course segment of the São Francisco River, located directly in the sub-basin of the Formoso River. This basin localization is determined and delimited by the coordinates of 17° 25' and 17° 56' southern latitude and 44° 56' and 45° 26' of western longitude, and it is totally included in the municipal district of Buritizeiro-MG, draining an area of nearby 826 km.

During the 60th decade, great part of the drained land in Formoso River Basin was destined also to the implantation of eucalyptus and pinus monocultures. This monoculture activities growth up with the decade of 90th, due to the introduction of the commercial cultures like soy, corn, and bean and, later on, the coffee, too. The original vegetation was practically extinguished, giving place to the entropic cultivated areas. However, introducing new agro-technologies, the production was more diversified and it won significant commercial character. Grains, especially soy, corn, bean, coffee and, nowadays the cotton monoculture, impress a new agricultural landscape in the northeastern part of Minas Gerais and Goiás states. According to (Alloway et al. 1997), the agriculture is one of the most important diffuse sources of heavy metals pollution, introducing contaminants principally by impurities and components of fertilizers (Cd, Cr, Mo, Pb, U, V, Zn); pesticides (Cu, As, Hg, Pb, Mn, Zn); preservation materials for wood (As, Cu, Cr) and solid and liquid dejections of animal creation (Cu, As, Zn). The objectives of this study are evaluate the concentration and the distribution of the selected elements (Cu, Cd, Cr, Ni, Pb and Zn), based on their parameters of potential toxicity for mankind and the aquatic biota; verify the origin of those elements (natural or anthropogenic; quantify the concentration, represent them graphically and compare it with guiding values established by CSeQGs (2002), adopted by the CONAMA Resolution n° 344/04 and describe the concentrations of the investigated elements in the sediment samples collected at the eleven sampling points...

2. Metodology

On the determination of the sampling points in the Rio Formoso Basin was taken in consideration the variations in the landscape, reflected in the different types of geological units, morphological compartments and their interfaces. Due to this observation were taken samples throughout the different units/compartments in representative places, tends as support the interpretation of orbital images and field campaigns.

At each field campaign a total number of eleven samples of 1.5kg each of sediments were collected totalizing 22 samples. For sampling was done respecting the norms of CETESB (1988). The samples were taken on the two margins of the river, 30 cm away from the margin. Bottom sediments were collected manually directly in the bottom of the fluvial channel by a wrought cylindrical steel collector, with capacity for 1kg of sediments, afterwards in laboratory, the samples were dried at room temperature, prepared, weighted and fractional in nylon sieves, in 8 fractions down until reaching the fraction of <0.063 mm, which was used for heavy metals determination. The samples was opened and dissolved by acid digestion (aqua regia) and the reading was done with an ICP-OES, model M 4165 - Epectroflame - Spectro of the (CPMTC/UFMG) on Argon flux. The mineralogical analysis of the sediments was executed at the laboratory of CDTN/CNEN, using the powder method of -X-Ray diffraction. 2 kg of selected fresh rock samples were collected with the purpose to obtain all existent linotypes in the region.

In the laboratory, the samples were dried at a temperature of 90°C, crushed down to 2 mm, quartered and homogenized. Pulverization was made in steel mill down to ~ 150 meshes. The

chemical opening was done by acid digestion and the determination realized by AAS, at the research laboratory of SGS-GEOSOL.

3. *Physiographical aspects*

The Rio Formoso Basin is located at the south-eastern portion in Sanfranciscana Basin, within the limits of the San Francisco Craton, more specifically belongs geographically to the Cretaceous Basin of Western Minas Gerais. The Mata da Corda Group (Upper Cretaceous), is formed by alkaline kamafugitic rocks (80-90 Ma) and vulcano-clastic sediments that occupy the southern portion of the basin. The Chapadão Formation (Cenozoic), composed by oxidized sandy sediments of a deep red color, resulting from the near recent fluvial reworking of diverse detritic materials present in the area of research. This cover is the product of the alteration of the rocks of the Mata da Corda Group, more exactly denominated in this region as Capacete Formation. The Sanfranciscana Basin presents a paleogeographic evolution strongly controlled by the sedimentary tectonic events and correlated magmatism, which conditioned the deposition periods, diagenesis and the erosion in the whole basin.

The Formoso River can be classified as an open channel, and his main flow is of the turbulent type with numerous rapids. In general, his turbulent flow is characterized by a variety of secondary movements and currents, contrary to the downstream part of the river (Christofolletti, 1977). Along the fluvial channel, the flow varies between turbulent currents and the turbulent rapids; this last one restricted to the passages of higher speed, in the great majority on the upper to middle segment of the course. The dynamic of the hydrographic basin of the Formoso River is responsible for the fluvial sedimentation, which includes the removal processes, transport and sedimentation of the particles in suspension. Some peculiar aspects of this fluvial sedimentation that happen mainly in the higher and lower segments are related to the intense removal of slope-debris, whose main cause is agriculture. Another fact that increases the sedimentation rates is the construction of local highways and roads.

4. *Results*

In a general way the data of the selected heavy metals analyzed in the river bottom sediments show a very heterogeneous compartment from very high to very low concentrations. The sampling points with the highest concentrations are located in the areas directly influenced by agricultural and cattle creating activities. These places receive directly the metal-organic residues generated by the enterprises, transported by wind and the pluvial waters. The sampling points with lower concentrations are localized in the middle to lower course of the river. It is stood out, once again, that until the moved away points of the area of direct influence presented lines of those heavy metals.

It becomes once more evident, that the fine sediment fractions (argillite, loamy) is the most favorable to incorporate the selected geochemical selected compounds to identify anthropic or natural sources connected to the different geomorphologic compartments and, consequently, containing the largest concentration of heavy metals.

All the investigated heavy metals in sediment show a permanent enrichment along the longitudinal profile, showing the solubilization of the smaller amount of selected elements of the litho types of the rocky substratum liberated by the processes of physical and chemical intemperism. The morphologic characteristics of the fluvial channel and the general hydrodynamic conditions of the basin are the most important mechanism for the distribution and transport of the selected metals in the sediments. The strong correlation among the six analyzed metals is in relation to the profile and to the geological-geomorphologic compartment. It is nearly clear that the hydrogenic potential is one important control mechanism for their sediment concentration in the Formoso River system determining their mobility.

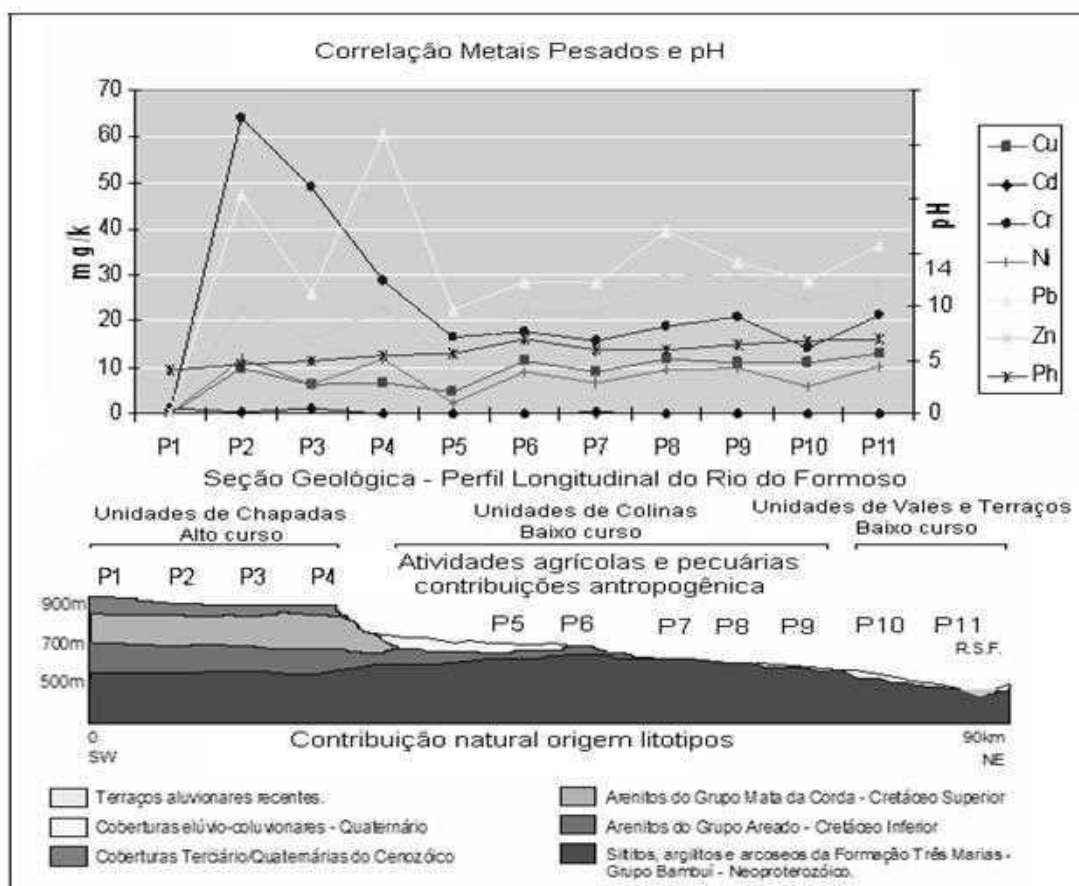


Fig. 1: The correlation between heavy metal and the connection to the geological-geomorphologic compartments.

The pH, of the sediment samples varied from 4.9 to 6.5, common values in continental areas, with predominance of slightly acid to acid conditions.

The colors, of the sediments samples maintained a tendency among YR and Y, tones from yellow-reddish to yellow. The colors are related to Fe-oxide-hydroxide minerals existent in the main litho types of the study area, especially goethite, hematite and magnetite. The sediment of Formoso River predominate a detrital quartz grains, follow by clay minerals, heavy accessory minerals and the autogenic minerals. The presence of clay minerals as Kaolinite in same samples, suggest an easier exchange between water column and sediment surface.

The concentration and distribution of the heavy metals in sediment samples along the longitudinal profile of the Formoso River are correlating with lithology, and human activities (fig. 1).

5. Conclusions

The results of the chemical analyses for the selected heavy metals in the river sediments, demonstrate that the loamy fraction is keeping very high concentrations of those metals, especially Cd and Cr, which passed level 1 for TEL for sediments (Resolution CONAMA 344/04). The other analyzed elements, especially Pb, Zn, Ni and Cu show concentrations lower than the limit determined by that resolution, but they demand special attention, because their concentration levels are close to the recommended limits. All the investigated selected metals show in the sediments a natural enrichment by natural liberation by physical and chemical intemperism along the longitudinal profile, tends as main source the trace minerals from the several rocks. It was verified that the predominant mineral is quartz; but the presence of clay minerals (Kaolinite), explain a variation of the concentrations in the samples, due to ion exchange processes. The morphologic characteristics of the fluvial channel and the hydrodynamic features of the basin are important mechanism for the distribution and transport of the metals the sediments. The obtained results

confirmed a higher concentration of some heavy metals and in the sediments of the river, and this can be connected to different human activities in this Sub-basin. Taking these results into consideration, a possible suggestion is the implantation of a strong monitoring program for all the analyzed heavy metals and an additional investigation of soil, plant and animal metal concentrations.

ACKNOWLEDGEMENTS

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HEAVY METAL VARIATION IN THE SNOW FROM BUCHAREST, ROMANIA

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Key words: heavy metals, snow, pollution, traffic, atmosphere

Introduction

The negative impact that developing industrial activities have on the environment and human communities which live in the respective perimeter is a well known fact. The development–destruction balance can not be maintained unless there is an active campaign for life quality monitoring, in which preventing and diminishing the effects of anthropic factors on the population would play a major role.

The extended industrial activity in the area of Bucharest, mostly implying an extremely intense traffic in many areas of the city, was and still represents one of the main pollution factors. This can cause major physical-chemical disequilibrium, expressed as increasing concentrations of noxious elements, especially heavy metals and other polluting compounds. In order to evaluate the impact of contaminating factors (industrial activities, car and air traffic, etc.) on the environmental state of Bucharest, field and laboratory investigations were conducted to determine the concentration of heavy metals in the water resulted from snow melting.

The study came as a response to the public concern that depositing snow taken from the roads of the city in gardens and parks would contaminate the groundwater with heavy metals and other polluting compounds that would leach through the soil. The aim of the research is to determine the lead and copper variation in the snow from a crossroad in the city and the causes of increased concentrations.

Research methodology and techniques

For this study, the crossroad between Iancului Street and Mihai Bravu Street was monitored from 9.02.2010 and 18.02.2010, when 25 samples were taken from the four corners of the crossroad (Fig. 1). Point C is used as a taxi station, where, during the winter, there is a large number of cars parked with the engines turned on, while point D is a parking lot. Some samples were taken around 9 a.m. and others around 5 p.m..

It must also be mentioned that during the sampling period there was a precipitation episode (after the third set of samples was collected) which consisted of snow and rain. During this time, no samples were taken.

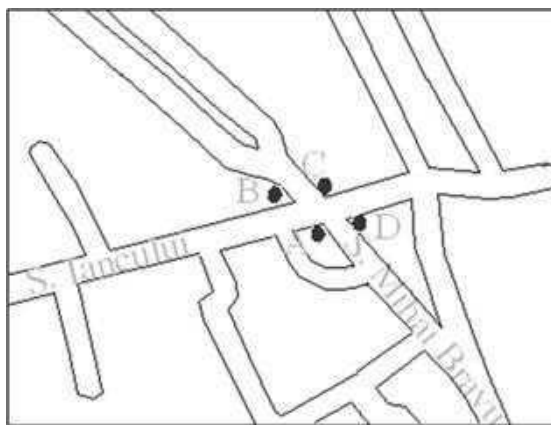


Fig.1 Localization of the samples taken from Iancului Street - Mihai Bravu Street crossroad, Bucharest

Each snow sample equaled to around 200 mL of water. In laboratory, HNO₃ 1M was added in the ratio of 1mL to 100 mL of sample for conservation. The water resulted from melting the snow samples was first filtered, to remove the solid residue and then investigated with an atomic

absorption spectrometer – ZEEnit-700 (AnalyticJena), graphic furnace technique, to identify the concentration of lead (Tab. 1) and copper (Tab. 2) .

The analytic data was processed using Microsoft Office (EXCEL), Ocad and Windsurf.

Results and discussions

Obtained results point out frequent values surpassing admitted concentrations by the national and European legislations. According to Decision number 188/2002, Pb should not surpass 200 µg/L and Cu - 100 µg/L in wastewaters discharged into natural receivers.

Tab. 1 Lead concentrations (µg/L) found in the water resulted from melting the snow collected from Iancului Street - Mihai Bravu Street crossroad, Bucharest

Loc.	1	2	3	4	5	6
A	9,12	11,48	58,66	28,55	114,70	135,20
B	16,09	7,63	41,52	49,57	39,66	5,61
C	16,38	3,80	31,62	39,81	69,18	269,20
D	20,00	30,44	39,04	75,10	94,55	227,60

Tab. 2 Copper concentrations (µg/L) found in the water resulted from melting the snow collected from Iancului Street - Mihai Bravu Street crossroad, Bucharest

Loc.	1	2	3	4	5	6
A	9,08	9,16	223,40	128,10	106,00	216,70
B	3,81	27,74	138,20	165,20	42,90	113,30
C	272,00	21,53	80,89	43,94	79,61	438,30
D	25,72	7,55	134,80	50,48	291,30	325,00

* values surpassing admitted concentrations of wastewater discharged into natural receivers (Decision number 188/2002)

Similar results have been obtained by Engelhard et al. (2007), who studied the eavy metal concentration in snow from Innsbruck, at different distances from the main road.

Another major concern, besides groundwater pollution, is direct contamination with heavy metals, as the snow is often ingested by children. For this reason, blank samples were collected, containing fresh snow, and they still had high concentrations of lead and copper, at the limit for admitted concentrations for potable water (Pb – 10µg/L, Cu – 100 µg/L, Law number 458/2002). Most of the samples collected from the crossroad, though, had values exceeding this regulation.

The second and the third sample sets were taken in the same day, the second at around 9 a.m. and the third at around 5 p.m., to point out the small variation over the course of the night, when the traffic is low, compared to the general increase during the day, for both elements and all points of the crossroad.

The effect of the rain and snow episodes is mostly causing the leaching of the metals from the upper part of the snow moulds, where the sampling was made, to the bottom part, so that the fourth set of samples usually have smaller concentrations than the previous one. The fifth and sixth sets of samples were collected when the rain and sun melted the snow, which was mixed with particles of dust from the road. Therefore, the concentrations of heavy metals increased dramatically on the last day of sampling, for most of the sets.

It is important to take into account that, both for Cu and Pb, the concentrations for points C and D are the highest at the last set of samples and can be easily presumable it is linked with the effect of cars, as in point C, a taxi station is organized, while in point D, a parking lot is used by the inhabitants of the area. The high concentration of heavy metals, especially lead, could bring up questions about the quality of the gasoline used by the drivers and whether or not it is lead – free.

Correlating the obtained concentrations, an ascendant trend is pointed out for the studied elements, being more obvious for Pb (Fig. 2).

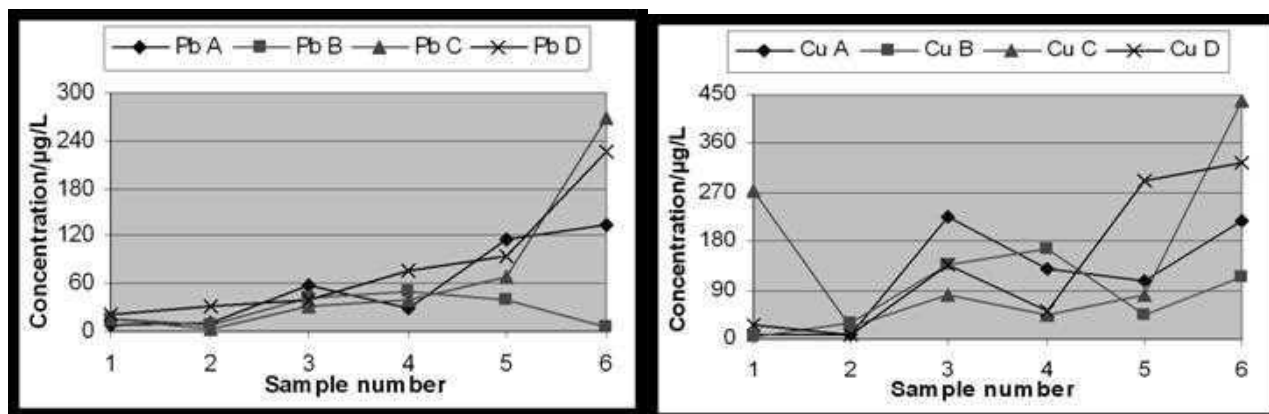


Fig. 2 Lead (left) and copper (right) variation in time, in the four corners of the Iancului Street - Mihai Bravu Street crossroad, Bucharest

Conclusions

The analytical investigation of water resulted from melting the snow samples from Iancului Street - Mihai Bravu Street crossroad, Bucharest, highlighted the presence of heavy metals, frequently surpassing admitted concentration by national and European legislation, pointing out the possibility of introducing relatively significant concentrations of heavy metals in the water system.

The accumulation and variation pattern of lead and copper suggest multiple pollution sources: (i) air pollution – industrial, air traffic – determining the accumulation, probably by adsorption of different elements on snow, (ii) intense car traffic, taking into account that the crossroad chosen is one of the most used in Bucharest, (iii) solid particles – dust which exists everywhere in Bucharest. The variation of concentrations can also be determined by the fluctuant character of atmospheric currents, and the wind direction can cause preferential accumulation of lead and copper.

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INFLUENCE OF OPERATING PARAMETERS OF CALCIUM SULPHATE DIHYDRATE FROM CALCITE AND SULPHURIC ACID

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Introduction

Gypsum is a mineral compound of first importance in the formulation of a wide range of building materials. To make up for the long term depletion of its natural resources, building material industry head more and more toward gypsum by-produced in other industrial sectors. Today, among such products, some are already added in different percentages to natural gypsum (phosphogypsum, desulfogypsum and titanogypsum for example). Though, some other are still studied, especially gypsum produced by neutralizing sulphuric acid with lime. That neutralization process is frequently encountered in mining, metal or dye industries. Nevertheless, if a lot of papers about gypsum crystallisation thermodynamics and kinetics have been edited since the last decades (among them Marshall et al. 1966, Witkamp et al. 1990, Freyer et al. 2003), very few contributions can be found in literature on the topic of calcium sulphate dihydrate precipitation from sulphuric acid taken as industrial wastewater and containing electrolytes at different valences (Singh & Garg, 2000; Gominšek et al. 2005). The aim of the present work (Bard 2006) is to lay the basis of a process for the production of synthetic gypsum valuable in plaster industry, and precipitated from sulphuric acid and limestone instead of lime to lower production costs.

Results of experimental study

Influence of temperature and acid concentration.

Crossed effects of temperature (25, 70, 80 and 90°C) and initial acid concentration (15, 20 and 30wt%) have been studied. FTIR spectrometry and XRD confirmed that only gypsum has been precipitated. We observed that increasing the temperature at constant initial acid concentration leads to an evolution of the crystal shape from an acicular (i.e. needle-like) to a tabular (i.e. platelet-like) facies. In the mean time, at constant temperature, an increase in initial acid concentration seems to result in decreasing the length/width ratio of synthesized crystals. From laser diffraction sizing (see Table 1), the mean particle size (d_{50}) of the formed solid has been found to increase with the temperature at constant initial acid concentration. On the other hand, the effect of the initial acid concentration at constant temperature is to be neglected. We can also assume that the temperature has the major effect on morphology and size of the precipitated crystals.

Table 1: Mean particle size of gypsum crystals precipitated at different temperature from a 20wt% calcite suspension and sulphuric acid at different initial concentrations.

Initial acid concentration (wt%)	temperature (°C)			
	25	70	80	90
15	15µm	34µm	45µm	63µm
20	12µm	35µm	49µm	58µm
30	14µm	33µm	42µm	50µm

For each solid sample 5g of washed and dried gypsum has been introduced in 100ml of pure water and kept 15 minutes in suspension. Measured pH is around a value of 8 for all solid samples. We suppose that this constancy despite differences in process parameters setting resides in the fact that all samples have been plentifully washed after filtration. All pulverulent samples present an apparent density of about 0.28 (Table 3). We can also assume that initial acid concentration and temperature have no influence on this powder's characteristic.

Influence of the agitation of the reacting medium

The effect of the propeller's rotation speed ω (in rpm) generating the medium's agitation has been studied at 90°C. It has been found to have neither influence on the crystals' shape and size nor on powder's apparent density (for 200rpm propeller's radial speed we have apparent density about 0.28 from a sulphuric acid at various initial concentrations 15, 20 and 30 wt%). As turbulence decreases appears a new population of smaller particles to the detriment of the former one. We noticed that the lower the acid's initial concentration, the stronger this phenomenon. This could possibly explain the increasing discrepancy between the mean particle sizes of the two populations as initial acid concentration decreases (Table 4).

Table 3: Apparent density of gypsum samples produced at different temperature from a 20wt% calcite suspension and sulphuric acid at different initial concentrations.

Initial acid concentration (wt %)	Temperature (°C)			
	25	70	80	90
15	0,275	0,280	0,285	0,280
20	0,280	0,285	0,280	0,285
30	0,275	0,280	0,280	0,280

Table 4: Mean particle size of gypsum crystals precipitated at 90°C with various propeller's radial speed from a 20wt% calcite suspension and sulphuric acid at various initial concentrations.

Initial acid concentration (wt%)	Propeller's radial speed ω (rpm)	
	200	400
15	36 μ m	45 μ m
20	35 μ m	49 μ m
30	40 μ m	42 μ m

Influence of the inlet flow of calcite suspension

Influence of the inlet flow of the 20wt% calcite suspension has been studied at 90°C with an initial acid concentration of 15wt% and a propeller's radial speed of 400rpm. We observed a decrease in the length/width ratio while decreasing the inlet flow from 20ml/min down to 5ml/min. We also noticed an increase in the contrast between the particle populations located at about 20 μ m and 100 μ m, coupled with an increase in the mean particle size as the inlet flow of the calcite suspension decreases (Table 5). We also observed that the mean particle size of the precipitated gypsum increases as the inlet flow decreases. We supposed that this increase in particle size is linked to the evolution of supersaturation. Indeed, the slower calcium is added to the reacting medium through the dissolution of injected calcite suspension, the lower the maximum supersaturation will be. Since a high supersaturation favours a high nucleation rate (that is to say the production of numerous but small crystals) we assume that decreasing the inlet flow of calcite suspension leads to the generation of a weaker supersaturation and then to the production of less numerous but bigger crystals.

Table 5: mean particle size of gypsum crystals synthesized at 90°C with a propeller's radial speed of 400rpm from sulphuric acid 15wt% and a 20wt% calcite suspension at various inlet flows.

Calcite suspension inlet flow (ml/min)			
20	15	10	5
63 μ m	70 μ m	105 μ m	166 μ m

As the inlet flow of calcite suspension decreases, the apparent density of the gypsum's powder increases. We assumed that such an increase in the apparent density is not resulting from the evolution of particles' shape and size. In this case, it would have been observed while studying the influence of temperature and initial acid concentration where modifications of crystal shape and sizes had already been observed. We better assumed that an increasing contrast between two well-

defined populations of gypsum crystals combined with a tabular facies results in a more compact stacking of the bigger particles in which the smaller can be stored easier.

Discussion

Variation of temperature induces a variation of morphology and size of the precipitated gypsum. As temperature increases, the length/width ratio decreases resulting in an evolution of the crystal shape from an acicular (i.e. needle-like) facies to a tabular (i.e. platelet-like) facies. The mean particle size is affected by temperature too as it increases with this parameter. An increase in the initial sulphuric acid concentration affects the morphology of produced crystals in the same way, but in contrary to the former parameter, that modification has no marked effect on the mean particle size of the gypsum powder. Both of these two process parameters have neither influence on the pH of the precipitated solid in water, nor on its apparent density.

Those results, more particularly the morphological evolution of crystals, lead us to focus on experiments conducted at 90°C with an initial sulphuric acid concentration of 15wt%, operating conditions for which crystals exhibit a shape the closer to those required by plaster industry. The influence of the agitation of the reacting medium studied through the radial speed of the propeller has neither effect on the morphology nor on the pH and nor on the apparent density of the precipitated solid. Nevertheless, as this speed decreases a new population of smaller particles appears to the detriment of the initial bigger one. This phenomenon becomes more important as the initial sulphuric acid concentration decreases. We also assume that working with low agitation speed is to be avoided.

Variations of calcite suspension inlet flow leads to a variation of length/width ratio as well as a variation of mean particle size of produced crystals. More precisely, a decrease in suspension s inlet flow makes crystal shape evolve from acicular to tabular facies and makes mean particle size increase significantly. The major evolution with regards to the product quality is certainly the improvement in its apparent density, which increases from 0.3 to 0.5 when decreasing the suspension s inlet flow from 20 down to 5ml/min. We also assume that the lower the suspension s inlet flow; the better the quality of the precipitated gypsum.

Conclusion

The present work focuses on the physical and chemical aspects of the semi-batch precipitation of gypsum by injecting a calcite aqueous suspension to a sulphuric acid solution. It helps in understanding the impact of process parameters such as temperature, initial concentration of reactants (which actually represent the solid/liquid ratio of the reacting medium), and agitation of the reacting medium and the inlet flow of reactants.

The operating conditions are set so that the synthesis is conducted at 90°C with an initial sulphuric acid concentration of 15wt% (i.e. a solid/liquid ratio of about 13%), with a propeller s radial speed of 400rpm and an inlet flow of calcite suspension of 5mL/min. These conditions lead to a good improvement of the product s apparent density, that is to say the better for valorisation in plaster industry.

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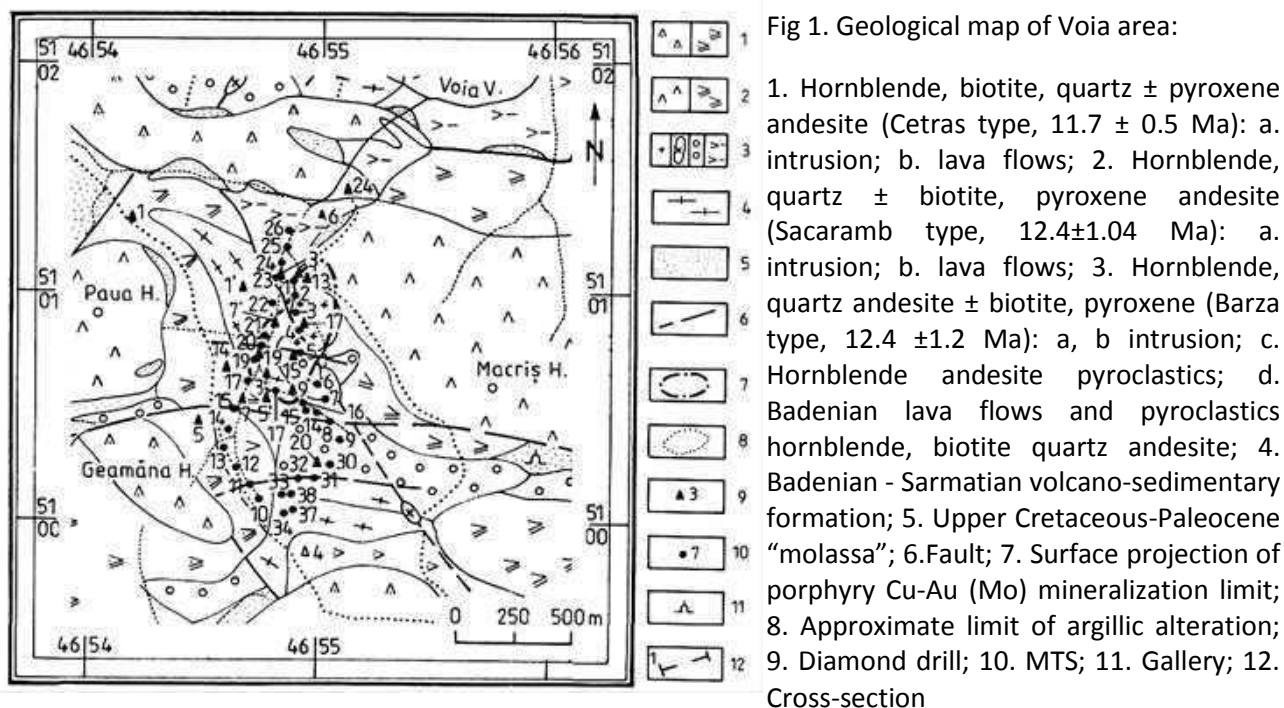
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DEEP NEOGENE VOLCANIC STRUCTURE AND RELATED MINERALIZATION FROM VOIA AREA, METALIFERI MOUNTAINS, ROMANIA

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Voia region is situated in south part of Tertiary Halmagiu-Brad-Sacaramb tectonic basin, Metaliferi Mountains (MM). The deep structure of Voia subvolcanic body (VSB) was the subject of diamond drillings and magneto-telluric soundings. Our attention will be especially for MTS information regarding the deep structure of Voia subvolcanic body (VSB) and related mineralizations: Ca-Mg pyrite skarns, porphyry Cu-Au (Mo) and epithermal HS and LS pyrite-gold and gold-base metal sulfides. This study was undertaken in order to extract all the relevant information from two MTS structural geologic imageries achieved until 5000m depth.



According to Balintoni and Vlad (1998) and Berbeleac (2003), MM are tectonically located in an active continental margin of a back-arc area, characterized by extension beginning with Upper Cretaceous and continued in Neogene with short and successive compressions and extensions. In Tertiary time the back-arc area has been affected by important rifting processes related to northwest-trending, right-lateral strike-slip faults and their subsidiaries. These faults are responsible for forming intra-mountain tectonic basins and served as main conduits in rising Badenian-Pannonian magma and ore fluids. In Voia volcanic region (~ 4 Kmp), at the surface, the Neogene volcanic products are widespread and consist of three main types of rocks and one formation: calc-alkaline K quartz andesite with amphibole, biotite $\pm$ pyroxene of Sacaramb types (ST) and Cetras types (CT) (12.4 - 10.27 Ma, Rosu et al., 2004), Upper Cretaceous-Paleocene molassa (UCPM), Sarmatian Barza type (BT) hornblende quartz andesite of VSB witch appears on a little surface in the right slope of Macris Valley and Sarmatian-Badenian volcano-sedimentary formation (SBVSF). Other types of Neogene volcanic rocks are present in this area (look the legend of the map). To the depth probably appear: Ardeu nappe (ArN), Techereu-Drocea nappe (T-DN), Curechi-Stanija nappe (?) (CStN), Biharia + Muncel nappes (?) (B+MN), Baia de Aries nappe (BAN) and Vidolm nappe (?) (VN) as an alternative to B+MN (Fig.1). VSB had a poly-stadial evolution and the andesite-microdiorite body is cross-cut by small dike of two younger sequences of hornblende quartz andesite. Large area of HS alteration with argillic minerals - pyrite $\pm$ gypsum and quartz alunite-pyrite appears in upper part of Voia Valley (Fig.1); towards depth it pass gradually to feldspathic

and propylitic assemblages, where, related to VSB is a magmatic - meteoric hydrothermal systems with Ca-Mg skarn-pyrite, porphyry Cu-Au (Mo) and epithermal HS (anhydrite-pyrite $\pm$ base metals) and LS (quartz-carbonate-Au- base metal sulfides) mineralizations are present.

Field measurements carry out with ADU-06 station using the LF1 and LF2 frequency bands. For each MTS the maximum resistivity values have been processing and modelings using the acquisition by purchase MAPROS soft and IPI-MTS inversion soft. MTS have been performed on three lines situated in upper part of Voia Valley, from witch only 1 and 2 are choice for interpretation data (Fig. 2a,b,c,d). They covered a surface of 0.70kmp. The field work conditions have been the followings: troubled relief with 45° - 5° ground slopes had electrical sensors situated at W and E of lines 1 and 3 and NE of line 2; 1-2m soil blanket and under it a very pronounced iron cap; 60-175m the distance between MTS; about 2,800m total length of lines; 5.50 h the total measurement time and 5000m the investigation depth. Through processing data have been obtained: 1) theoretical and measurement curves of resistivity and phase after N-S direction and at 0.01-3.00 s period; 2) the average values of resistivity, the thickness and the depth for each line and sounding and 3) the inversions for each sounding.

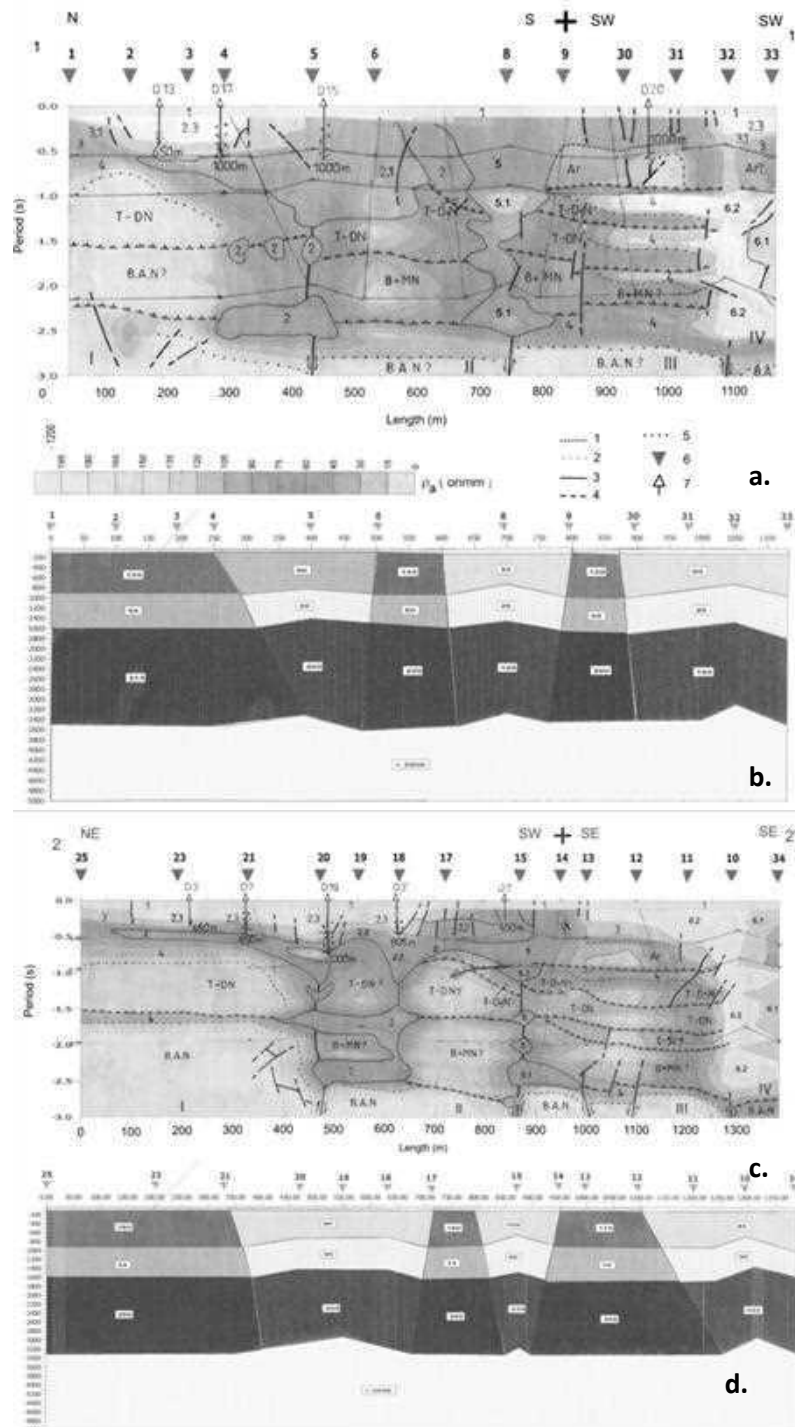


Fig. 2: Cross-section resistivity along line 1 and 2 and geologic interpretation (a, c) of resistivity average values (b, d). Fig. 2 a,c have traced the limits of 5 "beds" (except "bed"1). 1. Geologic boundary; 2. Unconformity boundary; 3. Fault; 4. Nappe; 5. Porphyry Cu-Au(Mo) mineralization; 6. MTS; 7. Diamond drill; Number of rock type: 1. Types of rocks intercepted at surface by the cross-section; 2-2.3 rocks of VSB: 2. dominant fresh diorite; 2.1. fresh to propylitic-feldspatic alteration and Cu-Au (Mo) in VSB; 2.2-2.3 dominant andesite with feldspatic-propylitic, porphyry Cu-Au (Mo) and HS and LS alteration and mineralization; 3.1. BSVSF; 3. UCP "molasa"; 4. Cover deposit; 5. Fresh or near fresh andesite-diorite of ST; 5.1. probable ST andesite with dominant argillic alteration; 6.1 and 6.2 probable CT andesite with HS type of alteration. Abbreviations: BAN, Baia de Aries nappe; T-DN. Techereu - Drocea nappe; TD1 N. Probable a digitated top of T-DN; CSt(?). Curechi- Stanija nappe; VN. Vidolm nappe(?).

Voia depth structural image (VDSI) is the result of 29 MTS processing data. Between 450-1,200m depth it was checked with 18 diamond drillings (~15,000 l m) data. The analysis of the resistivity values distribution for each MTS and their cumulate values for each line (cross-section) allow us to do, in brief, the following general remarks (Fig. 2a, b, c, d): 1) Voia area has been divided in four tectonic micro-blocks noted from I to IV, each block being separated by three important E-W vertical crustal faults; crustal faults serve as conducts for rising magma and ore fluids. Blocks II and III are complete exposed in the cross-sections, while blocks I and IV continue out of them; 2) tectonic control exercised by the crustal faults and nappes in localization, form and dimension of three andesite volcanic-subvolcanic structures, formally noted and composed of following main type of rocks: 2-2.3 - BT andesite, named VSB, 5-5.1 – ST andesite (?) and 6.1-6.2 CT andesite (?); 3) in each block, there are five lithological entities, named, from upper to base, 1 to 5 beds. The variation of resistivity average values with the periods and depth of these beds are given in Fig. 2a,c. The lithologic content of the beds is noted from 1 to 6 (alterations increase from 2 to 2.3, 5 to 5.1, 6.1 to 6.2), that mean (in bracket depth in m and number of rock): a) bed 1 (0-125 m) high oxidation and HS of Barza andesite, Sacaramb lava flows, pyroclastics and VSD rocks (1); b) bed 2 (125-900m) – in general similar contents as bed 1, dominantly T-DN and ArN and intrusive rocks (2.1, 5, 6) VSB (2-2.3) with porphyry Cu-Au (Mo) (2.1; c) bed 3 (900-1500 m) – Cretaceous cover deposits; (4) of T-DN, Jurassic ophiolites and limestones of T-DN and Barza andesites-microdiorites with porphyry Cu-Au (Mo) mineralizations, ST (5, 5.1) and CT rocks (6, 6.1, 6.2), VSB, LS assemblages and porphyry Cu-Au(Mo) (2, 2.1); d) bed 4 (1,500-1,600) – 3,000 (3,300)-dominantly Jurassic ophiolites (TD₁N, TDN), partially Mesozoic sedimentary rocks (4) of three subvolcanic intrusions (ophiolites of TDN, crystalline schists of BAN?) and Neogene intrusive rocks (2) partially as magma mini-rooms (2, 5) and e) beds 5 (3,000 (3,300)-5,000m) - dominantly Precambrian-Paleozoic rocks probably belong to BAN? and VN?, Neogene intrusions (2, 5) and Permian rocks (?) (4). The name of the metamorphic formation support many discussions; 4) two tectonic-subsidence basin - like graben structure and pull-apart type, one in the northern part and the other one in the southern part. They are well expressed in cross section Fig. 2 a (MTS1 + 50m - MTS5 + 50m; MTS9-MTS33) and Fig. 2 c (MTS25 +100m- MTS18+75m; MTS14+50m- MTS10) and are named north, and respectively, south basin. The age of the subsidence is probably Upper Cretaceous-Pannonian time because the UCP molassa, SBVSF and BT are affected by two faults related to subsidence processes.

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CHARACTERIZATION OF BRAZILIAN PHOSPHOGYPSUM

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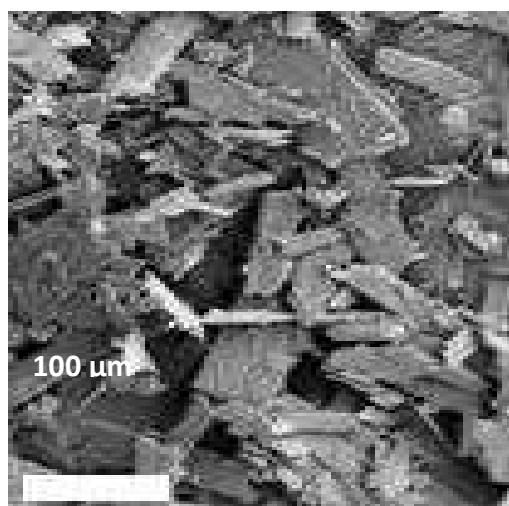
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1. Introduction

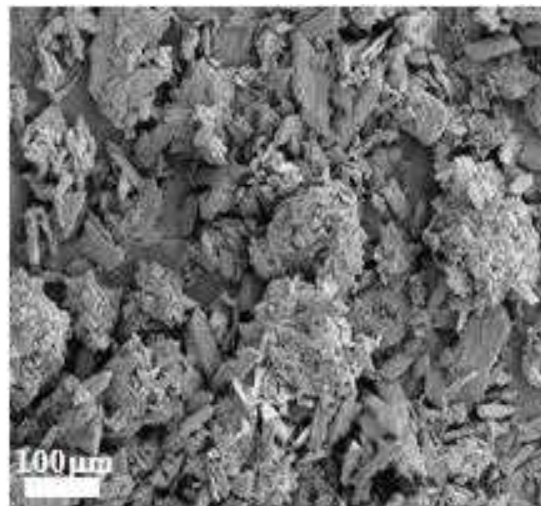
The Phosphogypsum by-product of the chemical fertilizer industry in some countries becomes a source of raw material for cement and plasters industry. However, it contains impurities contents varying according to the nature of the rocks used in downstream manufacturing of chemical fertilizers and the type of process used to manufacture phosphoric acid. The main problems of phosphogypsum are the free moisture, low pH, HF acid; P_2O_5 , radioactivity and heavy metals. These last two years we have seen in Brazil use of phosphogypsum in construction of housing. This work is an approach to decision support for the risks assessment in using some phosphogypsum in construction. For those, we took samples in the main production site Brazilian phosphogypsum to assess the appropriateness of the use of this product in construction.

2. Materiels et methods

Samples of Phosphogypsum come from the production centers of Brazilian chemical fertilizers. Each sample is representative of the production 2007 - 2008 in stocks pile of different companies chosen for this study. The phosphate ore proceed from the apatite s veins into the Brazilian carbonatites, his origin is magmatic.



Group 1



Group 2

Fig. 1: Scanning Electron Microscope (SEM) Jeol 6400 equipped with Energy Dispersive X-ray Spectrometry (EDS). The Images showing a different characteristic texture of group 1 and group 2 Brazilian Phosphogypsum.

We effect a global characterization of these products by morphological analysis (SEM), chemical (XRF, ICP-AES, XRD and IR spectroscopy), thermal dehydration by TG / DSC, conductivity coupled with pH meter, calorimetry and radioactivity. The samples were homogenized and packed in cylindrical containers with a volume of 20 ml. A spectrometer of high purity germanium (HPGe)

CANBERRA brand, characterized by a relative efficiency of 30% and a resolution of 1.8 keV to 1332 keV was used for quantification of ^{40}K and families of ^{238}U , ^{235}U and ^{232}Th . Calibration standards were prepared in the same geometrical conditions as the samples to analyze. They are: A multi-gamma source liquid containing several radionuclides (high energy range) and whose activities are certified by the supplier (Amersham) for the calibration efficiency. Reference materials certified by the IAEA, containing families (Uranium, Thorium), for quality control analysis. The results given are those corresponding to ^{226}Ra analysis performed after 21 days of effective sealing of samples, the ^{222}Rn has been trapped and ^{214}Pb , ^{214}Bi and ^{226}Ra are in equilibrium with each self. The phosphogypsum samples were analyzed at CNESTEN (Morocco).

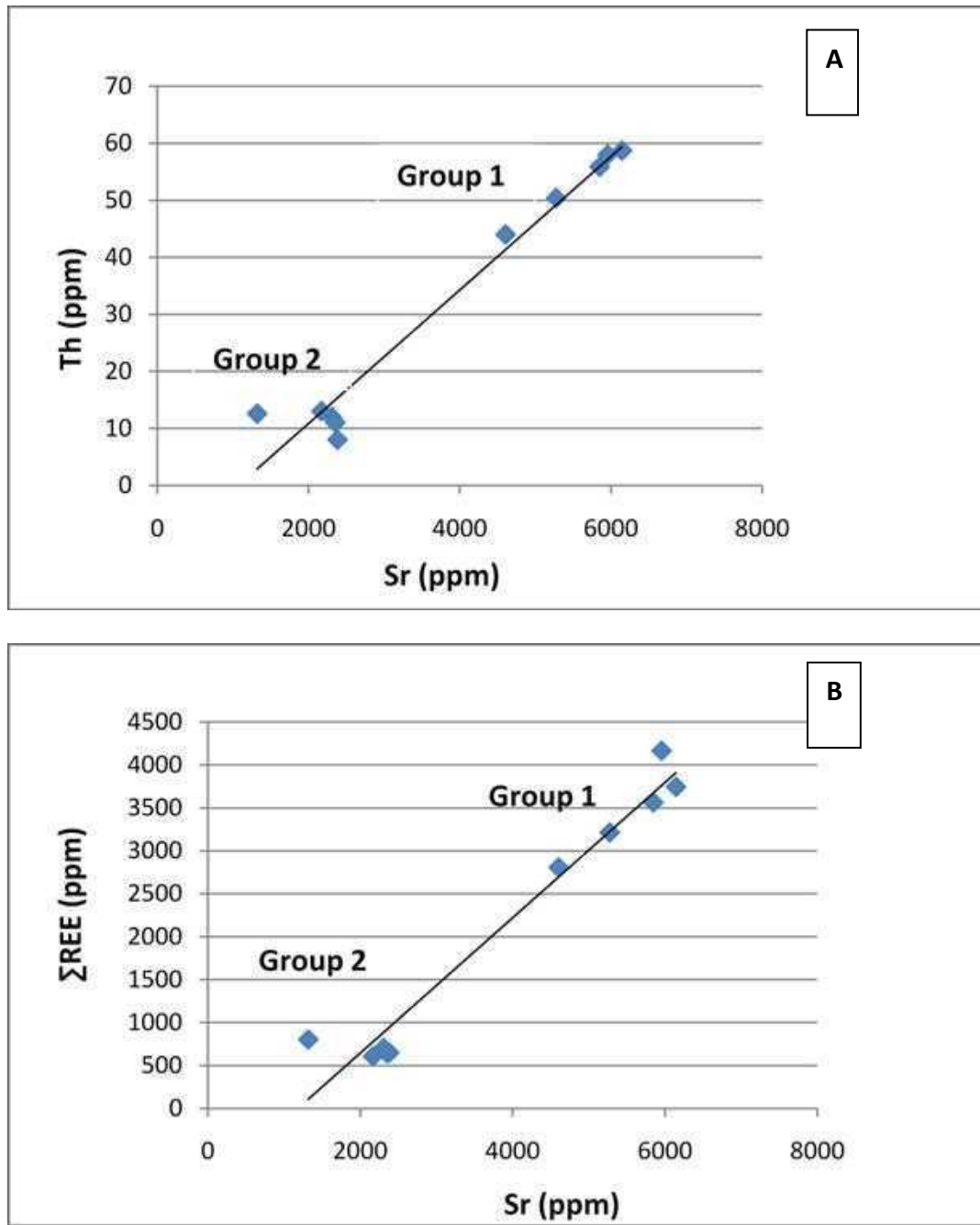


Fig. 2: Relation between Th (4A) and ΣREE (4B) and Sr contents in Brazilian phosphogypsum.

3. Results

We have distinguished two morphological groups (fig. 1), the first group is characterized by needle-shaped crystals with a uniform distribution between fine needles and platelets elongated sizes varying from 10 to 120 μm with crystallites ranging from 393-554 nm. The predominant phases in this group are gypsum, basanite and traces of anhydrite. The second group is characterized by a texture of fine agglomerated needles 5 to 30 μm in size and crystallites ranging from 73-300 nm. This second group consists exclusively of gypsum.

The study of conductivity of the two groups confirmed the XRD data, we have the conductivity curves in three stages to a rapid increase in conductivity to 1.6 mS / cm (dissolution) for the majority except one sample that reached 4.4 mS / cm and a gradual decrease in conductivity and conductivity stabilize around 2.6 mS/cm after half an hour while other samples of both groups rapidly stabilized to a minute between 1.5 and 2.3 mS / cm. The thermogravimetric analysis shows that the exothermic peak is nevertheless strongly shifted to higher temperatures and more spread out and the appearance of another peak around 120 ° C probably due to impurities. The spread of the curve between 85 ° and 100 ° C is related to the residual moisture in the Phosphogypsum.

The spectra of Fourier transform infrared TFIR revealed the presence of a peak slightly above 3600 cm^{-1} which is justified by the hemihydrates presence in some samples and the peaks at 836 cm^{-1} and 872 cm^{-1} different from what we observe in natural gypsum and related to the absorption of HPO_4^{2-} group (Hanna et al. 1999; Bilal 2010; Bilal et al. 2010).

The differences between the values of loss on ignition of various Phosphogypsum we show the presence of small quantities of semi-hydrate and anhydrite. The P_2O_5 contents are less than 1.5%, the Phosphogypsum is characterized by abundances of Sr, Th and REE, very high in the first group (fig. 2). The levels of heavy metals are insignificant.

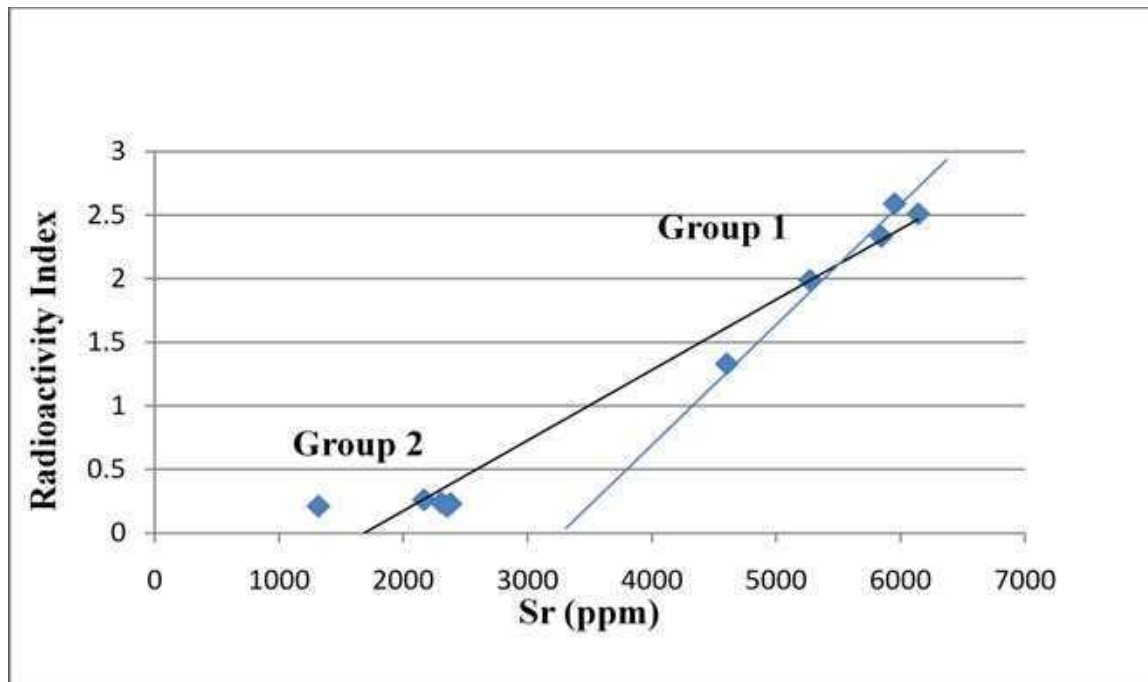


Fig. 3: Relation between radioactivity index ($I = (\text{Ra}/300) + (\text{Th}/200) + (\text{K}/3000)$) and Sr contents in Brazilian phosphogypsum.

Radioactive elements ^{226}Ra , ^{232}Th , ^{40}K discriminating both groups was the first one I radioactivity index ($I = (\text{Ra}/300) + (\text{Th}/200) + (\text{K}/3000)$) between 1.33 and 2.59 and the second group has an index between 0.24 and 0.45 (Fig. 3). The second group shows an index of Phosphogypsum radioactivity below the accepted standard ($I < 1$) for building materials established

by International Commission on Radiological Protection. Considering the radioactivity, we conducted on the same site in 1997; we specify that indices were significantly higher radio activities: 3.54 to 2.02 for the first group and 1.90 to 1.07 for the second group. However, the modernization of the tool and the manufacturing process led to lower radioactivity and impurities contents. The radioactivity measurements on different sites have shown that fine particles are richer in Radon than fractions above 30 μm . There remains the problem of solving Th. Some Phosphogypsum who suffered a wash, showing a decrease in levels of heavy metals, Th, REE, P_2O_5 , but Na_2O and K_2O .

4. Conclusion

The physico-chemical characterization of Brazilian phosphogypsum showed that some phosphogypsum, the group 2, may be used as building materials. The thoron levels are high in Brazilian phosphogypsum. Fine particles of phosphogypsum have also an elevated radioactivity. We must be careful about using these raw materials in the construction without a prior study of phosphogypsum stockpiles. It seems important that a map of the radioactivity inventory is required before any use of phosphogypsum.

ACNOWLEDGEMENTS

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CHARACTERIZATION OF MORTAR AND RENDERING OF MEDRESE RACHIDIA BUKHARA (OUBÉKISTAN)

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1. Introduction

Bukhara (Uzbekistan) has more than 2 000 years listed in 1994 of World Heritage by UNESCO. It is the most complete example of a medieval city of Central Asia whose urban structure mainly remained intact, with many monuments whose many celebrates Medrese of the XVIIe century. In the present work, the mortars from several parts of the Medrese Rachid of Boukhara at Uzbekistan, are characterize their nature as well as to study the technological aspects involved in the manufacturing processes of mortars and rendering in Uzbekistan. It is also a question of defining the state of degradation of these mortars to define the future restorations of Medrese Rachidia.

2. Experimental

2.1. Instrumentation and operating conditions

Powder dispersed on double-sided sticky tape and gold coated was also checked for chemical composition on a JEOL JSM 840 scanning-electron microscope (SEM-EDS) fitted with a TRACOR Northern 2000 energy-dispersive system. The apparatus was set at 15 keV, 5 nA beam current and a 10 μm raster were used. The same apparatus was used for acquiring SEM images. X-ray powder diffraction (XRD) analysis was performed on a Siemens D-5000 Kristalloflex automated diffractometer equipped with a graphite-diffracted beam monochromator (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$).

For thermogravimetric analysis (TG–DTG), samples were dried at room temperature for at least 48 h. The TG–DTG curves were obtained using a thermo balance from TA instruments (SDT 2960) with temperature and weight precision of 0.1 °C and 0.1_g, respectively. The sample was varied between 5 and 10 mg and weighed on ceramic pans. TG–DTG experiments were performed in flowing dry nitrogen atmosphere (100 ml min^{–1}) at a heating rate of 10 °Cmin^{–1} within the temperature range of 25–1000 °C.

2.2. Sampling

Sampling was accomplished in conjunction with the archaeologists and performed on the basis of architectonic considerations during April 2003 per Nicolas Detry. Information regarding sampling location and architectural use are provided in Fig. 1 show the map of the Medrese Rachid of Bukhara (Ouzbékistan) with the corresponding sampling locations.

The traditional mortar for the building is made from plaster with a mixture of clay and ash or sand and clay. Internal coatings are made with a special plaster called *Gunch* that comes from cooking alabaster low temperature (260 °). Some special mortars are designed to withstand water, as in the steam and are then made based *Gunch* and with a resin mixture of almond, then they are polished with metal spatulas.

The plaster has the advantage of being very flexible binder for mortars which helps resist structures during earthquakes. But it is a hygroscopic material highly resistant to moisture.

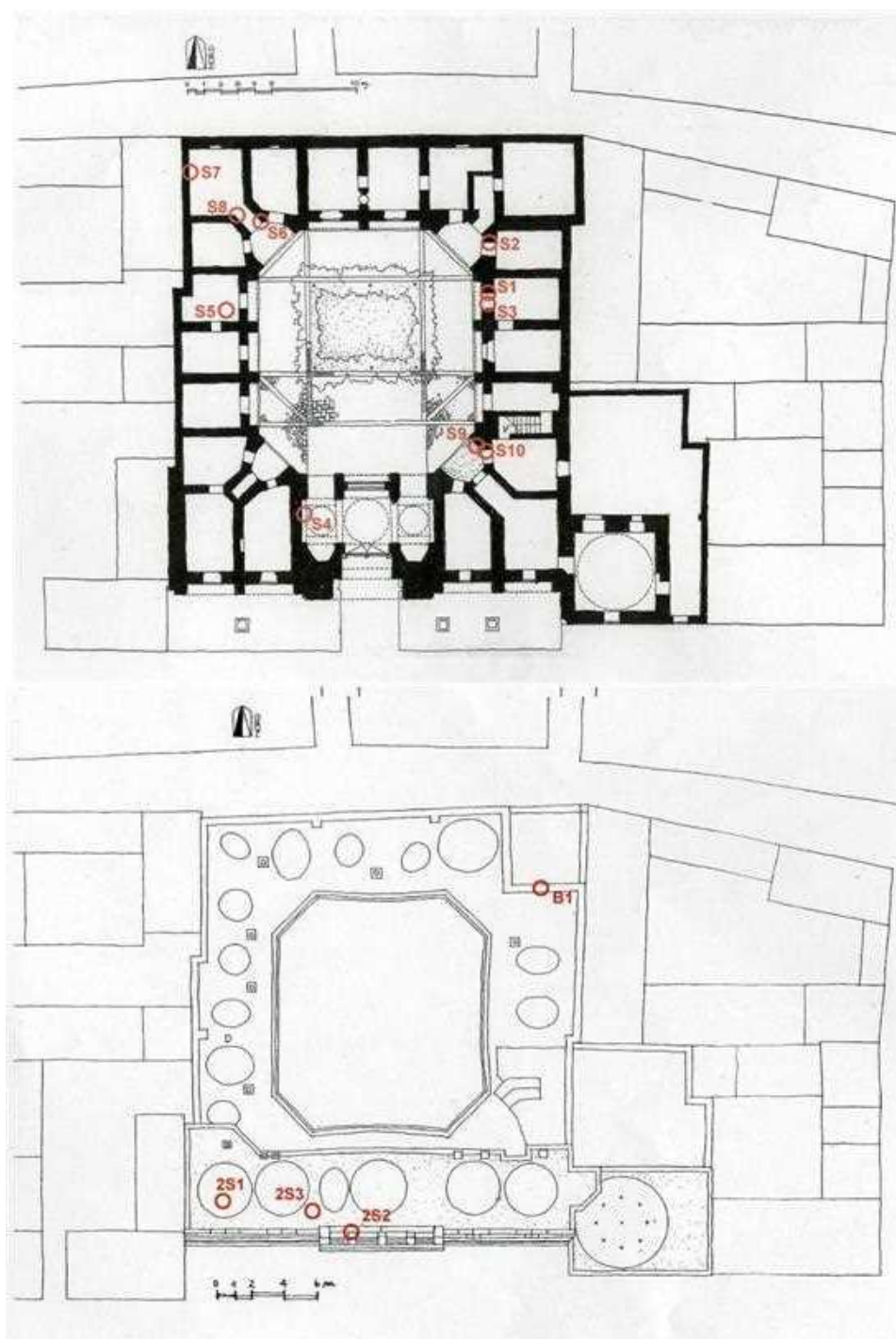


Fig.1: Map of the Medrese Rachid of Bukhara (Ouzbékistan) and sampling point
Nicolas Detry 2003. A: level 0 and B: level 1

3. Results

The TG-DTG analysis is used as a tool for characterization of old mortars. Indeed, it can easily detect the presence of compounds of hydraulic characteristics and provides the information that allows identification of the type of mortar.

Table 2 shows the percentage of weight loss estimated from the TG-DTG curves as a function of temperature ranges selected. Between 30 to 120 °C, the weight loss is due to adsorbed water; of 120-200 °C, the weight loss of water from hydrated salts; between 200 and 600 °C, the weight loss is due to water structurally related compounds from water and from 600 to 800 °C, the loss of CO₂ as a consequence of the decomposition of calcium carbonate (CaCO₃). The CO₂ to structurally bound water ratio in relation to CO₂ percentage (% weight loss in the temperature range

of 600–800 °C) is between 15 and 24%. We can observe that samples S2 and S7, S6, S8, S10 and 2S1 containing calcite or dolomite.

Table 1: XRD mineralogical composition of mortar and rendering from Medrese Rachidia.

Sample	Type	Mineralogy
S1	rendering	Gypsum , Zn_2SiO_4
S2	rendering	Gypsum, quartz, dolomite, iron oxyde
S5	rendering	Gypsum, quartz, chlorite
S7	rendering	Gypsum, calcite
S6	Mortar	Gypsum, quartz, calcite, chlorite
S8	Mortar	Gypsum,
S9	Mortar	Gypsum, quartz
S10	Mortar	Gypsum, quartz, dolomite, chlorite, muscovite
2S1	Mortar	Gypsum , calcite, dolomite, quartz
2S2	Mortar	Gypsum, quartz, chlorite, illites
2S3	Mortar	Gypsum, quartz, chlorite, illites

Table2: TG–DTG weight losses (wt.%) as a function of the temperature range.

Sample	Type	30–120 °C	120–200°C	200–600 °C	600–800 °C
S1	rendering	0.81	19.78	0.84	0.00
S2	rendering	0.81	7.03	2.69	16.25
S5	rendering	0.81	14.83	0.9	0.00
S7	rendering	1.41	18.81	4.0	24.09
S6	Mortar	1.15	2.80	7.6	18.72
S8	Mortar	1.08	20.04	2.6	21.44
S9	Mortar	0.84	20.29	2.67	0.00
S10	Mortar	0.9	3.02	5.46	15.41
2S1	Mortar	1.29	10.16	3.01	19.51
2S2	Mortar	1.12	20.01	2.01	0.00
2S3	Mortar	1.11	20.47	1.97	0.00

The term refers to water two specific properties: the property of hardening when water is added to the dry binder, and also the ability to harden under water. The hydraulic compounds are obtained from the reactions of $\text{Ca}(\text{OH})_2$ with natural or artificial bland are not available. The hydraulic mortars include all materials with a quantity of water structurally bound to hydraulic components are higher than 3% (S6, S10, S7), while the typical lime mortars are characterized by less than 3% of structurally bound water to hydraulic components. The obtained results enable the classification of the mortars studied hydraulic lime mortars with aggregates of siliceous and calcareous nature.

The physico-chemical characterisation of mortars and rendering samples of Medrese Rachidia reveals differences in the mortars employed and contributes to the knowledge of the Uzbékistan construction mode of the XVII^e century.

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CONTRIBUTION TO THE GOLD GEOCHEMISTRY FROM THE PORPHYRY CU-AU MINERALISATION OF BOLCANA DEPOSIT, METALIFERI MTS.

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Abstract

Bolcana ore deposit is characterized by the association of two types of mineralisation: the porphyry copper-gold type, spatially overlapped on the microdioritic subvolcanic stock, the other one is the polymetallic gold veins type that crosses the subvolcanic structure and the surrounded rocks. The gold is present in both types of mineralisation, but native gold is microscopically identified only in the porphyry mineralisation as inclusions in chalcopyrite, bornite and quartz minerals. Geochemistry of the gold grains is different in relation with the host minerals. The gold from chalcopyrite is enrichment in silver and tellurium, whereas the gold included in bornite and quartz has a higher purity grade. We consider that gold from bornite and quartz is a secondary generation resulted by mobilization of the gold from chalcopyrite in the upper level of the ore deposit, where a intensive argilizations was recognized, and was re-precipitated in the bonanza zone as high purity nativ gold in bornite and quartz.

Mineralisation

The porphyry copper-gold mineralisation forms impregnations or small veins (stockwerk network) into microdioritic/andesitic rocks of the Bolcana subvolcanic structure. It is the result of the Neogene metallogensis from Brad-Săcărâmb District (Metaliferi Mts) (fig.1). The main metallic minerals of this mineralisation are chalcopyrite, magnetite, pyrite and subordinate bornite, molybdenite, native gold, etc. These minerals are commonly small, not visible in hand specimen. The polymetallic-gold mineralization, that is associated with the porphyry type, is disposed as a vein network, distributed to two directions: NNW-SSE and E-W. The latter direction is less developed.

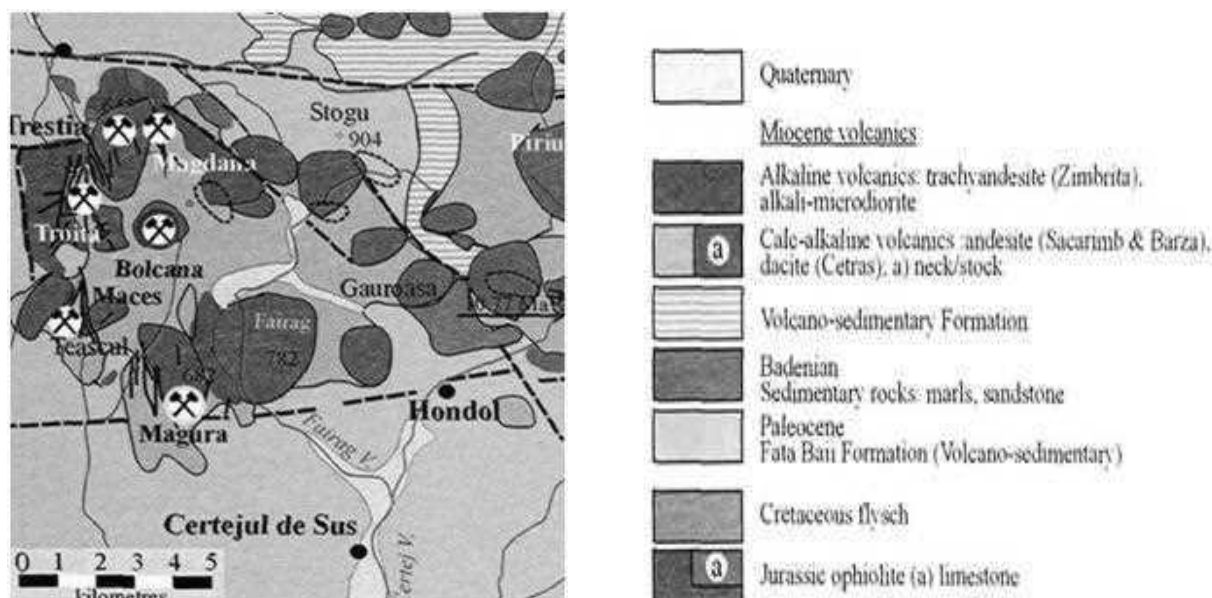


Fig 1. Geological map of Bolcana area and deposit locations; compiled from Ghițulescu and Socolescu (1941), Udubașa et al. (1992); the „Geological map of South Apuseni Mts, Alpine and Magmatism and related Ore Deposits (IGR, 2001) in Ciobanu et al., 2004

These veins have approximately 0.3 m in width and cross the subvolcanic body and the intruded andesitic rocks. The veins contain an ore mineral assemblage including sphalerite, galena, pyrite, tennantite-tetrahedrite, chalcopyrite, marcasite, bournonite.

The native gold was identified microscopically only in the porphyry-type mineralization, where it appears as small inclusions in chalcopyrite and bornite, and only rarely in quartz. (fig. 2, 3). Gold was not identified in the polymetallic mineralization, but was mentioned in former studies. (Udubaşa et al., 1981).

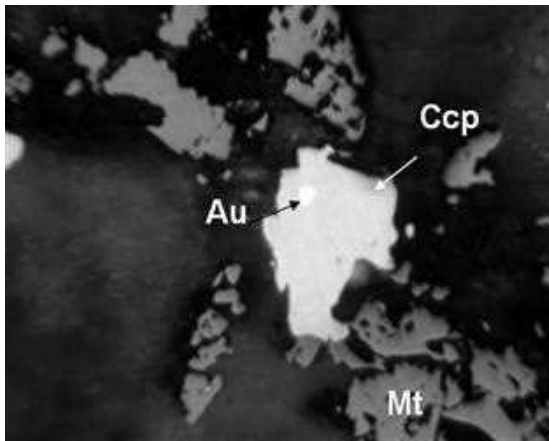


Fig. 2 Gold inclusion in chalcopyrite

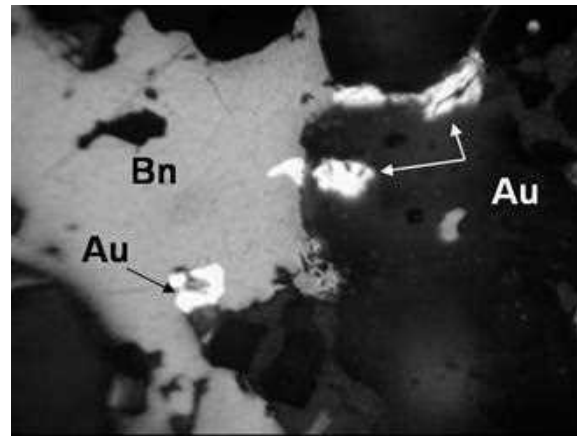


Fig. 3 Gold grains hosted by bornite and quartz

Analytical data

The chemical composition of some grains of native gold was analyzed using the scanning electron microscope (JEOL JXA-8600). The measurement was performed in the Mineralogy Department of Salzburg University on a number of 4 gold grains hosted in chalcopyrite, 2 grains

Table1. Chemical composition of the gold grains from the porphyry copper mineralisation

	Chemical composition (%)			
	Ag	Te	Au	Total
Gold in chalcopyrite	20,94	0,21	77,04	98,19
	19,67	0,1	80,18	99,95
	20,76	0,05	79,04	99,85
	14,56	0,01	84,03	98,60
	3,19	0,00	94,92	98,11
Gold in bornite	0,65	0,00	98,05	98,70
	3,88	0,00	96,53	100,4
Gold in quartz	3,86	0,01	96,47	100,35
	1,98	0,00	97,28	99,26

included in bornite and 3 grains included in quartz. Where the size of the grains allowed more than one measurement for one grain, no significant difference between measured spots has been remarked.

The results show variable concentrations for the Au, Ag and Te in different grains, as a function of the host mineral.

(a) The gold from bornite and quartz has a similar composition, with a higher purity grade, with means $\text{Au} > 93 \text{ wt. \%}$, while the silver shows low contents (below $\text{wt. \%} 4$) and tellurium is below detection limit. (b) The native gold hosted by chalcopyrite has an average Au content of 78 wt. %, with values of 70-85 wt. %. The silver displays contents between 14 wt % and 24 wt %, and the tellurium has values less than 0.2 wt. % for all the analyzed gold grains. It was observed that the tellurium correlates positively with the silver; in consequence the highest content of tellurium is recorded in the grains with highest silver content.

Discussions and conclusions

The measurements show the existence of two generations of native gold with different chemical compositions. The first generation is associated with chalcopyrite and contains ca. 20 wt% Ag and 0,2 wt% Te. The gold of the second generation appears as inclusions in bornite and quartz and has a small content of Ag; Te is below detection limit. The host bornite forms large grains, with chalcopyrite relics and covellite and chalcocite substitutions. This Au-bearing bornite is found in the enrichment zone.

Mann 1984, Nahon et al, 1992 (in Robb L., 2004) propose a model to explain the presence of an important content of high purity gold in a typical lateritic profile. They show that gold and silver become soluble in high Eh - low pH conditions and the gold re-precipitates as high purity native gold when finds specific conditions below water table (low Eh, more alkaline pH). This model could be used to explain the change in the geochemistry of gold in the upper level of the Bolcana porphyry copper deposit.

The first generation (gold from chalcopyrite) has its origin in the magmatic-hydrothermal fluids and its precipitation is determined by the change of the initial physical-chemical parameters of the primary hydrothermal system. The gold from bornite and quartz can be considered as secondary, the result of mobilization of the primary gold in the high Eh - low pH conditions from the upper level of the deposit. These conditions are confirmed by the presence of the intermediate argillic alteration with caolinite, illite, smectite, quartz, oxi-hydroxide iron assemblage. According to the model given by Mann (1984) and Nahon et al. (1992), gold re-precipitates as a high purity native gold below water table, in places where the secondary copper minerals (bornite, covellite, chalcocite) form a characteristic mineralization.

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MINING WASTE DEPOSITS, LEGAL AND INSTITUTIONAL FRAMEWORK

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1. Introduction

The specific processing, mining industry after mining mass separation of useful components, result in large amounts of mining waste (tailings) which should be stored near the site of extraction.

Dry storage dumps have relative large dimensions, they are placed in valleys having permanent character and generate optimal conditions for material they are placed on to slip.

Mud-setting ponds are large moist landfills loaded with noxious which can become water polluting sources by their content in suspension substances, flotation reagents and metallic ions. Represents a high risk causing increase over the critical threshold of hydraulic gradients, generates uncontrolled seepage leading to damage or ever destruction of retention dam with serious consequences (sometimes catastrophic) upon downstream utilities.

Following the restoration programs the mining activity under the administration of 13 companies and national societies from mining industry ceased. Under their administration there is a large number of industrial waste landfills, respectively 71 mud-setting ponds having an overall volume of 289,94 millions of m³ and 557 mining dumps with an overall volume of 1,421 billions m³ falling under OUG no. 244/2000 on safety of dams, approved by Law no. 466/2001, OUG no. 152/2005 on integrated prevention and control of pollution, approved by Law no. 84/2006 on the basis of which must be provided monitoring of stability and quality of discharged effluents as well as providing measures for its safety, closure and greening.



Figure 1. Location of closed tailing ponds from mining industry

compliance with regulatory powers under provisions and coordinates this process at national, regional and local level by Regional Agencies for environmental protection and Environmental Guard.

GD no. 112 of 2009/02/18 Art.14.-item (1)

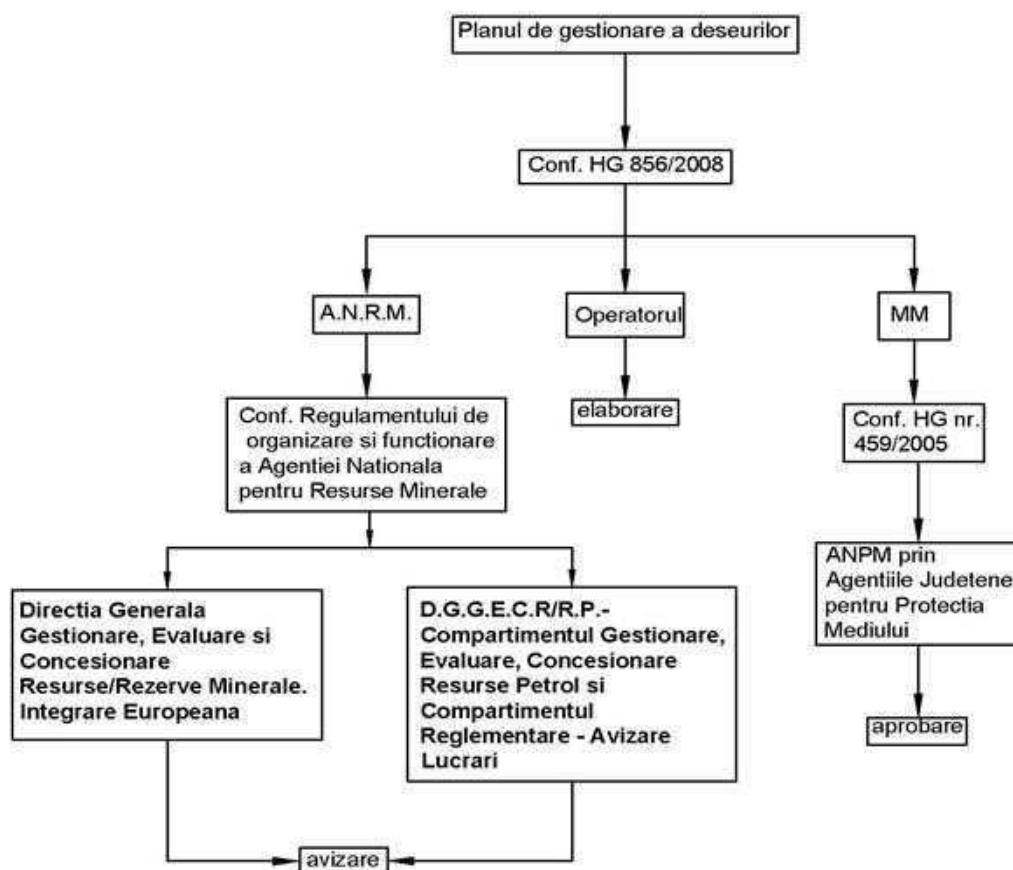
GNM has the following main attributes:

a) establish actions representing contraventions and apply sanctions on environmental protection, notify the competent criminal prosecution authorities and colaborates with them in finding facts which according to environmental legislation are crimes;

b) control the compliance with legal provisions in developing regulatory documentation, approvals, permits, environmental agreements/ integrate environmental agreements and has access to all documentation representing the basis of those agreements at request of the head of public central authority for environmental protection;

c) propose to issuing authority the suspension and/or cancellation of approval/agreement/environmental permit/ environmental integrate permit as appropriate issued in breach of legal provisions.

3. Responsibilities scheme of competent authorities/ operators regarding the waste management plan



STUDIES OF GOLD MINERALS FROM METALIFERI MOUNTAINS USING X-RAY FLUORESCENCE METHODS

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The X-Ray Fluorescence (XRF) elemental analysis methods require no sample preparation (not only polished samples – as for optical microscopy – but all kind of samples – crystals, amorphous, powder, etc. and also liquids can be analyzed), providing a non-destructive, sensitive and fast measurement on sample areas from 1 cm² (X-ray tube XRF) down to few micrometers diameter points (micro Synchrotron Radiation induced X-Ray Fluorescence – SR-XRF).

We focused on two samples – polished sections - from Rosia Montana and Musariu ore deposits.

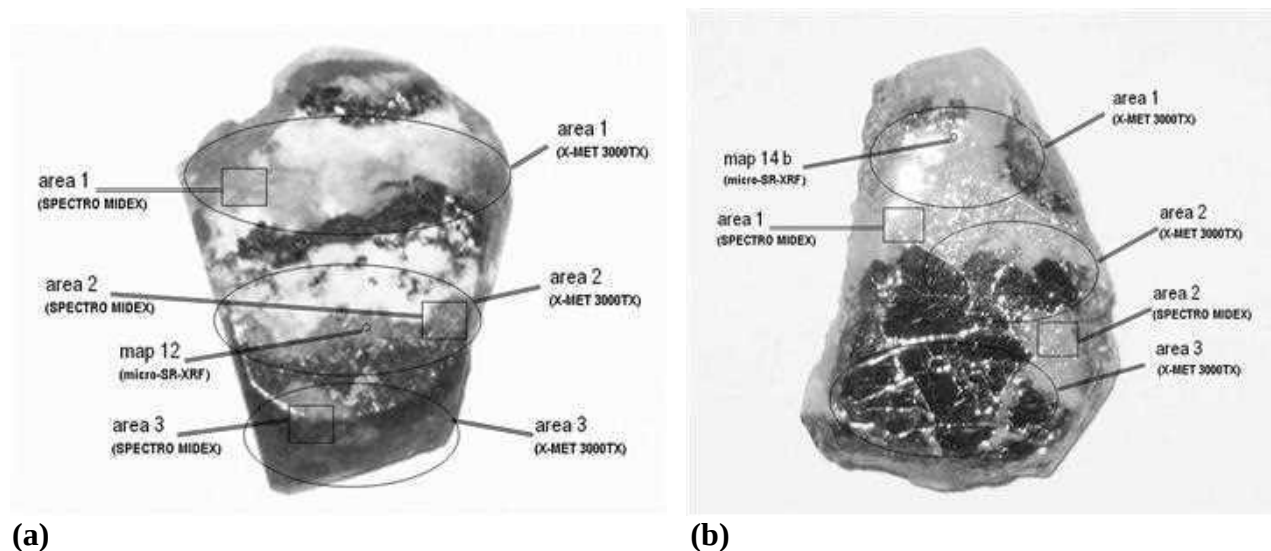


Fig. 1 - Rosia Montana (a) and Musariu (b) samples – areas and points of measurements

In the case of the first method we used two X-ray tube XRF spectrometers: a portable one - X-MET 3000TX (which can be used practically in all locations – mines and ore processing plants including) and a stationary one - SPECTRO MIDEK.

For the portable spectrometer, the exciting X-ray beam is generated by a 40 kV tube with Rh-anode. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the K α line of Mn (5.89 keV). The measurement spot size is about 30 mm². The X-MET XRF analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage. It was used for a preliminary investigation, providing only a rough sample characterization due to the large measurement spot size (6 mm x 5 mm). The general results are the following:

For Rosia Montana, the Au/Ag/Cu ratio is strongly variable - from 14.2/4/2.9 in Area 2 to 1.7/2.1/0.8 in Area 3. As associated minerals, we suppose to have Sphalerite, Pyrite, Chalcopyrite, Galena and Alabandite in all three areas, but in different concentrations.

For Musariu, the Au/Ag/Cu ratio is strongly variable from 57.8/16.7/- in Area 3 to 33.00/23.00/2.40 in Area 2. As associated minerals we suppose to have for Area 1 Sphalerite, for Area 2 Pyrite and Chalcopyrite, and for Area 3 again Sphalerite.

The stationary spectrometer has a 50 kV Mo-anode tube and a Peltier cooled Si drift chamber detector, with 170 eV resolution for the K α line of Mn (5.89 keV). The typical diameter of

the measurement spot is 0.7 mm, but it can be optimized for different tasks to 0.2 mm, 0.6 mm, 1 mm or 2 mm with four integrated - software controlled – collimators. The results for both samples are summarized in Table 1.

Table 1. Rosia Montana and Musariu samples - elemental composition - SPECTRO MIDEX spectrometer

	Au(%)	Ag(%)	Cu(%)	Pb(%)	Fe(%)	Mn(%)	Al(%)	Zn(%)	S(%)	Si(%)	Traces
Rosia Montana - Area 1	-	-	-	-	3.35	0.15	-	-	-	82.45	Ti, Ca, P, S
Rosia Montana - Area 2	49.72	11.94	0.1	-	-	37.6	-	-	-	-	Al, S,
Rosia Montana - Area 3	traces	traces	8.76	52.94	16.78	13.98	-	-	-	0.24	Sb, Ni, Te, P
Musariu - Area 1	traces	0.40	traces	-	0.71	-	11.1	66.04	3.8	12.96	Cd
Musariu - Area 2	6.05	1.88	-	-	traces	-	0.77	traces	0.2	91.76	K, Ca

For Rosia Montana, from these measurements, we can estimate as associated minerals:

- in Area 1– an important quantity of Mn (Alabandite, Rhodonite or Rhodochrosite), but also Si (Quartz) and Pb (Galena)
- in Area 2 - Au and Ag, Mn (see Area 1), Zn (Sphalerite) and Fe, Cu (Chalcopyrite)
- in Area 3 - Fe (Pyrite), Pb (Galena), Fe and Cu (Chalcopyrite) and Mn (see Area 1).

For Musariu, the minerals associated with gold are estimated to be:

- Area 1: is very rich in Zn (Sphalerite), and also some Quartz is present
- Area 2: an important amount of Si (Quartz) is detected.

For a more detailed examination (down to micrometric level), more advanced experiments, especially focused on Sb, Sn, Te detection, were performed at BESSY Synchrotron Radiation Facility, Berlin, due to the improved conditions offered by its high-energy X-ray beam. Point spectra – approx. 10 microns diameter - were acquired at 35 keV excitation energy. The samples were mounted in air in a special frame for *passé - partout* on a motorized xyz stage at an angle of 45° to the X-ray beam allowing to scan 2mm x 2mm areas. Fluorescence signals were collected for 300 s each by an HPGe detector, with no filtering. A video system and a long distance microscope allowed monitoring and selection of samples analyzed points. Data analysis was performed by means of the PyMCA software.

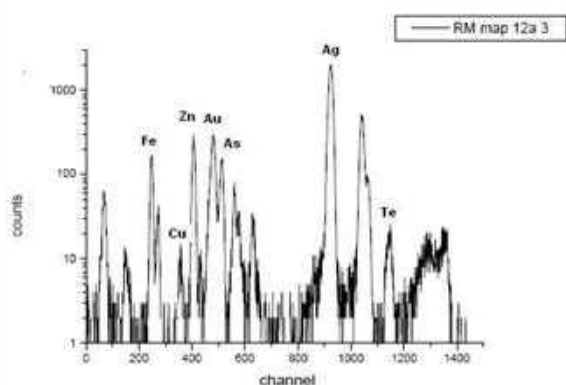


Fig. 2: Micro-SR-XRF spectrum for the Roșia Montana sample (10 microns diameter area)

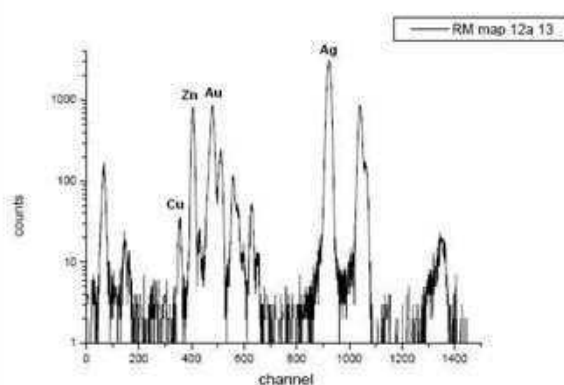


Fig. 3: Micro-SR-XRF spectrum for the Roșia Montana sample (10 microns diameter area)

For Rosia Montana we observe in some points the presence of Au-Ag tellurides – probably Silvanite (Au,Ag)Te₄, Petzite (Ag₃AuTe₂) or Krennerite (Au,Ag)Te₂ – surrounded by Sphalerite and

Pyrite areas (see Figure 2). In Figure 3 we observe an increased gold presence, the absence of tellurides and of Pyrite. In Figure 4 we observe the presence of Te, Sb and Pb, suggesting the appearance of Nagyagite - $\text{Pb}_5\text{Au}(\text{TeSb})_4\text{S}_{5-8}$. In Figure 5, beside Nagyagite it is also possible the presence of a silver telluride (Hessite?). We remark the strong inhomogeneity of the „gold” area from Roşia Montana sample – from point to point (10 microns diameter), not only the ratio Au/Ag is variable but also the presence of gold&silver tellurides is strongly different. The existence of Nagyagite can be also mentioned.

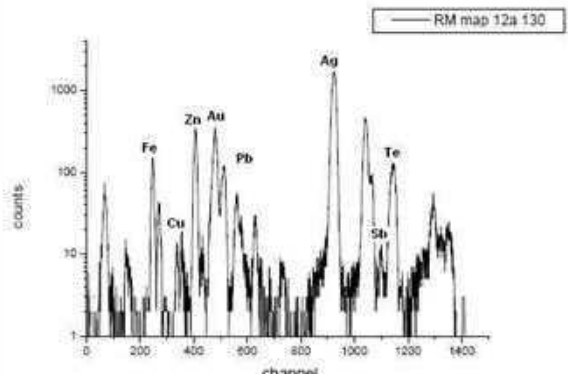


Fig. 4: Micro-SR-XRF spectrum for the Roşia Montana sample (10 microns diameter area)

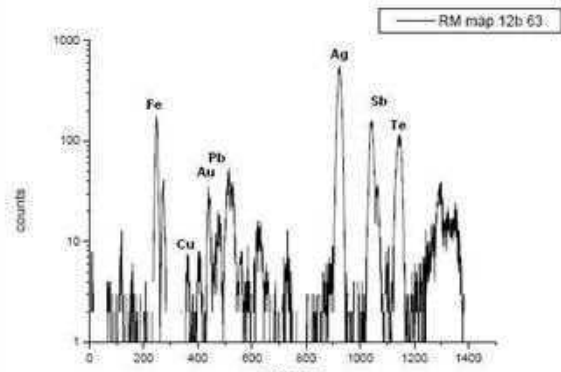


Fig. 5: Micro-SR-XRF spectrum for the Roşia Montana sample (10 microns diameter area)

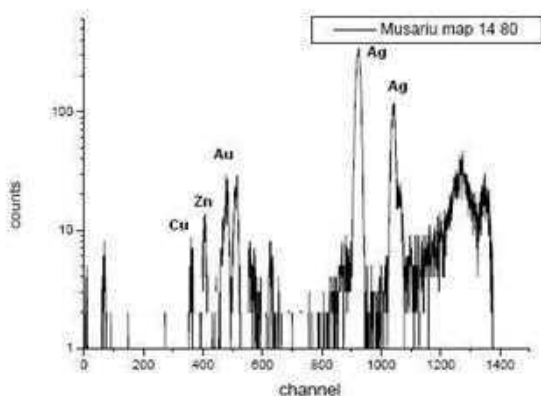


Fig. 6: Micro-SR-XRF spectrum for the Musariu sample (10 microns diameter area)

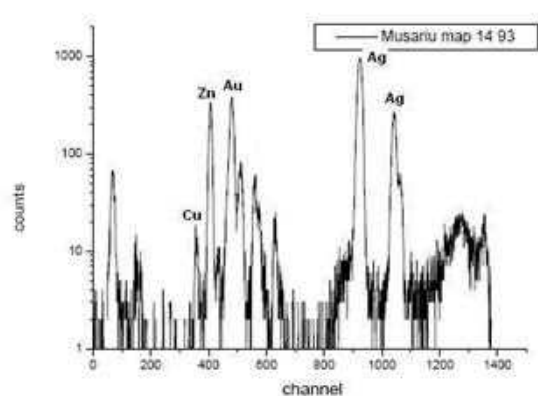


Fig. 7: Micro-SR-XRF spectrum for the Musariu sample (10 microns diameter area)

For Musariu the most relevant result is the strong variation of Au/Ag ratio from point to point. In Figure 6 silver is high, in Figure 7 silver is lower but Sphalerite is increased.

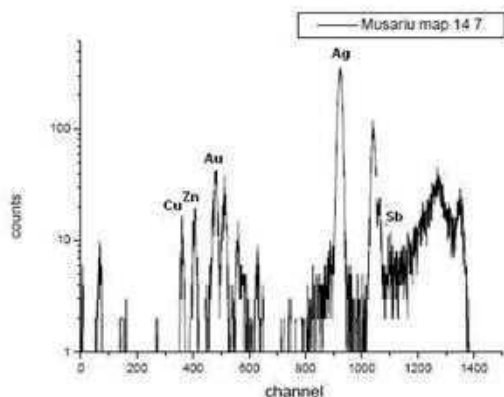


Fig. 8: Micro-SR-XRF spectrum for the Musariu sample (10 microns diameter area)

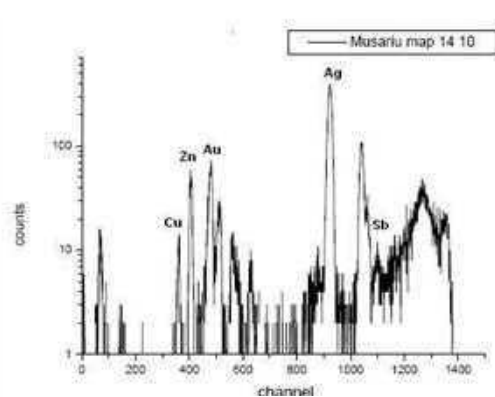


Fig. 9: Micro-SR-XRF spectrum for the Musariu sample (10 microns diameter area)

In Figure 8 we observe the presence of antimony, probably from a Sb-Ag compound – e.g. Stephanite - Ag_5SbS_4 . In Figure 9 beside the presence of a Sb-Ag compound we see the increased Sphalerite content. We remark the strong variation of Au/Ag ratio (stronger than for Rosia Montana) and the presence of Sb-Ag compounds in some micronic areas.

In conclusion, together with classical geological investigations based on optical microscopy, the use of X-Ray based analytical techniques - X-Ray Fluorescence (XRF) based on X-ray tubes, micro-Synchrotron Radiation X-Ray Fluorescence (micro –SR-XRF) - gives the opportunity to perform a complete characterization of gold geological samples. These methods require no sample preparation (not only polished samples – as for optical microscopy – but all kind of samples – crystals, amorphous, powder, etc. and also liquids can be analyzed). The portable XRF spectrometers can be used practically in all locations – mines and ore processing plants including. Micro-SR-XRF provides micro-structural analyses, very important for gold&silver minerals (tellurides, Sb compounds) determination, such information being very useful for geochemical – metallogenetic interpretation.

THE X-RAY DIFFRACTION ANALYSIS OF ATMOSPHERICAL PARTICLES IN INDUSTRIAL AREA OF IASI

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Abstract

Mineral compositions of aerosol particles were investigated for 24 sample collected in August 2009 and April 2010 in the industrial area of Iasi. Quartz and calcite are the most important minerals that occur in the air particles and the minor phase content: feldspars, dolomite, muscovite and zincite. Also we have found organic material, cement waste, dye, plants fragments, textile fragments and glass. The main source of mineral particles was found to be the soil suspension in addition to the metallurgical production industries in the area.

Introduction

Air pollution is one of the most serious problems of contemporary society, both in terms of time - affects both the short and medium term and long term, but also space - mobility and large areas are affected. Many studies have been done on the chemical composition of solid air pollutants. Some authors have used scanning electron microscopy (SEM) with X-ray energy dispersive (EDS) to examine particles in morphological and chemical terms, or elucidate their mineralogy (Esbert et al., 1996; Umbria et al., 1999; Chabas and Lefevre, 2000; Bernabe and Carretero, 2003; Zhenxing S. et al. 2009). Several important studies on the distribution of suspended particulate matter and heavy metals associated with them and their sources in different places in the world have been made recently (Cabada et al., 2004, Kawanaka et al., 2004). But there are few studies on the mineralogy of solid pollutants. Thus Esteve et al., 1997, Querol et al., 1999; Queralt et al., 2001; Ekosse et al., 2004 have studied mineralogy of the dusty particles. In some cases the mineralogy studies of atmospheric particles may indicate much more than chemical composition (we can determine the origin of particles and their effects on health).

Industrial platform of Iasi is the second largest in the country. Predominant industries are: energy industry (east platform), chemical industry (west platform), metallurgy and heavy machinery (south and east platform).

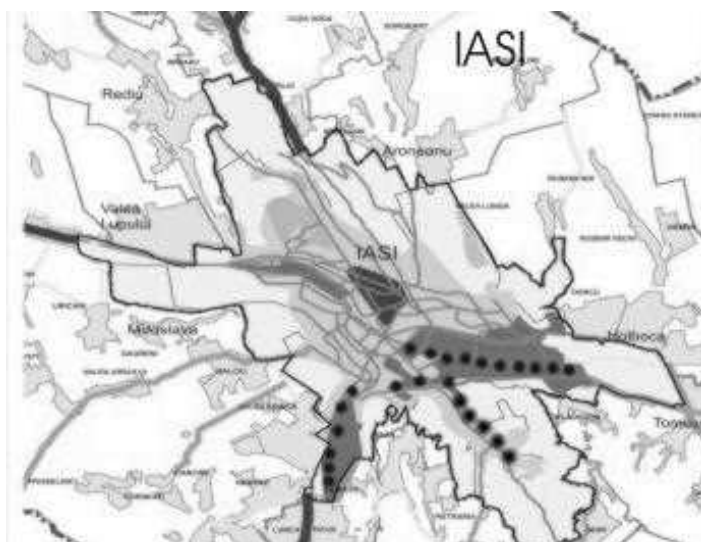


Fig. 1 Location of sampling sites

Samples and methods

Samples were collected from industrial area of the city of Iasi in August 2009 and April 2010. The samples were sieved to obtain the finest fraction. Initially samples were examined microscopically at the Department of Mineralogy, the device being used Olympus microscope. X-

ray experiment was carried out using X PERT MPD PAN analytical diffractometer using Cu K α radiation at 40 kV and 40 mA. Scans were performed from 2° to 120° (2 θ) step size 0.02, step time 30 sec

Results

Analyzing thin sections under a microscope we determine that the predominant minerals are quartz, muscovite, feldspars, calcite. Also we have found organic material, cement waste, dye, plants fragments, textile fragments and glass. Quartz appears as a constituent detritic allogenic isolated granular, on the surface of some granules can noticed some friction ridges which suggests that those grains were transported by wind. Muscovite is a very stable mineral, occurs as isolated crystals hipidiomorf shape, habitus lamellar. Carbonates represent by calcite occur in the anhedral form.

The most abundant mineral phases on the samples detected by XRD were quartz and calcite, which were present in all samples. Minor phases included: feldspars, dolomite, muscovite. In 4 samples provides from the south industrial platform we found zincite (ZnO) in that zone there is a important metallurgical company who made ferrous metal foundries. Zn is assumed to contribute to the toxic potential of atmospheric particles. Several studies have demonstrated that the speciation of Zn has an large influence on lung lesions: soluble Zn phases, e.g. Zn sulfate, aggravate lung inflammation, as opposed to less soluble Zn species.

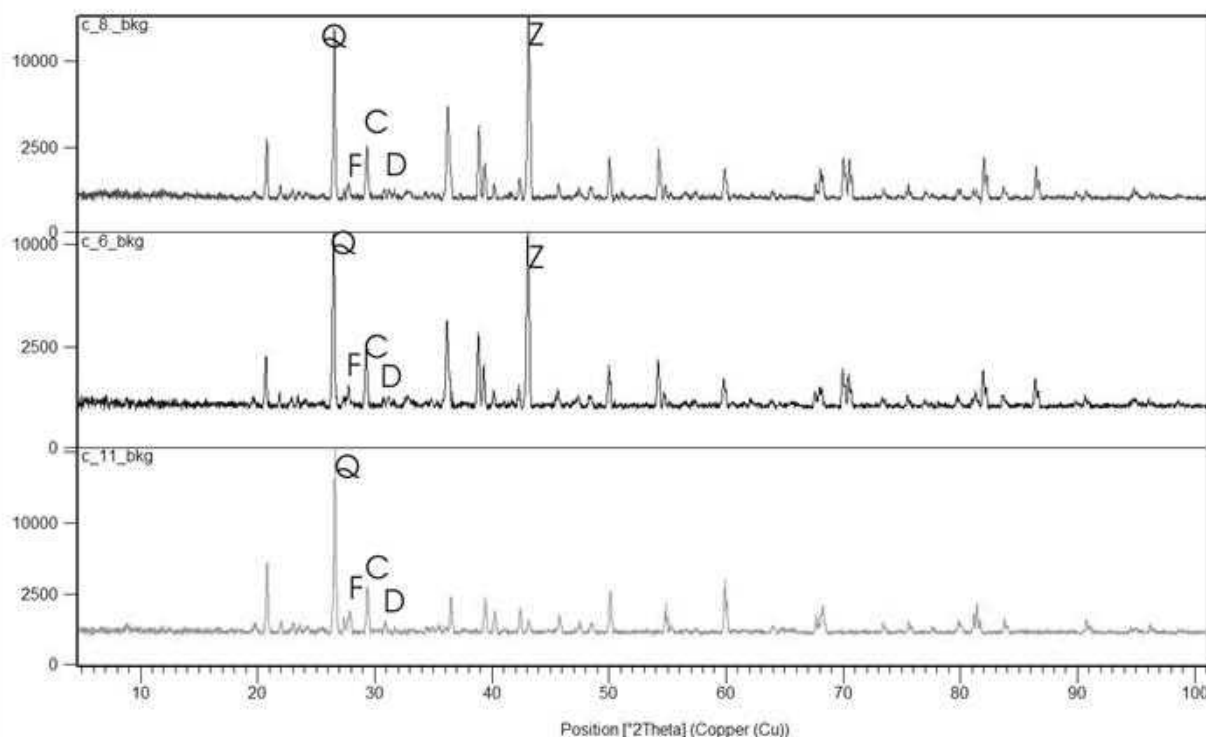


Fig. 2 Quartz(Q), feldspars(F), calcite (C), dolomite (D) and zincite(Z)

Conclusion

Using XRD analysis we conclude that the most abundant mineral phases in the samples were quartz and calcite, which were present in all samples. Feldspars, dolomite, muscovite and zincite appear in a small proportion.

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BENTONITE RESOURCES AT “ORASUL NOU” AND MEANS OF USING THEM IN THE FIELD OF ENVIRONMENT PROTECTION

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The bentonite resources are being increasingly used in the field of environment protection. In Romania, in the area of Oraşul Nou commune (Satu Mare district), there are large amounts of bentonite resources. This area has been prospected through drill holes, which have shown significant quantities of bentonite rocks. The bentonite-bearing formations were explored in detail by Bârlea et al., (1969). Currently, there are a few open-pits that have been developed and subsequently abandoned because of the low demand for such resources on the internal market.

1. Geological framework .

The geological formations in Oraşul Nou area are of Neogene age, and they consist of sedimentary and volcanic deposits. The sedimentary formations belong to the Sarmatian, Pannonian and Quaternary periods. The volcanic formations are made of lava flows intercalated in sedimentary formations, that Sagatovici (1968) and Bârlea (1969) identified as being of Badenian age. At a later date, Rădan et al., 1995 established that they were of Pannonian age. The part that has significant amounts of bentonite resources is the northern end of the volcanic rocks in the Oraşul Nou – Medieş Vii area, represented by ignimbrite facies formations.

The bentonite resources are hosted in the volcanic formation. The bottom and top parts of this formation host ignimbrite-facies rhyodacites. The middle-section complex is of perlite-pyroclastic nature, made of a predominantly pyroclastic central level, represented by lapillic tuffs and volcanic ash, intercalated between two levels of perlite-facies rhyodacites. The pyroclastic rock fragments are made of the following: hyaline rocks, fluidal volcanic rocks, metamorphic rocks, marls and siltstones. The matrix is represented by volcanic ash and crystal fragments. The perlites consist of volcanic glass (over 95%), which includes plagioclase crystals, sanidine, quartz, biotite. In certain spots, in the form of enclaves, there are andesite fragments, microdiorites, quartz-muscovite schists. In individual spots, the perlites are replaced by montmorillonite and cristobalite.

The current mineralogical composition has resulted from several simultaneous mineralogenetic processes, that include primary components, devitrification products and minerals of hydrothermal and supergene origin. Among the primary components, glass takes over 95% of the rock volume. Primary minerals are represented by plagioclase feldspar, quartz, biotite, sanidine. Devitrification products occur mainly as various types of silica (cristobalite and tridymite), and, as secondary minerals, there are also occurrences of adularia, montmorillonite, kaolinite, halloysite, carbonates and sulphides.

2. The quality of the bentonite and of the rocks altered to bentonite.

The perlites, bentonites and rocks altered to bentonite may be used as commercial rocks. The most important ones are the bentonites. The mineralogical composition of the bentonites and of the rocks altered to bentonite is similar in terms of quality. The differences arise from the various ratios of the montmorillonite to other components. In the case of bentonite, the minimum amount of montmorillonite is of 60-65%, whereas in the case of the rocks altered to bentonite, the amount of montmorillonite is of 20-25%.

Determining the content of montmorillonite is rather difficult. Visual methods have limited applicability, whereas determining the content based solely on the chemistry of the rock leads to erroneous data. The method that only incurs minimum errors is the use of X-rays diffraction. Taking this fact into account, we have developed a method based on X-ray diffraction analyses, which uses

reference standards. The tests and measurements made using this method have been presented, in summary, in the previous paragraph.

The montmorillonite is the prevailing mineral in the bentonite, but only occurs as a less significant part of rocks altered to bentonite. The main form occurs as calcium montmorillonite; to

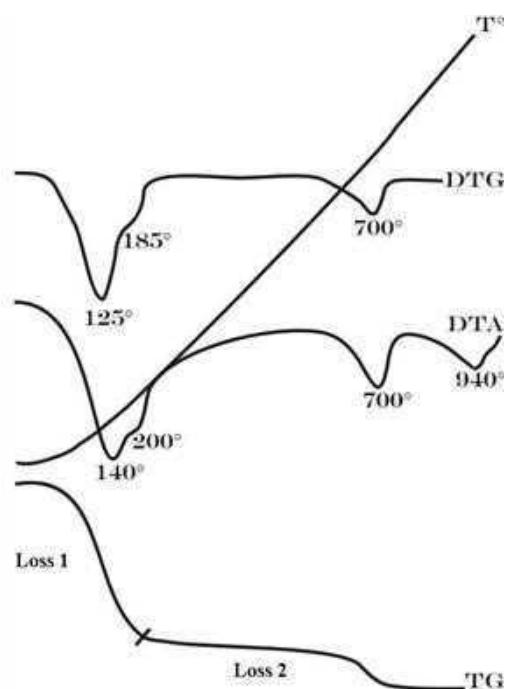


Fig. 1. Derivatogram of the Cheto montmorillonite – Oraşul Nou

a lesser extent, there are also intermediary types of montmorillonite and Wyoming montmorillonite (Fig. 1). The data provided by X-ray diffraction have shown the presence of a well crystallized montmorillonite, with a low degree of structural disorder.

The silica occurs in the transformed form of cristobalite, which is associated to montmorillonite. The amount of cristobalite increases in direct proportion to the intensity of the transformation to bentonite. The content of montmorillonite is higher in the fine fractions of the rocks altered to bentonite (<0.01mm), exceeding 95% in some cases. The cristobalite tends to concentrate in grain size fraction, as same as the quartz, feldspars and carbonates.

The tests determined several specific properties which have an impact on the use of these resources for various industrial fields and with regards to

environment protection. These properties are influenced by the mineralogical composition, the structure of the minerals and chemistry of the rock. The values for some of these properties are as follows: specific gravity – 2.3g/cm³; CEC for Ca²⁺ - 46%; degree of whiteness 70-75%, plasticity – 68.87, suspension stability 89.

3. Bentonite genesis.

Mineralogical and chemical data suggest that the process of altering to bentonite was mainly a hydrothermal-deuteric process. Deuteric weathering affected the pyroclastic materials and the perlites in watery mediums with an alkaline pH and a high concentration of Mg and Ca, but lacking K, (Grim and Güven 1978). The presence of rare iron, mercury, and zinc sulphides is representative for bentonitization of the pyroclastic material by the hydrothermal solutions. Related to the known genetic patterns of bentonite deposits, it may be assumed that they fit into the category of deuteric-hydrothermal alteration.

The alteration to bentonite has taken place when the silica and alkali metals were removed by a significant amount of water. The silica may remain in situ, in the form of cristobalite associated to clay minerals, or it may be mobilized upwards or downwards and redeposited. From a mineralogical point of view, the chemical transformations occur mainly as formation of clay minerals, the montmorillonite being the prevailing one. This mineral has formed through the breakdown of feldspars and mass of volcanic ash, as well as of the volcanic glass in the perlite.

4. Considerations with regards to the bentonite potential of the area

The deposit is tabular-lenticular in shape, average width being of approximately 5 m for the bentonite level and about 10 m for the level of rocks altered to bentonite, missing about 25% of the

leachable part. Taking this into account, the deposit is one of the largest ones in the country. The possibility for open-pit mining is yet another significant advantage in terms of capitalizing on this deposit. According to data provided by specialized literature, (Meunier 2005, Alther 2004) bentonite may be used in the following fields:

- Within the petrochemical industry, as catalyst for refining crude oil and for purifying fractional distillation products;
- When preparing drilling fluids;
- Within the paper industry, for making white and glossy paper;
- Within the drug industry and cosmetic products industry, for making balms, wet wipes, soaps, powders, make-up products, face creams and mud wraps;
- Within the food industry, for clearing and purifying water, wines, beer, vegetable oils;
- Within the manufacturing of refractory products, for obtaining refractory cement and as a plasticizer in the field of porcelain manufacturing;
- Within the ironworks industry, when casting on plastic cores;
- For making white cement and Portland cement;
- Within the agricultural field it is used as carrying agent when spraying fungicides and insecticides and for improving sandy soils.

5. Usage options with regards to environment protection.

The use of bentonite in the field of environment protection is significantly lower than the use of natural zeolites. Bentonite may be used for detoxify processes, for purifying the waste water from a town s sewerage system, for the protection of waste-storage areas, for purifying industrial gases. It is also possible to use bentonite as amendment for fly ash, for covering waste disposal areas, (Mollamahmutoğlu and Yilmaz 2001). Recently, bentonite has also been used in research related to removing ammonium and heavy metals ions from waste waters, and in particular for retaining chrome. The adsorption properties depend on the value of the cation exchange capacity, (Ayari et al., 2005). The removal of heavy metals from aqueous waste is due to the high hydraulic conductivity of the bentonite-zeolite mixture, (Kayabali Kamil and Kezer Hasan 1998).

Due to the bentonite clay s strong negative ionic charge, it makes it possible to attract any substance with a positive ionic charge, such as bacteria, toxins, heavy metals etc., that reach our system from the more and more polluted environment. These substances are both adsorbed on the surface and absorbed within by the clay molecules (Abehsera, 1986; Knishinsky, 1998).

Perry (2006) suggests both a digestive cure, as well as an external use. The author claims that the human body does not digest the bentonite clay, therefore, it only passes through our system, collecting and removing the toxins and, afterwards, the clay is eliminated, playing the role of a little internal vacuum cleaner.

6. Conclusions.

The deposit of rocks altered to bentonite, formed in Orasu Nou area, has resulted from the hydrothermal-deuteric alteration of the median perlite-pyroclastic complex within the volcanic formation. In terms of quality, the bentonite resources are characterized by the presence of well crystallized calcium montmorillonite. The deposit s conditions are such that open-pit mining is favoured.

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GEOLOGICAL DATA FOR PIETROASA GYPSUM DEPOSIT (CLUJ COUNTY)

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Introduction. Pietroasa Gypsum deposit is a part of Badenian deposits present in the western part of Transylvanian Basin, Romania. The deposit begins on north of Turda town and continues toward the south passing through the villages from Cheia, Moldovenesti, Pietroasa, Podeni, and Aiud. The study of Pietroasa Gypsum deposit began with geologic field work, starting with geologic mapping, 44 drill holes, core sampling, and collection of outcrop samples.

Geology of the region

The investigated region is distributed at the contact between two different structural units – Apuseni Mountains in the west and Transylvanian Basin in the east.

Apuseni Mountains. Turda – Moldovenesti – Pietroasa region is situated at the eastern extremity of Apuseni Mountains and from a petrographic point of view this region is characterized by the presence of eruptive basic and sedimentary rocks – Jurassic limestone.

Eruptive rocks can be found on north of Arieșului Valley towards the south up to Aiudului Valley. This rock, the age of this has been attributed as being Upper Jurassic, sustains in the west side Stramberg Tithonic limestone, and in the east they are covered by transgression the badenian formations of Transylvanian Basin.

In Pietroasa region, the ophiolites are well developed along the lower course of Pietroasa brook, in front of the entrance from Moldovenesti locality. They appear likewise north of the Pietroasa village, where it constitutes a patch of small dimensions. The rock is massive, with areas of disintegration, has a greenish-black color that leans towards brownish-red with a high resistance.

The sedimentary rocks belong to Upper Jurassic age and appear in the western part of the researched region. In the Jurassic limestone, north of Arieșului Valley, are dug out Cheile Turzii and continue towards the south in the crest of Piatra Secuiului. At the inferior part of the Jurassic deposits interchange, limestone with intercalations of stratified calcarenite can be found, after which follows massive limestone of the Stramberg type, partly crystallized, of about 700 m thickness. The limestone is arranged as transgression on top of the previously described ophiolites.

Transylvanian Basin. The eastern part of Turda – Moldovenesti – Pietroasa region belongs to Transylvanian Basin and consists of neogen (Badenian, Sarmatian, Pannonian) and quaternary sedimentary rocks.

Badenian deposits are found transgressed on top of the ophiolites. The contact between the two formations can be followed from Cheia locality towards the south, to Moldovenesti, Pietroasa and Podeni and follows a sinuous line, with indentations in the form of gulfs in the ophiolitic strip, amongst which the greatest can be seen in Pietroasa region.

Badenian begins with an onshore facies consisting of conglomerates, calcareous breccias and sandstone after which the limestone horizon follows with Lithothamnium (organogenic limestone, rich in coral, foraminiferal assemblage, lamelibranchia, gastropods and echinida). In certain areas of the sediment basin, where there were favorable conditions, a lagoon-like facies was established, represented by the saline clays, saline breccias (in the surrounding town of Turda), massifs of salt (Turda, Valea Florilor) and gypsum lenses (at Copaceni, Cheia, Pietroasa, Valea Florilor).

Towards the centre of Transylvanian Basin the lagoon-like facies is missing, the badenian being present in neritic facies (greyish-blue or blackish argillaceous marl, clay and sandstone with thicknesses of a couple hundred meters).

In the Pietroasa – Podeni region the badenian sea water has shifted a lot to the west, creating a small gulf in which firstly sediments with onshore facies characteristics were deposited and then, after the separation of the rest of the basin, sediments with lagoon-like facies characteristics.

The sarmatian deposits make up the eastern part of the researched region, and in view of this, Buglovian and Volhinian – Bessarabian were separated.

Buglovian has a reduced spatial development and is represented by a uniform series of sand and sandy marl encompassed between two horizons of tuff: tuff of Hădăreni at the base and Ghiriș tuff at the superior part. Volhinian – Bessarabian with a wider spread than the preceding consists of schistose marl, greyish-blue marl, ferruginous clays and sandstone with brackish fauna.

The pannonian deposits develops in the east of the sarmatian deposits and is encompassed in a succession of greyish-black clays, sandy clays, ferruginous clays, sandstone and sand.

The newest deposits in the region are of a quaternary age and are represented by:

- The upper deposits of the Arieș terrace consists of rocks and thick sands of about 10 – 30 m that are of Upper Pleistocen age;
- The recent alluvial of the Arieș river and of the more important brooks in the area consist of rocks and sands of the Holocen Upper age;
- The clay deposits of the land slides that characterize the area and the bajada deposits at the mouth of the brooks and of the slopes affected by the torrents.

Geology of the deposit

Badenian has within the perimeter of the deposit a stratigraphic succession which presents at the base arenaceous limestone with Lithothamnium, on top of which greenish tuff, tuff sandstone and clay can be found.

The gypsum facing continuous sedimentation presents a stratiform–lenticular character with an inclination towards NE with 10 – 15°. Across the gypsiferous horizon Badenian ashen clays can be found, on top of which, at the superior section quaternary clays are disposed (sandy clays accumulated at the base of the plants, alluvial clays along the length of the valleys as well as clays resulting from landslides that encase within themselves bits of rock).

Deposit form

The deposit presents within its structure two separate gypsum lenses – a lens in the northern part of the deposit and another in the southern part thereof.

Northern lens. This is contoured in the northern half of Iancului Hill and occupies a surface area of about 8 ha. The thickness of the gypsum varies between 10 – 15 m at the crest of the hill and decreases on the flanks reaching 1 – 2 m at the downhill. Since the thickness of the gypsum along the flanks is greatly reduced the gypsum no longer presents a point of interest in terms of exploitation. The gypsum covering predominantly consists of clays with a maximum thickness of 12 m. An important part of the lens is even at the crest of the hill, thereby reducing the covering volume for the calculated gypsum resource with good overburden/gypsum ratio being for current exploitation.

Southern lens. Presents much greater dimensions than the northern lens, circa 37 ha, and is situated in the southern half of Iancului Hill from where it continues towards the east on flank under Hidiș Bilt peak. The gypsum has a greater thickness than the northern lens frequently reaching 15 – 20 m. It can be noted that, in this lens, the greatest thickness of the deposit of 33,5 m in the F15 drill soil log is recorded. Overburden/gypsum ratio is accepted for the current exploitation.

Gypsum usage

The quarrying products resulting from the future gypsum quarry will be designed for complying with the demand of the production in the plants, as follows:

- 0–50 mm white gypsum sort is utilized for plaster fabrication (over 90% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$);
- 0–30 mm white gypsum sort is utilized for plasterboard fabrication (over 80% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$);
- 0–30 mm grey gypsum sort is utilized for cement fabrication (55 - 80% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$);
- 0–1 mm sort is utilized for pharmaceutical industry.

Conclusion

Pietroasa gypsum deposit has been outlined within Badenian deposits existing in the western part of the Transylvanian Basin. The resource in Pietroasa deposit is important, and the gypsum is utilized for plaster, plasterboard and cement manufacturing.

MINING WASTES - SAMPLING, PROCESSING AND USING IN MANUFACTURE PORTLAND CEMENT

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Introduction

A sustainable economy will use more efficient resulted wastes, will reduce wastes to a minimum level and will be based more on recycling, reusing and renewable energies technologies (M. Michael, J. Petruska, 1982). Various settling ponds in Romania were sampled for sterile mineral wastes, which in its turn underwent chemical and mineralogical investigation so as to reveal any possible ways of employing it in cement manufacture. The criteria for selection consisted in the content in SiO_2 and Fe_2O_3 and the requirements in the standards for cement manufacture. The mining wastes were selected to be employed as an addition to the raw mix in cement manufacture. The laboratory investigations regarding the use of the mining wastes from tailing ponds as a corrective addition to the raw mix in cement manufacturing have led to obtaining of clinkers with ordinary modular composition. From structural - mineralogical point of view, the quality of the obtained clinkers is good, being typical alite Portland clinkers. Cements of type CEM I, obtained through grinding of the clinkers with gypsum, at a fineness of about $3500\text{cm}^2/\text{g}$ have presented physical mechanical characteristics in accordance with quality requirements imposed by SR-EN 197-1:2002 norm.

Mining wastes - sampling, processing and characteristics

Tailing ponds from Romania territory (Fig.1) represent deposits of sterile made through hydraulic transport of tailings slurry from the preparation plants. In each phase of exploitation mining tailings ponds should have a sufficient space to ensure proper settling of the tailings slurry, so that clarified the water which is discharged to be according to the rules in force regarding water guiding in emissary or technological conditions relating to installation of preparation. Tailing ponds used for the research were obtained by sampling operations. Sampling operations was done by prospection with the sampling probe on pond surface (Fig.2). Amount of the sterile from pond thus obtained was subjected to mixing and quartation operations in order to obtain representative samples for laboratory analysis and testing.

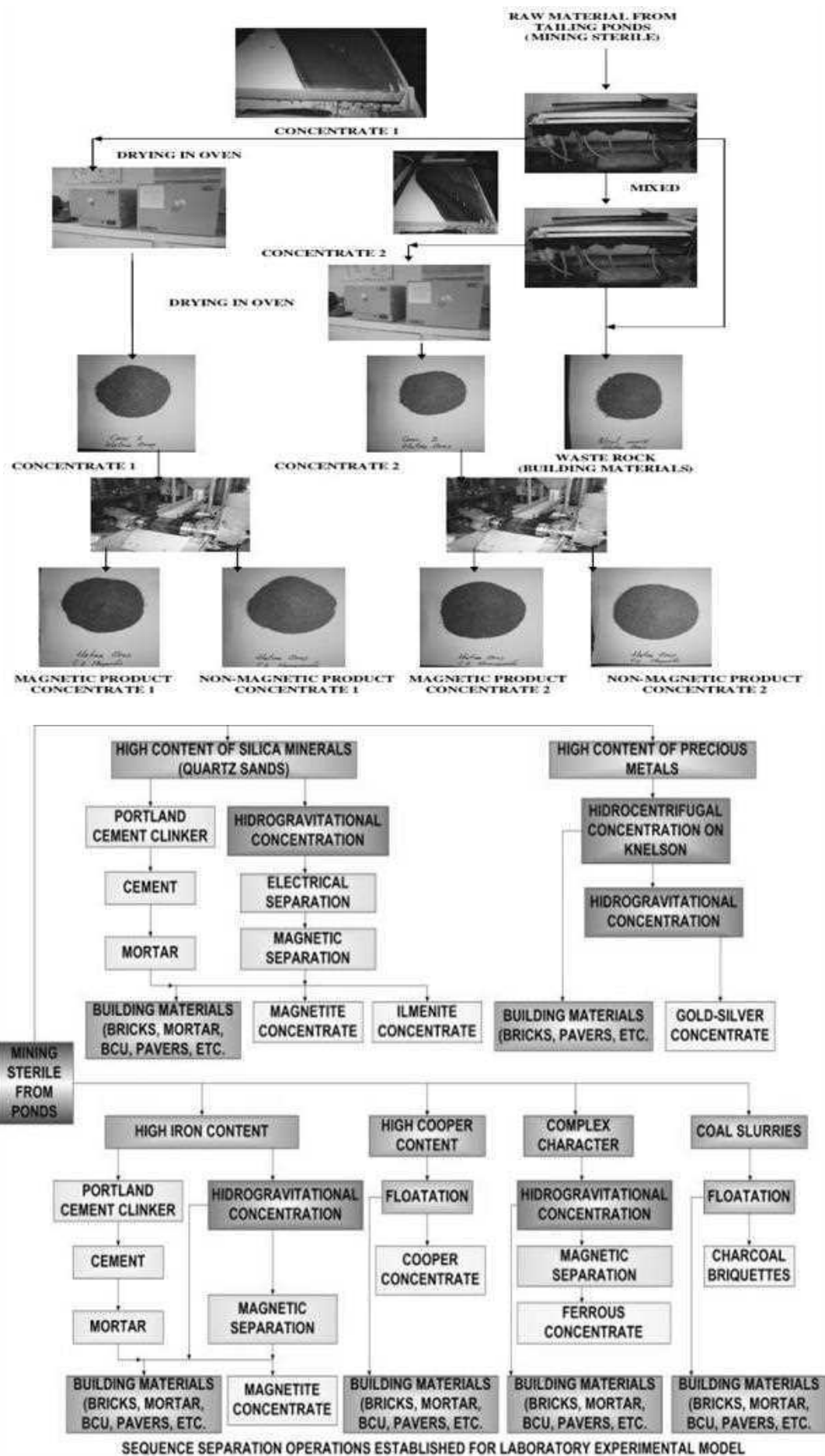


Figure 1: Tailing ponds from Romania territory from tailing ponds



Figure 2: Sampling from mineral sterile

Obtaining of representative samples for laboratory analysis was made using the divider for reduce the sample (Jonson type divider), and with samples divider, Reach type, respectively. With such evidence divider, type Reach PT 100, it were selected both representative samples for each type of laboratory analysis and also standard sample. Separation methods based on physical concentration of useful minerals such as hydro - centrifugal concentration on the centrifugal concentrator 7.5 type Knelson (fluidization water pressure, processing ore quantity on one concentration cycle) (Zlagnean M, Tomus N., 2006).



The sterile minerals occurred as powdery material with sizes from microns up to millimeters, with moisture between 6% and 11,19%, which supposed samples drying in order to be reused in cement manufacture. The tonality of the samples color varies according to the place of sampling and the mineral composition, high content in iron oxide give to samples a more pronounced reddish color. Samples were studied from chemical and mineralogical point of view. By processing of these tailings types concentrated ferrous minerals (magnetite), titanium (illmenite) were obtained, which are used in metallurgy, concentrates of high quality quartz sand (quartz sand for glass industry), quartz sands for metallurgical industry and copper concentrates for sale (Zlagnean M.).

Experimental results

Thus, in using the mining wastes from settling ponds to obtain raw mixes in cement manufacture, the basic relevant requirements were taken into account:

- the raw materials should be homogeneous so as to allow smooth operation of the technology and to obtain clinker of high quality
- the ratio between the silica ratio and the alumina ratio should be effective.

The criteria for selection consisted in the content in SiO_2 and Fe_2O_3 and the requirements in the standards for cement manufacture. An eloquent example is the using of mining wastes from tailing pond, which represented a higher content of iron oxide, as corrector addition in the raw mix. The raw materials (limestone and clay) used to carry out the laboratory investigations came from the industrial process of cement clinker manufacture and included mining wastes from tailing pond. The silicate and aluminate component of the raw materials consisted of clay which geologically pertains to Eocene. Mixed with high purity limestone, the clay led to obtaining a various range of cement sorts according to the standards. Again geologically, the limestone pertains to Jurassic, and it has a high content in CaCO_3 . The raw materials samples were assayed not only for the main oxide components but also for the minor components. The mineral sterile from the pond were employed to obtain two raw mixes (Z1 and Z2). The raw mixes were ground up to a fineness value of 10% residue on the 90 μm sieve and the resulting raw mixes underwent characterization in terms of chemical composition and clinker burnability (Fechet R.). The chemical characteristics of the raw materials employed to obtain the raw mix is shown in the Table 1. The raw mixes were obtained by grinding the raw materials according to the formulation in Table 2.

Table 1

Name	Lime stone	Clay	Mineral sterile
% L.O.I.	43.47	11.59	4.13
% SiO_2	0.42	50.61	77.79
% Al_2O_3	0.51	13.87	5.28
% Fe_2O_3	0.20	6.55	8.65
% CaO	53.48	10.59	0.81
% MgO	0.80	1.70	0.39
% SO_3	0.00	0.08	1.19
% S sulphides	0.03	0.02	0.01
% Na_2O	0.42	1.52	0.13
% K_2O	0.13	2.50	1.52
% S total	0.03	0.05	0.49
% Cl^-	0.009	0.027	0.004

Table 2

Name	Raw mix	
Dosages	Z1	Z2
% Limestone	74,18	75,16
% Clay	22,04	18,90
% Mineral sterile	3,79	5,94
Modular composition	Z1	Z2
SR	2,45	2,65
AR	2,00	1,80
LSF	0,96	0,96
Clinker potential mineralogical composition	Z1	Z2
% C_3S	61,51	63,98
% C_2S	15,23	14,34
% C_3A	10,55	9,06
% C_4AF	8,89	8,95

The clinkers obtained from burning the raw mixes underwent chemical and mineralogical investigations in order to obtain a characterization. The obtained clinkers had good quality and high contents in tricalcium silicate (Fechet R.). Tables 3 presents comprehensively the chemical characteristics on the basis of which the modular, the clinker potential mineral composition were calculated, and the mineral composition of the clinkers as determined by optical microscopy examination (Fechet R.).

Table 3

Name	Clinker Z1	Clinker Z2	Modular composition	Clinker Z1	Clinker Z2	Clinker potential mineral composition (%)	Clinker Z1	Clinker Z2
% L.O.I	0,7	0,24	SR	2,31	2,59	C ₃ S	67,93	70,33
% SiO ₂	21,15	21,93	AR	1,72	1,51	C ₂ S	10,69	11,13
% Al ₂ O ₃	5,79	5,09	LSF	0,98	1,009	C ₃ A	9,68	7,82
% Fe ₂ O ₃	3,35	3,35				C ₄ AF	10,18	10,18
% CaO	66,91	67,80				Mineral phase, obtained (%)	Clinker Z1	Clinker Z2
% MgO	1,39	1,19				Alite (C3S)	65	65
% SO ₃	0,00	0,00				Belite (C2S)	15	15
% Na ₂ O	0,15	0,10				Masostasis	20	20
% Res. Ins. HCl-Na ₂ CO ₃	0,29	0,00						

Grinding the clinkers Z1 and Z2, obtained in the laboratory, with highly pure gypsum led to cement CEM I. The cements were ground up to a fineness of approx. 3500 cm²/g. The obtained cements underwent determinations of physical and mechanical properties (Fechet R.). Table 4 presents the results.

Table 4.

Characteristics	Cement Z1	Cement Z2
Water demand, %	23,8	23,6
Setting time		
Initial, min	160	160
Final, h-min	4-00	4-00
Soundness, mm	0.0	0.0
Flexural strength, N/mm ²		
2 days	4,34	4,04
7 days	7,04	6,93
28 days	9,02	9,00
Compressive strength, N/mm ²		
2 days	20,2	19,8
7 days	39,1	39,4
28 days	60,4	57,7
Resistance class	42,5R	42,5N

Conclusions

- The cements obtained with mining wastes are according to the requirements imposed by quality norms in force.
- The cements including mining waste enter a higher resistance class, namely 42,5 N and 42,5 R.

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PRELIMINARY GEOCHEMICAL DATA OF THE GEHLENITIC SKARNS FROM ORAVIȚA

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The occurrences of high temperatures skarns are quite rare in the world. Various authors have reported over thirty examples of such rocks, worldwide. The occurrence of skarns from Ogașul Crișenilor, Oravița, circumscribes the classic mineral association of high temperature skarns and includes, as representative species, gehlenite, calcic garnet, monticellite, ellestadite-(CaOH), vesuvianite. Two other occurrences of high temperature skarn have also been described in Romania, at Măgurea Vătei and Cornet Hill. In the skarns from Ogașul Crișenilor, Oravița, associated with the Upper Cretaceous magmatism in the South Carpathians of Romania, Constantinescu *et al.* (1988) reported a small occurrence of rocks, mainly composed of gehlenite-rich melilite. On every side and even in places inside this area, the gehlenite rocks are altered to vesuvianite and subordinately monticellite and clintonite.

The aim of this paper is to offer some preliminary geochemical data on the main mineral association from this occurrence.

The skarns of Oravița are developed at the expense of Cretaceous limestones and marls of the Crivina Formation, folded in a system of N–S-trending anticlines and synclines, belonging to the Reșița anticlinorium in the Getic nappe. At Oravița, this series is intruded by a small elongate body of Late Cretaceous diorite, with some variations toward quartz diorite and monzonite that belong to the banatitic belt. The Late Cretaceous to Paleocene banatitic magmatic and metallogenetic belt (BMMB, Berza *et al.* 1998) extends from western Romania (Apuseni Mountains and Banat) to the Black Sea, through the Timok area in Serbia and Srednogie zone in Bulgaria (Fig. 1).

At Oravița, the skarn cover is preserved at many places over the intrusion. Most of the skarns are barren, with a striking predominance of yellow-brown vesuvianite on the inner side of the intrusion and of some coarse grained wollastonite on the outer side, toward the metamorphosed limestone. Where the limestone is not magnesian, the vesuvianite postdated a stage characterized by an extensive development of grossular associated with diopside. In contrast, coarse clintonite, some monticellite and Al-bearing clinopyroxene occur at the contact of the intrusion with magnesian marble (Katona *et al.* 2003).

The occurrence from Valea Crișenilor, described by Constantinescu *et al.* (1988) and Ilinca *et al.* (1993), and recently studied by Katona *et al.* (2003) represents an exception to the general scheme just described. Almost monomineralic gehlenite skarn occur in a very restricted area along the contact of the dioritic intrusion (Fig. 2). The gehlenite skarn is known only in a 22 X 11 m area, limited to the north and south by other types of skarn. To the west, they disappeared by erosion, and to the east, they are covered by overlying inner endoskarn zone or by the igneous rock (Katona *et al.* 2003).

The determination of the chemical composition of the skarn samples from Oravița was performed using a JEOL J.S.M. 840 scanning electron microscope (SEM) equipped with a Tracor – Northern TN 1710 device for microanalysis. The analytical conditions were 15 kV acceleration voltage and a beam current of 40 nA.

The samples from the study have been collected from the endoskarn zone. Late-stage metasomatic replacement of gehlenite by vesuvianite is common as a result of late hydrothermal processes, although an altered surface another than vesuvianite has been identified and is probably representative for a phase (phase x) issued from the weathering process. Selected compositions of the most representative samples of gehlenite and vesuvianite are given in Table 1, and plotted in a ternary (Al) – (Mg+Fe) – (Si) diagram (Figure 3).

Fig.1: Geological sketch of the Banatitic Belt
(Berza *et al.* 1998)

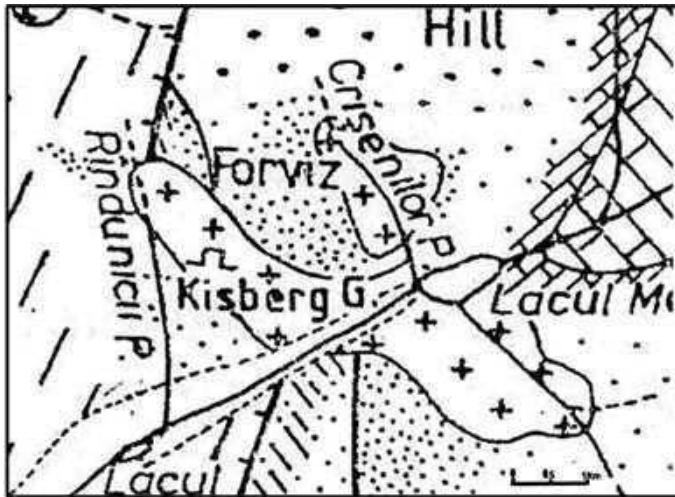


Fig.2: Geological sketch of Oravița area
(after Constantinescu *et al.* 1988)

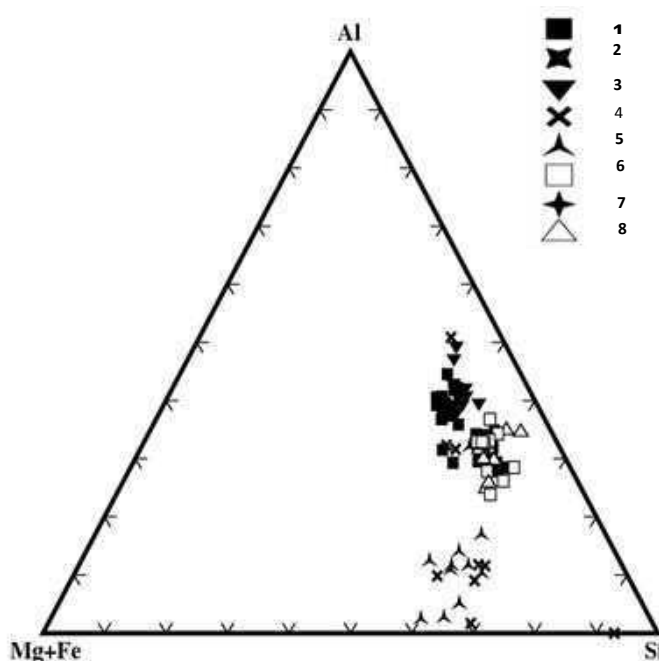
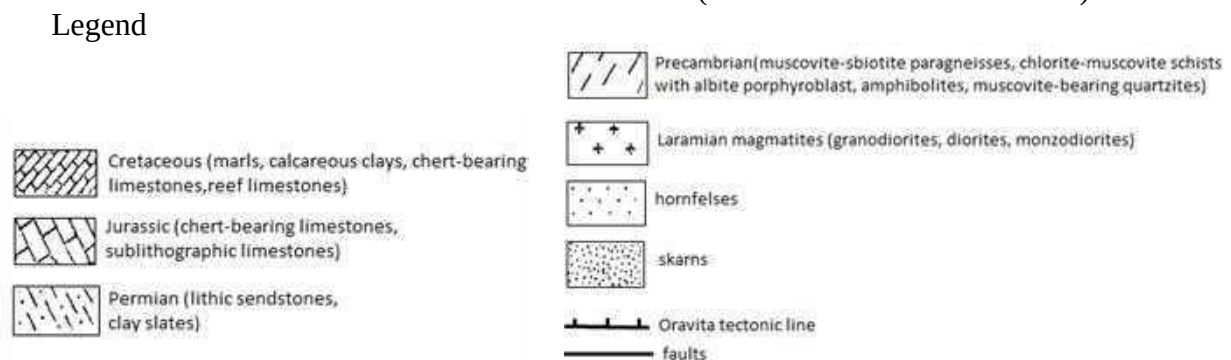


Figure 3. Ternary diagram (Al) – (Mg+Fe) – (Si) for the main Ca-Al phases from Oravița. Symbols represent: 1– gehlenite, present study; 2 – gehlenite, Katona *et al.* (2003); 3 – gehlenite, Marincea *et al.* (2001); 4 – melilite, Deer *et al.* (1962); 5 – altered gehlenite, present study; 6 – vesuvianite, present study; 7 – vesuvianite, Katona *et al.* (2003); 8 – vesuvianite, Deer *et al.* (1962).

Table 1: Selected EDX compositions of gehlenite and vesuvianite from Ogaşul Crişenilor (wt.%)

Sample	Mineral	CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	Na ₂ O	K ₂ O
A 1-1	Geh	30.39	20.57	42.28	5.2	1.53	0	0
A 5-6	Ves	36.16	18.74	38.87	4.32	1.90	0	0
A 1-4	phase x	24.03	17.64	49.02	2.71	6.60	0	0

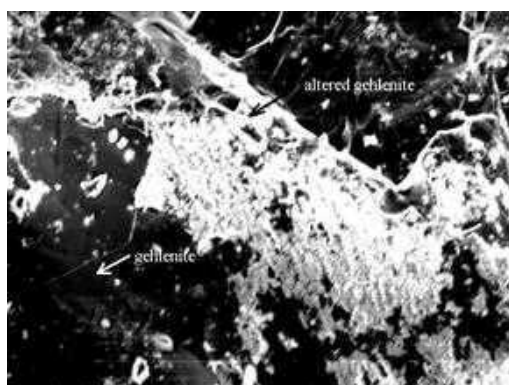


Fig. 4: SEM image of altered gehlenite (phase x)

This present study is part from a larger one entitled Mineral genesis of the high temperature skarns from Ciclova-Oravița, Banat – a mainly mineralogical study which aims to bring new chemical and physical data about the mineral species of this occurrence in order to understand the complicated succession of the processes generated by the intrusion at Oravița.

The chemical components of the system within which the pyrometasomatic processes took place are very numerous but here were limited to the system SiO₂ – Al₂O₃ – MgO – FeO (Fig.3). The results that were obtained at the electron microscope for the main mineral species (*i.e.*, gehlenite and vesuvianite) are in a good agreement with the data in literature (Deer *et al.* 1962, Marincea *et al.* 2001, Katona *et al.* 2003). Beside these two minerals, a group of minerals show a different chemical composition and probably represents an altered product on gehlenite (Fig. 4). The research will continue in order to see if this product is an intermediary phase between gehlenite and vesuvianite (OH-gehlenite?), rather than a preexistent Si-rich mineral or a weathering product.

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CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF RESIDUES FROM THE RECYCLING OF ACCUMULATOR BATTERIES WASTED

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Abstract: Because the greening of environment become priority, many scientific research aim to obtain information about the potentially polluting materials to develop more efficient technologies for the recovery of useful elements contained in these materials. This paper presents the chemical and mineralogical characterizations by X-ray diffraction and optical microscopy in polarized light of the slags from the recycling of wasted accumulator batteries. Results have a decisive role in choosing the method of the lead recovery and stabilization of the slag dumps resulted from the recovery processes.

1. Introduction

The waste accumulator batteries that contain the lead as metals, sulfates and oxides are used for the recovery of this element.

The recovery technology of the Pb from the batteries involves reducing melting of the components above mentioned. After the melt results considerable quantities of slag which also contain traces of metallic Pb, oxides and sulfates. These slags are deposited in dumps. The metallic Pb and as oxides and sulfates from these slags can be mobilized by atmospheric agents (wind, rain) causing environmental pollution. To avoid pollution, the slags must be treated to be stabilized before to be deposited on dumps.

To make this stabilization, the slags must be characterized to highlight the chemical and mineralogical composition and the ratio of component minerals.

The paper presents the ways and methods of characterization of slags. To characterize slags were used as methods: chemical analysis, phase analysis by X-ray diffraction and optical microscopy in polarized light. Because studied slags are powders, the microscopic study using polarized light require special sample preparation methods- immersion in nitrobenzene for the study in transmitted light and embedding in epoxidic resin, in vacuum, for the study in reflected light. For the phase analysis by X-ray diffraction the integral samples were analyzed. Afterwards because of the high complexity of the sample, the soluble fraction was separated by solubilization in distilled water. The soluble and insoluble fractions were characterized.

2. Analysis

The Chemical Analysis were made in the Chemical and Physical Analysis Laboratory from INCDMNR-IMNR, using the FAAS, ICP-OES, gases methods.

The X-Ray Diffraction Analysis were made in the XRD Laboratory from INCDMNR-IMNR. Through X-ray diffraction, a qualitative and quantitative analysis of the phase composition has been made. The data acquisition was made with the BRUKER D8 ADVANCE diffractometer with the software DIFFRACplus XRD Commender (Bruker AXS), using the Bragg-Brentano diffraction method, $\Theta - \Theta$ coupling in vertical configuration.

The Microscopical Analysis were made in the Microscopical Characterizations Laboratory from INCDMNR-IMNR, using a AXIO IMAGER. A1m with polarized light.

3. Results and discussion

Chemical Analysis shows for the analyzed sample (S1) next composition (Tab. 1):

CODE	MU	Pb	Cu	Cd	Cr	Fe	Mo
S1	%	7.6	0.083	0.004	0.035	13.6	0.002
CODE	MU	Ni	SiO ₂	Zn	Sb	Na	CaO
S1	%	0.008	18.65	0.55	1.04	22.2	0.30
CODE	MU	C	S _{TOTAL}	SO ₄ ²⁻	As	Ba	Hg
S1	%	1.01	4.78	8.18	0.057	0.29	<0.001

Table 1. The results of chemical analysis for S1 sample.

XRD Analysis (Fig. 1) shows for the analyzed sample (S1) the phasis composition from Table 2.

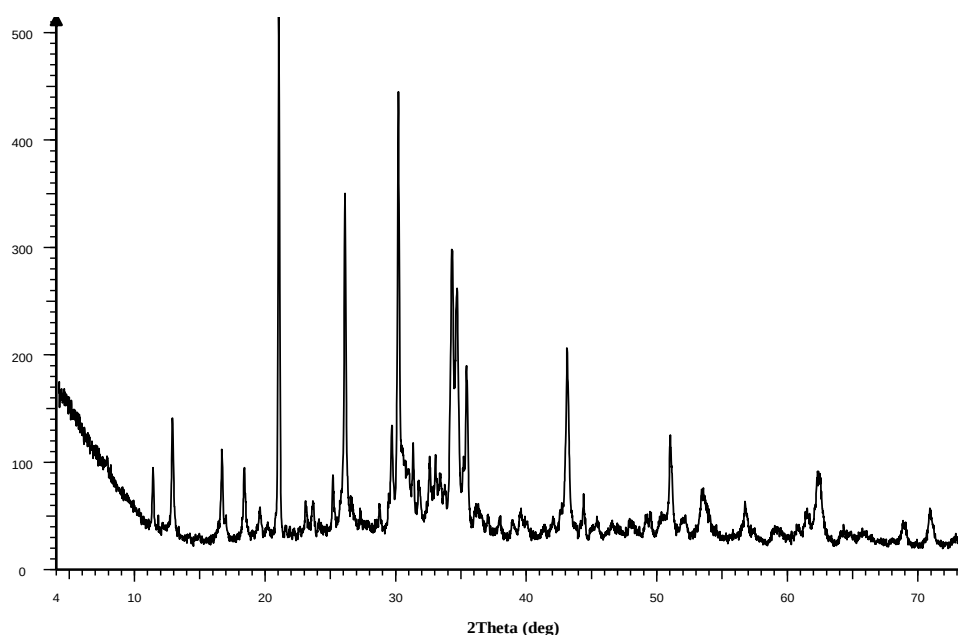


Fig.1: XRD Analysis for S1 Sample

Compound Name	Formula	S-Q	PDF Reference
Carnegieite (Low)	Na ₂ Al ₂ Si ₂ O ₈	53.3	00-049-0008 (*)
Magnetite	Fe+2Fe ₂ +3O ₄	11.7	00-019-0629 (*)
Erdite	NaFeS ₂ (H ₂ O) ₂	12.1	01-083-1323 (N)
Hydrocalumite	Ca ₂ Al(OH) ₆ Cl(H ₂ O) ₂	6.0	01-078-1219 (N)
Carnegieite (High)	NaAlSiO ₄	5.1	01-076-0909 (I)
Galena	PbS	6.9	01-077-0244 (*)
Calcite	Ca(CO ₃)	2.4	01-071-3699 (*)
Halite	NaCl	1.9	00-005-0628 (*)
Lead	Pb	0.6	00-004-0686 (*)

Table 2. Phasis composition resulted from the XRD Analysis

Microscopical Analysis shows that the sample consists largely of glass and microcrystalline material as aggregates (Fig. 2). In the aggregates appear galena – PbS, magnetite- Fe₃O₄, gudmundite – FeSbS, metallic lead (Fig. 3) and coke (graphite) (Fig. 4). Sometimes the lead and galena form an eutectic mixture (Fig. 5) Always galena and gudmundite appear together.

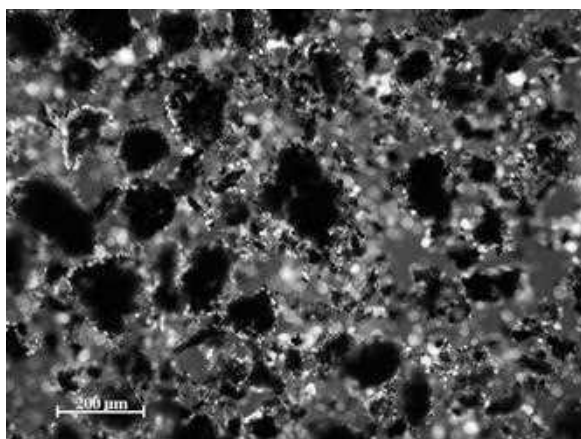


Fig. 2. N+, transmitted light. Glass and microcrystalline material as aggregates

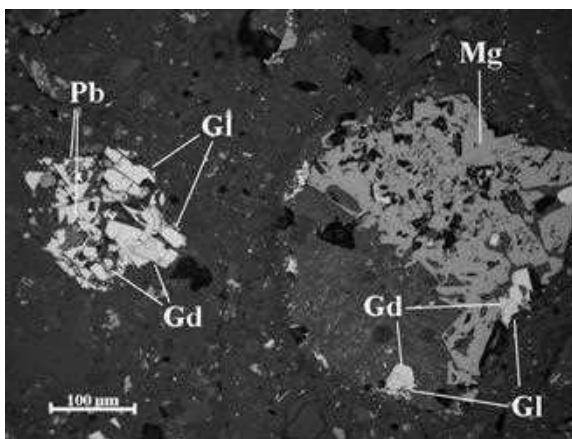


Fig. 3. NII, reflected light. Gl-galena, Gd-gudmundite, Mg- magnetite, Pb- lead

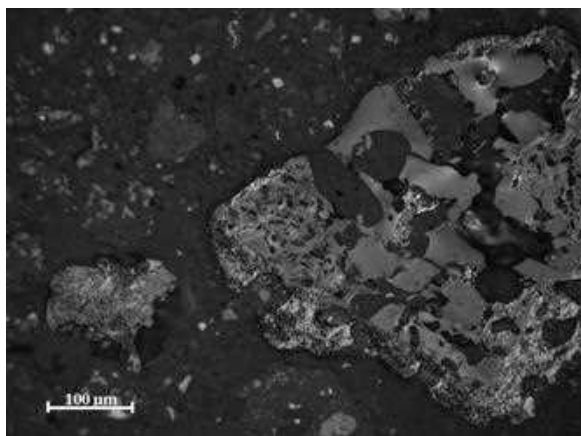


Fig. 4. N+, reflected light. Coke

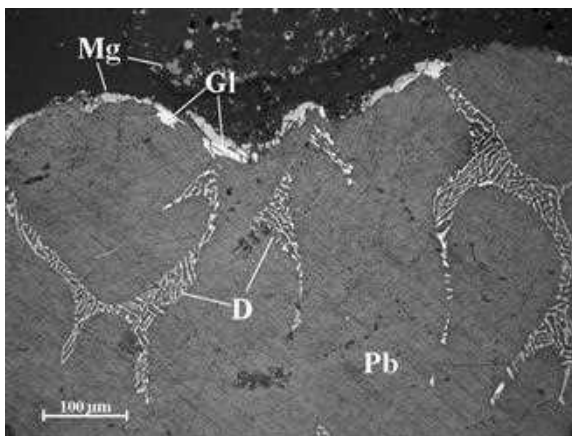


Figure 5. NII, reflected light. Gl-galena, Mg- magnetite, Pb- lead, D- eutectic mixture.

4. Conclusions

Given the two types of analysis phase, results do not coincide entirely, but they complete each other.

There are micron size phases which can not be determined by optical microscopy. These can be determined by X-ray diffraction. Other phases with low percentage and having micron order size - hundreds of microns can be determined by microscopic study, but not by X-ray diffraction.

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THE INDICATOR OF ENVIRONMENTAL QUALITY OF SAO MIGUEL'S RIVER OF ALTO SÃO FRANCISCO, MINAS GERAIS, BRAZIL

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Introduction

The hydrographical basin of São Miguel River is situated in the south portion of São Francisco basin, in the southeast of Minas Gerais State, Brazil, (figure 1). The basin is in a karstic region which natural conditional is extremely fragile and very susceptible to the exploitation of carbonic rocks, mainly the extraction and limestone refining. This fact highly increased the growth of the mining sector from the 90's on. Many big and small mining companies extract and refine the limestone in the region, in order to produce derived products, mainly used to lime production and cement.

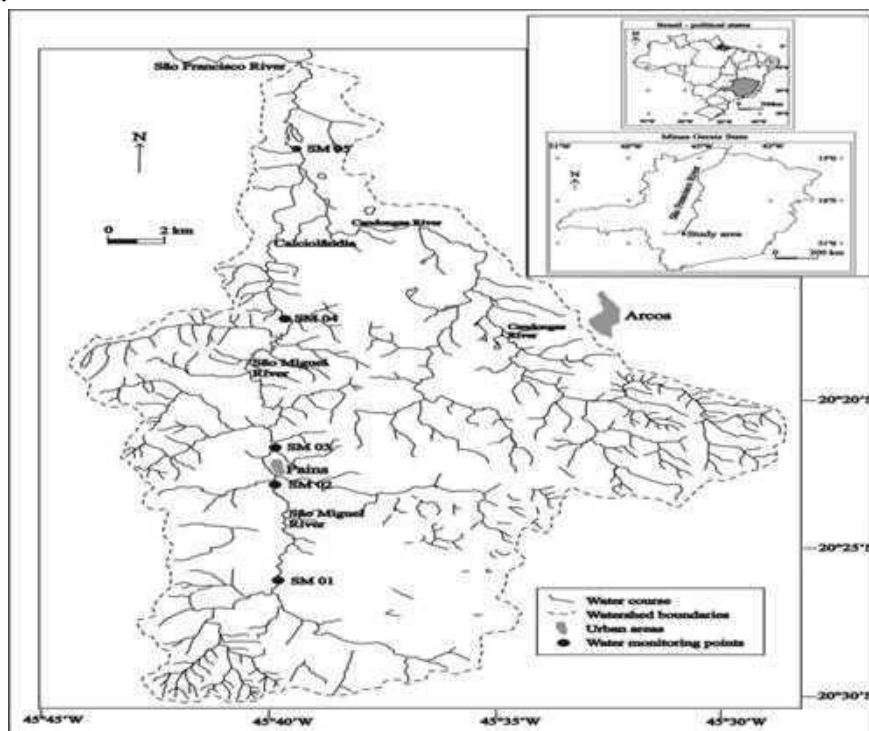


Figure 1: Location of the São Miguel River basin in the karstic region of Alto São Francisco, Minas Gerais, Brazil.

The mining is relevant in the regional economic sector, being responsible for great part of the jobs generation and the financial resources of the region. The cattle raising and the agriculture are other economic activities developed in the region.

They also contribute to the anthropic alteration of the landscape, being the fields used to cattle in 40% of the area, biggest percentage of ground using in the basin, followed by agriculture with 16% of the area's occupation. The mining and the human occupation have low percentage values, less than 2% together (Cherem 2006). The economic exploration of the region brings a strong susceptibility to air, ground, and fluvial waters pollution. This is due, mostly, to the own karst hydrologic characteristics, which typical formation enables the connection between the surface flow and the subterranean, enabling, this way, the contamination of the phreatic water. The urban

sewage, also represents a focus of potential degradation of the basin's water, reflecting the Brazilian reality marked by a high percentage of non-treated sewages and in some cases they are not even collected. The agriculture activities are, equally, potentially harmful to the region's environment, considering that the agriculture potential is attractive in the region (Lages et al. 2002). On it, many agro-chemicals are used and they are carried to the watercourses by rainwater, mainly when they are excessively used in the plantations.

The air quality may also indicate the environmental quality and the human activities impacts on the region. Certain processes of limestone extraction and refining are potential pollutants due to the emission of gases and particles. Among those pollutants are the heavy metals, present in certain fuels used in the calcination of the limestone rock and the dioxanes that are derived from the incomplete combustion of part of the fuels used in the regional furnaces (tyres, plastics and others).

Even with high environmental fragility and the presence of a strong mining sector, the region of São Miguel River's basin and Alto São Francisco karst are not well known in relation to the environmental impacts. For instance, Rede Hidrometeorológica Nacional has only one monitoring point in all the course of São Miguel River, in which are made campaigns every three months (Instituto Mineiro de Gestão das Águas - IGAM 2005). This paper intends to contribute to the investigation of the human activities reflexes, mainly the mining and refining of limestone, as well as the production of lime and cement, to the environmental quality of the basin by monitoring the parameters of the fluvial waters from the ground and the air.

The state of water, ground and air were here used as indicators of river São Miguel's basin environmental quality, which is situated in the karstic region of Alto São Francisco, SW of Minas Gerais, Brazil. That basin has its fragile natural picture threatened by mining activities and limestone benefiting. The hydrologic karstic dynamics make its aquifers highly susceptible to pollution. This study identified the impact of those activities in the local environment quality. The monitoring of the areas was made between 2004 and 2006, and the analysis was made in the Governo do Estado de Minas Gerais' laboratories. The ground samples were collected and analysed in 2007 and the atmospheric pollutants in 2004 and 2005. The results indicate that the air quality is impacted by mining activities, calcination and the fluvial waters reflect the effects of the agriculture and urbanization.

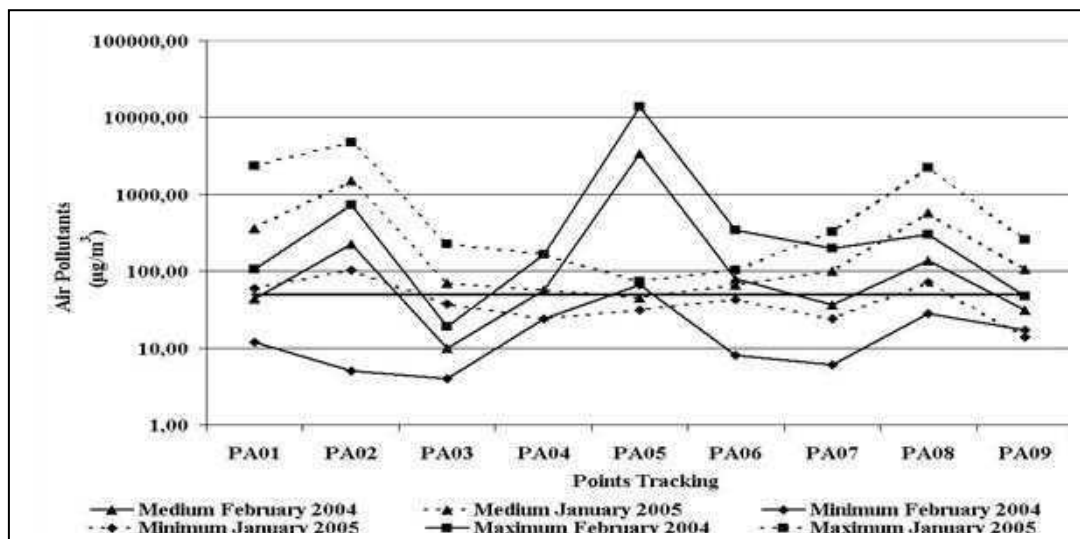


Figure 2 Concentration of inhalant particulates. The continuous line ($50 \mu\text{g}/\text{m}^3$) matches to the limit established by legislation (WHO 2005).

The ground presents metal values above the intervention value. However, the waters do not reflect adequately the mining impacts on the environment, a fact that may be explained by the peculiarities of this activity in the region.

Table 1: Total percentages from some heavy metals on the soils samples

Samples	Metals mg/Kg				
	Cr	Co	Cu	Cd	Zn
	88,5P	3,2A	5,0Q	5,5P	1,02,3Q
17	11,4,6P	4,0,4A	6,7,2P	1,3P	1,32,3Q
7	20,4,4A	2,4,9Q	8,2,8P	1,6P	1,11,5Q
5	46,0,0I	3,2,1P	7,8,3P	1,0P	1,19,3Q
14	13,5,7P	3,6,8A	5,0,5Q	1,2P	1,66,3Q
16	20,6,1A	3,5,8A	7,3,7P	1,0P	1,51,9Q

On the other hand, the chrome values call the attention on sample 5, once the intervention values exceed to the industrial area. This sample matches to a sink-hole where no sink-hole was found. The concentration itself is rather worrying and demands new collections and analysis for a more detailed study. Otherwise, the non-existence of sink-hole and the consequent presence of soils - with components that can retain this heavy metal - lead to believe that the underground water damages are, in a certain way, minimized.

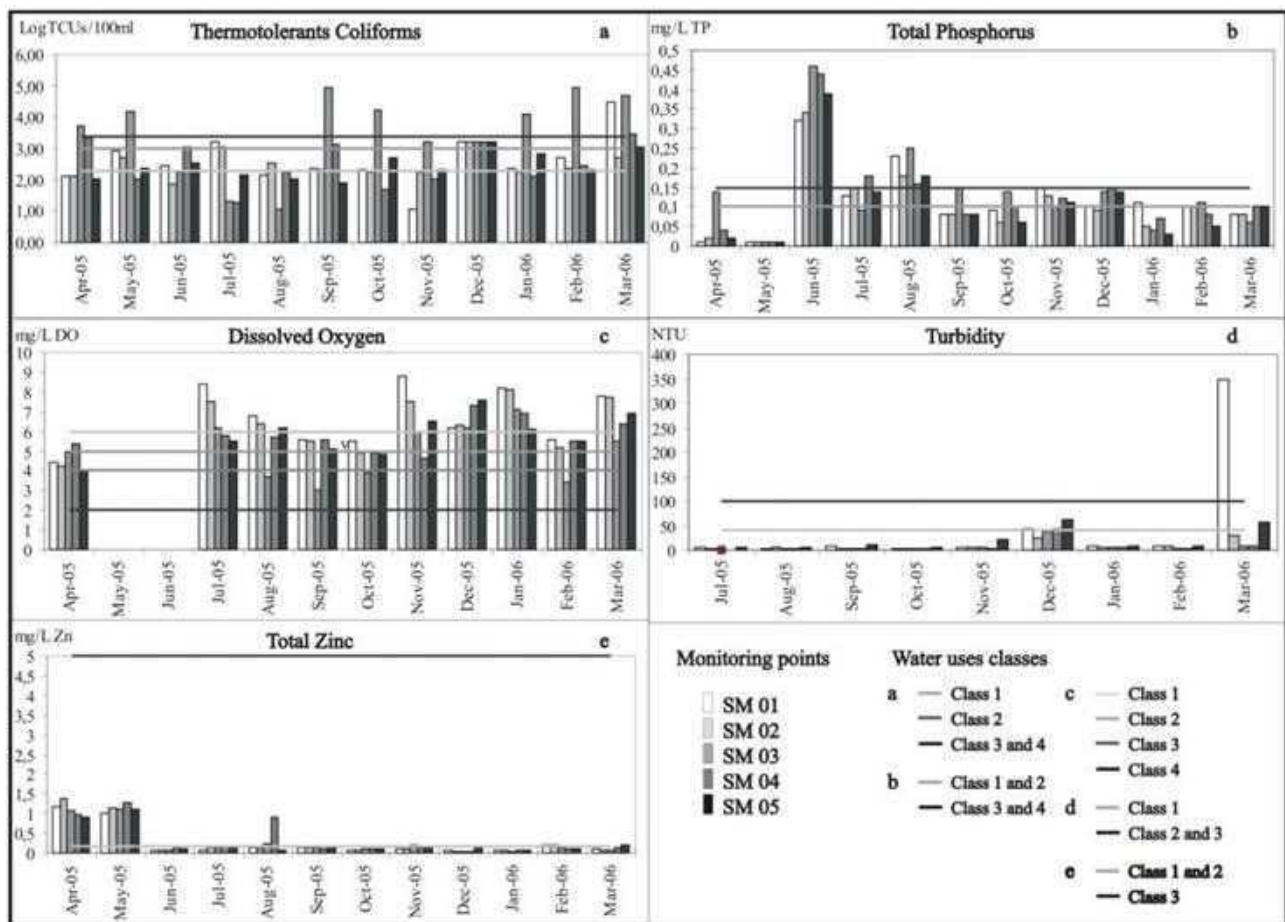


Figure 3: Results of concentrations of water quality parameters and use of water classes, São Miguel river - from April 2005 to March 2006.

The chemical components of soils show reactions that keep heavy metals on the soil profile. Considering that the underground and surface waters from the São Miguel River basin should be protected, the soil composition may contribute to the heavy metals' retention, making their lixiviation difficult to happen by the waters. Understanding that the high concentrations of metals (Table 1) and if the basin soils are inefficient to retain the metals, it is inferred that the waters may be compromised

Conclusions

The assignment allowed to evaluate some relations between human activities developed in the region and the local environmental characteristics from the study of the air, soil and fluvial waters' quality parameters. The São Miguel River basin is an area where economy and employment generator depends on the mining activities and limestone refining. This economical and social dependence on local districts, in reference to mining, may compromise the fight against the impacts of these activities. However, as soon as possible, it is necessary to know the existence and the reach of these impacts, and that is the study to which this paper was made for.

The hydric pollution occurs mainly in the medium part of the São Miguel river where the urban centre of Pains is settled, and its sewers and domestic effluents are launched in natura into the river. The relation between the high counting of thermo-tolerant coliforms, of total phosphorus, and the decrease of the levels of dissolved oxygen was verified regularly in this part. The results indicate the regular compromise of more demanding water uses according with international standards, notably the less demanding, such as sailing and landscape harmony, are excluded. However, more seriously, the restriction of the usage for bathing resorts purposes, should be observed, once the district shows significant occurrences of schistosomiasis parasite.

The physical alteration of the body water was proved with the turbidity increase, dangerously associated to coliforms increment. It is necessary to recover the vegetation riparian zones on the critical parts of the river.

Regarding the water reflex proceeding from mining activities and limestone refining, the total zinc was the only parameter that varied with the legislation that can be, a priori, associated to the potential impacts of the enterprises. Such fact indicates the necessity to deepen the researches.

After the analysis and interpretation of the results regarding the atmospheric pollutants, it is obvious the necessity of urgent measures, by competent authorities, meaning supervise and control the emission of pollutants in the studied place. The exposed data are from 2004 and 2005 and, until this moment, there is nothing that indicates that efficient actions were taken.

As for the soils, studies about the retaining capacity of heavy metals by its components will indicate the temporary contamination on the waters from São Miguel River basin. It is obvious that the pollutants - meaning the metals - are present. It is still necessary the evaluation of the local environment's vulnerability and connecting this vulnerability with the metal percentages and then the evaluation of the risks.

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MINERALOGICAL AND GEOCHEMICAL PECULIARITIES OF PHOSPOGYPSUM FROM TURNU MĂGURELE (ROMANIA)

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The aim of this paper is the mineralogical and geochemical description of phosphogypsum from a Romanian location for an accurate assessment of its environmental impact. The investigated samples were carried out from the deposit at Turnu Măgurele. The samples were analyzed by X-ray powder diffraction (XRD), by scanning electron microscopy (SEM), by X-ray fluorescence (XRF), by Fourier-transform infrared absorption spectrometry (FTIR) and by inductively-coupled plasma atomic emission spectrometry (ICP-AES).

The paper aims to investigate the chemical, mineralogical, morphological and crystallographic properties of phosphogypsum from this occurrence as a first step toward the characterization of the huge deposits of phosphogypsum from Romania. By defining the geochemical, radiometric and mineralogical peculiarities of the deposits of phosphogypsum the study is supposed to arrive at an accurate assessment of their environmental impact and to an accurate evaluation of the possibility of rehabilitation of these deposits.

The chemical composition of phosphogypsum is directly influenced by the type of phosphate ore used to produce the phosphoric acid. The phosphate ore used may be of sedimentary origin or of magmatic origin. The sedimentary phosphate ores (phosphorites), represent about 85 % of the known phosphate rocks (Habashi, 1980) and are generally related to the easily-to-mine deposits from the large sedimentary basins of Cretaceous age (- 70 Ma) where the phosphorous was concentrated by the biotic activity (Becker, 1989); such kind of ore was particularly used in the production of phosphoric acid at Turnu Măgurele. Subordinately, magmatic ores from the deposits from Kola Peninsula (Russia) was also used. There are big differences between compositions and quality of the two types of phosphate ores. Even if apatite is the main phosphate mineral (Lehr and McClellan, 1972), there are considerable differences between the chemical patterns of the magmatic ores, containing essentially apatite-(CaF), and the sedimentary ones, containing essentially carbonate-bearing apatite-(CaOH) (francollite).

The physical, chemical and crystallographic particularities of apatite samples, of both magmatic and sedimentary origin, directly influence their reactivity during the sulfuric acid attack used to produce phosphoric acid (Lehr and McClellan, 1972). The reactivity of carbonate-bearing apatite-(CaOH) (francollite) is superior, since $\text{CO}_3(\text{OH})$ groups replace PO_4 or coupled substitutions $\text{Ca} + (\text{PO}_4) \leftrightarrow \text{Na} + (\text{CO}_3)$ permit the fulfilling of the charge balance (McClellan and Lehr, 1969, Lindsay et al., 1989). The main minor components of the sedimentary phosphate ore (*i.e.*, quartz, fluorite, zircon, tourmaline, montmorillonite, kaolinite, titanite and pyrite according Gulbrandsen, 1967) could influence its reactivity during the acid leaching, but also permit the identification of the leached ore, because of the remnants in the phosphogypsum mass. In the case of magmatic ores, Ti-bearing minerals (*e.g.*, rutile, ilmenite, perovskite) could resist in phosphogypsum (Grenmillion and McClellan, 1980). Very few relicts fit with the magmatic origin of the ore used at Turnu Măgurele.

The mineralogical composition of the phosphate ore directly influences the composition of the phosphogypsum; the reactivities of different phases during the sulfuric attack. The acid easily decomposes apatite, carbonates, organic matter and oxy-hydroxides, and partially decomposes muscovite, illite, montmorillonite and kaolinite with formation of quartz, whereas the primary quartz is inert. A look at chemical analysis indicates that the phosphate ore used to produce the phosphogypsum from the Turnu Măgurele area had a predominantly sedimentary origin, indicated by the relatively large quantities of silica and low TiO_2 contents.

The chemical analysis of selected samples from the Turnu Măgurele deposit, performed by XRF and ICP-AES, showed that the chemistry of different samples is quite similar: the chemical differences between samples from different deposits are minor, and all the analyzed samples have chemical compositions indicative for a production by the hemi-dihydrate (HDH) or dihydrate (DH) procedure (relatively low contents of CaO as compared with the phosphogypsum obtained by the hemihydrate procedure). The XRF analysis reveals variations of the main oxide contents as follows: SiO₂ between 1.04 and 4.04 wt.%, TiO₂ between 0.03 and 0.16 wt.%, Al₂O₃ between 0.06 and 0.28 wt.%, Fe₂O₃ between 0.15 and 1.73 wt.%, MnO between 0.00 and 0.01 wt.%, MgO between 0.11 and 0.27 wt.%, CaO between 30.25 and 34.63 wt.%, Na₂O between 0.00 and 0.30 wt.%, K₂O between 0.01 and 0.13 wt.%, P₂O₅ between 0.52 and 3.71 wt.%, loss of ignition between 18.80 and 20.93 wt.%.

XRD analyses of phosphogypsum from the four occurrences, corroborated with Fourier-transform infrared absorption spectra, showed that the main crystallized phases in this kind of material are gypsum (CaSO₄·2H₂O), and bassanite (CaSO₄·0.5H₂O), reaching up to 90 wt.% and 5 wt.% from the mass, respectively. A phosphate-bearing phase identified as ardealite or brushite is common. Impurities consists of quartz, calcite (probably resulted from the treatment of the plants with CaO, in order to reduce their acidity) and minor clay minerals.

The infrared absorption spectra of representative phosphogypsum samples from the four occurrences show vibrations which could be assumed to gypsum or bassanite, quartz and rarely calcite. The bands assumable to molecular water (the H-OH stretching vibrations at about 3610, 3550, 3405 and 3240 cm⁻¹, the corresponding bending vibrations at ~1685 and 1620 cm⁻¹ and the composed modes at 2220 and 2130 cm⁻¹) are particularly well developed, suggesting a high level of hydration of the samples. The bands at ~1430 and ~870 cm⁻¹, assumable to the antisymmetric stretching and to the in-plane bending, respectively, of the carbonate group, are indicative for the presence of calcite. A band recorded around 800 cm⁻¹ can be assigned to the Si-O-Si antisymmetric stretching in silica (quartz).

The stacks of phosphogypsum from Turnu Măgurele are generally old as compared with most of the similar stacks in Romania, which conduce to the idea of utilization alternatives. As suggested by Arman and Seales (1990), this kind of phosphogypsum could be used by the cement industry, if the relicts of phosphate rock are minor and the radioactivity is low. At Turnu Măgurele, the radioactivity of the measured samples, induced mainly by the radium-226 isotope, is of the order of 40-8750 Bq/kg, and the content in toxic elements (*i.e.*, Cd, U, Th) is relatively low.

Table 1. Mineralogical composition of phosphate rock used to produce phosphoric acid at Turnu Măgurele, as determined by XRD

Crt. no.	Sample	Origin	Mineralogical composition
1	P 1 Mc	Morocco	carbonate-bearing apatite-(CaOH), calcite, quartz
2	P 1 - TM	(?)	carbonate-bearing apatite-(CaOH), calcite, dolomite, quartz, illite, dickite
3	P 2 - TM	(?)	apatite-(CaF), quartz, dolomite, xenotime, illite
4	P 3 - TM	(?)	carbonate-bearing apatite-(CaOH), calcite, dolomite, quartz, illite, montmorillonite
5	P 1 Sy	Syria	carbonate-bearing apatite-(CaOH), calcite, quartz, illite

The content in some minor elements, such as Sc (0.00 – 19.75 ppm), V (20.71 -154.05 ppm), Cr (0.03 – 148.07 ppm), Ga (3.85 – 23.39 ppm), Co (2.09 – 21.05 ppm), Ni (6.45 – 85.25

ppm), Cu (34.86 – 187.14 ppm), Zn (19.84 – 144.60 ppm), Zr (26.18 – 220.45 ppm), Nb (3.54 – 11.86 ppm), W (3.08 – 19.15 ppm), Pb (3.86 – 31.88 ppm), As (0.01 – 0.09 ppm) could be correlated with the presence of iron and Al sesquioxides and parallels the abundance of Fe, Al and Mn. Some other minor elements such as Sr (106.31 – 224.59 ppm), Cd (0.01 – 0.12 ppm), Ba (304.90 – 599.68 ppm), Rb (49.95 – 139.75 ppm), Cs (0.00 – 214.29 ppm), Y (0.00 – 30.17 ppm), La (0.00 – 40.20 ppm), Th (6.76 – 48.73 ppm), should be imagined as replacing Ca in the structure of gypsum.

The XRD analysis of some phosphate rocks used for producing phosphoric acid at Turnu Măgurele is given in Table 1. The composition is a classical one as compared with that given by Gulbrandsen (1967) for similar ores, and generally fits well with those of the sedimentary deposits from Morocco and Syria, also analyzed.

The composition of one of the samples (P 2 - TM) fits with those reported for magmatic phosphorites and suggests the importation of the raw material from the Kola Peninsula (Russia) as reported for the charges from the early '80 s.

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MINERAL AND ROCKS' RESOURCES IN THE OPHIOLITIC COMPLEX, OF THE MEHEDINTI PLATEAU; A CASE STUDY OF BASALT

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The Mehedinti Plateau with its three structural components – the Getic Unit, the Danubian Unit and the Severin Unit, justifies the separation of several metallogenetic districts (Fig.1):

1. one in the Parautohton of Severin, closely correlated with ophiolitic rocks complex
2. a patch of cover Bahna, in the Getic Unit
3. a patch of cover Portile de Fier, in the Getic Unit.

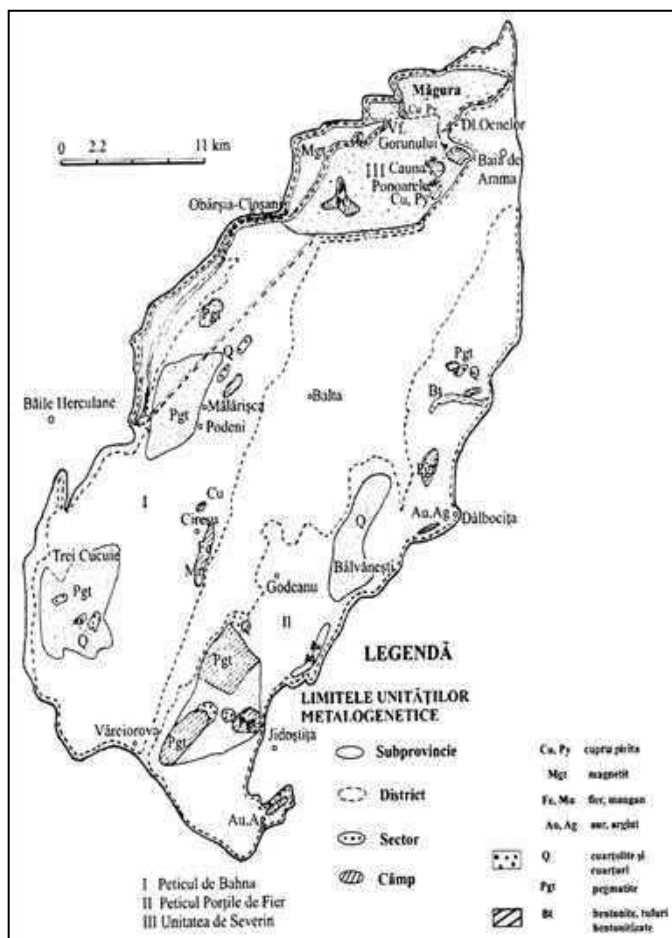


Fig. 1 - Metallogenetic units of the Mehedinti Plateau (Popescu, 1988)

I. Petrography of Ophiolitic rocks in the Severin Unit

Together with sedimentary rocks, magmatic rocks with mineralogical structures and similar compositions with those of classic ophiolitic associations are known in the Severin Unit. The ophiolitic rocks have the particularity that their occurrence is a tectonic melange of the petrographic types, so it can't be recognize the common ophiolitic succession (tectonic ultramafite rocks-ultramafite and cumulate mafite rocks – differentiated intrusive complex – vein complex - efusive complex with pillow lava), the absence of some terms being a fact (cumulate mafite rocks, intrusive differentiated and vein complexes). The tectonic melange of ophiolitic and non ophiolitic rocks (sedimentary or metamorphic rocks) is obviously revealed by their association way. Only an important tectonization could explain a lot of sedimentary argilitic blocks or high mylonitized

metamorphic rocks included within ultramafite rocks. Another result of the same process, proved by contacts with mylonites, is ultramafite rock within basalts or argilous schists.

1.1. Ultramafite Complexes

The ultramafite complexes have a non homogenous distribution. The most large area is in the right slope of the Brebina Valley , between Piatra Verde-Godeanu and Gerului Valley. There are isolated or small occurrences in Ogaşul Turcului – Topa Peak, Dragu Valley – Băroaia Valley, Gagii Valley– Sorăzii Valley and Borloveanu Valley – Ocna Hill. The compositional stratification is one of the primary structural elements, rarely observed in relict zones preserved within ultramafite rocks with massive textures. This is the result of an alternance of some cm or dm levels of rocks having dunitic, may be harzburgitic compositions, with rocks having a lherzolitic composition, sometimes with a wehrlite tendency. The position of the stratification plane is very variable and doesn't correspond with any of the other planar measurable elements and with any sorted limits of the complexes. The second noticeable structural element is the primary foliation, characterizing primary lithotypes. Foliation is the result of the plan-parallel disposition of pyroxene crystals (Foto 1), mainly orthopyroxene and chromite (Foto.2), mainly observed in harzburgites.

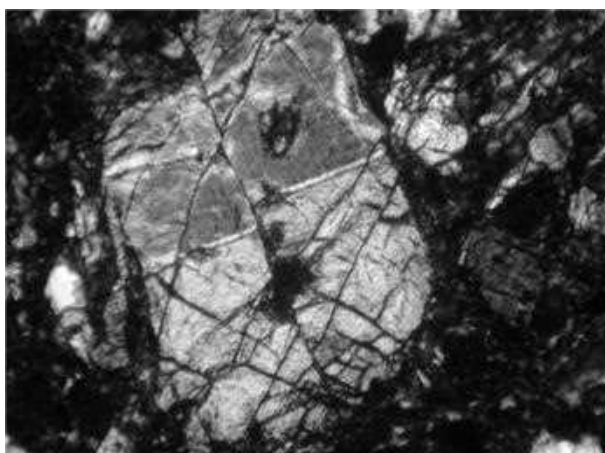


Foto 1. Twinning pyroxene, Măgura Valley;
x 60 , N+



Foto 2. Divided chromite partially substituted by carbonates and phyllosilicates, Bradului Valley; x20 , NII

1.2. Basalts

In the Severin Unit outcrop rocks of basaltic composition, mainly in the left side of the Brebina Valley and Ponoare - Măreşteşti area on the Borloveanu Valley. Basalts show a highly deformed character.

The metamorphic transformations are confirmed by the presence of neoformation minerals, especially pumpellyite (see analysis "Rx" - Fig. 2 and 3).

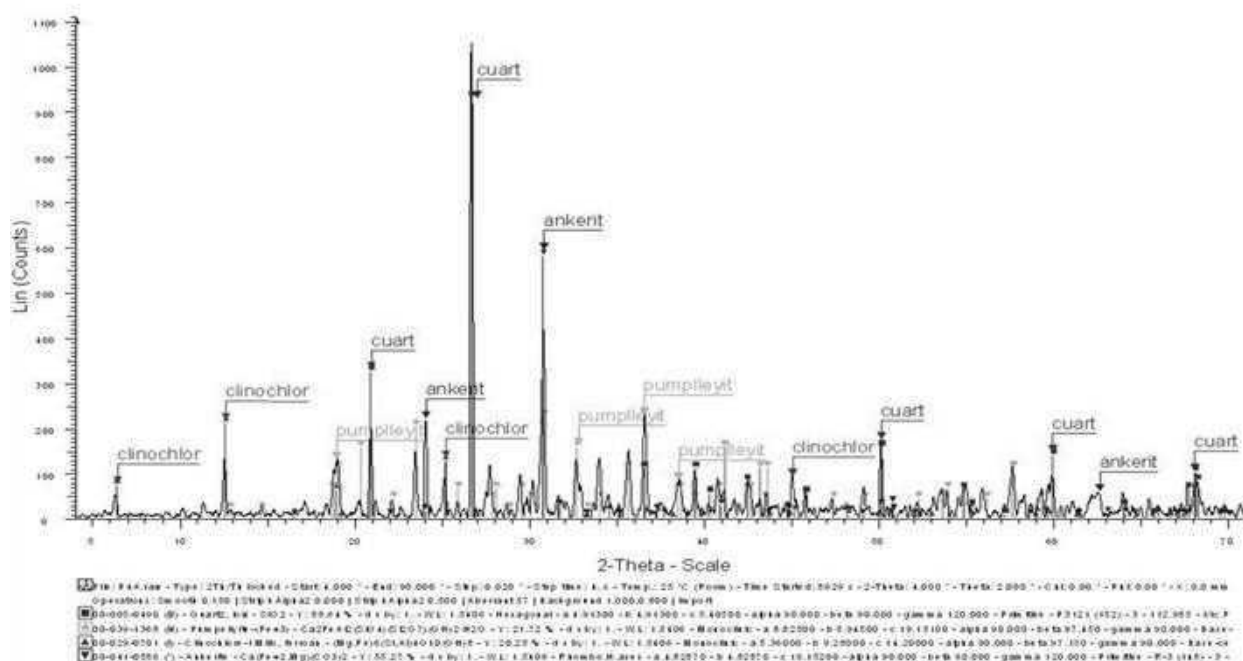
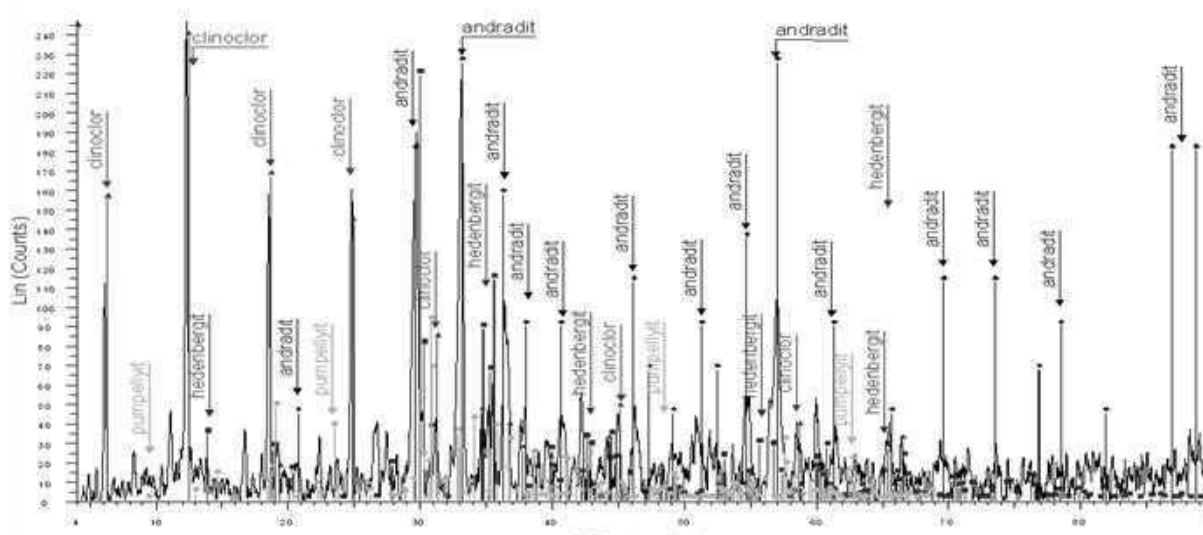
Areas where basalts are developed are the Dragu, Băroaia, Măgura Valleys, or "Ocnei - Măgura Coarbei" Hill, being characterized by a strong fragmentation of their blocks, because of the many intercalations of sedimentary, metamorphic or ultramafite rocks.

Most of the basalts belong of the aphyric, compact type. There are rare porphyria type, resulting by a large crystals growing of clinopyroxene or plagioclase. Basalts are generally microgranular, holocrystalline, with intergranular or subophitic texture. Lithophysae occur mainly filled by chlorite, rarely by quartz, chalcedony and zeolites.

Mineralogically, basalts are composed of plagioclase, clinopyroxene and opaque minerals.

Rarely, euhedral phenocrysts of olivine appear. Plagioclase is generally highly transformed, being replaced mainly by albite. The presence of pseudomorphoses suggests the existence of euhedral phenocrysts of olivine and also of euhedral substitutions of magnetite by chlorite.

Although the basaltic rocks of Mehedinţi Plateau are strongly secondary transformed, their physical and mechanical characteristics are similar to the Quaternary basalts (Racoş, Magura Sârbi, Sanoviţa).



the table no. 1.

Unlike the others, basalts of the Mehedinți Plateau are often transformed in secondary rocks.

The similarity of the physical and mechanical properties of the two types of basalts can be explained by the fact that, overall, the association of secondary minerals (pumpellyite, epidote, carbonates, chlorites, etc.) has physico-mechanical properties comparable with the primary ones (pyroxenes, plagioclase feldspar, etc.) (Foto. 1 and 2).

Table no. 1 – Physico - mechanical properties of basaltic rocks in the Mehedinți Plateau in comparison with other types of basalts from Romania

Line no.	Characteristic of basalts	U.M.	Racoș	Măgura Sârbi	Sanovița	Obârșia Cloșani
1	Apparent density	g/cm ³	2,83	2,58	2,40-2,77	2,85*
2	Water absorption at normal temperature and pressure	%	1,05	0,60	0,71-2,11	0,54*
3	Compressive strength – dry	N/mm ²	170	81	75-180	141,4*

*Arithmetic average of 10 samples

In the same way, it might be explained the similarity of compressive strength and water absorption.

The metamorphism process increases their cohesion through intergrowths of secondary minerals (quartz, carbonates, chlorites, epidote, pumpellyite).

As previously discussed, referring to the characteristics of basaltic rocks in the Mehedinți Plateau, they can be exploited as a dimension stone, aggregates for concretes and mineral binders, similar as basalts from Racoș, Măgura Sârbi, Sanovița.

Conclusions

The structural components, geological characteristics of hosted formations, genetic characters and qualitative properties of the accumulations has determined a separation in districts, sectors and metallogenetic fields in the Mehedinți Plateau.

The physico-mechanical properties of basaltic rocks of the Mehedinți Plateau, in comparison with other types of basalts (Racoș, Măgura Sârbi, Sanovița), shown in Table no.1, prove that they can be exploited for construction and for concrete aggregates and mineral binders.

Due to the metamorphism process, basalts increase their cohesion, cementing the secondary minerals (quartz, carbonates, chlorites). All these explain the physico-mechanical characteristics of basaltic rocks in the Mehedinți Plateau (apparent density, compressive strength, water absorption).

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AN OVERVIEW OF THE OAȘ AND GUTÂI NEOGENE METALLOGENETIC DISTRICTS

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The North Transylvanian Neogene mineral deposits constituted since the Middle Age one of the most important source of base-metals and Au-Ag ore for the mining industry.

The present paper intends to comment some characteristic features of The Neogene Oaș and Gutâi Metallogenic Districts in the context of the recent geological investigations.

Geologic and geophysical researches point-out that the Tertiary subduction and related volcanism of the Carpathian Arc evolved in connection with the Miocene, diapyric, uprise of the asthenospheric mantle of the Pannonian Basin, with a back-arc role (Kovács et al. 2002). Together with Tokaj (in Hungary), Vihorlat-Beregovo (Ukraine), the Oaș and Gutâi Neogene volcanic rocks occupy the NE border of the Pannonian Basin and belong to the Central Segment of the Carpathian Neogene Volcanic Chain (Seghedi and coworkers, 2005).

Some geochemical and isotopic data for the Central Segment reveal differences concerning the parental source of the magmatic products: mantle and/or crustal material. This is revealed, for example, by the Sr-Nd correlation (Seghedi et al., 2005).

The petrographic terms of the Neogene magmatites are illustrated by the total alkali-silica diagram (Fig. 1) for both districts, including the Kibler and Big-Shaian from the Vâshkovo area (Ukraine), within Oaș District.

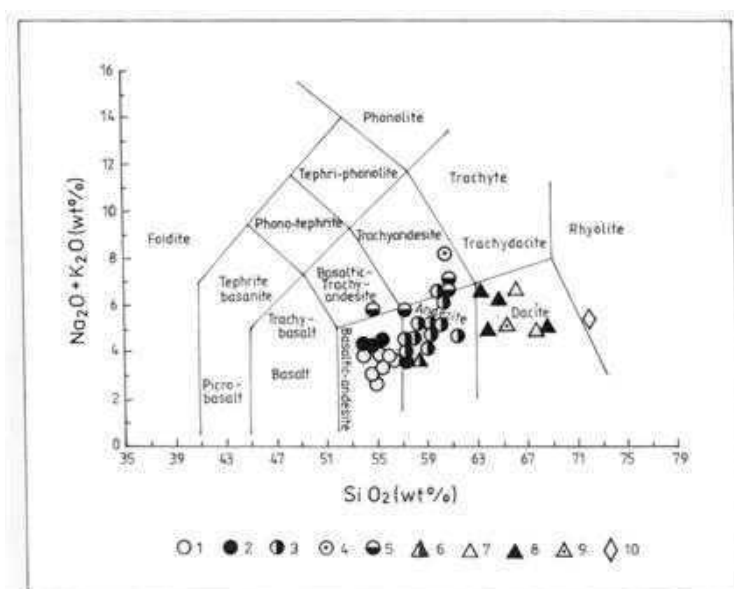


Fig. 1: Plots of the Neogene magmatic rocks from Oaș and Gutâi Mts., in the total alkalisilica diagram of the Bas et al. 1986. 1 and 2 – two pyroxene andesites and basaltic andesites; full circle, for Oaș volcanic rocks; 3 – pyroxene, hornblende ± biotite qz – andesites; 4 – Piscuiatu „qz-andesite”; 5 – hypersthene or trachy – andesites varieties of vulcanites; 6 – Ursoi and Kibler qz – diorite porphyry; 7 and 8 – dacitic rocks; full triangles, for Oaș samples; 9 – Bârlești and Șaiun (Vâshkovo) granodiorite – porph; 10 – Dănești rhyodacite

Characteristic of the Neogene volcanites from the Oaș and Gutâi Mountains there is the prevalence of the mafic-pyroxene varieties: two-pyroxene andesites, basaltic andesites, hypersthene andesites, pyroxene-hornblende andesites, even basalt occurrences. These „mafic” varieties constitute three or more volcanic sequences interposed and /or juxtaposed with the intermediate and felsic ones: qz-andesites, dacites, and rhyolites. All the volcanic products, including the ignimbritic rhyolites from Ilba-Băița (Alexandra Fülöp, 2001) cover the interval from Badenian and Pontian (15-7 Ma). The succession of the Neogene magmatites today is better defined due to the recent radiometric data published by Edelstein et al (1992), Lang (1994) and Kovács et al. (1998).

Significant are, also, the plots of the chemical analyses in the AFM diagram (Fig. 2). This reveal the trend of the majority of the analyzed samples to the calc-alkaline series terms plots in the tholeiitic domain that may suggest different origin of the parental magmas.

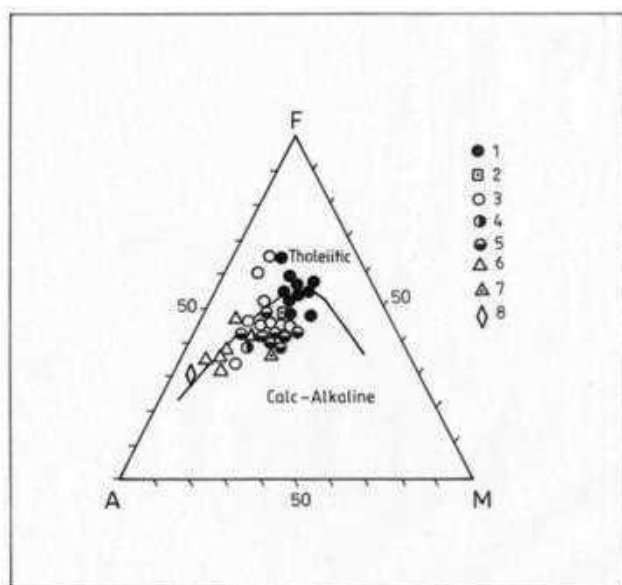


Fig. 2: AFM [Alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) – $\text{F}(\text{FeO} + \text{Fe}_2\text{O}_3)$ – $\text{M}(\text{MgO})$] diagram showing the calc-alkaline and tholeiitic distribution of the Neogene volcanites from the Oaş and Gutâi Mts. 1 – two pyroxene and basaltic andesites; 2 – qz – diorite porphyry; 3 – pyroxene-hornblende andesites; 4 – qz-andesites and biotite-quartz-andesites of Gutâi; 5 – trachy andesites and hyperstene andesites; 6 – dacites; 7 – granodiorite porphyry; 8 – rhyodacites.

It is noteworthy to mention for the Oaş District the outcrops of shallow magmatic intrusions, represented by diorites and qz-diorite-porphyries (Ursoi-Călinești), granodiorite-porphyry (Bârlești-Cămârzana, Pleșcuț near Bătarci) on the Romanian territory, as well as diorites and qz-diorites (Kibler hill) or granodiorite-porphyry (The Big Shaian) in the Vâshkovo area (Ukraine). The last intrusions are integrated by the Ukrainian geologists in the category of the „Hypoabyssic complex” (Lazarenko et al 1993; Zaitzeva, 1966) (Fig. 3)

The Oaş Metallogenetic District

The hydrothermal metallogenesis related to the Neogene volcanism from Oaş District, including those of the Vâshkovo area (Ukraine) generated concentrations of Pb, Zn, Cu; Pb, Zn, Ag; Au, Ag and occurrences of mercury minerals.

The great majority of the mineralizations are distributed in a field of geophysical-gravimetric maxim (positive) anomaly (S. Fotopulos 1964, 1967, unpublished data). This anomaly was interpreted as a risen area (block) of the pre-Neogene basement, accompanied by magmatic intrusions (Fotopulos, 1967, Jude, 1986).

Four mineralized structures were intensively investigated in the second half of the last century: Gruicul Socilor – Afinet Viezuri (Ghezuri, a local idiom); Băile Turțului and Bătarcel, to which may add the Au-Ag veins with some occurrences of cinnabar (Fig. 3) at Bixad-Oaş.

In the Viezuri hill, the Sarmatian and Pannonian sedimentary formations are pierced as a diapire, by a subvolcano (a risen stock) of dacites which pass to microgranodiorite porphyry. It carries diorite-monzodioritic enclaves up to 30-40 cm in size.

The polymetallic mineralization occupies the western side of the intrusion and constitutes a principal vein (Mihai Vein) with some branches at the upper part and a network of veins inside of the magmatic intrusions, at depth.

The earliest, a deep seated sequence of mineralization consisting of quartz, ilvaite, actinote and chlorite association with pyrite, chalcopyrite (with exsolutions of cubanite), hematite and pyrrhotite. This former sequence is followed by massive bands of galena with some sphalerite and by chalcopyrite and pyritic bands with quartz, siderite and dolomite as gangue minerals. The last sequence, at the upper part of the Mihai Vein consists of pyrite, marcasite, sphalerite, wurtzite, galena, some chalcopyrite, with quartz, chalcedonic and kaolinic minerals as gangue. The native gold may be found in all the named sequences, even as inclusions in ilvaite (Damian, 1995). But the richest ore grade occurs at the upper part, associated with adularia, into an argillitic facies of alteration of the wall rocks. This is a feature of the low sulfidic style of the epithermal gold deposits.

The first K-Ar radiometric dating on the adularia samples, performed by M. Soroiu at

I.F.I.N. Măgurele yields 8.8 ± 0.6 M.a. (Jude, 1986).

At *Băile Turțului*, the Emerik vein was mined long time for Pb, Ag and Au (Hauer, 1855). In this area, the Pannonian sedimentary and volcanic formations are cut by microdiorite and micromonzodiorite intrusions of subvolcanic facies.

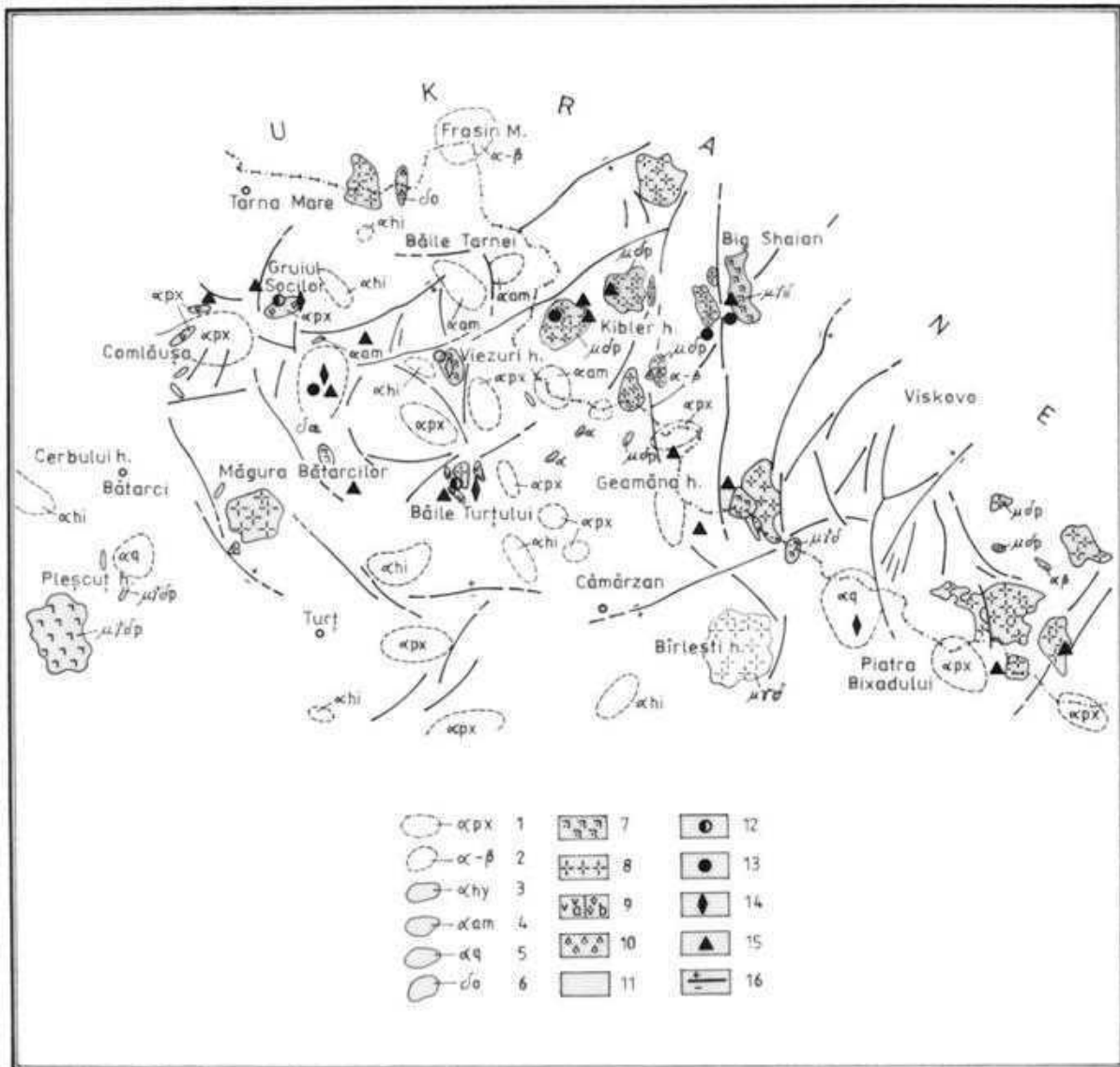


Fig. 3: Structural and metallogenetic sketch of the Oaș District, inclusive Vîshkovo area (Transcarpathian Ukraine)(modified from R. Jude, 1986). 1 – 6 – margins of volcanic structures: 1 – pyroxenic andesites; 2 – basaltic andesites; 3 – hyperstenic andesites; 4 – amphybol ± pyroxene andesites; 5 – qz – andesite; 6 – dacites and hyalodacitic rocks. 7 – 10 – intrusive magmatic rocks: 7 – granodiorite and microgranodiorites porphyry; 8 – qz – diorites a microdiorite porphyry; 9 – andesites (a) and microdiorite porphyry (b); 10 – dolerites (δo); 11 – Sarmatian and Pannonian sedimentary formations; 12-15 – hydrothermal mineralisations: Pb-Zn-Ag mineral paragenesis; 13 – Pb-Zn±Cu ore deposits; 14 – Au-Ag mineralizations; 15 – Hg ± Sb occurrences of mineralizations; 16 – fault.

The mineralization coincides in the principal vein – Emerik vein – with NE – SW direction with some branches and veinlets, connected to the main subvolcanic intrusion. The one vein contains Pb + Zn Sulfides with pyrite, subordinate chalcopyrite, arsenopyrite, marcasite, pyrrhotite and gold. Characteristic there are the frequent occurrences of the Sb and Ag minerals and

occasionally cinnabar in outer zones; quartz, calcite, sometime adularia, barite and fluorite as gangue minerals.

Afinet-Gruicul Socilor ore field

Southwards of Tarna Mare locality a group of veins and two mineralized breccia pipes are hosted by the Pannonian pyroxenic andesites in relation with a subvolcanic andesitic intrusion.

The mineralization, similarly to the Băile Tușului group veins has a Pb+Zn+Ag+ character. The Ag and Sb minerals occur in a later paragenetic sequence, with some barite and fluorite as gangue minerals. The richest values in Ag came from the silver-bearing galena and, on the other hand from the silver minerals: proustite, pyrargirite, polybasite, and argentite. It is noteworthy to mention that the microprobe analysis of the globular gold within pyrite from depth level of Vezuri deposit contain 9% Ag (a high fineness); the gold associated with quartz from the upper horizon of the mine, has a content of 13% Ag, whereas the gold associated with Ag minerals from Băile Tușului contains 20% Ag (Jude, 1986).

The Vein area of Bătrâcel

Near Bătrâcel locality, eastern side of Bătrâcel Valley the geologic investigations point out a group of gold quartz veins emplaced in a volcanic edifice of dacite and hyalodacitic rocks, these veins, around 200m long consist of pyrite, Pb-Zn sulphide and gold, occasionally cinnabar with quartz, calcite and kaolinic minerals as gangue. Some apophyses and little dikes of qz-andesite mark the presence of subvolcanic intrusions.

At Bixad, nearby Ukrainian frontier, the geologic investigations reveal some gold-quartz veins emplaced in Pannonian qz-andesites. They consist of pyrite, sphalerite, galena, tethradrite, micrometric grains of gold and occasionally fine grains of cinnabar in quartz and calcite gangue minerals (Ioana Gheorghită, in Borcoș et al. 1972).

In the Oaș District *the mercury minerals*, especially cinnabar, may be found in the hydrothermal paragenesis of the ore deposits (Gruicul Socilor, Bătrâcel; associated with stibnite in the outcrops (Penigeri stream of the Turț Valley) and frequently as impregnations or veinlets in massive volcanic rocks with argillic hydrothermal alterations, as well as in volcanoclastic rocks. On the other hand the cinnabar was found in majority of the streams within this territory, even from Frasin Valley, with occurrences of basaltic andesites (Jude, 1986) (Fig. 3).

The published data on The Vâshkov metallogenetic fields (Ukraine) mention six mercury deposits and around 30 occurrences of cinnabar and four Hg+Pb+Zn mineral occurrences (Lazarenko 1963; Sasin, 1966; Merlici a. Spitkovskaia, 1974).

Gutâi Metallogenetic Districts

The Neogene mineral deposits southern of the Gutâi Mts. are distributed in an elevated zone of preneogene basement, marked by a series of outcrops of Paleogene sedimentary deposits under the Neogene sedimentary and volcanogenic formations (Giușcă, 1958). They occur on the Mesteacăn creek (upstream of the Ilba Valley), on the Ulmoasa Valley (Băița), Romana stream (tributary to the Firiza Valley) a.s.o. It may be seen as an „Extended metallogenetic district” in a tectonised zone eastern of Băiș, make junction with the Dragoș Vodă regional fault.

However, their mineral and geochemical paragenesis as well as the geologic features lead to consider more adequate three metallogenetic districts: the Ilba-Nistru district, Băița-Dealul Crucii and Herja-Băiș District. A similar grouping was adopted by Popescu (1986) in three metallogenetic entities. All these mineral deposits are integrated according to radiometric analyses to the Pannonian metallogenesis (Kovács et al., 1998).

The Ilba-Nistru District includes all the mineral deposits hosted by the Sarmatian pyroxenic andesites - Seini andesite (Rădulescu, 1958), of 12.1 – 13.4 M.a. age. The radiometric data for the ore veins (adularia) show around 11 M.a. (Kovács et al., 1998). The difference of age between the host rocks (Seini andesites) and the mineral deposits (adularia) requires petrologic considerations.

Three type of mineralisations are characteristic for this district: Cu+py, with a small proportion of Pb+Zn sulphides; Pb+Zn±(Cu, Au, Ag) mineralisations and Au+Ag+py in which the Pb-Zn minerals lack or are insignificant (Jude, Popescu, 1997).

For the Cu-py mineralisation main characteristic there is the *Mihai-Nepomuc vein*; a mineralised fissure, along a fault, with NW-SE direction in chloritized andesitic rocks. The mineralisations consist of pyrite, chalcopyrite in chlorite, quartz, some adularia and argillitic minerals; subordinate, sphalerite, galena, arsenopyrite, hematite and marcasite occur. The Mihai-Nepomuc vein, with a length of 1.6 km, continues in the Țapu hill with Alexandru vein and with „Copper impregnation zone” within the Valea Colbului (Socolescu, Rădulescu, 1971).

Characteristic for the Pb-Zn mineralization are the Firizan, Aluniș, Venera (40, 41, 42) veins in the Aluniș hill and 170, 171, 173 veins in the Fața Mare hill in silicified, adularised and argillized wall rocks. The mineral paragenesis consists of galena, sphalerite, chalcopyrite, hematite, ± magnetite, gold and sometime sulphosalts of Sb, in quartz, calcite, siderite, chlorite eventually adularia, barite and kaolinic mineral gangue.

The Au-Ag-py mineralisations are distributed in the peripheral areas of the Ilba-Hondol mineral deposits, in the Valea Băilor (Racșa), Cetății Stream (Seini) etc. On the other hand, a latter vein generation formed by chalcopyrite, pyrite, gold with quartz and adularia penetrates the Pb+Zn+Cu type of the Venera vein (Jude, Popescu 1997).

Nistru ore deposit comprises two groups of ore veins: one with polymetallic character, to NW of Piatra Hondol volcanic centre, the other to E and SE, of Cu+py±Au, Ag compositions (Nepomuk, Domnișaoara etc.).

NE of Nistru mining locality, the Sarmatian-pyroxenic andesite is traversed by some subvolcanic intrusions of propylitized microdiorites, micromonzodiorites and qz-andesites. In the same area, new geologic investigations pointed out a distinctive paragenetic sequence of Cu-Au-Bi minerals. The Bi-sulphosalts include members of bismuthine-aikinite series (Damian, 2003) and some occurrences of tetradymite ($\text{Bi}_2\text{Te}_2\text{S}$) as intergrowths with chalcopyrite, gustavite and gold (Plotinkaia, Damian et al. 2009). The gold occurs as microscopic grains in chalcopyrite, as well as globular gold in pyrite; the latter is a gold with high fineness (83.30% gold and 15% Ag). The secondary ion mass-spectroscopy analysis (ISMA) reveals an arsenic pyrite containing invisible gold (Floarea Damian, 1999).

Băița-Dealul Crucii District comprises Au-Ag is hosted by deposits related to the Pannonian qz-andesite and dacite (10.5-11.3 M.a.). The great majority in the Piscuiatu qz-andesite from Poprad Hill and Valea Roșie (Red Valley); another, especially the Wilhelm ore veins in the Ulmoasa dacite (eastwards of Băița Valley). The radiometric data show around 10 M.a. of the gold mineralization (Kovács et al. 1998).

Characteristic there are the vein field of Poprad hill: The Sofia X, XXV, Alexandru Veins a.s.o belong to the Săsar mine and the Valea Roșie golden veins.

The ore veins consist of varieties of silica minerals (quartz, amethyst, chalcedony, even opal) with collomorphic and banded textures containing sulphides, native gold and silver minerals in varied proportions; to this paragenesis may add carbonates and adularia. The mineralogical studies (Petrușian et al., 1960) reveal two stages of the metallogenetic processes; the former generated gold, pyrite, Pb, Zn, Cu sulphides in silica minerals; the second stage is marked by silver minerals (proustite, pyrargyrite, polybasite, stephanite, argentite), argentiferous gold (electrum) with native silver in the carbonate minerals gangue. Some occurrences of free gold of Valea Roșie deposit is similar with the Metaliferi gold deposits (H. Helke 1938).

Observations on the fluid inclusions within quartz crystals from Sofia Veins point out the Th values of 200-232°C (Pomârleanu, 1971). All these features mark typical characteristics for the Low sulphidation epithermal style of gold deposits (White, Hedenquist, 1995).

Dealul Crucii ore deposit

North of Baia Mare town an important ore vein of approx. 1200 m long cuts the Sarmatian pyroxene andesites, Pannonian qz-andesites and pyroxene-hornblende andesites.

The ore vein consists of polymetallic and Au-Ag mineralization, long time mined, up to 1950. Ghițulescu (1950), on the ore grade data, establishes a notable vertical zonality of the mineralization: a golden quartz zone at the upper part of the mine, somewhat similar to Valea Roșie gold deposit; a silver rich zone and La zone des lamprites aurifères (zone of gold bearing

sulphides) to deeper horizons of the mine (Ghițulescu, 1935). Helke (1938) explains the argentiferous ore shoots of the mineral deposit by the presence of thin veins of pyrargirite; accompanied by other Ag and Sb minerals, telescoped into the polymetallic mineralization of the main vein. So, there is a sequential feature of the Dealul Crucii hydrothermal mineralization.

Herja-Băiuț District

The mineral deposits within this metallogenetic district are related to the Pannonian pyroxene and pyroxene hornblende andsites (Jereapăn type) of 10.1-10.9 M.a. The radiometric analysis on the adularia and illite related to ore minerals (8.8-9.3 M.a.) show a good correlations with the host andesitic rocks (Kovács et al., 1998).

Herja mineral deposit, South of the Igriș Mts.

A group of ore veins, rich in Pb-Zn-Ag ore minerals ore connected to a shallow magmatic (subvolcanic) intrusion. A propylitised intrusion of andesites, that pass to microdiorites and micromonzodiorites at deeper horizons of the mine are accompanied by some andesitic dikes (Damian, 1996). The magmatic bodies cut Eocene and Sarmatian sedimentary formations with a weak thermic metamorphisms (biotite hornfelses) induced by the magmatic bodies. The ore field is constituted by a group of about 260 veins and veinlets, fourteen more interesting, with ENE-WSW direction; the vein nr. 10 (Șălan) and 60 (Clementina) in the middle part reaches aprox. 800 m in length.

The mineralization, somewhat with an atypical feature is characterized by an excessive concentration of metallic minerals with a deficiency of gangue: sphalerite, galena, pyrrhotite, pyrite, marcasite, arsenopyrite, chalcopyrite, tetrahedrite, stibnite, berthierite, semseyite, plumosite (Petrulian, 1934), bournonit, fülöpit, freibergite, pyrargyrite, proustite, polibasite, gold, etc. and quartz, calcite, siderite, dolomite, fluorite, barite, adularia, ilvaite etc. as gangue minerals (Damian, 1996). The veins are rich in Ag and Sb minerals, but deficient in gold, that may be correlated with scarce occurrences of the adularia. The tourmaline (Szöke, 1968) and fluorite (Damian, 1996) suggests the presence of the volatile substance in the hydrothermal processes.

The mineral and geochemical paragenesis as well as the geologic context leads to consider the Herja mineralization in the category of the meso-epithermal mineral deposits.

Baia Sprie mineral deposit

The Herja, Baia Sprie and Șuitor ore deposits are located in a tectonized zone with E-W trend, southern of the occurrences of Paleogene formations.

There is an important ore vein – Filonul principal - aprox. 2000 m long and E-W direction, with many branches at upper part mined since Middle Age in the Gros Grube from Mons Medius town (Baia Sprie). It occupies the northern border of a Pannonian volcanic edifice of hornblende-pyroxene andesite and traverses 97 andesites and dacites. Another vein – the Filonul nou is located on the southern side of the same andesitic body.

Baia Sprie mineral deposit summarises the main characteristics of the Baia Mare districts : Cu-py paragenese with chlorite as essential gangue mineral constitutes the former mineral sequence, with scheelite and wolframite as exotic minerals ; sphalerite, galena, arsenopyrite, hematite, siderite, dolomite, calcite occur in subordinate proportion; the Pb+Zn+Cu paragenesis represents the second mineral sequence that, in the lower horizons of the mine traverses the former vein sequences. The third, Au-Ag sequences of mineralization, occupy especially the upper part of the vein are accompanied by Sb-minerals (Ghițulescu, 1935; Helke 1938; Manilici et al. 1965).

From Baia Sprie mineral deposit originate over 60 minerals, with some rarities; the wolframite has been identified by Krenner in 1875, a.s.o.

The last sequences are marked by crystals of barite and stibnite, penetrating in the Pb+Zn+Cu formation; metacinnabarite, cinnabarite or realgar over baryte crystals (Helke, 1938) a.s.o.

Wide hydrothermal-metasomatic aureolas in the propylitic, adularia-sericite-silica minerals and argillitic-pyritic halos accompany the above mentioned mineralizations.

The geothermometric studies of the fluid phases inclusions within quartz, published by Manilici et al. (1965) and Pomârleanu (1971) reveal the Th values of 200-250°C to deeper levels

of the mineral deposit. So, the mineralization has the features of meso-epithermal polymetallic ore deposits.

Cavnic mineral deposit

Southwards of Gutâi Summit, aprox. 30 ore veins, from which 12-15 most valuable constitute the Cavnic Pb-Zn-Cu (Au, Ag) mineral deposit. There is a system of quasi-parallel veins, majority of NE-SW trend, which cut the Pannonian sedimentary and volcanogene formations: Șuior qz-andesite and hornblende-pyroxene andesites (Jereapăn type) (Jude, 1970). The principal veins (Kelemen, Josif, Gheorghe, Sfinți, Ungar) may exceed 1200m long and are connected to some magmatic intrusions of andesite-microdiorite porphyry; a small intrusion of biotite-qz-andesite (or dacite) and a breccia pipe may be seen near the Voevozi vein (Jude, 1970).

The geologic observation in the lower horizons of the mine (-300, -400m) reveal petrographic transitions from subvolcanic to hypabyssal facies of the magmatic rocks: diorite, qz-diorite, even granodiorite terms, which induce an effect of thermic metamorphism on the nearly Paleogene and Neogene sedimentary rocks (Mariaș, 1996).

The hydrothermal processes evolved in three or many paragenetic sequences or stages and produced Pb, Zn, Cu sulphides, Ag, Sb sulphosalts, native gold and oxidic minerals associated with quartz, carbonates, silicates, sulphates gangue minerals.

Observations over the geometric relations of the veins ore textures point out three principal paragenetic sequences or stages of mineralization (Jude, 1970). The first stage constitute the „Ramura vestică” vein and the former sequence of the Cristofor, Iosif, Gheorghe veins and consist of chalcopryite, pyrite, sphalerite, galena, some arsenopyrite, pyrrhotite, tetrahedrite, gold and hematite ± magnetite in quartz (red quartz), chalcedony (fibrous quartz), chlorite and siderite. It seems to correspond to the Greenstein sequence with gold mentioned by Helke (1938) within Francisc (Gheorghe) vein.

The second stage produced notable concentrations of sphalerite, galena, subordinate chalcopryite and pyrite with quartz as massive bands and nests.

The third stage, generally, correspond to the Sb and Ag mineral paragenesis (tetrahedrite, bournonite, stibnite, semseyite, enargite, proustite, pyrargyrite) occasionally bismuthinite and germanite; gold, belong to one or several generations (Petrulian et al., 1976). Helke (1938) mentioned kaprothite – $\text{Cu}_6\text{Bi}_4\text{S}_9$, containing grains of gold. Characteristic to this stage is the abundance of the rhodocrosite and rhodonite associated with some adularia, quartz, calcite, barite, occasionally fluorite, sometime gypsum.

The latest minerals may be found in geode of quartz and (or) barite: crystals of sphalerite, stibnite, jamesonite, realgar, occasionally cinnabar.

L. Mariaș (1996) extended to seven moments (M1-M7) the long mineralization processes.

The geochemical observations and ore grade data lead to the conclusion that the Cu tends to increase towards the deeper levels of the mine. As concern the trace elements in the main sulphide minerals, the high content of In and Sn in sphalerite, correlated with Bi in galena and with Co and Ni in pyrite; all crease towards the magmatic intrusions and deeper horizons of the mine. It is worth of mention some content of Au and Ti in pyrite and, on the other hand, W in the quartz containing hematite from the first paragenetical sequence.

The published data about the geothermometric analysis (Borcoș, 1964, Pomârleanu, 1971) established temperatures T_h from 242 to 305°C, a mesoepithermal domain of the metallogenesis.

Conclusions

The polymetallic and Au-Ag mineral deposits from Oaș and Gutâi metallogenetic districts frequently are associated to the Neogene magmatic intrusions of subvolcanic facies: hornblende-pyroxenic andesites, microdiorites, even monzodioritic rocks (Nistru) or granodioritic composition (Viezuri). The mineralized structures are distributed in the tectonized areas and of elevated basement.

The geologic and petrographic context and the geochemical constraints lead to idea that these mineralized structures may derive from the mixing of the ascending-pyroxenic-basaltic melt with crustal matter, evolved in secondary magmatic chambers. As concerns the hypersthene

bearing volcanites, it is accepted that the assimilation of meta-aluminous crustal matter by the mafic melts increases the proportion of the orthopyroxene at the expense of the monoclinic (calcic) pyroxene. (Deer et al. 1969 in Jude, 2008)

The high value of the Rb/Sr of the magmatic rocks denotes a significant contamination of the ascending magma (Damian, Ciprian, 2009).

The occurrences of the exotic minerals of W and Bi in some hydrothermal paragenesis (Baia Sprie, Căvnic, and Nistru) may have a geochemical significance. They denote an additional substance of felsic nature. The W show a strong affinity for the granitic rocks, as wolframite, whereas the scheelite, frequently occur in Ca-skarns related to granitoides.

The Bi, also, has a strong affinity for the granitoidic rocks. The obvious examples may be found in the Mo-Bi or Mo-Cu-Bi mineral deposits related to the Iaromic-banatic granitoids from Banat and Bihor regions (Cioflica et al. 1977, 1993).

As concern the frequent occurrences of the in situ cinnabar as well as in the heavy minerals alluvial samples (Jude, 1986), from Oaş and Baia Mare districts. They show an elevated geochemical threshold of Hg.

The mercury's metallogeny postulates the frequent occurrences of the Hg-mineral deposits within island tectonic arc setting of basaltic (tholeiitic) volcanites as in Japan a.s.o. They may be a result from the volcanic gases emanation.

The gold finesses are a function of the geochemical and mineralogic paragenesis: high finesses in a high temperature hydrothermal sequence (the globular gold from the pyrite); a lower one, as argentian gold (electrum) in epithermal deposits.

The region is scarce in telluride minerals.

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EXPLORATION PROBLEMS IN SEDIMENTS OF POLISH FLYSCH CARPATHIAN

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The majority of fields previously discovered in the Polish Flysch Carpathians occur in shallow-lying, steep, narrow, and often flaked and displaced folds. Oil and gas fields discovered up to now are characterized in general by not very big reserves and in addition the discovered and documented deposits of hydrocarbons are exhausted to a significant extent. This situation shows the impasse in which oil exploration in the Carpathians is at present.

Ineffective exploration in the Polish Flysch Carpathians shows lack of significant, commercial discoveries within the last years. Moreover, Carpathian projects are expensive and burdened with a considerable risk due to the fact that seismics does not provide sufficiently reliable interpretations of geological structure and forecasting of occurrence of reservoir rocks remains at too high level of generality. The assessment of exploration perspectives of the West Carpathians is very controversial.

In this situation it should be stated that explorations in the Polish Flysch Carpathians require methodological progress in petroleum prospecting, new technologies in exploration geophysics and seismic data interpretation. Perhaps new exploration concepts are needed. It is worthwhile discussing the idea of reactivating deep research wells, essential to the scientific and industry progress, once performed by the Polish Geological Institute.

A question should also be put whether it is possible to discover relatively large deposits of hydrocarbons in the Carpathians (e.g. 5 million tones of crude oil, 5 billion m³ of natural gas)?

In the light of previous results of exploration of oil and gas fields the best reservoir rocks are: Ciężkowice and Istebna sandstones in the Silesian Unit, Wierzowskie and Lgockie sandstones in the Sub-Silesian unit and Kliwa sandstones and sandstones from Kuźmina (Lower Cretaceous) of Cretaceous in the Skole Unit. It is also important to remind the thesis that lack of large discoveries of hydrocarbons in the Carpathians results from poor reconnaissance of the structure of deeper "structural stage" of the flysch.

It is connected with minimal seismic reconnaissance and a small number of previously performed deep holes such as Paszowa – 1, Kuźmina – 1, Gorlice – 13, Sieklówka – 1 in the eastern part and Słopnice – 1, Leśniówka – 2, Chabówka – 1, Zawoja – 1, Sól – 8, in the west.

Majority of previously discovered fields occurs up to the depth of 1500 m in complicated geological conditions what determines quantity of documented reserves of these objects. Nevertheless above 1 million tonnes of crude oil was produced from several fields. The largest of them are the fields: Dominikowice-Kryg-Lipinki (1.7 million tonnes), Bóbrka-Rogi and Grabownica in the Silesian unit, the Węglówka field in the Sub-Silesian unit. The greatest production of natural gas was obtained from the folds of Potok (6.0 billion m³) and Strachocina (4.4 billion m³).

This „shallow structural stage is relatively well recognized and at present it is difficult to count on discovery of larger fields in this zone. However richer deposits of hydrocarbons may occur in deeper, open fold structures of Carpathian nappes but exploration of them requires performing a significant scope of preceding seismic works as well as research and exploration drilling.

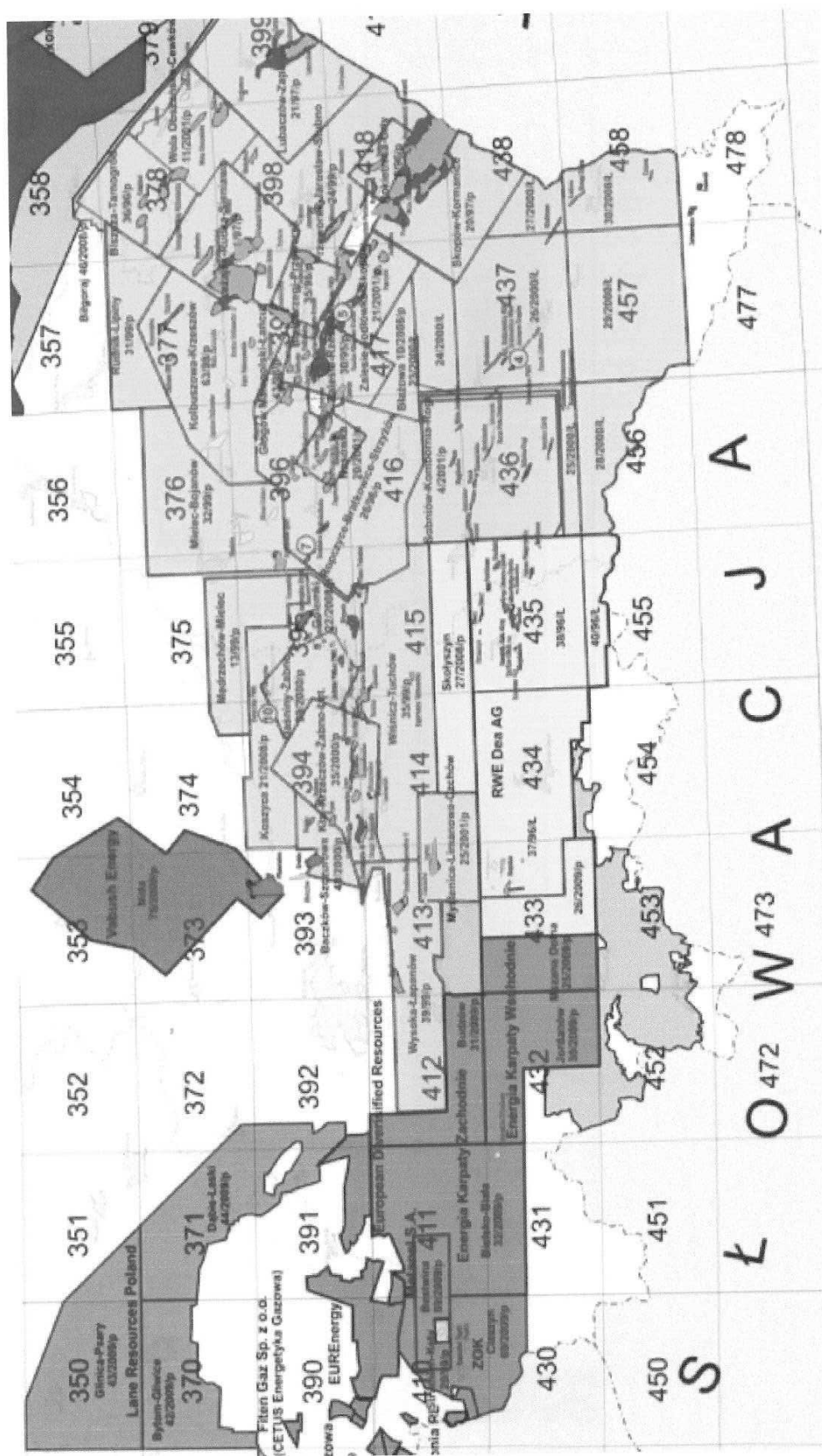
From previous geological and deposit recognition of Carpathian sediments it results that obtaining positive exploration outcomes in certain zones which are considered as the most perspective may helpful in programming of regional exploration works. The region of Kostarowce Zahutyń to the south from Sanok as well as the region of the Iwonicz fold and its extension belongs among others to such perspective zones. New 2D seismic surveys have been performed in these regions and geological interpretation allows separating several large structural objects at depths up to 5000 m with potential reserves of 1 million tonnes of crude oil. These zones will have been

prepared to exploration drilling already this year.

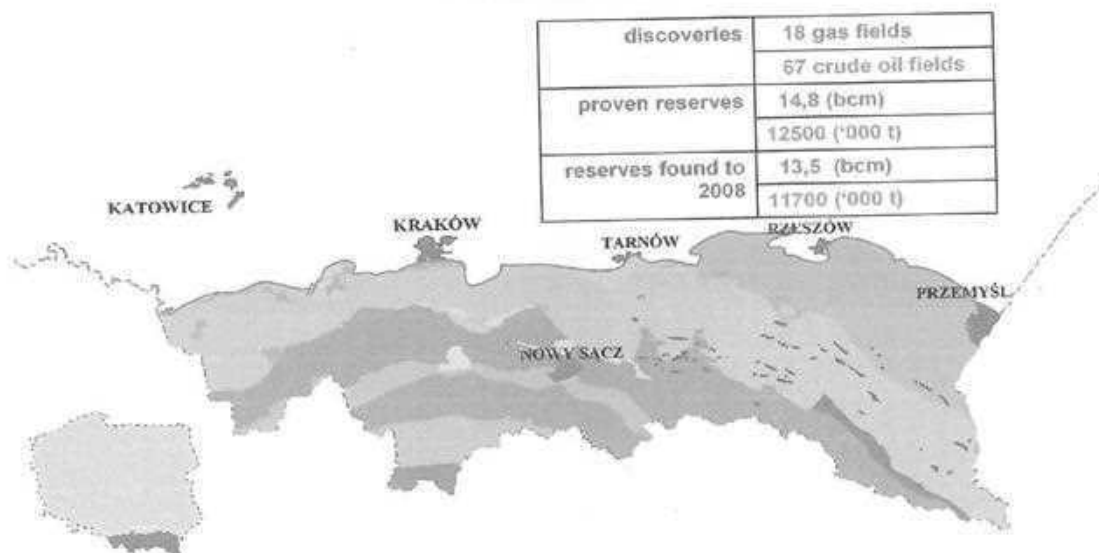
The concept of complex determining the geo-dynamic model of the Carpathians must be reminded in order to solve exploration problems in the flysch. This model should be connected with studies of the type of generation-migration-accumulation in successive structural series of flysch units of the Carpathians. Previous initial works have allowed determining a high generating potential in the Carpathian flysch sediments connected with Oligocene menilite layers and sediments of Lower Cretaceous.

Developing of a new exploration concept in respect to the above-mentioned regions, supported by an appropriate methodology of seismic surveys (in the scope of registration as well as data processing) should contribute to the progress of petroleum explorations in the Carpathian flysch sediments.

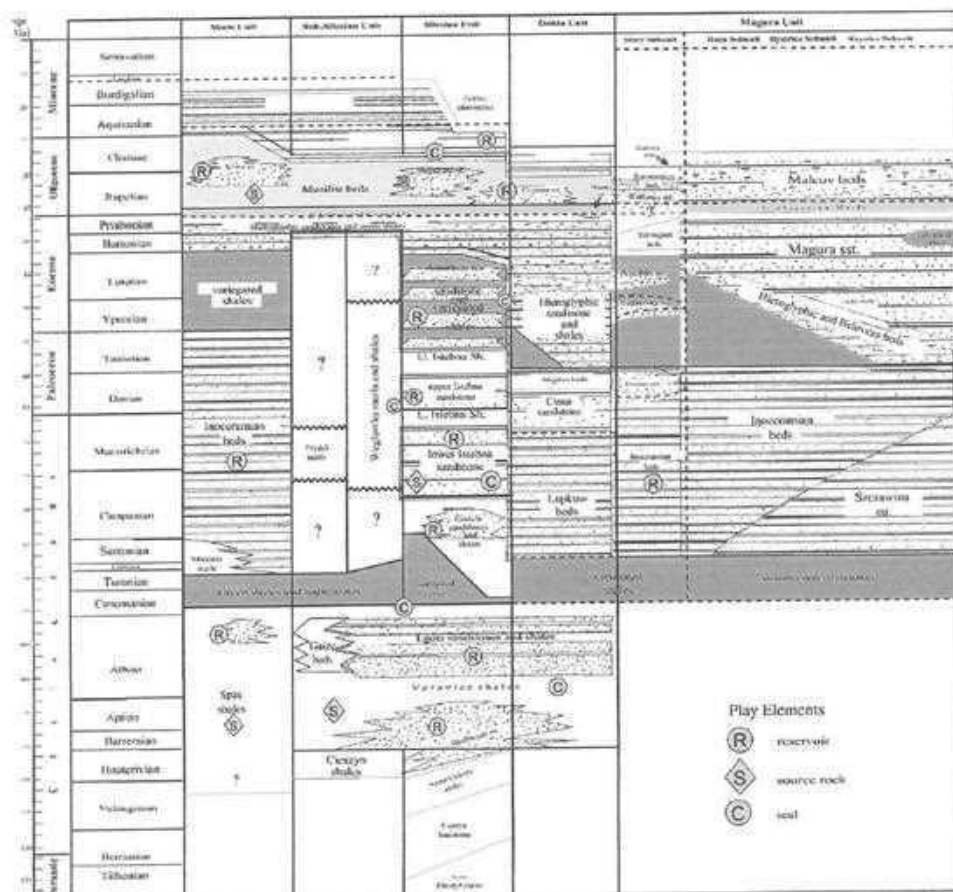
Simultaneously there are conducted concept, research as well as exploration works aimed at successive preparation of next objects in the region of Paszowa and Węglówka in the Carpathian flysch which may secure future exploration and production activity in the south of Poland.



THE CARPATHIANS



The Polish Carpathians –discoveries and reserves



The Polish Carpathians - lithostratigraphy

BIOGEOCHEMICAL EVALUATION OF A PASSIVE ACID MINE DRAINAGE TREATMENT SYSTEM FROM ILLINOIS, USA

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1. Introduction: Acid coal-mine drainage (AMD) is a widespread environmental problem in Illinois basin, one of the most important coal producers in the U.S.A., because extensive coal mining was carried throughout the basin during the last century. The cause of AMD is the weathering of pyrite (FeS_2) and other sulfide minerals when exposed to atmospheric conditions, that results in the production of sulfuric acid with subsequent mobilization of other toxic elements (metals, metalloids) and their compounds into groundwater and surface water. Additional concerns associated with acidic coal-mine drainage include sedimentation of chemical precipitates enriched in metals and other toxic elements, soil erosion, and loss of aquatic habitats in contact with waters with high sulfate and metal loads. The biogeochemical interaction between the low-pH AMD solutions and the local rocks are generally very complex and involve (i) redox reactions in solution and/or surfaces which are catalyzed by microbes, (ii) mineral dissolution and precipitation, and (iii) gas exchange reactions.

Two main treatment methods are currently used to mitigate AMD associated with abandoned coal mines, namely the active and passive treatment methods. Active treatment methods use the addition of chemicals to the AMD (e.g., hydrated lime $\text{Ca}(\text{OH})_2$, caustic soda NaOH , ammonia NH_3 , pebble quicklime CaO , and soda ash Na_2CO_3) to treat the contaminated waters. Passive treatment methods use anaerobic biotreatment cells built with naturally occurring materials

(e.g., limestone CaCO_3 and organic matter rich in bacteria) to substantially increase pH and reduce metal and sulfate concentrations in the contaminated waters. Passive treatment systems are typically man-made ecosystems that are designed to handle a specific range of metal loading conditions and AMD geochemistry. Even though passive treatment techniques require longer retention time and larger treatment area, they are relatively less expensive than typical active treatment methods because they generate smaller volumes of treatment residuals and do not require continuous monitoring and maintenance.

2. The Tab-Simco acid mine drainage treatment system: The Tab Simco is an abandoned coal mine site located in Jackson County, Illinois, U.S.A. (Fig. 1). The acid mine solutions discharged from the abandoned mine workings have low pH (~2.4) and high average concentration of dissolve ions: $\text{Fe} = 597 \text{ mg/L}$, $\text{Al} = 140 \text{ mg/L}$, $\text{Mn} = 39.7 \text{ mg/L}$, and $\text{SO}_4^{2-} = 3,540 \text{ mg/L}$. To abate this significant environmental challenge, a passive-type treatment system was constructed in 2007 by the Illinois Department of Natural Resources, Office of Mines and Minerals. The principle technology

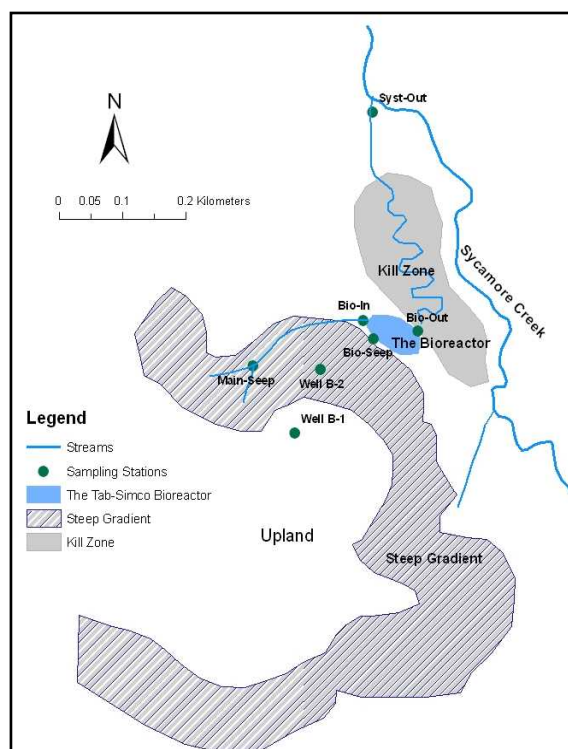


Fig. 1: Map of the Tab-Simco site and the location of sampling stations.

employed was a 0.75-acre sulfate-reducing bioreactor, which is one of the first full scale system employed for the treatment of acidic, coal mine drainage in the U.S.A. The bioreactor was constructed in three layers: a shallow acid impoundment, an underlying thick layer of compost, and

finally limestone with embedded drain pipes. A series of oxidation cells follow the bioreactor unit before discharge into Sycamore creek.

The performance of the Tab-Simco AMD treatment system in removing acidity, dissolved metals and sulfate, and the biogeochemical processes that occur within it, was investigated by analyzing samples taken from the site between July 2008 and Sept 2009. At each sampling station (Fig. 1), the following in situ parameters were measured: pH values, specific conductance (Sc), dissolved oxygen (DO), oxidation reduction potential (ORP) and flow rate. In laboratory we measured the alkalinity, major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), major anions (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , and PO_4^{2-}), and dissolved metals (Fe, Al, Mn, Cd, Cu, Pb, and Zn)

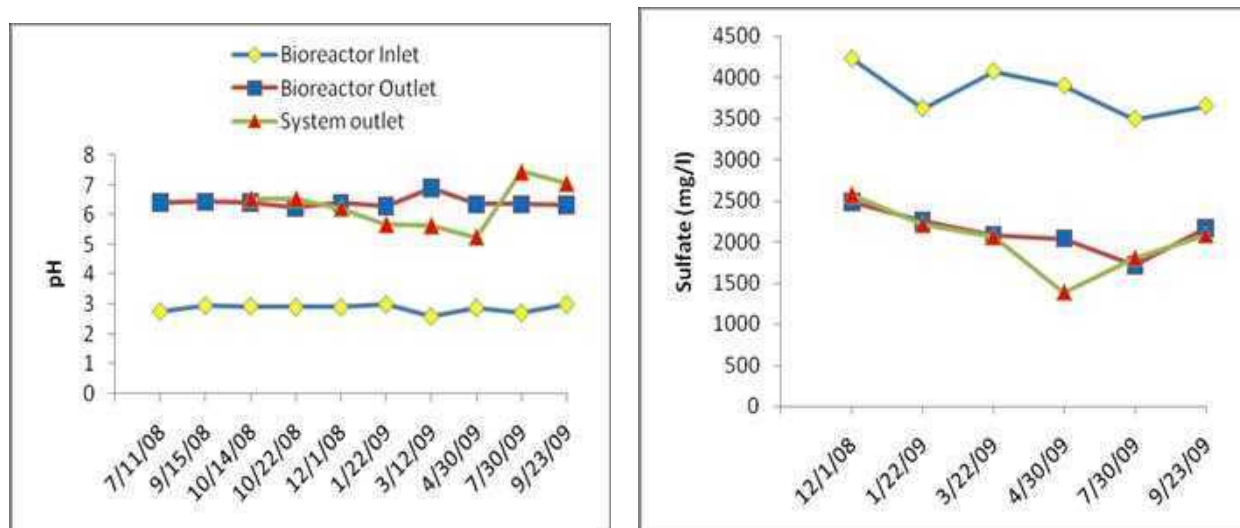


Fig. 2: Temporal variation of Tab-Simco AMD field parameters.

Treatment processes in the Tab-Simco bioreactor include production of alkalinity through bacterial sulfate reduction (BSR) and limestone dissolution followed by metal precipitation. The produced alkalinity neutralized the acidity, bringing it to lower levels and increasing the pH of the water (Fig. 2). The BSR also decreased the SO_4^{2-} concentration in the AMD (Fig. 2). Upon pH increase, the metals in the AMD precipitated mainly in the form of metal sulfides, oxides, and possibly carbonate. Results of chemical analyses indicated that the passive bioreactor decreases acidity from 3,386 to 74.4 mg/L, dissolved sulphate from 45890 to 2020 mg/L, total Fe from 884 to 3.48 mg/l, and Al from 207.4 to 2.10 mg/l; the pH increases from 2.8 to 6.4. Alkalinity is generated in the bioreactor by both limestone dissolution and bacterial sulfate reduction (BSR).

3. Biologically-mediated sulfide oxidation reactions: Recent studies have shown that microorganisms can survive and even thrive in environments that were previously thought voided of life, because they have finite nutrients and extreme living conditions. Such environments are associated with unusual physically or geochemically extreme conditions that are detrimental to the majority of life on Earth, such as extreme acidity, including very low or very high pH, extreme temperature, and high concentrations of sulfate and toxic metals. Bacteria are among the few forms of life that can tolerate these extreme environments.

In acid drainage environments, eukaryotes (protists, fungi, and yeasts), archaea, and bacteria form a chemo-autotrophically-based biosphere largely responsible for the oxidation of sulfide minerals. Microbial activity can impact rates of sulfur oxidation during dissolution of pyrite and other metal sulfides. The feedback between metabolic activity and mineral dissolution and/or precipitation can drive the pH down to values <2 , thus selecting for community members optimized for life in acid. DNA-based studies of organisms populating acid drainage environments have provided insights into the diversity of acidophilic, metal-tolerant species. The genera *Thiobacillus*,

Acidithiobacillus, and Leptospirillum contain numerous species that can utilize various sulfur compounds as electron donor. This group of organisms is largely responsible for the oxidation of sulfide minerals and includes iron- and sulfur-oxidizing bacteria. Sulfate-reducing bacteria are another important group of anaerobic bacteria that can oxidize organic compounds and reduce dissolved sulfate in the AMD to sulfide. The metabolic products of sulfate-reducing bacteria are bicarbonate HCO_3^- and hydrogen sulfide H_2S . Much of the HCO_3^- reacts with protons H^+ to neutralize water acidity and H_2S reacts with metal ions (e.g., Fe^{2+}) to produce metal sulfide precipitates.



Fig. 3: Microbial diversity of site based on molecular analysis of the 16S rDNA. The phylogenetic tree was constructed using the neighbor-joining method with Jukes-Cantor parameter.

Microbiological profiling of the Tab Simco site was performed by molecular analysis of the 16S rRNA gene clone libraries. This analysis indicated an abundance of sequences closely related to bacteria capable of Fe^{2+} oxidation in waters from both the monitoring wells and the constructed AMD oxidation pond (Fig. 3). Sequences closely related to *Acidithiobacillus ferrooxidans*, an organism that can not only oxidize Fe^{2+} but can also couple Fe^{3+} reduction to the oxidation of sulfur, is found in seeps that feed the bioreactor. The predominant phylotypes present in the samples collected from the bioreactor discharge post-treatment oxidation pond were related to sulfur and Fe^{2+} oxidizing bacteria.

However, sequences related to bacteria necessary for metabolizing the compost into simple carbon sources (a requirement by sulfate-reducing bacteria-SRB) were identified. To determine if SRB were present at the site, but in numbers too low to be detected by the initial sampling size, the *dsrAB* gene specific for sulfate-reducing bacteria was targeted. Sequences related to SRB were present in the bioreactor outlet and the post-treatment pond.

While this finding is expected due to the presence of compost in the bioreactor, it suggests that simple dissolved organic carbon sources often utilized by sulfate reducers, such as lactate, may not be available to promote efficient bacterial sulfate reduction. Thus, the relatively high level of sulfate detected in the post-treatment pond is likely due to both the available organic substrate and the presence of nitrate. These results will be used to improve bioreactor design and ultimately the water quality at the Tab-Simco treatment site.

A GEOLOGICAL OVERVIEW ON ARCHAEOLOGICAL BRONZE ARTEFACTS; SOME POSSIBLE LOCAL RAW MATERIAL SOURCES - CASE STUDY ON MUREȘ BASIN AND PRAHOVA COUNTY (ROMANIA)

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The human society was developing more and more tools for with they needed stronger materials and the stone was hard to shape, had no flexibility and was not so resistant. The need of metal started The Age of Cupper by using the row material from the nature: native cupper and sometimes natural alloys. Some tools and weapons where stronger than the others and when the man discovered the answer to that question begun the Bronze Age when man made the first intentional alloy with copper.

This studdy is a geological point of view on bronze from archaeological objects found in the Romanian territory and it is intended to determine, if so, the local origin of the raw material.

In Europe the only big study on copper and bronze was carried out by Junghans S. (1968). The paper included elemental analyses.

I prelevated from the Museum Complex of Arad – Archaeology section, 37 samples: 11 pieces and 26 powder samples. The samples have been weight measured and photographed. The samples came from 28 artefacts are: 2 axes (Păuliș and Felnac, Arad county), 3 reaping hooks (Sântana, Arad county and Gușterița, Sibiu county), 2 belt ornament (Pecica and Sântana, Arad county), 5 bracelets (Sântana and Păuliș, Arad county), 2 small blades (Sântana, Arad county), 3 slabs of smelting (Sântana, Arad county and Șpălnaca, Alba county), 3 celts (Sântana and Păuliș, Arad county), 3 spearheads (Păuliș, Arad county), 1 solar disk (Cicir, Arad county), chisel (Socodor, Arad county), 1 javelin head (Păuliș, Arad county) and 2 needles (Felnac, Arad county). From the Romanian National History Museum I ve prelevated another 28 samples from 16 reaping hooks of Draja, Prahova county deposit: 12 dust samples and 16 small pieces.

First I have chosen to do a X-Ray Fluorescence (XRF) elemental analys on the samples because this is a non-invasive one and I can use the samples for farther analyses. This was carried out at the Horia Hulubei National Institute of Physics and Nuclear Engineering with a XRF spectrometer – XMET 3000TX. The annalized area was about 5 mm².

If we expose an object to the natural corrosion we find that the copper lives the system, and we have also enrichment in tin, arsenic and iron. (up to 50% of the initial percent of Cu is lost). This can be estimated using a factor, f_{Cu} (Robbiola L, 2006). In the case that were analyzed both alteration and fresh metal, the percent of iron shows that if the original material had no iron, the alteration contained almost 2%, this shows enrichment, probably due to the environment.

The XRF analyze concluded the type of alloy used in those objects. The average percent of Cu is 90%, tin is present in a significant percent in the hand-made objects, and almost absent in the smelting (one from Arad surroundings and one from Șpălnaca). We have a good correlation between Zn and Pb (0.73), a week correlation between As and Ni (0.33) and a negative correlation between Cu and Sn (-0,55).

Table 1: Analyze on Sample P37 by the XMET 3000TX

P37	Cu%	Sn%	Pb%	As%	Ni%	Fe%	Sb%
	85.5	traces	traces	2	0.7	6	5.3

The next step in the analising process was to make polished sections from the extracted pieces. The microscopic analyse of the surface is important for the historians because this can give

information on the manufacturing techniques and the amount of usage of the object, but also, the aspect of the inside structure of the material can tell how it was made and especially from what. In this abstract I present as an exemple a polished section of a smelting from Șpălnaca (P37); its chemical composition given by the XMET 3000TX is presented in table no. 1. This was made on the fresh material, not on the alteration.

The polished sample was put under the microscope to see the internal structure (Fig.1).

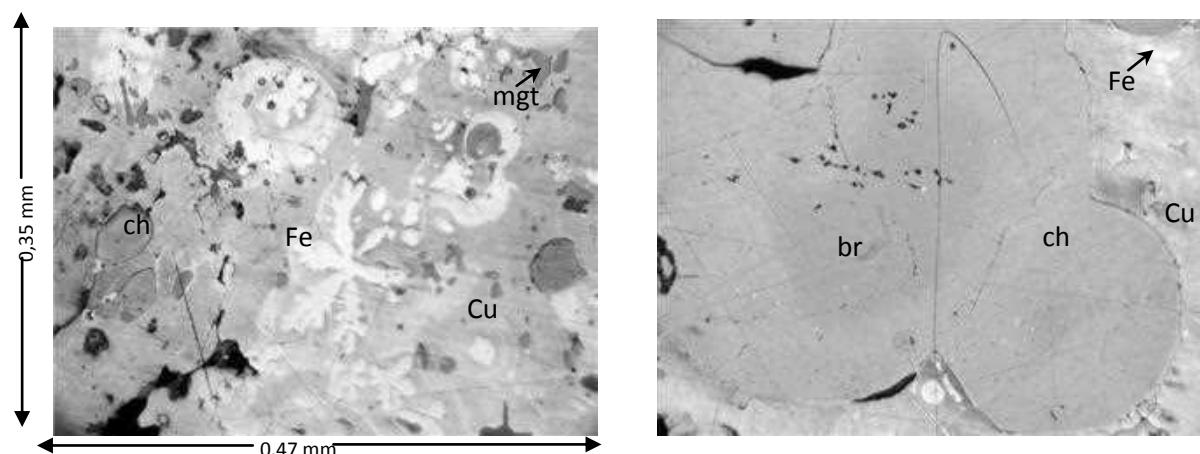


Fig. 1: Sample P37 under reflected light (N//): Fe-iron, Cu-coper, mgt-magnetite, ch-chalcocite, br-bornite.

The principal minerals identified were copper, chalcocite, bornite, iron and magnetite. Around the iron are formed halos of iron depletion. What is called Cu, is not native Cu, is in fact an alloy. To clarify the distribution of the chemical elements I ve made a XRF analize more detailed with a XGT-7000 X-ray Analytical Microscope (Tabel 2).

Table 2: Analyze on Sample P37 by the XGT-7000 X-ray Analytical Microscope

Elem.	Line	Mass[%]	3sigma	Atomic[%]	Intensity[cps/mA]
16 S	K	0.14	0.04	0.29	7.89
26 Fe	K	7.98	0.15	9.52	1352.8
28 Ni	K	0.64	0.07	0.73	80.54
29 Cu	K	77.44	0.58	81.17	8432.04
33 As	K	1.8	0.13	1.6	95.92
48 Cd	L	3.2	0.4	1.89	27.28
51 Sb	L	8.8	0.52	4.81	114.47

After Buzatu and Moldovan, (2009) all the analyzed bronzes are classified as bronzes with tin, and by having other elements (under 3%) they gain a greater refractivity and corrosion resistance. Exception makes those 3 bracelets from Păuliș which are made of brass, and the interpretation for them is under discution. The big percent of lead in these 3 bracelets is explainable because it couldn t be separated from the zinc, so they are lead brases bracelets. Also exception makes the three slabs of smeltings which presents no tin, or very small traces (may be from the oven).

It is obvious that the material wasn t made by a standard recipe, and also it could be seen that the ore was used as found and not very refined. The shape or the destination of an object is very little relevant for the raw material used. Most authors consider that arsenic is not intended in the bronzes, so this must be found only in those bronzes which came from a source with arsenic (Rovira

and Montero, 1994 in Eiroa, 1999). All of the bronzes that I have analyzed contain a small amount of arsenic (between 0.04 – 2%).

We have objects from the same archaeological site, very similar as aspect and yet we can have a very big difference regarding the raw material (In addition, we have two spearheads with very little percent of tin. We have some objects that has a lower percent of Cu, and similar compositions, they are not from the same site, but the archaeological sites are not too far from each other – 3 bracelets from Păuliș (that are very similar both as material and aspect), a reaping hook from Sântana and another bracelet from Sântana.

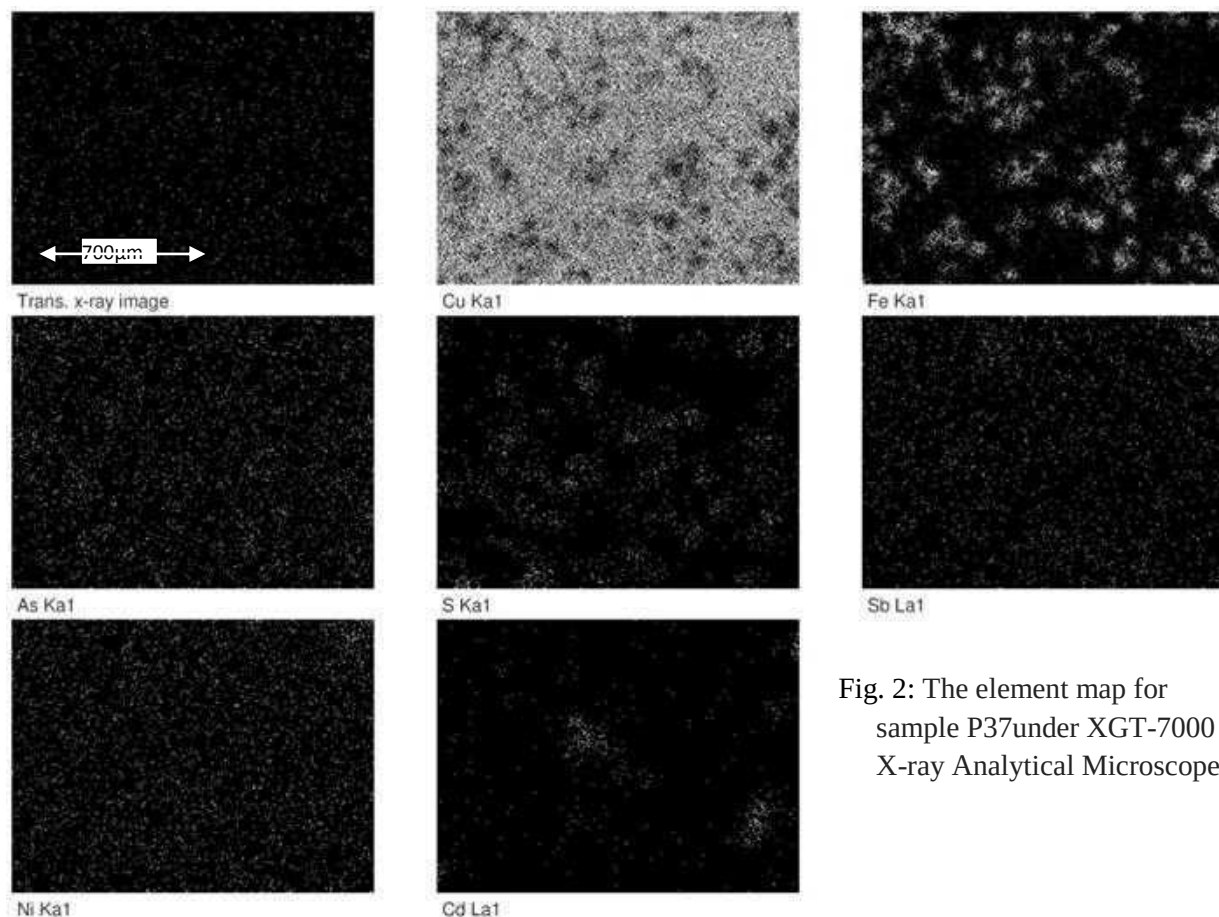


Fig. 2: The element map for sample P37 under XGT-7000 X-ray Analytical Microscope

At the superior part of the copper ores deposits from Romania the native copper and the chalcopryite, the principal mineral from which copper is extracted, is associated with arsenic minerals. Copper minerals occurring in deposits large enough to mine include azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), tennantite ($(\text{Cu},\text{Fe})_{12}\text{As}_4\text{S}_{13}$), chalcopryite (CuFeS_2), and bornite (Cu_5FeS_4), rarely chalcocite (Cu_2S) and covellite (CuS). That means that the first bronze ever made from a local source in Romania is most probably bronze with arsenic (Manilici & Manilici, 2002 in Neacșu Antonela, 2008). In the Bronze Age the ores from Baia de Aramă and Altân Tepe began to be exploited.

At Drajna it seems that the archaeological deposit is a gathering of artefacts from different sources, so they remain just as statistical information, with no certain area of provenance, most likely they are not locally manufactured. The discussion that allows is concentrated on Arad area.

The following occurrences have at the upper part an oxidation area with copper enrichment, those could have represented a local source for the raw material used in bronze artefacts manufacturing.

Metallogenetic, the area is located between the Apuseni Mountains Metallogenetic Province and Meridional Carpathian s Metallogenetic Province. (Popescu, 1986)

If we follow the Mureş river course we can suppose as possible source for raw material the areas in the Metallogenetic District of Concentrations Associated with Granitoids from Highiş-Drocea with copper mineralisation in Păiuşeni epimetamorphic crystalline schist and in granites and late-orogenic alkaline rocks that are interacting with the Păiuşeni suite. Chalcopyrite, pyrite, hematite and rarely sphalerite and galena are occurring in quartz and carbonate dikes (the Şoimuş-Highiş sector has polymetallic mineralisation, Secaş-Valea Prundului also has a polymetallic mineralisation where the chalcopyrite plays an important role), Drocea-Roşia Nouă Metallogenetic District (The Metallogenetic Sector with pyrite and copper, nickel sulphides from Căzăneşti – Roşia Nouă – Pietriş), Săvârşin-Cerbia-Măgureaua Vătei Metallogenetic District has a relative low potential as a source with rare polymetallic sulphides and some chalcopyrite, Tămăşeşti-Dealul Mare Metallogenetic District (polymetallic mineralisation). (Popescu, 1986)

It is well known that in the past the rivers were the principal way of transportation, so a supply of raw material from upstream is very possible. In the south the presumptive area for the raw material is the Metallogenetic District Deva where the copper mineralisation is located in the andesitic body under Pârâul Băilor stream; the mineralisation had at the upper part a more significant copper concentration and even some gold.

In the south can be mentioned the Metallogenetic Sector with Polymetallic Mineralisation Muncelul Mic-Veţel where the mineralisation suffered intensive mobilisation, cataclasis and pyritisation of the surrounding rocks. Here can also add some occurrences of polymetallic mineralisation at Româneşti (Popescu, 1986). Another probable source of copper may be found in the Metallogenetic Field Ocna de Fier-Dognecea where we have a well-known ore deposit, exploited probably from the Bronze Age - Ocna de Fier/Moraviza/Eisenstein/Vascö. In the XVIII century this was one of the most important suppliers of copper (Ciobanu, 1999).

For Şpălnaca it can be assumed as a possible source the Metallogenetic District of Metamorphic Crystalline Schist Baia de Arieş.

The iron from the artefacts is not intended, because we can find iron in the ores, and also in the environment (we also have, at the surface of the archaeological object, enrichment in iron).

Some Neolithic copper pits and mines were found at Şoimuş-Cosliac and modern pits and mines for copper at Milova (www.cimec.ro). Also, for the artefact from Şpălnaca are recorded some mining activities at Răchita, these activities are dating from Prehistory (Boroffka, 2006).

The global comparison between the raw material from the analyzed archaeological artefacts and the possible sources states that they may have a possible local source for the raw material, but also we definitely have some foreign material brought into the manufacturing process (tin). The source for the tin from Romanian bronze remains in discussion, because there are no tin ores in our territory. Bader, (1978) states that the tin may have been imported from other parts of Europe in exchange for salt (the salt began to be exploited in the same period, and our country had big amounts of a very good quality salt). The types of alloy used in Romania in the Bronze Age were not established yet; there are just a few analyses on the bronze objects.

As a statement for a local source we have the three slabs of smelting which have no tin, and further analysis may certify that.

Acknowledgements

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SPURRITE AND ASSOCIATED MINERALS IN THE INNER EXOSKARN ZONE FROM CORNET HILL (METALIFERI MOUNTAINS, ROMANIA)

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The high-temperature skarn occurrence from Cornet Hill (Metaliferi Mountains, Romania) is known as one of the rare occurrences of spurrite and tilleyite worldwide. The Cornet Hill area is located approximately 20 km west of Brad, and 40 km northwest of Deva. The high temperature skarn occurrence herein contains essentially spurrite- tilleyite- and gehlenite-bearing skarns that develop at the contact of a monzodiorite - quartz monzonite body, of Upper Cretaceous age. The skarn protolith consisted in Tithonic - Kimmeridgian reef limestones (in fact micritic reef limestones with clastic interlayers) of the Căpâlnaș-Techereu unit. The skarn from Cornet Hill is clearly zoned, the zoning being, from the outer to the inner part of the metasomatic area: calcite (marble) / tilleyite / spurrite / wollastonite + gehlenite + vesuvianite / wollastonite + grossular / quartz monzonite (Istrate *et al.* 1978, Pascal *et al.* 2001). This paper will offer a short description of the primary phases in the inner, spurrite-bearing, exoskarn zone based on optical, X-ray powder and electron-microprobe analyses.

Spurrite from Cornet Hill concentrates in the outer endoskarn zone, corresponding to the inner exoskarn. It practically defines a monomineralic zone where this mineral accounts for 90-95% of the rock volume. A minute study shows, however, that the typical assemblage is spurrite + perovskite, with minor proportions of tilleyite, wollastonite, gehlenite, grossular, titanian andradite and hydroylellestadite. The spurrite-bearing skarn is characterized by a massive appearance with medium-grained crystals of grayish blue to pale gray spurrite that exceed generally 5 mm in their largest dimension, without preferred orientation. Some of the larger patches of spurrite are, however, altered by thaumasite and afwillite and cross cut by microveins containing scawtite, plombièreite, tobermorite, calcite and secondary aragonite. The optical constants of a representative sample are $\alpha = 1.637(2)$, $\beta(\text{calc.}) = 1.675(2)$, $\gamma = 1.680(3)$ and $2V = 39^\circ$. The measured density of the same sample [$D = 3.02(2) \text{ g/cm}^3$] agrees perfectly with the calculated density ($D_x = 3.022 \text{ g/cm}^3$). The cell parameters, obtained as mean of 6 different sets of individual values obtained by least-squares refinement of X-ray powder data are $a = 10.493(15) \text{ \AA}$, $b = 6.716(9) \text{ \AA}$, $c = 14.179(16) \text{ \AA}$ and $\beta = 101.36(4)^\circ$. The chemical composition, obtained as average of 23 electron-microprobe spot analyses on different samples is (in wt% oxides): $\text{SiO}_2 = 26.84$, $\text{TiO}_2 = 0.03$, $\text{Al}_2\text{O}_3 = 0.01$, $\text{FeO} = 0.03$, $\text{MgO} = 0.05$, $\text{CaO} = 63.11$, $\text{Na}_2\text{O} = 0.07$, $\text{K}_2\text{O} = 0.01$, CO_2 (calculated) = 9.83.

The chemical-structural formula, calculated on the basis of 11 oxygen atoms, is: $(\text{Ca}_{5.010}\text{Mg}_{0.002}\text{Mn}_{0.003}\text{Fe}^{2+}_{0.002}\text{Ti}_{0.002}\text{Na}_{0.011}\text{K}_{0.001})(\text{Si}_{1.990}\text{Al}_{0.001})\text{O}_{8.015}(\text{CO}_3)_{0.995}$, which closely approximates the ideal formula $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$.

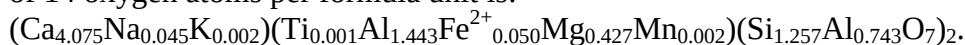
Granular inclusions of **perovskite** in the spurrite mass are common in most of the samples, and are particularly abundant in the close vicinity of the gehlenite-bearing endoskarn. The grain sizes commonly vary between 0.01 and 0.05 mm. The physical constants of a selected sample are $\alpha = 2.302(2)$, $\beta(\text{calc.}) = 2.341(2)$, $\gamma = 2.383(2)$, $D_x = 4.049 \text{ g/cm}^3$, $D = 4.04(1) \text{ g/cm}^3$. The average composition taken as mean of 15 point analyses on various crystals is (in wt.% oxides): $\text{SiO}_2 = 0.36$, $\text{TiO}_2 = 57.25$, $\text{Al}_2\text{O}_3 = 0.28$, $\text{FeO} = 1.19$, $\text{MnO} = 0.02$, $\text{CaO} = 40.23$, $\text{Na}_2\text{O} = 0.02$, $\text{K}_2\text{O} = 0.01$ and leads to the chemical-structural formula:

$(\text{Ca}_{0.983}\text{Fe}^{2+}_{0.023}\text{Mg}_{0.002}\text{Na}_{0.001})(\text{Ti}_{0.982}\text{Si}_{0.008}\text{Al}_{0.008})\text{O}_3$, approaching the stoichiometry.

The unit-cell parameters, obtained by least-squares refinement of the X-ray powder dataset obtained for a spurrite-included perovskite separate are: $a = 5.382(3) \text{ \AA}$, $b = 5.437(3) \text{ \AA}$, $c =$

7.634(4) Å. The refinement was carried out accepting the orthorhombic symmetry of the mineral, space group Pbnm.

Gehlenite occurs scarcely in the spurrite-bearing zone, as clusters of crystals interstitial to the spurrite mass. They are very irregularly distributed and probably express the former presence of Al-bearing silicate veins or beds in the protolith. The crystals are locally embedded in a matrix of vesuvianite that penetrate their cleavages and is probably the result of the interaction between gehlenite and a later stage aqueous fluid. The unit-cell parameters of a representative sample of gehlenite from the spurrite-bearing exoskarn, as refined from the X-ray powder data accepting the tetragonal symmetry of the mineral, space group $P\bar{4}2_1m$, are: $a = 7.684(3)$ Å and $c = 5.061(2)$ Å. The chemical composition of a gehlenite sample from the spurrite-bearing zone, expressed in wt.% oxides, is: $\text{SiO}_2 = 27.18$, $\text{TiO}_2 = 0.01$, $\text{Al}_2\text{O}_3 = 26.87$, $\text{FeO} = 0.64$, $\text{MgO} = 3.10$, $\text{MnO} = 0.03$, $\text{CaO} = 41.12$, $\text{Na}_2\text{O} = 0.25$, $\text{K}_2\text{O} = 0.02$. The resulting chemical-structural formula, calculated on the basis of 14 oxygen atoms per formula unit is:

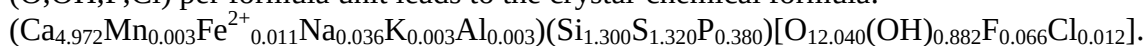


As well as the other gehlenite samples from Cornet Hill (Marincea *et al.*, 2001) the structural formula generally displays an incomplete tetrahedral occupancy and a slight excess of cations in the octahedral O sites, suggesting that some Ca may be present in the tetrahedral T sites (notations after Louisnathan 1971). The composition in end-members corresponds to a gehlenite (57.52 mol.%) with substantial åkermanite (34.21 mol.%) and minor Na-melilite (3.14 mol.%) and Fe-åkermanite (5.13 mol.%).

Wollastonite-2M occurs as rod-shaped crystals, of up to 5 mm in length, which generally are grouped in bunches and forms veins or nests (remnants?) isolated in the spurrite mass. The chemical composition of a selected sample (P 55) is (in wt.% oxides): $\text{SiO}_2 = 51.27$, $\text{Al}_2\text{O}_3 = 0.15$, $\text{FeO} = 0.02$, $\text{MgO} = 0.10$, $\text{MnO} = 0.01$, $\text{CaO} = 48.30$. The resulting chemical-structural formula is $(\text{Ca}_{6.020}\text{Fe}^{2+}_{0.002}\text{Mg}_{0.017}\text{Mn}_{0.001})(\text{Si}_{0.5964}\text{Al}_{0.021})\text{O}_{18}$. The indices of refraction measured for the same sample are $\alpha = 1.619(2)$, $\beta = 1.630(1)$ and $\gamma = 1.634(2)$. The mineral is optically negative, with $2V$ (measured) = 62° , which perfectly matches with the calculated value ($2V_{\text{calc}} = 61.83^\circ$). The unit-cell parameters, as obtained by least-squares refinement of the X-ray powder data are $a = 15.400(5)$ Å, $b = 7.318(3)$ Å, $c = 7.061(2)$ Å, $\beta = 95.31(2)^\circ$.

Calcic **garnets** occur as euhedral to subhedral crystals up to 1 mm in diameter, surrounded by the spurrite mass. The crystals are compositionally zoned, but the variations are very modest; Ti and Fe are slightly enriched in the outer zones. Two of the three generations of garnet described by Marincea *et al.* (2001) may be recognized on the basis of textural relationships. A first generation of garnet consists in Ti-poor grossular, in fact a solid solution of grossular (74.05 mol.%), andradite (25.19 mol.%), and minor "pyralspite" (0.76 mol.%); this garnet generation was considered by Pascal *et al.* (2001) to be in equilibrium with gehlenite. Another generation of garnet, which locally rims perovskite, corresponds to the third generation identified by Marincea *et al.* (2001) and is a titanian andradite that generally displays an increase in both andradite and morimotoite contents, compensated by a slight decrease of the grossular component, from core to rim. The mean chemical composition indicate an andradite (62.08 mol.%), with significant grossular (28.67 mol.%), high morimotoite component (8.35 mol.%) and minor pyralspite (0.80 mol.%).

Hydroxyllellestadite occurs as scattered at random grains surrounded by the spurrite mass. The mineral has euhedral to subhedral, equant to short prismatic habit. Grains have an average diameter of 0.1 mm with a maximum length of about 0.2 mm. No chemical or optical zoning was observed. The average chemical composition recorded for a selected sample of hydroxyllellestadite from the spurrite exoskarn is (in wt.% oxides): $\text{SiO}_2 = 15.57$, $\text{SO}_3 = 21.05$, $\text{P}_2\text{O}_5 = 5.38$, $\text{Al}_2\text{O}_3 = 0.03$, $\text{CaO} = 55.58$, $\text{FeO} = 0.17$, $\text{MnO} = 0.04$, $\text{Na}_2\text{O} = 0.23$, $\text{K}_2\text{O} = 0.03$, $\text{F} = 0.25$, $\text{Cl} = 0.09$, H_2O (calc.) = 1.58, $\text{O} = (\text{F}, \text{Cl}) = -0.13$. This composition, calculated on the basis of 3 (Si+S+P) and 13 (O,OH,F,Cl) per formula unit leads to the crystal-chemical formula:



The assemblages of metasomatic minerals described before may be ascribed to a paragenesis that corresponds to early metasomatic events. Textures such as the growth of vesuvianite on

gehlenite or the growth of titanian andradite on perovskite indicate that the primary assemblages were locally overprinted by secondary ones, defining a subsequent metasomatism and consequently a late metasomatic paragenesis. As observed by Marincea *et al.* (2001) subsequent hydrothermal and weathering overprint on the primary assemblages resulted in the formation of three secondary parageneses (1) an early hydrothermal one that includes scawtite, xonotlite, afwillite, thaumasite and hibschite; (2) a late hydrothermal one that includes 11 Å tobermorite, riversideite, thomsonite, gismondine, aragonite, calcite and (3) a weathering paragenesis that includes plombière, portlandite, and allophane. All these events contributed to the actual appearance of the spurrite-bearing exoskarn which is, however, the less altered rock from Cornet Hill.

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FOUR IMPORTANT NATURAL HAZARDS FROM ROMANIA

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1. Hazards In Romania

In time, all subgroups of natural hazards (cosmic, geological, hydro-meteorological and biological) have been recorded in Romania. Types of natural hazard are very numerous (over 50). Sometimes, some of them have acted in periods of maximum vulnerability of the society and of the environment, causing real disasters. The most numerous ones have been the hydro-meteorological and perhaps the biological subgroups, followed by geological ones and, finally, with negligible frequency and consequences, by the cosmic hazards. An attempt to classify the natural hazard group known in Romania is presented in Table 1, detailed on subgroups, and subcategories.

Table 1. Natural hazards which affected or which may affect Romania.

SUBGROUPS	CATEGORIES	SUBCATEGORIES	TIPES
1.Cosmic (astrophysics) hazards	Cosmic corps fall		Meteors fall
	Cosmic corps clink		Comets, asteroids, stars clink
	Cosmic corps blast		Gamma radiations
2.Geological hazards	Hazards produced by internal factors of the Earth		Earthquakes
			Volcanic eruptions
	Hazards produced by external factors of the Earth	Movement of released soils, roks and sediments masses	Landslides
			Falls, rolling land-slide or crumblingof rocks
3.Hydro-meteorology- cal hazards		Movement of snow and ice masses	Avalanches
	Movement of air masses		Storms, Blizzards, Tornados
	Movement of water masses	Movement of fresh water	Water flow, Torrents, Floods
		Movement of sea water	Storm waves
		Movement of fresh and sea waters	Floods on the Danube
	Electrical discharges		Lightnings, Thunders
	Frost phenomena of water	Frost water in air	Fogs, Hails
		Frost water on rivers	Ice floes, Ice bridges
	Moisture deficiency		Droughts
	Excessive temperatures		Very high temperatures
			Very low temperatures
			Arsons of forest
4.Biological hazards	Epidemics		Arsons of land
		Epidemics caused by bacteria	Plague, Cholera, Anthrax, Leprosy, Brucellosis
		Epidemics caused by viruses	Smallpox, Encephalitis, Meningitis, Malaria, Influenza, West Nile, SARS, HIV
		Epidemics caused by rickettsii	Foot and mouth disease, Typhus
		Epidemics caused by toxins	Botulism
		Epidemics caused by unknown causes	Balkan endemic nephropathy (NEB)
	Epizootics	For people and animals	Cholera, Plague, Brucellosis, SARS, Foot and mouth disease, Glanders, Ornitoza-psittacosis
		For animals	Pig pesta
	Invasions of insects		Caterpillars invasion
			Grasshoppers invasion

Various natural hazards (cosmic, geological, atmospherically, hydrological and biological) have been recorded in Romania. Nevertheless, four from the most important hazards, regarding the

number of dead or affected persons, or economic damages, are the earthquakes, floods, droughts and excessive temperatures.

2. Earthquakes

In connection with earthquakes felt in Romania, there are several main epicenter areas (Vrancea, Fagaras, Banat, and Black Sea), some minor areas and regions in the neighborhood countries. The most important, by energy and frequency effects, are Vrancea earthquakes. The seismic activity is mostly located at depths of 70-160 km (intermediate depth), in an epicenter area of approximately 2000 km²

There is also some minor crustal activity with depths down to 40 km, extending on an area up to 7000 km². Inside the Carpathian arc, they felt relatively weak. Usually, intermediate depth earthquakes of moderate magnitude are single shock ones, but the strong events are accompanied by numerous replicas. The November, 10th, 1940 event has a magnitude of 7.4.

Fagaras earthquakes are polikinetik ones (multiple shocks). They have a long duration and moderate intensity, reaching up to VII (Lazarescu, 1980). The hypocenter depth is crustal one (10-20 km), they being connected to several major fault systems separating Transylvania from the Fagaras Mountains. Banat earthquakes (Danubian ones) are generated along the fractures of the basement, being located between the Varset Massif (in Serbia), Vinga and Moldova Noua. They are polikinetik events (multiple shocks) with normal depth. They have reached the intensity up to VII and their macro seismic area is narrow.

The Pontic earthquakes are located in the proximity of the Black Sea coast, usually between Mangalia and Sabla area (Bulgaria). They occur frequently (2-3 per year), are polikinetik ones and have a low energy. Their occurrence is at the intersections of several important faults, both on land and on the sea self. Almost twice the millennium such destructive earthquakes have been recorded on the Bulgarian territory.

The secondary epicenter areas are related to faults of the basement, occurring at depths of 10-20 km. They have a local nature. Most active are those connected with parallel fractures limiting the East-European Platform, after then it goes down in steps to Carpathian orogen (Botosani Dorohoi and Avramesti Barlad); the ones related to the extension towards North and East, at a basement level, of several faults of North Dobrudja orogen (Tecuci-Tudor Vladimirescu, Marasesti-Focsani-Namoloasa, Tulcea-Isaccea-Galati); also the earthquakes located in the area of faults placed in the basement of the central part of Transylvania Depression (Tarnavelor area).

On the Romanian territory, earthquakes having the epicentral area in neighboring countries (Bulgaria, Serbia) or in Greece or Turkey are also recorded. The Bulgarian ones are placed on the trench structure existing along Marita river, or are linked to the fault system limiting Rhodopi Mountains. Earthquakes in Serbia are associated to the trench existing along Morava valley.

3. Floods

Floods are among the most popular in the area and most common hazard that occur in Romania, sometimes having great economic and social consequences. Floods usually take place over the course of internal rivers and of the Danube. In these cases a small river having usually small debits, increase dramatically the amount of transported water, producing on overflow and filling the major riverbed. Annual occurrence is around 10-15 floods, with greater frequency at medium altitudes (in the mountains and Sub-Carpathians) and lower frequency towards the plain. Catastrophic floods are produced every 50 -100 years because of torrential rains combined with sudden snow melting. They are most frequently occurring in the western part of the country.

Spring held regularly floods by melting snow, above which the overlap of spring rains. At the beginning of summer, they are wide spread in the country, being due to heavy rain. Autumn are rarer, due to rainfall during October-November and having a higher frequency in Banat and Oltenia. It is estimated that the maximum exposed flooding in our country is about 3.5 million ha, representing 15% of the country. In 2005, damage to the national economy has exceeded 1.7 billion dollars. For the floods from 2010, the damage was not yet calculated.

4. Droughts

Droughts occur in May and have drastic effects in the areas of plain, non-irrigated land. In Baragan and Dobrogea, the average duration of dry intervals is over 20 days, in the Romanian Plain, in the Plateau of Moldavia is 15-19 days, and for the rest of the country is about 17 days. Although droughts can register throughout all the year, the most numerous are produced in late summer and early autumn. The territories, which are exposed to drought, are in the Southeast of the country (Baragan, Dobrogea, Moldova Southern Plateau).

Throughout the whole country, drought in the summer of 2000, extended until the winter of 2001, has been the strongest of the past 100 years. It affected over 3.7 million hectares of land. The river has fallen considerably, the Danube has been the lowest level from 1840 onwards (when it started to be monitored its level). It was affected also the national energy system due to a low level in lakes. Damage to the national economy has exceeded 3 billion dollars.

5. Excessive Temperatures

Excessive temperatures which is not usual in the area of Romania, with temperate climate, those are either too high during summer or in winter too low. They persist for several days in a row. Temperatures too low or too high are not proper to human bodies when persist a longer period.

Very high temperatures accompanied by excessive moisture, are usually caused by warm air masses, coming from Africa across the Mediterranean Sea. They may cause, especially in urban areas, a number of deaths among young children, and aged, sick and disabled people. When the heat wave persists for a longer period, drought can occur, triggering fires (in the woods or areas with dry vegetation). Alternatively, they are activated epidemic outbreaks of epizootic diseases, putting in danger the agricultural-forest fund.

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REGENERATION OF ENDOGENOUS ORE DEPOSITS IN THE FRAME OF GLOBAL TECTONIC CONCEPT

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Generalities

The word regeneration (lat. *regenerare*) has an extremely broad use in Earth Sciences. According to various authors the meanings of this concept suggest the diversity of its fields of application, but usually involving the significance of remake-restore or rejuvenate in mineralogy, petrology, ore deposits, geochemistry, tectonics etc. Consequently, magmatic, post-magmatic, metamorphic, or tectonic regenerations have been notified.

Even a brief analysis of the use of this term in Geological Sciences allows to discern that behind it are hidden too many geological processes. Our contribution aims to make a revision of the geological conditions that favor and produce the regeneration, to stress the genetic type of regeneration and to clearly describe the newly formed products (regenerated).

Regeneration of the ore deposits

The regeneration of the ore deposits as stated by Schneiderhöhn (1953; 1962) is of high scientific interest for the understanding of the geological processes but it poses also an important practical significance. The statements made by the above cited author were more or less restricted by the general level of knowledge of its times. The huge progress made since the 60ies certainly asks for revision and reconsideration of the concept in accordance with the up to date petrometallogenetic interpretations and in close relationships with the global tectonic theory. A first attempt in this direction was made by Mârza (1999): *the regeneration of the ore deposits must be faced and examined in the light of the actual geological concepts (global tectonics, petrometallogeny)* (p. 329).¹⁾

The father of the regeneration of the ore deposits (Schneiderhöhn, 1953; 1962) interpreted the magmatism and the related metallogeny as a result of geosynclinal evolution, in accordance with the accepted theories of the moment. He used the hypothesis of Hans Stille who admitted the regeneration of ancient folded areas, which rises again to the surface by tectonic regeneration.

The expression regeneration of the ore deposits is not entirely correct because the term ore deposit imply also an economic aspect. Of course, we are not denying the real significance of Schneiderhöhn's statements which refer in fact to the re-concentration of the metals that is similar with the genesis of the new ore bodies/mineralizations. Furthermore, the classic theory refers only to the metals, but in the nature the metals/metallic minerals are tightly related to their host rocks and the regeneration acts both on rocks and ores (orthomagmatic, skarn, hydrothermal, volcanogenic etc.).

Regenerative processing

Essentially, the theory of regeneration as stated by Schneiderhöhn stress on the re-concentration of mineral resources, mainly metallic, formed during a previous geotectonic cycle by subsequent endogenous geologic processes (magmatic, metamorphic). Certainly these transformations took place but some authors talk also about exogenous regeneration, and consequently, the real significance and the specific paths of the regenerative process are not entirely delineated. This is the reason why Mârza (2010) integrates the regeneration of the mineralizations in the broader concept of concentrative petrometallogenetic processing and re-processing of metals. Taking into account this consideration ... the primitive terrestrial crust was born tabula rasa in

¹⁾ See also:- Popescu C., G. Metalogenie aplicata si prognoza geologica. Partea I-a , Centrul de multiplicare al Univ.Buc., 1981-Note of eds.

respect of mineralizations and their formation is due to the set up, the evolution and the petrometallogenetic processing of regional geotectonic provinces (Caledonian, Hercynian, Laramian, Alpine etc.) .

Below will be examined the regeneration of the endogenous related mineralizations in the framework of the concept of selective and concentrative petrometallogenetic processing within the mantle, and the crust as well as within the main geotectonic settings.

Mantle

The physical-chemical changes from the mantle are very important for the evolution of the crust and the geological process developed within the crust. Within the upper mantle takes place the proto-petrogenesis of peridotites (plagioclase, spinel, or garnet bearing). Deep mantle plumes contribute to partial melting of the upper mantle, too. The result is a continuous episodic melting and local crystallization of these products including also their bulk metallic minerals component in accordance with ultrabasic petrometallogenetic affinity. The presence of dunitic xenoliths in massive orthomagmatic chromite deposits certifies the movements of ultrabasic melts with already segregated metallic minerals or with the segregation in progress. This situation corresponds to orthomagmatic mantle-level regeneration.

Mantle-crust interaction

The mantle-crust boundary represents an area of permanent interaction in both senses, and consequently the regeneration is permanent. Furthermore, close to its boundary with the mantle the crust is dominated by intense granitisation and migmatites formation. Towards the surface, the intensity of the endogenous petrometallogeny diminished and the petrometallogenetic concentrative and selective processing and re-processing are controlled by the main geotectonic settings (drift, subduction zones, hot spots etc.).

Drifts

Generally speaking, the petrometallogeny of drift zones is characterized by a certain stability of oxidic ores (chromite, ilmenite, magnetite etc.). By contrast, the sulfide bearing ores formed by liquation (Cu-Ni, Co, PGE etc.) show an important capacity of migration. The less stable are the volcanogenic mineralizations (Fe-Mn) formed at the level of the ocean floor, which are subjected to many transform factors. Similar peculiarities show the transform faults, too. The regeneration can occur either during the formation of the above mentioned ores, either during subsequent tectonic, magmatic or metamorphic processes. Among the regenerative changes we can mention zonality, crystals corrosion, reaction coronas, changes of the morphology of the ore bodies etc.

Subduction zones

The Andean-type subduction zones represent the most active and spectacular tectonic setting with metallogenetic implications. Within the subduction zones the regenerative petrometallogenetic post-magmatic reprocessing is represented by greisens, skarns, hydrothermalism. The subduction zones are the most favorable tectonic setting for intermediate and acid magma genesis, and related metallogeny. The source of metals is represented by the melted – re-melted rocks and surrounding rocks, the metals being re-concentrated by post-magmatic, meteoric, connate or other types of fluids. The petrogenesis of subduction zones may last for tens of millions of years and consequently the related metallogeny may cover long time intervals with recurrent re-processing and re-concentration of the metallic budget of the geotectonic structure in accordance with geochemical and thermodynamic specificities.

Many examples of regenerated mineralizations and ore deposits are known in mineralogy and ore deposit literature. The more frequent refers to regenerated hydrothermal sulfide deposits (Cu, Pb-Zn, Cu, Sb, As, Hg etc.), precious metals (Au, Ag), while the oxidic deposits (magnetite, hematite, uraninite) are less present.

Island arc subduction zones follow a similar petrometallogeny, with important petrometallogenetic regeneration especially during the so-called *regenerative island arc stage* (Mitchell and Bell, 1973). This evolution stage is dominated by intensive tectonic activity, with important fault structures subsequently transformed in large scale ore bodies (veins, breccia dykes, and breccia pipes).

The regeneration of subduction zones can be also faced at a different level: reprocessing of ancient subduction zones in subsequent tectono-magmatic cycles, like Laramian subduction zones reactivated and reprocessed during Neogene within Apuseni Mountains. In fact this type of observation was highlighted by Schneiderhöhn when he proposed the theory of *the regeneration of the ore deposits*. It is more than obvious that cyclic geotectonic reprocessing led to metal(s) selective enrichment that finally contribute to the formation of the ore bodies. The examples from Romania are more than representative, with anomalous enrichment in base metals (Baia Mare), Au-Ag $\pm$ Te (South Apuseni Mountains) or uranium (Băița Bihor).²⁾

Conclusions

The endogenous petrometallogeny can act also as regenerative process. This peculiarity is responsible for selective re-concentration of mineral resources (metallic and non-metallic) from previous protors and the result is the genesis of new/enriched mineralizations/ore deposits.

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CORRELATION OF THE EARLY PALEOZOIC METALLOGENESIS IN THE WESTERN AND EASTERN CARPATHIANS

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The Carpathian Mountains comprise numerous fragments of pre-Alpine continental crust, present in all segments of the orogen, although with variable extent and lithologic composition. Such pre-Alpine terranes contain rocks that recorded tectono-thermal events with various ages: Precambrian, early Paleozoic (Caledonian) and late Paleozoic (Variscan). Early Paleozoic formations are known for a long time in the Western and Eastern Carpathians. Although similarities between these terranes were mentioned occasionally (e.g. Kräutner et al., 1980;1987), they are still perceived as different entities and referred to under different names. Here we plead for the equivalence of the early Paleozoic formations of the Eastern and Western Carpathians, which also implies an initial continuity of the early Paleozoic metallogenic zones in the two orogenic sectors.

The pre-Alpine terranes of the Eastern Carpathians occur between the flysch belt (to the east) and the Neogene volcanic chain (to the west), forming the basement of the Crystalline-Mesozoic zone. The pre-Alpine crust of the Eastern Carpathians was sliced by Alpine thrusts, which generated the Bucovinian nappe, the Sub-Bucovinian nappe and several Infrabucovinian nappes. The basement of the Bucovinian and Sub-Bucovinian nappes contains successions with ages from late Proterozoic to early Paleozoic. All these rocks were involved in an Ordovician collision (Pană et al., 2002; Munteanu and Tatu, 2003; Balintoni et al., 2009).

The early Paleozoic successions of the Eastern Carpathians were subjected to greenschist facies metamorphism and form the Tulgheş Group. The age of the Tulgheş Group is Ordovician (e.g. Vaida, 1999, Pană et al., 2002). The Tulgheş Group was accumulated in volcanic arc geotectonic setting (e.g. Kräutner, 1997; Munteanu and Tatu, 2003). The Tulgheş Group is divided in four formations based on the dominant conditions of accumulation, corresponding to different protoliths. Tg1 is psammitic (sericite quartzite and sericite-chlorite schists). Tg2 is characterised by the presence of graphitic rocks (sericite-chlorite ± graphite schists, graphitic quartzites ± Mn mineralisation ± barite mineralisation, carbonate rocks, metabasites). The Mn deposits hosted in the black quartzites of the Tg2 formation have been mined for ca. 200 years, in several places (e.g. Dadu, Oiţa, Tolovanu, Arşiţa, Teresia, Sărişor, Dealul Rusului). The Tg2 formation is supposed to have formed in a back-arc basin (Munteanu and Tatu, 2003). Tg3 is a prevalently volcanic formation (felsic volcanics, sericite-chlorite schists, rare basic rocks). The Tg3 formation contains stratiform volcano-sedimentary base metal deposits of Kuroko-type (e.g. Burloaia, Fundul Moldovei, Mănăilă, Leşu Ursului, Bălan). Tg4 is a lithologically varied formation (sericite-chlorite schists, metagreywackes, greenschists, acid volcanics, metacherts, carbonates), possibly gathering parts of a fore-arc complex (Munteanu and Tatu, 2003).

The Tulgheş Group has a lithostratigraphic correspondent in the Gelnica Group of the Western Carpathians. The volcano-sedimentary Gelnica Group builds up a substantial part of the early Paleozoic in the Gemeric Unit. It is composed mainly of flysch sedimentary successions with dominant fractions of redeposited acid volcanoclastic material, which were metamorphosed under greenschist facies thermobaric conditions. The age of the Gelnica Group is Ordovician (Vozarova et al., 2008). It contains metabasalts with various geochemical signatures: back-arc, E-MORB/intraplate and calc-alkaline (Ivan, 1994). The Gelnica Group contains graphitic rocks with Mn mineralisation (Rojkovic, 2001), similar with the Tg2 formation of the Tulgheş Group, and felsic volcanics with stratiform volcano-sedimentary base metal deposits, similar with the Tg3 formation of the Tulgheş Group. According to the descriptions in the literature (Hîrtopanu and Scott, 1999; Rojkovic, 2001; Munteanu et al., 2004), the Mn mineralisation in the Gelnica and Tulgheş Groups are very similar in their lithology and mineralogy.

The similar features of the Gelnica and Tulgheş Groups indicate an initial continuity between the early Paleozoic terranes from the Eastern and Western Carpathians. This continuity argues for an extended early Paleozoic metallogenetic province in the Carpathians, which was arc-related and can be divided in two areas with distinct types of mineralisation: Mn ± Ba associated with graphitic rocks, and syndepositional (stratiform) volcano-sedimentary base metal sulfides. The early Paleozoic terranes inherited by the Carpathian Mountains were fragmented during the Alpine orogenic cycle.*) The Alpine dispersion of the pre-Alpine terranes in the Carpathians was caused by Triassic-Jurassic rifts, which evolved to ocean basins (Meliata, Vardar-Transylvanian, Căcin-Ceahlău-Severin). The re-assembly of the dispersed terranes was accomplished during the middle Cretaceous collisional processes in a new configuration, which explains their present discontinuity.

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EUROGEOSOURCE – A EUROPEAN UNION INFORMATION AND POLICY SUPPORT SYSTEM FOR SUSTAINABLE SUPPLY OF EUROPE WITH ENERGY AND MINERAL RESOURCES

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The INSPIRE Directive (Infrastructure for Spatial Information in the European Community) 2007/2/EC issued a set of recommendations regarding the administration of the spatial databases in the countries members of the European Union, on the purpose of an effective environmental protection. This implies the achievement of the interoperability and harmonisation of spatial data sets and services from member countries.

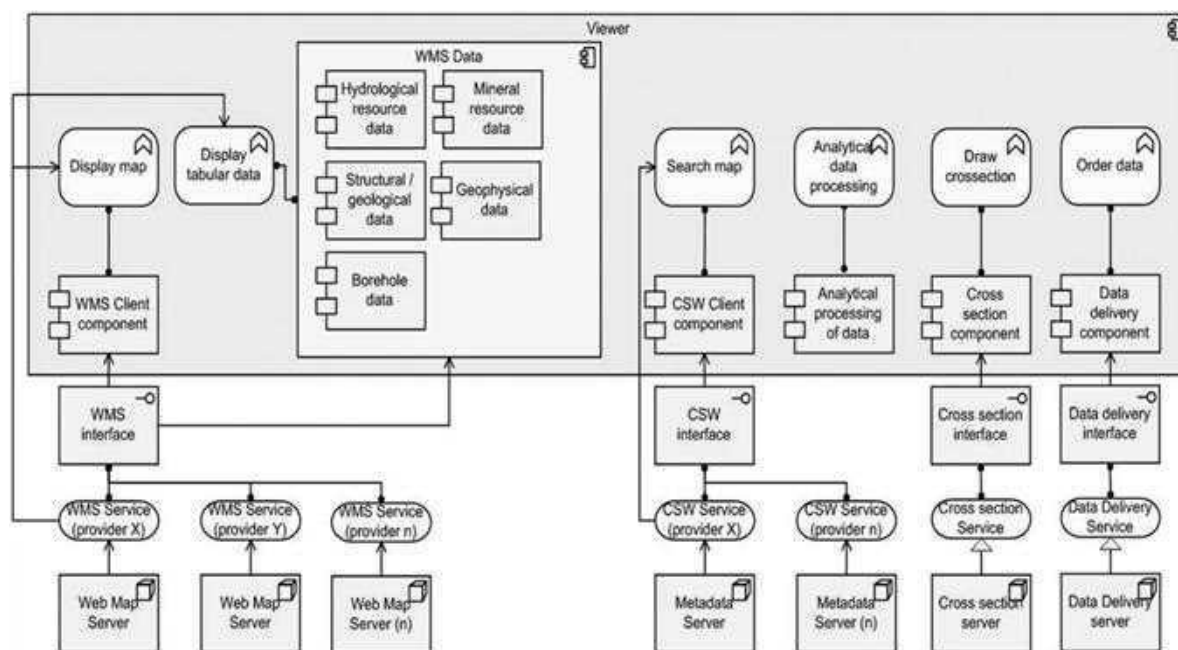


Fig. 1. Conceptual architecture of the EuroGeoSource system.
CSW = catalog service-web; WMS = web map service

There are themes of the INSPIRE Directive, which refer to geology, energy resources and mineral resources. These themes are addressed to by the EuroGeoSource project, co-financed by the European Union under the Information Communication Technologies Policy Support Programme (ICT PSP), part of the Competitiveness and Innovation Framework Programme (CIP). The main objective of the EuroGeoSource project is to develop the EU information and policy support system for a sustainable supply of Europe with energy and mineral resources. This implies the harmonisation of the data formats and classification between the participant countries.

The information will be accessed through a data portal (Fig. 1), which allows the access by Internet to the aggregated geographical information on geo-energy (oil, gas, coal etc.) and mineral resources (metallic and non-metallic minerals, industrial minerals and construction materials: gravel, sand, ornamental stone etc.), coming from a wide range of sources in a significant coverage area of Europe (the countries participating to the EuroGeoSource project are indicated in Fig. 2).



Fig. 2. Map of Europe with the countries that participate to the EuroGeoSource project

The EuroGeoSource portal will facilitate an easier harmonisation between the offer and demand on the market of mineral/energy resources. The users of the portal can be data/service providers or beneficiaries from a large spectrum of socio-economic affiliations: EU institutions, governmental organisations, private investors, academic institutions, NGOs, etc. Any organisation implied in the research and beneficiation of the energy/mineral resources could, on the one hand, use the portal in order to provide information about own activity and offer of services and products and, on the other hand, get information about other data and metadata providers of the portal. The information of the EuroGeoSource portal will be protected in order to restrict the public access only to data offered by the owners free of charge (Fig. 3).

The use of the EuroGeoSource portal would include the following basic sequence of operations:

- (1) The user selects the language.
- (2) The user browses the list of maps and chooses the dataset of interest based on the associated metadata; the dataset of interest is added as a layer to the geo-data viewer.
- (3) The dataset layer is queried at desired degree of detail in the map viewer.
- (4) The user collects the data of interest either free of charge or upon a fee, depending on the provider's requirements.

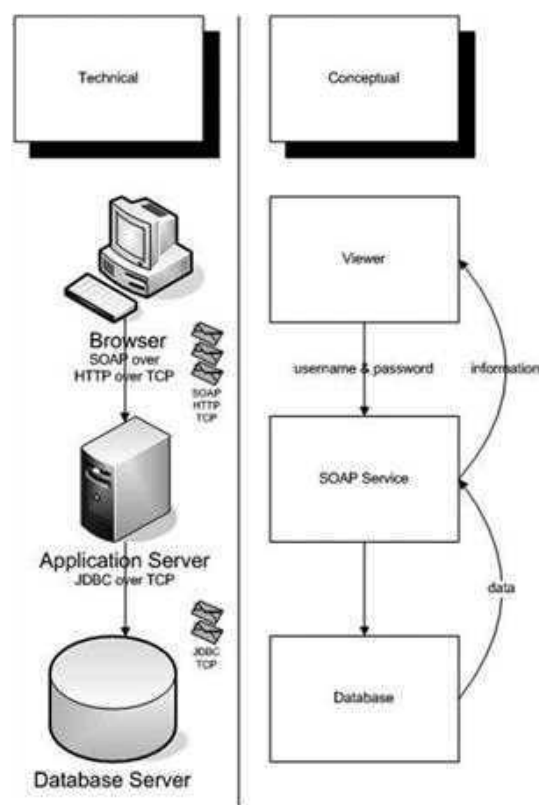


Fig. 3. EuroGeoSource technical and conceptual security scheme.

HTTP = hypertext transfer protocol; JDBC = Java database connectivity; SOAP = simple object access protocol; TCP = transmission control protocol.

Using the EuroGeoSource portal, investors will have an easier way of finding the information on the resources they need and on the Governmental institutions they have to address to, in order to get access to certain resources. The Governmental institutions in charge with the administration of the energy/mineral resources will be able to advertise their services to a broader segment of potential users. The regional and European organisations will have access to a larger and more homogeneous database on the energy/mineral resources in order to make socio-economic forecasts and development plans.

Information on the EuroGeoSource project can be found on the web page <http://www.eurogeosource.eu/>, created by the Geological Institute of Romania, the coordinator of the Workpackage 11 Awareness, Dissemination and Exploitation of the project.

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<http://www.inspire-geoportal.eu/index.cfm/pageid/241/documentid/468/doctype/0>

UNE MINÉRALISATION DU TYPE MISSISSIPPI VALEY LOGÉE DANS LE DÉVONIEN SUPÉRIEUR ÉPIMÉTAMORPHIQUE DE LA PARTIE NO DU MASSIF POIANA RUSCĂ (CARPATES MÉRIDIONALES)

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La minéralisation qui fait l'objet de notre article est située dans la partie de NO de l'Unité épimétamorphique du Massif Poiana Ruscă, développé dans l'extrémité de NO de la courbure des Carpates Méridionales. Les formations environnantes de la minéralisation ont l'âge dévonien supérieur (données palynologique – Kräutner et al., 1973 ; Mureșan, 1998), qui ont subi l'épimétamorphisme régional sudet (données d'âge absolu K/Ar – Kräutner et al., 1973). Du point de vue lithostratigraphique, la minéralisation est logée (Mureșan, 1973) dans les quartzites à séricite du Niveau des Quartzites Noirs de Scaunu, au-dessus et près des Calcaires de Tomești-Groși.

La minéralisation en question apparaît à 5 km vers SE de localité Românești. Elle se situe près et à l'est de Sommet Scaunul, étant connue dans la site Poiana Știolnii (en roumaine populaire, « știolna » signifie galerie), c'est-à-dire dans le versant droit de la partie supérieure de Vallée Palcului (affluent gauche de la Vallée Fărășești).

Schafarzik (1906) mentionne dans ce lieu, pour la première fois, un minéral à galène enlevé antérieurement par quelques anciennes escavations. Plus tard (1960-1963), l'Entreprise de découvertes géologiques (ISEM) a effectué des travaux miniers et de surface (tranchées, puits et des galeries courtes). Des descriptions du minéral ont été faites par Mureșan (1960, 1964, 1973), Hanomolo (1962, 1963), Chivu (1963) et Superceanu (1967).

Les travaux miniers anciens et récents ont montré que la minéralisation présente une concordance vis-à-vis des schistes cristallins environnants, étant orientée N-S / 30-35° O (dans une succession nonrenversée tectoniquement). La zone minéralisée a une longueur connue à peu près de 200 m et une épaisseur moyenne de quelques mètres, l'épaisseur maximale (25 m) étant observée dans la galerie III (orientée E-O, transversalement sur la minéralisation). Là, la coupe transversale de la minéralisation relève principalement la zonalité de la celle-ci (de l'est vers l'ouest, c'est-à-dire de la partie inférieure vers la partie supérieure du corps minéralisé): **(a)** quartzite à barytine (7 m), **(b)** quartzite (3 m), **(c)** quartzite à fluorine et barytine (5 m), **(d)** quartzite à barytine, fluorine et galène (10 m) – tous ces quartzites représentent des gels siliceux métamorphisés (voir la description du quartz). Selon nous, cette succession représente en même temps la situation antémétamorphique et aussi l'ordre de la déposition existante pendant la formation du corps minéralisé; il en résulte que celui-ci a une structure primaire multistratifiée. Du point de vue économique, la dernière sous-zone (celle supérieure) est la plus intéressante. La zone minéralisée dans son ensemble est complètement dépourvue de géodes.

Les minéraux primaires métallifères sont représentés principalement par la galène et par des petites quantités de pyrite, chalcopryrite, tétraédrite, blende, hématite, sidérite); **les minéraux primaires nonmétallifères**: dominants: quartz, barytine, fluorine; subordonnés: calcite, dolomite, séricite, rarement withérite. Le trait minéralogique principal du minéral est la triade barytine, fluorine, galène, qui domine nettement (en dehors du quartz) dans la minéralisation en question.

La barytine, à l'extinction ondulatoire, est finement grainulaire, constituant fréquemment des zones compactes (en association avec la galène et la fluorine), des agrégats, des plages ou des grains. **La galène**, toujours à cristallinité fine; constitue des lentilles, des petits nids à l'aspect de boudines; ce minéral contient souvent des grains petits et des inclusions de blende, de freibergite (Superceanu, 1967) et des grains de pyrite. La galène présente toujours une structure schisteuse qui est, parfois, plissée, constituant des microplis centimétriques, du type B1 (synmétamorphique), rencontrés aussi dans les roches cristallines environnantes. **La fluorine** a, comme d'habitude, la couleur violacée, rarement ayant une nuance verte; elle constitue des masses compactes ou des grains associés aux agrégats de barytine. **Le quartz**, le plus fréquent minéral dans la zone minéralisée (voir au-dessus la coupe transversale offerte par la galerie III), constitue des masses stratoïdes de quartzites à une structure finement mosaïquée (pavimenteuse), représentant des

anciens gels silicieux metamorphisés. Les individus de quartz présentent fréquemment une extinction ondulatoire. **La pyrite** apparaît comme des individus isolés, tant dans le minéral (sous forme de grains irréguliers) que dans les roches terrigènes cristallines immédiatement environnantes, ou constitue des cristaux idiomorphes, à l'axe A3 orientée parallèlement avec les linéations et les microplis B1 (synmétamorphiques, sudets) existantes dans les roches terrigènes et dans les calcaires.

Dans la zone supergène, ont pris naissance des minéraux secondaires: **pyromorphite, cérusite, krokoïte, anglésite**, toutes provenant par l'altération de la galène (Superceanu, 1967), **chalcosine, bornite, malachite, azurite** (les derniers quatre minéraux provenant par l'altération de la chalcopyrite), **limonite** (produite par l'oxydation de la pyrite et de la chalcopyrite).

Les analyses chimiques connues sont seulement partielles, faites sur les épreuves du minéral (récoltées dans quelques galeries, puits et tranchées, exécutées par ISEM); elles sont exécutées dans l'ancienne Entreprise de Prospections et de Laboratoires – Bucarest. Ces analyses relèvent les participations importantes du SO₄Ba (de quelques per-cent, jusqu'à 78 %), du Pb (des quelques dixièmes de per-cent, jusqu'à 22 %) et les quantités réduites de Cu (de traces, jusqu'à 1,66 %), Zn (des traces), As (des traces), CO₃Ba (très rare).

Il y a quelques aspects qui démontrent le métamorphisme régional subi par cette minéralisation: **(1)** la schistosité de la galène et le microplissement (centimétrique) de la celles-ci; l'axe des ces microplis est orienté NS, comme la structure B1 synmétamorphique B1 (sudète) existante dans les épimétamorphites environnantes; **(2)** l'extinction ondulatoire de la barytine et du quartz; **(3)** l'existence, parfois, de boudines dans les portions riches en galène; **(4)** la forme différente de la pyrite en fonction de la .contexte minéralogique (Ramdohr, 1969): **(a)** dans le minéral, constitue des grains irréguliers; **(b)** dans les schistes, constitue des individus idiomorphes; **(5)** l'inexistence des géodes dans le minéral. Les mobilisations hydrothermal-métamorphiques sont représentées par des rares et courts filonets à galène.

Pour établir la genèse primaire (antémétamorphique) de la minéralisation décrite, nous tenons compte de: **(1)** la concordance de la zone minéralisée avec la schistosité de stratification des roches cristallines environnantes; **(2)** sa composition minéralogique; **(3)** l'existence sous la zone minéralisée des roches calcaires épaisses (les Calcaires de Tomești-Groși); **(4)** sa ressemblance avec les minéralisations protérozoïques de plomb et zinc métamorphisées, logées dans les roches carbonatées du Groupe Rodna (par exemple, les gisements Valea Blaznei et Gușet) des Monts Rodna (Carpates Orientales), du type Mississippi Valley (étudiés par Udubașa, 1970, 1996). Tous ces aspects nous montrent que la minéralisation décrite est aussi du type Mississippi Valley. La genèse des gisements du type MV est encore disputée, surtout en ce qui concerne l'origine des éléments métallifères existants dans ce type de gisements. Il y a deux conceptions différentes qui admettent soit une origine continentale pour ceux-ci, soit une origine endogène (hydrothermale-sédimentaire). Puisque le transport sur la route continent-mer, est difficile à expliquer, tenant compte de l'instabilité des ions métallifères dans la présence des électrolithes existants dans les eaux marines, nous admettons la deuxième conception. Dans notre cas, ça signifie qu'auparavant, dans le milieu marin du Dévonien supérieur, débordaient un hydrotherme à une charge polymétallique (les éléments nonmétallifères, Si ; F, Ba etc y compris), qui a flocculé en contact avec les électrolithes de la mer. Dans notre cas, la nature colloïdale des hydrothermes est prouvée par: **(a)** la structure générale finement grainue du minéral; **(b)** la structure mosaïquée (pavimenteuse) finement grainue des masses quartzeuses. Ces aspects démontrent la recristallisation métamorphique de la masse géloïforme du minéral primaire. La minéralisation syngénétique résultée était concordante avec la stratification des sédiments environnants.

Nous mentionnons que dans le Carbonifère inférieur de l'Unité Épimétamorphique du Massif Poiana Ruscă, il y a aussi une minéralisation du type Mississippi Valley (Kräutner, 1964) représentée par les dolomites à blende et galène, logées dans la Vallée Dobra. Quoique cette minéralisation et celle décrite par nous ont la même genèse, elles diffèrent tant par leur position stratigraphique que par leur composition minéralogique, plus simple (seulement blende et galène) pour celle de la Vallée Dobra.

Avec cette occasion, nous dénommons l'entité métallifère décrite: « **la minéralisation de**

galène, barytine et fluorine Valea Ştiolnii – Româneşti » ou simplement: « la minéralisation Valea Ştiolnii – Româneşti ».

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THE SELENIUM AND SE-MINERALS IN THE SĂCĂRÂMB ORE DEPOSITS – METALIFERI MOUNTAINS., ROMANIA

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Telluride bearing gold and silver ore deposit at Săcărâmb is part of the Golden Quadrilateral area situated in the Metaliferi Mountains and this is the largest telluride mineral accumulation in Romania and Europe. Genetically, it falls within the gold–silver hydrothermal deposits with tellurides hosted into quartz veins. At Săcărâmb, the base–metal ore veins are hosted into an andesitic stockwork generated by the Neogene calc-alkaline magmatic events in the Metaliferi Mountains. The ore body extends over 1 km strike and about 600 m in depth.(Fig. 1)

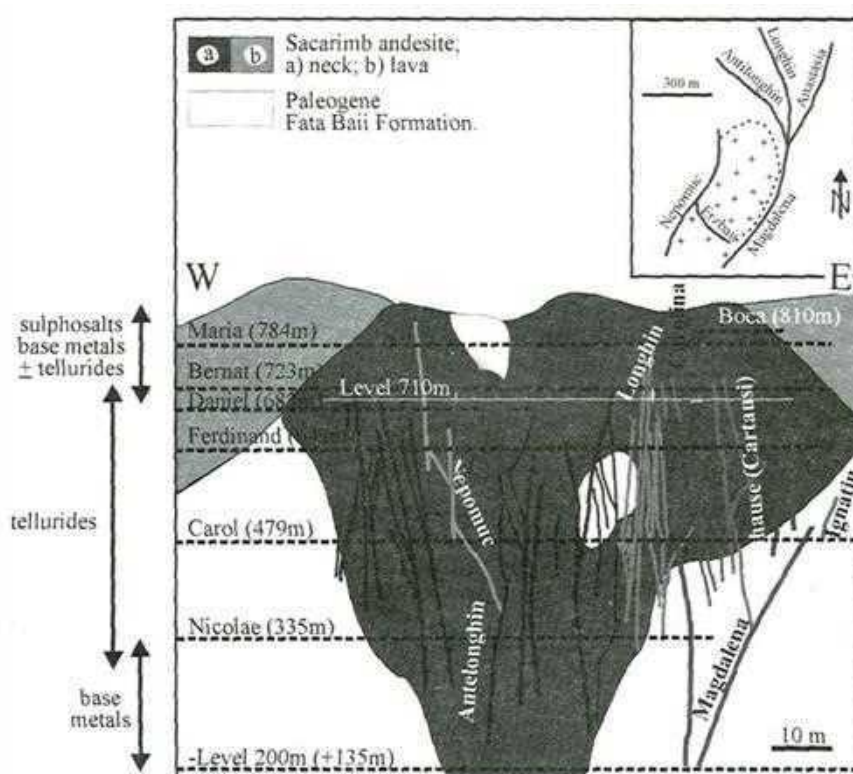


Fig. 1. Schematic cross-section of the Săcărâmb deposit. Inset shows a plan view of central part of the sistem illustrating vein branching at or near the contacts of the intrusive bodies (after Udubașa et al., 1992 and Berbeleac et al., 1995)

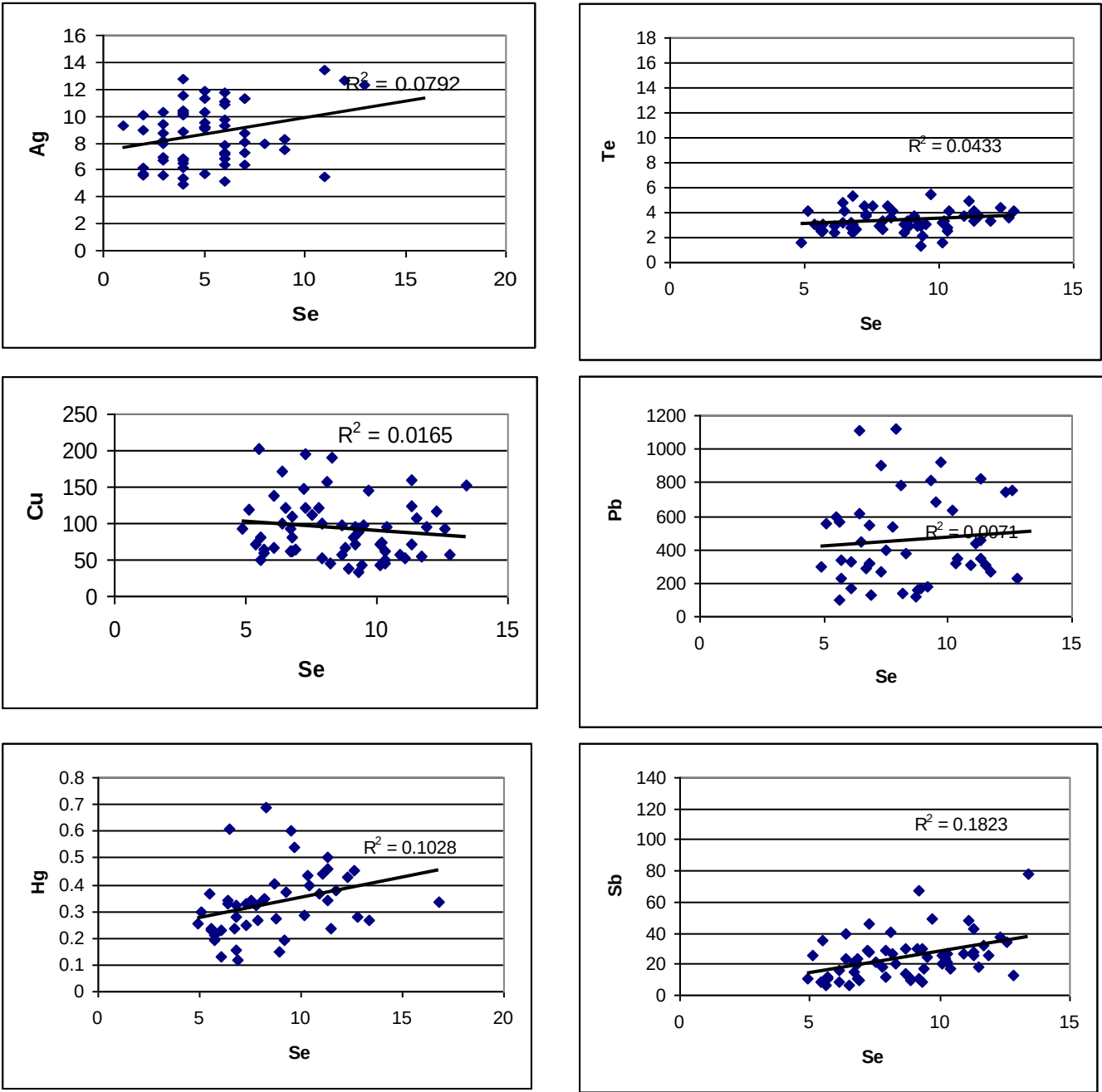
Over 100 mineral species have been identified in the Săcărâmb ore deposit and a total of 14 minerals contain Au, Ag, Te; some of them have been firstly described in the world (nagyagite, petzite, krennerite, stuetzite, muthmannite, museumite).

Since recently, tellurium was considered only from scientific – mineralogical point of view and there was no interest for its resource estimation in Romania. Only in 2005 this element started to be considered as a useful component, when it was used by the company First Solar, USA, in the construction of solar panels using photovoltaic cells based on Cd-Te technology. For more details see Popescu Gh., Neacșu A. (2008).

Our paperwork presents the results of the researches looking resources hosted into three waste dumps (Sectors I, II and III – at Săcărâmb) and into the Iazul Avariatic / Damaged Tailings Dam at Certej. Tellurium and selenium grades have been determined using ICP-MS method on the previously analyzed samples using Au-AA26 method for Au and Ag.

PLATE 1.

The correlation diagrams of selenium from the three waste dumps of Certej



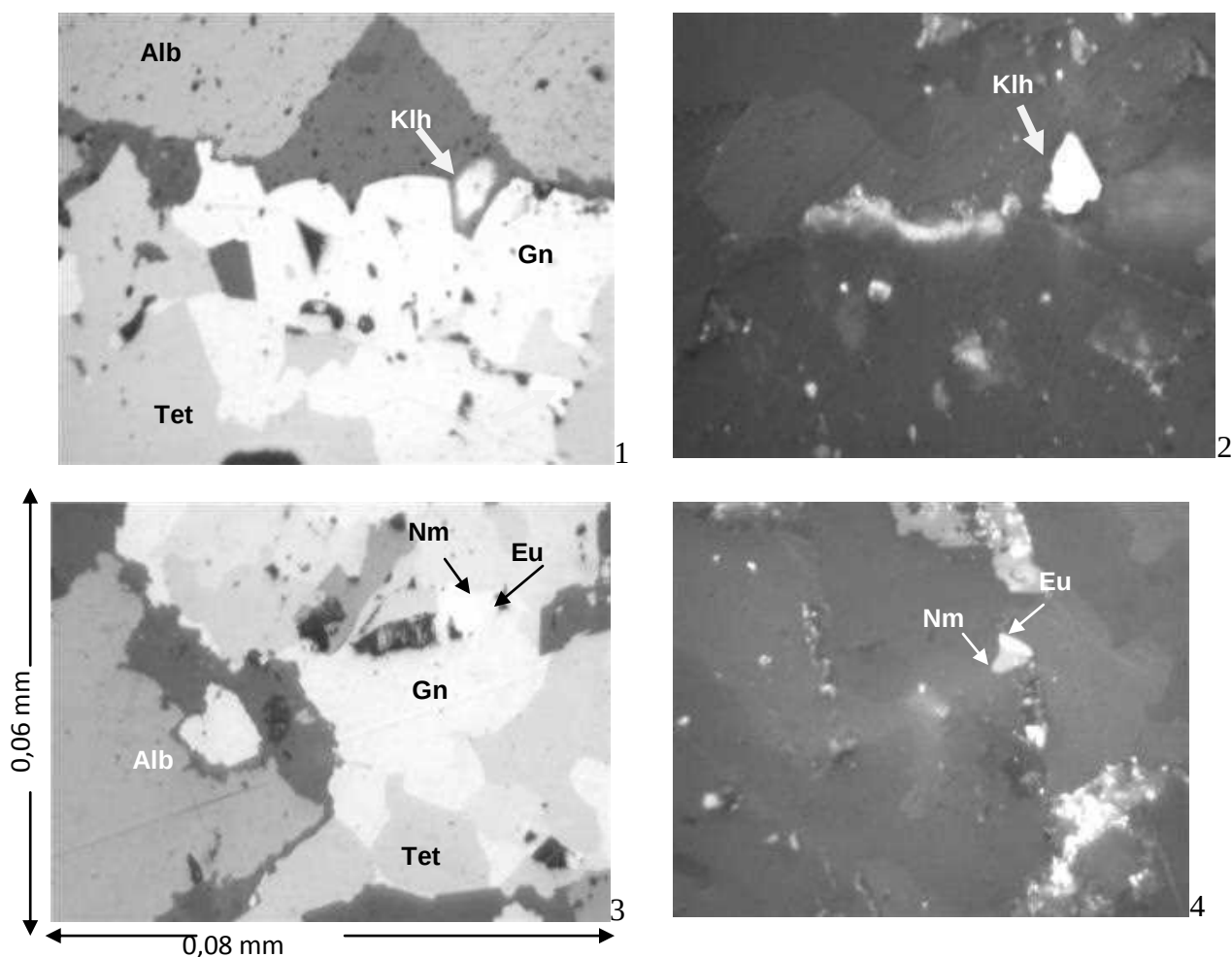


Fig. 2. Microscopic image with klockmannite (foto 1, NII and foto 2, N+) showing a strong pleochroism and anisotropism;naumannite and eucairite are associated with galena, hessite, tetraedrite and alabandite (foto 3, NII and foto 4, N+).Gn – galenite, Tet – tetrahedrite, Alb – alabandite, Klh – klockmannite, Nm – naumannite, Eu – eucairite.

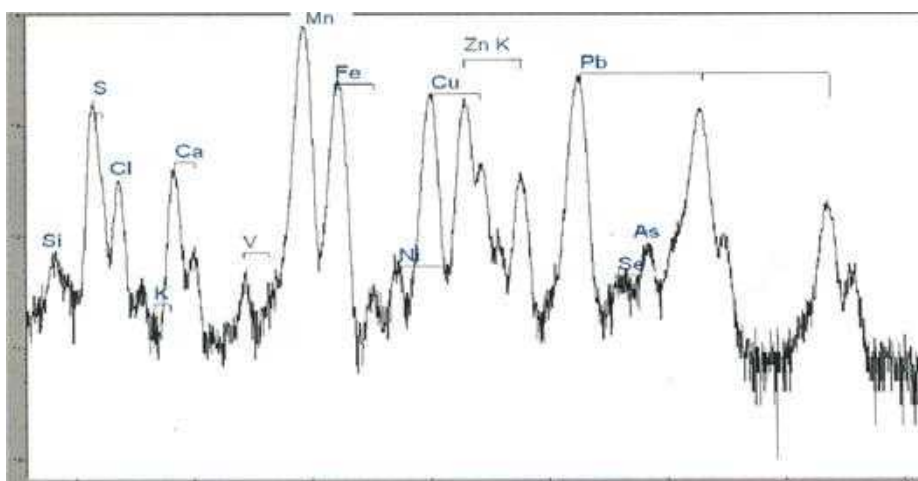


Fig.3: The XRF spectral analyse on aprox. 1mmx1mm area of a polished section with falowing mineral association: galena, tetraedrite, alabandite, carbonates (ankerite) and Se-minerals

Selenium forms selenides with lead, silver, copper and iron, but its correlation is not good with any of the analyzed elements ($R < 0.30$). A weak correlation tendency can be seen in the case of silver ($R = 0.28$). This aspect is due to selenium produced in the Au-Ag ore deposit at Săcărâmb,

such as those of copper and silver selenides (see minerals identified in this study, Fig. 2). A larger value, but insignificant too, of the correlation degree ($R=0.42$) between selenium and antimony was obtained, as in the diagrams presented on the plate I.

Because of the relatively high content of Se and Cd in the analyzed samples, it is possible to identify the association of these elements with other analyzed elements; together with they can form mineralogical compounds.

A mineralogical new fact that may be emphasized is the presence of selenides at Săcărâmb. Despite that eucairite (CuAgSe) was mentioned in 1853, it can't be confirmed by now. This is a thin white with a faint creamy tinge microscopically, with a weak pleochroism and a strong characteristic anisotropism, from olive-brown to steel-blue with a purplish tinge. Eucairite is associated with an anisotropic mineral, possible naumannite (?) (Ag_2Se) (fig. 2, foto 3, 4). The third selenide was observed in a carbonate vein, on the limit between galena and alabandite; its white color with a strong pleochroism and also its strong anisotropism, from blue to brown and finally from green to red-brown (fig. 2, foto 1,2) indicate klockmannite (?) (CuSe). To demonstrate the presence of selenium a XRF investigation was made, on a polish sample where the selenium minerals are associated with galena, alabandite and tetradrite (fig.3).

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COMPARATIVE STUDY OF PHYSICAL AND MECHANICAL PROPERTIES OF BASALTS EXPLOITED IN ROMANIA

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Abstract

Basaltic rocks have been widely used as aggregate for various purposes. They show a variety of textural and mineralogical characteristics that may affect their physic-mechanical properties as well as their use as construction material. The study presented in this paper was carried out on basalts that are spread in 5 geological regions of Romania. To establish their better suitability as aggregate used for asphalted mixture, were selected Late Scythian - Unisia pillow basalts from Niculițel Formation, the Tithonic – Early Aptian Mureș Valley basalts, the Pliocene - Quaternary continental flood basalts from Perșani Mountains – Racoș Area–Bogata Valley–Comana, the Pliocene - Quaternary continental flood basalts from Lucareț-Șanovița in the East area of Timiș Departement and the Dogger-Aptian pillow basalts from Mehedinți Area.

The experimental studies were conducted on these rocks. The samples were collected as being representative from 5 different quarries. The physic-mechanical properties of the basalts of different compositions and textures, and physical and mechanical properties of their aggregates were determined. The results were then compared with the typical acceptance limits in international usage. Although the pillow basalts have better aggregate quality compared to flow basalts, all of the basalts studied, were found to be suitable for production of crushed rock aggregates for bituminous mixtures production.

Introduction

Exploitation of basalt and its industrial processing in order to use materials (aggregates) as building materials must meet several important concepts like: good knowledge of mineralogy and petrography composition of basalts, sequence stratigraphy, tectonics basalt deposits, physical and mechanical characteristics, thermal and geometrical characteristics of the material obtained after the basaltic rocks industrial processing.

Basalts, because of their mineralogical and chemical properties are widely used as building materials. Thus, they are used for entering into the composition of civil concrete, bituminous mixtures slurry seal for surface finishing used for the construction of roads, highways, airports and other traffic areas; as unbound aggregate materials and related hydraulic use in civil engineering and road construction and aggregates for railway ballast or raw stone used for: rock fills. Thus, its widespread utilization is very important in current economic development. To be used in the fields listed above, raw basalt result of quarrying activity is machinable - crushing and sieving processes.

Basalt products are processed in the following classes defined as particle size (granularity mineral aggregates) *sand fraction* 0/2 mm, 0/4 mm, 0/8 mm used primarily for bituminous mixtures (asphalt) used in construction road traffic or airports zones; crushed fractions 4/6 mm, 4/8 mm, 4/10 mm, 8/16 mm 10/14 mm 16/25 mm 16/22,4 mm for, both, concrete and bituminous mixtures used in construction areas, airports and traffic, for slurry seal finishing coat for surface areas of traffic, *crushed stone - main fractions*: 0 / 25 mm, 0 / 16 mm, 25/40 mm 0 / 40 mm, 0 / 63 mm 25/63 mm 40/63 mm - used as ancillary or related aggregates for hydraulic base layer, road foundations, foundations, civil engineering, base layers stuffed with bituminous split, natural aggregates stabilized with pozzolana or hydraulic binders, in gravel, gravel and concrete medium penetrated, penetrated and cement for all ranges of traffic roads, and *crushed stone fractions* 31.5 / 50 mm, 31.5 / 63mm used for ballast tracks. Raw basalt, resulted from actual mining processes, industrial raw (uncrushed) is used for rock fill dams.

Furthermore, basalts have a use in the manufacture of wool and mineral fibers and basalt glassceramic industry.

Generally, aggregates are vital for road infrastructure constructions and for construction industry. Detailed knowledge of the physical-mechanical characteristics of basalts, leads to the choice of processing method to obtain proper materials to be used in bituminous mixtures fabrication respecting National and European Quality Standards.

Short geology description of basaltic areas

In Romania, basic igneous rocks (basalt rocks *largo sensu*) are found in different rocks complexes and are parts of various tectonic structures: basaltic rocks transformed into crystalline schists (amphibolites, serpentines and talc schists eclogite etc.), in the Carpathian crystalline series of the Danubian and Getic terranes, as lower Paleozoic ophiolite sutures (e.g. Iuți gabbros peridotites and dunites from Plavișevița that are associated with the Corbu crystalline series in Banat region), old obducted ophiolite complexes (pillow-lava basalts from Buceava crystalline Paleozoic series of Getic Nappe).

In Banat region, Paleozoic Variscan Orogeny and Apuseni ends with distensional tectonic regime in which the post-tectonic basins appear elongated filled with sediments in continental facies, but significant stockpiles of acidic volcanic rocks (red rhyolitic porphyrys), but also basic (basalts from Moneasa and Beiuș- Apuseni Mountains). Perhaps, we are in the presence of "bimodal" acid-base volcanism, which is accompanied by a specific metalogeny (mineralizations of the Ștei uranium or Ciudanovița)

Mesozoic Era, when the Carpathians has evolved and has finalized, contains numerous impressions of an evolution in terms of geological subduction – collision process. In this context, basaltic rocks and associated suites of rocks (peridotites, gabbros, the fosse turbiditic sediment types etc.) represents an "important marker" in deciphering the "setting" of these tectonic units of rocks and their paleogeographical position.

Geological and geochemical details on basaltic rocks in these structures show a great petrographic diversity (basalts, pillow-lava-type variolites, anamesites, dolerites, gabbros, harzburgitic peridotites in different serpentinization degrees sometimes associated with more acidic differentiated type oligophires, trachytes, keratophyre tuffs as Mures area or Perșani areas). Also, the associated sedimentary rocks have a great variety of facies: siliceous rocks, cherts, radiolarites, red or green deep-sea fine clay sediments, coarser clastical flysch associated with fine clays and tectonic blocks (klippe) of basalt and limestone karst, making a formation of specific "mélange" for precollisional accretion prisms. Compositional variety of basalts is expressed geochemical. Analyses of major and minor elements, and more recently, isotope geology studies show a great variety among them and thus different tectonically settings.

Hence, we deduce an associated geological diversity in a relatively small space. We conclude, therefore, that basalts rocks are trapped in allochthonous tectonic structures in category of obducted overthrust nappes (when serpentinized peridotites are present) or basalts and ophiolitic flysches or nappes (when serpentinized peridotites are lacking). Flysches with ophiolitic fragments can be considered as a *mélange* formation. The allochthonous position of these ophiolitic structures is inferred from the geophysical data that are showing reduced gravity anomalies in their area of outcrop, so they sit on a crust socle at least 30 km crustal thickness.

Triassic basalts of the simatic Tulcea socle that was formed in connection with activation of lower Triassic rift, which separates the continental crust, between the corresponding Macin and Tulcea Nappes in the west and the east and they are the result of the the progress oceanic rift crust composed of basalt-lava textures pillow (subsea flow characteristic), accompanied by pyroclastic material. These are crossed by gabbros bodies and dolerite. Consequently basalts may represent Niculițel area as an remnant oceanic crust from Plaeotethys ocean consumed in the suduction process.

Ophiolitic rocks in the Apuseni Mountains form a belt about 200 km length of Zarand Mountains (east of Lipova) till the Trascău and Metaliferi Mountains, near Turda.

In the Southern Carpathians, Severin Nappe (Obârșia-Baia de Arama Formation may represent a classic example of obduction nappe).

In the Eastern Carpathians, "Black flysch" Formation of Maramureş Mountains and debris of Transylvanian nappe in Rarău, and especially Bicaz and Perşani Mountains (Augustine area, Ormenis, Lupşa) may be examples of the allochthonous ofiolitic rocks from the overthrust nappe.

There are two ages of these ofiolitic rocks. Transylvanian Nappe (Perşani and Rarău) has developed from Triassic and Severin and Metaliferi Mountains Nappes begin their developments in upper Jurassic (Dogger) and are put into place in Upper Aptian Orogeny.

Another category of basaltic rocks is related to "deep fault" (South Transylvanian Fault) are very new and are trapped in Quaternary lacustrine and terrace formations. There is an initial explosive phase which brings with orthopyroxenes mantle nodules (wherlite), followed by basalt lava flow separation with characteristically prismatic columns. At Racoş and Lucareţ-Şanoviţa (Banat) are the most characteristic.

To accomplish this research, we studied the physical and mechanical properties of the 5 different types of basalts: Late Scythian - Anisian pillow basalts from Niculiţel Formation, the Thitonic – Early Aptian Mureş Valley basalts, the Pliocene - Quaternary continental flood basalts from Perşani Mountains – Racoş Area–Bogata Valley–Comana, the Pliocene - Quaternary continental flood basalts from Lucareţ-Şanoviţa in the East area of Timiş Departement and the Dogger-Aptian pillow basalts from Mehedinţi Area.

Investigation methods

To determine the physical and mechanical properties of the basalts in order to use them as building materials, it was taken samples of raw basalt material (after the drilling and blasting process) from the following areas: Revărsarea Quarry - Tulcea county (Late Scythian - Anisian pillow basalts from Niculiţel formation), Brănişca Quarry - Hunedoara county (Thitonic – Early Aptian Mureş Valley basalts), Racoş Quarry - Braşov county (the Pliocene - Quaternary continental flood basalts from Perşani Mountains), Şanoviţa Quarry - Timis county (the Pliocene - Quaternary continental flood basalts from Lucareţ-Şanoviţa), and Obârşia Cloşani Quarry – Mehedinţi County (the Dogger-Aptian pillow basalts from Mehedinţi Area).

The samples were investigated in a specialized Laboratory and the main physical-mechanical analyses were: Specific density (g/cm^3) and Water Absorption (%) following the requirements of SR EN 1097-6/2002, The Los Angeles Coefficient (mass losses %) - the result of the resistance to fragmentation determination, following the requirements of SR EN 1097-2/2002, The Micro Deval Coefficient (mass losses %) - the result of the wear resistance with Micro Deval Test following the requirements of SR EN 1097-2/2002, Compressive strength (N/mm^2) following the requirements of SR EN 1926/2000, Freeze –thaw resistance (% mass losses) at 10 frost-thaw cycles in the temperature range following the requirements of $(-20^\circ\text{C} / +20^\circ\text{C})$. SR EN 1367-1/2002 (Although this laboratory test determines the thermal and weathering properties of the natural aggregates, the results show the behavior of natural aggregates used in construction industry during phenomenon of freeze-thaw).

Results

Type of test	Revărsarea Basalt	Brănişca Basalt	Obârşia Cloşani Basalt	Sanoviţa Basalt	Racoş Basalt
Specific density (g/cm^3)	2,915	2,780	2,850	2,650	2,500
Water Absorption (%)	0,163	0,60	0,54	1,15	1,05
Los Angeles Coefficient (mass losses %)	14,0	16,8	16,5	18,0	17,0
The Micro Deval Coefficient (mass losses %)	5,0	5,9	5,7	8,0	7,2
Compressive strength (N/mm^2)	172,0	161,0	141,1	155,0	170,0
Freeze –thaw resistance (% mass losses)	7,6	8,2	7,9	8,5	7,2

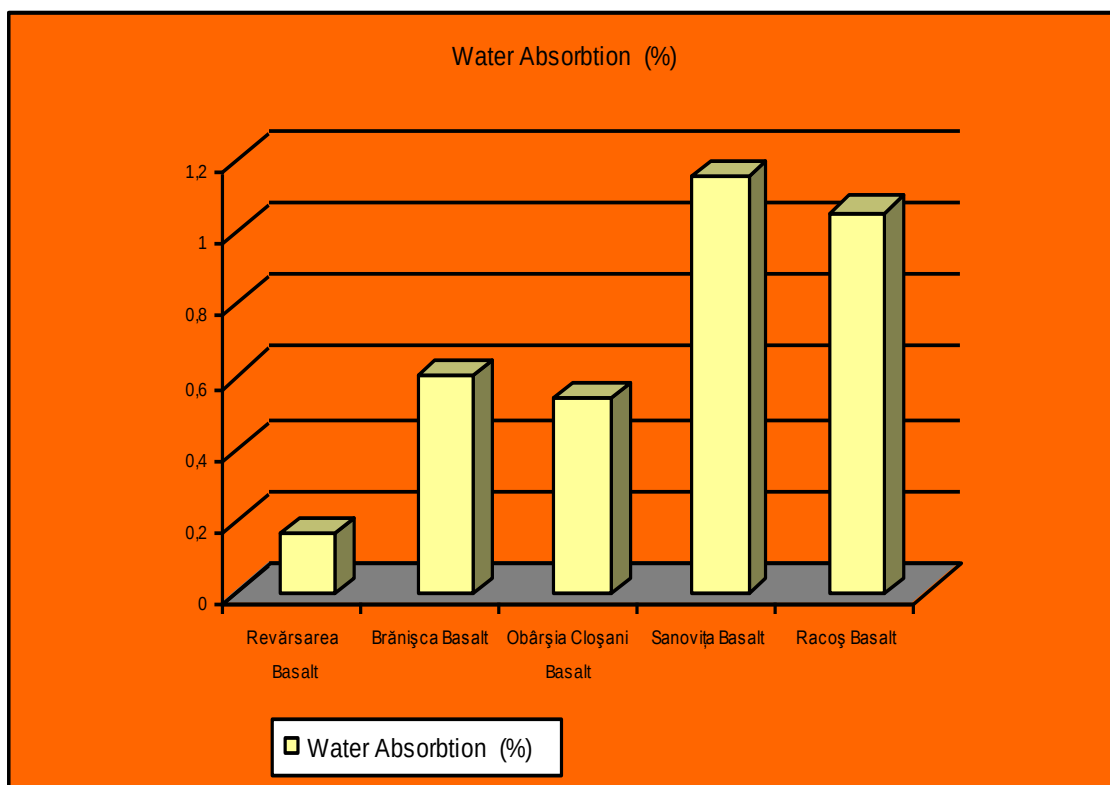


Fig.1 Graphic representation of the different basalts water absorbtion propriety

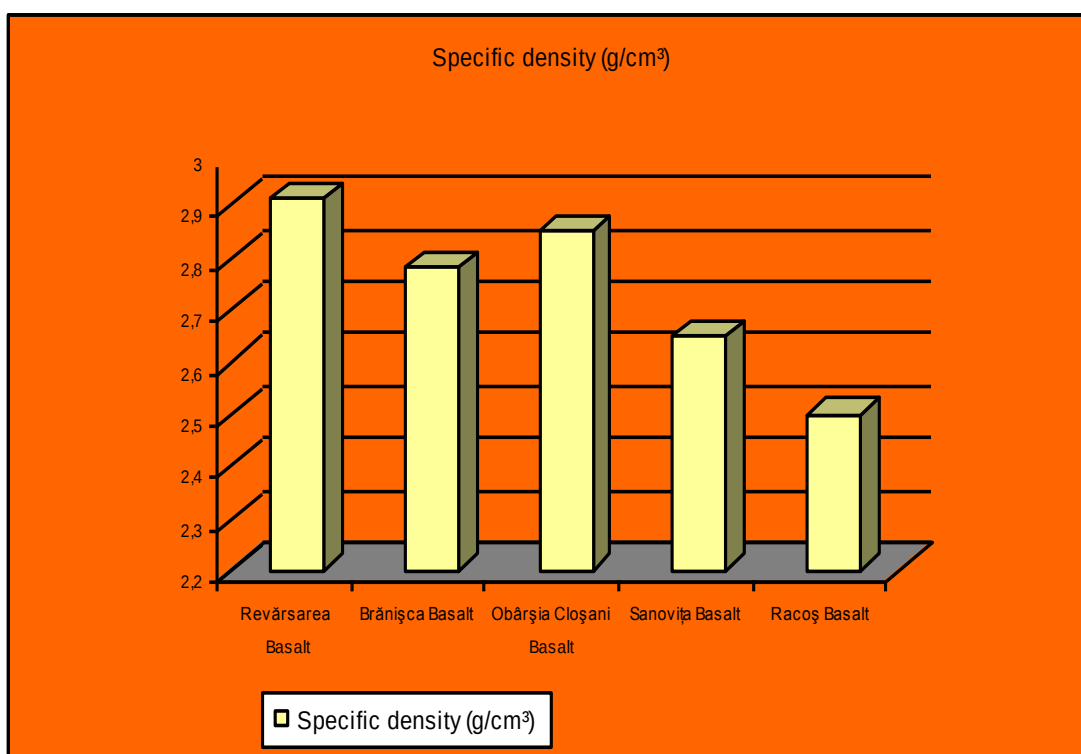


Fig.2 Graphic representation of the different basalts specific density

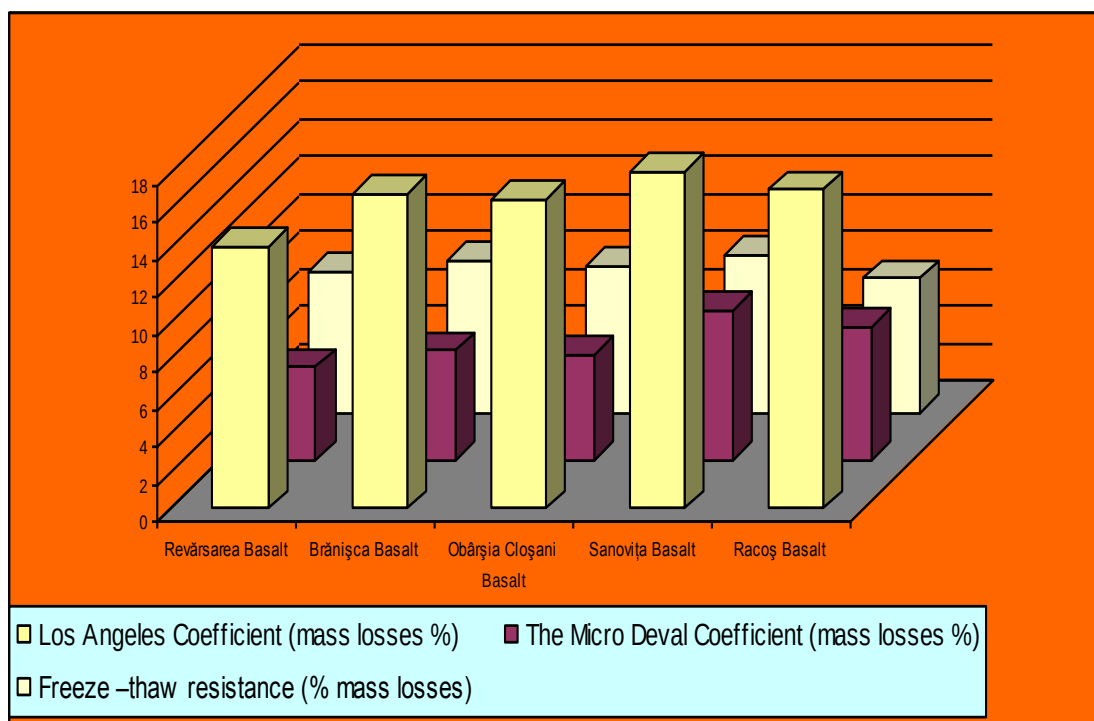


Fig.3 Graphic representation of the different basalts Los Angeles Coefficient, MicroDeval Coefficient and Freeze –thaw resistance (% mass losses)

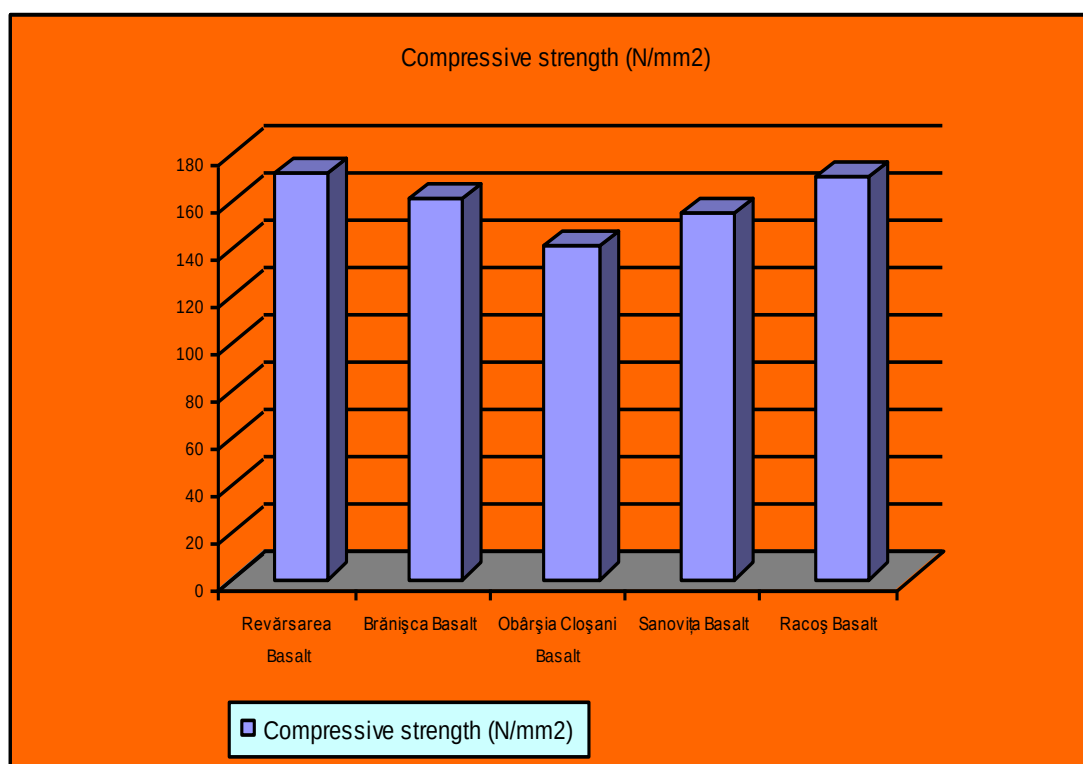


Fig.4 Graphic representation of the different basalts compressive strength

Conclusions

Properties, such as mineralogy and chemistry, linear thermal expansion with temperature, high stability and hardness in different environments made basalts to be used for different purposes in construction.

Basalts from Romania are widely used as construction materials, such as raw and industrial processed material because they have: high hardness, freeze-thaw resistance, thermal resistance, low absorption, resistance to corrosion, resistance to radiation, mechanical strength, resistance to shock, resistance to acids and bacteria, good conductivity properties.

The vacuoles from the structure of some basaltic rock types provide thermal protection, good waterproof protection.

The basalts, also, can be processed by cutting into various shapes, sizes and colors. Because of these properties is of great versatility in use and covers a very wide range of products used in building materials industry.

From the above graphs, it is noted that the basaltic rocks from the Pliocene-Quaternary areas Perșani,, Lucareț-Șanovița and are less resistant to crushing and compression than the rocks of others who are stationed in Mesozoic basalts provinces (Triassic – Revărsarea from the Niculițel formation, Jurassic - Brănișca from the Mures Valley, Cretaceous-Obârșia Cloșani). Also, their water absorption is much higher compared to those of Mesozoic basalts.

It can be seen as ofiolitic Mesozoic basalts are more suitable used in the manufacture of asphalt, cement concrete, for railways ballast, road and airport infrastructure. Pliocene-Quaternary basalts may be used in road construction, airport, railway, civil, if their exploitation and processing oriented compact basalt levels and less to the scoria levels.

Quaternary basaltic rocks from Pliocene alkaline volcanism but may be used with good results in the production of basalt ceramic glass industry (peak areas were used in the global economy in both construction and military purposes), fiber products and mineral wool; in carrying out parts of basalt melt and cast, able to replace steel parts, the development of glazes containing basalt, resistant to wear.

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STRATEGIES FOR MINING PERIMETERS CLOSURE, ECOLOGIC RESTORATION AND ENVIRONMENT INTERNATIONAL PRACTICES

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1.1. Introduction

Development strategy for mining industry promoted before the year 1989 was based on self support concept in providing for economy mineral resources in order to reduce imports. The result was the development of mining activity without considering the geo-economic analysis for the entire life cycle of exploitation determining that in 1989 this branch of industry to be unprofitable from economic point of view. The mining sector which developed more than the potential of national mineral resources allowed involved directly 350.000 persons and 700.000 persons indirectly.

The situation generated after 1989 needed state support for this branch, requiring a large financial support. During 1990-2005 the state spent for the mining sector \$ 5.950,7 millions adding a an exploitation loss of \$ 1.547,3 millions.

The results of restructuring actions for this period generated a set of new problems:

- sudden drop in economy for mining regions affected by the sector restructuring;
- enhance social problems in these regions;
- enhancing environmental issues;
- increased poverty.

1.2. Situation of recoverable solid mineral resources base and state intervention level

Mineral resources which in various knowledge stages can be exploited with mining technologies are presented in the table below:

Substance	Mineral resources		Level of state intervention
	M.U.	Quantity	
lignite	millions of tons	2800	reduced by underground exploitation subsidies of social transfers and partly by capital allowances
coal	millions of tons	900	increased by providing operating subsidies, social transfers and capital allowances
gold-silver ores	millions of tons	40	very large by providing operating subsidies, social transfers, capital allowances and staggering debt to electricity suppliers
polymetallic ores	millions of tons	90	
copper ores	millions of tons	900	
uranium ore	millions of tons	*	Increased by operating grants, social transfers and capital allowances
salt	millions of tons	4000	without intervention
mineral water	millions m3/day		without intervention

* quantity of resources has a special regime

1.3. Closure of unviable mines and performance of closure and greening process

Over sizing of mining sector in the period prior the year 1990 and applying the market economy principles lead in short time to serious debts produces by suppliers and state budget causing imminent restructuration in mining industry and closure of a large number of mines.

In this context, starting from 1998 according to the enforce legislation was implemented the process of conservation and closure of unprofitable mines and quarries. Up to date, on the basis of Mines Law by Governmental Decisions was approved the final closure of 550 mines/quarries and establishment of funds required for conservation, closure and greening of surfaces affected for these objectives.

Closure of mining objectives and ecologic restoration of surfaces affected is one of the most complex activities related to exploitation and recovery of mineral resources and consist of performance of a set of specific activities. All these stages/ activities included in closure process are physically and value assessed by technical operation designs which are developed in the first phase of the program related to mining objectives closure. Financing is made from funds provided annually by S.C. CONVERSMIN S.A. with the Ministry of Economy, Commerce and Environment of Affairs (on the basis of DGRM – MECMA).

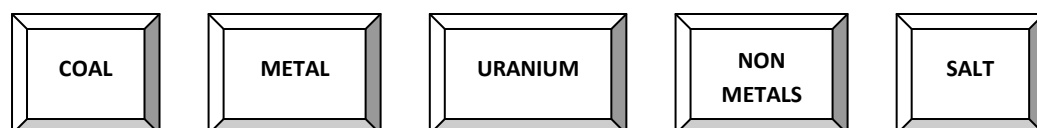
The main stages/ activities related to closure of unviable mines are:

- a. Conservation
- b. Closure of mining activities
- c. Decommissioning and clean up areas affected
- d. Monitoring after closure

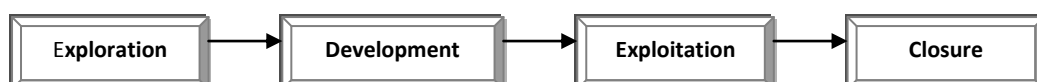
1.4. Environmental international best practices on closure and ecological restoration of mines

The best practices can be translates as the best way of doing something but in other words the term of best practices describe a management approach including an arrangement to obtain results beyond those expected in compliance with legal decisions. In order to obtain the best practices it is expected that an operator to develop a management system providing the identification of improvement opportunities and to ensure that changes are implemented, monitored and assessed.

Best practices were set by compiling information from several sources and mainly from the Australian environment publications representing a valuable information source regarding environment management, by modules The best environment practices in mining branch . These are the best practices applied in mining sector for companies concerned about improving and also can provide a referential degree measuring the mining industry progress. Rehabilitation and restoration of vegetation are just some aspects of mine closure plan. This plan should also include aspects as counselling mine staff regarding re-employment option for the period prior to activities cessation. The intention is to help the staff to transfer to other industries or to develop own business.



- Closure management plan -



The final intention is create after mining activities closure conditions involving a negligible risk for local residents and environment both on short and long term. In this respect it is recommended to set a closure provisional plan when commissioning the activity which should be revised and finalised during mining exploitation. In order to provide implementation of viable actions during and after mining activity has become increasingly common that during the license development for mining operator to be requested among other conditions, financial warranties on the basis of assessed restoration and decommissioning costs.

Guidelines developed include the following principles:

- Cost for restoration of field affected by mining activities (mainly during operations on large scale) will be borne by mining operator or by the exploration license holder and/or mining exploitation. Rehabilitation/restoration activities should:
 - ✓ revitalize land used during mining activities for other beneficial use;
 - ✓ provide safety for subsequent users of the land;
 - ✓ be self-sustainable
- Mine rehabilitation plan should be part of project planning phase and should also be part of the revising and approval process.
- Restoration costs should be included in operation costs of design.
- Progressive, continuous restoration should be encouraged.
- The risk of supporting costs from public funds following the premature closure or failure to comply the accepted rehabilitation plan should be reduced by financial warranties for rehabilitation.

ON THE NECESSITY OF THE INDUSTRIAL SYSTEMATIC EXPLOITATION OF THE SALINE SPRINGS IN THE CARPATHIAN AREA

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Key words: Miocene salt, salt deposit, salt solution, saline springs, halokarst, mineralized rivers

Our previous synthesis papers in the saliferous formations and salt deposits in the Carpathians area, supplemented with other detailed studies made us consider that the industrial systematic exploitation of some saline springs of this area is preferable because of several distinct reasons. The most important one is the fact that the salt resources are continuously diminishing by their ceaseless dissolution. This process is very well reflected by the great number of saline springs known from the distant past in the Carpathians area. This phenomenon is very much favoured by the fact that most of our salt deposits appear exposed are situated at small depths. This situation is complicated by the great number of faults affecting the salt massifs which are in fact open ways for the fresh water infiltrations inside them, inducing natural karst systems. In this way numerous saline springs, many of them with great flow rates can easily appear. The water of these mineral springs affects the water of the creeks, rivers and aquifers which acquire abnormal mineralization. This phenomenon is known as "natural saline pollution" (an improper term). This can lead to a secondary mineralization of the soil if these waters are used for irrigations. From this point of view the exploitation of the saline springs becomes useful for the decreasing of the mineralization of the surface hydrographical systems or of the underground waters. Another critical reality is the instability phenomena which accompany either the "dry" exploitation of the salt massive, or their exploitation by water dissolution through drilling wells. Finally, the saline springs exploitation could be very much favoured by the tradition of their (pre-industrial) exploitation in many ways, which in fact has never ceased till now.

Next we will present some general data on the Miocene saliferous formations and on the salt massifs within them.

The Miocene salt appears at two different stratigraphic levels: Lower Miocene (Aquitanian) and Middle Miocene (Badenian). The Aquitanian salt is connected to the "Lower Salt Formation". The Aquitanian salt facies is to be found only in the outer Carpathians area. Between Ozana and Putna valleys, at the top of the "Lower Salt Formation" there is a salt clays complex containing lenticular layers of potassium salts. The Badenian salt is connected to the "Upper Salt Formation". This formation is to be found not only in the outer Carpathians area but in the Transylvanian Basin and in the Maramures Depression as well.

In the Miocene salt formations of the Carpathians area a lot of salt deposits have been delimited. There are 194 deposits, 107 of them in the external part of the Carpathians chain, 83 of them in Transylvania and 3 in the Maramures Depression. Most of the Aquitanian salt deposits exhibit complicated diapiric shapes (blades, tears, pillows). The Badenian salt deposits are less complicated in shape than the Aquitanian ones. Often they are pillow or layer shaped. The salt rock of the most deposits contains 70-90% NaCl. For some deposits the percentage is of about 95-98%. The number of salt deposits open by human exploitation is small. The number of deposits exploited in historical times is even smaller. In the present in Romania only 7 salt deposits are in exploitation (4 of them in the external area of the Carpathians chain and 3 of them in Transylvania).

The new synthesis studies on the geodynamics of zones with Miocene salt formations in the Carpathians area clearly showed that the salt deposits (bodies) are the most vulnerable (sensitive) areas in the entire structural edifice which completes the Carpathians chain to the interior (Transylvania) and to the exterior (Muntenia and Moldavia). The explanation is the continuous and intense process of salt dissolution under the action of the fresh water, especially of meteoric origin. These waters act on the salt rock surface or inside the salt creating inside the salt rock a system of

empty spaces of karstic (halokarstic) nature. The continuous dissolution of the salt represents a peculiar type of erosion, specific for the rocks made entirely of soluble salts minerals, a chemical suffusion process combined with a mechanical suffusions one.

The existence and the amplex of this process is demonstrated by the great number of salt springs (chlorosodic springs), many of great NaCl concentration and with variable flow rates which are to be found in the external part of the Carpathians chain and in Transylvania to the margins of the basin. This process is also demonstrated by the great number of more or less heavily mineralized rivers and also by the vast areas whose underground waters have a great salt content. Another consequence is the accumulation of salt in the soils of the low plain zones where often there are to be found extended salty areas with no vegetation or with halophytes only. Such areas can be found along the rivers in the north-eastern part of the Romanian Plain, in the Pannonian Plain near the Hungarian border and in some zones of Transylvania.

In the cases where the intense solution process inside the salt massive has created an advanced karstic system (large caving) it can arrive to surface land leading to collapsing (through endokarstic re-equilibrations).

In the Carpathians region the exploitation of the salt resources started in the prehistorically times (Neolithic, even Palaeolithic). It is most likely that the exploitation in those old times consisted in using the water of the numerous concentrated salt springs, directly or for obtaining solid salt by evaporation. This type of exploitation is being used even in the present days by the inhabitants in zones with salt springs for conserving food and fodder or for food preparation. At the same time the "dry" exploitation of salt was initiated in areas with exposed salt rock. At the beginning this exploitation was rather primitive but technologies have been continuously diversified and modernized. The dry salt exploitation or by underground salt dissolution with drilling rigs led to the production of great, various shaped hollow spaces inside the salt massifs. This is a peculiar type of karst which we could call anthroposaline karst. This type of karst weakens to a great extent the stability of the salt massifs and can lead to endokarstic equilibrations and re-equilibrations which are completely out of human control, especially in the abandoned exploitation sites. During all salt exploitation periods a great number of accidents and incidents have been produced which culminated with the great land collapse at Ocnele Mari (Teica).

Generally speaking and taking into account both the strictly natural effects of the salt massifs presence and those induced by human intervention we can say that the only reasonable way in salt exploitation should have been the rational exploitation of the salt springs in the entire Carpathians area, without direct intervention on the salt rock of the salt formations. The direct dry or wet exploitation only led to the emergence of vast zones which are absolutely unpredictable from the point of view of land stability in the areas connected to exposed or underground Miocene salt formations.

We can appreciate now that the most interesting area for salt springs exploitation is comprised between Trotus and Prahova valleys. Here important springs are located along Rimnicu Sarat (Jitia especially), Slanicul de Buzau (Sarile Bisoca) and Cricovul Sarat (Singeru zone). In these zones it can arrive very fast to establish the perimeters in which will work the desalinization stations or points in which the salt water can be put in bottles or other containers. The technical data about the salt obtaining by evaporation at Cacica and Baltatesti (in the past) or at Bazna (in the present) could be very useful.

CU - NI MINERALIZATION FROM NĂDRĂG - POIANA RUSCĂ MOUNTAINS (ROMANIA)

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Generalities

The area is located on the North-East side of Poiana Ruscă massive (Romania), between Nădrăg and Hăuzești localities. Continuing a previous series of researches, the author initiated geological prospections in 1990, when there was identified a Cu-Ni mineralization, with platinoide elements content, which represents a new metallogenetic type for the Western side of Poiana Ruscă massive. The latest researches performed by Berghes and collaborators (1987, 1988) and Tudor and collaborators (1989, 1990) showed the separation of a mesometamorphic retromorphosed unit. A series of obtained informations determined, on one hand, a modification of the existent rock types classification and, on the other hand, a re-interpretation of the geological evolution. The metallogenetic temporal scale was extended and completed, by highlighting a new mineralization occurrence submitted to a new type for this area, the Cu-Ni mineralizations associated with regional metamorphosed ultrabasic rocks.

The geological context of the mineralization

The metamorphic rocks consist of retromorphosed mesometamorphic schists, which are overlapped over epimetamorphic rocks from the north side, along a fracture with a WNW – ESE direction, disposed between Padeș-Bordaru ridge and Gladna Montană locality. There were separated four formations, disposed in an apparently monoclinic structure and having specific lithological characteristics: the orthoklastic gneisses and lower quartzites formation (South from Gladna Montană); the plagioclastic gneisses formation (South from Hauzești); the eruptive basic and ultrabasic metamorphosed rocks formation (Nădrăgel valley basin); the orthoklastic gneisses and upper quartzites formation (Bordaru ridge area).

The Cu-Ni mineralization is cantoned in the eruptive basic and ultrabasic metamorphosed rocks formation (into the lower part of some green-blue rocks, which represent the regional metamorphosed term of some ultrabasic rocks, determined as tremolite-antigorite schists). The cyclic alternation of the metaeruptive rocks levels, concordant with clastic rocks shows that the formation resulted from flows of basic and ultrabasic lava associated with cineritic products, consolidated in submarine conditions. It was separated along a distance of about 5 km, the average width being circa 500 meters (fig. 1). The stratigraphic succession was established on basis of the transversal profiles geological surveys and there were outlined three sequences, separated by the clastic rocks levels (metasediments).

The types of the rocks chemical analysed are hornblendite, mineralized tremolite-antigorite schists, metabasalts with gabbroic metamorphic structures and metasediments. Their content variation is shown in the ternary diagram MgO - CaO - Al₂O₃ (fig. 2), the komatiitic rock field is taken after Naldrett and Turner (1977), from Green and Naldrett (1981). In the komatiitic series, the superior touched limit corresponds to the piroxenitic komatiites, while the metabasalts are grouped in the area of the basaltic komatiites or limitrophe areas. The diagram MgO - Al₂O₃ - TiO₂, used by Mishkin (2009) for the delimitation of the komatiitic rocks, shows the disposal of some metabasalts in the komatiitic basalts area. The secondary processes, observed by means of the microscopic study of the rocks are strengthening the hypotheses that the rocks have chemical variations attributed to the carbonatization (ankerite dolomite), feldsparization, serpentinization and then biotitization. The compositional differences of the ultrabasic rocks, on one hand and the metabasalts and metasediments, on the other hand, have determined the creation of some metasomatic reaction areas with enrichments of CaO, MgO, Al₂O₃ and alcali, as an effect of mobilizing these elements during the regional metamorphism.

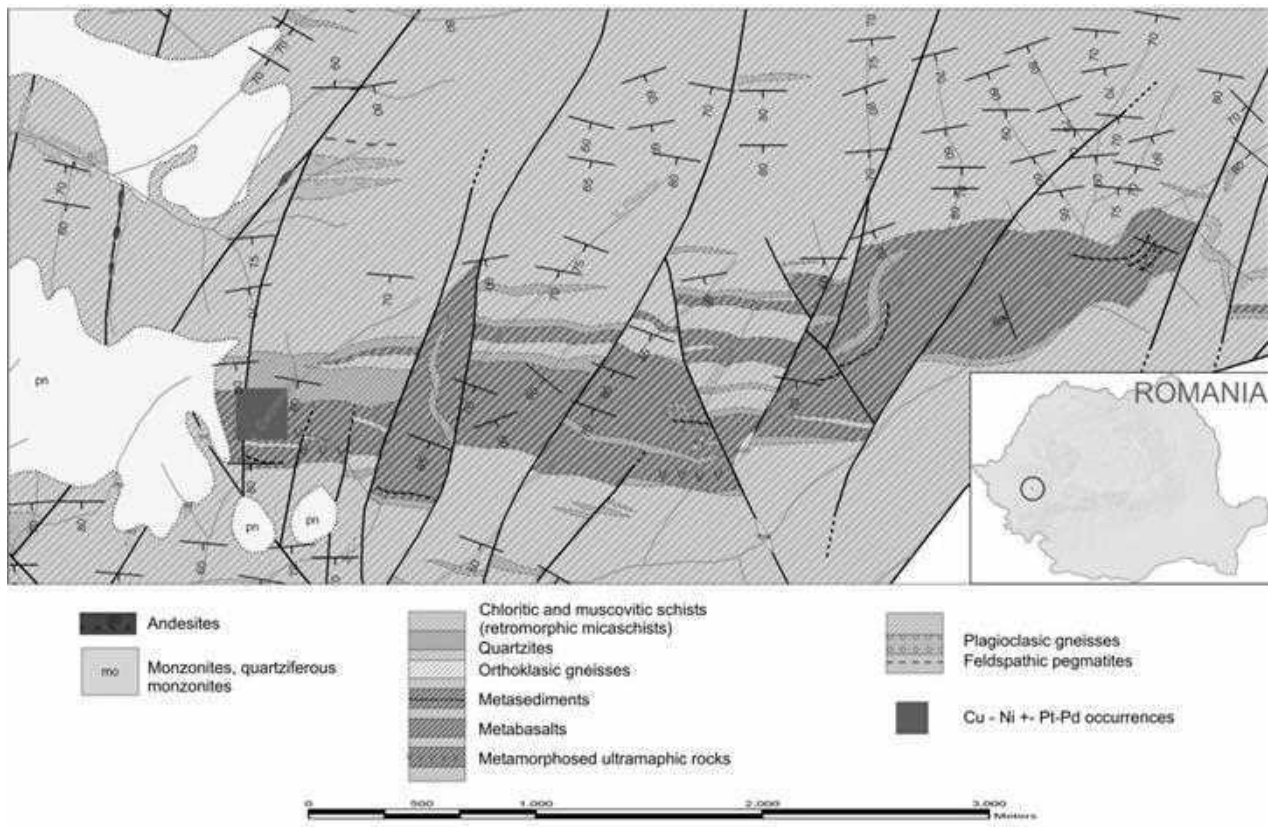


Fig. 1: The geological map of the northern area from Nădrag.

Mineralization description

The copper-nickel mineralization is situated in the base of the metamorphosed ultrabasic rocks (tremolite-antigorite schists). It was observed, on a width of 8 m, limonitized in a proportion of about 50% due to the fact that it is situated at the limit of the hydrostatic level. The metallic minerals form nests, schlieres or matrices (3-10 mm), within the ultrabasic rock, having as interstitions the silicates which form the spinifex texture of the rock (tremolite, antigorite).

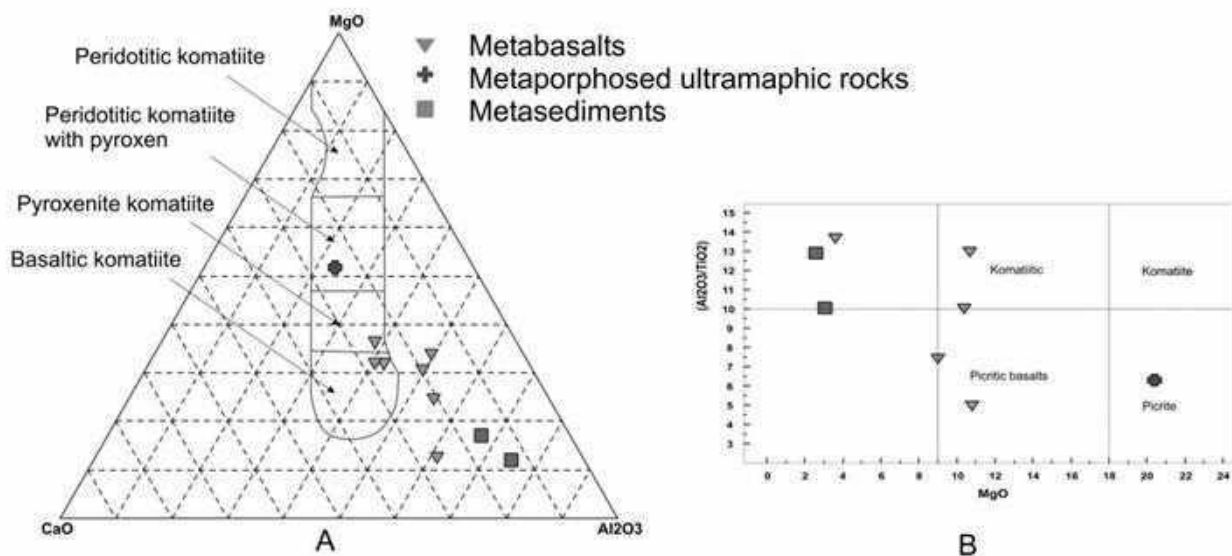


Fig. 2 : Rocks separation diagrams from the northern side of Nădrag area (A – after Naldrett and Turner (1977), B – after Mishkin (2009)).

The paragenesis observed in polished sections is formed from minerals of Fe, Ni and Cu. Thus, there appear, in a crystallization consequence, magnetite, pentlandite, pyrotine, chalcopyrite

and sphalerite. Following some secondary transformations, there appear: hematite, limonite, pyrite, bravoite and malachite. The percentage content within the mineralization is: pentlandite (40-60%), pyrotine (5-20%), chalcopyrite (10-30%), bravoite (10-20%), pyrite (3-5%), magnetite (1-3%), sphalerite (1-3%). The totality of the metallic minerals and limonite resulted from sulphurs, represent 20-40% of the rocks' volume.

The pentlandite is the main component of the mineralization and it appears in the form of maced granules, of a shiny white-yellow colour, izotrope. It is characteristic – the octahedral type cleavages, within or on the edges of the crystals, with sides in angles of 80-85°. Often, it is transformed in bravoite. The pentlandite also appears, in an isolated manner, in other basic and ultrabasic rocks. Pyrotine appears permanently and contains Ni, judging by the transformations in the bravoite. In many cases, it is transformed in pyrite in the marginal area of the granules. The chalcopyrite is also a main component of the mineralization, appearing in the form of some euhedral crystals of yellow colour. In conditions of superficial alteration, it is transformed in malachite.

The ulterior transformations suffered by the primary minerals are mainly happening due to the regional metamorphism, which had as an effect the apparition of some ulterior minerals (bravoite in well-developed granules, pyrite around the pyrotine crystals). The secondary minerals appeared as a result of the superficial alteration are the limonite and malachite.

In order to verify the high contents of Pd and Pt obtained during the chemical analyses, there was performed a study with electron microprobe analysis on a group of minerals containing pentlandite, pyrotine and limonite and there was observed that the main primary nickel mineral is the pentlandite, followed by pyrotine, and also that the Pd is contained by pentlandite.

The transformations suffered by the host rocks (serpentinization, carbonatization) have been accompanied by transformations of the pyrotine into pyrite, magnetite and bravoite. The regional metamorphism affected the mineralization in three ways: modifications of the sulphurs content due to the reactions from the host rocks, modifications and recrystallizations of the sulphurs due to the temperature changes during the main phases of the metamorphism, physical deformations which had modified the spatial configuration of the minerals.

The study of the contents of utile and minor elements of the mineralization from Nădrag and of the regional metamorphosed basic and ultrabasic rocks was performed by analysing 41 point and linear samples. The analyses method is the emission spectrography, completed by the chemical method (for the samples with high content of Ni, Cu, Zn), the spectral docimasy (Pt and Pd analysis) and the absorbtion spectrography (Au analysis).

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MINING WASTES – TIME FOR PHYTOMINING AND/OR PHYTOREMEDIATION

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The huge amounts of waste dumps and tailing ponds in Romania appeared after centuries long mining are distributed over large areas of Carpathians Mts. The total amount of such waste materials probably exceeds 200 mil. km². They cause landscape modification and in some cases a severe impact on water quality, also can produce soil contamination as well as plants growth disturbances. This is why any attempt to remediate such negative environmental aspects in this post-mining period should be more and more undertaken and financially sustained.

The Leaota Mts. display a mosaic of different types of ore occurrences: the most typical is the pentametallic ore type (Co-Ni-Bi-Ag-U), developed mostly in the south-western part (i.e. Valea lui Neguleţ and Valea lui Dăniş); gold-quartz ores are known in the northern part (Ghimbav Valley); Cu-Co-pyrite ores form the most typical shear-zone related occurrences (Tibra and Tâncava brooks, both tributaries of Bădeanca Valley); Pb-Zn ores sporadically occur also in the catchment area of the Bădeanca Valley. A new type of ores, Pb-Zn-Cu-Ti (with brookite as dominant mineral) has been recently described by Udubaşa (2004) on the Purcăreţu brook (left tributary of the Bădeanca Valley). U-carbonaceous matter occurrences have been explored both in the Bădeanca Valley (No. 2 Bădeanca adit, where also polymetallic ores and pentametallic ores are also likely to have been occurred) and in the Zănoaga Valley (eastern part of the mountains).

The Bădeanca No. 2 adit was probably the biggest exploration mining works producing the largest waste dump of the area (approx. 10000 m²). Systematic sampling of the waste dump was undertaken in order to establish a methodology to recover the metals by using plants (phytomining). In addition to the sparse ore minerals found in the 70 years old waste dump (pyrite, ilmenite, hematite, chalcopyrite, marcasite) a lot of nanominerals have been identified by using high resolution structural techniques (NGR, TEM/SAED), i.e. maghemite, greigite, lavendulan, gold, gold-silver alloys as well as silver carbonates (that is the first natural occurrence of such compounds: both alpha and beta forms).

A large part of the of the waste dumps (more than 70 years old) is covered by vegetation: both trees (*Alnus incana*) and small plants (*Fragaria vesca*, *Centaurea biebersteinii*, *Thymus globulescens*, *Ranunculus repens*, *Bellis perennis*, *Cirsium ciliatum* etc.). Nevertheless, for the phytomining experiments two other plants have been chosen: *Zea mays* and *Trifolium repens*. Grown on artificial ores (neutral soils enriched in Au, As, Cu, U) these plants have shown good capabilities for metals uptake, however with different biases towards certain plant parts (roots, trunks, leaves). *Trifolium repens* shows the highest uptake of gold, especially when the plant has grown on U-enriched soils. Uranium solution in soil seemed to facilitate the gold uptake, in a way not completely understood yet.

A quite similar approach has been undertaken by a team of specialists from the Faculty of Biology at the University of Bucharest (Stancu et al., 2010). However, the methods applied were different, with the main aim at solving the phytoremediation of some tailing ponds in the Zlatna area.

It seems to be clear that the already started postmining period in Romania, maybe as a substitute of mining, should be continued and new methods should be applied and refined in order to achieve at least two goals: either phytomining, i.e. recovery of metals for further use (especially precious metals) and of other heavy metals found in the waste dumps (for the purpose of decontamination) or phytoremediation aiming at the neutralization of the substrate (tailing ponds materials) necessary for chemical fixation or stabilization of heavy metal compounds.

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SUSTAINABLE AGGREGATES RESOURCE MANAGEMENT – A PROJECT FROM THE SOUTH EAST EUROPE TRANSNATIONAL COOPERATION PROGRAMME

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1. The South East Europe Transnational Cooperation Programme

The South East Europe Transnational Cooperation Programme is a unique instrument in the politics objective of regional territorial cooperation, having as main purpose the improvement of integration and competitiveness in a certain area, as much as complex as diversified. It sustains the developed programmes in the 4 priority axes (innovation, environment, accessibility and sustainable growth of areas), according to Lisbon and Gothenburg priorities and contribute to the process of integration for the states that are not part of the European Union.

The European Commission approved the Transnational Cooperation Programme South-East Europe for the interval 2007-2013 on 20 December 2007. This program gathers the largest number of participant countries, 16 in total. From those, 8 are member countries of the European Union, 6 are candidates and potentially candidates and 2 are countries that participate to the Politics of European Vicinity. It is a very complex program, which assumes different challenges regarding the maintenance of a good contraction mechanism made of different instruments: ERDF (European Regional Development Fund), IPA (Instrument for pre-accession) and ENPI (European Neighborhood and Partnership Instrument).

The final objective of this program is to realize a connexion bridge inside the European Union, a bond with cohesive politics of EU and an instrument for dissemination of good practices for candidate countries. The project Sustainable Aggregates Resource Management (SARMa) is part from Priority Axis 2: Protection and Improvement of the Environment, being framed in the Intervention Area 2.4: **Promoting energy** and resource efficiency.

2. Project objectives and the way to meet them

Aggregates, like crushed stone, sand and gravel are very important for infrastructure and constructions. States from South East Europe have important reserves of aggregates, but the offer and the supply are not coordinated inside them and between them.

The illegal and destructive quarries represent challenges from the aggregates area, by their limited recycling and their opposition to local communities. To ensure the demand it is need for an efficient and sustainable supply chain (planning, extraction, transport, use and recycling). Aggregate operation must have a social environment, to prevent opposition on extraction, gaps in the procurement process and increase restrictive.

Aggregate management occurs in all regions (regions or countries), but nowhere at the level of good practice. The project is based on previous projects, and studies on best practices and partners programs.

There project have are two main objectives. The first is related to a preoccupation and common approach towards sustainable aggregate resource management (SARM). It follows to develop a common concept throughout South East Europe.

The second main objective seeks sustainable supply planning aspect (OSH) at three levels (local and regional, national, transnational) to ensure an efficient and safe supply in South

East Europe. It aims a better distribution of costs and benefits on the production, use, waste disposal and recycling of aggregates to increase resource and energy efficiency and quality of life.

Objectives will be achieved through coordination in the management of aggregate resources, increasing the transfer of know-how, capacity building, developing a unique information infrastructure and a common understanding on aggregates, based on directives and guidelines of EU. Activities will connect institutions, policy makers, politics and economics, operators of quarries, civil society and non-governmental organizations through workshops and target results.

Specific objectives include capacity building, obtaining information on infrastructure and planning a regional center in the SARM and SSM. Local activities will focus on mining with minimum environmental impact by using best practices, reducing illegal exploitation and recycling in order to reduce production and consumption of primary aggregates. Regional and national activities will create a SARM framework for effective management and will define SSM, as it is and recommend for implementation under the law.

SARMa project is part of the Priority Axis 2: Protection and improvement of the environment, being framed in the area of intervention 2.4: **Promoting energy** and resource efficiency, having as lead partner Geological Survey of Slovenia. It is the first transnational project in South Eastern Europe, based on SARM and SSM.

3. Project participants

In the project are to be found participants from EU countries (Austria, Bulgaria, Greece, Italy, Slovakia, Slovenia, Romania and Hungary) and neighboring countries (Albania, Bosnia-Herzegovina, Croatia, Montenegro, Serbia).

Among the participants are universities, national geological institutes, ministries, associations of producers of aggregates, prefectures, mining and geology agency. Trained specialists are engineers geologists, mining engineers, engineers of exploitation, engineers of preparations, economists and managers.

The participants from Romania are the Faculty of Geology and Geophysics (University of Bucharest) and Geological Institute of Romania. The project has undergone the first stage of development and it is found in the second stage. Three meetings were held, one in Ljubljana (Slovenia), one in Bologna (Italy), and another one in Split.

4. Expected results

Results will include at local level the increase in the efficiency of extraction of aggregates in order to maximize profit and to obtain a sustainable life cycle of aggregates, frequent adoption of best practices, as few phenomena of illegal extraction as possible and use of a database to find them; increase the recycling rate to be used as aggregates.

Regionally, the results will include the use of several policies and legislation that incorporates the principles of SARM and SSM, a more consistent management of aggregates and of recycling; a better recognition of the need for SSM plan based on planned actions, increased efficiency of information dissemination to stakeholders and affected groups, the adoption on a large scale of GIS support structure and SARM and SSM, creating several maps and databases for aggregates transport.

At the transnational level, results will include capacity building through knowledge transfer, a comprehensive policy regarding coordinating within SARM and SSM between countries of SE Europe, efficient transport of aggregates, continuing the partnership between project members and observers representing the mining ministries, local authorities, chambers of commerce and industry.

Transnational activities aim to harmonization of policies and legislation in South East Europe, the transfer of information and creating an intelligent system of aggregates. The project represents the base for creating a regional center for the management and sustainable aggregates supply. Transfer policies at local, regional and national levels are provided through regional and local authorities.

Currently, states of SE Europe manage aggregate inconsistently, sometimes without considering efficiency of energy or resources, or alternative materials. Transnational partnership of experts and participants from different levels will help transfer of knowledge from areas with more experience to those with lower resource capacity.

Partners will adopt and adapt EU policies in order to create a common framework for sustainability management and supply. Recommendations will be tested and the results will be applied in the area of SE Europe, allowing countries to implement the harmonized approaches, thus increasing the sustainability of quality of life, resource efficiency and long-term cooperation.

Results will be disseminate to level of expertise and public events and will be made available in electronic form and in the form of textbooks and through the Intelligent System of Aggregates. Regional Centre will monitor the results and knowledge transfer to the industry, government and in the end to civil society.

Details about the project and its results obtained during the performance to date can be obtained from the website www.sarmaproject.eu

SOLUȚII POSIBILE PENTRU UN MANAGEMENT DURABIL AL AGREGATELOR

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Legislația în vigoare asigură cadrul de desfășurare pentru extracția de agregate și roci de construcție prin legea minelor și normele de aplicare a acesteia. În acest cadru, în deplină concordanță cu ultimele directive ale Uniunii Europene, urmează să fie construit un nou sistem, stimulat și atractiv din punct de vedere economic, însă și restrictiv, prin care deținătorii de licențe pentru substanțe minerale utile să fie interesați, dar și îndrumați spre cooperare.

La nivelul Uniunii Europene se urmărește cu tărie implementarea managementului durabil al resurselor de agregate pentru că agregatele (piatra concasată, nisip și pietriș) sunt cruciale pentru infrastructură și construcții. Țările membre ale UE, iar între ele cu precădere cele din Sud Estul Europei, sunt bogate în agregate, dar se constată că aprovizionarea nu este coordonată în interiorul acestor țări sau de-a lungul acestei arii. Satisfacerea cererii presupune un lanț de aprovizionare eficient și durabil (planificare, extracție, transport, utilizare și reciclare), și o exploatare socio-economică rațională, pentru a înlătura opoziția față de extracție, blocajele de aprovizionare și restricționarea dezvoltării. La nivel local, extracția rațională are în vedere protejarea mediului prin promovarea celor mai bune practici, reducerea numărului carierelor ilegale, și reciclare pentru reducerea utilizării agregatelor primare.

Institutul Geologic al României, recunoscut la nivel european pentru atribuțiile de Serviciu Geologic, face parte din consorțiul de realizare a proiectului SEE/A/151/2.4/X cu titlul „*Sustainable Aggregates Resources Management*” – SARMA (www.sarmaproject.eu), finanțat prin Programul de Cooperare Transnațională „Europa de Sud-Est” .

Rezultatele scontate prin implementarea proiectului SARMA includ următoarele aspecte:

- a) dezvoltarea unor politici și a legislației care să înglobeze principiile managementului și ofertei durabile a agregatelor;
- b) dezvoltarea unor strategii consistente pentru managementul durabil al resurselor de agregate și a reciclării în regiunile/țările Europei de Sud-Est;
- c) o mai mare recunoaștere a necesității existenței unui plan privind oferta durabilă de agregate;
- d) o mai mare atenție privind diseminarea informațiilor către grupurile interesate sau afectate de această activitate;
- e) adoptarea mai largă a structurilor GIS ca suport pentru managementul și oferta durabile de agregate.

În România, conform legii, deținătorii de licențe de explorare/exploatare au exclusivitate pe perimetrul concesionat și din această cauză nu se pot desfășura alte activități miniere fără acordul lor. Însă Legea Minelor, Nr. 85 din 18 martie 2003 precizează la CAP. 3 (Regimul de punere în valoare a resurselor minerale) la Art. 25 : *În limitele unui perimetru de explorare/exploatare, autoritatea competentă poate acorda, în condițiile legii, unor persoane juridice, altele decât titularul licenței, dreptul de explorare și/sau exploatare pentru alte resurse minerale, cu acordul titularului. De asemenea la Art. 24 se precizează: Titularul unei licențe poate transfera unei alte persoane juridice drepturile dobândite și obligațiile asumate numai cu aprobarea prealabilă și scrisă a autorității competente. Orice transfer realizat fără aprobare scrisă este nul de drept. Totodată, în aceeași lege la CAP. 4, drepturile și obligațiile titularului, Art. 38, litera e, se*

precizează că *titularul licenței poate să se asocieze cu alte persoane juridice în vederea executării activităților miniere prevăzute în licență, cu aprobarea prealabilă a autorității competente*. Responsabilitatea îndeplinirii obligațiilor din licență revine în exclusivitate asociatului care are calitatea de titular de licență. În vederea emiterii aprobării asocierii, autoritatea competentă va avea în vedere cel puțin următoarele elemente: capacitatea tehnică și financiară a celui cu care se încheie asocierea, obiectul asocierii, modul de delimitare a drepturilor și obligațiilor asociaților. Companiile și societățile naționale care execută activități miniere vor obține aprobarea autorității competente numai cu acordul prealabil al ministerului de resort.

Modalitatea în care se poate face asocierea unor firme pentru realizarea, în parteneriat, a exploatarea unor substanțe minerale diferite în cadrul unei singure licențe deținute unilateral doar pentru o substanță utilă se regăsește în: HG Nr. 1208 din 14 octombrie 2003 privind aprobarea Normelor pentru aplicarea Legii minelor nr. 85/2003 la CAP. 6 (transferul licenței), Art. 109-117.

Din cele arătate mai sus rezultă că există toate premisele legale pentru exploatarea rocilor și agregatelor de construcție, pe arealul unei licențe obținută pentru alte substanțe minerale utile.

În cele ce urmează vom prezenta câteva situații posibile prin care volume imense de roci excavate și depozitate pot fi introduse în circuitul economic și valorificate ca agregate.

Cazul 1: În suprafața licenței sunt roci mineralizate și sterile în locații diferite iar pe zonele cu roci sterile sunt lucrări vechi și/sau halde vechi de steril.

Soluție: se separă suprafața cu roci sterile și se acordă noului investitor.

Consecințe: Taxele primului investitor scad prin reducerea suprafeței perimetrului din licență. Noul investitor va participa în mod natural, la refacerea drumurilor din zonă. Totodată, dacă, primul investitor are lucrări în derulare, poate scăpa de sterilul nou și poate lua, la înțelegere cu noul investitor, un procent de pe sterilul din perimetrul lui. Astfel dispar volume de steril din noile halde ale primului investitor. Costurile de cercetare geologică necesare celui de al doilea investitor, scad, substanțial, folosind lucrările și documentațiile primului investitor (cu respectarea legilor în vigoare).

Stimulente: statul ar putea acorda niște facilități primului investitor care a acceptat această soluție ecologică.

Presiuni: Statul ar solicita anumite taxe de poluare, pentru cine depune steril și nu îl valorifică, ori taxe pentru suprafețele nou ocupate cu haldele de steril. Măsurile ar putea obliga primul investitor măcar la o grosieră sortare a sterilului depozitat.

Cazul 2: În suprafața licenței, rocile mineralizate sunt amestecate cu rocile sterile

Soluție: Se acordă dreptul primului investitor să păstreze întreaga suprafață, dar, la înțelegere cu noul investitor, să-și dea acordul de exploatare a rocilor sterile de către al doilea investitor, cu condiția împărțirii taxelor, în mod, proporțional.

Consecințe: primului investitor îi scad taxele. Rocile sterile vor fi luate de al doilea investitor, care, la înțelegere, poate oferi un procent primului investitor.

Stimulente: statul ar putea acorda niște facilități primului investitor care a acceptat această soluție ecologică. Statul ar solicita documentații simplificate celui de al doilea investitor, dacă cele obținute de primul investitor, care este responsabil în fața autorităților, sunt actuale și acoperă în totalitate perimetrul.

Presiuni: Statul ar solicita anumite taxe, de poluare, pentru cine depune steril și nu îl valorifică, sau taxe pentru suprafețele nou ocupate cu haldele de steril. Statul poate institui o penalitate care se aplică celui care nu separă rocile utile de cele sterile în halde diferite.

Cazul 3: În perimetrele în care sunt, doar lucrări de cercetare.

Soluție: Se solicită de către ANRM primului investitor situația actuală a lucrărilor și, în prezența unor premise favorabile pentru agregate, cedarea acestor suprafețe.

Consecințe: Se va realiza o gestionare mai eficientă a zonelor cu potențial pentru materiale de construcții.

Stimulente: Statul ar putea oferi unele stimulente investitorilor care ar prelua aceste zone.

Presiuni: Dacă deținătorul de licență nu cedează aceste zone, cu toate că se demonstrează că nu prezintă un alt fel de interes economic, poate fi sancționat, până la retragerea licenței. .

Cazul 4: În perimetrele exploatate nu se desfășoară lucrări, din diferite motive, dar mai există licență pentru o firmă.

Soluție: ANRM va solicita, de urgență, proprietarului licenței situația actuală și va demara procedurile legale de retragere a licenței. În acest fel se va actualiza situația perimetrelor libere.

Consecințe: În cazul că perimetrele sunt poluate cu halde vechi sau zone degradate, ANRM poate scoate perimetrele la concurs pentru exploatare de materiale de construcții.

Stimulente: Statul ar putea oferi unele stimulente investitorilor care ar prelua aceste zone.

Presiuni: Dacă deținătorul de licență nu cedează aceste zone, cu toate că se demonstrează abandonul, poate fi sancționat, prin amendă și retragerea licenței de către ANRM

Cazul 5: Prezența teraselor aluvionare sau a depozitelor de pietrișuri și nisipuri actuale, din râurile care traversează perimetre pentru care s-a acordat licența pentru alte substanțe.

Soluție: ANRM va decide, împreună cu Ministerul Mediului și Regia Apelor Române, dacă este cazul exploatare a acestor substanțe. Numai dacă aceste exploatare au ca scop reabilitări ale albiei râului și ecologizarea zonei, ANRM poate decide scoaterea la concurs a perimetrelor.

Consecințe: În această situație titularul de licență va prezenta un punct de vedere și disponibilitatea de colaborare. Eventualul investitor va împărți cu primul proprietar taxele către stat, conform suprafeței ocupate din licență și va amenaja drumurile aferente activității lui. Primul investitor va beneficia de reducerea taxelor, reducerea costurilor de întreținere a drumurilor și eventual va negocia un procent din materialul extras de noul investitor.

Stimulente: Statul poate acorda niște facilități ambilor investitori pentru ecologizarea zonei.

Presiuni: Statul, mai ales prin organele de control de la mediu și ape, va monitoriza strict activitatea celui de al doilea investitor și va lua măsuri, conform legii, în cazul unor abateri de la proiectul avizat.

Cazul 6: Vechi areale miniere, abandonate, aflate la dispoziția ANRM.

Soluție: ANRM va scoate la concurs aceste zone, pentru valorificare, ca materiale de construcții, a rocilor depozitate în vechile halde de steril.

Consecințe: Potențialul investitor are acces la informațiile geologice din perimetru (plătind taxele legale la ANRM). Își poate face un calcul de rezerve cu lucrări geologice mai puține. Materialul din haldă este deja extras și necesită doar concasare. În acest fel se reduc costurile extracției. Se elimină poluarea fonică și riscurile generate de exploziile folosite în cariere. Acest aspect permite derularea activităților miniere aproape de localități sau rezervații naturale fără a afecta populația și mediul, așa cum fac marile cariere actuale.

Stimulente: Statul ar putea oferi unele stimulente investitorilor care ar prelua aceste zone

Presiuni: Statul, mai ales prin organele de control de la mediu și ape, va monitoriza strict această activitate și va lua măsuri, conform legii, în cazul unor abateri.