

Romanian Journal of MINERAL DEPOSITS

continuation of

DARI DE SEAMA ALE SEDINTELOR INSTITUTULUI DE GEOLOGIE SI GEOFIZICA
COMPTES RENDUS DES SÉANCES DE L'INSTITUT DE GÉOLOGIE ET GÉOPHYSIQUE
(2. Zacaminte)

Founded 1910 by the Geological Institute of Romania

ISSN 1220-5648

VOL. 86
No. 1

CONTENT

page

- Gheorghe C. POPESCU, Antonela NEACȘU, Grigore BUIA, Gheorghe DAMIAN, Floarea DAMIAN**
Perspectives of rare metals and dispersed elements ore deposits in Romania. A review 1
- Paulina HIRTOPANU, Ion STANOIU**
Stefanu manganese and iron occurrence, Parang Mts., South Carpathians 15
- Florentin STOICIU, Viorel BADILITA, Mihai GHITA, Lenuta Jana ENACHE**
Physico-chemical characterisation of a copper slag from metallurgical plant Zlatna 31



Geological Institute of Romania
Society of Economic Geology of Romania
București – 2013



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ISSN 1220-5648

PERSPECTIVES OF RARE METALS AND DISPERSED ELEMENTS ORE DEPOSITS IN ROMANIA. A REVIEW

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Abstract. Rare metals represent a valuable group of ore mineral resources who play an essential role for the multitude of high-tech products. Before the year 1990, during state exploration, some noneconomic accumulations have been discovered in Romania, referring to the technologic possibilities before the ninety decade. Geologic and metallogenic characteristics of the Romanian territory offer many arguments in order to understand the rare metal forming processes and their spread, and also to discovery new ore deposits. This kind of accumulation was formed both intracontinental rift stage - case of the Ditrău Massif, East Carpathians, with some rare and radioactive metal occurrences (Nb, Zr, Y, Th, U), and during the collision between the Getic Unit and the Danubian Realm, when conditions for generating rare metals (Nb, Y, Zr) and radioactive metals in the shear zone of Getic „blocks” from the South Carpathians have been developed. Other rare metals are Te, Se and Cd, which are found into base-metal ore veins related to an andesitic stockwork generated by the Neogene calc-alkaline magmatic events in the Metaliferi Mountains at Săcărâmb, and in the waste dumps of the old mine area. Telluride bearing gold and silver ore deposit at Săcărâmb is included in the Golden Quadrilateral area and it is the largest telluride mineral accumulation around Romania and Europe.

Keywords: rare metals, industrial applications, Romanian metallogeny, metallogeny of strike-slip faults in the Southern Carpathians, carbonatite-type rare metals concentrations of Ditrău Alkaline Massif, East Carpathians, telluride mineral accumulation in the Metaliferi Mountains.

1. Introduction

The classic acceptance of rare metals (“RMs”) is referring only to a small number of elements, *e.g.*, Ta, Nb, Be, Zr, Li (Petrulian, 1973). Modern authors extend the term, including more than 30 metals/semimetals of alkali elements (Li, Rb, Cs), light elements (Be), rare earths elements-lanthanide and similars („REEs”, Y, Sc), hard fusible elements (Zr, Hf, Nb, Ta), and dispersed elements mainly concentrated in sulphides (Ge, Tl, Cd, In, Te, Ga, Se). This group includes elements which appear as independent minerals, but also as isomorphic substitutions within the network of common minerals, having a limited spreading, from where the term *rare* is coming (Murariu, 2002). Due to their geochemical properties, these metals are extremely valuable, explaining interest for discovering, mining and processing similar ore deposits. The European Commission Report from June 17, 2010 mentioned that access to mineral resources will be more and more difficult in the future for the European Union, despite their essential role for the multitude of high-tech products, *e.g.*, mobile phones, iPods, hybrid auto motors, wind energy turbines, radar and missile systems, Li-ion batteries, optics, energy fluorescent light bulbs, synthetic fuels. The previsions making by the European Council for the period till to 2030 indicate a *critical group* of at least 14 elements and raw products (http://www.consilium.europa.eu/ueDocs/cms_Data/docs/pressData/en/ec/115346.pdf).

This is the consequence of economic development in some countries and of the new emergent technologies. RMs resources are located only in few countries (where is more and more difficult to mine and extract them), *e.g.*, Democratic Republic of Congo for cobalt and tantalum, Brazil and Russia for niobium and tantalum, China for antimony, USA for tellurium, selenium, lithium, Chile for lithium, etc. In many cases this strong demand for RMs requires difficult and costly processes, meaning large amounts of energy, toxic emissions and residues. The recycling rate is still reduced, the rank of substitution too. Moreover, many of the emergent economies have their own strategies of industrial development, based on commercial, fiscal and investment instruments, so that resources can be used for internal purposes (Buia & Lorinț, 2011).

2. Demand and uses

As we know, demand for RMs is a consequence of developing high technologies, IT, and communications especially. Several uses correspond with every element, based on its properties.

Lithium

Although lithium and its compounds have several industrial applications and nuclear physics, the main use is related to lithium batteries and lithium-ion batteries. It is used extensively in non-linear optics application, telecommunication products, IT, electric and electronic devices. Researchers sustain that the future of this metal will be in auto industry, by increasing application of the Li cells in hybrid electric, plug-in hybrid electric and battery electric vehicles. Lithium-ion batteries are also growing in popularity for aerospace and navy industries, where miniaturising of circuits and energy storage devices are essential (http://en.wikipedia.org/wiki/Lithium-ion_battery).

Niobium and tantalum

Niobium, formerly columbium, is a soft, grey, ductile transition metal. Niobium becomes a superconductor at cryogenic temperature. It has the largest magnetic penetration depth of any element. Niobium alloys are used for superconductors and in electronic components. It is a microalloying element for steel (ferro-niobium). Because it absorbs easily gases, niobium is used in getters. About 60% of the worldwide production of niobium and tantalum are used in mobile phones and electronics. Appreciable quantities of the element are used in superalloys for jet engine components, gas turbines, rocket subassemblies, turbo charger systems, air frame systems, medical devices, teleguide guns. The chemical inertness of tantalum makes it a valuable substance for laboratory equipment and a substitute for platinum, but its main purpose is for electrolytic capacitors and electronic equipment industry. Tantalum is also used to produce high quality alloys and superalloys for jet engine components, nuclear reactors, missile parts, rocket subassemblies. Since it is nonirritating, tantalum is widely used in making surgical instruments and implants (<http://en.wikipedia.org/wiki/Niobium>).

Tantalum is always together with niobium and occurs in minerals like tantalite, columbite and coltan (a mix of columbite and tantalite).

Tellurium

Until recently a by-product of mining industry, tellurium is widely used our days in energetic industry (thermoelectric devices), metallurgy (steel industry), metallic alloys, color ceramics, glass and plastics (<http://en.wikipedia.org/wiki/Tellurium>). The most important use of tellurium is in solar panels and semiconductors. The CdTe photovoltaic cells are obtained using a high advantageous *CBD technology*, involving wafers of crystalline silicon. Thin films are based on using semiconductor layers to absorb and convert sunlight, and used to surpass crystalline silicon photovoltaic in cheapness and efficiency. (http://en.wikipedia.org/wiki/Cadmium_telluride_photovoltaics).

Selenium

This element is a semiconductor and it is used in some types of solid-state electronics, as well as in rectifiers devices which convert alternating current electricity into direct current electricity. Because of their photovoltaic and photoconductive properties, selenium is used in photocopying, photocells and solar cells. Selenium compounds are popular in the glass-making industry. Commercially, selenium is produced as a byproduct in the refining of Pb, Cu and Ni ores. It is used in light meters, because pure selenium increases 1000 times its conductivity from dark to strong sun light exposure (<http://en.wikipedia.org/wiki/Selenium>).

3. Geological and metallogenic characteristics of Romanian territory which generate rare metal occurrences

From the geological point of view, RMs form economic deposits in specific conditions, as a consequence of some particular geological-metallogenic processes. So, if we refer to the crustal-lithospheric processes, then hot spot and intracontinental rift zones are the most indicated for generating RMs ore deposits in the light of plate tectonics. The East-African rift is assimilated with the intracontinental rift stage, longways where few of the most important RMs ore deposits are formed (Ta, Nb, REEs, Y, etc.) (Neacșu, Popescu, 2009).

The Romanian metallogeny describes both crustal geological processes (continental drift, oceanic crust expansion and convergence of lithospheric plates), and also local processes (tectonogenesis,

magmatogenesis, metamorphism and hydrothermalism), which have been developed in a particular way, based on the action of the first major processes (Popescu, 1986).

According to the geological structure of Romanian territory, its metallogeny is different as forming and organisation. There are specific metallogenic units in the Carpathians and vorland (Fig. 1). Thus, the vorland metallogeny, in Dobrogea, where metallogenic processes are mainly pre-Alpine related, is characterized by iron and base metal ores in crystalline schists, and by iron, barite and sulphide mineralization associated to Triassic magmatites. The RMs and minor elements are less important, but produced minerals like monazite, molybdenite, or mineral indicators as fluorite.

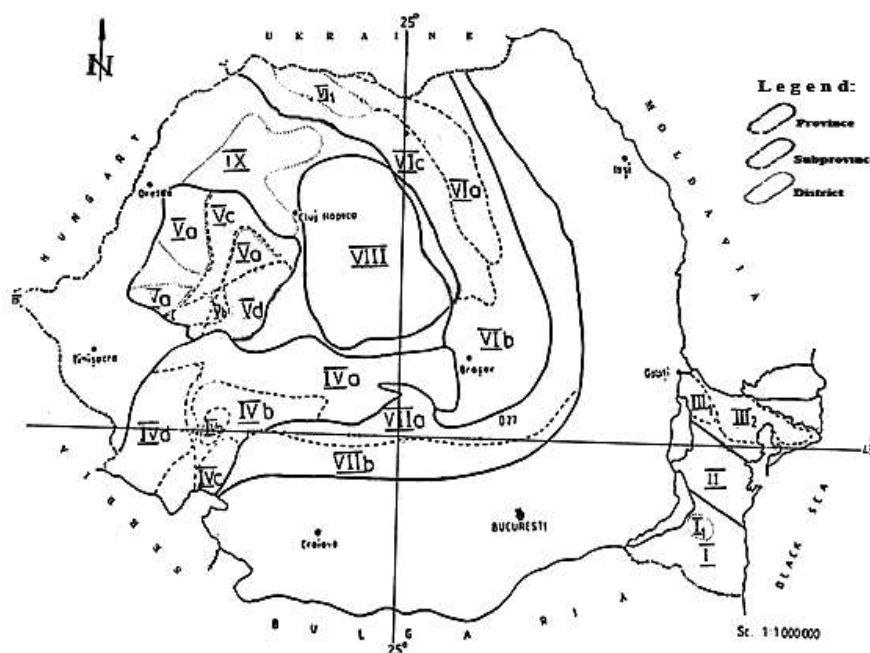


Fig. 1. Metallogenic units of Romania

Vorland domain: I. South Dobrogea province, I.1. District with phosphorites and glauconite, II. Central Dobrogea province, III. North Dobrogea province, III.1. Măcin district, III.2. Tulcea district. Carpathians Realm, IV. South Carpathians 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 banatites, V.d. Subprovince associated of Neogene volcanics, VI. East Carpathians 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-Carpathians through province, VIIa. Subprovince with evaporites, VII.b. Subprovince with Ti-Zr placers, VIII. Transylvanian Basin province, IX. Gilău Mezeș-Preluca district (according to Popescu, 1986, simplified).

The metallogeny of the Carpathians displays a great variety of mineral deposits, both Alpine and local regenerating Pre-Alpine ages. The Carpathian domain has its own metallogenic individuality, related to the convergence process, in fact to the subduction stage, during K₂-Pg in the South Carpathians and in the Apuseni Mountains (giving up Cu, Bi, Mo, Fe, Pb, Zn as major metals, and rarely Ni, U), and during Miocene-Pliocene (with Pb, Zn, Cu, Au, Ag as major metals and Cd, Bi, Ge as minor elements) in the East Carpathians, and also in the Apuseni Mountains (with Au, Ag, Cu, Pb, Zn as major metals, and Te, Se, Cd as minor elements).

There are only few references looking the metallogenic consequences of plate tectonics for Romanian territory. A general presentation about Alpine ore deposits and metallogenic units from the NE of Mediterranean region in the light of plate tectonics, is made by Jankovič in 1990, and recently by Neubauer et al., in 2005. They discuss the Romanian metallogeny in relationship with the metallogeny of the neighbouring Alpine terrains.

There are other studies (Popescu, 1977) where particular aspects of plate tectonics are presented, such as the kimmeric North Dobrogea metallogenesis (Somova, Iulia) and its correlation with epigenetic mineralization from the eastern part of the crystalline-Mesozoic terranes of East Carpathians (Ostra-Gemenea-Delnița). The result is that the North Dobrogea is considered a relict of an intercontinental rift,

which has been preceded by a hot spot with consequences in the Măcin District of the North Dobrogea Province (Fig. 1). If we add that this district includes alkali-sodic granites, then it is clear that it could be interesting for tackling RMs.

Due to the existence of the Ditrău Massif, East Carpathians, where alkali-rocks are formed (alkali-granites, syenites, nepheline syenites) in relationship with a carbonatitic system, a special effect of intracontinental rift stage passed in Triassic-Low Cretaceous may be considered (Borcoş et al., 1998; Cioflica and Vlad, 1984), and consequently, particular RM and REE mineralization in a such context.

In order to explain metallogenic aspects of the Carpathians Domain, the elaborated models are local and focused on the every Carpathian unit.

Evidences of the dismembering of the pre-Alpine metallogeny are observed in the South Carpathians, as a result of the collision between the Getic Unit and the Moesian platform. The two units have been separated at the beginning of the Mesozoic Epoch by the Severin Unit, and the convergence process continued from Middle Cretaceous until Upper Cretaceous. The most significant metallogenic result is the dismembering of the Pre-Alpine metallogenic unit related to the Getic crystalline rocks (manganese and iron metallogenic unit), so relicts of manganese metallogenesis are found within the Getic „blocks”, created as a result of the collision process (Fig. 2). Another result is the presence of Au-Ag mineralization and some rare and radioactive metal occurrences (Li, Nb, Zr, Y, Th, U).

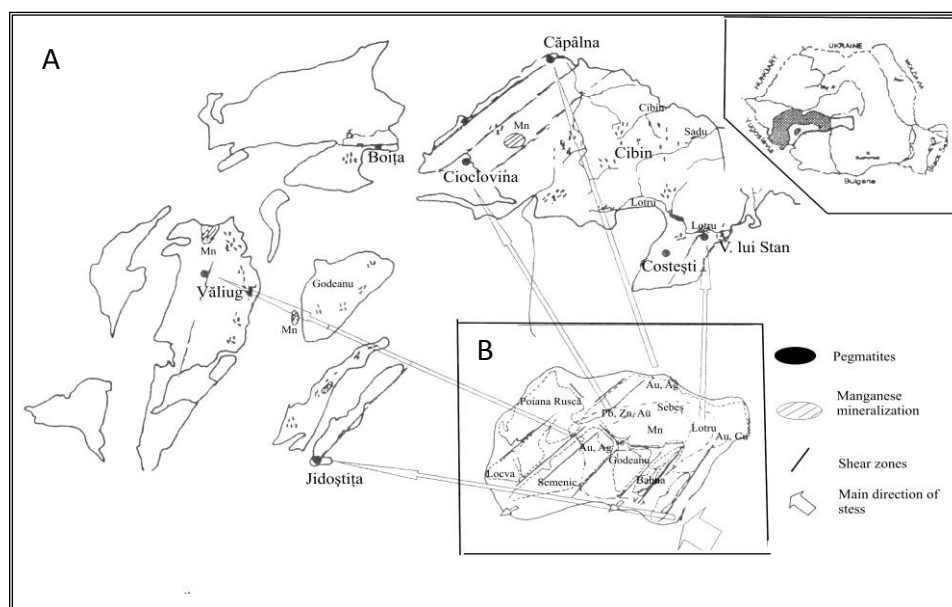


Fig. 2. A. Getic „blocks” resulting by collision process between the Getic Domain and the Moesian platform, and mineralization associated to shear zones. B. The Getic Domain before the collision process with the Danubian Domain (strike slip faults which facilitate the Getic Domain dismembering are observed) (according to Popescu, Tămaș-Bădescu, 1998).

4. The Romanian metallogenic units with deposits of rare metals and dispersed elements

4.1. Metallogenic units related to the riftogenesis process

There are mineral deposits related both to the incipient stage of the expansion process, when hot spots, intracontinental rifts eventually, were created, and also to the intercontinental rifts. Despite its Alpine age, metallogenesis has a relict character for the Vorland Domain and also for the Carpathian Domain, as a consequence of the younger geodynamic process, meaning transcurrent motions with a convergent character (Popescu, 1997).

4.1.1. RM deposits in relationship with the intracontinental rift stage

There is a well-known metallogenesis only in the Ditrău Alkaline Massif zone, consisting of Mo and carbonatite-type REE concentrations.

Magmatites and their metallogenesis represent particular aspects in the Crystalline-Mesozoic subprovince of East Carpathians (see VI.a in Fig. 1) (Constantinescu et al., 1983; Pál-Molnár et al., 2010). There is an

intrusive alkaline massif with a quasi-ring structure, where central part is represented by foidic rocks, followed discontinuously to the periphery by syenites, monzonites, monzodiorites, granites and alkaline-granites (Fig. 3). The NW part of the massif, the Jolotca-Tarnița Sector, is detached in comparison with the main intrusive core, revealing particular petrographic and metallogenic features, due to the deeper level of erosion.

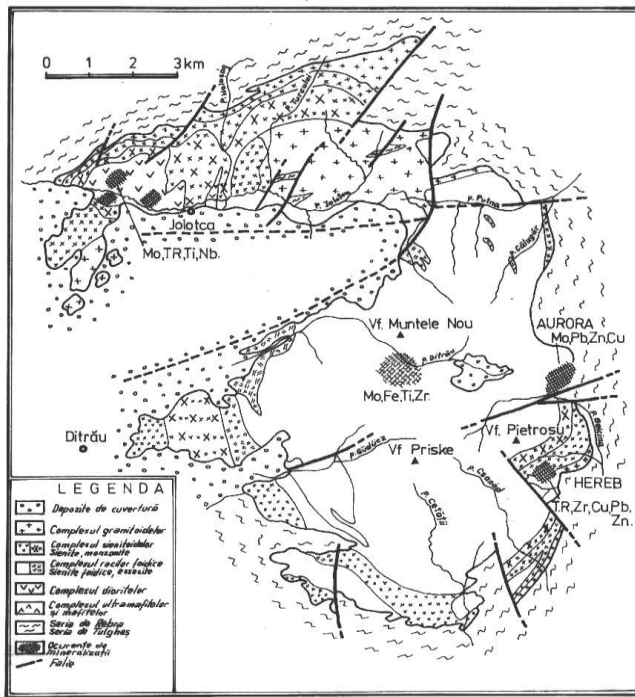


Fig. 3. Geological sketch of the Ditrău Massif (according to Constantinescu et al., 1983, with additions)

Thus, the magmatic products are syenites and monzonites in the central core, and diorites and granites separated by lenticular hornblendites in the peripheral part of the massif.

Various petrographic vein rocks are observed through the Ditrău Alkaline Massif, controlling spatial development of related metallogenesis. So, lamprophyres, microsyenites, foidites, alkaline-granite and aplite dykes are found, together with albitite and sulphide carbonatite veins.

New petrological studies revealed that the formation of the Ditrău Alkaline Massif can be related to a continental magmatic activation. The process started in the Middle Triassic at the southern passive edge of the European continent in an extensional tectonic environment by the uplift of mantle-origin magma; this produced the rocks of the Tarnița Complex (peridotites, gabbros, diorite), and comagmatic products (nepheline syenites and granites). By the Jurassic detachment of the Getic-Bucovinian "microcontinent" from the European platform, a new mantle origin intrusion developed. Due to the mixing of the resulting syenites with the cogenetic rocks of the first magmatic phase, a series of hybrid rocks (diorites, monzonites) were formed (Pál-Molnár, 2010).

The metallogenesis associated to the Ditrău Alkaline Massif is complex, its main characteristic being the presence of RMs (e.g., Zr, Ti, Nb, Th, Mo) and REEs.

From the genetical point of view, primary concentrations formed by magmatic segregation are seen, related to the Tarnița Complex magmatites, represented by Fe, Ti, P, V, Ta, and postmagmatic mineralization related to syenites and foidite syenites, e.g., Zr, P, Nb, Th, REEs, Mo, Pb, Zn.

Two metallogenic sectors are drawn (see Fig. 3): the northern Jolotca-Tarnița Sector, and the southern Aurora-Hereb Sector.

- The Jolotca-Tarnița Sector includes "primary" Fe, Ti, P, V, Ta mineralization, related to ultramafites, mafites and diorites, represented by disseminations and nests of vanadiferous magnetite, ilmenite, sphene, apatite; it includes also postmagmatic mineralization of Mo, REEs, Ti, Nb, Pb, Zn, spatially associated to vein rocks (lamprophyres, albitites, carbonatites). Last mineralization contains quasiparallel system veins,

but also disseminations and net veinlets with molybdenite, xenotime, loparite, monazite, ilmenite, pyrite, sphalerite and galena;

- *The Hereb-Aurora Sector* is situated on the SE zone of the Ditrău Massif, and consists of postmagmatic RMs mineralization, associated to syenites and foidite syenites, grouped in two vein fields:

- *The Hereb-Balasz Lőrincz field* with Zr, P, Nb, Ti, Th, REE vein mineralization (zircon, apatite, ilmenite, orthite, xenotime, pyrochlore, columbite, and sulphides);

- *The Aurora field* contains Th, V, REE, Zr, F, Mo vein mineralization, spatially associated to lamprophyre veins, syenites, granites and crystalline schists. The mineralization includes pyrochlore, bastnaesite, thorite, xenotime, niobotantalite, zircon, fluorite, and Pb, Zn sulphides.

A modern and detailed mineralogical study of RMs from the Ditrău Massif is published by Hârtopanu et al., 2010. On this occasion, more than 100 new minerals were described and were added to the 85 already described REE, Y, and also Th, U, Nb, Ta, Zr minerals.

4.1.2. Occurrences of rare metals and minor elements in the northern area of Dobrogea (Măcin Mountains, the Pricopan Massif)

With a less clear geodynamic situation is the Măcin Unit mineralization (Fig. 1), with no economic importance for the moment, consisting of monazite, fluorite, molybdenite and copper sulphides, in relationship with hercynic granitoidic rocks.

The presence of molybdenite and monazite mineralization associated to alkaline-granites in the Pricopan Massif, similar to the Ditrău Massif, shows that both metallogenesis were formed under conditions of an incipient stage of the expansion process. For the moment, there are no petrological data for convinced sustaining this point of view.

There are two hypotheses regarding the genesis of intrusive rocks in the Măcin Unit, one for explaining the genesis of the Pricopan-Greci calc-alkaline rock type, and other for the Iacobdeal alkaline rock type. The molybdenite mineralization is associated to the Pricopan granitoidic rocks, but REE and sulphide mineralization to the Iacobdeal granitoidic rocks. Two possibilities exist: both metallogenesis types and hosting granitoidic rocks can not be related to the same stage of geodynamic evolution, or they are created in the protorift stage, but in a different geological-petrological context. In agreement with the last interpretation is the situation of the Ditrău Massif area, where granites and diorites of the northern part host molybdenite mineralization, and syenites and monzonites of the southern and eastern part include REE mineralization. Despite a lot of opinions referring to the genesis of the Ditrău Massif, all geologists admit an unitary genesis. In this spirit, we think that in the case of metallogenesis and magmatogenesis of the Măcin Unit, it is possible an unique, successive and evolutive interpretation of them, in the geodynamic conditions of an intracontinental rift, followed by an intercontinental rift stage, with metallogenic consequences in the North Dobrogea Tulcea Unit, where bimodal magmatites and *Red Sea type mineralization* are found (Popescu, 1977). The age of the Ditrău complex has a middle Triassic age of 231.5 ± 0.5 Ma (Dallmeyer et al., 1997). Preliminary unpublished zircon U-Pb age data on alkaline granitoid from the Iacobdeal region of south-western North Dobrogea yield a concordant age of 233 Ma ± 2 Ma, which is identical, within analytical uncertainties with the Ditrău alkali massif (M. Ducea, 2013, pers. comm.), and indicate both for Dobrogea and Ditrău alkali magmatites a strong argument for unitary genesis.

4.2. Occurrences of RMs and minor elements, the Sebeş Mountains, Grădiştea de Munte

Evidences of the dismembering of the Pre-Alpine metallogeny are observed in the Southern Carpathians, as a result of the collision between Getic Unit and Danubian Realm. From Middle Cretaceous until Upper Cretaceous, the Getic Unit has been fragmented in tectonic blocks – „terrane”, resulting the dismembering of the Pre-Alpine metallogenic units related to pegmatites and manganese schists (see Fig. 2A and 2B).

The motion of the Getic blocks has been realized alternatively on E-W and NE-SW directions, resulting strike-slip faults, which prolonged within some blocks as shear zones, having a metalloctect role, especially for Au-Ag mineralization, but also for RMs (Fig.4A), all these forming new Alpine metallogenic units, with a lineimentary disposition (Fig. 4B).

4.2.1. Grădiştea de Munte

On the Cioclovina – Strungari – Căpâlna allignment in the northern part of the Sebeş Mountains, four mineralized microclitic gneiss bodies have been discovered based on gamma radiation intensity

measurements, presenting high values of radioactivity, as a consequence of the existence of REEs and RMs (Fig. 4).

Mineralization is included within one of this body, having a tabular-like aspect, a thickness between 5-6 m and up to 35 m long. Ore deposit is concordant with surrounded formations, having E-W trending and 75-80° dips, sometimes vertically disposed. The exploration activity emphasized the presence of RMs (Zr, Nb, Th, U, Rb, Sn) and REEs (Y, Ce, La). These elements form their own minerals, but they are also included as isomorphic substituents in other mineral network structures (see Plate I).

RM and REE minerals have been identified (Popescu et al., 2003) *e.g.*, zircon, monazite, xenotime, allanite, törnebohmit, pyrochlore, fergusonite, thorite, cassiterite, etc., as hypidiomorphic to xenomorphic grains, with very small sizes, even microscopic ones, extremely difficult to detect. These minerals are preferentially concentrated along fissures in rocks or on borders of grains, as aggregates with nest-like aspects or disposed along schistosity planes in rocks (Plate I, Fig. 1, 2). They are also observed as inclusions in feldspar, quartz and biotite. The genesis of mineralization is due to pneumatolitic process, as a consequence of potassium rich supracritic solutions transport along the Subcetate-Căpâlna shear zone, and with regional development in the northern part of the Sebeş Mountains (Popescu et al., 2003).

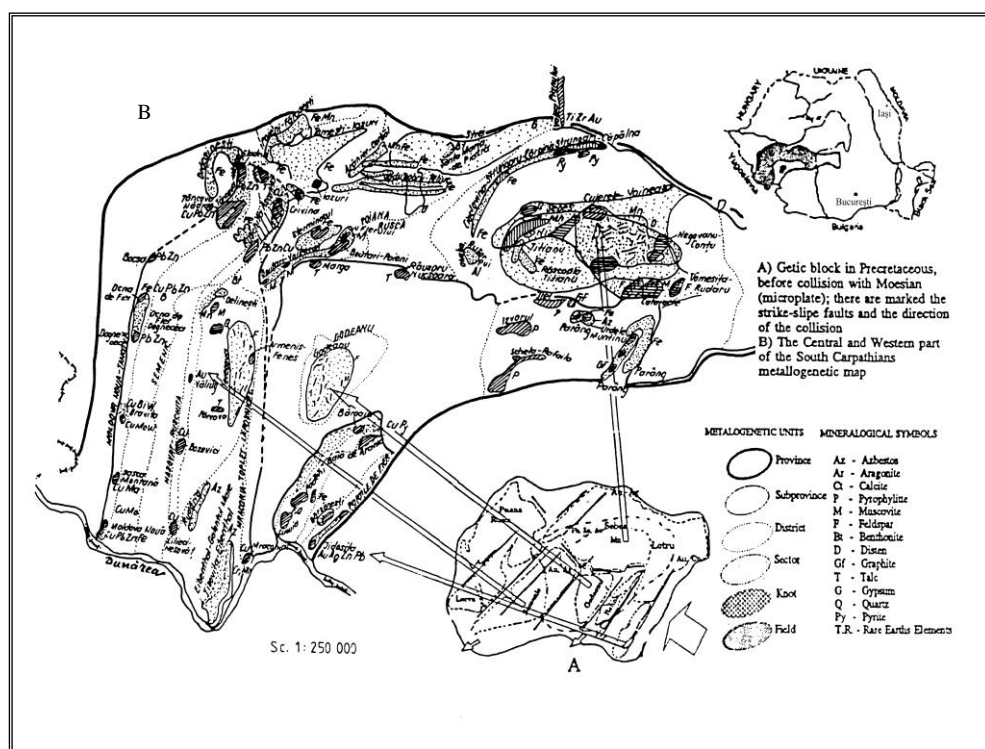


Fig. 4. Metallogenetic units of the Getic Realm before pre-Alpine events (A) and after its collision with the Moesia (microplate) (B) (according to Popescu et al., 1998).

4.2.2. Conțu Li-bearing pegmatites, the Cibin Mountains

Representing a part of pegmatitic district Cujerele-Voineasa, this is one of the most important metallogenetic units of the South Carpathians (Fig. 4). The lithiferous amounts have been identified in two close pegmatite bodies: inferior Conțu and superior Conțu. Li-bearing minerals from pegmatites in the Conțu field display widespread pegmatite bodies in various sizes (Androne, 2005), in depth as vein and lens-shaped or tabular bodies, highlighted by drilling and mining, but also isometric-tabular bodies, generally outcropping on the surface (Fig. 5). Associated minerals are albite (cleavelandite), spodumene, quartz and muscovite. Spodumene is the main Li-bearing mineral (Hann, 1987), accounting for large aggregates, distributed in pegmatite body, of several tens of centimetres in length; it is associated with tabular white-shiny feldspar mass (albite); quartz occurs as glassy white-lilac aggregates, and greenish muscovite bundles. Subordinately, nests with Li, Fe, Mn and Ca phosphates are observed: lithiophyllite-

triphylite, ferrisicklerite-sicklerite (Călin, 2012), amblygonite-montebrazite, but also tavorite and phyllosilicates (lepidolite, cookeite) (Androne, 2005). Subordinately, together with lithophilous minerals Sn, Nb and U minerals appear: cleavelandite – a variety of albite, uraninite, columbite, cassiterite (Călin, 2012). Beryl occurs in the Li-bearing pegmatites as microscopic grains, and boron occurs as tourmaline and dumortierite (Săbău et al., 1987). The Sebeș-Lotru sequence, which hosts the Li-bearing mineralization, is around 329 M.a. (Dallmeyer et al., 1994) by the isotopic methods ^{40}Ar - ^{39}Ar , who argued Hercinian age for Conțu metallogenesis.

The genesis of Li-bearing pegmatite was first considered to be magmatic, due to the complex mineralogy with REEs. Based on relationship between pegmatite and host rocks, on interminerals relationship, but also on the absence of magmatic bodies, the genesis of the Conțu pegmatites is considered to be metamorphic (Hann, 1987), as they seem to have originated mainly as a result of segregation under metasomatic-preanatectic conditions, by crystallizing within a pegmatitic fluid, without a tangible melting (Săbău et al., 1987).

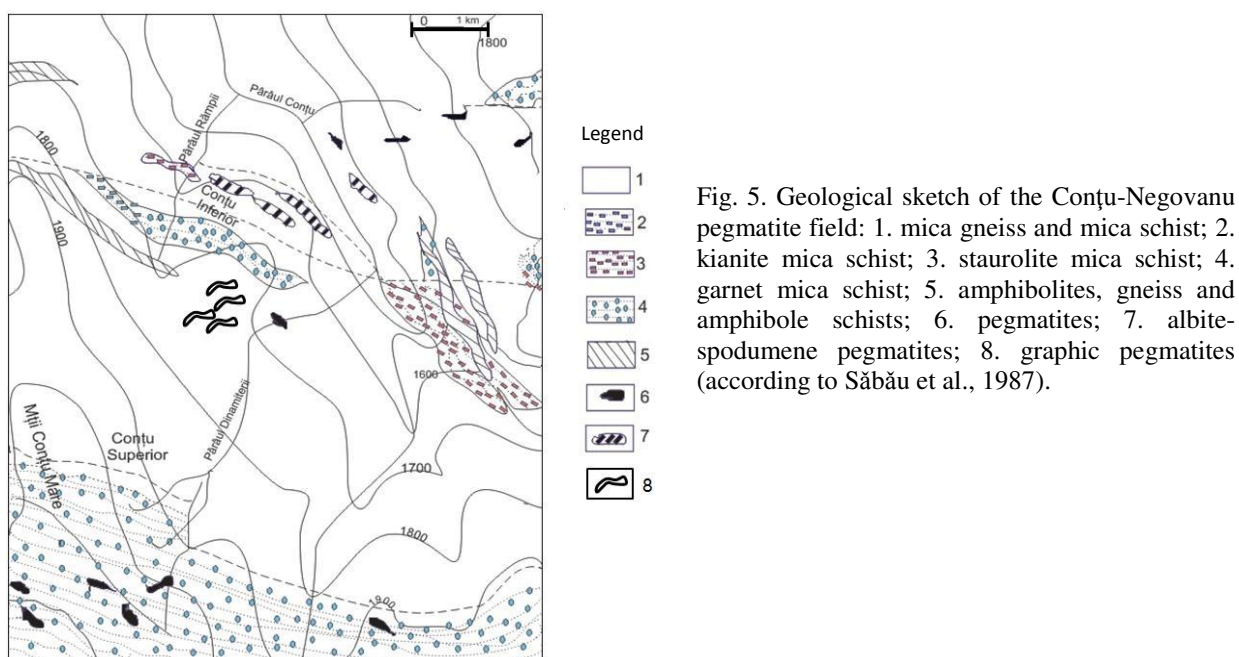


Fig. 5. Geological sketch of the Conțu-Negovanu pegmatite field: 1. mica gneiss and mica schist; 2. kyanite mica schist; 3. staurolite mica schist; 4. garnet mica schist; 5. amphibolites, gneiss and amphibole schists; 6. pegmatites; 7. albite-spodumene pegmatites; 8. graphic pegmatites (according to Săbău et al., 1987).

This process involves temperatures and pressures belonging to the Precambrian metamorphic event, affected the Sebeș-Lotru sequence, and developed under conditions of the amphibolitic facies, within the staurolite-kyanite zone (Hărtopanu, 1994). For the moment, a connection between these pegmatites and the Jiu-Sibișel shear zone, crossing the getic block Sebeș-Lotru on a NE-SW trend, is more probable (Fig. 4). Pegmatites have been formed by a similar mechanism as RM and REE mineralization in Grădiștea de Munte (Popescu et al., 2003).

4.3. Tellurium, selenium and cadmium resources in Apuseni Mts.

Since recently, tellurium was mentioned only from scientific-mineralogical point of view, without any interest for estimating geological resources in Romania. Only in 2005 this element started to be considered as a useful component, when it was used in the construction of solar panels using photovoltaic cells based on Cd-Te technology. Telluride bearing gold and silver ore deposit at Săcărâmb, Metaliferi Mountains, is the largest telluride mineral accumulation in Romania and Europe. Genetically, it falls within the class of gold-silver hydrothermal deposits with tellurides hosted into quartz veins. The base-metal ore veins are hosted into an andesitic stockwork generated by the Neogene calc-alkaline magmatic events in the Metaliferi Mountains (Fig. 6). A first estimation, regarding tellurium resource in Săcărâmb ore deposit was made taking into consideration Au: Te ratio (*i.e.* 1:2), from the most common tellurides - nagyágite and sylvanite, and the amount of gold extracted from Săcărâmb deposit over 1746-1941, estimated as being approx. 30 t Au. Therefore the amount of Te mined and unprocessed – just dumped, would be of approx. 60 t (Udubașa & Udubașa, 2004). Our paperwork presents the results of the

explorations conducted over the last 4 years on the tellurium resources hosted into three waste dumps (I, II and III Sector) at Săcărâmb (Fig. 5) and into the “Iazul Avariât” / “Damaged Tailing Dam” at Certej. Tellurium grades have been determined using ICP-MS method on the previously analyzed samples, using Au-AA26 method for Au and Ag. As concern the Au:Te ratio, it should be mentioned that this is approx. 0.25 in case of the Damaged tailing dam and 0.35 in case of the three waste dumps; these values are different against the theoretical values mentioned above.

There is a difference as concern the grades of useful elements in all four investigated zones, meaning that the waste dumps have higher Au and Te grades compared to the ore deposit. According to new data, accepting an average Au:Te ratio of about 0.3, for all perimeters it would result an estimated resource of approx. 85.7 t of tellurium. Regarding the correlation degree, tellurium is well, directly correlated with gold and silver (Fig. 8), and this confirms that tellurium is related to gold and silver mineral compounds.

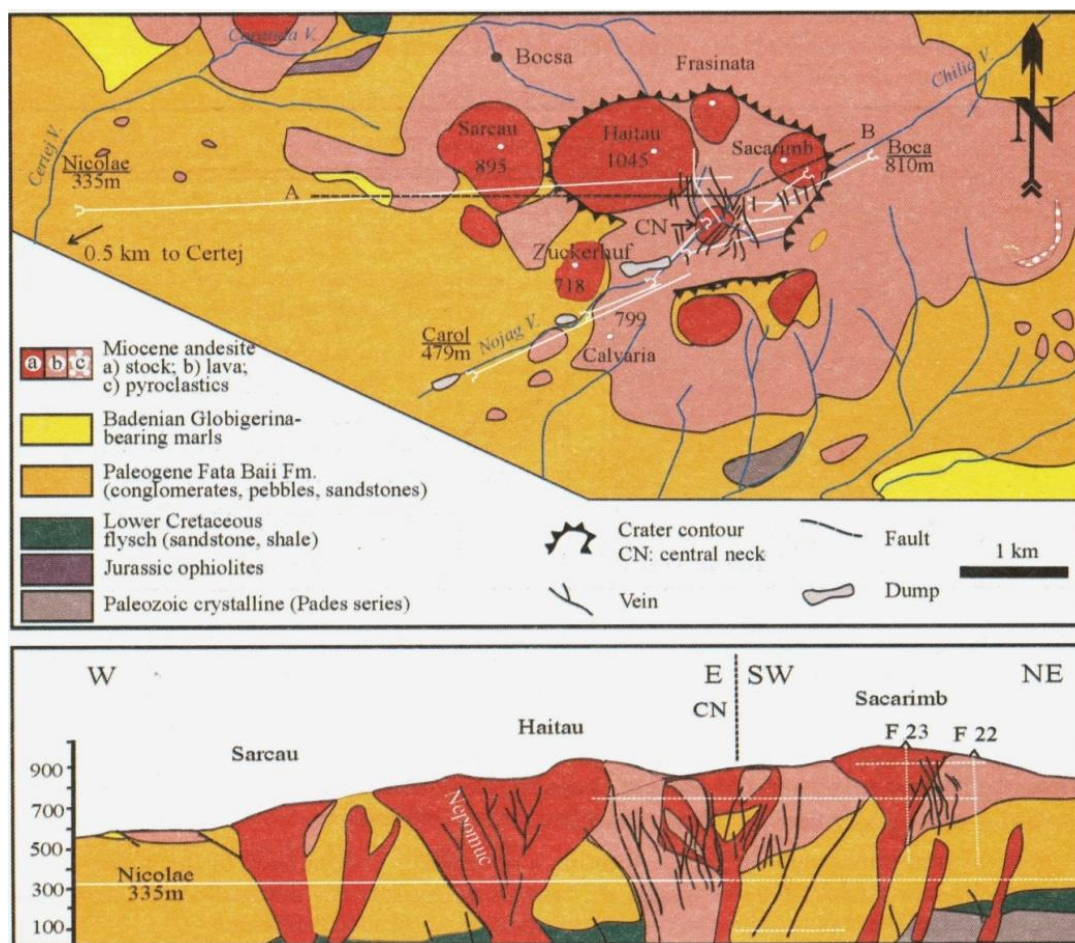


Fig. 6. Geological sketch map of the Săcărâmb area where waste dumps are placed (Udubaşa et al., 1992; Popescu et al., 2013).

Actually, the Au, Ag and Te distribution map into the tailings dam area and waste dumps area indicate overlapping of the enrichment zones for all those three elements (Fig. 7).

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 (Fig. 8).

A mineralogical new fact that may be emphasized is the presence of selenides at Săcărâmb. Despite that eucairite (CuAgSe) was mentioned in 1853, it could not be confirmed by now. Eucairite is associated with naumannite (Ag_2Se) and klockmannite (CuSe). The selenium minerals are associated with galena, alabandite and tetrahedrite (Popescu et al., 2010).

5. Conclusions

Data and theoretical speculation that we dispose for the moment offer an optimistic image on the potential of the rare metals and dispersed elements on the Romanian territory.

There are doubtless mineralogical, petrological and geodinamic elements of this statement. Last of them give a good support for considering the future development of the exploration activities – based on analogy: new ore deposits are found where old, well-known ore deposits have been found. This analogy is valid for similar areas with the Săcărâmb ore deposit zone in the Metaliferi Mountains, where significant amounts of tellurium have been discovered, and also associated rare elements (Se and Cd), *e.g.*, Stăniș and Baia de Arieș.

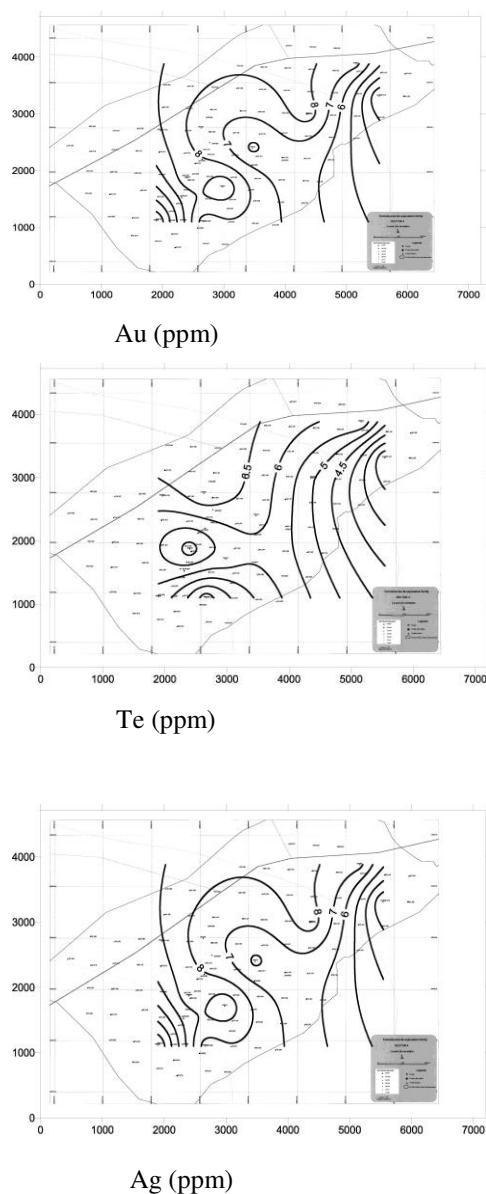


Fig.7. The distribution of Au, Ag and Te in the waste dumps of the Sector II Certej
The isoline values are in ppm.

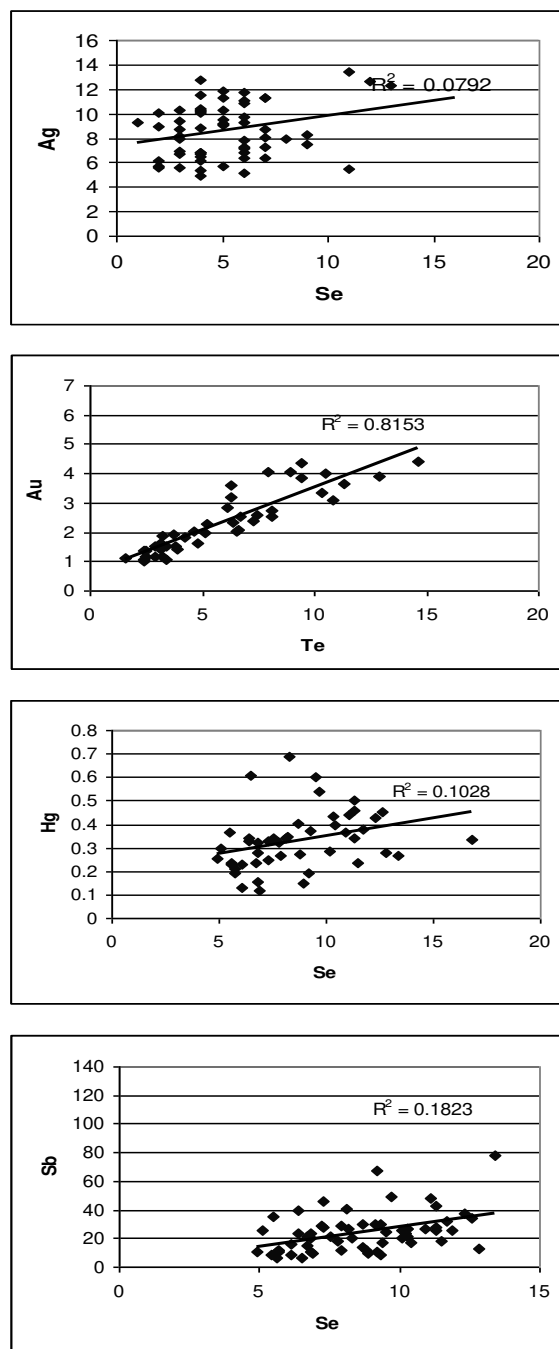


Fig. 8. The correlation diagrams of selenium and tellurium from the three waste dumps of Certej.

In the same category, there are shear zone areas of the Getic Unit in South Carpathians, especially in the Sebeş Mountains. All these areas should be carefully investigate in extention, from the mineralogical, geochemic and geophysical point of view, in order to establish the potential for rare metals and dispersed elements.

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- <http://en.wikipedia.org/wiki/Niobium>

PLATE I

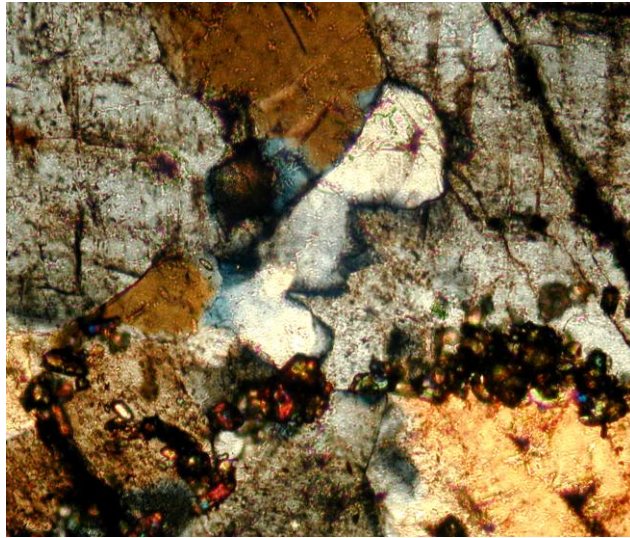


Photo 1. Aggregates of rare minerals from pyrochlore group (?), disposed along fissures and on the feldspars borders. Transmitted light, N+, x60

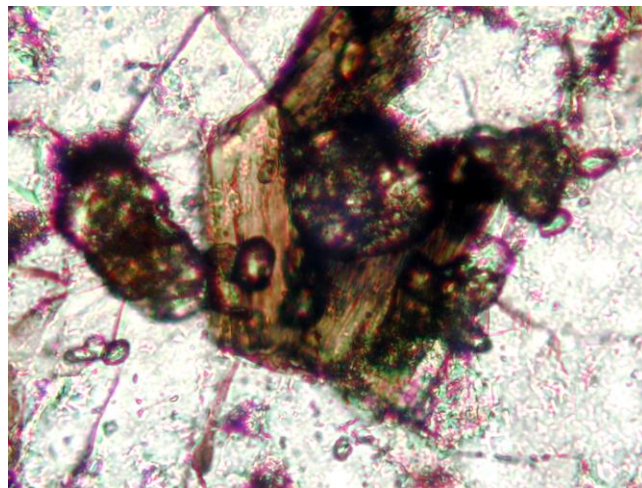


Photo 2. Inclusions of rare minerals (zircon and allanite) in biotite and feldspars. Transmitted light, N+, x60

STEFANU MANGANESE AND IRON OCCURRENCE, PARANG MTS, SOUTH CARPATHIANS

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Abstract. The Stefanu occurrence of manganese and iron mineralisations are situated in the Parang Mts, being encompassed in the Danubian Realm formations. They occur as lens bodies associated to Stefanu-Carbunele lithostratigraphic entity within Urdele Complex/Urdele Nappe. The rocks that occur on the peak between the origins of the Lotru and Latorita valleys belong to the Austrian Getic Nappe, represented by Sebes-Lotru and Ursu groups, intensely metamorphosed crystalline schists. The Puru Nappe Obarsia Nappe is represented by a tectonic melange formed mostly of ophiolitic rocks. The Urdele Nappe consists of a pre-Liassic crystalline basement and a Jurassic-Cretaceous Alpine cover. The crystalline basement of the Urdele Nappe is represented by the Paleozoic Polatistea Formation/Polatistea Nappe, (constituted by micaceous greenschists retromorphosed with carbonate rocks lens bodies), and by the Urdele Complex of ophiolitic type (constituted of greenschists, metabasics and ultrabasics rocks), hosting manganese and iron mineralization. The Cerna Zone of Upper Danubian, is represented by a crystalline basement of Dragsan Group+Latorita Granitoid, and Alpine Cover constituted by Upper Jurassic-Lower Cretaceous Boului Valley and Oslea Formations. The Stefanu Mn-Fe occurrence includes a Mn mineralization and a Fe one. The Mn mineralization consists of rhodonite, pyroxmangite, rhodochrosite, piemontite, barite, parsettensite, pyrophanite, Mn-ilmenite, and various manganese oxides. The quartzites with magnetite, stilpnomelane, phengite, ilmenite, hematite, goethite, lepidocrocite and siderite form the Fe mineralization, that also contains apatite, K-feldspar and various Fe-chlorites. The rhodonite-pyroxmangite are the main constituents of Mn mineralization, occurring together as reduced assemblage. The two polymorphs, rhodonite and pyroxmangite seems to be in equilibrium, but there are some indications that rhodonite precedes pyroxmangite, since it forms the core of the crystals of the latter. The rhodonite structure is stabilized with respect to that of pyroxmangite by Ca, at low P and high T, whereas Fe and Mg increase the stability of pyroxmangite, at low T and high P, with respect to rhodonite. The Stefanu rhodonite, belong to the first metamorphic event, under the conditions of up greenschists facies, at T higher than 500⁰C, and relative low P. In the same time in the Fe-quartzites formed ferrostilpnomelane. The pyroxmangite formed on rhodonite structure, under low blueschists facies metamorphism, at low T and high P (more than 8Kbar). Piemontite appears contemporary with pyroxmangite, in oxidized assemblages. The appearing of pyroxmangite coincides with that of phengitic mica and ferristilpnomelane (formed by ferrostilpnomelane oxidation) in Fe-quartzites, both of high P and low T minerals. In the last metamorphic event, of low greenschists facies (T<400⁰C), occur barite and Mn calcite, as veins in manganese assemblage, and various Fe-chlorite in Fe-assemblage, respectively. The spessartine, tephroite and mangangrunerite are missing because probably the precursor sediments and metamorphic conditions for their forming were unfavorable. The Fe-quartzites were originally, premetamorphic a chert and the Mn assemblages were probable a hydrothermal submarine deposits, linked with a chert+ophiolite sequence, affected by at least three metamorphism phases. The genesis of Mn-Fe mineralization is volcanogen-sedimentary metamorphosed, belonging to greenschists facies, at the limit with biotite zone, at the first event, followed by lowest blueschists facies of second metamorphic event. The last retromorphic event in Stefanu occurrence determined the appearance of vein minerals in both mineralisations.

Key words: Danubian Realm, Parang Mts, Urdele Nappe, Polatistea Formation, Mn-Fe Stefanu occurrence, pyroxmangite, rhodonite, piemontite, pyrophanite, barite, parsettensite, Mn-oxides, Fe-oxides, phengite, ferristilpnomelane, Fe-chlorites.

Introduction/History

Popescu-Voitesti (1923) described the Urdele Nappe, whose definition is almost identical with that of the late Severin Nappe (Codarcea, 1940). Streckeisen (1930) showed that the Liassic Schela Formation overlies the Neo-Jurassic limestones. Stanoiu (1984) separated the rocks of the upper part of the Urdele Nappe under the provisional name of Puru Nappe, considered by him a more intensely metamorphosed equivalent of the Obarsia Nappe on the Mehedinti Plateau. Berza et al. (1986) separated the Lainici Nappe, Urdele Nappe, Vidruta Unit, Petrimanu-Stefanu Unit (identical with the Puru Nappe) and Getic Nappe. Strusievicz, Strusievicz (1988) described the Lainici Unit, Urdele Unit, Vidruta Unit, Petrimanu-Stefanu Unit and Getic Unit. Stanoiu et al. (1991) pointed out the presence of the radiolarian within the metasilicolites and red green metapelites in the Puru Nappe, and stated that the Urdele and Vidruta units represented one Alpine tectonic unit (Urdele Nappe) – taking into account that there is a pre-Liassic tectonic contact between the basements of the Urdele and Vidruta units. Stanoiu (unpublished

data) identified a fragment of *Calpionella alpina* in the rocks of the Severin Nappe (Azuga Beds associated with Sinaia Beds) in the Manaileasa Valley. The Mn-Fe mineralization in the zone of origin of the Stefanu-Carbunele Valley was mentioned first time by Berza et al.(1986) and Strusievicz, Strusievicz (1988).

Geology of the region

The rocks occurring in this area belong to several Alpine tectonic units: Cerna Unit, Urdele Nappe, Obarsia Nappe, and Austrian Getic Nappe. The Cerna Unit (Codarcea, 1940) consists of a Proterozoic intensely metamorphosed crystalline basement of Dragsan Group, and an Alpine unconformable weakly metamorphosed cover represented by Upper Jurassic (?)–Neocomian Valea Boului Formation, consisted of quartz-feldspar, whitish sandstones with a carbonate matrix belonging to Purbeckian-Weldian Group, and the Upper Barremian-Aptian Oslea Formation formed of grey, recrystallised limestones of Urgonian Group.

The Laramian Urdele Nappe consists of a pre-Liassic basement and an very weakly metamorphosed Alpine cover, formed of unconformable Vidruta-Rostovanu Formation (Liassic) in Gresten facies, Lupeni Formation (Neojurassic-Eocretaceous) represented by recrystallised limestones, and the metadetrital Upper Turonian-Lower Maastrichtian Isroni Formation. The pre-Liassic basement is represented by two lithostratigraphic “entities”, separated by a pre-Liassic tectonic contact: Polatistea Proterozoic Formation, mostly formed of micaschists, paragneisses and crystalline limestones associated with Slima Granitoids, Stevia Granitoid and Urdele Paleozoic Complex of ophiolite type, formed of greenschists, metabasics and metaultrabasics. The Polatistea Formation, which forms the Polatistea Nappe, tectonically overlies the Urdele Complex. In the study area, Polatistea Formation and Urdele Complex have been tectonically mixed in the tectogenetic phases subsequent to the formation of the Polatistea Nappe. The Urdele Complex probably represents a Paleozoic or Proterozoic ophiolitic suture.

The Obarsia Nappe/Puru Nappe, of Austrian (?) and Laramian age, is represented by a Jurassic (?)–Lower Cretaceous weakly metamorphosed ophiolitic complex (Puru Complex), a better metamorphosed equivalent of the Obarsia Complex in the Mehedinti Plateau, mostly represented by metabasics, ultrametasbasics and metapelites+metasilicolites with radiolarians.

The Austrian Getic Nappe, is represented by the metamorphites of the Sebes-Lotru Group and of the Ursu Group. The Austrian Getic Nappe and Puru/Obarsia Nappe form Laramic Getic Nappe.

The Mn-Fe mineralization

The manganese and iron occurrence is situated in the Stefanu area and the origin zone of the Carbunele Valley being encompassed in the crystalline basement of the Urdele Nappe, represented by the Urdele Complex. The Polatistea Formation/Nappe, that tectonically overlies the Urdele Complex, consists of micaceous chlorite greenschists with intercalated lens between recrystallised limestones. The Mn-Fe Stefanu mineralization forms lens bodies with thicknesses up to 0.5m, associated with brick-red banded quartzites. Most of the sample were collected from numerous blocks situated along the Carbunele Valley.

In the Stefanu occurrence were determined two distinct mineralizations:

A. The manganese mineralization consists of rhodonite, pyroxmangite, rhodochrosite, piemontite, parsettensite, apatite, barite, pyrophanite, various Mn-oxides, manganian brown chlorites (caryopile?), quartz. The rhodonite-pyroxmangite-rhodochrosite constitute a reduced assemblages, and the piemontite-hematite-quartz association, characterized by presence of Mn^{3+} , is an oxidized one.

B. The iron mineralization contains magnetite, ilmenite, hematite, ferristilpnomelane, phengite, apatite, goethite, lepidocrocite, pyrite, chamosite, various green ferric/ferriferous chlorites and quartz. Accessory occurs K alkali feldspar and albite (?). The iron mineral assemblage is oxidized one. Generally, the iron mineralization is situated in the marginal areas of lens, and the manganese one is situated in their central areas. The ore/rock of iron mineralization has a banded texture, constituted of quartz-magnetite-hematite-phengite banding, quartz-magnetite-hematite-apatite banding, quartz-magnetite-hematite-ferristilpnomelane banding, as can see in Figs 2, left and right photos, and 3, left and right photos. The quartz is the commonest mineral occurring in iron quartzites. The primary quartz is fine-grained, granoblastic to xenoblastic and shows wavy extinction (Fig. 3 left). It is known that in low grade metamorphic zones the quartz has small grains and they are bigger in blueschists grade metamorphic. So, the grain size of quartz in chert-rich or quartz-rich horizons, could be a good indicator

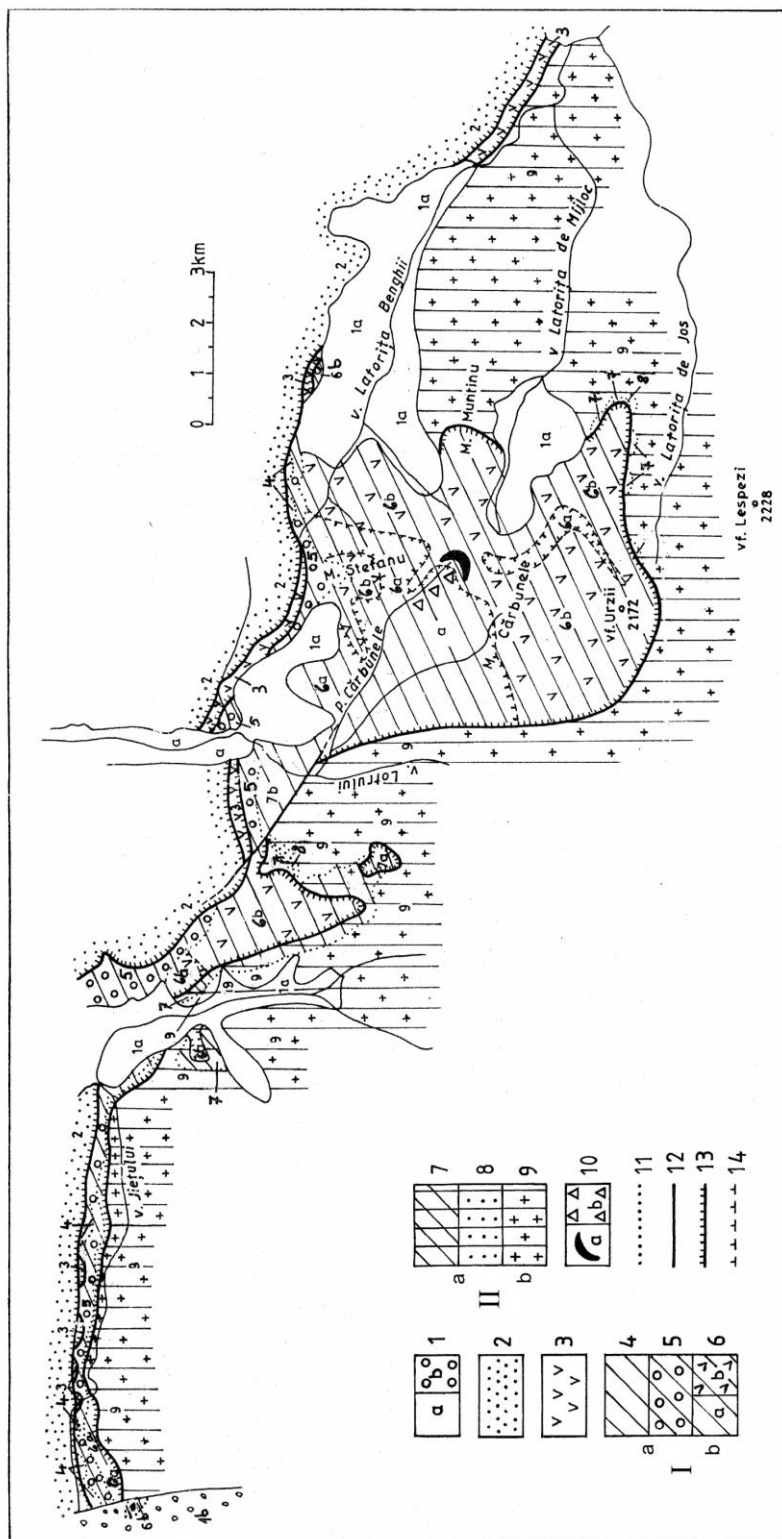


Fig. 1. Geological map of the region in the spring zone of the Jiet, Lotru and Latorita Valleys (According to Paliuc, 1937; Schuster, 1978; Apostoloiu et al., 1988; Stanoiu, 1984; Stanoiu et al., 1989; Stanoiu et al., 1990, with completions). 1, Quaternary; 2, Neogene; 3, Austrian Getic Nappe; 4, Urdele Nappe; 5, Puru Nappe (Obarsia Nappe); 6a, Jurassic-Cretaceous Alpine Cover (4, Lupeni Formation; 5, Vidruta-Rostovanu Formation); 6b, pre-Liassic crystalline basement; (6a, Polatistea Formation; 6b, Urdele Complex Upper Jurassic Neocomian). II. Cerna zone (Lower Danubian): a, Lower Cretaceous Alpine Cover; (7, Oslea Formation, Barremian-Aptian; 8, Valea Boului Formation, Upper Jurassic-Neocomian); b, Crystalline basement; (9, Dragan Group: Latorita Granitoids). 10, Mn-Fe mineralization: a, lenticular intercalations in the Urdele Complex, Barremian; b, slope blocks. 11, Unconformity limit. 12, Fault line. 13, Alpine overthrust line. 14, Pre-Liassic overthrust line (probable Paleozoic).

of metamorphic grade. In addition, the high lamination of quartz grains in Fig. 3 left was caused by high P metamorphic conditions. In contrast with iron quartzites banded texture, the Mn-assemblage constituted mainly from rhodonite-pyroxmangite-rhodochrosite, shows a granoblastic texture, slightly oriented (Fig. 4 right and left photo).

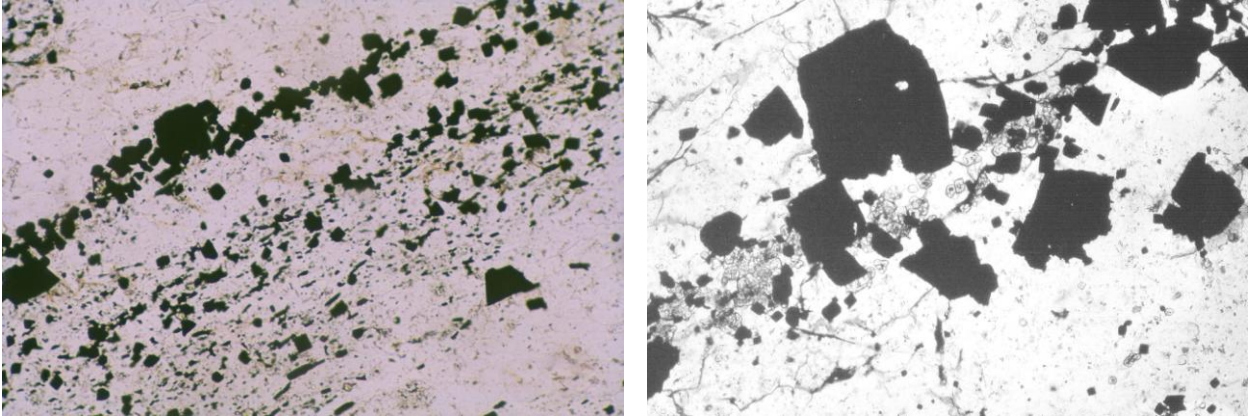


Fig. 2. Banded quartz (grey) with magnetite (black), ferristilpnomelane (brown), NII, sample St118, x35 (left photo); banded magnetite (black) + apatite (small grey grains) with quartz + very little stilpnomelane (needles), NII, sample St6, x 35 (left photo).

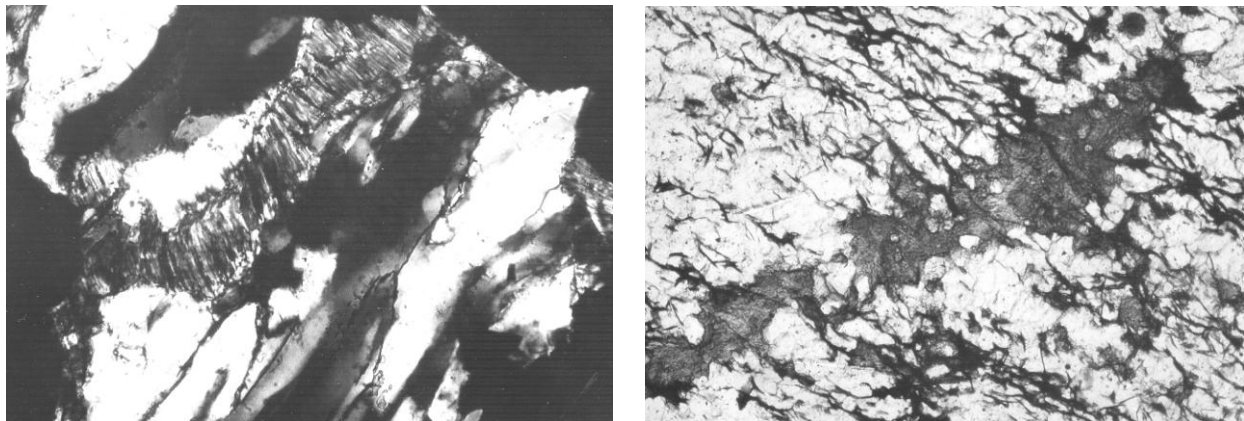


Fig. 3. Banded quartz (laminated) - phengite (perfect cleavage), N+, sample St3, x30 (left photo); banded stilpnomelane (needles, dark grey) - quartz (white), magnetite (black), cut by Fe-chlorite vein, NII, sample Sta, x35 (right photo).

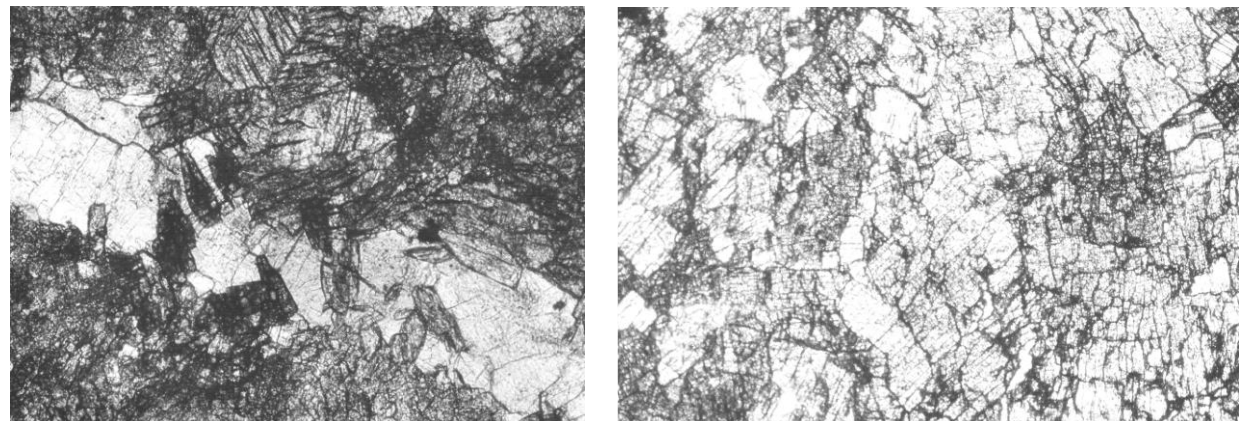


Fig. 4. Pyroxmangite (black grey, cleavages, slightly bended crystals) with rhodonite relics (light grey, small), cut by barite (white) vein, NII, sample St2 (left photo), x30; rhodonite mass with massive texture, slightly oriented, NII, sample St1 (right photo), x30.

A. Manganese mineralization

The rhodonite (Mn,Ca)SiO₄ is the prevailing manganese minerals. It occurs as crystals of up to 1cm, of a pure pink colour. The rhodonite was determined optically, chemically and by X-ray analyses. It seems to be the oldest mineral, being earlier than pyroxmangite. The pyroxmangite occurs as interbanded grains between that of rhodonite, or intersects rhodonite crystals (Fig. 5 right photo). They have not the same crystallographic orientation. At first view, the pyroxmangite seems to be relics in rhodonite, but it is conversely: the pyroxmangite is neoformed (newly formed) on rhodonite. It is frequently associated with pyroxmangite, rhodochrosite, parsettensite, pyrophanite and very rarely with various secondary manganese oxides. Like pyroxmangite, it is penetrated by barite veinlets. The association pyroxmangite-rhodonite in Stefanu occurrence is subsaturated, the quartz is missing from it. It occurs only tardive, as very little veins, sometimes associated with barite. Even if it is subsaturated association, the manganese olivine tephroite is missing. Also, rhodonite-pyroxmangite-rhodochrosite assemblage is a reduced assemblage, because the manganese is present only as Mn²⁺.

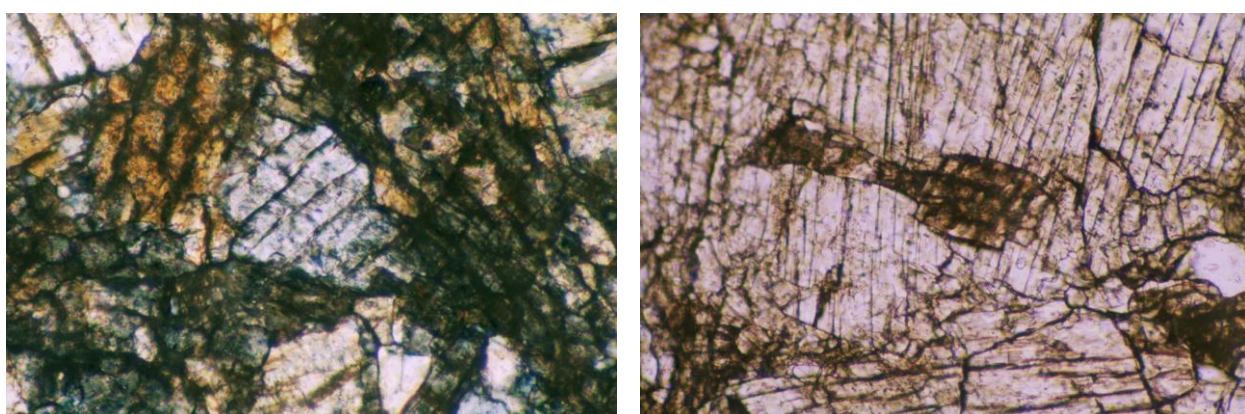


Fig. 5. Pyroxmangite, (3 cleavages, high refringence and birefringence, slightly altered), N+, around rhodonite (grey, centre) sample St2 (left); rhodonite (3 cleavages, lower refringence, cleavage), cut by pyroxmangite (centre, slightly altered, two cleavages), NII, sample 2St (right), x30.

Under the microscope, the rhodonite presents idiomorphic grains with 3 pyroxenoid cleavages (Fig. 5 right photo). It forms frequently massive, monomineral agglomerations. The chemical composition of Stefanu rhodonite is shown in Table 1, in comparison with the Delinesti rhodonite (Semenic Mts) (Hirtopanu and Hartopanu, 1996a) and Dadu rhodonite (Bistrita Mts) (Hirtopanu et al., 1996b). The chemical composition of these three types of rhodonite are showed in Table 1.

Table 1. Chemical composition (%) of the Stefanu rhodonite (St1 and St2) in comparison with the Delinesti (D47) and Dadu (BD100) rhodonites (wet chemical analyses).

Oxides: Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	Total
St1	42.19	0.09	0.41	0.28	3.70	45.83	0.55	5.90	0.02	0.02	0.24	99.21
St2	44.93	0.03	0.53	1.15	3.26	43.65	0.46	5.49	0.01	0.00	0.30	99.84
D47	46.00	0.06	0.52	1.76	1.23	43.63	1.74	4.66	0.02	0.00	0.63	99.84
BD100	45.09	0.80	0.00	1.24	3.36	43.79	1.44	3.80	0.04	0.00	0,05	99.61

Analyst: Erna Calinescu

Their chemical composition is quite similar, the only slight difference being observed in the MgO content, which in the case of the Stefanu rhodonite is three times lower than for the Dadu and Delinesti rhodonites. The low Mg content characterizes the rhodonites formed in blueschists facies (Mottana, 1986). Also, according to experimental data, the high CaO content indicates high X_{H₂O} and lower temperature of forming all metamorphic Stefanu manganese paragenesis. It was formed in the first metamorphic event, happened probable in the upper greenschists facies.

Pyroxmangite, (Mn,Fe)MnSiO₃, triclinic, occurs in pink grain aggregates. The crystals have dimensions from a few mm up to 1cm. Like rhodonite, the pyroxmangite crystals are colourless on

microscope and presents 3 pyroxenoid cleavages. The high refringence and birefringence (Fig. 5 left photo) and the small optical 2V, distinguish it from rhodonite. The Stefanu pyroxmangite has some alterations on cleavages, because of its Fe content. The bended and contorted pyroxmangite crystals (Fig. 4 left photo and 5 left photo) were grown under relative high pressure required for the transformation of rhodonite in pyroxmangite. This transformation happened in the second metamorphic event, situated at least in the lower part of blueschists facies and the final of the greenschists facies. For this transitional metamorphic event between the two metamorphic facies could be estimated a $P \approx 8$ Kbar and a temperature less than that of rhodonite appearance, $< 500^{\circ}\text{C}$, around 400°C . So, the relationship with rhodonite is of substitution, pyroxmangite being younger than rhodonite (Fig. 5, right photo). The two minerals differ in composition (they do not represent pure MnSiO_3 : pyroxmangite has some Fe content and rhodonite some Ca content), thus showing the existence of a compositional miscibility gap between the two minerals. The Bistrita pyroxmangites and rhodonites compositions were plotted in the triangle diagram Mn-Fe+Mg-Ca, where the two minerals formed different compositional fields (Hirtopanu, 2004). The two minerals have different stability fields, according with PT conditions: the pyroxmangite proves to be a high P low T polymorph of the rhodonite. The pyroxmangite and rhodonite had different evolutions in different associations, maintaining the feature of univariant polymorph terms. The Stefanu pyroxmangite did not evolve in mangangrunerite, like Bistrita and Delinesti pyroxmangite (Hirtopanu, 1996a). But, like the later two pyroxmangites, the Stefanu pyroxmangite is substituted by large barite grains as vein and nests (Fig. 7, left and right photos).

The **rhodochrosite**, $(\text{Mn,Ca})\text{CO}_3$, primary mineral develops as porphyroblast grains (Fig. 6 left and right photos). It is associated with rhodonite and pyroxmangite, in reduced assemblages, being precursor of these Mn-silicates.

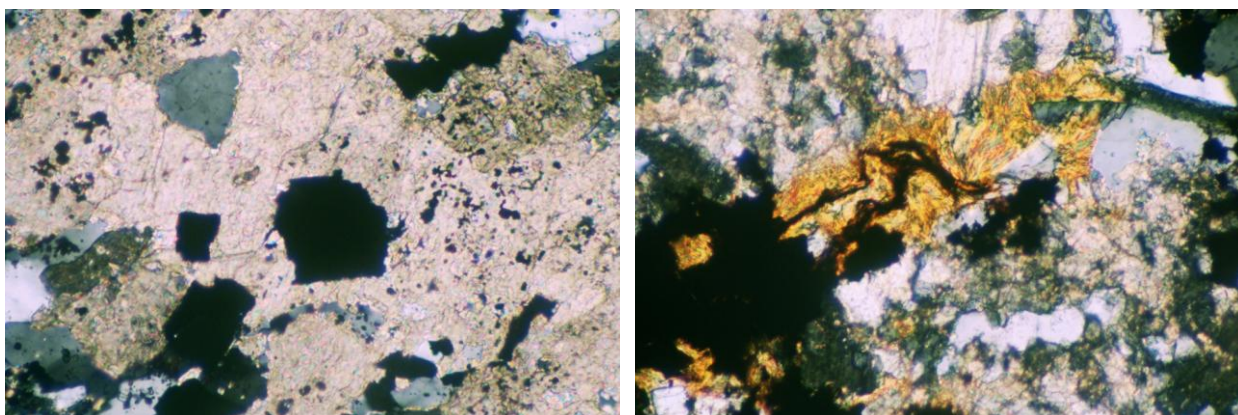


Fig. 6 Rhodochrosite (high birefringence), Mn oxide (black), quartz (grey), N+, sample St118, x35 (left photo); parsettensite (foliated, yellow) + Mn-secondary oxide (brown black), vein in rhodochrosite (high birefringence), quartz (grey), N+, sample St1, x35 (right photo).

Mn-calcite, $(\text{CaMn})\text{CO}_3$, occurs in little veins (that cut the rhodonite-pyroxmangite assemblages), associated with barite and quartz. Also, the kutnahorite, $\text{CaMn}(\text{CO}_3)$, could be present as little veins.

Parsettensite, idealized formula: $\text{Mn}_5\text{Si}_6\text{O}_{13}(\text{OH})$, with some K, Na, Al and H_2O . Also, this mineral contains probable some Ba, judging by the high and constant presence of barite in this ore/rocks. The parsettensite occurs as fibrous radiating aggregates with distinct pleochroism, from brown to light yellow colour. In transmitted light it has a relative high birefringence, similar to that of mica. It has perfect cleavage and occurs as vein in rhodochrosite (Fig. 6 right photo). It is substituted by red/black secondary Mn oxides.

Pyrophanite, MnTiO_3 , rhombohedral, is manganese equivalent of ilmenite. In Stefanu occurrence it occurs rarely, only in reduced manganese carbonate assemblage, as red brown translucent microscope grains. Some MnTiO_3 component could be incorporated in ilmenite (Fig. 10 left photo) as Mn-ilmenite. In oxidized assemblages of Fe-quartzites, the pyrophanite place is taken by rutile.

Piemontite, $\text{Ca}_2\text{Al}_2\text{Mn}^{3+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, monoclinic. It is the Mn^{3+} epidote, belonging to the epidote series. It contains Mn^{3+} dominant at one site. Piemontite has been described from a broad spectrum of rock types and geological environments. The piemontite, manganian epidote (i.e., Mn^{3+}

bearing) has the characteristic strong red-yellow-violet-brown pleochroism, while manganoan epidote (i.e., Mn^{2+} bearing) do not exhibit the characteristic reddish hue. The Stefanu piemontite occurs as very small short prismatic grains, with cleavage perfect on (001) and poor on (100). It was determined only optically. The pleochroism is strong and varies from light yellow, orange, red to deep red (Fig.7 left and right photos). Optically it is biaxial (+) with $2V \approx 70^\circ$, having a maximum birefringence around 0.07. Piemontite is predominantly the product of low grade metamorphism. The restricted and sporadic occurrence of piemontite suggests that other factors than temperature, pressure or whole rock composition control its crystallization. Several lines of evidence from studies of natural parageneses suggest that oxygen fugacity and fluid composition may be critical factors in crystallization of piemontite. Piemontite occurs in metamorphic rocks, metamorphosed under highly oxidizing conditions. The high oxygen fugacity required for piemontite formation in Stefanu occurrence. It is associated with hematite/magnetite and quartz, forming an oxidized assemblage. The juxtaposition of this oxidized assemblage with the pyroxmangite /rhodonite reduced one, implies a very low oxygen mobility during metamorphism. The presence of hematite coexisting with piemontite proves a very high oxygen fugacity for piemontite formation.

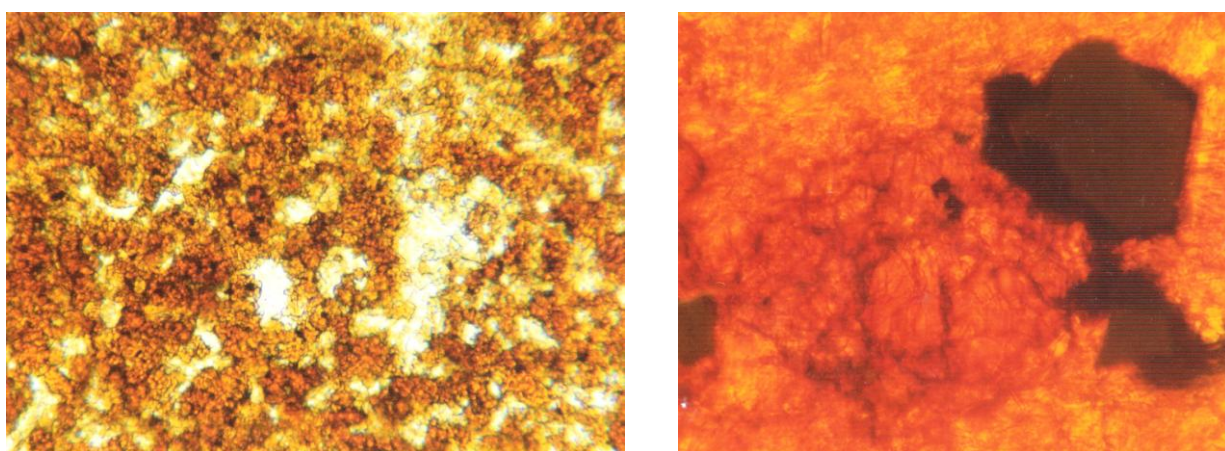


Fig. 7. Piemontite (yellow red grains), quartz (white), NII, sample St5b, x35 (left photo); piemontite (orange yellow), magnetite-hematite (black), NII, sample St5c, x40 (right photo).

Barite, $BaSO_4$, orthorhombic, is found as large crystals, with sizes up to 1cm or even larger (Fig. 8 left and right photos). Under microscope, barite presents pyroxmangite/rhodonite relics, left after their substitution by barite. Also, barite is almost permanently accompanied by a yellow pyrosmalite type phyllosilicate, in rosettes, having to a small size to be accurately determined. This secondary mineral grown on/with barite could be **caryopilite** $(Mn,Mg)_3Si_2O_5(OH)_4$, or **friedelite** $Mn_8Si_6O_{15}(OH,Cl)_{10}$.

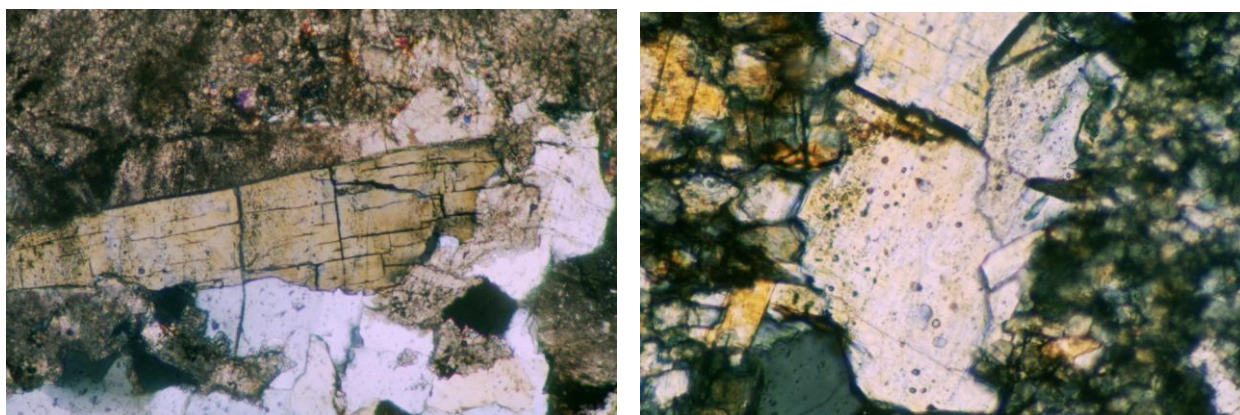


Fig. 8 Barite (large grain, yellowish, two cleavages), substituted pyroxmangite (light brown), quartz (white) + rhodochrosite (grey), NII, sample St1 (leftphoto); barite (reddish white) vein in pyroxmangite (high refringence and birefringence), N+, sample St2 (right photo).

The late character of barite is also evident by its occurrence of centimeter veinlets and cavity fillings, that penetrated both the rhodonite and pyroxmangite aggregates (Fig. 8 left and right photos). It is associated with Mn-calcite, kutnahorite and secondary quartz. Barite is typical epithermal mineral precipitated from low temperature hydrothermal solutions (below 400°C). So, the older minerals than barite from this occurrence, were formed at temperature higher than 400°C.

B. Iron mineralization

The iron mineralization has the following mineralogical composition: magnetite, hematite, ilmenite, phengite, ferristilplomelane, apatite, goethite, lepidocrocite, various Fe-chlorites and quartz.

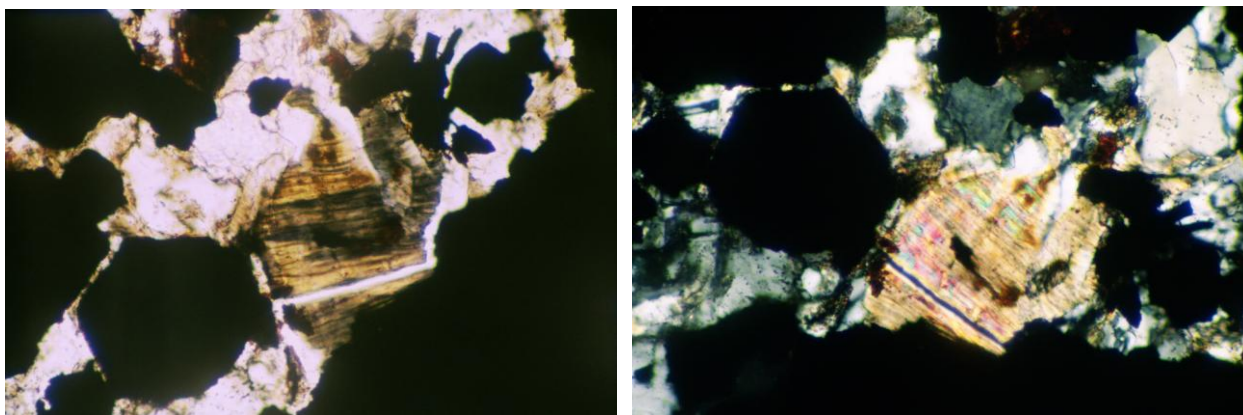


Fig. 9. Magnetite (black), phengite (yellow dark grey/medium birefringence), quartz (white/grey), magnetite (black), NII (left) and N+ (right), sample St3, x35.

Magnetite, (Fe_3O_4) and **hematite** α -(Fe_2O_3) are found in the proximity surrounding of rhodonite-pyroxmangite assemblages, in red brick quartzites. These minerals are found in big amounts, so the rock can be considered an iron ore, the Fe-oxides occupying sometimes, more than half of the rock/ore mass. As one can see in Fig. 9, the magnetite is idiomorphic, occurring as small octahedral crystals, generally well-developed, whereas the hematite is xenomorphic, occurring as elongated grains. The hematite is a very important constituent because it is simultaneously an indicator of temperature as well as oxygen fugacity. In ferriferous quartzites hematite formed at the very beginning of diagenesis and remains stable throughout all stage of metamorphism (Mottana, 1986). Extensive field and petrographic evidence from many metamorphic iron deposits show that quartz-magnetite, quartz-hematite and quartz-hematite-magnetite assemblages persist through high grade metamorphic conditions without reactions. The originally finely banded quartz-magnetite, quartz-hematite and quartz-hematite-magnetite assemblages and their coarser grained metamorphic equivalents generally show no replacement of hematite by magnetite, or vice versa. Generally, there is no textural evidence for one iron oxide having given way to the other. The quartz-magnetite horizons do not produce silicate assemblages upon metamorphism. In Stefanu occurrence magnetite/hematite are associated with phengite and apatite (Fig. 10 left and right photos), ferristilplomelane (Fig. 2 left and right photos) and apatite (Fig. 10 left and right photos), all minerals being oriented after the major schistosity of the rock/ore. In the presence of Mn^{3+} -bearing silicate phase, the hematite could be equilibrated, occurring in Stefanu area in oxidized association with piemontite (Fig. 7, right photo).

Ilmenite, FeTiO_3 , rhombohedral, is rich in Ti and has some Mn content, being a manganese ilmenite, but not with sufficient Mn content to be pyrophanite. Its EDS spectrum can be seen in Fig. 11, left image. It is constituent of oxidized assemblages, where it does not coexist with pyrophanite.

Apatite, $\text{Ca}_5(\text{PO}_4)_3$ (F, OH, Cl), hexagonal occurs in the manganese ore type as an accessory mineral and as a constituent mineral in iron mineralization. It has small to up a few mm (and more) dimensions grains associated with magnetite, stilplomelane and K-feldspar (Fig. 10).

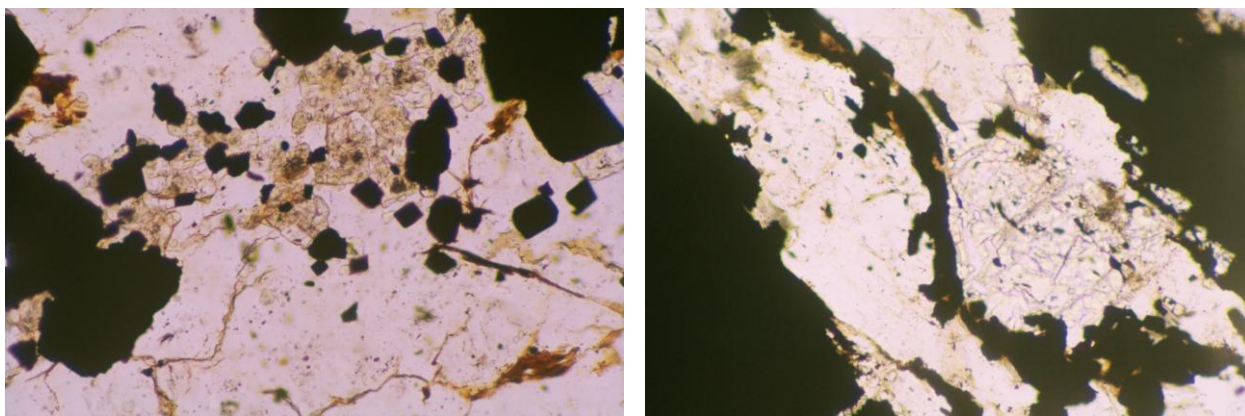


Fig. 10. Apatite (hexagonal grains, light yellow), magnetite (black), quartz (white grey), sample St119 (left); Fe-oxides vein (black,centre) around apatite (big white grain) and K-feldspar (white with cleavage, low refringence), sample 3St (right).

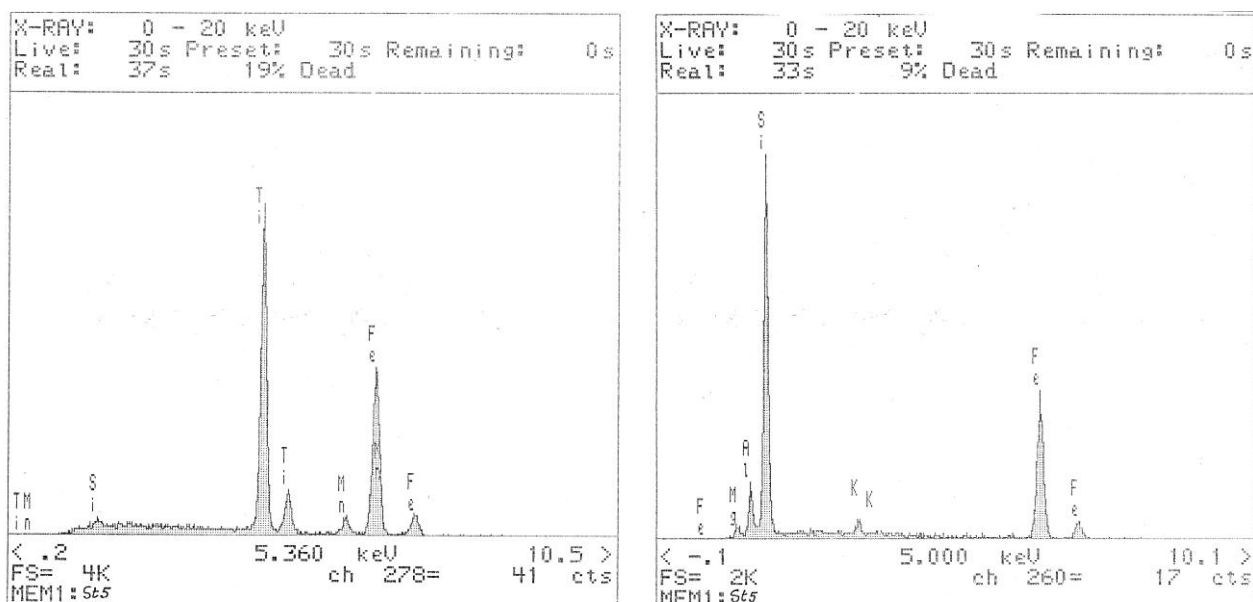


Fig. 11. EDS spectra of Mn-ilmenite (left) and ferristilpnomelane (right), sample St5.

Ferristilpnomelane, $(K, Ca, Na)(Fe, Mg, Al)_{12}(Si, Al)_6(O, OH)_{54}.nH_2O$, triclinic. The ferristilpnomelane occurs in the magnetite quartzites rock, in radiating clusters, needles and sheaves, of microscopical size grains up to a few mm, generally orientated on the schistosity of the rock/ore (Figs 2, 3). The pleochroism from yellow to red brown is similar to that of ferristilpnomelane member of stilpnomelane group. Its EDS spectrum is presented in Fig. 11 right. It is associated, beside magnetite, with hematite, ilmenite, phengite and large amounts of quartz. It is known, that the ferristilpnomelane appears only in high FeO/MgO rocks. The coexisting chlorites formed secondary on ferristilpnomelane, have also a high ratio Fe/Fe+Mg. Stilpnomelane is stable in muscovite free rocks throughout the biotite zone. In Stefanu occurrence occurs in the earlier stage of metamorphism and persists through the greenschist facies, where it is associated with phengite, magnetite, hematite, quartz, chlorite. There is no indication that stilpnomelane replaces another phases, so it belongs to the primary metamorphic assemblages. Phase equilibria in the system K_2O -FeO-MgO- Al_2O_3 - SiO_2 - H_2O - CO_2 and the stability limit of stilpnomelane in metamorphosed Precambrian iron formations were studied by Takashi & Klein (1989). Their petrologic data together with available experimental and predicted thermodynamic data on the associated minerals place the upper stability limit of stilpnomelane in iron formation at about 430-470°C, and 5-6Kbar. The Fe end member stilpnomelane can persists to a maximum temperature of 500°C and pressure up to 6-7Kbar, although it is unlikely to occur in metamorphosed iron formations (Takashi & Klein, 1989). If the value of K^+/aH^+ is smaller stilplomelane decomposes to chlorite, (how it happened in

Stefanu occurrence), but if larger, it is replaced by biotite (Takashi & Klein, 1989). Biotite is not present in Stefanu occurrence. At pressures less than 4Kbar the zussmanite $[K(Fe,Mg,Mn)_{13}(Si,Al)_{18}O_{42}(OH)_{14}]$ field is restricted to a very high value of $a(K^+)/a(H^+)$, where iron formation assemblages are not stable. In other occurrences stilpnomelane is found in metapelites of the pumpellyite-actinolite facies and the chlorite zone of the greenschists facies, but only rarely in the biotite zone of the green schists facies. Also, stilpnomelane could be precipitated from hydrothermal solutions. In to P,T and bulk composition, the stilpnomelane izograd is controlled by variations in K, Fe^{3+}/Fe^{2+} , O/OH and H_2O contents (Takashi and Klein, 1989). The ferristilplomelane was formed by oxidation process of ferrostilplomelane. So, originally was formed first ferrostilplomelane, most probable contemporary with rhodonite, then ferristilplomelane, contemporary with pyroxmangite, both from manganese assemblages.

Phengite, is a series name for dioctahedral micas of composition $K(AlMg)_2(OH)_2(SiAl)_4O_{10}$, similar to muscovite but with addition of magnesium. It is a term between muscovite and celadonite. Phengite is the product of particular type of metamorphism involving low T and high P ($\approx P_{H_2O}$), typical of blueschists and eclogites. The well growth of orientated phengite crystals, between laminate quartz grains (Fig. 3 left photo) could be a good evidence that the last stage of metamorphism in this area was produced by relative high P.

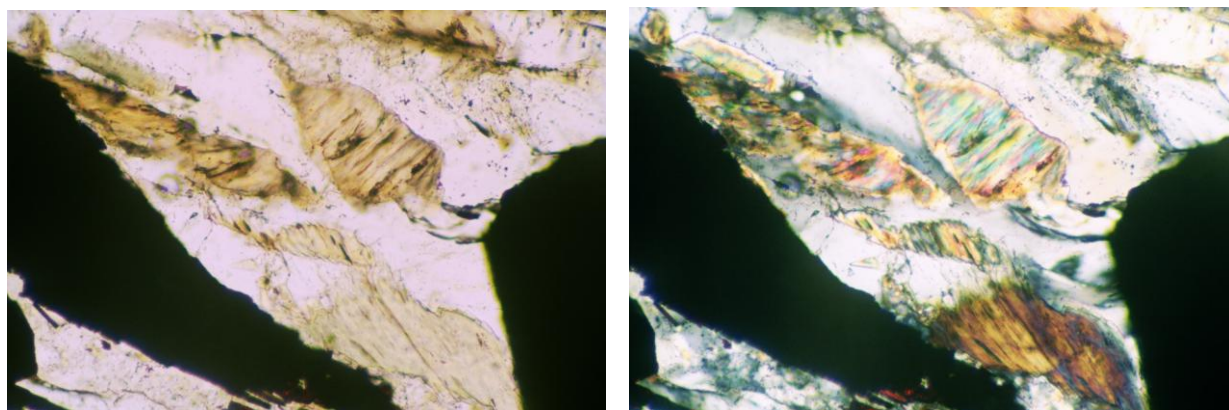


Fig. 12. Phengite (yellow brownish, yellow light, perfect cleavage), grown on schistosity between laminated quartz hematite (black), quartz (white), NII (left photo), and N+ (right photo), sample 3St, x35.

In transmitted light the phengite is either colourless, but also has light grey, light blue green, light gray greenish, light brownish and light yellow, depending on the Fe or Mn contents (Fig. 12). It occurs as foliated aggregates, with perfect cleavage (001). It has a moderate pleochroism, relative high birefringence, similar to that of mica. Associated with magnetite, hematite, ferristilplomelane, K-feldspar, and quartz. The brown phengite contains 1.5-2% MnO and its field is close to the boundary with celadonite (Mottana, 1986).

In the rich quartz zones of the banded quartzites described above, a widely developed **goethite**, α -FeO(OH), occurs (Fig. 13 left photo). It is formed on pyrite and magnetite crystals. Under microscope in the large goethite crystals one can observe, beside pyrite relics, a strongly anisotrop mineral, which is **lepidocrocite** γ -FeO(OH). These two minerals, goethite and lepidocrocite, cause the brick reddish colour of the quartzites that host iron and manganese mineralization. The idiomorphism of crystals is due to their later forming, being contemporary probable with vein minerals from manganese assemblages with barite. The goethite and lepidocrocite could be also a hydrothermal products.

Chamosite, $[Fe^{2+}Mg,Fe^{3+}]Al[Si_3Al]O_{10}(OH,O)_8$, monoclinic. The chamosite has usually very small tabular, microgranular, prismatic grains. It forms a series with clinocllore. The chamosite is the iron rich end member and the clinocllore is the magnesium rich end member. The Fe^{3+} and Fe^{2+} contents are variable, and their variations could be seen in the Stefanu chamosite color. From this point of view, this chamosite presents two varieties, very well distinguished on microscope. The ferric chamosite with a high Fe^{3+} , is yellow brownish, light brown and a ferrous chamosite with high Fe^{2+} , are green, dark green. The chamosite is associated with magnetite, hematite and stilpnomelane. The magnetite/hematite-chamosite assemblage is very common. Some grains with the medium birefringence and refringence, intimately associated with magnetite could be **cronstedtite** $Fe^{2+}Fe^{3+}(SiFe)_2O_5(OH)_4$, and some green

yellowish chlorite which intersects the quartzites with fine brown grained stilpnomelane (Fig. 14), could be **ripidolite**.

The Fe-chlorites from oxidized assemblages of Fe quartzites are mostly secondary, being widespread in the late veins, generally in the form of fans and rosettes. In these veins crossing the rocks/ores, and in oxidized assemblages, Fe-chlorites are poor in manganese, and sometimes, can span the entire Fe-Mg series.

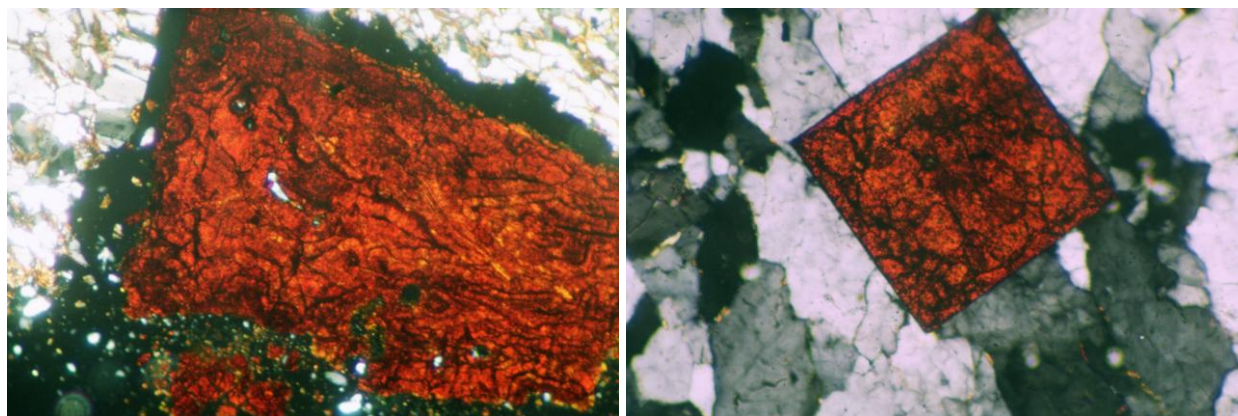


Fig. 13 Goethite (grown probable on magnetite), big red grain in ferristilpnomelane quartzit, N+, sample 6St (left), x30; goethite (red) grown probable on cubic pyrite face in quartz (grey), N+ sample St7 (right), x30.

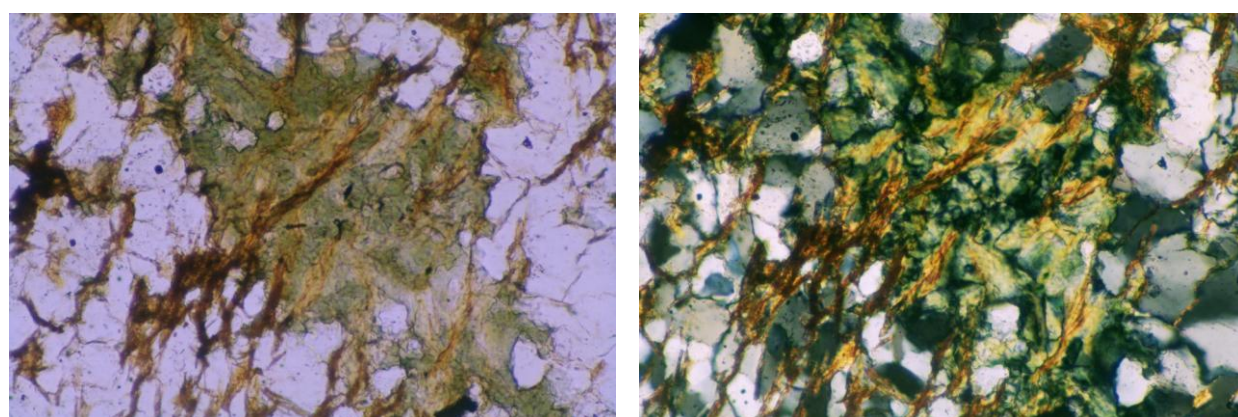


Fig. 14 Ferristilpnomelane (brown yellow/high birefringence), transformed in Fe-chlorite (green/low birefringence), quartz (white/grey), NII (left photo) and N+ (right photo), sample 6St, x35.

Other minerals

Alkali K-feldspar, $K(Si,Al)_4O_8$ can be observed in the quartzites with a higher content of hematite, associated with apatite (Fig. 10, right photo). According to the optic features, it is an alkali feldspar of low temperature. It displays twins formed of two individuals. Similar parageneses appear in the quartzites that accompany the manganese ores in Bistrita Mts, with the mention that there they are more complex association, due to the occurrence of alkali pyroxenes and amphiboles (Hirtopanu, 2004).

Pyrite, FeS_2 , occurs as accessory mineral. It has been transformed into goethite and lepidocrocite due to the high fugacities of the oxygen (f_{O_2}) and of the water (f_{H_2O}). The outline of lepidocrocite/goethite crystal is similar to that of former pyrite (Fig. 13, right photo).

Quartz, SiO_2 , rhombohedral, is the commonest mineral occurring in Fe-quartzites. The primary quartz is fine-grained, granoblastic to xenoblastic, and shows wavy extinction. The deformed laminate quartz crystals (Fig. 3, left photo) are associated with magnetite, phengite, stilpnomelane, which grown orientated on schistosity. Large nondeformed quartz crystals occur in veins, in both manganese reduced assemblages and iron oxidized assemblages.

Genetic remarks

The genesis of the Stefanu Mn-Fe formations can be explained on the basis of the results of their mineralogical study:

a. The occurrence can be regarded as an association between a manganese and iron assemblages. This is an important feature of volcanogenic-sedimentary metamorphic manganese deposits (Roy, 1976). In these deposits, iron and manganese ores are found in mixed or well differentiated assemblages. In the Stefanu Mn-Fe occurrence the two mineralisations are distinct, having well differentiated assemblages. Also, like Stefanu occurrence, the volcanogenic-sedimentary metamorphic deposits have small dimensions, compared to very large nonvolcanogenic-sedimentary metamorphic deposits, because the concentration of Mn/Fe was not a continued process but was rather sporadic. Manganese deposits were formed at a greater distance from the volcanic centre than those of iron due to higher mobility (Strakhov, 1967).

b. The tephroite, spessartine and mangangrunerite are missing from this occurrence. The lack of tephroite can be explained and by the lack of a adequate protolith for its appearance, that is a carbonate Mn rich medium with very few silica. Generally, the appearance of spessartine is highly dependent on the Mn content. It occurs by reaction between quartz and Mn-chlorites, at about 400°C, $P=P_{\text{fluid}}$ exceeds 1Kbar (Hsu, 1968). In the initial premetamorphic sediments, the Mn-chlorites, the source of spessartine formation, between other conditions, were missing. So, the spessartine garnet is not present, because probably to the lack of Al in initially sedimentary/volcanogene deposits. Its stability is controlled by bulk composition, being restricted to aluminous rocks. On the other hand, the spessartine appears to be irrelevant to the aim of petrological reconstruction within the blueschists or the upper greenschists facies. In closely associated domains of lens, Dasgupta et al., documented that pyroxmangite+tephroite assemblage was stabilized in relatively high iron bulk composition and low X_{CO_2} , and pyroxmangite without tephroite appeared at higher X_{CO_2} . So, the lack of tephroite in Stefanu occurrence is due to the unsuitable X_{CO_2} and some iron in premetamorphic sediments. Several studies have documented the role of bulk composition in determining stabilization of Mn silicates and carbonates and partitioning of major elements among them: X_{Mn} in the bulk controls stabilization of Mn garnet and tephroite, X_{Fe} controls tephroite and X_{CO_2} controls on the appearance of Mn carbonates. The mangangrunerite occurs only in higher metamorphic grades, that were not reached in this occurrence.

c. Rhodonite and pyroxmangite occur together in the Stefanu occurrence, in bladed intergrowth and their equilibrium conditions are difficult to decide. There are some indications that rhodonite precedes pyroxmangite, the last being newly formed on the first. In this case, rhodonite is older than pyroxmangite and it belongs to the first metamorphic stage of greenschists facies and pyroxmangite belongs to the second metamorphic event, to the blueschists facies, at least in its lower domain. Pyroxmangite of pure MnSiO_3 composition has been shown to be a high pressure and low temperature polymorph with respect to rhodonite of the same composition (Maresch and Mottana, 1976). The transformations are reversible in presence of water at 3Kbar/ $T=425-450^\circ$, 6Kbar/ $T=475-525^\circ$, 20kbar/ $T=500-900^\circ$ and 30Kbar/ $T=1000^\circ\text{C}$. For the first stage of metamorphism, for the reduced Stefanu Mn carbonatic assemblages, when rhodonite appears, one can estimate a $T\approx 525^\circ\text{C}$ and a $P\approx 6\text{Kbar}$. In the same stage and conditions in the iron quartzites oxidized assemblages, could be formed the ferrostilplomelane, contemporary with rhodonite.

d. The rhodochrosite is found only in reduced rhodonite-pyroxmangite assemblages, where quartz is missing, the rock/ore being subsaturated in silica. In these restricted areas the quartz occurs secondary, only as veins. In this assemblages the Mn is only divalent. Piemontite associated with hematite, magnetite and various Mn-oxides with Mn^{3+} , is present in oxidized assemblages, juxtaposed to those reduced rhodonite-pyroxmangite assemblages. In the Fe-assemblages, the quartz is present in large amounts, per total of this mineralization, thus the ore/rock is suprasaturated in silica.

e. Pyroxmangite and rhodonite occur in reduced carbonatic assemblages. In the Stefanu occurrence the pyroxmangite precedes rhodonite, since it forms the core of the crystals of the later. The two polymorphs, rhodonite and pyroxmangite are in divariant equilibrium, since rhodonite concentrates Ca relative to pyroxmangite; the latter is enriched in Fe^{2+} and Mg. The rhodonite precedes pyroxmangite, since it forms the relics /the core of/in crystals of the latter. Abrecht (1988) confirmed that rhodonite and pyroxmangite have very small differences in entropy and Gibbs free energy of formation and, hence, metastable persistence of each of this phases is possible.

f. Most metamorphic occurrences of piemontite are in high pressure or high pressure to intermediate facies terrains. In Stefanu occurrence piemontite coexists with hematite, magnetite and ferristilplomelane. Because spessartine is missing, this association could be placed in low temperature of blueschists facies, at $T < 400^{\circ}\text{C}$. If the spessartine could be present, the association could be placed in high temperature side, at $T > 450^{\circ}\text{C}$.

g. As regards the evolution of the quartzites with magnetite and hematite in the surrounding Mn ore, one may consider that it was initially a quartz volcanogen-sedimentary material with many iron oxides and hydroxides, and with very little clay material with very low magnesium content. The metamorphism of these deposits led to the formation of magnetite/hematite, phengite, apatite and stilpnomelane in a quartz gangue. The firstly formed stilpnomelane was ferrostilplomelane, contemporary with rhodonite from manganese assemblage. The phengite and ferristilplomelane typical minerals for relative high pressure, appeared in the second metamorphic event, at the same time with the appearance of pyroxmangite in the manganese assemblage. This second metamorphic event belongs to high pressure low temperature blueschists metamorphism, at least in its lower part. In iron formation occurrences the stilpnomelane stability is bordered by four equilibrium reactions with assemblages (Takashi and Klein, 1989): stilpnomelane-zussmanite-chlorite-minnesotaite; stilpnomelane-zussmanite-chlorite-grunerite; stilpnomelane-biotite-chlorite-grunerite; stilpnomelane-biotite-almandine-grunerite. The stability field of stilpnomelane is reduced by increasing X_{CO_2} and $X_{\text{Mg}}^{\text{stil}}$ and it is also a function of a $a(\text{K}^+)/a(\text{H}^+)$ in the metamorphic fluids. If the value of $a(\text{K}^+)/a(\text{H}^+)$ is smaller than that defined by the above assemblages, stilpnomelane decomposes to chlorite, but if larger, it is replaced by biotite. At pressure less than 4Kb the zussmanite field is restricted to a very high value of $a(\text{K}^+)/a(\text{H}^+)$, where iron formation assemblages are not stable.

The various Fe-chlorites and goethite/lepidocrocite from Fe-quartzites, and the barite from manganese assemblages, occurring as veins, belong to the last retroromorphic event of this assemblages. The occurrence of barite as veins in pyroxmangite-rhodonite association is another piece of good evidence for hydrothermal activity in this area. Barite is typical of epithermal suites precipitated mineral from low temperature hydrothermal solutions, below 400°C .

The juxtaposition of oxidized assemblages (hematite-magnetite-piemontite-quartz) and reduced assemblages (rhodochrosite-rhodonite-pyroxmangite) in manganese mineralization shows the big importance of the oxygen fugacity in forming and evolution of these minerals. In the Fe-quartzites, the hematite-magnetite association fixes the oxygen fugacity at a value close to 10^{-12} atm.

Conclusions

The association of the metamorphosed manganese ore with the iron one, and the small dimension of this occurrence are two arguments in favor of the initial volcanogenic-sedimentary origin, associated with submarine volcanism, most probable of basic type (spillite, diabase ?). Usually in a volcanogenic-sedimentary sequence, iron and manganese ores are found in mixed or well-differentiated assemblages. Generally, in the Stefanu occurrence the iron and manganese assemblages are well-differentiated and rarely they are found mixed.

The present mineralogical association from Mn-Fe Stefanu occurrence mainly constituted of Mn pyroxenoids (rhodonite and pyroxmangite) and rhodochrosite, as well as the lack of tephroite, spessartine and mangangrunerite, indicate a first metamorphic event in the low greenschists facies, following by a blueschists facies metamorphism situated at least at nearly limit with the upper part of greenschists facies, marked by the appearance of pyroxmangite and piemontite in manganese assemblage. In the Fe quartzites, the first metamorphic event was marked by the appearance of ferrostilplomelane, and the second one, of high pressure, was established by appearance of phengite and ferristilplomelane, both being high pressure minerals.

The original manganiferous sediments possible contained beds of nearly pure manganese carbonate and oxides, hydrous manganese silicates admixed with silica. Upon regional metamorphism the rhodochrosite may break down under relative chemical potential of CO_2 and react with quartz to form rhodonite to low greenschist facies, and this gave rise to pyroxmangite on it. The tephroite, spessartine and mangangrunerite are missing. The Stefanu Mn and Fe ores are well separated, the former being associated with Mn carbonate and the latter with siliceous (jasper) rocks. Sometimes they occur in alternate beds. During sedimentation and diagenesis formed rhodochrosite, opal, calcedonie, Mn-

hydroxides, Fe-hydroxides, leptochochlorites, Fe-disulfides formed. During metamorphism occurred pyroxmangite, rhodonite, rhodochrosite, piemontite, pyrophanite in manganese assemblages, and hematite, magnetite, ilmenite, goethite, stilpnomelane, phengite, various Fe-chlorites, pyrite in iron assemblages. The barite, goethite, lepidocrocite and pyrite occurrences as veins are connected probably with hydrothermal activity. It is known that blueschists facies cherts are enriched in easily mobile elements, such as Ba and Sr with respect to chert metamorphosed under zeolites facies or greenschists facies. Moreover, there is a contribution from the underlying metabasites undergoing prograde metamorphic reactions involving release of water-rich fluids previously incorporated in the basalt during the oceanic stage (Mottana, 1986).

Acknowledgements. We are very grateful to Prof. Dr. Gheorghe Udubasa, member of the Romanian Academy, for its careful reviews and valuable suggestions.

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PHYSICO-CHEMICAL CHARACTERISATION OF A COPPER SLAG FROM METALLURGICAL PLANT ZLATNA

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Abstract. Copper extractive metallurgy produce great quantities of residues - slags, flie dusts, etc. These materials contain many elements in concentrations that could justify their processing to extract. To process these materials by classical methods require a large energy ammount. Following, the operation is unprofitable and materials are stockpiled. In this circumstances there is a danger of environmental pollution due to waste alteration under the influence of the external factors. Knowing the phase composition of the residues in question, a recovery or neutralization technology to protect the environment can be developed. This paper presents the characterization by chemical analysis, X-Ray diffraction and optical microscopy in polarized light of a sample of slag from the former copper plant Zlatna.

Keywords: copper extractive metallurgy, slag, flie dust, Cu-Fe-S system

1. Introduction

The metallic copper production from sulfide concentrates involve multiple operations as listed below:

1. Oxidizing roasting.
2. Concentrate melting
3. Copper matte converting
4. Refining of copper after converting

The first two operations produce the most of the residues.

The flash smelting process of the copper concentrates, applied in Zlatna, simplifies the technology by performing the first two operations in the same installation. In this installation, the temperature reaches 1300 degrees Celsius.

Resulted residues, flie dusts, slags, comprise a wide variety of minerals, starting with those of concentrates and continuing with the minerals occurring in the successive stages of processing of those concentrates.

2. Analitical Methods

The Chemical Analysis were made in the Chemical and Physical Laboratory from INCDMNR-IMNR, using the DCP, FAAS, ICP-OES and 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 DIFRACplus XRD Commender (Bruker AXS), using the Bragg-Brentano diffraction method.

The Microscopical Analysis were made in the Microscopical Characterzations Laboratory from INCDMNR-IMNR, using an AXIO IMAGER A1m microscope with polarized light, reflected and transmitted.

Slag specimens as powder (also containing flie dust) from the metallurgical plant Zlatna were embedded in epoxidic resin and then prepared by grinding and polishing. Prepared specimens were microscopically studied in reflected polarized light.

Subsequent to the determination of the global mineralogic composition of the specimens by XRD and microscopic method, the study of the fine structure was performed using microscopic observations in cedar oil immersion.

3. Experimental Part

3.1. Chemical analysis of the sample

The results of the chemical analysis are presented in Table 1.

Table 1. Chemical composition of the sample.

Element (%)	Cu	Fe	Al	Cr	Mg	Mn	Ni	Pb	Sb
	23,4	24,1	1,69	0,13	0,83	0,2	0,08	1,62	0,09

Element (%)	Sn	Si	Ti	Zn	Ca	Na	K	C	S
	0,49	7,80	0,07	5,06	1,36	0,24	0,46	0,4	4,15

3.2. XRD and optical microscopy

The sample revealed, by X-ray diffraction and optical microscopy, the following minerals (which can be observed in the Figures 1-14):

- Chalcocite – Cu_2S
- Chalcopyrite – CuFeS_2
- Magnetite – Fe_3O_4
- Metallic copper
- Bornite – Cu_5FeS_4
- Glass
- Pyrite – FeS_2
- Sphalerite – ZnS
- Pyrrhotite – Fe_{1-x}S
- Fayalite – Fe_2SiO_4
- Cuprite – Cu_2O
- Quartz – SiO_2
- Digenite – Cu_9S_5
- Covellite – CuS
- Willemite – ZnSiO_4
- Gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Hexahydrite – $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
- Picromerite – $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
- Konyaite – $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$
- Halite – NaCl
- Hydrocalumite – $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$
- Langite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$
- Tenorite – CuO
- Galena – PbS
- Biotite – $\text{KFeMg}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

3.2.1. XRD for integral sample:

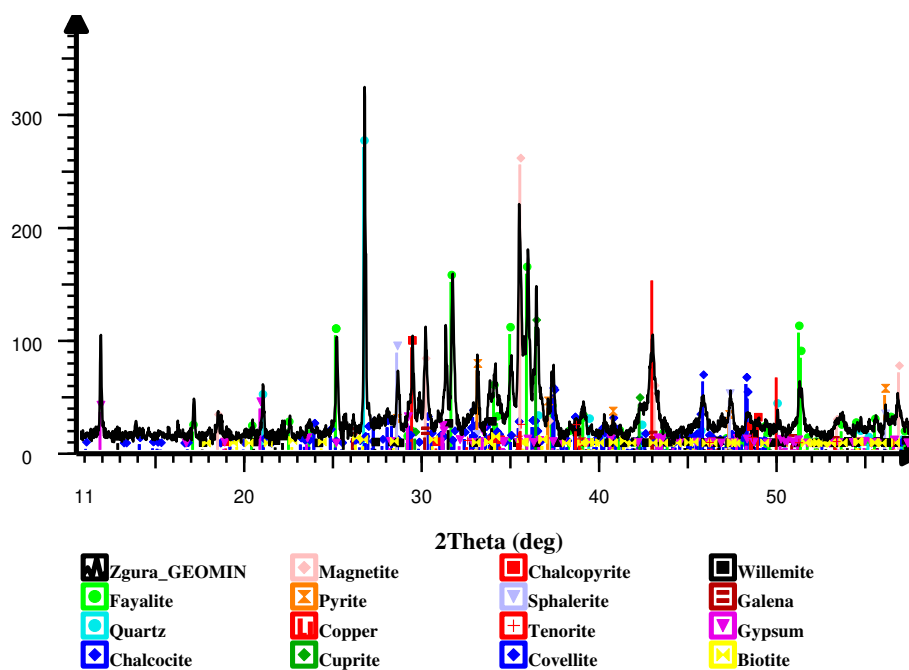


Fig. 1. Graphical presentation of qualitative analysis phase

3.2.2. XRD for soluble fraction:

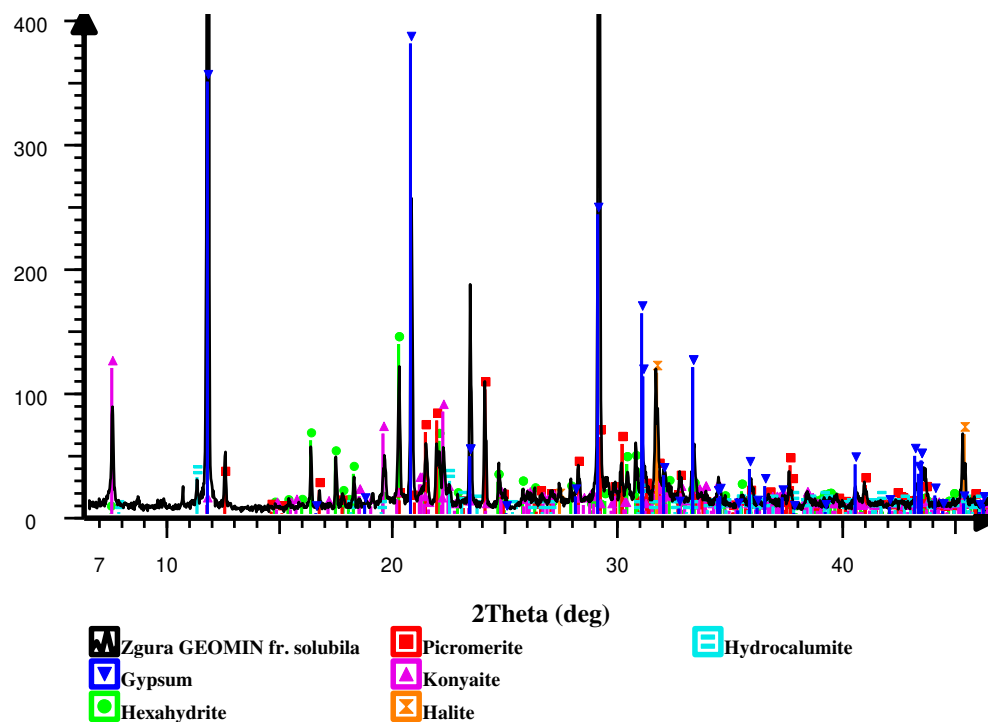


Fig. 2. Graphical presentation of qualitative analysis phase

3.2.3. Microscopical Analysis

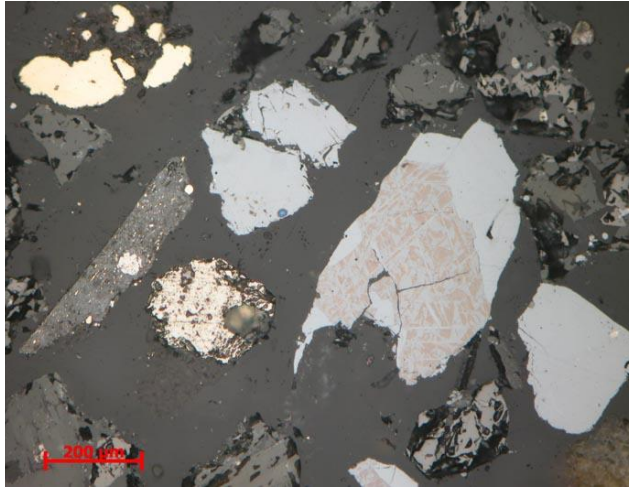


Fig. 3. Chalcocite, chalcopyrite, copper, pyrite, bornite, magnetite, fayalite. NII, reflected light.

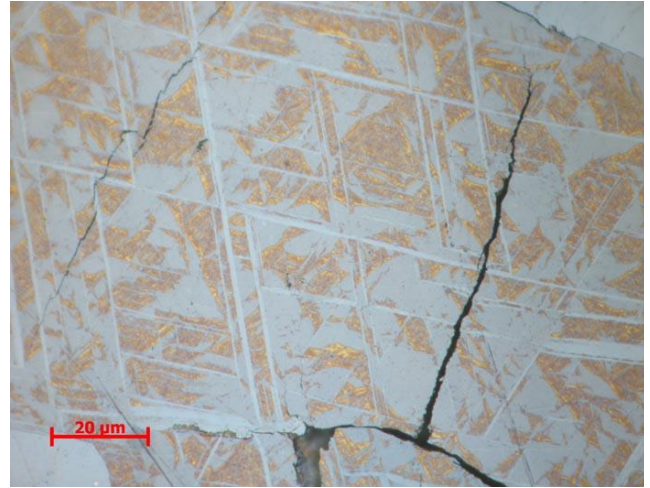


Fig. 4. Chalcocite exsolved from bornite. NII, reflected light, cedar oil immersion.



Fig. 5. Chalcocite, bornite, chalcopyrite, copper containing interdendritic cuprite, glass with magnetite. NII, reflected light.

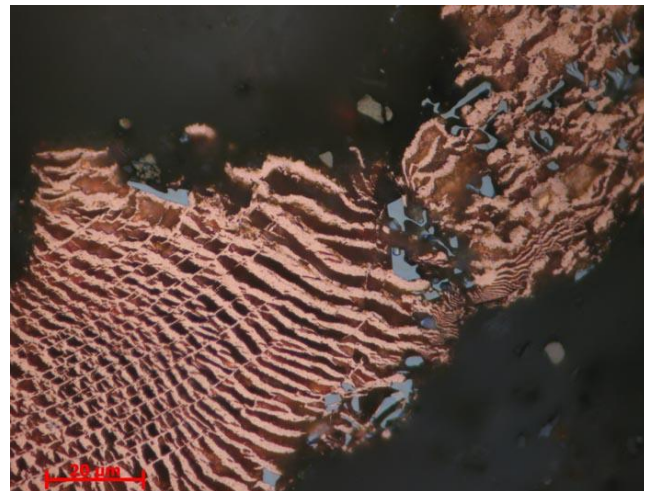


Fig. 6. Dendritic copper containing interdendritic cuprite. NII, reflected light, cedar oil immersion.

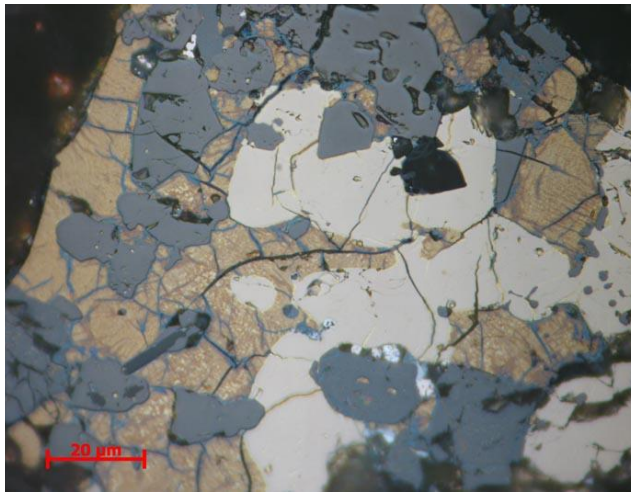


Fig. 7. Bornite, chalcopyrite, pyrrhotite, magnetite, digenite on the cracks. NII, reflected light, cedar oil immersion.

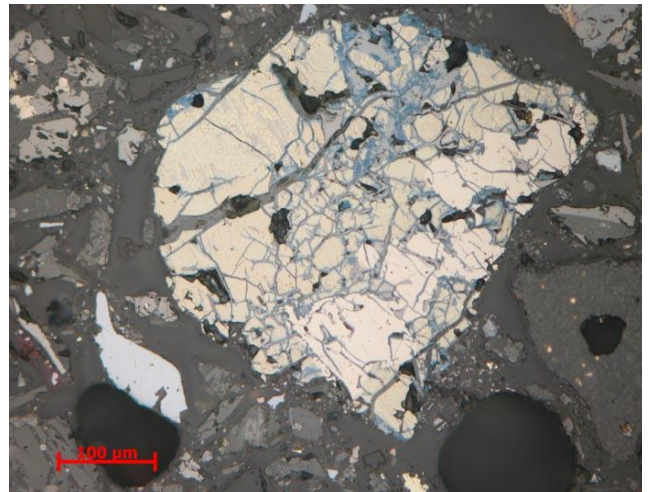


Fig. 8. Chalcopyrite, bornite, chalcocite, sphalerite+chalcopyrite in glass, magnetite, covellite on the cracks. NII, reflected light, cedar oil immersion.

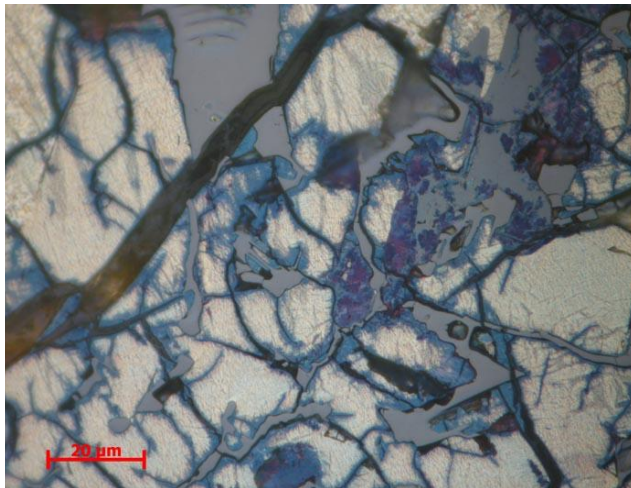


Fig. 9. Chalcopyrite, bornite, magnetite, covellite, on the cracks. NII, reflected light, cedar oil immersion

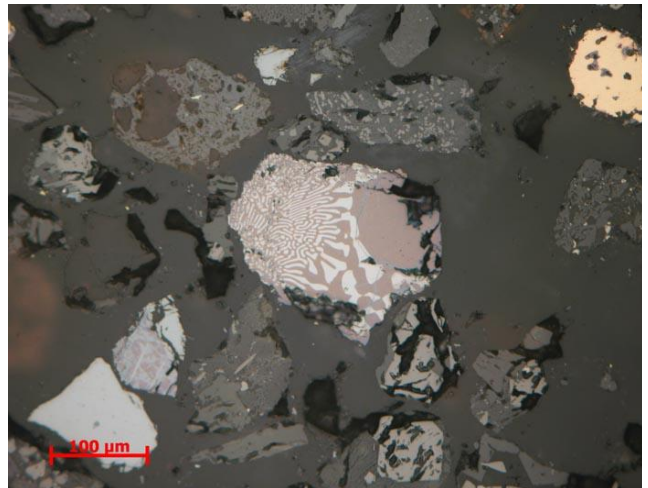


Fig. 10. Vermicular intergrowth of bornite and chalcocite. NII, reflected light

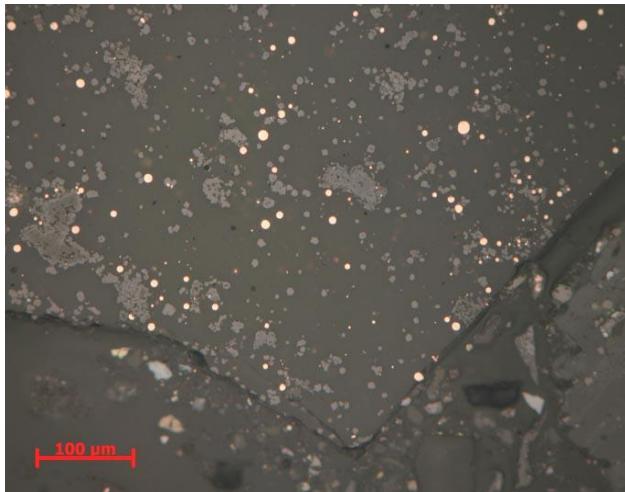


Fig. 11. Copper drops, magnetite crystals in glass. NII, reflected light.

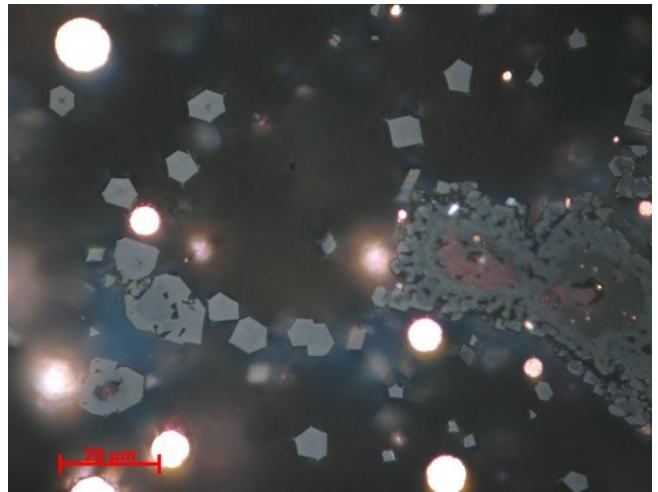


Fig. 12. Copper drops, isometric magnetite crystals in glass. NII, reflected light.



Fig. 13. Prismatic fayalite and magnetite in glass, copper drops. NII, reflected light.

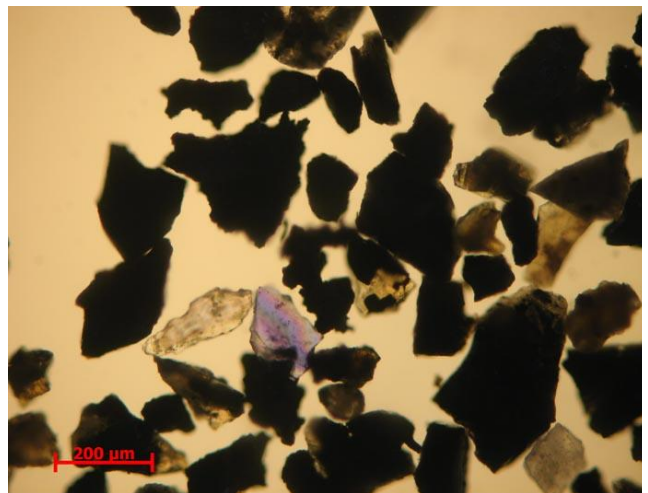


Fig. 14. Fayalite, willemitte (colored), glass, sulfides. NII, transmitted light.

4. Discussions

The bornite appears in all the studied samples, alone, or associated with others sulfides and oxides (Fig. 3–5, 7-10).

The theoretical formula of the bornites is Cu_5FeS_4 , but the natural bornites depart from this formula. The natural bornites partly contain CuFeS_2 and Cu_2S at high temperatures, because of the bornite lattice that is very similar to that of digenite and chalcopyrite. These bornites may decompose, forming high temperature mixed crystals of bornite and chalcopyrite (Ramdohr, 1969).

A rapid cooling of the bornite containing CuFeS_2 and Cu_2S at high temperatures leads to the formation of the digenite (in the studied material on the cracks – Fig. 7).

The digenite, the stable form of the Cu_2S above 450°C (Raghavan, 2006), below this temperature it transforms in the other form, hexagonal one, chalcocite (Fig. 3-5, 8, 10, 13). This form is almost always paramorphic and “it can be recognized in polished sections... by the presence of... a segmental pattern... of the orthorhombic form” (Ramdohr, 1969). From this lamellar paramorphic chalcocite evolves “mirmekitic” intergrowths bornite-chalcocite (Fig. 10), by recrystallization – consider a lot of authors noted by Ramdohr.

Under oxidative conditions chalcopyrite may decompose resulting the covellite (Ramdohr, 1969). In Fig. 8, 9, covellite and magnetite are together on the cracks of the mixing chalcopyrite and bornite.

During the flash smelting process of the copper concentrates the temperature reaches 1300°C . In the temperature range 800°C - 900°C , in the Cu-Fe-S system, metallic copper and iron may coexist (Raghavan, 2006). Under oxidative conditions the metallic copper (Fig. 3, 5, 10-13) and iron are oxidized (Constantin, 2009) to cuprite (Fig. 5, 6), and magnetite (Fig. 3, 5, 7-9, 11-13). In the same Cu-Fe-S system in the terms of high concentrations of Fe and S, at temperatures of 700°C - 900°C bornite and pyrrhotite coexist (Raghavan, 2006). This associations together with magnetite formed due to the oxidative conditions, appear by the rapid cooling of the copper matte (Fig. 7).

The slags appear from the flash smelting and the bessemerizing processes (Gâdea et al., 1978). These slags train the impurities, gangue minerals in the first case, of flash smelting, and other elements outside of copper, in the second case, of bessemerizing process. The structure of the slags is vitreous (glass), and this glass train a lot of the minerals from the concentrate and the copper matte (Fig. 5, 8, 11-14). In the glass prismatic crystals of fayalite develop, a specific mineral in iron rich slags (Fig. 3, 13, 14). Rarely, the willemite was founded (Fig. 14).

5. Conclusions

- Most part of the sample consists of glass, the main element of the slag, resulting in the process of copper obtaining.
- Some of the determined sulphides (chalcopyrite, pyrite, sphalerite) came from the copper concentrate, the raw material of copper extractive metallurgy.
- Most of the sulfides which belong to the Cu-Fe-S system, occur in association as they formed by different cooling rates of liquid particles of matte and slag.

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**Volume printed with the support of
SAMAX Romania S.R.L.
and
the “Munții Apuseni” Professional Association, Brad**

Computer layout:
Sorin Silviu Udubaşa