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CONTENT

- continued on the outside back cover -

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A SELF-PERSPECTIVE RESEARCH TOPIC REVEALED DURING THE ELABORATION OF THE ATLAS "FLUID AND MELT INCLUSIONS FROM ROMANIA"

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Motto:

> *"From a drop of water, a logician could infer the possibility of an Atlantic or a Niagara without having seen or heard of one or other"(Sherlock Holmes in A study in Scarlet- Bottomley et al., 2003)*

Abstract. Compulsory self-perspective research topic were envisaged during the elaboration of the atlas of "Fluid and Melt Inclusions from Romania", which is still under construction at Romanian Journal of Earth Sciences (RGES) from Geological Institute of Romania (IGR). This is in the nowadays trend in fluid inclusion research worldwide, although specific processes would be emphasized in this paper. They includes fluid (FIA)-, and melt inclusion (MIA) associations concept; fluid phase separation, immiscibility, ore fluid phase evolution, volatile exsolution from magmas; intermediate density fluid inclusion; destructive and non destructive methods; data acquisition and interpretation; main applications in Geology, Mineralogy, Petrology, Metallogeny, Sedimentology and Geologic hazard, Industrial application, "high-tech" and critical mineral exploration etc.

Key words: fluid and melt inclusion types, atlas, Carpathians, rocks, ore deposits, research topic, Romania

Introduction

The geological history of Romania's territory spanned ca. 2.0 Ga from Proterozoic to the present time (Balintoni, 2000). There are plenty of geological events where one or more fluid/melt phases were involved during their formation time. Metamorphic, magmatic and sedimentary rocks are characterized by various fluid mixtures trapped as carbonic, aqueous and melts inclusions in petrogenetic and hydrothermal or evaporate ore minerals. A complex fluid assemblage could be also encountered in the upper mantle peridotite nodules and in the high to low grade metamorphic rocks in all crystalline chains of the Carpathians. In this work the fluid and melt inclusions trapped in mineral formed during various geological processes and ages from Carpathian area from author's sample collection are presented, based mainly upon petrography and microthermometry. The atlas of fluid and melt inclusions from Romania is under construction at the Romanian Journal of Earth Sciences (www.igr.ro). There are 140 Figs yet, containing more than 1600 microphotographs of fluid and melt inclusions with specifications mainly about their petrography and microthermometry to date, from various geological formations from Romania (Pintea 2015, unpubl). In this paper there are summarized several important features about their occurrence and PVTX characteristics, useful in various geological application issues; these are the followings:

1. Silicate melt inclusions as variety of assemblages, containing glass, crystals and vapour phases (mainly $H_2O±CO_2$) are characteristic in all subvolcanic and volcanic environments from Eastern to South Carpathians, and Apuseni Mountains from multiple ages from Permian to Quaternary, from rhyolites to alkali basaltic alkaline rocks. The most important feature on this category is evidentiated by the presence of silica rich magmatic vapour phase (supercritical, Fig.1a) possibly originating deep in the lower crust and upper mantle region evolved as immiscible carbonate/silicate phases (e.g. Chalot Prat and Arnold, 1999; Pintea, 2014a). These probably were also involved in the epithermal alteration-mineralization processes and trapped as multiphase fluid inclusions in the low temperature quartz crystals from veins and stocks. "Foam-like" silicate glass inclusion were described and measured by microthermometry as valuable geothermometer of the subvolcanic and eruptive events related to the Dej Tuff formation (Pintea, 2013) and it is possible that an unmixing-like process was initiated by decompression in the upper "bubble-rich" layer on the top of the magma chamber, at the base of the volcanic conduits. Magma mixing/mingling processes is evidentiated by complex silicate melt inclusions (Fig. 1bd) suggesting temperature of andesitic melt formation around ≥1050° -1150°C (Pintea, 2014b). It is envisaged that during such heterogeneous processes immiscible Fe-S-O melts were trapped as various globular inclusions in the petrogenetic minerals (i.e. feldspar, quartz, amphiboles and pyroxenes) showing large wetting angle variations on the silicate surface, up to 180°, after several decrepitation experiments. High density "bubbles"of aqueous fluid (± liquid ± solid(s)) in the same minerals seem to be a very useful methodology in magmatic-hydrothermal ore deposit exploration (e.g. Naumov et al., 1996; Davidson and Kamenetsky, 2007) and would be necessary applied in the current research topic from different prospecting and exploration fields in Romania.

2. Hydrous salt melt inclusions exolved from silicate melt generated a range of heterogeneous single or coeval fluid and melt inclusion assemblages in porphyry copper deposits from Metaliferi Mountains and Eastern Carpathians and in the Upper Cretaceous porphyry and granite-pegmatite formations (Pintea, 2012). Sometimes, overestimated because heterogeneous trapping or post entrapment modifications, their real formation conditions could be measured from coeval silicate melt and hydrous salt melt pairs, as shown in Fig.1, where salt melt start to exolved at 1085°C from silicate melt (i), and silicate melt segregated at 1086°C (j), in good accord with data presented in the literature (e.g. Steele-MacInnis and Bodnar, 2013) which postulated that: "at any temperature greater than 1100°C aqueous fluid inclusions cannot be trapped in quartz, because quartz would melt in the presence of an aqueous

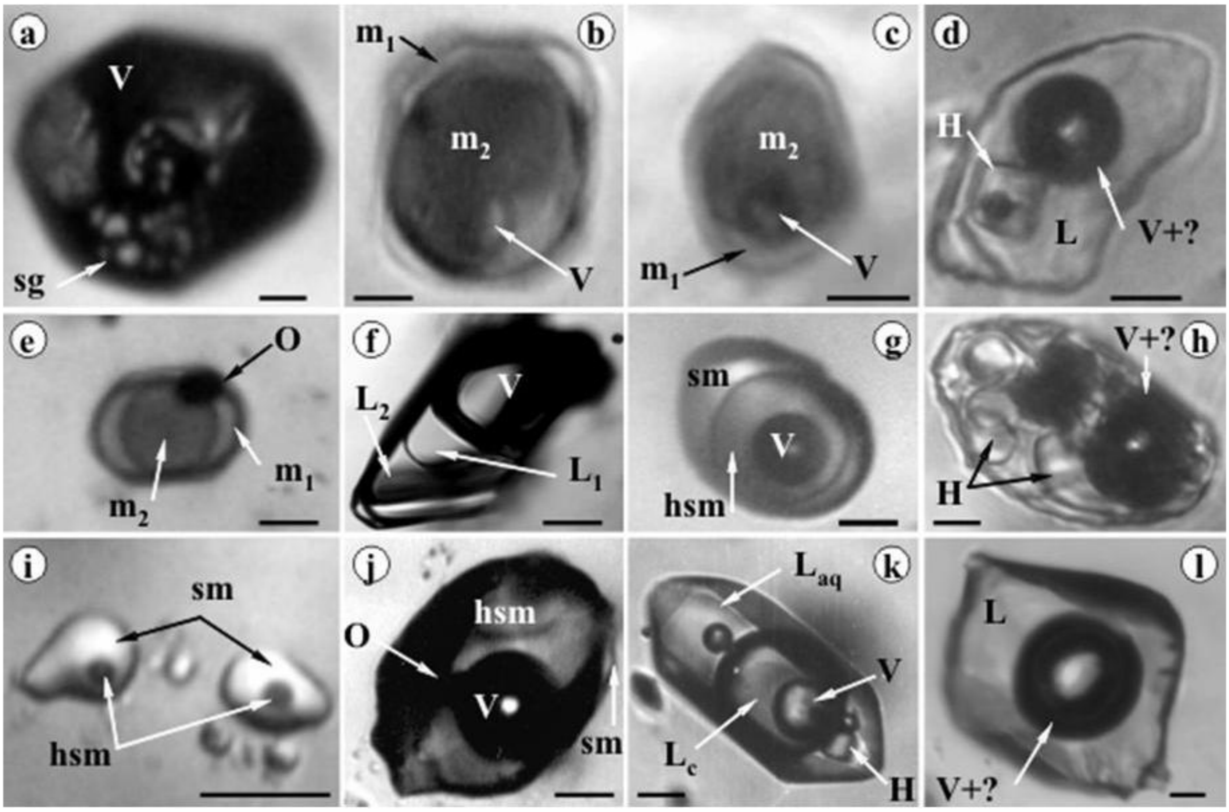

Figure 1. Selected types of fluid and melt inclusions from various geological formations from Romania, suggestive for immiscibility in various geological conditions; V- vapor, sg- "in situ" sublimated silicate roe, m_1- acidic silicate melt, m_2-mafic silicate melt, O- opaque, sm- silicate melt, hsm- hydrous saline melt, L_1, - liquid hydrocarbon (?), L_2, L_{aq}- aqueous liquid, Lc- CO_2 liquid, H- halite; **a, b**- Săpânta quartz xenoliths; **c, k**- Ditrău alkaline massif; **e**- Rosia Montana beta-quartz; **g**.- Deva "porphyry copper" deposit silicate melt - salt melt - vapor immiscibility at 1300°C; **i.** Th= 1085°C in silicate melt and **j.** Th = 1086°C in contemporaneous hydrous salt melt inclusion trapped in quartz; **f.** Bocşa-Săcărâmb epithermal ore deposit; **d**, **h**. a rind around the vapour bubble (pin point) together with solid microphase(s) at T = 25°C (**d**) and around 400°C (**h**), suggesting a second immiscible Fe-rich chloride (ferric) phase inside the brine inclusions in porphyry copper from Bolcana (**d**) and Rosia Poieni (**h**); Carbonic liquid- like phase (or a rind of reaction between aqueous vapour interface) around vapour bubble in aqueous inclusion from the miarolitic quartz from Vladeasa granite. Scale bar: a, b, c, d, e, g, h, i, j, k, l - 10µm; f.-70µm.

phase". Several pulses of Fe- chloride rich fluids exolved directly from the magmas and/or released during the endogenous metasomatic processes are also envisaged based upon complex brine inclusions microthermometry and their physico-chemical characteristics in accord with the recent published data worldwide (Pintea, 2014b; Kodera et al., 2014; Lecumberi-Sanchez et al., 2015a; Steele-MacInnis et al., 2015). The presence of supercritical water environment at high T-P conditions based upon published experimental works (e.g. Mibe, 2001; Martel and Bureau, 2001), precipitating of micro-halite crystals (and other salt and ore microcrysts) and nano silica globules was tentatively emphasized in several alpine porphyry copper deposit from Romania (Fig. 2). Probably many of these microphases (i.e. nano particles) were trapped in solid state in complex hydrous salt and silicate melt inclusions, known as typical heterogeneous trapping phenomena (e.g. Pintea, 2010; 2012; Lecumberi-Sanchez et al., 2015b).

3. Aqueous-rich fluid inclusions are characteristic for fluid evolved in epithermal, skarn and metamorphic terrains with low salinity (< 23.18 wt % NaCl eq) low temperature (< 350 - 400^{o}C) and low pressure (<50 - 100bars). Nevertheless, suggestive brine and vapour rich inclusions formed in secondary trails from magmatic quartz phenocrysts (or phenoclasts) from Danesti-Piatra Rosie dacite were recorded recently (Pintea, 2015 unpubl.). Possible high salinity fluid were envisaged also in a quartz -sphalerite paragenese containing "chalcopyrite disease" microtexture at Cavnic (Pintea, 2015 unpubl). These inclusion types and microtexture features are the result of fluid evolution (magmatic influx, meteoric

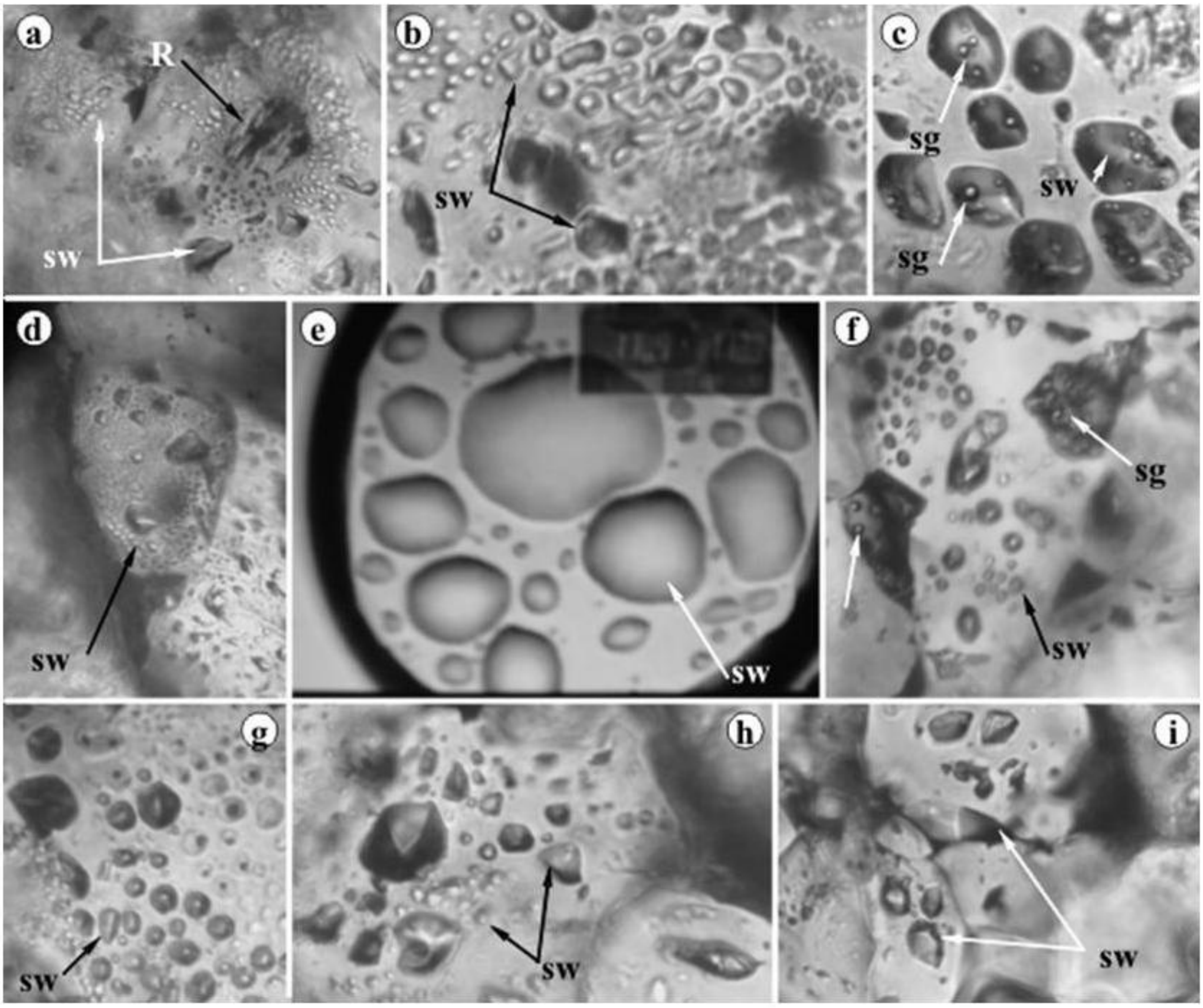

Figure 2. Presumed former supercritical water droplets (liquid cluster assemblage) trapped in the coarse grain quartz from Metaliferi Mountains (**a.** Larga – Dl Roatei ; **b**. Talagiu; **c**, **d**, **f**, **g**, **h**, **i** – Deva) analogous to the supercritical water shoved in diamond anvil cell experiment under critical pressure (Mibe, 2001; 2010-http//www.youtube.com/kenmibe). R- solid restite, sw- liquid (vapour) water, sg- silica globules. Not to scale.

convective waters) by boiling and/or mixing processes. Condensation or effervescence in veins and brecciate bodies during ore mineral precipitation and hydrothermal reactive alterations are also common. A hydrocarbon-rich component as liquid, gas (mainly CH_4) and/or solid bitumen (pyrobitumen) seems to be a common feature in hydrothermal fluid geochemistry that did not receive too much attention, but their presence is ubiquitous in many of such epithermal deposits from Romania, especially where gold is present (Fig.1e).

4. Complex carbonic fluids (CO_2-H_2O-NaCl) associated with REE-MoS_2 mineralization in the external-ring from Ditrău massif (Triassic-Jurassic) were trapped in (re)crystallized quartz crystal as spectacular heterogeneous mixtures being the favorite fluid inclusions assemblages in the atlas content. Based upon low temperature microthermometry a CH_4-rich fluids is probably present in the carbonic phases from various fluid inclusion types in quartz from Jolotca (Ditrau massif) and Vladeasa miarolitic quartz crystals (Fig.1 and Fig. 2). CO_2 - rich fluid trapped as primary and secondary fluid inclusions in olivine and orthopyroxene from the peridotitic nodules from the basaltic alkaline lavas brought out from the upper mantle in the Perşani Mountains (Quaternary) are special geothermobarometers too. Amphibolites and granulites metamorphic terrains including pegmatite (Pomarleanu, 2007) contains carbonic fluid assemblages besides low salinity and low temperature secondary trails especially in quartz veins and pods.

5. Monophase liquid inclusions (mother seawater) from preserved sedimentary primary growth zones as chevron assemblages, offer the only one possibility to estimate paleotemperature and to study paleo-geochemistry of the precipitation conditions from the marine/lagunar basins during Miocene salt deposit formation in the Transylvania Basin and extra Carpathian areas (Pintea, 2008). Moreover, recent preliminary work on brine and aqueous-rich inclusions (Fig 3) trapped in the barite nodules from the bentonite deposit from Valea Chioarului (Paleogene rhyolitic rocks) indicated a possible hydrothermal vent evolution under seawater environment (down to 1000m).

6. Hydrocarbon-rich fluids trapped as complex fluid inclusion assemblages in “dragomites” (bypiramidal quartz crystal known as “Marmarosh diamonds”) from Neocomian-Albian argillaceous blackshale from the Transcarpathyan flysh are useful tool to study basin fluid migration and hydrocarbon maturation process (Pintea, 1995). Despite the fact that Romanian territory host some important oil and gas prospects the fluid inclusion study in these fuels deposits and occurrences are scarce or missing at all. Advanced field and laboratory works based upon modern methodology (i.e. fluid inclusion stratigraphy - *www.fittulsa.com*) would be necessary to be planed in the next research project topics.

Conclusions.

The most complex geological process generated the most spectacular fluid inclusion assemblages and in this respect porphyry copper, granitic-pegmatites and REE- bearing mineralization are the favorites in the present content of the “Fluid and Melt inclusion atlas from Romania”. The self-perspective research methodology must be based on fluid (FIA)-, and melt inclusion (MIA) associations concept; fluid phase separation, immiscibility, ore fluid phase evolution, volatile exsolution from magmas; intermediate density fluid inclusions, destructive and non destructive methods; data acquisition, interpretation and modelling with main applications in Geology, Mineralogy, Petrology, Metallogeny, Sedimentology, Geologic hazard, Industrial application, “high-tech” and critical mineral exploration etc. The work is in progress.

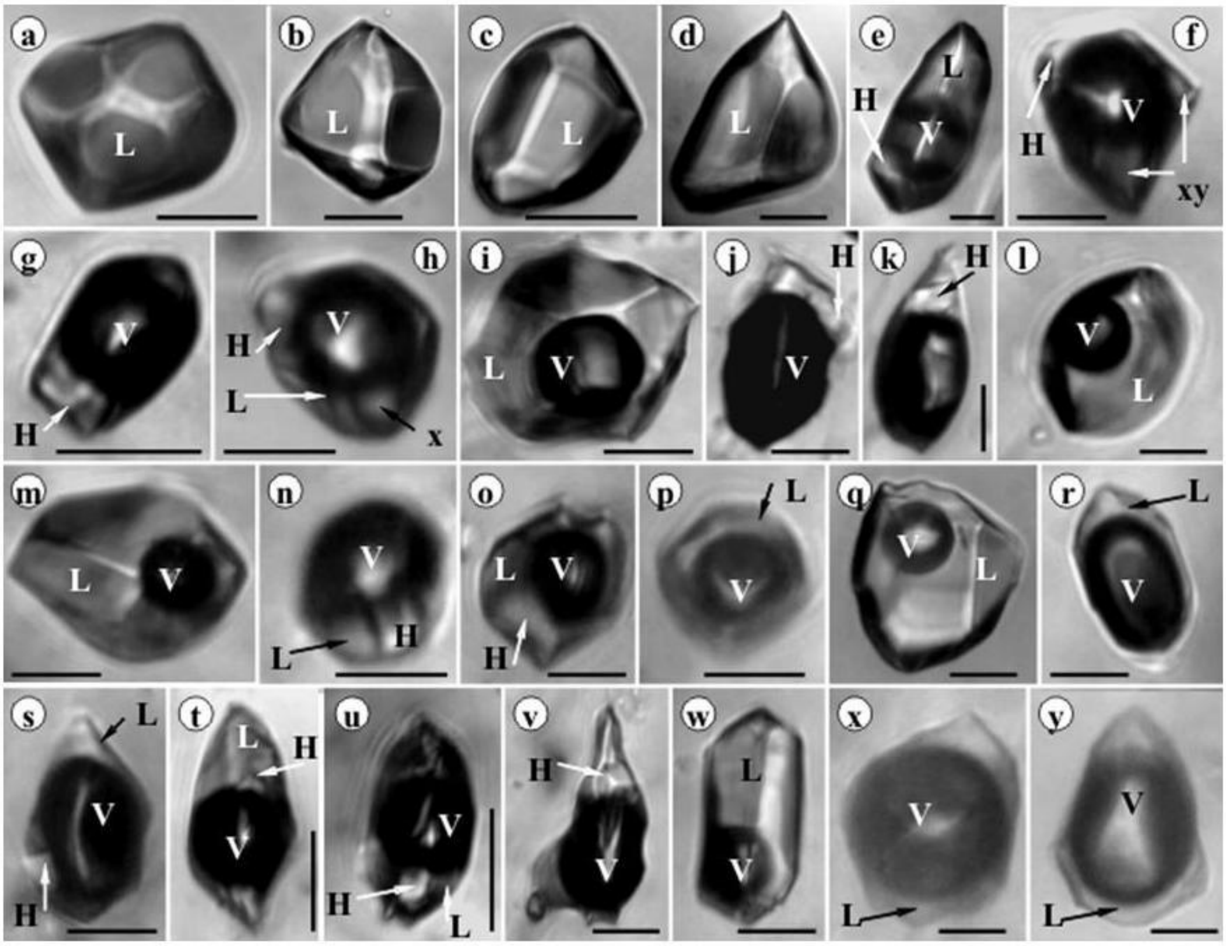

Figure 3. Liquid monophase-, (a, b, c, d) – biphasic-, (i, l, m, p, q, r, w, x, y) and triphase-, (e, f, g, h, j, k, n, o, s, t, **u**, **v**) fluid inclusions in barite nodules from the bentonitic Valea Chioarului mining prospect (geol. V. Todoran, 1997 - sample courtesy). Notations: L-liquid, H- halite, V- vapour. Homogenization temperature in un-stretched biphasic fluid inclusions ranged between 154^{o} and 240^{o}C (n = 30). Rarely, triphase fluid inclusions (n=4) showed Th= 263-330^{o}C, with estimated salinity of 30-34 wt% NaCl eq., and formation pressure between 28 and 96 bars. Scale bars: 10 µm.

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 7-12

ARGYRODITE OCCURRENCE IN ROȘIA MONTANĂ EPITHERMAL Au-Ag DEPOSIT, APUSENI MOUNTAINS, ROMANIA - EPMA DATA

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Abstract: Two occurrences of argyrodite within Roșia Montană ore deposit were certified by electron microscope (SEM) and electron probe microanalysis (EPMA) data. Both argyrodite occurrences are located in the southern part of the ore deposit in the underground workings from Cârnic massif within quartz veins crosscutting two different breccia structures. The ore bodies containing argyrodite have been mined during Roman times. The access in the underground and the sampling of the argyrodite bearing ores was facilitated by the mining archaeological research carried out in Cârnic massif (1999-2006). Argyrodite is associated with electrum and other Ag-minerals, *i.e.* acanthite, native silver, stephanite, proustite-pyrargyrite, polybasite-pearceite, Ag-tetrahedrite, and Ag-bearing galena, as well as common sulfides (pyrite, chalcopyrite, and sphalerite). The calculated chemical formula of argyrodite from Roșia Montană is $Ag_{8.35}GeS_{7.02}$ indicating a S excess as compared with the ideal formula Ag_8GeS_6.

Keywords: argyrodite, electrum, breccia dyke, Cârnic Roman mine, Roșia Montană, Apuseni Mountains

Introduction

Argyrodite is the germanium rich end member of the argyrodite (Ag_8GeS_6) - canfieldite (Ag_8SnS_6) series, which contains also putzite $(Cu_{4.7}Ag_{3.3})GeS_6$ and alburnite $Ag_8GeTe_2S_6$ (Paar et al., 2004; Tămaș et al., 2014). Moëlo et al. (2008) consider argyrodite a chalcogeno-salt type thiogermanates (Ge^{4+}) together with barquillite, briartite, calvertite, germanite, and putzite, while canfieldite is considered a chalcogeno-salt type thiostannate (Sn^{4+}). The available chemical composition of argyrodite with values in wt% for the main elements (Ag, Ge, and S) and the common impurities (Fe, Sb, and Sn) is given in table 1.

Table 1 - Analytical data (in wt %) for argyrodite according to Mindat mineralogical data base (http://www.mindat.org/min-331.html).

Element	Ag	Fe	Ge	S	Sb	Sn	Total	Occurrence
Value	74.20	0.68	4.99	16.45	trace	3.36	99.68	Aullagas, Bolivia

Several authors have already mentioned the occurrence of argyrodite in Romania, their identification being based on optical microscopy and/or semi quantitative analysis. On the basis of optical microscopy and etching Andronescu (1962) mentioned the questionable presence of canfieldite-argyrodite associated with enargite and germanite in Bucuresci-Rovina ore deposit, Ge minerals being related to chalcopyrite. According to Socolescu et al. (1963) the presence of argyrodite is undoubtful within Cu mineralization from Pârâul lui Avram ore deposit. The same authors emphasized that this occurrence represents the first mention of this mineral in Romania. The identification of argyrodite from Pârâul lui Avram ore deposit was made by optical microscopy in immersion and was subsequently confirmed by spectral analysis. According to the above mentioned authors, argyrodite from Pârâul lui Avram deposit occurs exclusively as inclusions in chalcopyrite, being closely associated with enargite-luzonite, famatinite, Bi-minerals (bismuthinite and galenobismutite), stannite, sphalerite, jamesonite, chalcocite and rarely covellite. Apart of the already mentioned minerals, the mineral association from Pârâul lui Avram ore deposit contains also pyrite, pyrrhotite, tetradymite, sphalerite, tennantite, melnikovite, and marcasite, accompanied by quartz, barite, and kaolinite (Socolescu et al., 1963). The third occurrence of argyrodite in Romania is Roșia Montană ore deposit and this occurrence was discovered by Tămaș (2002). The presence of argyrodite was stated on the basis of semi quantitative chemical data obtained by electron microscope (SEM) investigations. Later on, Te-argyrodite was described by Ciobanu et al. (2004), Tămaș et al. (2004 and 2006) and Bailly et al. (2005) from Cârnic and Cetate massifs according to EPMA data. However, Tămaș et al. (2014) proved that the above mentioned so-called Te-argyrodite is in fact a new mineral, alburnite ($Ag_8GeTe_2S_4$). Summarizing, the presence of argyrodite at Roșia Montană was indicated by Tămaș (2002) on the basis of SEM data, while the present contribution offers for the first time accurate EPMA data supporting the occurrence of argyrodite at Roșia Montană. It is also worth to mention that Popescu and Neacșu (2010) reported the presence of two tin-sulfosalts (canfieldite and pirquitasite) in Roșia Montană ore deposit.

The mining archaeological research carried out during several years in Roșia Montană underground developments allowed the discovery of an important network of Roman workings exceeding 6 km of cumulative length (Cauuet and Tămaș, 2012).

Geological and mineralization settings

Roșia Montană is an emblematic Au-Ag epithermal deposit located in the Apuseni Mountains, Romania. The ore deposit is situated in the northernmost Neogene ore district of South Apuseni Mts., precisely Bucium-Roșia Montană-Baia de Arieş. Previous works by Mârza et al. (1997), Tămaş and Bailly (1998, 1999), Leary et al. (2004) and Tămaş et al. (2006) pointed out the low sulfidation and respectively intermediate sulfidation character of the deposit. According to the last authors and Baron et al. (2011), at the ore deposit scale there is a clear passage from an early Au-Ag rich low sulfidation to a late Ag-rich intermediate sulfidation character. The ore deposit is hosted by 13.65 ± 0.63 Ma dacite bodies (Roşu et al., 2004), Cretaceous flysch (clays, sandstones), Neogene sedimentary rocks and synchronous vent breccias (Leary et al., 2004; Minuţ et al., 2004). The volcanic activity in Roșia Montană area ended at 9.3 ± 0.47 Ma (Roşu et al., 1997) with the emplacement of andesite lava flows and volcaniclastics. More details concerning Roșia Montană area (geology and ore deposit data) are given by Tămaş (2010).

The geological study of the Roman workings as well as of other underground workings allowed the identification of four ore deposition events within Cârnic massif from Roșia Montană (Tămaș et al., 2006). According to the previous mentioned authors and Baron et al. (2011), Ge bearing minerals are present within the third and the fourth mineralization events. The occurrences of argyrodite presented here belong to the third mineralization event, and are both located within Roman mining sites (stopes) from Cârnic massif.

Materials and methods

More than one thousand polished sections made on ores from Roșia Montană were studied during almost a decade using optical microscopy, electron microscopy and electron microprobe and only six of them contain several argyrodite grains.

The argyrodite was identified using only SEM spectra in the samples 1572 and 2175, while for the remaining three samples (1551, 1580 and 1660) a preliminary diagnosis was made by SEM but afterwards it was confirmed by additional microprobe data. The electron microscopy investigations (SEM, JEOL 6360LV, using a voltage of 20 kV) were done on the basis of preliminary optical microscopy observations. The SEM is coupled with an energy-dispersive spectrometer (EDS, PGT Sahara), which allowed the acquisition of several spectrums indicating the presence of a Ge-bearing mineral containing also sulphur and silver. Semi quantitative chemical compositions of several argyrodite grains have been also acquired prior the microprobe analysis. The EPMA data were gathered with a CAMECA SX50 electron microprobe using an acceleration voltage of 25 kV, a beam current of 20 nA, a 3 x 3 micrometers analysed area, and a counting time of 10 s for peaks and 5 s for background. Two programs used for argyrodite included S, Fe, Cu, Ge, As, Se, Ag, Sn, Au, and Sb. As standards were used natural and synthetic minerals, pure metals and alloys. The SEM and EPMA investigations were carried out at GET laboratory (former LMTG) from Paul Sabatier University, Toulouse (France).

Results

The presence of argyrodite in Roșia Montană is really very minor. At present, argyrodite was identified by the means of electron microscopy and microprobe data only within two ore bodies from Cârnic massif. These occurrences are located in two Roman networks, *i.e.* Cârnic 2 and Cârnic 10, as defined by Cauuet and Tămaș (2012). The argyrodite from the first occurrence consists in a breccia dyke-vein structure crosscutting a breccia pipe body from Cârnic 2 Roman network (sample 2175). The second occurrence is represented by a quartz vein crosscutting a breccia dyke structure from Cârnic 10 Roman network (samples 1551, 1572 and 1580 from Cârnic 10 Lower and 1660 from Cârnic 10 Upper). It is worth to mention that the sample from which Tămaș (2002) reported argyrodite on the basis of SEM spectra was picked up from Cârnic 2 breccia body (sample 228) but unfortunately it was accidentally destroyed after SEM investigations during subsequent additional polishing needed for microprobe analysis.

The present mineralogical study validates the existence of several minerals already reported from Roșia Montană and gives quantitative chemical data concerning argyrodite from two ore bodies from Cârnic massif, Roșia Montană epithermal ore deposit, *i*) a breccia dyke-vein structure crosscutting a breccia pipe located in Cârnic 2 Roman network, and *ii*) a quartz vein crosscutting a breccia dyke situated within Cârnic 10 Roman network. According to Tămaș (2002 and 2010) the breccia pipe structure partially mined out in Cârnic 2 Roman network contains common sulfides (Ag-bearing galena, chalcopyrite, sphalerite, and pyrite), electrum, acanthite, native silver, polybasite-pearceite, stephanite, tetrahedrite and argyrodite. The breccia dyke structure from Cârnic 10 Roman network has a mineralogical association composed of several Ag-minerals (polybasite, proustite-pyrargyrite), electrum, Ag bearing tetrahedrite, common sulfides (chalcopyrite, sphalerite, galena, pyrite), and argyrodite. All the above mentioned minerals from the breccia dyke mined out within Cârnic 10 Roman network have been firstly identified by the means of optical microscopy (Fig. 1) and then they were confirmed by SEM (Fig. 2 and Fig. 3) or/and EPMA data, but the present contribution presents chemical data for argyrodite only.

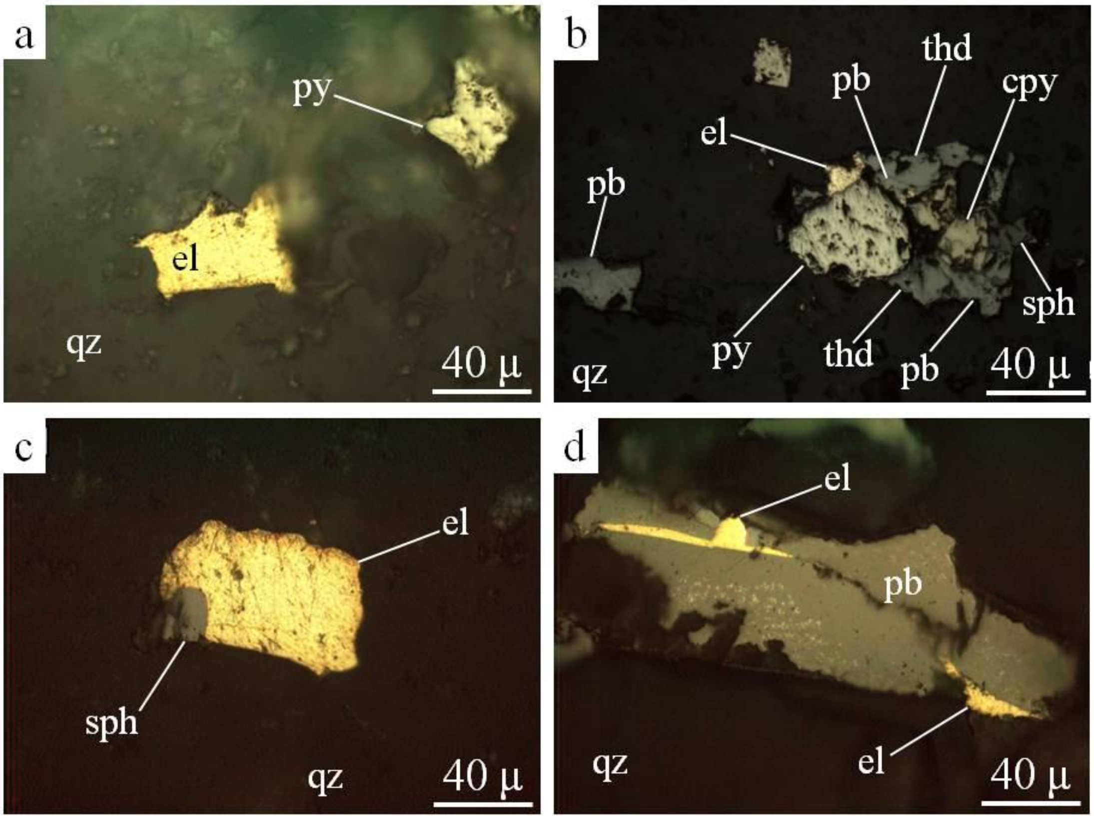

Fig. 1. Microscopic view (polished sections, plane polarized light) of the mineralogical association from the ore body mined out in Cârnic 10 Roman network (breccia dyke and overprinting quartz veins), Cârnic massif, Roșia Montană: a - electrum and pyrite in quartz gangue; b - electrum, polybasite, tetrahedrite, chalcopyrite, sphalerite and pyrite; c - electrum covering sphalerite; d - electrum crosscutting and deposited on polybasite. Abbreviations: cpy - chalcopyrite; el - electrum; pb - polybasite; py - pyrite; sph - sphalerite; thd - tetrahedrite; qz - quartz.

Several argyrodite grains were first noticed and then confirmed by SEM analysis within the breccia dyke structure from Cârnic 10 Roman mining network (Fig. 3 and 4). Argyrodite occurs as up to 30 micrometers isolated grains hosted within quartz gangue. It is sometimes closely associated with electrum, either occurring as individual grains or as composite grains composed of argyrodite and electrum inclusions (Fig. 3). Argyrodite as well as electrum have been deposited mostly within the open spaces of the quartz vein crosscutting the breccia dyke body and thus the argyrodite grains have irregular shapes.

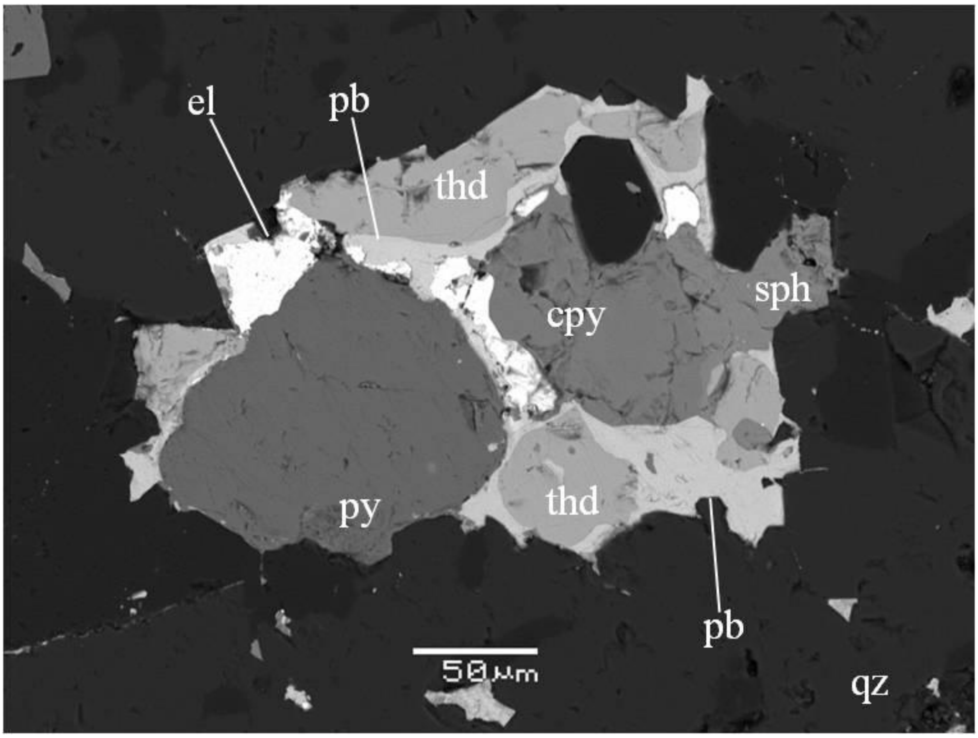

Fig. 2. SEM image of the mineral association consisting of electrum, Ag minerals and common sulfides from the ore body exploited within Cârnic 10 Roman network. The image represents a detail of Fig. 1b. Abbreviations: cpy - chalcopyrite; el - electrum; pb - polybasite; py - pyrite; sph - sphalerite; thd - tetrahedrite; qz - quartz.

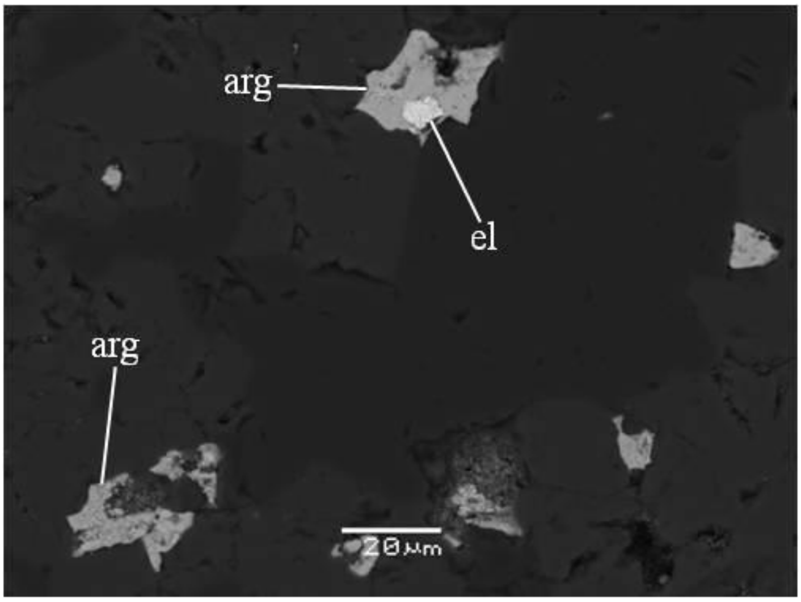

Fig. 3. SEM image of argyrodite - electrum association from a quartz vein overprinting the breccia dyke body exploited within Cârnic 10 Roman network (sample 1660). Abbreviations: arg - argyrodite, el-electrum.

Several spectrums of a Ge-bearing mineral have been acquired from several mineral grains within five polished sections (*e.g.* Fig. 4). Each spectrum indicated the presence of Ag, Ge and S elements only without any traces of other metallic/non-metallic elements pointing thus that the likely mineral candidate is the argyrodite.

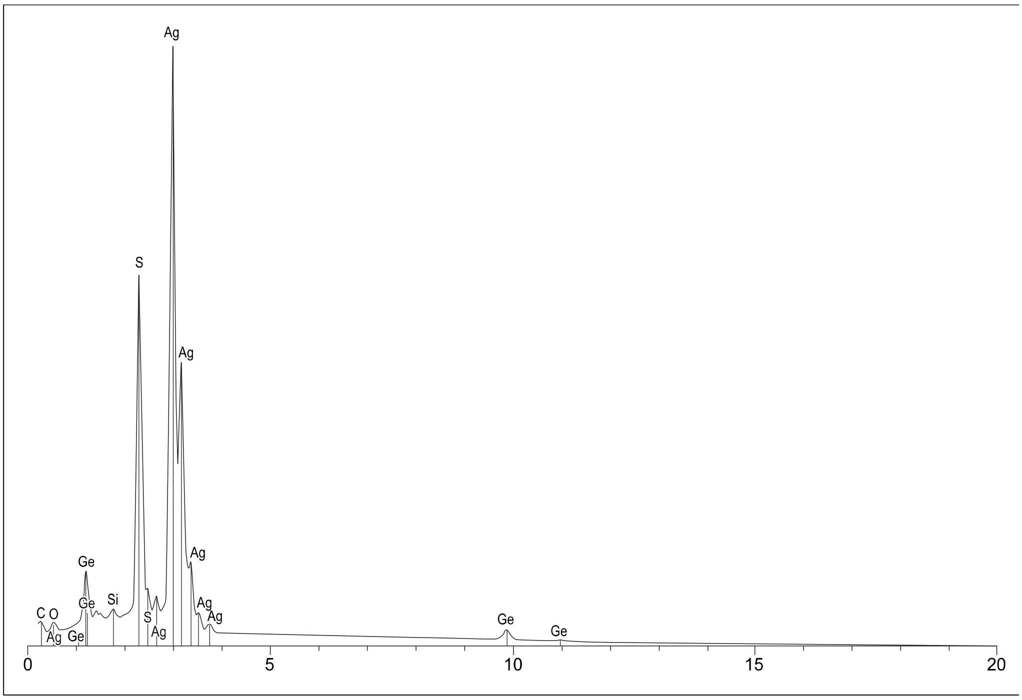

Fig. 4. SEM-EDS spectrum of argyrodite (sample 1572), showing the peaks of the chemical elements defining this mineral: Ag, S, Ge.

The mineral grains containing Ge were subsequently analysed by electron microprobe. The Table 2 summarizes the chemical data acquired for the samples 1551, 1580 and 1660. Due to the small size of the mineral grains and the high Ag content, the accuracy of the data is not always perfect but still significant for the chemical interpretation. The calculated formula of argyrodite, taking into account only the main elements (Ag, Ge, S) is $Ag_{8.35}Ge\ S_{7.02}$ showing a slight S excess as compared with the ideal formula Ag_8GeS_6. Taking into account all detected substitutions/impurities, the calculated chemical formula is $(Ag, Cu, Au)_{7.16}(Ge, Fe, As, Sb, Sn)_1(S,Se)_{6.21}$.

Table 2 - EPMA data (wt %) for argyrodite, Roșia Montană; n - no. of point analysis; g - no. of analysed grains.

Sample	S	Fe	Cu	Ge	As	Se	Ag	Sn	Au	Sb	Total
1551; n=5; g=3	18.72	0.09	0.28	5.56	0.76	0.85	72.87	0	0.03	0.77	99.93
1580; n=7; g=2	19.3	0.86	1.76	6.38	0.31	0.89	71.34	0.01	0.61	0	101.46
1660; n=2; g=1	18.29	0.02	0	5.88	0.53	0.39	77.38	0	0.09	0	102.58
Average	**18.77**	**0.32**	**0.68**	**5.94**	**0.53**	**0.71**	**73.86**	**0**	**0.24**	**0.26**	**101.31**

Conclusions

The occurrence of argyrodite in Roșia Montană ore deposit was confirmed by SEM and EPMA data. Tămaș (2002) mentioned for the first time the presence of argyrodite in Roșia Montană ore deposits, precisely within Cârnic 2 breccia pipe. Our study validates two new occurrences of argyrodite, both located in Cârnic massif from Roșia Montană. The first occurrence is represented by a hydrothermal breccia dyke-quartz vein structure crosscutting the Cârnic 2 breccia pipe while the second one consists in a quartz vein cutting a breccia dyke body situated in Cârnic 10 Roman network. Argyrodite is associated in these occurrences with electrum, Ag-minerals (native silver, acanthite, polybasite, and proustite-pearceite), Ag- tetrahedrite and common sulfides (chalcopyrite, sphalerite, galena, and pyrite). The EPMA data confirmed the absence of Sn from the analyzed argyrodite grains (maximum 0.01 wt %) and a slightly S excess.

Acknowledgements

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COMMON AND SPECIFIC PROPERTIES OF WASTE FROM THE TAILINGS PONDS OF FUNDU MOLDOVEI – LEȘU URSULUI MINE DISTRICT, ROMANIA

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Abstract: The study of waste in the tailings from the Fundu Moldovei – Leșu Ursului mine district shows some common properties, as follows: (i) pyrite controls the acidity and production of hydrated Fe-sulfates; (ii) the ratio between Fe_2O_3 and MgO is related to halotrichite-pickeringite solid solutions; (iii) Pb and As contents are related to goethite and jarosite occurrence. On the other hand, the peculiarities of the waste deposits have resulted in some specific properties, such as: (i) the detritus in the tailings ponds from the Leșu Ursului mine district is coarser and richer in pyrite; (ii) the lower abundance of soluble fraction in the tailings of Pârâul Cailor is explained by a less intense evaporation and a pronounced removal by the temporary stream that appears during heavy rains; (iii) the tailings of Dealul Negru and Pârâul Cailor are less acidic because of the smaller waste grains, which buffer the oxidation process; (iv) especially in Suha Valley tailings, the hydrated sulfates appear through the evaporation of two types of leachates: pore-hosted leachates within detritus and leachates accumulated as shallow pools on the beach of the waste deposit.

Keywords: tailings, sulfates, grain size, soluble fraction, toxic elements, Fundu Moldovei, Leșu Ursului.

1. Introduction

The purpose of the study is to emphasize the common properties and those that differentiate the detritus of four tailings ponds (TP) built up in the Fundu Moldovei – Leșu Ursului mine area, Suceava County. The four waste deposits are: TP of Dealul Negru and TP of Pârâul Cailor, located in the mine field of Fundu Moldovei, and TP of Suha Valley and TP of Straja Valley, located in the mine field of Leșu Ursului. The comparison lays on mineralogical, physical and chemical properties of waste.

The tailings ponds were built up of waste resulted from the processing plants of Fundu Moldovei and Tarnița, which were extracting Cu, Pb and Zn from the ore deposits of Fundu Moldovei and Leșu Ursului metallogenic fields. These fields are parts of the Cu-rich Polymetallic Belt of Eastern Carpathians, which stretches over a length of about 200 km. The ores of this metallogenic belt are hosted by the rocks of the metamorphic Tulgheș Group, which is a sequence of quartz-sericite-chlorite schists, silicic volcanics, carbonate schists, greenschists and metagreywacke. In the Polymetallic Belt of the Eastern Carpathians, three metallogenic districts were described, as follows (from NNW to SSE): (1) Borșa-Vișeu; (2) Fundu Moldovei-Leșu Ursului, and (3) Bălan-Fagu Cetății. The ore deposits in the metallogenic district of Fundu Moldovei – Leșu Ursului consist of sulfides that were accumulated as massive strata, lenses or tabular bodies of disseminated metallic minerals. The most common sulfides in the ores are Cu-rich pyrite, sphalerite and galena, showing various abundance.

The residues resulted from the ore processing plant of Fundu Moldovei were stored in two tailings ponds, i.e. the waste deposit of Dealul Negru, which is of side-hill type, and Pârâul Cailor, which is a cross-valley impoundment. The tailings pond of Dealul Negru covers a surface of about five hectares and displays a beach of 200 × 120 m. The waste deposit of Pârâul Cailor is 30 m high and has a beach of 350 m long and 280 m wide. The northern sector of the beach is crossed from west to east by a temporary stream, appearing during heavy rains, when it removes and transports the tailings outside the waste deposit.

The tailings ponds of Suha Valley and Straja Valley contain the residues of the Tarnița extraction plant. The waste deposit of Suha Valley is of side-hill type, it has a maximum thickness of 12 m and a beach of 200 × 90 m. The peculiarity of this waste dam is given by the 3 to 4 m high piles, scattered especially over the northern sector of the beach. The waste deposit of Straja Valley is a 25 m high dried impoundment of cross-valley type, with a triangular-shaped beach, which stretches over about seven hectares.

2. Materials and methods

For the present study, the samples were exclusively collected from the beaches of the four tailings ponds, following rectangular sampling grids; afterwards, the samples were stored in plastic bags until they were analysed. Data on 60 samples were used, i.e. 15 samples collected from each waste deposit.

The microscopic observations of waste were carried out using a Meiji 9400 ML stereomicroscope, while the particle-size analyses were performed using the sieving method. For this purpose, the samples were previously dried in an air oven, at 50ºC, for 24 h. The sieves of 1 mm, 0.5 mm and 0.063 mm were used to separate the following four grain-size classes: coarse sand, medium-coarse sand, fine and very fine sand, and silt + clay fractions.

XRD analyses were performed after a previous grinding of samples, using a mechanical agate mortar. The waste was analyzed using a PW 1739 X-ray diffractometer, equipped with monochromatic CuKα (λ=1.54 Å), the power settings being of 40 kV and 25 mA. The scan settings were 5–65° 2θ, 0.5° step size and 2 s count time per step.

To determine the pH and soluble fraction, leaching tests were carried out. The chemical composition of tailings was determined by energy-dispersive X-ray fluorescence (EDXRF). For this purpose, the previously ground samples were mixed with Hoechst wax, then analyzed with the help of an Epsylon 5 XRF spectrometer. The spectrometer calibration was performed using data for river sediments as reference materials.

The statistical analyses of the physical and chemical data were carried out with the help of the XL Stat Pro 7.5 software.

Table 1. Mineralogy of detritus from the tailings pond* (based on XRD patterns)

	Fundu Moldovei mine field		Leșu Ursului mine field	
	Dealul Negru	Pârâul Cailor	Suha Valley	Straja Valley
Quartz	●●●	●●●	●	●●
Chlorite	●●●	●●●	●	●●
Sericite	●●	●●●	●	●●
Pyrite	●	●	●●●	●●
Sphalerite	●	●	●●	●●●
Illite	●●●	●●●	●	●●
Kaolinite	●●●	●●●	●	●●
Goethite	●●●	●	●●	●●●
Pickeringite	●●●	●●●	●	●●
Halotrichite	●●●	●●	●●	●●
Apjohnite	●●●	●●●	●	●●
Alunogen	●●●	●●●	●	●●
Hexahydrite	●●●	●●	●	●
Jarosite	●	●	●●●	●●

* the abundance of a mineral in the detritus of a tailings pond, relative to the abundance of the same mineral within the other waste deposits. ●●● – the most abundant; ● – the least abundant

3. Results and discussion

3.1 Mineralogy

The microscopic observations together with XRD analyses showed that the mineral composition of detritus from all tailings ponds is dominated by primary minerals, i.e., the minerals of the ore-hosting schists (quartz-, sericite- and chlorite-schists) and polymetallic ore (pyrite, sphalerite and accidentally galena). The microscopic approach also showed a larger abundance of pyrite in the waste of Straja Valley and especially at Suha Valley. The waste mineralogy is completed by associations of secondary minerals, as follows: clay minerals (illite and kaolinite), hydrated oxides (goethite) and highly soluble hydrated sulfates of Al, Fe and Mg. The latter have precipitated either from acidic pore-water of tailings or through evaporation from shallow pools accumulated on the beach. They appear as efflorescent mineral aggregates or crusts consisting especially of pickeringite, halotrichite, apjohnite, alunogen, hexahydrite and jarosite (Table 1). XRD patterns of römerite, coquimbite, butlerite and ferrihydrite were also identified.

3.2 Grain size data

Data in Table 2 indicate a larger abundance of fine and very fine fractions of waste, compared with the coarse detritus. This is more obvious for the tailings ponds of Dealul Negru and Pârâul Cailor, where the ratio coarse/fine fraction is 1/14 and 1/18, respectively. Compared to this, ratios of 1/2 and 1/3 were found in the Suha Valley and Straja Valley tailings (Table 2). The latter ratios especially result from a much larger coarse fraction, i.e. up to 30 wt%, compared with only 5-6 wt% as recorded for the tailings from the other two waste deposits. The explanation may consist in the technological procedures of metal extraction that followed different parameters or metal extraction with different degrees of efficiency.

Table 2. Grain size analyses (average wt% determined on 15 samples from each of the tailings ponds)

	Coarse sand size	Medium sand size	Fine sand size	Silt+Clay
DN	0.72	5.95	53.18	40.15
PC	0.05	5.14	63.56	31.25
ShV	10.05	20.23	43.81	25.91
StV	8.30	19.01	52.91	19.78

DN-Dealul Negru; PC-Pârâul Cailor; ShV-Suha Valley; StV-Straja Valley

3.3 Soluble fraction

The soluble fraction of waste consists of secondary minerals, mostly hydrated sulfates, as already stressed in the mineralogical section of the study. Except for the waste deposit of Pârâul Cailor, the abundance of the soluble fraction is similar in all tailings ponds and its mean ratio is around 10 wt% (Table 3). Three aspects regarding the waste of the Pârâul Cailor may explain the much lower amount of soluble fraction, compared to the other tailings ponds: (i) the abundance of pyrite, whose oxidation and hydration lead to highly soluble sulfate formation, and which is much lower in comparison with the tailings from Suha Valley and Straja Valley; (ii) the position of the tailings pond relative to the topography of the area, which prevents the waste exposure to wind and, therefore, slows down the evaporation process; (iii) the removal of the soluble fraction by the temporary stream that crosses the beach of the waste deposit from west to east, during heavy rains.

3.4 Acidity

The acidity of the detritus is normal for this type of waste, its pH ranging between 2.5 and 3.2 (Table 3). The comparative analysis of tailings acidity indicates pH values of 0.5 units, higher for the waste from the tailings ponds of Fundu Moldovei mine field (Dealul Negru and Pârâul Cailor). The lower abundance of pyrite in the latter tailings ponds and, therefore, a less intense subsequent oxidation, as well as the higher content of silicates lead to this variation of acidity. The reduced oxidation may also be explained by the larger abundance of the fine fraction in the waste of Fundu Moldovei mine field. This results in smaller pore spaces within the waste and leads to a reduced contact of oxygen with the primary minerals, pyrite included.

3.5 Chemical properties

The major elements of the waste from all four tailings ponds are SiO_2, Al_2O_3, Fe_2O_3 and MgO. As most of SiO_2 comes from quartz, which has a low susceptibility to weathering, data on silica are missing in Table 3. The detritus of the tailings ponds from the Fundu Moldovei mine field contains similar amounts of Al_2O_3, Fe_2O_3 and MgO (Table 3). Moreover, the abundance of Al_2O_3 and MgO in the waste of this mine field is larger compared to tailings from the Leșu Ursului mine field. This is due to a higher abundance of silicates (chlorite and sericite) and their weathering products: clay minerals (i.e. illite and kaolinite) and hydrated sulfates (pickeringite, hexahydrite, alunogen and apjohnite). On the contrary, the detritus collected from the tailings ponds of the Leșu Ursului mine field (especially that of Suha Valley), which has the largest content of pyrite, displays a larger abundance of Fe_2O_3. Pyrite not only increases the Fe abundance in the waste, but also the quantity of secondary iron minerals developed on its account, as a weathering result: goethite, halotrichite, jarosite (Table 1), and also römerite, butlerite, coquimbite and ferrihydrite.

The abundance of Cu, Zn and As within the tailings from the waste deposits of Dealul Negru and Pârâul Cailor is similar, but lower in comparison with the detritus of the other two dried impoundments under study (Table 3). This is because of the larger contents of Cu-bearing pyrite and sphalerite recorded in the detritus of the latter waste deposits (Table 1). Moreover, in terms of Cu, Zn and As, the comparison between the tailings ponds of Leșu Ursului mine field shows differences, as following: (i) Cu is more abundant in the waste of Suha valley, where higher contents of Cu-bearing pyrite were recorded; (ii) the higher content of As within the waste of Suha valley is also due to pyrite abundance, as this mineral can incorporate large amounts of arsenic (Blanchard et al., 2007); (iii) the waste of Straja valley is richer in Zn, because of its larger amount of sphalerite. The mean lead amounts in the investigated waste deposits range roughly between 1200 and 1600 $mg\cdot kg^{-1}$. The highest contents were determined in the tailings of Dealul Negru and Straja Valley waste ponds; there, the XRD analyses indicate a larger quantity of goethite, which is an important sink of Pb and other toxic elements (Murciego-Murciego et al., 2012).

Table 3. Chemical composition of tailings

	Al_2O_3	Fe_2O_3*	MgO	Cu	Pb	Zn	As	Cd	SF	pH
	(wt %)			($mg\cdot kg^{-1}$)					(wt %)	
Fundu Moldovei mine field										
Tailings pond of Dealul Negru										
Min	5.07	6.32	2.18	193	659	96	104	0.03	2.33	2.64
Max	18.92	14.05	5.81	1090	2674	265	296	0.12	27.51	3.49
Mean	**12.55**	**9.85**	**4.07**	**458**	**1508**	**162**	**188**	**0.06**	**10.29**	**3.14**
Kurtosis	-2.006	-1.017	-0.890	-0.263	-1.363	-0.385	-1.457	-1.177	-1.824	-1.065
St.dev.	5.95	2.30	1.05	283	700	48	64	0.03	5.60	0.28
Tailings pond of Pârâul Cailor										
Min	2.90	6.64	1.79	211	534	124	94	0.05	0.89	2.60
Max	18.62	11.80	5.21	1492	1817	223	225	0.10	24.44	3.49
Mean	**11.80**	**9.02**	**3.52**	**498**	**1283**	**166**	**173**	**0.06**	**4.54**	**3.04**
Kurtosis	-1.714	-1.809	-1.542	1.145	-0.957	-0.833	-1.258	-0.551	**3.061**	-1.629
St.dev.	5.89	1.90	1.17	394	387	29	43	0.02	**7.14**	0.32
Leșu Ursului mine field										
Tailings pond of Suha Valley										
Min	1.54	12.26	0.09	323	304	109	190	0.09	3.45	2.30
Max	9.92	21.00	0.82	3041	6613	2172	2188	0.83	20.75	3.03
Mean	**4.11**	**18.40**	**0.32**	**1327**	**1314**	**626**	**462**	**0.28**	**9.98**	**2.59**
Kurtosis	-0.830	-0.491	-0.223	-0.968	**3.099**	-0.203	**3.370**	-0.626	-0.798	-1.388
St.dev.	2.83	2.86	0.23	935	**1898**	**696**	**611**	**0.27**	5.35	0.25
Tailings pond of Straja Valley										
Min	3.28	11.51	0.05	344	219	56	84	0.26	3.78	2.53
Max	11.67	18.43	1.95	1270	4073	1648	309	3.74	19.40	2.89
Mean	**8.16**	**13.24**	**1.23**	**805**	**1587**	**955**	**155**	**2.46**	**11.57**	**2.66**
Kurtosis	-1.525	2.191	-1.423	-1.372	-0.456	-0.251	0.680	0.402	-1.833	0.558
St.dev.	2.80	1.94	0.65	300	1168	427	64	0.94	5.90	0.10

Fe_2O_3* = FeO + Fe_2O_3

The normality tests, performed on all data, without considering the waste deposit from which the samples were collected, have indicated non-normal distribution for all chemical elements under study. This may be the expression of differences between the physico-chemical properties of waste from the four waste deposits. On the contrary, the descriptive statistics performed on data regarding samples collected from the same tailings pond show kurtosis and standard deviation that suggest unitary statistical populations (Table 3). This suggests common physical and chemical properties of waste collected from the same waste deposit. However, larger values of kurtosis and standard deviation were determined for the soluble fraction within the tailings of Pârâul Cailor, which is explained by the formation of two generation of hydrated sulfates: older sulfates, precipitated on the main beach surface, and younger sulfates, developed within the sectors affected by the temporary stream, during rainfall periods. Data on Pb, Zn and As contents in the waste of Suha Valley also suggest non-unitary populations. The explanation may consist in the occurrence of at least two types of hydrated sulfates, known as sinks for toxic elements: (i) sulfates developed through the evaporation of pore-waters in tailings from the waste piles flanks; and (ii) sulfates precipitated through the evaporation of leachates accumulated as shallow pools on the beach surface.

The Pearson correlation matrix (not shown in the paper) highlights some common geochemical properties of waste under study. Thus, the positive correlation between Al_2O_3 and MgO ($r^2 = 0.800$) is due to their presence within the structure of some primary (chlorite) and secondary (illite and pickeringite) minerals. The tendency of iron oxide and MgO to a negative correlation ($r^2 = - 0.660$) may be explained by the formation of either halotrichite [$FeAl_2(SO_4)_4 \cdot 22(H_2O)$] or pickeringite [$MgAl_2(SO_4)_4 \cdot 22(H_2O)$] within waste, as terms of a solid solution series. The coefficient of correlation between MgO and pH ($r^2 = 0.680$) suggests that less acidic environments are favorable to pickeringite formation. This is in agreement with the three-stages sulfate evolution model of Velasco et al. (2005), which showed that pickeringite appears after alternative dissolution and precipitation processes, during the neutralization episodes of stage III. The correlation of Pb with As ($r^2 = 0.760$) supports the hypothesis of simultaneous accumulation of the two elements within goethite (Murciego-Murciego et al., 2012) and jarosite (Hammarstrom et al., 2005; Asta et al., 2009).

4. Conclusions

The purpose of the study was to identify the common properties and those that differentiate the tailings from the Fundu Moldovei – Leşu Ursului mine district.

The properties that make the waste from all four tailings ponds similar are: (i) the abundance of pyrite controls the acidity of waste and generally the production of hydrated oxides and sulfates involving Fe; (ii) the weathering of primary minerals leads to similar secondary phases, such as hydrated iron oxides, hydrated sulfates and clay minerals; (iii) the abundance of Al_2O_3 and MgO is controlled by both primary minerals (chlorite) and secondary minerals (illite, pickeringite); (iv) the abundance of Fe_2O_3 relative to MgO results from the formation of mineral terms of the halotrichite-pickeringite solid solutions; (v) the MgO content is larger in less acidic environments; (vi) goethite and jarosite are sink minerals for Pb and As.

Among the properties not common to all the investigated waste deposits, the most relevant are: (i) the tailings from Straja Valley and especially from Suha Valley contain significantly more pyrite than those from the other deposits (ii) the waste of Suha Valley and Straja Valley tailings ponds is coarser, probably because of some differences in the extraction procedure; (iii) the waste of Pârâul Cailor contains less soluble fraction than the other waste deposits, because of its reduced formation through evaporation and pronounced removal by the temporary stream during heavy rains; (iv) the tailings of Dealul Negru and Pârâul Cailor is less acidic because of the lower abundance of pyrite and also larger abundance of smaller waste grains, which buffer the oxidation process; (v) when the land relief of the waste beach shows significant differences (as for Suha Valley tailings pond), hydrated sulfates appear as a result of evaporation affecting two types of leachates: leachates in the detritus pores and leachates accumulated in shallow pools on the lower parts of the beach.

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 19-24

MODERN LIGNITE EXPLORATION IN THE THRACIAN BASIN AND WESTERN ANATOLIA/TURKEY

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Abstract: During the Tertiary several lignite horizons were deposited in Thracia and Western Anatolia under lacustrine to fluviatile conditions. These lignites occur mainly as coal lenses in the Thracian basin. In Western Anatolia coal occurs mainly as coal seams. DMT started working in Turkey in 2006 after the privatization of the Turkish mining industry and the introduction of international reporting codes like JORC as basis of resource reports. DMT regularly uses inter alia geophysical borehole measurements to correlate lignite seams or lenses and 2D seismic-surveys to delineate the structural framework which were not used in Turkey as tools in non-governmental exploration of the private industry. Both methodologies save costs and time and lead to a better understanding of the paleo-environment and hence to the understanding of the deposits.

Keywords: lignite lenses, correlation, borehole measurements, deposit structures, geophysics.

1 Introduction

Following the First World War the young Turkish Republic nationalised bigger parts of the Turkish industry. Between 1928 and 1940 the mining industry was also nationalised by the Turkish government. In parallel the government established in 1935 the Mineral Research & Exploration General Directorate (MTA), with the aim of conducting scientific and technological research on mineral exploration and geology. In 2004 the Turkish government moved to privatize the mining companies. Over a period of around 70 years until the liberalization of the Turkish mining industry in 2004 no private investors were able to invest into mining projects. The booming economic growth in the last 15 years in Turkey produced a class of industrial magnates, which use their financial resources to invest in mining and exploration projects. As a result DMT explored many sites in Turkey in the last 10 years.

1.1 Geological setting

1.1.1 Thracian basin

The Thracian basin is an intra-mountain Tertiary basin in the European part of Turkey. Following Keskin (1974) Eocene to Pliocene units build-up the filling of the basin. Ignoring discontinuities and erosion, sedimentation continued until very recently. The main lignite deposits occur in the Danişmen Formation of the Upper Oligocene/Lower Miocene. Some low grade lignite horizons were deposited in the Upper Miocene. Following own research and Perinçek et al. (2015) the lignite fields in the N of the Thracian basin are generally found on flanks of the Istranca massif (İstanbul-Silivri-Sinekli; Tekirdağ-Saray-Küçükyoncalı; Tekirdağ - Saray - Safaalan; Tekirdağ - Saray – Edirköy fields). The lignite deposits at the southern rim of the basin include the coal fields of Keşan, Malkara, Uzunköprü and Meriç. The lignites N and S of the basin gradually deepen to the center of basin and attain a depth of 600 m within the 10.000 m-thick sequence (Şengüler, 2013). The lignites of the Thracian basin were deposited in delta swamps of lacustrine environments. Due to higher sedimentation rates the lignite deposits in the Thracian basin vary extremely in respect of thickness and structure. Another problem to interpretation is caused by the change of fluvial conditions during the formation of Danişmen Formation (Perinçek et al., 2015). Fluvial condition hamper strongly lignite sedimentation and correlation of coal seams in the Thracian basin (Şengüler, 2013) is, therefore, difficult. Following own research and results of exploration campaigns most lignite deposits in the Thracian basin occur as coal lenses and not as continuous coal seams. Sometimes these coal lenses can be correlated with neighboring lenses, sometimes not. The Thracian basin contains approximately 2 Gt of coal resources.

1.1.2 Western Anatolia

Following Yağmurlu et al. (2004) the lignite-bearing continental Neogene basins of Western Anatolia are divided into three groups according to their time of formation, tectonic setting, and sedimentary facies. These are, in ascending time/tectonic order, the NE, the NW and the EW-trending basins which opened during the uplift of the Menderes Mountains.

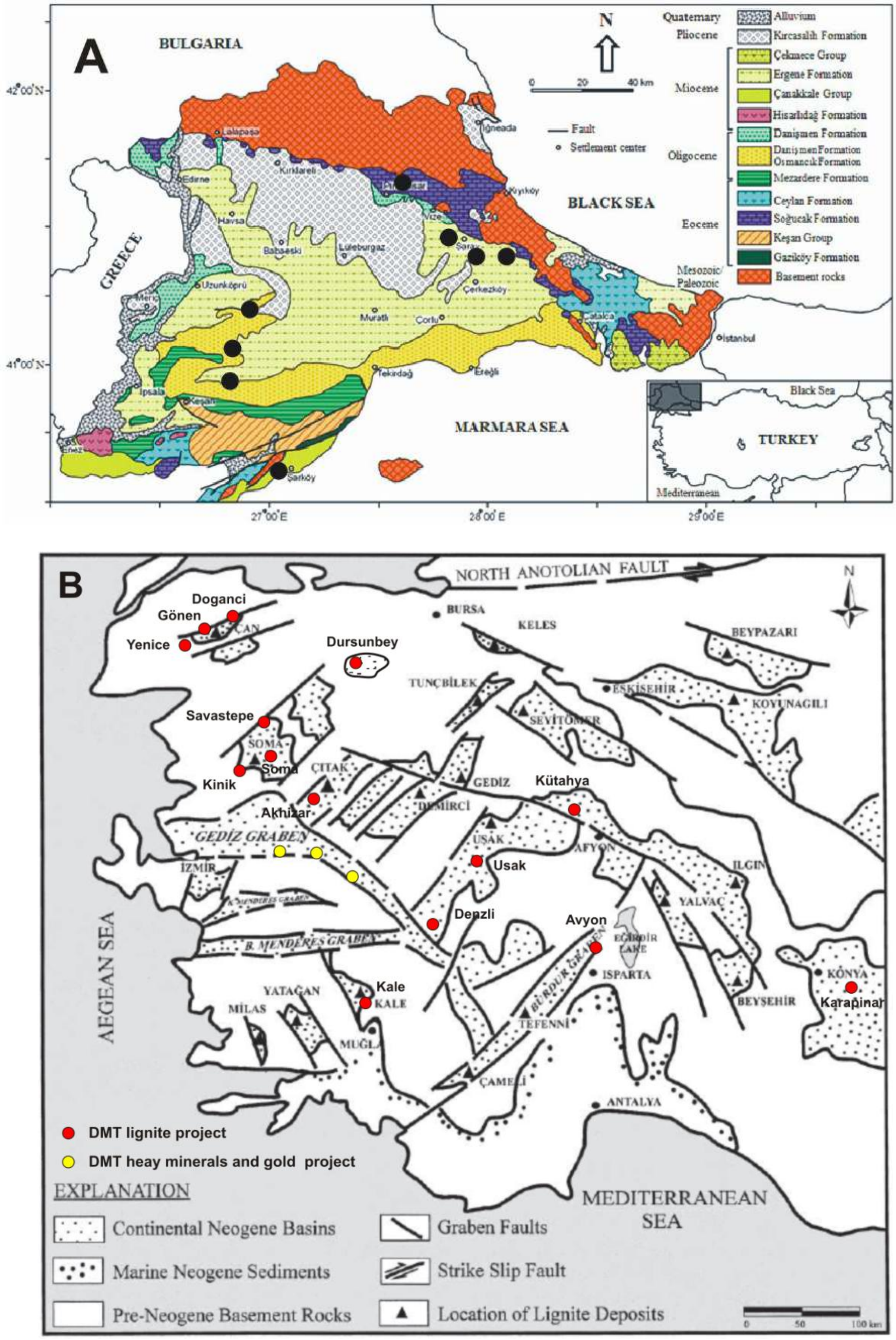

Fig. 1: a) Geology map of Thracian basin (from Perinçek et al., 2015). b) The lignite-bearing Neogene basins of Western Anatolia (modified from Helvacı and Yağmurlu, 1995).

While the NE and the NW-trending Neogene basins of Western Anatolia are filled with Middle to Upper Miocene sedimentary sequences respectively, the EW-trending basins are filled with Pliocene-Quaternary sediments only the latter basins have parallel trends from west to east.

Generally, the boundaries of the basins are controlled by faults which have influenced the thickness and spreading of the sedimentary sequences and lignite seams. These sedimentary sequences of the continental basins consists mainly of fan, fluvial, lacustrine, and volcanoclastic sediments. Most of the economic lignite deposits in the Neogene continental basins occur in the uppermost part of the fluvial sequences which are concordantly overlain by lacustrine sequences.

The NE-trending Neogene lignite basins of Western Anatolia, have a relatively high calorific value compared to those of the NW-trending lignite basins. The EW-trending Pliocene-Quaternary basins do generally not contain economic lignite deposits. The total lignite resource of Western Anatolia amounts to approximatively 3 billion tones (Helvacı and Yağmurlu, 1995). In the Western Anatolian basins the coal occurs in bigger coal seams and only partly in lenses. Due to the ongoing uplift and fragmentation of the Menderes Mountains these lignite seams are faulted intensively.

2 Exploration in Turkey

All exploration work in Turkey until the privatization of the Turkish mining industry was done by the state-owned MTA based in Ankara. The absence of private consulting companies led to exploration techniques without modern scientific background. Normally, only boreholes without geophysical logging were used to interpret the complex geology of the coal fields.

In their own projects DMT provides Standard Operation Procedures (SOPs) for drilling and core logging following international standards with the objective to be able to report resources compliant to international reporting standards, like JORC. In addition, DMT recommended a transformation of exploration results to international standards, including hydrogeology, geophysical borehole measurements, methane measurements, geotechnical studies and, for clarification of the structural framework and the depth relationships, 2D seismic surveys.

2.1 Seam correlation

Historic data often miss legends of lithologies. In addition, the unclear situation of core losses influences re-interpretation of the historic boreholes. Correlation of lignite is ideally based upon the documentation of core losses and the reconstruction of the stratigraphy by using geophysical borehole measurements like natural gamma, gamma-gamma (specific weight), deviation, neutron, caliber etc. This is demonstrated below. Figure 2 shows an example of a correlation of a historic borehole and a new borehole. It clearly shows the benefits of the documentation of core losses in the new drill hole and the reconstruction of the lithology using natural gamma measurements. These measurements were carried out by a local contractor using the DMT's SOPs. Results from the southern Thracian basin near Malkara show the higher value of geophysical borehole measurements:

- The core recoveries are generally poor in lignite and coal. Parts of the coal are destroyed by the drilling tool and washed out by the drilling mud. Hence, intersection of coals do contain only parts of the actual coal developed. Without geophysical measurements these losses are not possible to reconstruct (s. Fig. 2: The second seam in the old borehole shows only half of the existing coal.
- New drill holes show always higher thicknesses of coal and interbedded clay-, silt- to sandstones in comparison with the historic ones.

The application of borehole geophysical measurements are not only useful for oil and gas exploration. German geophysists use these methodologies to prospect German coal and lignite field since years. These geophysical tools help to interpret the structure of geologically difficult deposits. These investigations, geophysical and correlation, are the base for 2D seismic field surveys.

2.2. 2D seismic field survey and 3D modelling of lignite deposits

During exploration campaigns 2D seismic surveys will be executed to save costs and time. If the drilling campaign is too difficult due to the surface conditions or is too time-consuming 2D seismic surveys are an efficient method to get the needed information much faster than drill holes could deliver. An example from Western Anatolia shows the way to save costs and time:

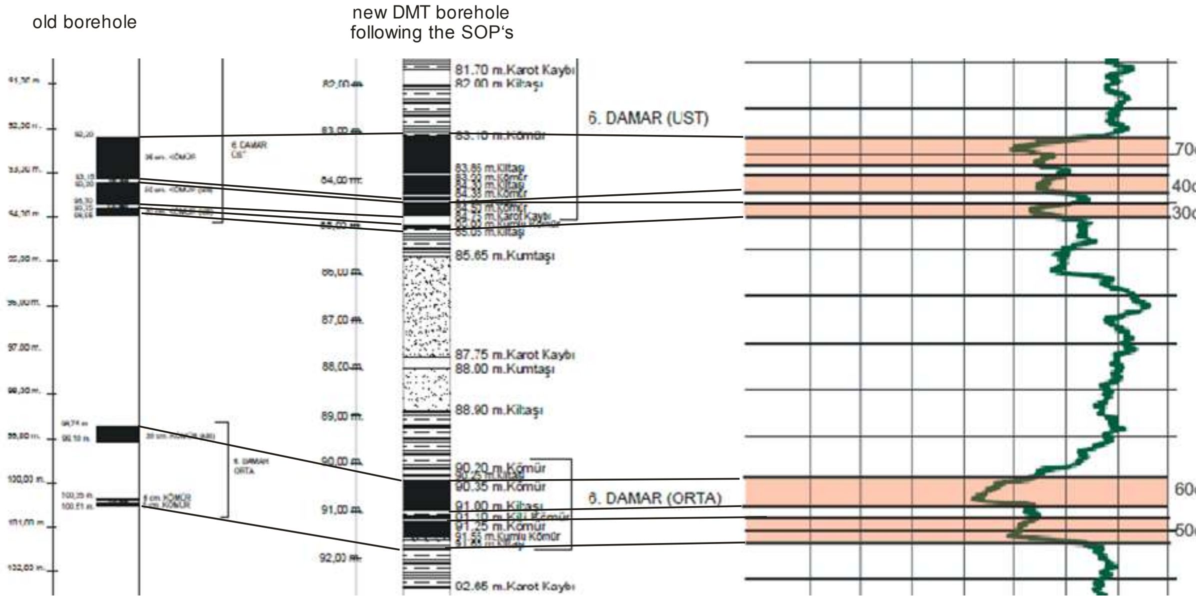

Fig. 2: Correlation between old borehole and a new borehole and a geophysical borehole measurement; example from the Thracian Basin near Malkara.

- DMTs geologists estimated that 25 additional boreholes were required to clarify the structure of the faulted deposit in the Menderes Mountains. The following calculation convinced the client of ordering a geophysical company to execute a 2D Seismic survey following 7 lines scouted by DMT:
  25 Boreholes needed, 1 borehole 1000 m depth ca. 200.000 $; Expenses of drilling: ca. 5.000.000 $
  Expenses of the seismic survey ca. 500.000 $

- The field work started in January and was completed after 6 weeks in March 2014. During the whole time DMT seismic specialists supervised the geophysical company to verify the quality of the work and data. The processing of the data was done by DMT's specialists in Essen from March to April 2014.
- These results were positive and following the successful data processing also the modelling of the data was executed by DMT geologists in Essen from April – May 2014. The analysis of the drilling led to a seam-like coal deposit with variable coal thicknesses, while the modelling of the 2D seismic led to a 3D model of the structure of the deposit (Fig. 3). As a result of the interpretation DMT geologists could define several fault-bordered resource blocks in the deposit. DMT mining engineers could use the 3D model to start the planning of the shaft location and the mine.

3 Conclusions

Cored boreholes, which were investigated using borehole geophysical measurements led to much more accurate results than boreholes without these investigations. The methodology facilitates the reconstruction of core losses, which are normal in exploration boreholes, and assist in the definition of the character and the structure of hard coal and lignite deposits.

2D seismic surveys and resulting 3D models save costs and time of exploration campaigns. During an exploration for lignite in Western Anatolia such a survey saved around 90% of the remaining exploration budget and enabled the mining engineers to start the planning of the shaft location and the mine.

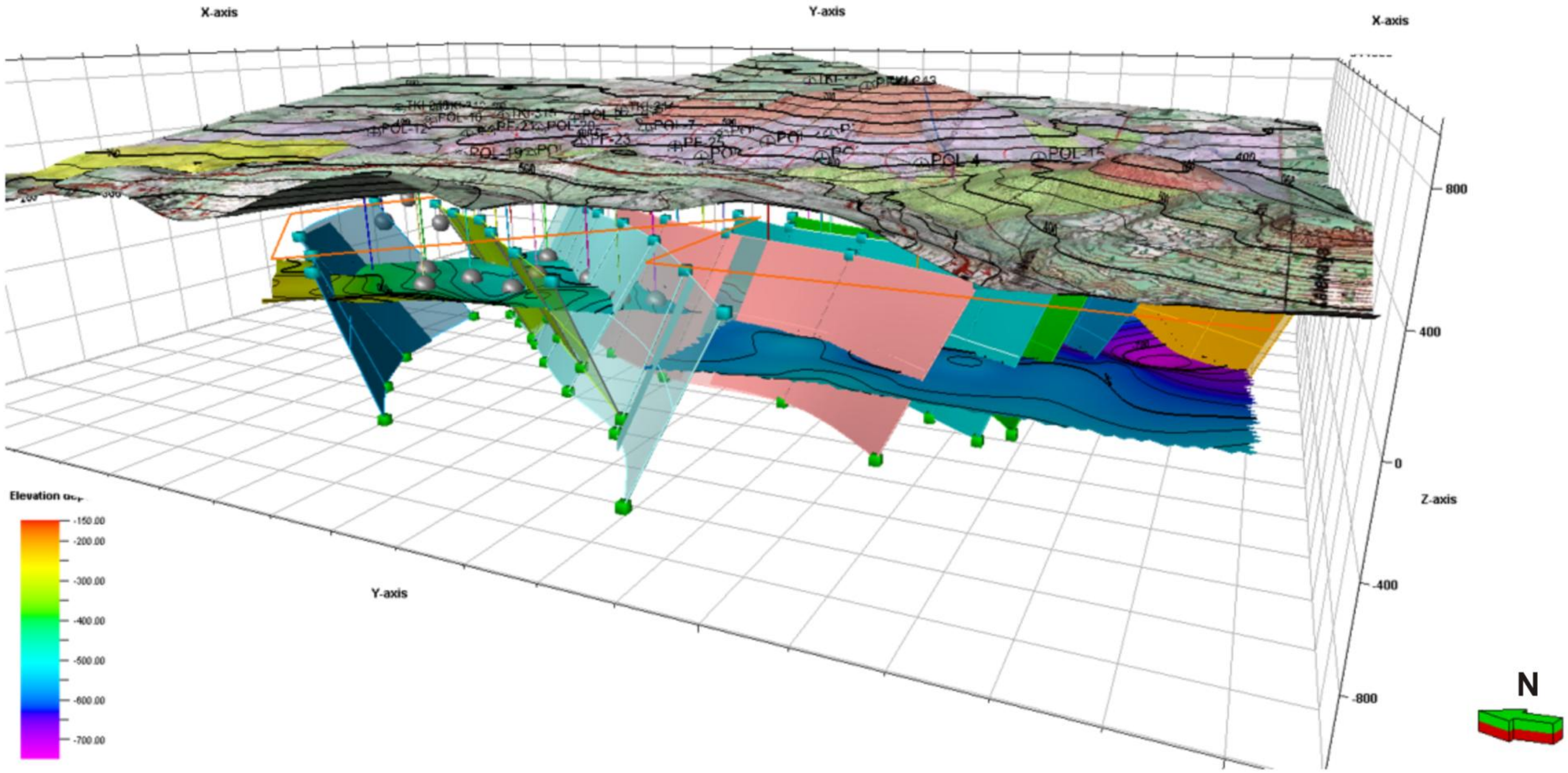

Fig. 3: Interpreted 3D model with structures of the deposit in the Menderes Mountains (from Gielisch & Gräßel, 2015).

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 25-28

ASSESSMENT OF METAL CONTAMINATION OF RIVER SEDIMENTS IN CONSERVATION AREAS: CASE STUDY OF CAPARAÓ NATIONAL PARK/BRAZIL

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Abstract. Metal contamination of sediments is a result of the increase of anthropogenic activities. Although relatively well discussed for different aquatic systems, there is a lack of studies about metal concentration in river sediments from conservation units. The main objective was to assess the metal contamination of sediments in a conservation unit in Brazil and to point out the sources of pollution. The results from this work showed that several samples had metal concentration that could cause damage to the aquatic organisms, and some samples had values that certainly would cause harmful effects to the biota (Cr: 236,5ppm; Cu: 1270ppm; Ni: 42ppm; Zn: 589ppm; Pb: 119ppm). Although the practices of fish farming and coffee plantation seem to be the responsible for the contamination, internal areas of the park also showed high concentrations. The surface runoff and atmospheric deposition may be the main mechanisms of metal input of metals to this conservation unit. The buffering zone of the park is not large enough to provide a barrier for anthropogenic influences that causes metal concentration measured in this study.

Key words: metals, sediment contamination, conservation areas, principal component analysis

1. Introduction

The main objective of this study was to assess the metal concentration in sediments from freshwater bodies in the buffer zone and inside the Caparaó National Park and set a relationship with local or regional sources and conditions.

1.1. Basic information

Sediments are an archive of past environmental conditions in sediments from water bodies (Smol, 1992) and can therefore be used to document natural or anthropogenic impacts through time (Smelzer and Swain, 1985). With the increase of anthropic activities, there has been a great interest in the scientific field for studying metal contamination of river sediments. The main sources of metals to aquatic environments are rock weathering and anthropogenic activities. The principal anthropogenic sources are the wastewater, atmospheric input, soil erosion from agriculture and industries. Natural occurring metals are associated to mineral structure and show low mobility, while the ones from anthropogenic origin show high mobility due to their weak fixation to the substrate.

Sediments contaminated with metals showing toxicological effects to benthic organisms and can affect by the trophic chain all aquatic organisms, animals and human beings and therefore limits were established (Long et al., 1995; MacDonald et al., 1996; CONAMA, 2004). To reduce or avoid the impacts it is necessary to find the sources, to obtain information about transport mechanisms and to indicate their effects over the investigated region.

1.2. Studied area

The Caparaó National Park is a conservation unit located between the Espírito Santo and Minas Gerais States, Brazil (Fig. 1). A centre and a surrounding buffer zone, both with different anthropogenic activities, build up this unit. A main part of these activities existed when the park was created. These activities include fish farming, coffee and eucalyptus plantations and pasture for livestock.

2. Materials and Methods

2.1. Sampling

To evaluate the impact of anthropogenic activities in the concentration of metals in river sediments in Caparaó National Park, 45 points were sampled (Fig. 1) in function of their position near to human activities or preserved areas. Sampling occurred at November 2013 and January 2014. The samples were retrieved with a non-metallic shovel, placed in plastic bags, transported and stored always < 4°C.

2.2. Analytical Methods

Sediments were dried at 30 °C for 24 hours. Silt-clay fractions were separated for metal analyses in accordance with NBR 7181 (ABTN, 1984). The fine fraction (<0.063 mm) was subjected to acid digestion in microwave MARS-CEM using method SW-846-3051 – US EPA (US EPA, 1998) and filtered through cellulose filter (0.45 µm).

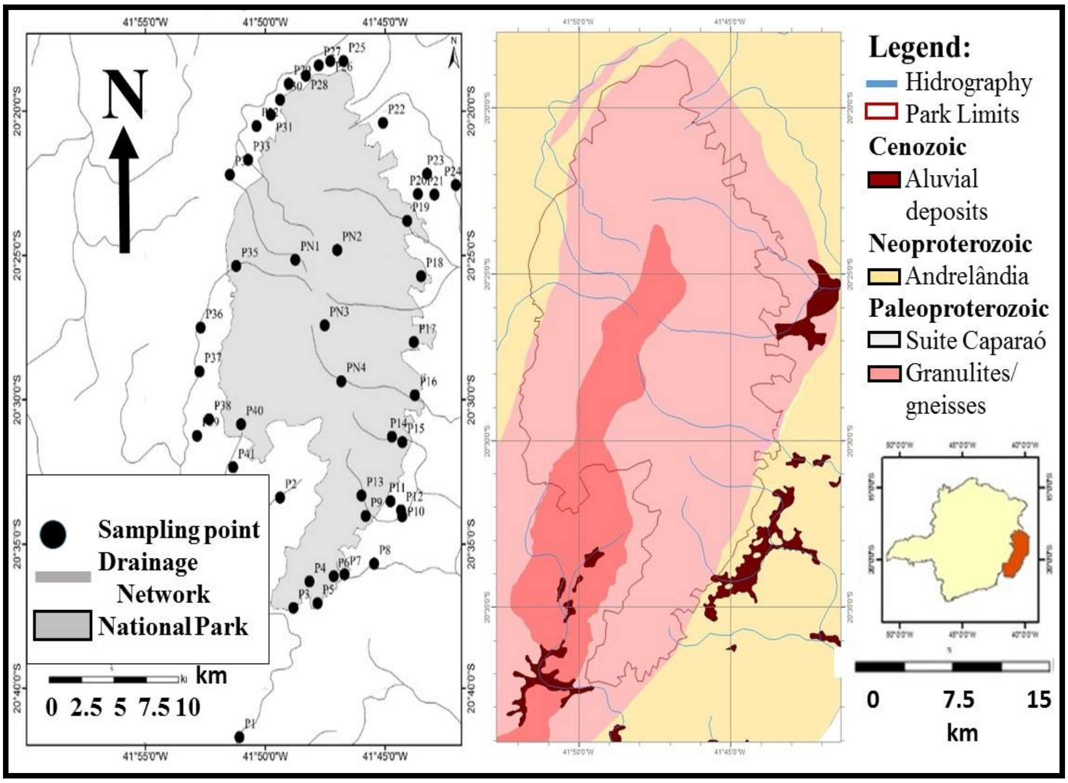

Fig. 1. Sampling map, location (left) and simplified geological map (right) of the Caparaó National Park (Horn, 2007; Rodrigues et al., 2015).

2.3. Statistical Data treatment

The results were submitted to statistical procedures including a Principal Component Analysis (PCA) to obtain information about dataset structures and correlations using "*Statistica"* software version 7.1 for Windows. This permit to define biological communities and areas or periods of the same ecological characteristics.

3. Results and Discussion

The means and standard deviations of the analysed metals by mg.kg^{-1} are shown in Table 1. The values vary for all elements in the different part of the investigated areas in function of rock chemistry, human activity and geographic location (Fig. 2 b, c, d). Some samples from the central part of the Park (higher altitude >1800m), show a significant higher concentrations of metals than expected. Al, Fe e Cd did not show variations overall samples but the other elements show variation due do local properties (Fig. 2, a, b, c, d, Table 1).

Table 1. Mean values and standard deviation of selected metal concentration from stream sediments of the Caparaó Nacional Park.

Location	Pressure	Mg	Al	Ca	Cr	Fe	Co	Cu	Cd	Ti	Mn	Ni	Zn	Ba	Pb
								mg.kg^{-1}							
East	Urban (N=1)	1520	387	899	108	96	9.5	58	0.0005	805	439	7.0	80	176	64
	Coffee/Eucalyptus (N=4)	807± 297	399± 21	1034± 106	156± 18	103± 12	8.5± 1.7	181± 96	0.0009± 0.0006	880± 128	297± 26	14.0± 4.9	125± 39	89± 24	80± 8
	Coffee (N=7)	587± 427	387± 0.00	704± 325	135± 32	96± 0.00	8.3± 2.5	333± 393	0.0005± 0.0001	797± 126	359± 150	12.3± 6.7	196± 164	109± 41	66± 15
	Fish Farming (N=2)	918± 189	432± 5	16± 4	174± 13	124± 0.02	21.1± 4.0	57± 9	0.0019± 0.0001	779± 77	777± 131	29.2± 8.1	94± 14	233± 64	70± 14
	Preserved (N=6)	731± 382	404± 23	861± 424	178± 40	106± 13	12.4± 2.9	305± 198	0.0010± 0.0007	772± 87	428± 96	22.8± 5.2	198± 83	155± 19	74± 14
West	Coffee (N=16)	283± 369	420± 23	527± 507	118± 33	118± 3	8.2± 5.0	258± 248	0.0019± 0.0001	833± 231	417± 159	23± 10	160± 119	129± 59	60± 16
	Coffee/Eucalyptus (N=1)	1148	436	21	191	124	10.0	78	0.0019	851	347	33	152	160	66
Center	Urban (N=1)	884	387	1651	223	96	8.8	489	0.0005	933	328	19	265	124	94
	Turism (N=1)	707	387	297	180	96	9.6	730	0.0005	694	253	3.1	316	35	70
	Preserved (N=3)	820± 136	387± 0.0	1145± 321	74± 4	96± 0	1.9± 0.2	155± 34	0.0005± 0.0001	540± 61	202± 30	0.23± 0.001	91± 17	79± 11	63± 1.2

The results were compared with international (Long et al., 1995; MacDonald et al., 1996) and national (CONAMA, 2004) sediment guidelines. Cu, Zn and Cr had considerable percentages of values above the usual guidelines, indicating sure effects. In the surroundings of the Caparaó National Park, the main anthropogenic activity is related to agricultural practices, indicating their contribution to the metals concentration in sediments.

The results of PCA statistical analyses are shown in Fig. 2 a, b, c, d. The first Axis explained 34,3 % of the total variability and selected the metals Al, Fe, Cd, Ni e Ba. The Axis 2 with 21.3 % of the total variability selected the parameters Cr, Cu, Zn e Pb, indicating that these metals showed similar distribution between the samples (Fig. 2a). Four distinct groups of metals are shown. Group1 (Ni, Ba, Al, Fe, Cd) and 3 (Zn, Cu, Pb) can be related to the use of pesticides at the agriculture practices. Group 2 (Co, Mn, Ti) is possible associated with fertilizers and group 4 can be linked to the use of dolomite and marble for pH correction in coffee plantations. Cr position may show direct anthropogenic activities and/or characteristics of mafic rock substrate (amphibolite, e.g.).

The plot of the single sampling locations (Fig. 2 b) shows that the points P15, P17, P33 and P37 (group 1) have highest values for the metals selected by Axis 1 and points P22, P6, P2, P4 and P13 (group 3) for the parameters selected by Axis 2. Other samples are influenced by of coffee plantation (P33, P37, P22 and P26) contaminated by Pb, Cd, Cu, Zn, Cr and Ni. Cu is used as a component in several fungicides and fertilizers explaining the behaviour of the points P6, P4 and P13 close to metals selected by Axis 2 (Zn, Cu and Pb). The high values found in preserved areas of the park, indicate atmospheric transport and deposition, possible from long distance. Low metal values at points PN2, PN3 and PN4, show that the central area of the park is well protected and preserved.

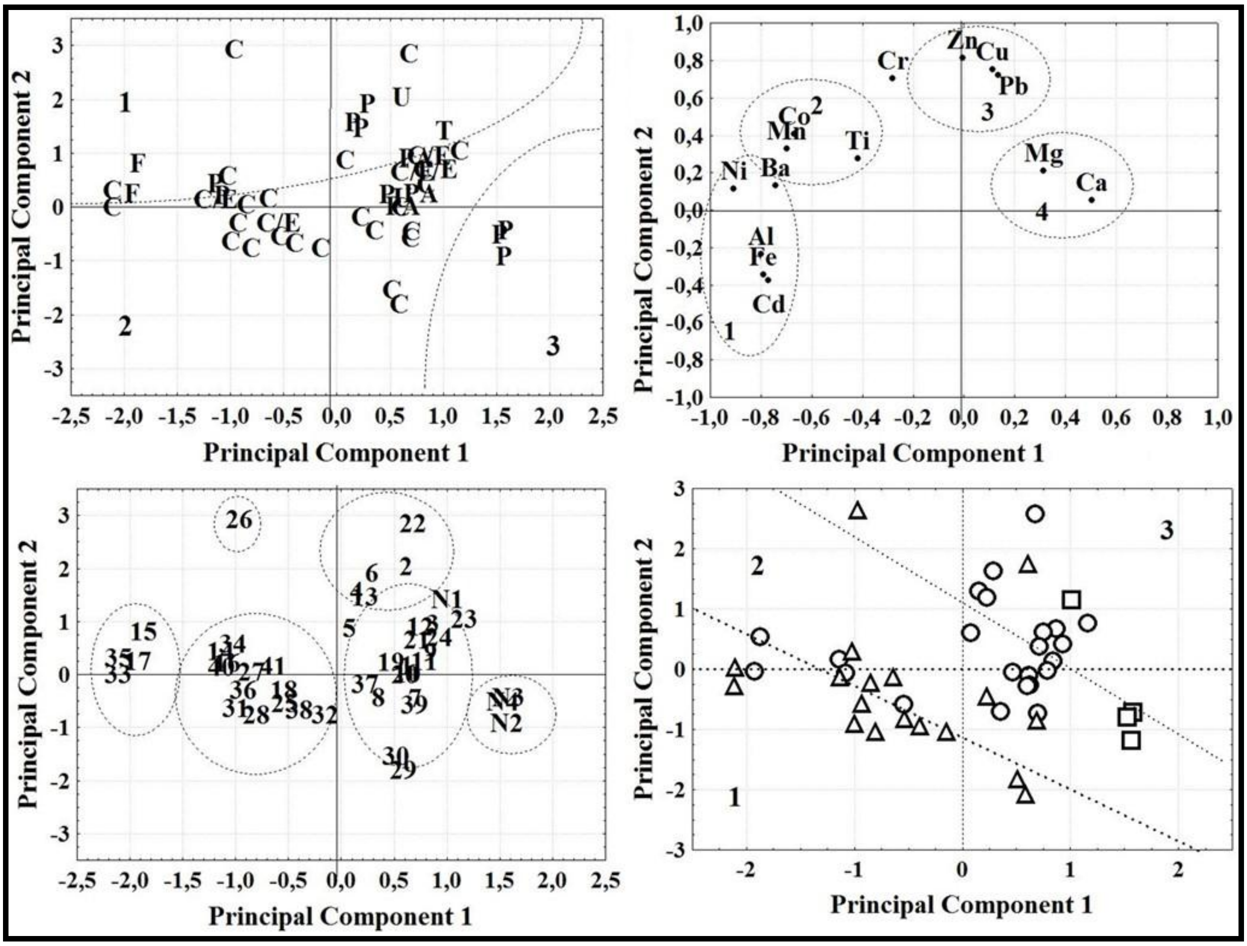

Fig. 2. Results from the Principal Component Analysis (PCA) of the samples of sediments from water bodies in the Caparaó National Park: a. for anthropogenic activity (C: coffee; C/E: coffee/eucalyptus F: fish farming; P: preserved; PA: pasture; U: urban, T: tourism); b. for elements; c. for the sampling points; c. for geographic location (triangle: western flank; quadrangle: central part; circle: east flank).

A distribution by geographic location (Fig. 2c) showed that similarity is well distributed. West side border is determined by elements of axis 1 indicating higher influence by Al, Fe, Cd, Ni and Ba. Sediments from the East side of the Park are connected to Axis 2, indicating higher concentration of Cr, Cu, Zn and Pb associated to fertilizer application during the rainy season. Points from the central part (e.g. PN1) show correlation with tourism or long distance contamination excluding direct local anthropogenic influence. Points (P6, P4, P13, P14 and P16) from the margin of the central area have significant concentrations of metals, indicating that the park's buffer zone is not large enough to minimize the anthropogenic influence. This study show that the Caparaó National Park is influenced by several possible contamination mechanism, like deposition of metals by short and long distance atmospheric deposition and surface runoff, resulting mainly from agricultural activities in the surroundings of the Park but with the possibility of contamination from eastern cities and industrial plants (Fig. 3).

4. Conclusions

The results indicated that the surface runoff and atmospheric deposition were the main mechanisms of metal input. The investigated elements are associable with different natural and anthropogenic sources, like use of fertilizer and pesticides, tourism and industry. Regional distribution of the samples shows clearly the variation of anthropogenic pressure over the park. The most sources are directly in the neighbourhood of the park, but some contamination from the inner and higher parts may be indicative for a long distance process from east with contribution from industry and the sea.

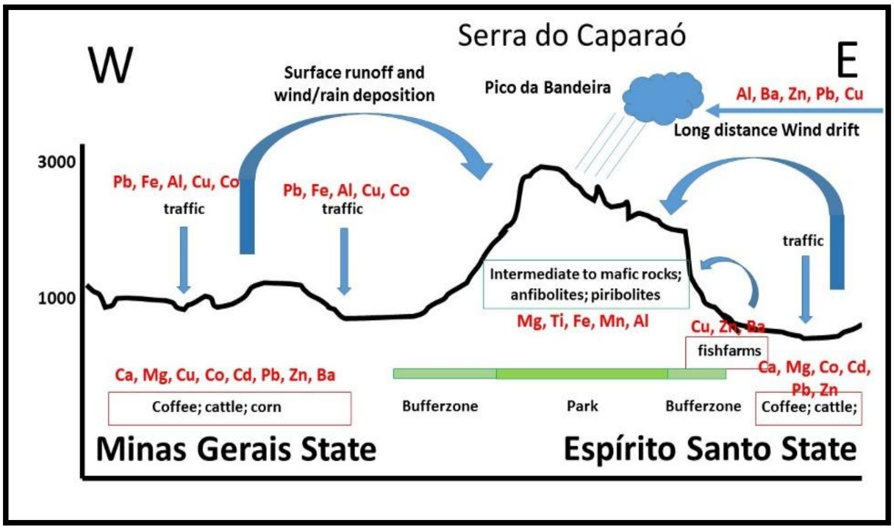

Fig. 3. Not to scale profile showing the principal contamination factors at the Caparaó National Park.

5. Acknowledgements

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THE ZIRCON/CYRTOLITE FROM GRADISTEA DE MUNTE OCCURRENCE, SEBES MTS, SOUTH CARPATHIANS, ROMANIA

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Abstract. Zircon is an important constituent mineral of Gradistea de Munte (GM) ore/rock, exceeding the quality of un accessory mineral. Mineralogical features of the GM zircon, the main ore mineral, demonstrate its long multistage crystallization. The multi-staged mineralizing process is supported by textural relationships of all rare minerals constituents of ore, where replacement of earlier minerals by later ones is common (Hirtopanu and Fairhurst, 2014). The textural relations between -Nb, -REE(Y), -Th, -U an -Zr minerals, and between the zircon and minerals of the host rock, show that zircon/cyrtolite shows many generations: the old zircon occurs as discrete grains in phlogopite and magnetite, is good crystallized, transparent, similar to igneous zircon; the zircon/cyrtolite have a texture consisting of a mixture of two microdomains, metamict and crystalline. The new zircon generations overgrown as small clean crystals, as a fringe on cyrtolite, baddeleyite, thorite, etc could be considered as resulting from hydrothermal processes.Their geochemical zoning indicates a different origin of each part of the crystal. Representative microprobe analysis of GM zircon/cyrtolite show high contents of Th, Y, Yb, Ce, Hf, U and less La, Nd, Sm, Dy and Nb. The heavy rare earth elements (HREE), specially Y, beside Th and sometimes Hf, are the predominant trace elements in GM zircon/cyrtolite, because of their similarity in ionic radius to Zr^{4+}. The baddeleyite occurrence as one of the oldest mineral, indicates that the first vein mineralizing solutions were subsaturated in silica. The absence of silica has stabilized baddeleyite and its presence has stabilized the zircon/cyrtolite.

Key words: zircon/cyrtolite, geochemical zoning, yttropyrochlore-(Y), uranpyrochlore, thorite, Y-silicates, cassiterite, baddeleyite, hydrothermal processes, Gradistea de Munte.

Geological setting

The Gradistea de Munte (GM) rare element minerals occurrence is situated on the north slope of the Sebes Mts, South Carpathians, in the upper course of the Orastie river. From a structural geological point of view the GM area belongs to Sebes-Lotru Series of the Upper Proterozoic Getic Crystalline. It is metamorphosed under amphibolite facies and in this area is represented by micaschists with kyanite and garnets, quartz-feldspar gneisses and amphibolites.The quartz-feldspar gneisses/" granites" represent here the most important petrographic type, being the host of mineralization.Their mineralogical composition is: microcline, albite, quartz, biotite and muscovite.They have a pink grey color or red because of the important presence of potassium feldspar, when the rock looks like a granite, constituted only by microcline and quartz. Sometimes, the quartz is missing, the rocks being formed only from microcline, with little albite and some accessory minerals. The mineralization is linked with this "granite". When this gneiss/granite is mineralized it becames typical dark red or brick-colored, easy to recognize on the field. The GM rare elements mineralization comprised IV bodies of microcline gneisses/ granites amongst them the body I was the best. It is of 3.5/0.5/0.05km in size and was explored by mining workings and drilling. The content of Nb+Ta established with these workings was more than 1.5 % wt, the content of REE(Y) was about of 0.5% wt (the Y content was much more than Ce). Also, the Th content (about 0.5% wt) was much more than U. The zirconium has the highest content amongst all these rare elements and its silicate mineral -zircon/cyrtolite is the most common mineral being omnipresent in high content in the ore/rock.

Mineralogy of GM occurrence

The gneiss/"granite", host of mineralization, contains magnetite and the zircon/cyrtolite as constituents minerals, while the other rare element minerals occur as accessory ones and sometimes even less.The mineralogy of GM rare element minerals is very complex (Hirtopanu & Fairhurst, 2014). The rare Nb,Ta, REE(Y), Zr, Sn, Th and U minerals belong to the following four classes: oxides, carbonates, phosphates and silicates. The oxides class is represented by 9 supergroup/groups: pyrochlore supergroup (with 2 groups, proper pyrochlore and betafite), fergusonite, columbite, euxenite, Nb-rutile, cassiterite, baddeleyite, uraninite+thorianite. The carbonates, although less widespread, are diversified, being represented by 6 minerals: bastnasite-(Ce), bastnasite-(Y), thorbastnasite, parisite-(Ce), synchysite-(Y) and synchysite-(Ce). Amongst rare earth phosphates, there are present the thorium phosphate, brabantite, and Y(REE) phosphates, represented by monazite-(Ce), xenotime-(Y) and cheralite-(Ce). In the GM occurrence the most widespread rare element minerals are the silicates, represented by Nb, LREE, Y, Th, Zr and U, and among them the Y-silicates and Th-silicates are predominant. The LREE-silicates are represented by allanite-(Ce), yttrifer allanite-(Ce) and cerite-(Ce). The Y-silicates are largely being represented by several terms: yttrialite-(Y), thalenite-(Y), rowlandite-(Y), tombarthite-(Y).

Physical and optical properties of zircon, $ZrSiO_4$/cyrtolite, $ZrSiO_4(OH)_4$

Zircon often alters chemically, especially when it contains U, Th, Y, Pb and cations of valence lower than four. It is characterized by the presence of water and by a deficiency of silica. These features provide the proof for suspecting the existence of an (OH)n:(SiOa) substitution in zircon such as that indicated for thorite. The substitution in the following manner: one OH substitutes for one O in SiO_4 tetrahedra, as Si(O,OH). The hydroxyl substitution in zircon and thorite make them prone to metamictization. So, a small substitution of (OH) for O as Si(O,OH) tetrahedra occurs in zircon and thorite, but the total water content is not higher than 5-6%. Kostyleva first (1946) established that the metamictic disintegration is the result of destruction of bonds in the lattice produced by alpha radiation from the radioactive elements present. The cyrtolite was first noted at Bedford, N.Y., by Luquer (1904) as being "a zircon which contains uranium, thorium and rare earth as well as the usual zircon constituents: zirconium, hafnium, silicon and oxygen". Since cyrtolite range from crystalline to amorphous, it is assumed that the originally possessed a definite crystalline structure which subsequently has been completely or partially destroyed. Cyrtolite, therefore, is a metamict substance. It has a weakly ionic structure which would be readily susceptible to changes into state of ionization (Norton, 1957).The GM zircon/cyrtolite forms veinlets and small nests of a few cm and bigger in the host rock. Most of the GM zircon/cyrtolite grains/aggregates range from 2-3mm to 1cm in diameter and much more. The hand specimens of samples are dark reddish brown, grey, green or blackish brown color. The zircon/cyrtolite grains are irregular in shape and boundaries. A few crystals show tetragonal symmetry, typical zircon-like prisms, most of them being flattened and distorted (Fig. 1A). The cyrtolite has microcrystalline granular to fibrous structure (Fig. 2A). Also, there were observed cauliflower-like aggregate of cyrtolite. Some crystals are roughly triangular or pseudohexagonal in outline. Their colours in thin sections are pale reddish, orange red, yellow, orange yellow (Fig. 2B), brown (Fig. 1B), greyish green, green to light green (Fig. 1A, 7B) and are sometimes colourless. A long yellow brown fibrous grain aggregate of cyrtolite with rounded shape is surrounded with small light yellow brown new zircon grains with good shape (Fig 1A). In the figure 2A and 2B one can see the zonation of the fibrous cyrtolite, which develops a cross texture in the centre of the grains (2A). In the Fig. 1B, big yellow brown microgranular aggregate of cyrtolite with low birefringence, is surrounded by another small later zircon crystals with high birefringence. No optical figure could be obtained for GM cyrtolite. The dark isotropic areas are metamict (Figs. 1B, 2B).

Association

The GM zircon/cyrtolite crystals are concentrated as small lens in magnetite, phlogopite/biotite and feldspars (albite and microcline), being associated with yttropyrochlore-(Y) (Fig. 4B), fergusonite-(Y), uranpyrochlore (Fig. 7B), monazite-(Ce), xenotime-(Y), many Y-silicates, thorite/ thorogummite (Figs. 3B, 4A), Zr-thorite, Nb-Zr-silicates, cassiterite (Fig. 6B) and has uraninite (Fig. 5B), baddeleyite thorianite and fergusonite inclusions (Fig. 5A). Some zoned clean zircons are associated with yttrocolumbite with oscillatory composition. The oldest zircon is enclosed in phlogopite and magnetite. Small grains of cyrtolite, together with apatite (Fig. 4B) and xenotime-(Y) are enclosed in Y-silicates, the latter minerals being amongst the newest formed minerals in the occurrence. Sometimes, the zircon grains grow around Y-silicates, belonging probably to another generation. Also, new grain zircons with good shape are associated with a mixture of apatite and thorium phosphate silicate (cheralite-huttonite) (sample G15BA/6). In the associations with secondary fibrous Y-REE-Ca carbonates, the zircon grains are clean and with good prismatic shape and zoned (sample G15BA/6), while in the associations with thorite /thorogummite and uranpyrochlore the cyrtolite is predominant. The old baddeleyite is surrounded by new small zircons grains as fringes (Fig. 3A), showing that the first vein mineralization solutions were subsaturated in silica. The absence of silica has stabilized baddeleyite and its presence has stabilized zircon/cyrtolite.The same as zoning of zircons/cyrtolites, the substitution relations zircon-baddeleite, demonstrates the sudden change in minor and major element contents of mineralizing solutions during rapid, late stage crystallization. Also, the other GM silicates, especially Y and Th change their composition even in the same crystal (as seen in their backscattered electronic images) and pass from one variety to another, because of the rapid change in composition of mineralizing solutions.

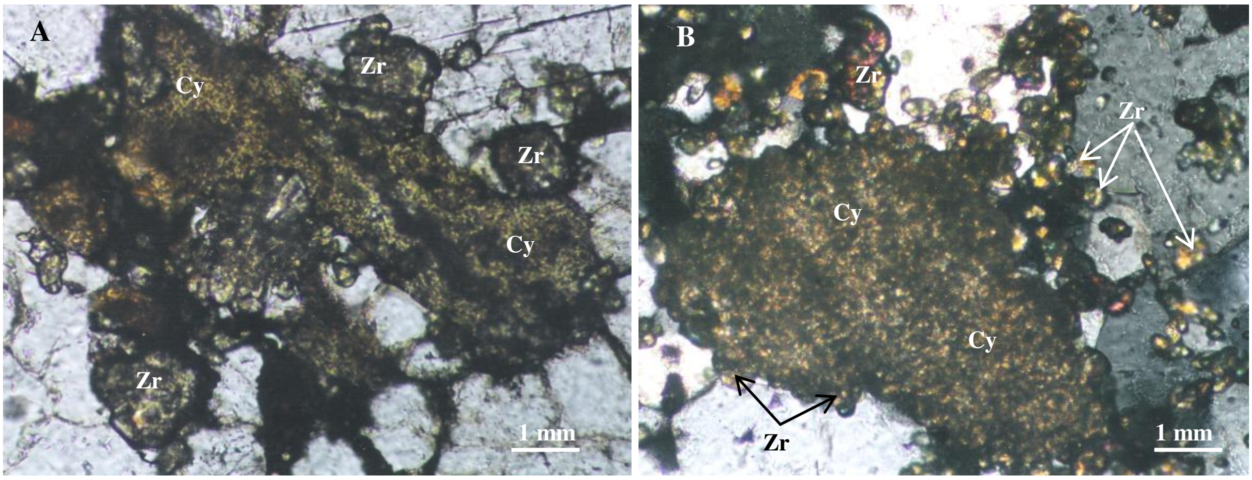

Fig. 1. Rounded, irregular shape of cyrtolite grain (Cy, big grain, yellow-green) with new zircon grains with good shape and high refringence around (Zr), TL, NII, sample G15-1/4 (A); Cyrtolite brown grain aggregate (Cy) with isotropic areas and low birefringence, and new small zircon grains (Zr) around with good shape and high birefringence, TL, N+, sample G15-4/3 (B).

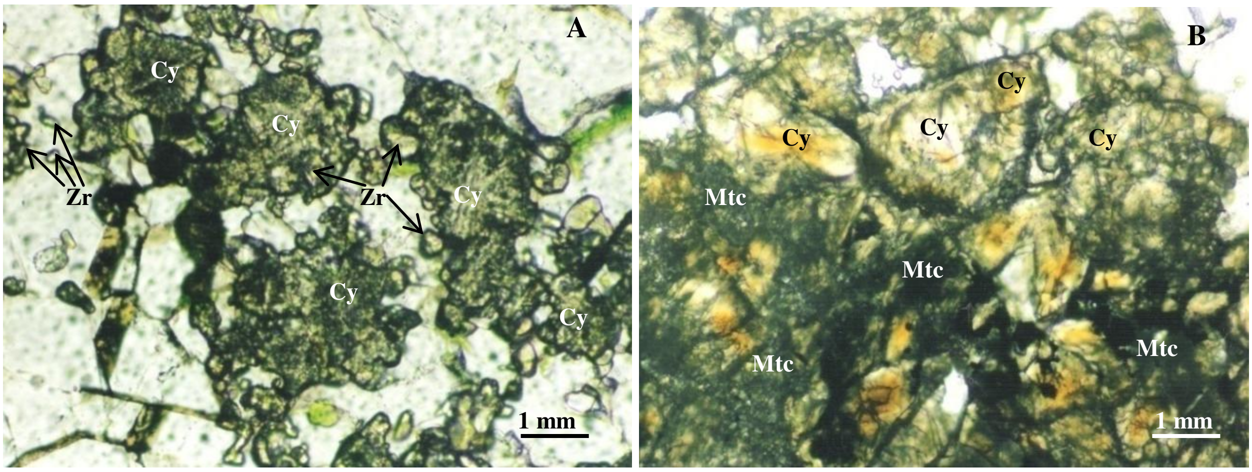

Fig. 2. Fibrous sectorial and marginal zoned of fibrous cyrtolite grains (Cy, green) showing a texture like of that of chiastolite cross, with new generation of small zircon (Zr, clean, no fibrous) grains around, TL, NII, sample G11-2 (A); Fibrous zoned marginal cyrtolite (Cy) with metamict areas (Mtc), with low birefringence TL, N+, sample GM15-1/8 (B).

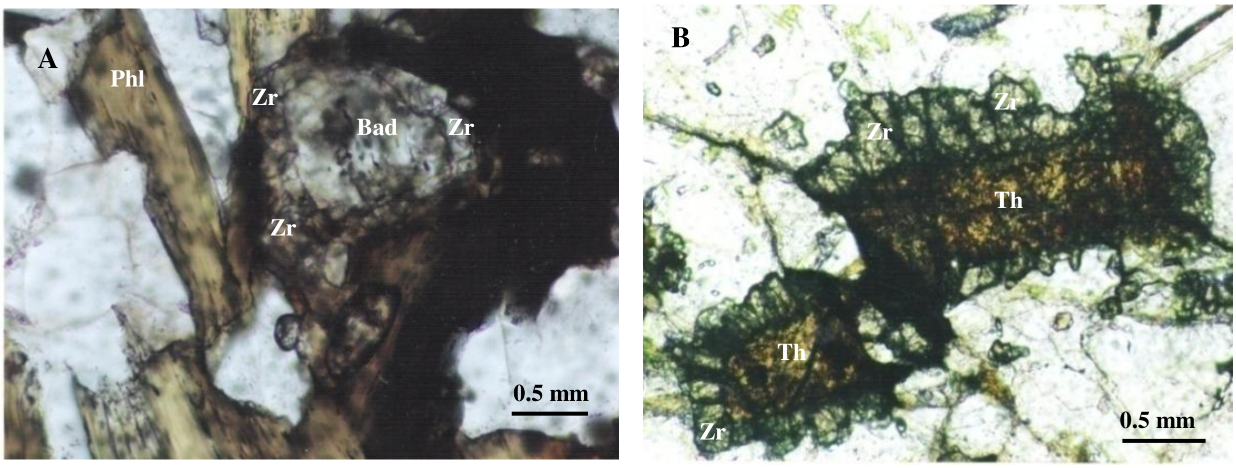

Fig. 3. Baddeleyite (Bad, big grain, centre, grayish white, clean, high refringence) with many small zircons around (Zr, grey), as a fringe, associated with phlogopite (Phl), and other new zircon grains around, NII sample G11-2-1/1 (A); Thorogummite (Th, yellow brown prismatic grain) with new small grains zircon (Zr) around, as a fringe, NII, sample G11-2/11 (B).

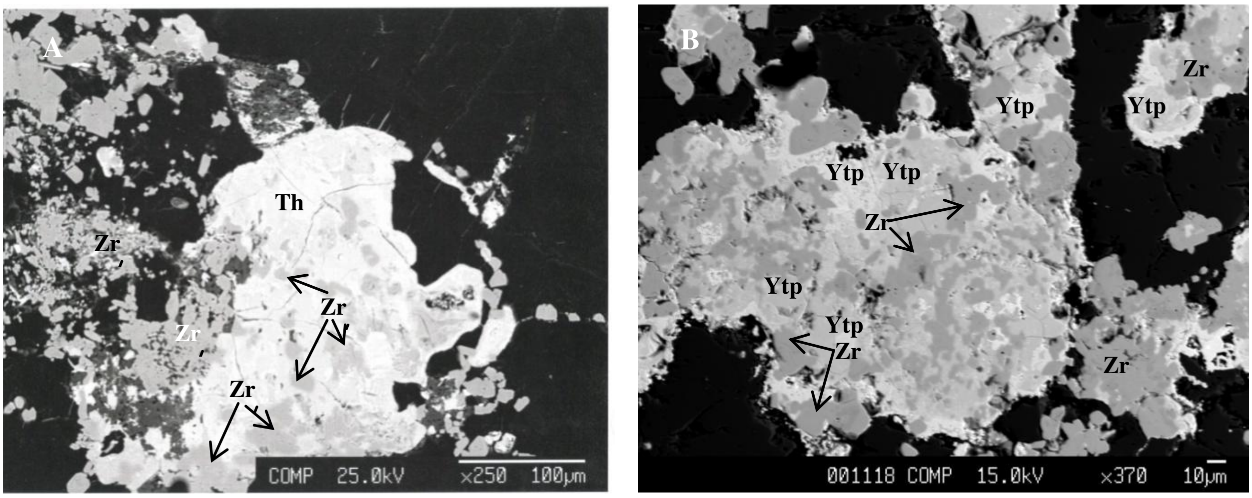

Fig. 4. BSE image of oscillatory composition in thorite (Th): white more Th, Nb, Y, Fe and white grey with more Si and Th and less Nb, Fe and Y, many zircons (Zr) inside and around, sample G11-5/2a (A); BSE image of zircons (Zr) enclosed in yttropyrochlore-(Y) (Ytp) with oscillatory composition: more Ta and less Y (white grey) and more Nb and Y (white), sample G15BA/1 (B).

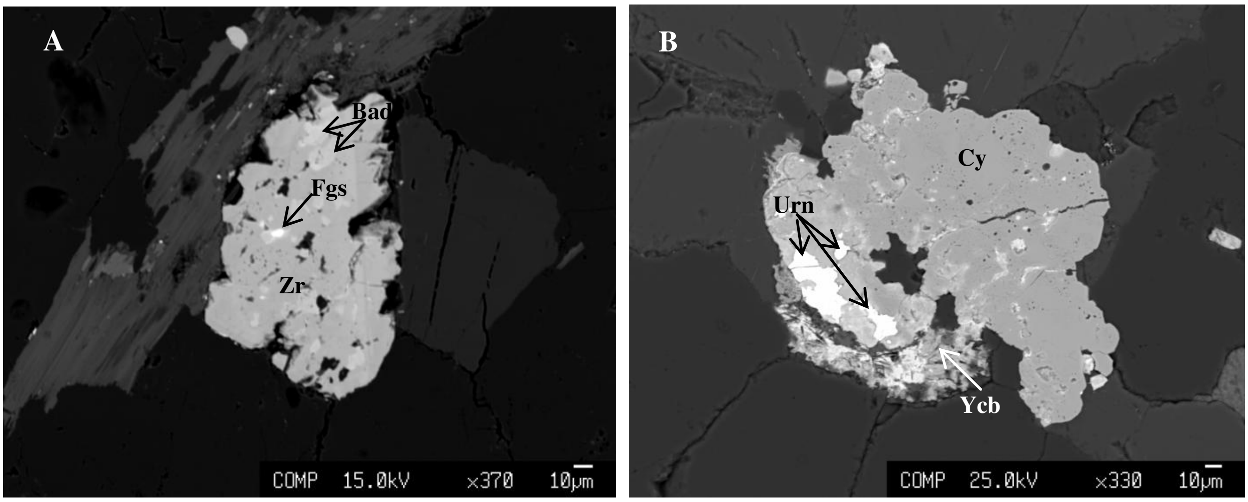

Fig. 5. BSE image of zircon/cyrtolite grain with baddeleyite (Bad, white grey, small) and fergussonite (Fgs, white bright, small) inside, sample G11-2-1(A); BSE image of zircon/cyrtolite grain with porous texture (Zr, grey), uraninite (Urn, white, enclosed in zircon), Y-carbonate (Ycb, fibrous,grey, below uraninite), sample GMC/2 (B).

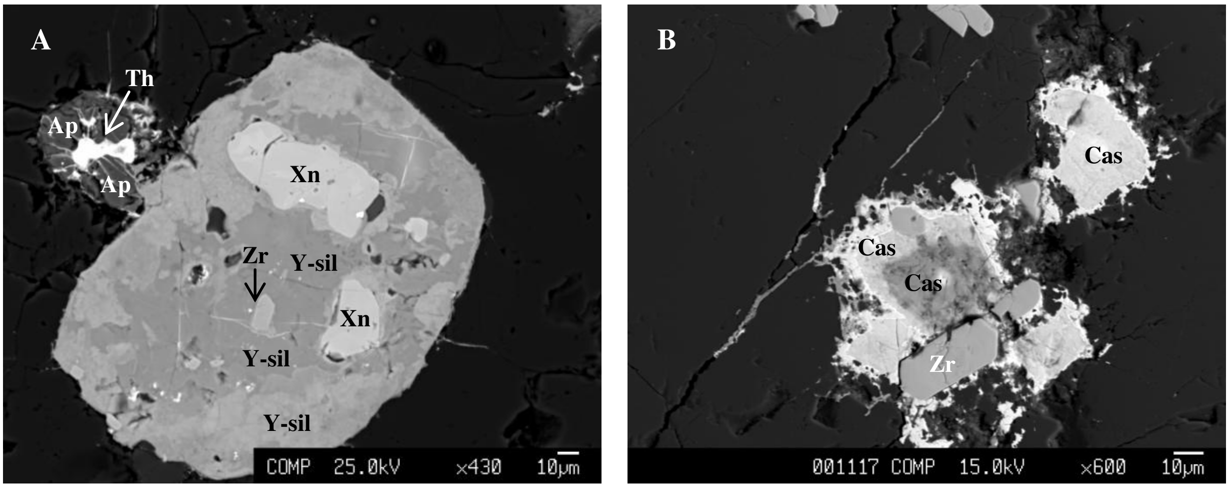

Fig. 6. BSE image of Y-silicate grain (Y-sil, prism, with oscillatory composition), with zircon (Zr) and xenotime (Xn) inside; in the corner up left thorite with zirconium (Th) with apatite (Ap) around, sample GM31/10, (A); BSE image of zoned cassiterite (white, grey white) with enclosed zircon (prismatic, grey), sample G11-4A/1, (B).

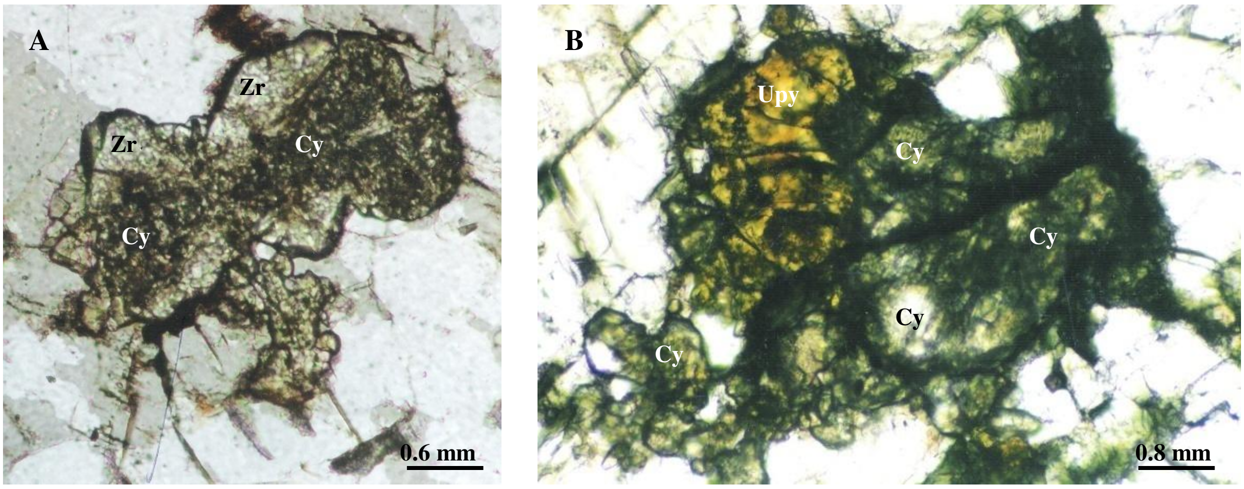

Fig 7. Zoned crystal:cyrtolite (Cy, core, high Hf), zircon (Zr, rim, clean, no Hf), sample GM31 (A); uranpyrochlore (Upy, yellow orange) associated with green radioactive cyrtolite variety (Cy), LT, NII, sample G15-1 (B).

Chemistry of GM zircon/cyrtolite

All the total percentages of microprobe analyses of GM zircon/cyrtolite are less then 100% (Table 1).This is because the water was not determined. Also, many important trace elements are below the detection limit of this method. The ability of zircon to incorporate and retain trace elements is largely determined by its crystal structure. The zircon structure has general formula *ATO₄*, in which high field strength *T*–sites cations occupy isolated tetrahedral, and *A*-site cations occupy larger eight coordinated structural sites. The zircon structure has two possible sites for cation substitution, a tetragonal (Si) and a triangular dodecahedral sites (Zr) (Speer, 1980). The predominant substitution involves replacement of

Table 1. Representative microprobe analyses of cyrtolite/zircon

Sample	G15-4/64	G15BA/4b/4	G11-2-1/6/1	G11-2-1/6a/2	G40-1b/2	G40/4/2	G40/7/1	G15BA/1a/3	G15BA/4/7
SiO_2	31.614	32.31	31.16	30.15	32.06	35.70	35.17	35.41	33.75
ZrO_2	62.268	55.94	58.16	58.17	57.62	56.87	54.68	45.05	55.95
Y_2O_3	0	2.64	2.63	2.65	2.63	2.61	0.09	2.13	2.62
B_2O_3	0	0	0	0	0	0	0.01	0.43	0
Ta_2O_5	0	0.06	0.12	0.12	0.05	0.11	2.97	0.43	0.25
La_2O_3	0	0	0	0	0	0	0.51	0.07	0
Nb_2O_5	0	0	0	0	0	0	0	6.02	0.62
P_2O_5	0.124	0.58	0.05	0.04	0	0	0.07	0	0.63
Ce_2O_3	0	0.06	0.04	0.07	0.04	0.03	3.05	0.79	0.10
Pr_2O_3	0	0.09	0	0	0	0.01	0.20	0	0
Nd_2O_3	0.024	0	0.03	0	0.03	0.01	0.79	0.28	0.07
Sm_2O_3	0	0.01	0	0	0	0	0.15	0.04	0.02
Eu_2O_3	0	0	0	0	0	0	0.09	0,01	0
Gd_2O_3	0.022	0	0	0.04	0	0	0.18	0.04	0.04
Dy_2O_3	0.001	0.12	0.04	0.01	0	0	0	0.08	0.04
Yb_2O_3	0.097	0.14	0.22	0.20	0.05	0.17	0.10	0.35	0.38
Tb_2O_3	0	0.03	0.01	0.04	0.04	0.02	0	0	0
Ho_2O_3	0	0	0	0	0	0	0	0	0
Er_2O_3	0	0	0	0	0	0	0	0	0
Tm_2O_3	0	0.03	0.04	0.05	0.02	0.03	0	0	0.04
Lu_2O_3	0	0.05	0.02	0.04	0	0.06	0	0.05	0
PbO	0	0.01	0.02	0	0.03	0.01	0.14	0.02	0
ThO_2	0	0.10	0.06	0.15	0	0.01	0	0.30	0.17
UO_2	0.010	0.05	0.11	0.34	0.23	0.18	0.01	0.51	0.46
HfO_2	0	0.09	0.03	0.20	0.10	0.11	0.08	0.40	0.16
F	0	0.15	0.12	0	0.08	0	0.01	0	0.03
Na_2O	0.071	0	0	0	0	0	0	0	0
K_2O	0	0.02	0	0	0.01	0.01	0.06	0.02	0.01
MgO	0.160	0.03	0.03	0	0	0	0	0	0
Cr_2O3	0	0	0	0	0.02	0	0.02	0.02	0
Al_2O_3	0.016	0.14	0	0.05	0	0	0.35	0	0.02
CaO	0.271	0.04	0	0	0	0	0.02	0.01	0.09
SrO	0	0	0	0	0	0	0	0	0
BaO	0	0	0.01	0.02	0	0	0.06	0.10	0.02
FeO	0	0.08	0.08	0.22	0.02	0.08	0.13	0.85	0.13
MnO	0.002	0.00	0.01	0.01	0	0	0.03	0.07	0.01
TiO_2	0.098	0.37	0	0	0.01	0.01	0.22	0.19	0.04
Total	94.780	95.38	95.19	96.71	94.90	95.91	94.25	94.17	95.63

Zr in the larger triangular dodecahedral sites. Zircon type compounds display variable degrees of solid solution among end members. Zircon/cyrtolite is isostructural with thorite/ thorogummite with which it forms a complete series. The ZrO_2 content in some GM thorite/thorogummite is around 15%wt, confirming an extent of solid solution between $ZrSiO_4$ and $ThSiO_4$. In some cyrtolites the ThO_2 have sometimes high values (5%wt), and it could be named Th-cyrtolite, $(Th,Zr)(SiO_4)(OH)_4$. Because the zircon is isostructural with xenotime, the Y and P will preferential enter in its structure in the agreement with the substitution: $Zr^{4+}+Si^{4+}\leftrightarrow Y^{3+}+P^{5+}$. The GM zircon/cyrtolite has the P_2O_5 content around 0-0.63 (Table 1), and Y_2O_3 has the highest contents, around 2.62%wt (Table 1). The Yb_2O_3 is always present, but with smaller contents than Y_2O_3. Another possible substitution in zircon is: $2Zr^{4+}\rightarrow (NbTa)^{5+} + REE^{3+}$. The substitution of Zr by REE-Nb in GM zircon occurs rarely, because the big difference between their ionic radius and the Nb-REE were finally concentrated in fergusonite. The incorporation of U and Th into zircon is primarly governed by coupling the thorite substitution with the coffinite substitution $U^{4+}+Th^{4+}\leftrightarrow 2Zr^{4+}$ (Mihoko et al, 2010). The HfO_2 has a large content variation, between 0-6.50%wt. The high content of Hf, has the cyrtolite from Fig 7A, with representative microprobe analysis: SiO_2=28.30, FeO=0.22, ZrO_2=64.96, HfO_2=6.50%wt, that could be a new variety of cyrtolite, hafnium cyrtolite $(Hf,Zr)(SiO_4)(OH)_4$. Because the cyrtolite grains have uraninite inclusions (Fig 5B), it is difficult to established for GM cyrtolite if its alpha emitters (Th, U and possible Sm^{152}) have been placed in the structure during the original crystallization of the mineral, or all the alpha emitters have been introduced secondarily. In this last case, metamictization might have occurred, but the degree of metamictisation would not represent the true age of the mineral. At least some of the U- as uraninite and Th- as thorianite from GM cyrtolite is secondary, forming veinlets and nests inside it (Fig 5B). The ThO_2 contents of zircon/cyrtolite in Table 1, have been placed in the structure during the original crystallization of the mineral. The variations of trace elements in zircons cause its zoning. In fig 7A the core of crystal is enriched in Th and U, transforming it into brown blackish cyrtolite, while the rims are transparent, devoid of visible imperfections of structure and no inclusions. Also, the zircon zoning reflects the sudden change of trace elements contents during rapid, late stage crystallization, being a geochemical zoning.

Conclusions

Zirconium, together with Nb and REE are high-field-strength elements (HFSE), i.e., their ions are relatively small and highly charged and they are considered to be among the most immobile elements in aqueous solutions. However, at least locally mobility of Zr has been reported in a variety of geological settings. Many studies have suggested that hydrothermal transport and deposition were the primary processes in creating some zirconium ores. The GM zircon was affected by metamict disintegration, consisting in progressive hydration and destruction of the crystalline network, probably due to the effect of the self-radioactive damage. The cyrtolite is surrounded by a fringe of a new zircon generation. This new zircon generation could be considered as resulting from hydrothermal overgrowth processes. Recognizing the hydrothermal nature of zircon is important for reconstructing ore-forming processes by U-Pb dating. The GM zircon/cyrtolite, especially the old generation, is not very good crystallized, presenting an intermediary degradation degree to a metamictic state, because of the presence of the radioactive element (U and Th) contents in its composition. Thus, frequently its structure consists of a mixture of the two microdomains: metamictic and crystalline. It was proved that the metamict zircon (with a serious degradation of crystalline structure) has a higher solubility than the zircon with a good structural network, that explains its presence in the hydrothermal later paragensis. The method of X-ray fluorescence and X-ray diffraction procedures are necessary to establish that the GM zircon/cyrtolite can be used for age determinations.

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ALLUVIAL GOLD IN THE SOUTH CARPATHIANS: ANALYTICAL DATA ON SOME NEW OCCURRENCES

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Abstract: Almost all the rivers crossing North-South the central South Carpathians (both on the southern and northern slope) contain alluvial material carrying gold either as (sometimes) mineable occurrences (e.g., Pianu in the Sebeş Mts., Cibin-Olt in the Făgăraş Mts., Râureni in the Vâlcea county) or as random presence of gold together with dominant heavy minerals. The source of gold was identified mostly in the western part of the area (shear zone related ores) whereas the gold source in the eastern part remains largely unknown, probably disseminated grains in rocks such as amphibolites, ultrabasites etc. The newly reported gold occurrences in the area between Topolog and Dâmboviţa rivers belong to the latter source type. Anyhow, high fineness of gold is a characteristic feature of all the alluvial gold occurrences in the area.

Keywords: alluvial gold, magnetite, rutile, micro-inclusions, X-Ray Fluorescence, micro-PIXE, Argeş county

Introduction

Primary (mostly shear zone related) gold ores as well as the thereto related alluvial gold occurrences generally show different fineness of gold. The shear zone related gold ores are hosted especially by the medium grade metamorphic rocks of the so-called Getic Realm, largely developed in the Sebeş, Căpăţâna, Leaota and Făgăraş Mts. A general view about the gold distribution in the central-eastern part of the South Carpathians has been given by Udubaşa and Udubaşa (2002). Some of the representative shear zone-related gold ores (Valea lui Stan/Brezoi and Costeşti/Horezu in the Căpăţâna Mts. and Jidoştita in the Mehedinţi Mts.) have been thoroughly investigated by Udubaşa (2004). The Valea lui Stan ore deposit was the only cost-effective gold mine in the area, operated by underground workings by the former “Mica” Society, mainly before the 2nd World War. Gold contents up to 100 g/t have been locally reported. However, the small reserves and discontinuities in the development of the ore bodies led to the closing of mines. Exploration undetaken in the 1970s did not succeed to discover new ore bodies (Udubaşa & Hann, 1988).

The geochemical signature of the two most important shear zone-related ore occurrences are given in Table 1.

Table 1. Geochemical signature of the Valea lui Stan and Costeşti ores.

Occurrence	Major elements	Minor elements
Valea lui Stan	Au-As-Cu	Cr-Ni-Pb-Zn
Costesti	Au-As-Bi	Cr-Ni-Se-Cd

Source: Udubaşa (2004)

Alluvial/detrital gold

There are relatively numerous gold ± heavy minerals occurrences in the central-eastern South Carpathians and their geochemical signature is quite different, the common elements being Au and Fe-Ti-Zr. As concerns the gold relative abundance, there is, however, a significant difference among the occurrences; some are gold-dominated, some other are mostly oxide/silicate dominated (Table 2) and this is related to the sources of minerals in the catchment areas of the rivers hosting the occurrences. The source of gold for some of the occurrences (e.g., Râureni, Cremenari on the Olt river) is related to the primary gold ores, i.e. the Valea lui Stan ores. The Pianu occurrence seems to have however multiple sources (shear zones, lineaments with kyanite-rutile/ilmenite-magnetite-gold in micaschists, ultrabasites, ortoamphibolites) as suggested also by the variable fineness of gold. Tămaş-Bădescu (2010) postulated in addition the redeposition of gold by Cretaceous sedimentary rocks covering the metamorphics of the Sebeş Mts. For the other Au-dominated occurrences, the primary source is seen to be the shear zone gold deposit at Valea lui Stan (along the Lotru river, tributary of the Olt river).

Table 2. Gold and heavy minerals occurrences in the South Carpathians.

Locality	Association	Host rocks/ formations	Location/ river	Distance from the limit of the cristalline schists[5] (km)
A. Gold-dominated occurrences[1]				
Pianu Valley	Au, Ti, Zr, Pt[4]	Cretaceous sedim. rocks, alluvia	Sebeş Mts. (N)	0
Cibin, Olt	Au, Ti, Zr, Fe	Alluvia, Quaternary	Făgăraş Mts.	0
Râureni	Au, Fe, Ti, Zr	Alluvia, Quaternary	Olt river	5
Cremenari	Au, Fe, Ti, Zr	Alluvia, Quaternary	Olt river	9
B. Heavy minerals ± gold occurrences[2]				
Tigveni	Ti, Zr, REE, (Au)	Dacian - Pontian	Topolog	8
Merişani	Ti, Zr, Au, Fe, V	Pliocene - Quaternary	Argeş	30
Mâzgana / Vultureşti	Ti, Zr, Au, Fe, V, Hg	Pliocene - Quaternary	Argeşel	27
Onceşti	Ti, Zr, Au, Fe, V	Pliocene - Quaternary	Dâmboviţa	15
Gemenea	Ti, Zr, Au, V, Fe	Pliocene - Quaternary	Dâmboviţa	15
C. New occurrences[3]				
Cicăneşti	Au, Ti	Alluvia	Argeş	4
Mioarele	Au, Fe, Ti, Zr	Alluvia	Argeşel	3
Boteni	Au, Fe, Ti, Zr	Alluvia	Argeşel	7

[1,2] Included in the Map of Mineral Resources of Romania, scale 1:1.000.000 (Borcoş et al., 1984).
[3] Newly reported.
[4] The presence of Pt at Pianu (first reported in 1855) has been mentioned by Udubaşa et al. (2004).
[5] Distances from the limit of the cristalline schists to the occurrences have been estimated in order to evaluate how far were transported the heavy minerals to their deposition and/or concentration sites. Such distances correspond in a way to the "negative metallotects" of Nicolini (1970).

The remaining occurrences (B and C in the Table 2) should be regarded as having disseminated sources of gold and heavy minerals. Nevertheless, they could hardly be considered as occurrences of economic value as the technological approaches did not show positive results, yet. Press release mentioned only an artisanal recovery of gold at Vultureşti/Mâzgana: "Mina Mâzgana", organized in 1980 by Eng. Gheorghe I. Ștefan.

The new occurrences

Recently (2014), gold nuggets or grains were found by "local seekers" in the area of Cicăneşti village (approx 15 km NW of Curtea de Argeş) and Argeş river (near Curtea de Argeş, where Cicăneşti stream joins Argeş). These samples have been collected by Acad. Gh. Păun and given to the specialists of the Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH). An interesting aspect is that the gold nuggets were always found together with approximately rhomboidal black-grey small grains (dark coloured "stones") (Figure 1).

Other gold grains were also found by "local seekers" on Topolog and Argeşel rivers (Boteni-Mioarele area) and given to the specialists of IFIN-HH.

The analytical procedures

The gold samples/grains were analysed by XRF and micro-PIXE methods.

The XRF (X-Ray Fluorescence) measurements were performed using a X-MET-TX3000 portable spectrometer; the exciting X-ray beam being generated by a 40 kV – Rh anode tube. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the Kα line of Mn (5.89 keV). The measurement spot size is about 30 mm^2. The spectrometer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage (Cristea-Stan et al., 2012a). Accuracy of the method varies between ± 2% for elements more than 10% concentration, ± 10% for elements between 1 and 10% concentration and ± 25% for elements less than 1% concentration.

For micro-PIXE (micro Proton Induced X-ray Emission) at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy, with a 2 MeV proton micro-beam (6 µm x 6 µm beam area, maximum beam current ~1000 pA) was used (Cristea-Stan et al., 2012b). The characteristic X-rays were measured with a Canberra HPGe detector (180 eV FWHM at 5.9 keV). An Al funny filter (80 µm thick

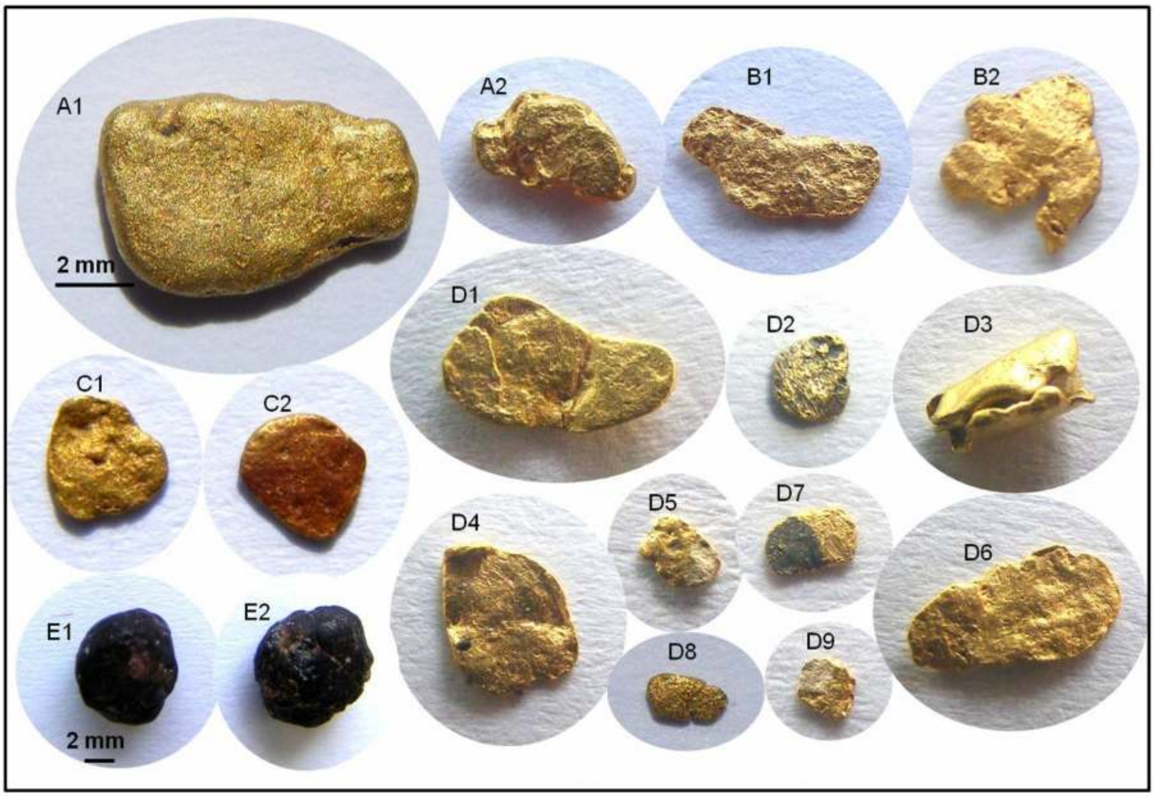

Fig. 1. Alluvial gold grains (nuggets) from Argeş (A1-A2), Cicăneşti (B1-B2), Argeşel (C1-C2) and Topolog rivers (D1-D9) and the polygonal dark colored grains from Cicăneşti (E1-E2).

and 8% hole) in front of the X-ray detector was used to reduce the intensity of the peaks in the low spectral region (below 4 keV). 2 mm x 2 mm maps and point spectra were acquired.

Results

The X-Ray Fluorescence analyses performed on the gold grains gave the compositions presented in Tables 3 and 4 and Figures 2 and 3.

Table 3. Elemental composition of alluvial gold from Curtea de Argeş area (Argeş and Cicăneşti).

Sample	Au%	Ag%	Cu%	Fe%	Pb%	Au fineness (‰)
1. Argeş 1 – "big" nugget	97.7	4.4	0.03	0.6	0.1	957
2. Argeş 2	97.4	1.3	0.03	1.1	0.2	987
3. Cicăneşti 1	92	7.2	0.05	0.7	0.1	927
4. Cicăneşti 2	98.6	0.6	0.03	0.7	0.1	994

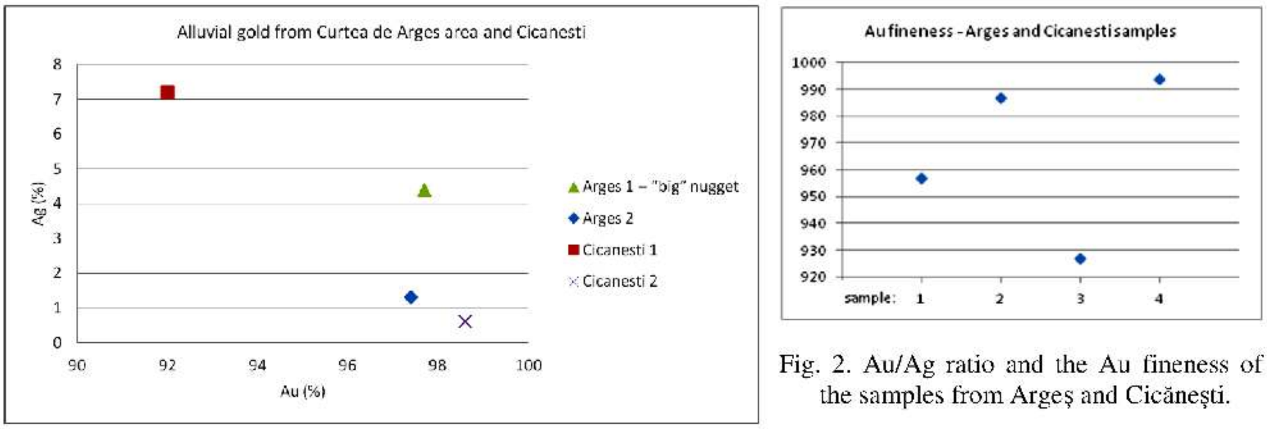

Fig. 2. Au/Ag ratio and the Au fineness of the samples from Argeş and Cicăneşti.

The samples from Argeş and Cicăneşti areas show high Au content and high fineness respectively (Table 3 and Fig. 2), except one sample from Cicăneşti. Traces of Cu, Fe and Pb have been detected.

Table 4. Elemental composition of alluvial gold from Argeşel and Topolog rivers (Boteni-Mioarele area)

Sample	Au%	Ag%	Cu%	Fe%	Pb%	Au fineness (‰)
1. Argeşel 1 ("yellow" colour)	97.2	1	0.1	1.5	n.d	990
2. Argeşel 2 ("red" colour)	90.4	2.1	0.1	7.1	0.1	977
3. Topolog 1	94.2	4.9	0.03	0.8	n.d	951
4. Topolog 2	96.2	2.6	n.d	0.8	n.d	974
5. Topolog 3	79.2	19.9	0.1	0.7	n.d	799
6. Topolog 4	93.7	3	0.03	0.6	2.6	969
7. Topolog 5	97.5	1.4	0.03	0.8	n.d	986
8. Topolog 6	93.7	5.2	n.d	0.6	n.d	947
9. Topolog 7	97.3	1.4	0.3	1	n.d	986
10. Topolog 8	92.9	5.4	0.2	1.1	n.d	945
11. Topolog 9	95.7	3	0.1	0.9	0.2	970

n.d. – not detected

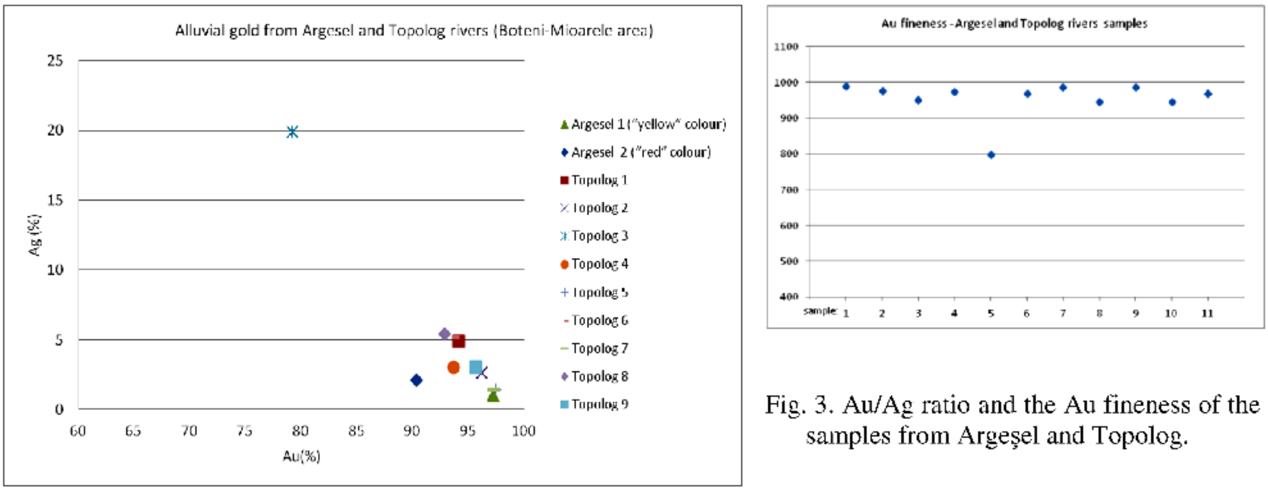

Fig. 3. Au/Ag ratio and the Au fineness of the samples from Argeşel and Topolog.

The samples from Argeşel and Topolog area show also a high Au content and fineness respectively (Table 4 and Fig. 3), except one sample from Topolog river area. This sample has higher Ag content than the similar sample from Cicăneşti, reaching almost 20% Ag. Traces of Cu, Fe and Pb have been detected in some of the samples.

In the samples from Cicăneşti, the rounded grains with polygonal outlines found together with the gold grains consist of magnetite with some Mn content (XRF data: 96.5% Fe and 3.2% Mn, with traces of Cu and Au) as well as rutile (XRF data: 97.2% Ti, 2.7% Fe, with traces of Cu and Au) (Fig. 1B).

A sample from the Topolog river has been analyzed by micro-PIXE and shows a quite homogeneous distribution of Fe and Sb and localized Pb contents (Fig. 4). Further analyses are needed in order to solve this unexpected results. The presence of magnetite and rutile composite grains reminds the kyanite-rutile-gold lineaments in the Sebeş Mts., which remain undiscovered, yet, in the Cicăneşti/Argeş area, however, highly probable.

Discussions and conclusions

Gold analyses have been performed by using both XRF and micro-PIXE methods on several new occurrences in the area between Topolog and Dâmboviţa rivers, on the southern slope of the South Carpathians. The results of analyses show the same high gold fineness as in the other gold occurrences in the area. In some places, rounded grains with weakly developed polygonal outlines have been identified in association with gold, whose compositions indicate the presence of magnetite and rutile. They are probably reminiscent of a liniament containing kyanite-rutile-ilmenite-magnetite and gold in the Sebeş Mts. Such a still undiscovered lineament could be presumed to exist also in the Făgăraş, Iezer and Leaota Mts., as a supplementary source of gold.

The gold provenance is still unknown in many occurrences of alluvial gold - heavy minerals in the South Carpathians (excepting, however, the Sebeş and Căpăţâna Mts.). Nevertheless, within the area covered by metamorphic formations, the rocks belonging to the Getic Realm contain gold in many places. In contrast, the metamorphic formations of the Danubian Realm seem to be devoid of gold or have very scarce primary ores or disseminated gold.

The distance from the boundary of the metamorphic rocks (presumed to be the source of the gold and heavy minerals) and the gold occurrences in alluvial material is quite different. The occurrences located within or near the areas consisting of metamorphic rocks show more abundant gold, which was occasionally recovered at industrial scale (Pianu, Cibin, Râureni). The gold occurrences situated far away from the boundary metamorphics/sedimentary cover are poorer in gold. The effect of "negative metallotects" (Nicolini, 1970) may act in parallel to the scarcity of gold sources.

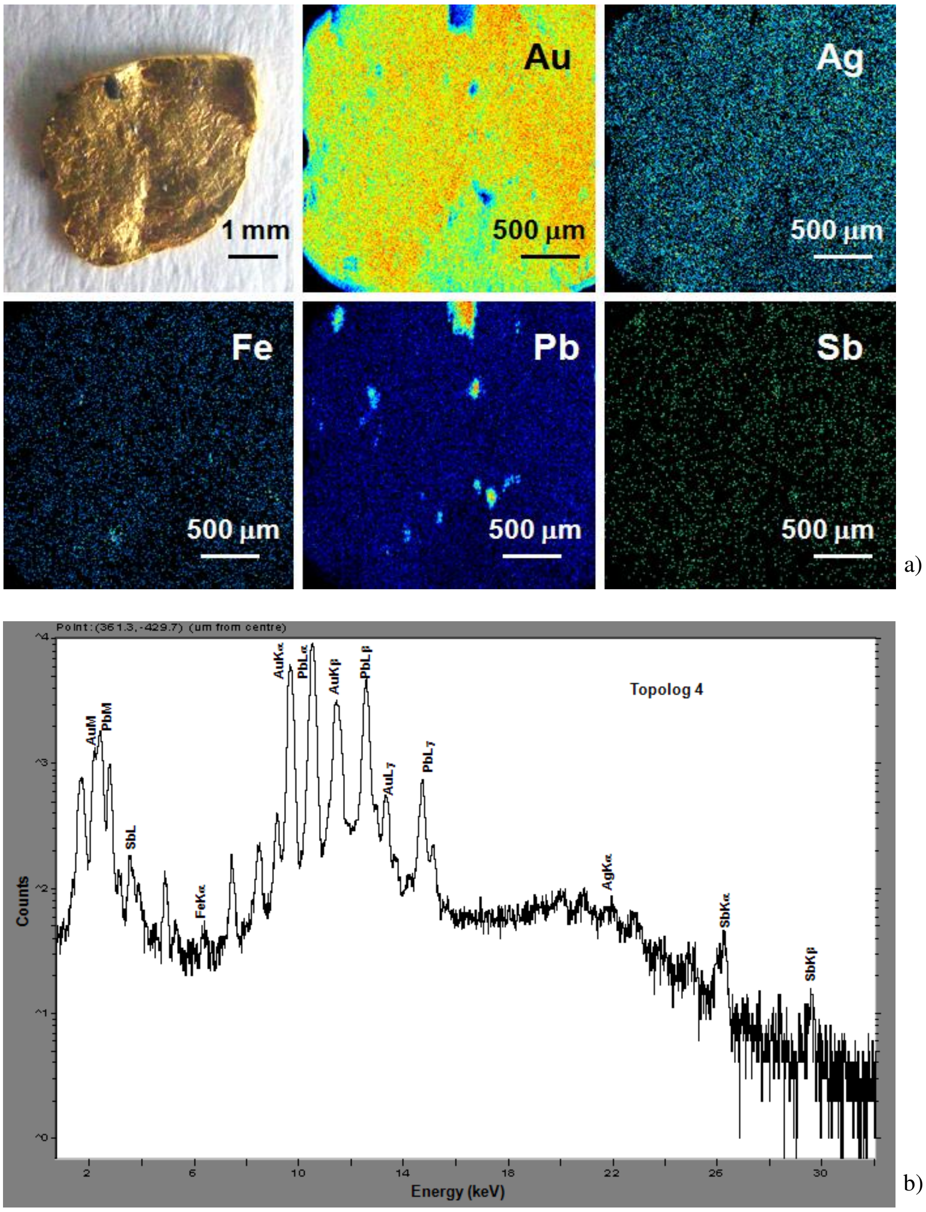

Fig. 4. Topolog 4 sample - micro-PIXE elemental maps (a) and point spectrum - Pb (b).

Comparison of the analyses presented here (high fineness of gold, with few exceptions) with the same type of analyses of gold from the hydrothermal deposits in the Metaliferi Mts. (highly variable fineness) shows the higher presence of Ag, Cu and other impurities in the hydrothermal gold (e.g., Cristea-Stan et al., 2012; Popescu et al., 2015).

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POSSIBLE USE OF Si-PHYTOLITHS IN METAL ANOMALY PROSPECTION. EXAMPLE FROM RIACHO DOS MACHADO REGION, CERRADO, MINAS GERAIS, BRAZIL.

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Abstract: This work investigates the distribution of selected heavy elements in soil samples and Si-Phytoliths from plants. The aim is to verify if metal contents are indicative for metal anomalies in the soil. Samples were collected in profiles near the Riacho dos Machados Goldmine. Granitic-gneissic rocks, in tectonized contact with the overlaying rocks, form the basis of the investigated region, which belongs to the Rio dos Machados Group of the Espinhaço Super Group. The whole rock substrate is covered by lateritic to arenitic soils with different exposure depths. Metal-rich fluid invaded this unit, forming metal anomalies, forming Zn-Pb-Au deposits, like that of Salobre-Porteirinha. After appropriate preparation, the samples were analyzed by ICP-OES (Si-Phytoliths) and XRF (soil). Anomalies in the investigated profile are indicated by high metal contents in the Si-Phytoliths of the selected species. Using different species, the metal concentration at different depths can be determined.

Key words: Si-Phytoliths; prospection; metals; Cerrado; plants

1. Introduction

Prospecting new mineral occurrences is a very expensive and extensive process. Many direct and indirect methods are in use. We will show here a new possibility of biological prospection using native plants to obtain information about metal concentration in subsoil by surface - soil evaluation of metal leaching during weathering. The transport and the enrichment processes in plants s.l. is described by a lot of authors such as Raven (1993), Turnau (2007) and Wuana and Okieimen (2011).

1.1. Basic data

Plants use the ions concentrated in soil to obtain their nutrients. In this process, all ions present are brought into the plant, heavy metals included. The excess of this elements, which are dangerous for the organism, is refused by the plant, which fixes them in Phytoliths of opal or oxalate composition. These fixed elements are trapped and permanently retained from the bio circuit.

These concentrations remain nearly uninfluenced by the changes of the external factors, like climatic changes, rainfall etc., in opposite compartment to the organic parts of plants that show changes in their metabolism (Fig. 1).

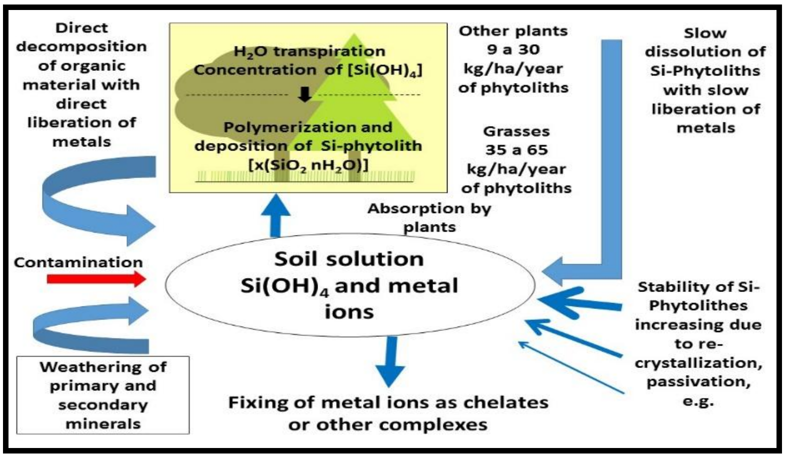

Fig. 1. Schematic flux diagram for Si-Phytoliths formation and process of trapping and stabilization of the metal ions. This organogram is the compilation of own results and data from literature (e.g., Iler et al., 1997; Wüst and Bustin, 2003; Fernandes-Horn et al., 2016).

1.2. Studied area

The studied area is located southwest of Riacho dos Machados and northeast of the mining plant of Ouro Fino Mine. The area is limited by the coordinates UTM 702600E-702300E and 8230750N-8230350N. The access to the area is made from Montes Claros, by the highway BR-251 (68km), then by the State Highway MG-120 (37 km away), covering a distance of 105 km in total to the city of Riacho dos Machados. From that point, secondary roads make access to the Tião Amaral Ranch (Figs. 2, 3).

The map and stratigraphic profile (Crocco et al., 2000) show the geological setting of the region (Fig. 2). Within the target region, anomalies of three elements were selected (Cu, Zn, and Pb) to test the methodology. Sampling was done over a region of about 0.5 km^2. Eighteen soil samples were collected as well as 58 plant samples, three of each species, at each point. Figure 3 shows the sampling area and the distribution of nine batches of samples over the isoline map of Riacho dos Machados Gold Mining group.

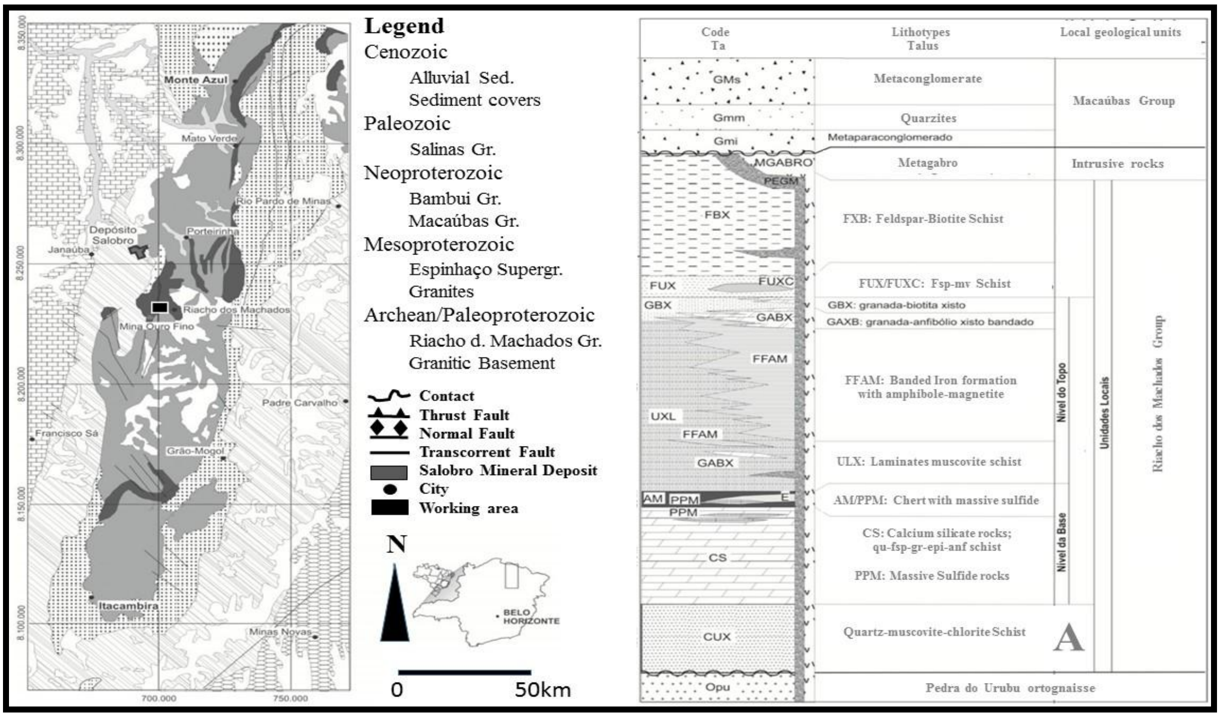

Fig. 2. Geological setting of the investigated area. The small black quadrangle indicates the investigated region and A in the column shows the stratigraphic position of the profiles (from Crocco et al., 2006).

2. Materials and methods

2.1. Sampling

Plants and soil samples were collected following two profiles oriented W-E (1 to 4) and NW-SE (5 to 9); they cross all known anomalies. The surfaces were cleaned of vegetation and every soil sample, 1 to 2 kg weight each, was taken from a depth of 3-10 cm. Five to ten plants of every different species (*Annona leptoptella; Piptadenia gonoacantha; Sida sp*) were collected close to the soil sample locations.

2.2. Sample preparation

The Si-Phytoliths from plants were separated using the method described by Parr et al. (2001), then dissolved within HF/HNO$_3$, retaken by 10% HNO$_3$, filtered and stored in a freezer at low temperature. After drying, crushing and sieving to <0,634 mesh, the soil samples were preserved at low temperature.

2.3. Analytical procedures

The solutions were analyzed by an ICP-OES spectrometer, type SPECTRA, using internal and international reference standards. The analyses were executed at the NGqA-IGC-UFMG.

The soil samples were submitted to XRF-analyses, using a Shimatzu spectrometer, at the Laboratory of LIPEMVALE-Federal University of Jequitinhonha and Mucuri Valleys (UFVJM).

2.4. Data treatment

The analytical data were submitted to a statistical evaluation, in order to homogenize group data, obtain usable mean values, to detect, and to separate the incorrect data from the set. The analytical soil and Phytoliths data were compared to the anomaly element data obtained from Carpathian Gold Inc.

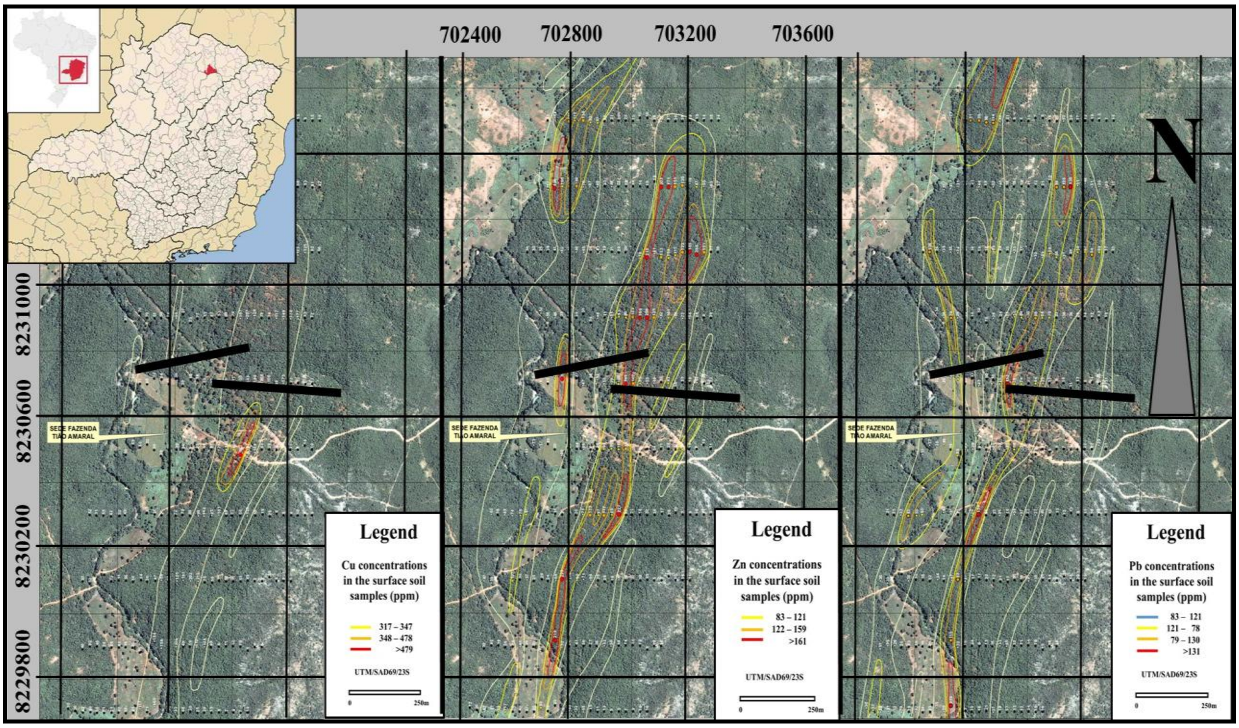

Fig. 3. Situation on the investigated site. Maps showing Pb, Cu and Zn distribution of the soils, provided by the Mining Corporation. The samples were taken on two E-W profiles (black lines; unified), cutting the metal-enriched zones (originals from Carpathian Gold Inc.; modified).

3. Results

The study consists in an integrated approach, which used field GPS information, analytical data of plants and soil samples and isoline-information from Riacho dos Machados Gold Mine (former: Ouro Fino Mine). The plants accumulate metals in different concentration, in their biominerals. For this purpose is used mean values of whole plant Si-Phytoliths concentrations, which are very close to the high contents found only in the leaves. The analytical data on soils show a good correlation with the isoline data of maps. Beside the three main elements (Pb, Zn, Cu), other ones were also evaluated (Mg, Al, Ca, Cr, Fe, Co, Cd, Ti, Mn, Ni, and Ba). Figure 4 shows the correlation between the different concentrations for the

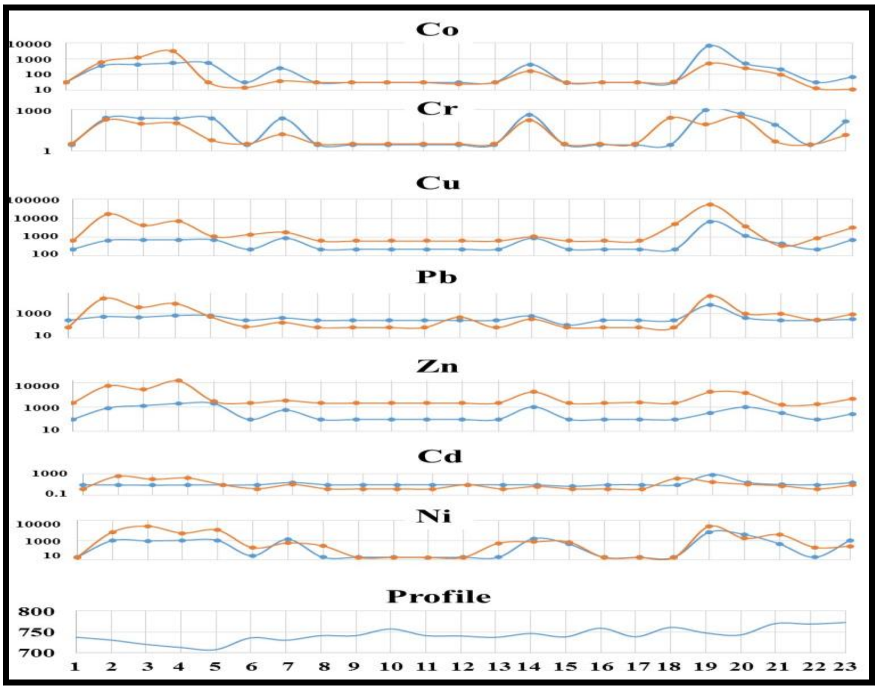

Fig. 4. Selected element concentration (ppm) in soils and Si-Phytoliths from plants along an E-W oriented profile (blue: soil samples; brown: Si-Photoliths data). The lowest profile shows the altitudes of sampling points (m). The numbers are the profile sampling points.

selected elements. Elements concentration in Si-Phytoliths from plants shows a slightly more complex behavior than that of soil samples, while a correlation between the two data sets were also found. The changes of natural factors like rainfall, insolation, and temperature changes influence the Si-Phytoliths less than the whole plant biomass.

4. Discussion and conclusions

The dense distribution of the selected plants and their high Si-Phytoliths production allow their use in the Cerrado/Caatinga region of whole Brazil.

This first investigation may stimulate the search for other plants of other biotopes for the same purpose.

The information are more exact than the soil sampling method due to the peculiarities of soil evolution and transforming process.

The variation of natural factors like rainfall, insolation, and temperature changes influences less the Si-Phytoliths than the whole plant biomass.

Si-Phytoliths show metal enrichment correlated with soil metal concentration.

The plants can assimilate metals at various concentrations, due to their physiology, the physical-chemical conditions of and the form of the metal compounds.

The Si-Phytoliths, due to their inorganic nature, are less sensitive to extreme weather changes, like poor precipitations/lack of rain, insolation or temperature changes.

5. Acknowledgements

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 45-48

USE OF MINING WASTE IN AGRICULTURE. AN EXAMPLE USING EMERALD MINING WASTE FROM MINAS GERAIS, BRAZIL.

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Abstract: After adequate treatment, a lot of waste materials can be used to fertilize the poor lateritic soils of the Bazilian central part. The emerald-bearing schist found near Nova Era in Minas Gerais, Bahia and Goias States is tested here. It is rich in Mg, Ca, K, Zn and other elements important for plants, which lack in poor laterite tropical soils. Different quantities of schist were added to the soil and the evolution of soil chemistry and plant raising was observed for corn. The laboratory and field investigations show the good chemical overall evolution of the soil. Investigations by microprobe of the schist minerals indicated the longtime liberation of interesting elements from minewaste to soil fluids and the retainment of undesired compounds. The tests show that the use of waste material alone or in blending is a good and cheap possibility to lower mining impact and to get higher and cheaper food production.

Keywords: Emerald mining, Mining waste, Soil corrective, Environmental impact, Laterite soils, Tropical climate, food production, fertilizer, soil correctives

1. Introduction

The growing world population demands a significant increase in the quantity of mining and industrial processes to guarantee the welfare of people. A consequence of this intensification is an extensive use of natural resources and the generation of a huge amount of residues. The mining groups which try to supply the world demand of raw materials are one of the major producer of waste tailings, causing landscape and physico-chemical environmental impacts. The formation of these tailings created a problem, being cosidered as an environmental passive of high cost and complex dealing for the involved bussiness groups from the present into future (Machado, 1994). On the other hand, due to the increase of the number of inhabitants of the planet, a larger production of foods will be necessary and also a more efficient and maintainable exploration of the natural resources (soils and minerals). A lot of mining wastes are composed of primary and secondary minerals which are able to liberate from their composistion chemical elements necessary for plants in their physiologic development (Aguiar et al., 2011). To obtain a good production rate and a recovery of the used substrates (soils), it is necessary to do fertilization and correction to prepare soils for planting, especially in tropical regions where high erosion and deep weathering results in acid and poor laterite type soils (Fernandes, 1996). To secure an adequate production, this demands a very high consumption of mineral input (fertilizers, correctives). The high percentage of importation has a negative influence over importation-exportation balance of the country. In this way, using tailing material alone or blended with industrial products, can reduce environmental impacts on the mining sites and industrial plants and also lower the cost of agricultural production. Here, are shown data of experiments using waste material from emerald digging tailings of a mining region in Minas Gerais applied on lateritic soils to reduce the cost and better the production for small farmers and to reduce the waste piles and tailings (Fig. 1). The biotite-, biotite-phlogopite-schists and amphibolites derived from metamorphosed rocks of the Archean ultramafic units (Leal, 1999) contain elements such as Mg, Ca, P, K, Zn, Fe, Cu and Co that are necessary in physiological processes of plant development. Brazil has three principal emerald provinces (Nova Era-Minas Gerais; Campo Formoso-Bahia; Santa Terezinha-Goiás) that can supply significant amounts of waste in the fertilizer industry.

The waste generated by the mining of emeralds in Brazil exceeded 45,000 tons in 2010, allowing to be used on >4,500 ha planted area/year. So the import of lime and fertilizer for agriculture can be reduced considerably, jobs can be generated by involving the workers in logistics, processing and distribution of the prepared material, which may increase the profits of industry and farmers.

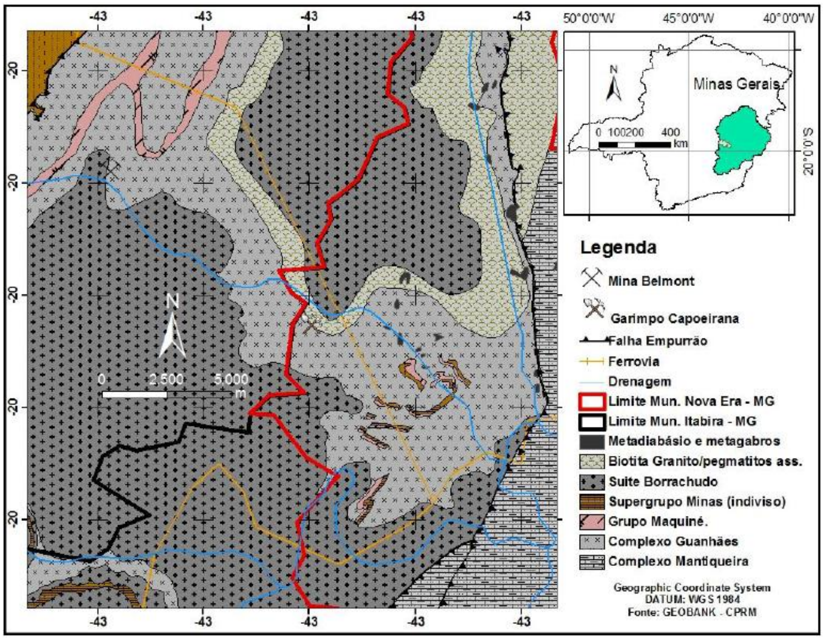

Fig. 1. Location and geology of the emerald mining district near Nova Era. The red line marks the area with ex-ploited rocks. The red circle represents the principal mining locality (Leal, 1999; modified; Machado, 1994).

2. Materiais and methods

2.1. Sampling

Fig. 2. Example of waste material used in the experiments. The material is composed of different schists, amphibolite and quartz veins.

In this work, was used waste material from different tailings of the emeralds mining region Nova Era County-MG (Fig. 2; Table 1) and agricultural soil collected at the experimental area of the agronomic department of the State University of Rio Doce Valley (UNIVALLE) at Goverandor Valadares-MG. The soil used in the experiments is a medium-sandy soil and in the agriculture related analysis were determined relevant parametres (De Felippo and Ribeiro, 1997) and are presented in Table 2.

The samples were collected in 0-20 cm depth interval (Fig. 3) and dried under normal conditions (25-30ºC; shadow), crushed down and homogeniezed by sieving (<5.0mm) to a uniform soil substrate. The mining residue was crushed and reduced to a granulometry <0.560 mm and mixed with the soils in different proportions.

2.2. Laboratory leaching tests

The waste and soil were mixed in the proportions 99.8 g of soil: 0.2 g of waste and 98.0g of soil; 2.0 g of waste, corresponding to the use of respectively 4 or 40 t/ha of the waste in field aplication (soil density ~1.00g/cm^3). After preparing, 100 g of sample were put in plastic beakers and irrigated until reaching 80% of the field capacity, leaving to incubation room for 60 days with controlled temperature varying between 27 and 33ºC with humidity control. The beakers were covered with transparent plastic blanket to reduce the evapotranspiration of the sample and to maintain the humidity. The experiments were repeated four times for each used waste dose. After the incubation period, the soils were collected and left to dry under normal conditions (TFSA: air temperature; darkness), and afterwards submitted to the preparation for routine chemical analyses according with the method described by De Filippo and Ribeiro (1997).

2.3. Greenhouse tests

To analyze the availability of nutrients for plants in the soil, a hybrid corn test in a greenhouse was organized at the experimental area of UNIVALLE with five treatments and five repetitions each. The following quantities of waste were used (0 t/ha, 5 t/ha, 10 t/ha, 20 t/ha, 40 t/ha). The greenhouse tests were performed at the experimental area of UNIVALLE in Governador Valadares-MG. The prepared materials (waste and soil) were placed in plastic containers of 63 dm^3 in the same proportions and two corn plants were planted in every pot. To determine the efficiency of the used waste as a nutrient source for plants, every month, the weight of dried roots, stems and fruit samples was determined.

Table 1. Composition of the mining waste used in this work.

Elements	Units	Concentration
Al2O3	%	9.27
CaO		4.37
Cr2O3		0.29
Fe2O3		9.79
K2O		3.14
LOI		2.53
MgO		19.17
MnO		0.16
Na2O		0.80
P2O5		0.02
SiO2		50.25
Pb	$mg \cdot kg^{-1}$	5.15
Cd		< 0.10
Cu		4.40
Ni		166.75
Ti		5.05
Zn		107.00

2.4. Open field tests

A field test was executed on a typical soil and with normal agriculture preparation at a farm near Divinopolis-MG. The used plants were the same corn species like in the other tests. The same soil-waste mixtures like in the greenhouse test were used. Fig. 4 shows photographs of different stages of evolution of the plants with varying waste application.

2.5. Chemical analyses

The analyses of leaching tests were done in the ICP-OES laboratory of NGqA-IGC, overall rock and soil chemistry in the ICP-MS laboratory of ACME, mineral composition in the DRX laboratory of CPMTC-IGC and soil specification in the soil laboratory of the University in Viçosa.

2.6. Microprobe analyses on waste minerals in the soil

The analyses were done on separated mineralspecimen from soil-mining waste mixtures after different periods. The periods were imediately after mixing, after six, twelve and eighteen months.

The investigated minerals are the most important compounds (mica; amphibole) for nutrient liberation from the mining waste (Fig. 5a, b).

Table 2. Agriculture-relatated parametres of the used soils such as pH, soluble match (P), potassium (K), calcium (Ca), magnesium (Mg), aluminum (Al), potential acidity (H+Al), Sum of bases (S), total CTC (T), CTC executes (t), Saturation of Bases (V) and saturation of Aluminum (m). Determination after De Filippo and Ribeiro (1997). This table also shows the parameters for the used soil-mine-waste mixtures.

	pH	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	SB	T	t
		mg/dm^3		$cmolc/dm^3$				$cmolc/dm^3$		
1. Areno soil	5.40	4.10	110.40	1.10	0.10	0.55	2.60	1.48	4.08	2.18
2. Areno soil 4t/ha.	5.33	4.50	142.64	0.90	0.68	0.53	2.68	1.94	4.62	2.47
3. Areno soil 40t/ha.	5.40	5.40	206.81	1.00	1.30	0.40	2.68	2.83	5.51	3.23

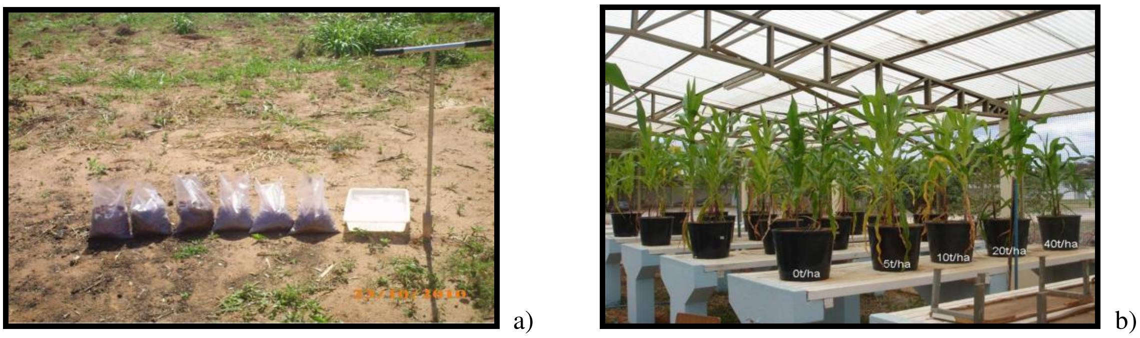

Fig. 3. a. Soil samples from UNIVALE used in the work.
b. Evolution of the plants from beginning untill after 3 month

3. Results

The results of leaching tests support the idea that in relation to the original soil (soil: 110.4 mg/dm^3K) can be observed considerable changes in the K-values of the soil for the different used mixtures with a variation about 29 to 87% for the treatments with 4 and 40 ton/ha, respectively. In relation to Al-saturation, the significant reduction was shown in the order of 70% (soil: 32.11% mixture: 9.94% for waste application of 40 t/ha). These may be caused by two factors, the reduction of the free Al and the increase of the base-saturation (Mg and K), due to the waste composition (Table 1) and the availability of elements in soil. The leaching tests show considerable liberation of important elements from tailing material like K, Ca, Mg,Co, Cu, Cr, Fe, Zn an Mn and considerable retention of other PTE´s with Cd, Pb. The material do not change significantly the pH of the original soils (acidity of the soil pH = 5.6; low acidity). There is a slow decomposition of the minerals all over the vegetation period of corn (120 days) which permits one aplication every year.

Fig. 4. Corn plant evolution in agricultural land after 1, 2 and 3 months. a) Preparation for seed; b) Application of waste; c) Planting of corn; d) 1 month; e) 2 month; f) 3 month; The application was done separately in four distinct rows from left to right in every picture with the application of 0, 10, 20 and 40 t/ha. The best result can be seen for plants with 30 and 40 t/ha application.

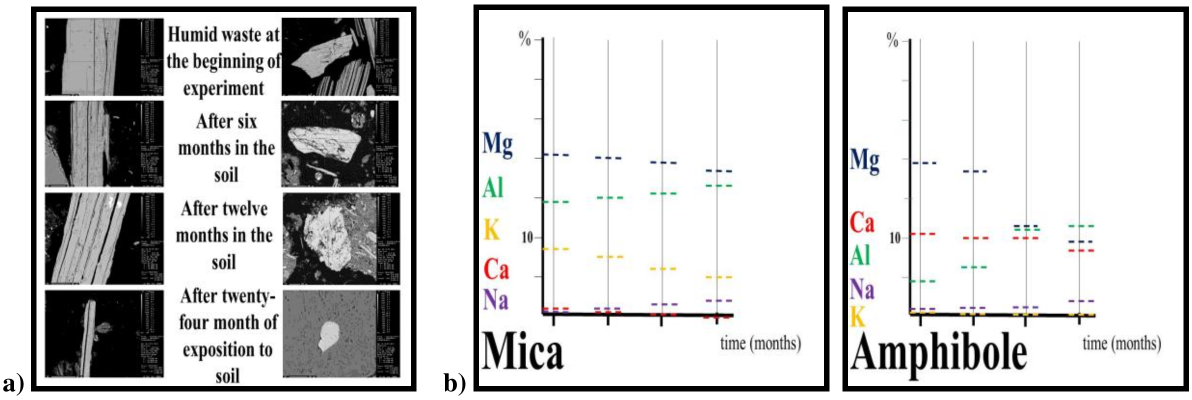

Fig. 5. a. Morphological evolution of the investigated minerals. b. The element evolution in the seelcted mineral versus time of soil exposure. The slow and continuous liberatio of nutrient elements is to observe. Elements like Na and Al are retained in the minerals. For every mineral type 25 grains were investigated and the results treated statistically.

4. Conclusions

The waste material from the tailings of emerald mining can, according to its amount, structure, location, mineralogical and chemical composition, serve as complementary inputs for the fertilizer industry, reducing in this way the costs of food production and also mitigate the problems caused by the deposition of the mining waste. The observed preliminary results confirm an increment in the disponibility of some elements like magnesium and potassium together with a low correction of the pH in soils for agricultural production. Field experiments with more plant groups (beans, eucalyptus) are in execution. It may be necessary to use also blending with industrial waste to obtain better pH-correction data, probably with limestone or gypsum from other mining activities in Minas Gerais. Taking in account the waste piles produced by this mining activity and the annual fertilizer import by Brazil it is poosible to spare a huge amout of money, beside the environental advantages.

5. Acknowledgements

Logistic and financial support was given by NGqA-IGC-UFMG, FAAG-UNIVALE and FAPEMIG.

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 49-54

A NEW OCCURENCE OF WOLFRAMITE – FERBERITE IN ROMANIA

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Abstract: Wolframite has recently been discovered in the Cisma ore deposit in the eastern part of Baia Mare area. The wolframite was identified at +680m level of the Cisma vein. Wolframite appears in quartz-hematite-pyrite-chalcopyrite assemblage. The FeO contents range between 23.54-23.94% and Fe between 18.32-18.61%. Manganese contents are very low: MnO = 0.78-1.08% and 0.61-0.84% Mn. This indicates the presence of the iron-rich member known as ferberite. The formula is very close to that of ferberite: $(Fe,Mn,Mo)_{1.027}(W,Nb)_{0.9913}O_4$. The low contents of Mo, in some analyses, may be explained by the substitution of W. Somewhat higher contents were obtained for niobium: Nb_2O_5=0.20-0.27% or Nb=0.14-0.19%. The small contents of niobium could indicate the presence of iron as Fe^{2+}. The presence of the Fe^{2+} in large amounts in fluids indicates that these were not heavily oxidized, being dominantly of magmatic origin.

Keywords: wolframite, ferberite, hydrothermal, ore deposits, Cisma vein, Baia Mare

1. Introduction

Wolframite is the name for the hübnerite - ferberite series. Woframite ore deposits are associated with granitic intrusions (Neiva, 2008). The tungsten is enriched by fractional crystallization, in the residual melts, associated with granitic intrusions of orogenic belts (Goldmann et al., 2013) Wolframite deposits are generally formed in ore deposit types including skarn, greisen and hydrothermal veins. The most common mineralization of these types is represented by: greisens, e.g., Western Krušné hory/Erzgebirge granites pluton (Štemprok et al., 2005); the quartz vein in greisen associated with granites, e.g., in Bohemian Massif (Dobes et al., 2011); quartz veins in Northern and Central Portugal associated with Hercynian granites (Neiva, 2008) and in Mesozoic ore deposits in South China, associated with different types of granite, that is world-class W-Sn province (Mao et al., 2013).

In the Romanian territory, the wolframite occurs in skarn deposits associated with Laramian Banatite magmatism at Oravița Ciclova, Southern Carpathians (Rădulescu and Dimitrescu, 1966) and in the hydrothermal ore deposits associated with the Neogene Volcanic Arc of the East Carpathians at Baia Sprie, Băiuț (Superceanu, 1957) and Văratec (Costin and Vlad, 2005). The presence of the tungsten minerals has been mentioned in Cavnic and Baia Sprie ore deposits, in the main mineralization stages, (Grancea et al., 2002). Wolframite in the Băiuț ore deposit has been mentioned as hübnerite and in the Văratec ore deposit as ferberite. The presence of hübnerite at Băiuț has not been revalidated by Udubașa et al. (1992).

In the other hydrothermal deposits in the Carpathian Arc, wolframite has been described at Banská Štiavnica, Slovakia (Kalinaj, 1992) and at Alsó-Rózsa adit, Nagybörzsöny, Hungary (Szakáll et al., 2012, Földessy, 2014), which are similar to those of Baia Mare metallogenetic district.

The wolframite has recently been discovered in the Cisma ore deposit in the eastern part of Baia Mare area.

2. General geology

The Baia Mare volcanic area and ore district are part of the Oaș-Gutâi volcanic mountains and are situated at the northeastern boundary of the Alcapa block with the Tisza-Dacia block, near the border with the European Platform (Săndulescu et al., 1993; Márton et al., 2007; Schmid et al., 2008). The Oaș-Gutâi volcanic mountains represent a segment of Neogene-Quaternary volcanic arc located inside the Eastern Carpathians and the border with the Transcarpathian Basin. The metallogenetic district of Baia Mare is the largest concentration of mineralization of the metallogenetic subprovince associated with the Neogene magmatism, (Popescu and Neacșu, 2010).

The metallogeny - generally with polymetallic character - is closely associated spatially and genetically with the Neogene magmatic activity, extending from west of Ilba (Seini) - as far to the east as Băiuţ and Ţibleş. The overall direction of the district is E-V and is, therefore, relevant its association with the crustal fracture Dragoş Vodă, in terms of both volcanism and metallogeny (Popescu, 1986; Măldărescu and Popescu, 1981).

The Cisma deposit from Băiuţ district is situated in the easternmost part of the Baia Mare area (Fig. 1).

Sedimentary rocks are represented by Paleogene sedimentary overlain by Lower Neogene sediments and Upper Neogene andesites. The predominant sedimentary rocks are the Paleocene ones, which belong to Tocila – Secu flysch (Bombiță, 1972). The sedimentary groups fall under the Trans-Carpathian Flysch, arranged in two structural units: Botiza Nappe and Lăpuş Paraautochonous. The sedimentary groups of the Upper Cretaceous and the deposits in pelagic facies of Upper Jurassic age appear in the form of tectonic klippes. These are frequent in the lower Botiza Nappe. Paleogene sedimentary is represented by the Eocene with three layers: inferior, middle and superior, constituting the petrographic background, where the bodies of magmatic rocks are intruded.

The sedimentary rocks are intruded by Late-Neogene quartz microdiorite porphyries (quartz micro-monzodiorite porphyries) and micro-granodiorite porphyries. The intrusive magmatic rocks are affected by hydrothermal alteration, in special propylitic and phyllic alteration. At the contact of the intrusive body with the sedimentary, there are hornfels in chloritic facies.

The Băiuţ area includes three Pb-Zn-Cu-Au deposits: Cisma, Breiner and Văratec (Borcoş and Gheorghiță, 1976). The Cisma Poiana Botizei deposit is hosted by Paleogene sedimentary intruded by Neogene quartz microdiorite porphyries and micro-granodiorite porphyries (Fig. 1).

3. Cisma ore deposit

The Cisma deposit occupies the easternmost part of the Băiuț area. Damian and Damian (2004) identified two mineralization stages at the Cisma deposit. The early stage is represented by: hematite-pyrite-chalcopyrite-tennantite-tetrahedrite-quartz associated with small amounts of sphalerite, galena, wolframite, pyrrhotite, lillianite-gustavite and native bismuth. The second stage is predominantly base-metal and contains: galena, sphalerite, pyrite, chalcopyrite, marcasite, native gold, stibnite, realgar, orpiment, semseyite, boulangerite, jamesonite. Native gold occurs as small grains in pyrite and is present predominantly in the upper part of the Cisma vein. It consists of two main veins: Cisma and Bandurița.

The Cisma vein, dipping to SSE, is 2 km in length and 600 m in depth and in the central zone its thickness is up to 5-6 m. Areas of greater thickness (up to 10 m) alternate with wedging-out zones with thickness of about 1 m. The main vein has several branches (Fig. 2). The vein is situated in the middle horizon of the Eocene flysch of Tocila – Secu. The texture of the vein is parallel, represented by zones with massive ore and zones with impregnation. Nonmetallic minerals are represented by quartz and small amounts of carbonates, chlorite and clay minerals. In the central part, the vein contains 2-3 zones with massive ore in alternation with bands of quartz or with intercalations of argillaceous and silicified sedimentary rocks of Paleogene age.

The Bandurița vein dipping NNW has a length of about 1500 m and the maximum thickness of 1.5 m. In this vein, frequently occurs the second mineralization stage with higher amounts of Pb and Zn. The vein is disposed in the area of contact between the intrusions and the rocks of Eocene middle flysch (Fig. 2). The mineralization consists of pyrite, galena, sphalerite, chalcopyrite, marcasite and arsenic minerals. Nonmetallic minerals are represented by quartz and high amount of carbonates. The texture of the vein is parallel, represented by a zone rich in pyrite and a zone rich in sphalerite and galena. The central part of the vein is predominantly composed of carbonates.

Sphalerite base-metal mineralization is represented by two generations (Plotinskaya et al., 2012). Sphalerite-1 has Fe contents 1.3 to 4.6 wt.% (2.3 to 7.9 mol.% FeS) and Mn (0.5 to 0.7 wt.%). Sphalerite-2 overgrows sphalerite-1 has similar Fe content (1.9 to 4.5 wt%), is low in Mn (to 0.2 wt.%).

In the Cisma vein is predominant the early stage. The vein contains bismuth minerals (Damian et al., 2010), being identical to other copper mineralization in the Baia Mare area (Damian, 2000). The marginal and the apical areas of the Cisma vein have elevated values for the Pb and Zn. Olimpiu branch has large quantities of stibnite. Bandurița vein has large quantities of Pb and Zn, typical for the second stage of mineralization. Also, on the Brandurița vein appear appreciable quantities of orpiment and realgar associated with marcasite.

4. Analytical methods

The chemical composition of wolframite was studied with a Cameca SX 100 Electron Probe Microanalyzer (EPMA). The analyses were carried out at State Geological Institute of Dionyz Stur (Bratislava, Slovakia). The analysis spots were selected using the backscattered electron (BSE) images. The measurements were performed on carbon coated polished sections using an acceleration voltage of 15 kV, 40 nA beam current, 5 µm beam diameter, 20s counting time for the peak and 7s for the background.

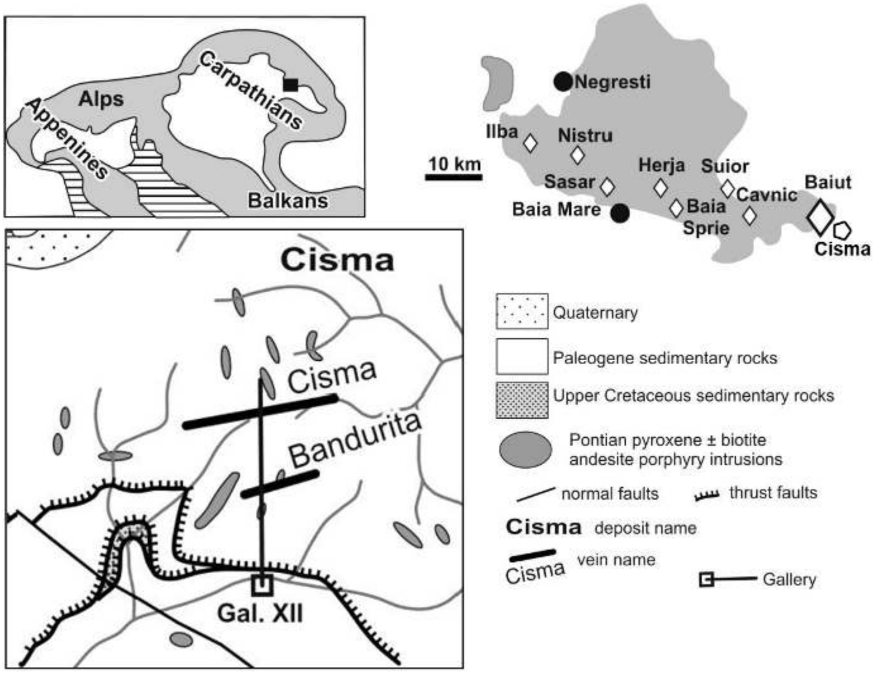

Figure 1. Geological sketch map of the Cisma area, after Plotinskaya et al., (2012) with minor changes.

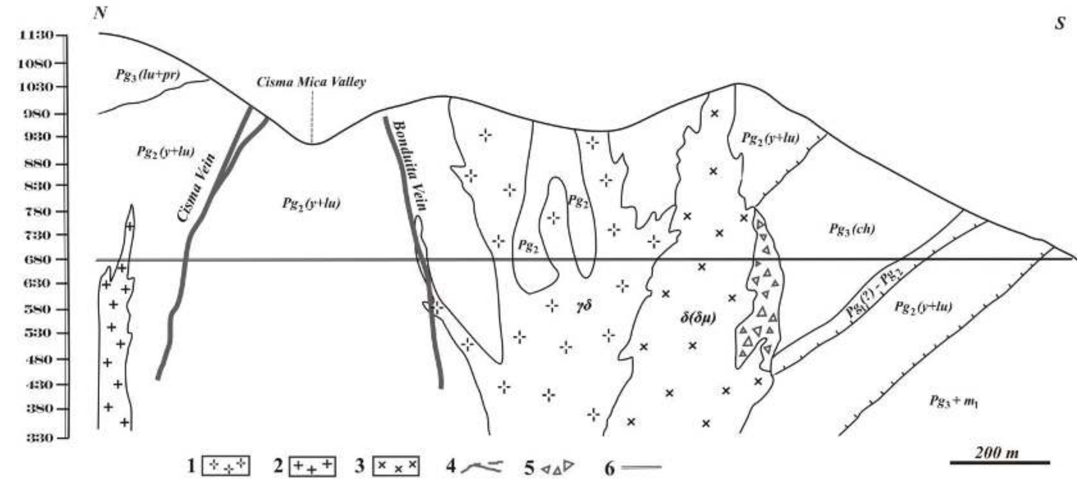

Figure 2. Cross section through the Cisma (Cisma Poiana Botizei) deposit: 1-microgranodiorite porphyries, 2-andesite, 3-quartz-microdiorite porphyries, 4-veins, 5-breccia, 6-gallery, Pg_{123}-Poleogene (Eocene) lower, middle and upper.

The following X-ray lines and natural (n)–synthetic (s) standards were used: W Lα ($CaWO_4$), Fe Kα (Fayalite), Mn Kα (Rodonite), Nb Lα ($LiNbO_3$), Mg Kα (Forsterite), Mo Lα ($CaMoO_4$). The typical minimum detection limits were: 1240ppm for W, 565ppm for Fe, 535ppm for Mn, 745ppm for Nb, 755 ppm for Mo.

5. Wolframite

This is the first occurrence of wolframite reported from the Cisma ore deposit. The wolframite was identified at +680m level of the Cisma vein. Wolframite appears in quartz-pyrite-chalcopyrite assemblage (Fig. 3 A, C). Wolframite occurs as prismatic or tabular crystals or subparallel clusters arranged in the form of bundles of up to 1 mm, visible with the naked eye. It differs from hematite by yellow tints to olive and especially by visible pleochroism and strong anisotropy (Fig. 3 B, D).

Wolframite from Cisma vein shows the composition of the ferberite component (Tables 1 and 2). Crystals of wolframite from Cisma vein have a homogeneous composition. On the backscattered electron images (Fig. 3 E, F) there is a clear distinction between crystals of ferberite. This is due to different orientation of the prismatic crystals and not from the compositional differences of these crystals. In contrast, the wolframite from Baia Sprie ore deposit, (Bailly et al. 2002) presents a hübnerite-rich core and ferberite-rich rim.

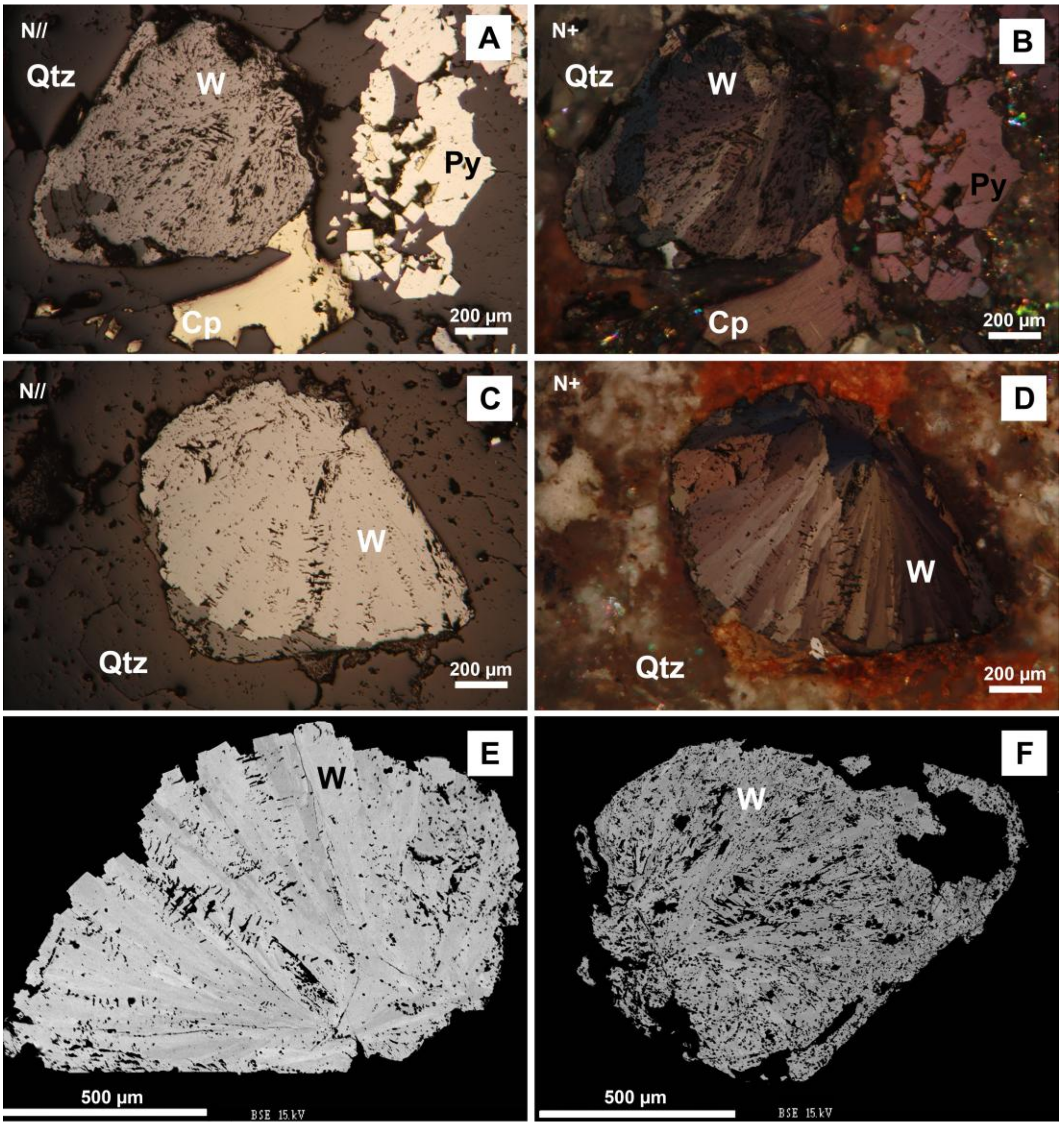

Figure 3. Wolframite (ferberite): A-wolframite associated with pyrite, chalcopyrite included in quartz parallel nicols, B same image as A, cross nicols, C-wolframite included in quartz, D-same image as C, cross nicols, E and F - Backscattered electron images (BSE) of wolframite.

Table 1. Chemical analyses (wt%)

Sample name	WO3	FeO	MnO	Nb_2O_5	MoO_3	Total
CS-721_an1	76.40	23.57	0.78	0.20	0.08	101.03
CS-721_an2	76.61	23.74	0.96	0.24	0.15	101.72
CS-721_an3	76.96	23.94	0.89	0.24	0.07	102.15
CS-721_an4	76.83	23.73	1.08	0.27	0.11	102.07
CS-721_an5	76.49	23.75	0.81	0.22	0.11	101.44
CS-721_an6	76.39	23.78	0.85	0.23	0.10	101.38
CS-721_an7	77.42	23.80	0.83	0.00	0.25	102.40

Table 2. Analyses of the main elements (wt%)

Sample Name	W	Fe	Mn	Nb	Mo	O	Total
CS-721_an1	60.58	18.32	0.61	0.14	0.05	21.34	101.04
CS-721_an2	60.75	18.46	0.74	0.16	0.10	21.50	101.73
CS-721_an3	61.03	18.61	0.69	0.17	0.05	21.58	102.16
CS-721_an4	60.93	18.44	0.84	0.19	0.07	21.57	102.07
CS-721_an5	60.66	18.46	0.63	0.15	0.08	21.43	101.45
CS-721_an6	60.58	18.48	0.66	0.16	0.07	21.42	101.39
CS-721_an7	61.39	18.50	0.64	0.17	0.05	21.63	102.40

Table 3. Cations recalculated from analyses in Table 1

Sample name	W	Fe	Mn	Nb	Mo	Total	Ox-base
CS-721_an1	5.93	5.91	0.20	0.03	0.01	12.07	24
CS-721_an2	5.90	5.90	0.24	0.03	0.02	12.11	24
CS-721_an3	5.91	5.93	0.22	0.03	0.01	12.12	24
CS-721_an4	5.90	5.88	0.27	0.04	0.01	12.11	24
CS-721_an5	5.91	5.93	0.20	0.03	0.01	12.10	24
CS-721_an6	5.91	5.93	0.21	0.03	0.01	12.11	24
CS-721_an7	5.93	5.88	0.21	0.03	0.01	12.07	24

The FeO contents range between 23.54-23.94% and Fe between 18.32-18.61%. Manganese contents are very low: MnO = 0.78-1.08% and 0.61-0.84% Mn. This indicates the presence of iron-rich member known as the ferberite. Low contents of Mo, in some analyses, may be explained by the substitution of W because both elements occur in the same valence state (Goldmann et al., 2013). Somewhat higher contents were obtained for niobium: Nb_2O_5=0.20-0.27% or Nb=0.14-0.19%. Niobium entered in wolframite in solid solution and is probably incorporated into the wolframite lattice by means of the coupled substitution $[(Fe, Mn)^{2+},W^{6+}]\Leftrightarrow(Fe^{3+},Nb^{5+})$ (Neiva, 2008).

Small contents of niobium could indicate the presence of iron as Fe^{2+}. Presence of the Fe^{2+} in large amounts in fluids indicates that these were not heavily oxidized, as they had predominantly magmatic origin.

The average ferberite composition corresponds to the formula calculated using cations at 24 ions of oxygen, (Table 3): $Fe_{0.985}Mn_{0.04}Mo_{0.002}W_{0.986}Nb_{0.0053}O_4$ or $(Fe,Mn,Mo)_{1.027}(W,Nb)_{0.9913}O_4$.

The formula is very close to that of ferberite.

6. Discussions and conclusion

The presence of wolframite in Cisma vein is specific to the mineralogical assemblage of the initial stage of mineralization silicate-oxide that after Neiva (2008) is often postdated by a sulphide-rich stage.

Microthermometric measurements (Plotinskaya et al., 2012) indicated the depositional temperatures of 270 to 316°C in the Bandurița vein and 143 to 344°C in the Cisma vein. The high temperatures are common to forming of minerals in the first stage of mineralization that includes ferberite and is similar with the generation of the sphalerite 1 (Plotinskaya et al., 2012, 2014). The fluids had low salinity, up to 10 wt.% − eq. NaCl, but usually less than 5 wt.% − eq. NaCl. Temperature and salinity are much lower than those reported by Neiva (2008) for hydrothermal mineralization associated with granite intrusions.

The pressure ranges from 50 to 80 bar (Plotinskaya 2012). This suggests formation depth of approximately 500 to 800 m for a hydrostatic regime (Plotinskaya et al., 2012). This depth roughly corresponds with the observation of Măldărescu & Popescu (1980) that maximum erosion interval in the area was 400-500 m.

The isotopic composition of sulfur, $\delta^{34}S$=+10:+18%, from pyrite of the first stage (Damian et al., 1998) indicates the presence of a magmatic source of the hydrothermal fluids. Temperature and high salinity are responsible for forming minerals in the first stage where magmatic fluids are dominant. The low temperatures and low salinities of ore-forming fluids responsible for forming the final stage at Cisma may indicate a mixing of magmatic fluids with a dominant meteoric water component.

Precipitation of wolframite was caused by the interaction of hydrothermal fluids with the sedimentary rocks. The ascent of these hydrothermal fluids was stopped by impermeable pelitic rocks causing mineral precipitation by the decrease of the temperature. The composition of these fluids and stable isotope data (Damian et al., 1998) indicate that the primary magmatic fluids were strongly modified by interaction with the sedimentary host rock. The sporadic presence of ferberite in the copper mineralization suggests for the first stage a mesothermal type of mineralization.

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NEW COMPOSITIONAL DATA CONCERNING AU-AG ALLOYS FROM THE NORTHERN PART OF ROŞIA MONTANĂ DEPOSIT, METALIFERI MOUNTAINS, ROMANIA

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Abstract: This paper presents the results of the new investigations by optical microscopy, scanning electron microscopy (SEM) and electron-probe micro-analysis (EPMA) performed on samples collected from Orlea adit from Roşia Montană Au-Ag deposit, Romania. Based on composition, three types of Au-Ag alloy were described. At Roşia Montană, galena, pyrite, chalcopyrite and sphalerite are intimately associated with gold, electrum and tellurium-bearing minerals. At Roşia Montană, the precipitation of Au-Ag alloy with variable composition can be assigned to compositional changes of the parent hydrothermal solutions during deposition due to boiling, fluid dilution and cooling.

Keywords: electrum, gold, Roşia Montană, Orlea, Metaliferi Mountains.

Introduction

The great variety of mineral deposits of the Metaliferi Mountains reflects the complex geotectonic environments and the intimate relationship between igneous and hydrothermal activities that have taken place during Miocene. These events are responsible for the formation of a very rich mining district so-called the "Golden Quadrilateral" (Fig. 1). This is one of the most productive mining districts of Europe for over 2000 years, concentrating over 60 gold deposits in about 900 km^2. Due to the Golden Quadrilateral, for many years, Romania was one of the main gold producers of Europe. Roşia Montană Au-Ag deposit is located in the northeastern part of the Metaliferi Mountains (Romania), in the Roşia-Bucium metallogenetic district. It is one of the largest Au-Ag deposits of Europe, being discovered during Roman times, known under the name of Alburnus Maior.

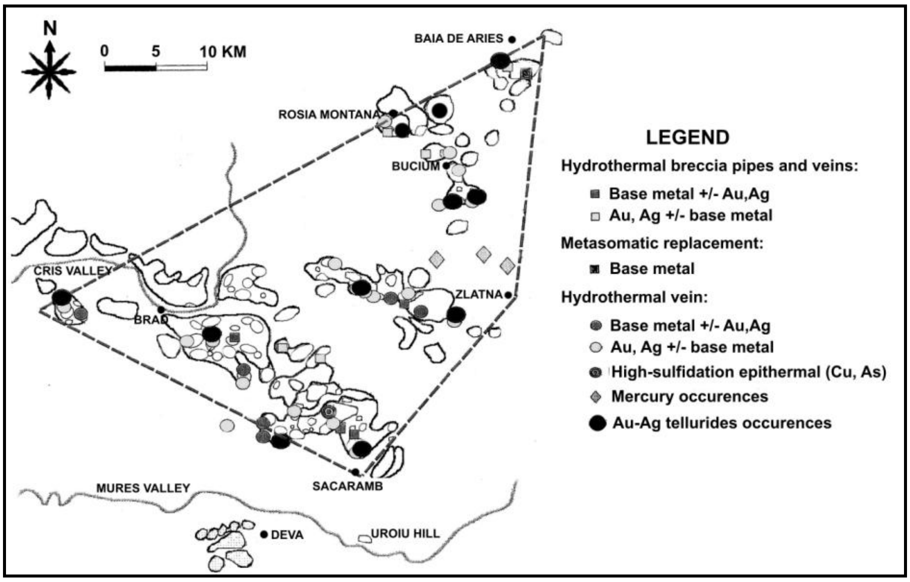


Fig. 1. Sketch map of the Golden Quadrilateral (after Udubaşa et al., 2001)

The remained reserves are estimated at 214.9 million tons of ore, with average contents of 1.46 g/t Au and 6.9 g/t Ag, representing 10.1 million ounces (314 t) Au and 47,6 million ounces (1480 t) Ag (as from Roşia Montană Gold Corporation).

This paper describes the occurrence and chemistry of Au-Ag alloy and its distribution inside the analyzed ore veins in order to understand the factors that led to deposition from the hydrothermal fluids.

Traditionally, the term "electrum" has been used to refer to Au-Ag alloys of a compositional range between 20 and 80 wt % gold, based on the classification of Boyle (1979). This distinction is ignored in the present paper, and the term of Au-Ag alloy is used as a synonym for all Au-Ag alloys present in our samples, including electrum, so-called "native" gold and "native" silver.

Geological setting

The Metaliferi Mountains in Romania cover an area of about 11000 km^2 situated in the South Apuseni Mountains.

The calc-alkaline Miocene magmatism in the South Apuseni Mountains was related to transtensional and rotational tectonics being focused within NW-SE oriented extensional basins (Roşu et al, 2004) that became hosts of major metallogenetic units strongly related to the extensional stress fields.

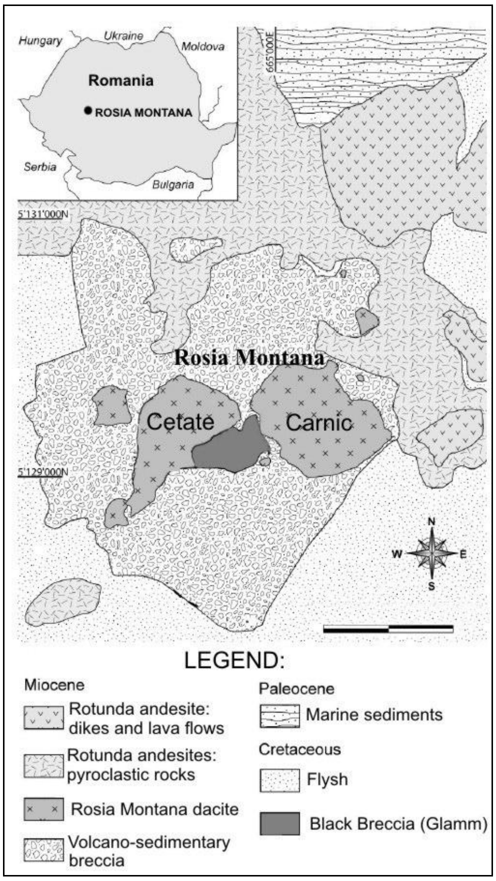


Fig. 2. Roşia Montană sketch map (after Kouzmanov et al., 2005)

The Neogene calc-alkaline magmatic rocks are widespread in the Metaliferi Mountains and host the major deposits of this region. The volcanic and intrusive activity took place, in three episodes, between 14.7 and 7.4 Ma and they were accompanied by metallogenetic processes (Borcoş et al. 1986, Roşu et al. 2004) resulting in the following metallogenic districts: Roşia Montană-Bucium-Baia de Arieş, Brad-Săcărâmb-Deva and Zlatna-Stănija.

Roşia Montană deposit (Fig. 2) is a breccia hosted epithermal system, spatially related to the Roşia Montană dacite bodies intruded during the Neogene, being followed by hydrothermal activity. The ore deposition at the Roşia Montană deposit evolved from an early Au-(Ag) low-sulfidation character to a late Ag-Te-(Ge-Au) intermediate-sulfidation character, and may be correlated with late magmatic pulses (Tămaş, 2010).

Alterations are widespread, four major types being distinguished by macroscopic observations and optical microscopy on transmitted light: phyllic, silicification, propylitic and argillic.

Materials and methods:

For the purpose of the present study, we have used 50 samples collected from the Orlea gallery, situated in the northern part of Roşia Montană Au-Ag deposit, during several field campaigns.

The optical microscopy observations in reflected light were made using a Nikon Eclipse LV100POL microscope with an attached Leica DFC 420c digital camera for the photomicrographs.

Following reflected light microscopy to identify the ore-mineral assemblages, the polished sections were studied with a JEOL JSM 6400 Scanning Electron Microscope (SEM) equipped with EDX detector at Ecole Nationale Supérieure des Mines, Saint Etienne, France. Reconnaissance quantitative compositional data were determined using a Cameca SX 50 electron microprobe with an acceleration voltage of 19.98 kV at G2R Laboratory (University of Nancy, France). Later analyses were done using Cameca SX 100 electron microprobe with an acceleration voltage of 15kv at the Magmas and Volcans Laboratory in Clermont-Ferrand, France.

Measurements were performed on polished sections coated with 2nm of carbon using EMS150R ES Rotary-Pumped Modular Coating Systems at Ecole Nationale Supérieure des Mines, Saint Etienne, France.

Results and discussions:

During optical microscopy observations on polished sections in reflected light and with the Scanning Electron Microscope, we could identify the following ore minerals (Fig. 3): gold, electrum, pyrite, chalcopyrite, galena, sphalerite, marcasite, tetrahedrite, arsenopirite, magnetite, tellurium-bearing minerals (hessite, altaite, sylvanite, petzite, cervelleite, alburnite, argyrodite) and uytenbogaardtite.

Quartz, carbonates (calcite, rhodocrosite) and adularia occur as gangue minerals.

In reflected light, it was observed that gold grains present various shades of yellow due to the variable composition and gave information about the presence of electrum (Au-Ag alloy) with different Au:Ag ratio. Later studies showed that almost pure gold is dark yellow. Electrum shows light to very light yellow nuances due to the presence of different amounts of Ag.

The Au-Ag alloys associated with pyrite, chalcopyrite and sphalerite present three different variable compositions as follows: 1. Gold-rich alloy, where Au concentration ranges between 65 and 88 wt%; 2. Alloy with Au-Ag concentrations in almost equal proportions, with Au ranging between 45 and 55 wt% and 3. Silver-rich alloy where Au concentration is between 22 and 35 wt% (Figs. 4 and 5). The SEM elemental mapping showed that the concentration of the two precious metals is variable inside a grain but with no clear pattern (Figs. 4-6).

We noticed that Au-rich grains (native gold) are usually associated with sphalerite and have Au content higher than 85 wt% (Fig. 6).

We could separate the following mineral assemblages in which gold occurs: Au-Ag alloy with pyrite and sphalerite, gold in sphalerite, Au-Ag alloy with chalcopyrite and pyrite, Au-Ag alloy in carbonates, gold in pyrite and gold and gold-silver tellurides in pyrite.

The most important depositional mechanism for gold in electrum is the boiling of ore fluids. This causes an increase of pH. Silver deposition in electrum is caused by this pH change as well as decreasing temperature, H_2 degassing and dilution (decrease of Cl concentration) (Shikazono, 2003).

Galena, sphalerite and chalcopyrite also precipitate due to the increase of pH induced by the breakdown of base metal complexes with Cl, accompanied by boiling (Shikazono, 2003).

Fluid inclusion studies indicate the dilution of the magmatic fluids (Wallier et al., 2006), the mixing of boiled fluid with meteoric water causing the deposition of gold and electrum in the Roşia Montană hydrothermal system. The abrupt cooling of the hydrothermal fluids caused the oversaturation in dissolved components and the precipitation of ore minerals.

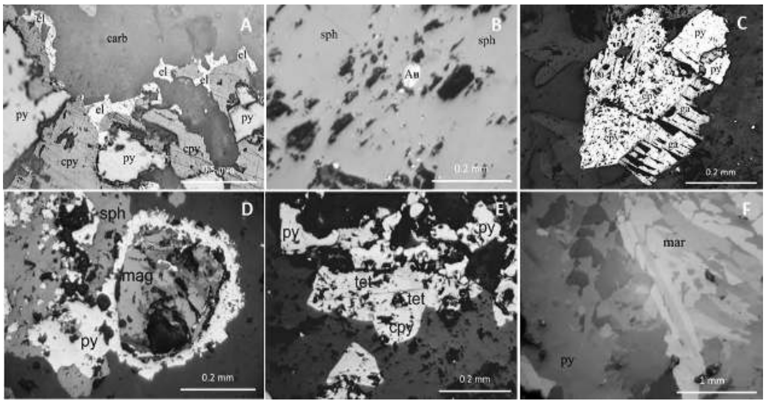
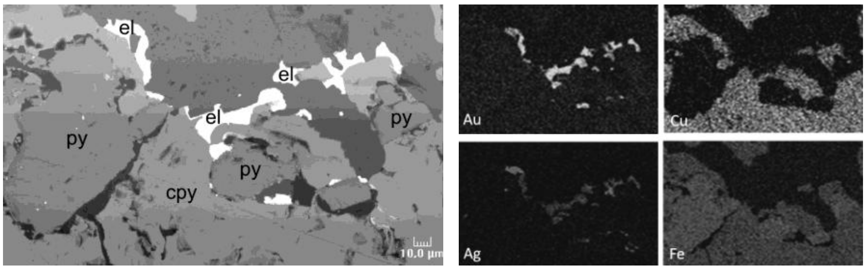


Fig. 3. Photomicrographs of the polished sections at the optical microscope. A. electrum-pyrite-chalcopyrite-carbonates assemblage, // nicols; B. gold in sphalerite, // nicols; C. pyrite-chalcopyrite-galena assemblage, // nicols; D. magnetite-sphalerite-pyrite assemblage, // nicols; E. pyrite-chalcopyrite-tetrahedrite assemblage, // nicols; F. pyrite-marcasite, *X* nicols. Abbreviations: Au-gold, carb-carbonates, cpy-chalcopyrite, el-electrum, ga-galena, mag-magnetite, mar-marcasite, py-pyrite, sph-sphalerite, tet-tetrahedrite.

Fig. 4. SEM photomicrograph of electrum-sulfides-carbonates assemblage (left) and elemental mapping for Au, Ag, Cu and Fe of the sample (right) showing the different content in Au and Ag of electrum grains.



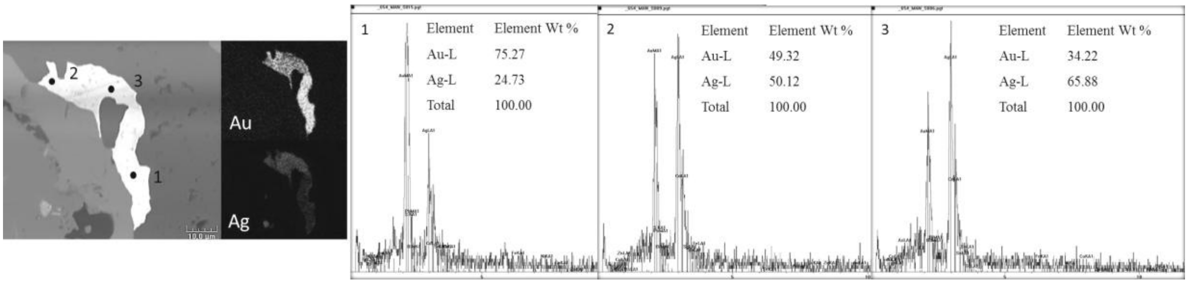


Fig. 5. SEM photomicrograph and elemental mapping for Au and Ag (left) of the electrum grain. SEM-EDX and EPMA analysis showing three different compositions within the electrum grain.

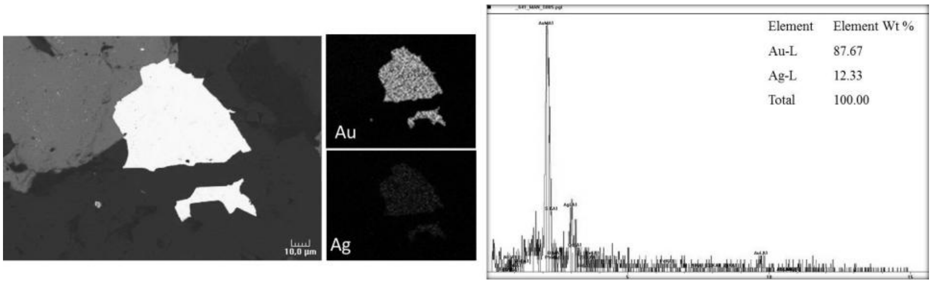


Fig. 6. Photomicrograph and elemental mapping for Au and Ag of a native gold grain associated with sphalerite (left). SEM-EDX and EPMA analysis of the grain (right).

Conclusions:

The precipitation of Au-Ag alloys with different Au:Ag ratios at Roşia Montană, can be assigned to compositional changes of the parent hydrothermal solutions during deposition due to boiling, fluid dilution and cooling. The resulting alloys may be Au rich or Au poor, depending on the temperature, chemical environment and mechanisms of ore deposition.

At Roşia Montană, the metallic load of the hydrothermal fluids is reflected by the wide range of ore minerals precipitated in veins, disseminated or forming stockworks: gold, electrum, pyrite, chalcopyrite, galena, sphalerite, marcasite, tetrahedrite, arsenopyrite, magnetite, tellurium-bearing minerals (hessite, altaite, sylvanite, petzite, cervelleite, alburnite, argyrodite) and uytenbogaardtite.

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MIOCENE MAAR AND FLOW DOME COMPLEX STRUCTURES FROM BUCIUM RODU AND FRASIN, METALIFERI MOUNTAINS, ROMANIA

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Abstract: Bucium Rodu and Frasin are two dacite maar-diatreme volcanoes, which penetrate 400-500 m in the Cretaceous flysch deposits. They are hosting epithermal gold mineralization as veins, disseminations, breccias and stockworks. Also, the two dacitic structures control the location of mineralizations. For instance, at Bucium Rodu, the veins follow the western contact of the diatreme with the Cretaceous flysch as NW-SE and N-S vein sets with shallow, moderate and near vertical dips to the west or east. They are accompanied by small breccia bodies and disseminations, occurring as "en échelon" tension veins. In contrast, at Frasin, the mineralizations are concentrated in or near the NW and SE dome contacts with polymictic breccias. The ore deposition has probably developed in three stages, and was associated with epithermal low sulfidation stages. Adularia, phyllic and carbonate alterations show close relationships with the gold mineralization.

Keywords: maar, flow dome, low sulfidation, gold deposits, volcanism, Metaliferi Mountains.

INTRODUCTION

The Miocene Bucium Rodu-Frasin volcanic structure and related gold deposits are located in the NE part of Metaliferi Mountains, within the so called "Golden Quadrilateral" and approximately 5 km SE of Roşia Montană, a world class gold deposit (Fig. 1 inset). Because of the close vicinity with Roşia Montană gold deposit, the structural complexity and the rich gold mineralization types made Bucium Rodu-Frasin a very attractive area for intensive/extensive prospecting and exploration works as well as for academic studies.

The geology and metallogeny of Bucium Rodu-Frasin zone have been described and discussed in several paper (Ghiţulescu and Socolescu, 1941; Borcoş and Vlad, 1997; Ștefan et al.,1998; Berbeleac et al., 2004, unpubl; Leary et al., 2004; Hewson et al., 2005).

This paper discusses, in detail, the issues concerning the occurrence of maar-diatreme and flow dome complex structures, and the positioning of the ore deposits in direct correlation with these structures.

GEOLOGICAL SETTING

Structural interpretation of detailed mappings, laboratory studies, mining and drilling works and magnetotelluric sounding data (Ghiţulescu and Socolescu, 1941; Ianovici et al., 1969; Roşu et al., 2001; Borcoş and Vlad 1997; Leary et al., 2004) suggests that Bucium Rodu - Frasin area represents, probably, a small Upper Cretaceous-Lower Miocene collapse basin and a complex maar-diatreme structure resulted from normal reactivation of older, steeply dipping fault structures partially related to the Vinţu-Arieş Fault.

The geology of Bucium Rodu-Frasin area and its surroundings consists mainly of the following outcropping lithologic units (Fig. 1): 1) the Lower Cretaceous marine sediments, 2) Badenian Frasin dacites as volcanogenic - sedimentary deposits, epiclastic deposits and volcaniclastic products mono- and polymictic breccias, 3) Badenian Frasin dacite intrusions, 4) Sarmatian (?) andesite lavas Barza type, 5) Detunata basalt - andesite (K-Ar ages, 7.4 ± 0.3 Ma, acc. to Roşu et al., 1997), 6) the intra - maar - diatreme and subsequent sedimentary deposits, and 7) Quaternary alluvial deposits. There are no isotopic analyses available for dating the Frasin dacite, thus it can be assumed that this has the age of either Conţu dacite, situated about 1 km to SE, or the Roşia Montană dacite (e.g., Borcoş et al., 1998).

MATERIALS AND METHODS

A great amount of data has been used in order to achieve our goals. The petrographic study performed on thin sections was based on the samples collected from outcrops and underground galleries. In addition, interpretation of data from surface mapping, surface and underground drillings, and magnetotelluric soundings, were performed. The majority of the primary data were obtained from Prospecting and Geological Exploration Company (I.P.E.G.) Deva (1980-1990) and S.C. Roșia Montană Gold Corporation S.A. (2000-2005) (R.M.G.C).

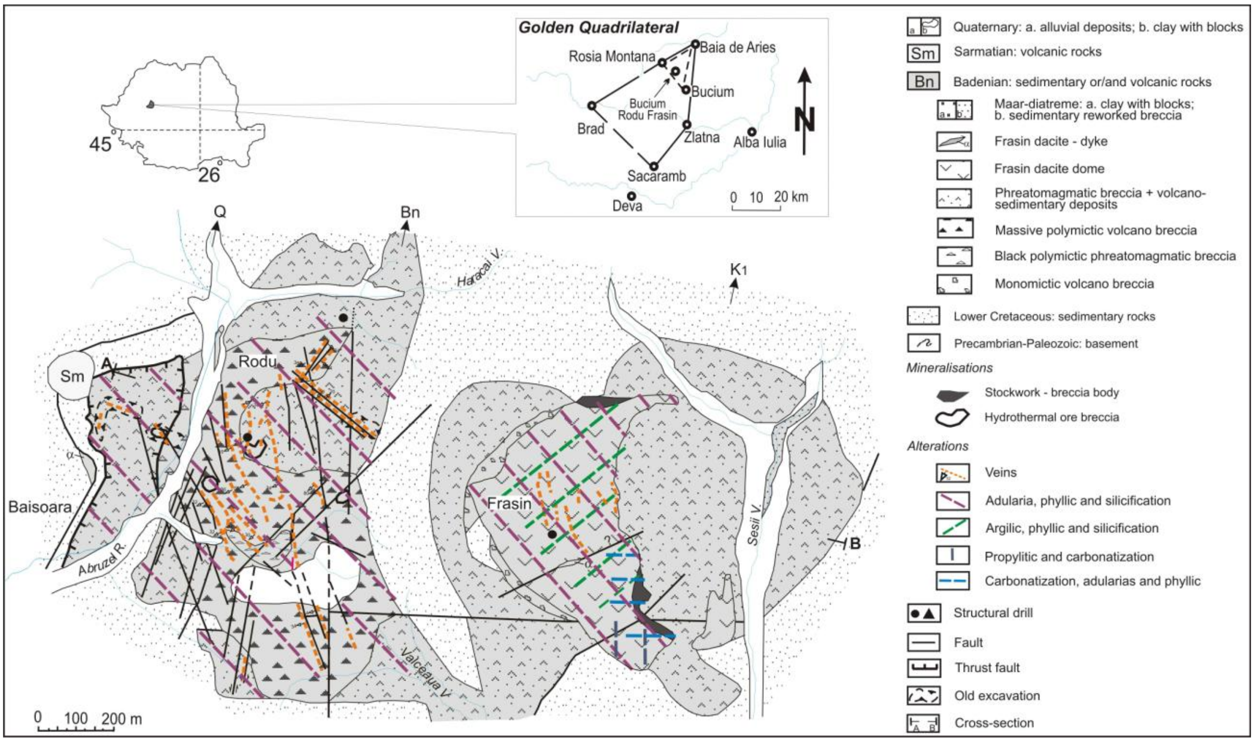

Fig. 1. Geological map of Bucium Rodu-Frasin area. Inset shows the location of the study area within the Romanian terrritory (after R.M.G.C. data with additions).

RESULTS AND DISCUSSION

1. Bucium Rodu-Frasin structure

There is a relationship between the volcanic activity and the volcanic rocks, the shallow ore deposits of the epithermal type and specific volcanic landforms. According to Sillitoe and Bonham (1984), precious and base metal, and lithophile element deposits show genetic, spatial and temporal connection with four types of high-level magmatic systems, and distinct volcanic landforms: stratovolcan, flow dome complex, caldera and maar.

In the Bucium Rodu-Frasin area only two volcanic landforms were identified: maars and flow dome complex, that display similar features with the ones described by Sillitoe and Bonham (1984). The maar has cone-shaped contour filled with a concave rock body known as diatreme. The flow dome complex is characterized by the presence of high-grade epithermal precious metal ± base metal deposits (veins, dissemination, breccias and stockwork).

2. Bucium Rodu-Frasin Maars

Maars are craterlike depressions with variable shape and size, which are surrounded by tuff rings (Sillitoe and Bonham, 1984). Diatremes represent the surface correspondent of maars. They are the result of repeated phreatomagmatic explosions and subsidence (e.g., Sillitoe and Bonham, 1984). The diatremes are cone-shaped rock bodies, which consist of mainly phreatomagmatic explosion breccias and base metal “vent breccias” (e.g., O'Connor et al., 2004).

The Bucium Rodu maar-diatreme has an elliptical shape (~ 1500/1000 m) with its long axis striking N-S, and the southern and eastern sides exhibiting an irregular contour. In contrast, the Frasin-Șeasa maar-diatreme is nearly circular in shape. Its diameter is about 1100 m. At the surface, between these two structures, there is a pile of Cretaceous sediments (~400 m thick) consisting mainly of sandstones, black shales and rarely conglomerates.

Both maar-diatremes are made up of poorly stratified breccias, which exhibit a polymictic character and a coarse-sorted appearance. Also, they may contain reworked pyroclastic rocks belonging to the diatreme walls (dacites, Cretaceous sedimentary blocks) and, only for Bucium Rodu maar-diatreme, hydrothermal products. Occasionally, inside the diatremes, there can be found the products of a Pliocene sedimentation, represented by argillaceous rocks with blocks and gravels with dominantly dacitic material. With thicknesses ranging from 8 to 10 m, they were recognized in the left slope of Radului stream, Șeasa Valley and Abruzel River. Many drillings performed in Rodu maar-diatreme area encountered levels of volcano-sedimentary deposits interbedded with intra-maar sequences, represented by fluvio-lacustrine siliciclastic deposits. The volcano-sedimentary deposits consist of interbedded pyroclastics and reworked breccias, sandstones and mudstones.

3. Flow dome complexes

Frasin Hill structure represents an endogene dacite dome with approximately N-S strike. It has a crescent shape that reaches 400 m in width in the central part. Other dacite occurrences lie in the right slope of Șeasa Valley and Abruzel River; small dacitic dykes were found in the drillings and outcrops from Rodu maar-diatreme and Frasin dome. Dome emplacement was, however, preceded by the pyroclastic eruption from diatremes. The ore deposits related to flow dome complexes are found as precious and base metals veins, stockwork, breccia fillings and replacement bodies. Ore deposits are located marginal or within the dome (Fig. 1), and were formed synchronously or postdate the dome formation.

4. Ore deposits

Ore deposition has been favored by: 1) the presence of shallow magmas rich in fluids; 2) the regime of high mobility and intense tectonic deformation, dominantly extension; 3) interacting master fault – strike-slip faults in a right-lateral system of extensional duplex; 4) gold-base metals mineralization occurrence in close genetic relationships with the hydrothermal breccias and phreatomagmatic fracturing; 5) existence of low-angle extensional faults; and 6) more permeable polymictic breccias at the lowest level of Rodu maar-diatreme complex.

The ore deposition had a pulsating character, and it probably developed in three stages. The mineralizing hydrothermal fluids probably had near neutral pH, the gold being transported as a bisulfide complex and deposited at temperatures of 150-230ºC (White, 2003 in Leary et al., 2004), while the main mechanism of gold precipitation seems to have been the first boiling (Hewson et al., 2005).

4.1 Composition of the ore deposits

The mineralisation belongs to the gold epithermal low-sulfidation style. The ore deposits consist of sulfides and precious metal minerals along with carbonates and quartz gangue minerals. The metallic minerals in the ore generally consist of fine-grained pyrite, marcasite, minor tetrahedrite, sphalerite, alabandite, manganese and iron oxides and gold.

Gold grains are associated with pyrite and sphalerite and are frequently included in carbonate minerals. They have irregular shapes and range in size from a few microns to visible grains. Usually, the gold grains can be found in small cracks, fissures and geodes, or inside the main conduit veins and fractures. Also, small concentrations at the intersection zones of the so called “chairs” (“scaune”) and veins with “crosses” (“cruci”) can be observed. According to White (2003, in Leary et al., 2004), the gold has been geochemically identified as “electrum”, and its fineness is between 695 to 740, averaging 722.

The most important mineral assemblages encountered in the Bucium Rodu-Frasin mineralization are the followings: a) pyrite - native gold in quartz - carbonate minerals; b) pyrite - native gold ± galena, sphalerite, chalcopyrite in quartz - feldspar - carbonate minerals; and c) in the Hărăcăi area, pyrite - native gold in clay minerals as veins, and pyrite - native gold in carbonate minerals as Au-Ag stockwork.

4.2 Mineralization

The mineralization contains minor pyrite, sphalerite, galena, chalcopyrite, tetrahedrite and gold in carbonate + quartz gangue. Magnetite and little hematite and sulfides probably formed in the mesothermal conditions (?) have been recognized only as metasomatic substitutions of some limestone clasts of supposedly Cretaceous age. The mineralization belongs to low sulfidation epithermal style (Leary et al., 2004) apparently emplaced in shallow conditions. It appears in the more permeable polymictic breccias at the lowest levels of the Rodu-Frasin maar-diatreme and flow dome complex structures. In addition, it is present within and immediately adjoining the Frasin dacite dome, as well as in Cretaceous sediments (Fig. 2). The mineralization can be classified, according to the deposition forms, in the following styles: 1) veins, 2) disseminations, 3) hydrothermal breccia in maar-diatreme breccias, and Cretaceous sediments, and 4) stockworks, in the Frasin dome and the contact breccias.

Mineralization in Rodu Frasin diatreme polymictic breccias and Frasin dome were formed syn- and post dome emplacement. According to accepted models of maar-diatreme formation (e.g., Lorenz, 1973), the mineralization within Rodu diatreme have been generated by a series of hydro-volcanic explosions triggered by the interaction of hot andesitic-dacitic magma and cool meteoric waters (c.f. Sillitoe et al., 1984). In contrast, the mineralization within Frasin dome occurred after the emplacement of the dacitic dome due to the circulation of hydrothermal fluids.

4.2.1 Veins

The pyrite-base metal sulfides-gold-carbonates (calcite, dolomite, rhodochrosite, aragonite) - quartz-adularia vein style is especially present in the Rodu maar-diatreme, where it occurs as single veins or/and vein sets, sometimes accompanied by Au-Ag disseminations and hydrothermal breccias.

The most important veins are mainly hosted by fractures concentrated in the western and eastern slopes of Meselor Hill. To the south, these veins do not extend beyond Radului stream. The total area covered by them is 400x400 m. The veins usually display NW-SE strikes. They show an “en échelon” tension veins distribution, being related to late normal movement on steeply east-dipping faults (acc. to Hewson et al., 2005). The most important veins are: Șperlea, Scaunul Cămarii and Scaunele Bradului, Crucile Bradului and Buhaiului (Ghițulescu and Socolescu, 1941).

In Frasin structure, the vein sets are located mainly in the northwestern part of Frasin Hill, where they form the Vipere vein system. This system consists of parallel veins with N and NW directions and 80-85° west dip (Berbeleac et al., 2004, unpubl.). They are approximately 50-150 m long, 0.15-0.40 m in thickness, and filled with carbonates, minor quartz, pyrite, marcasite and gold.

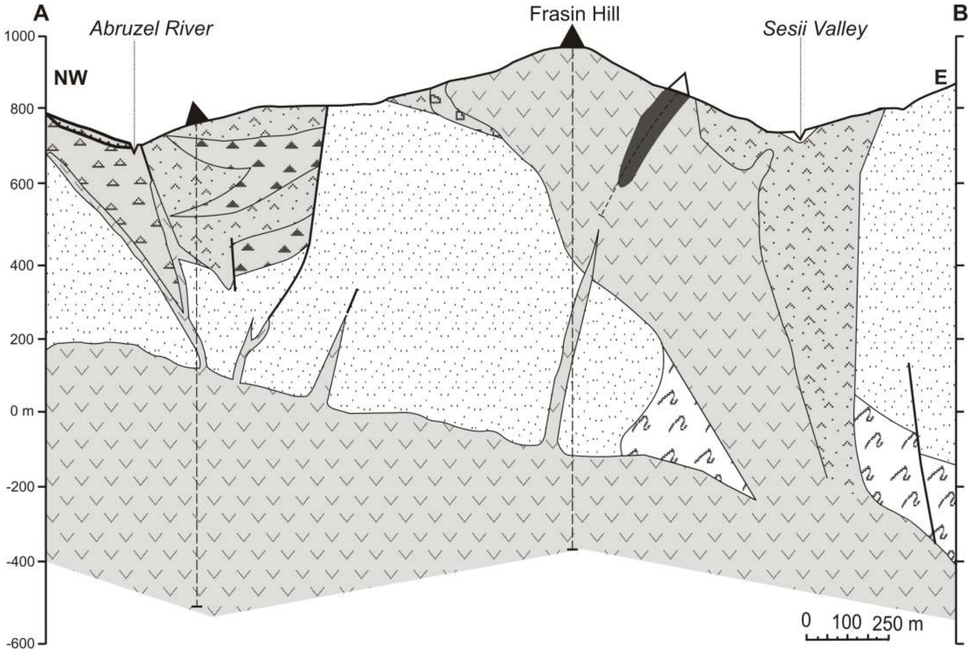

Fig. 2. Cross-section through Bucium Rodu-Frasin area (compiled using the drill core data from R.M.G.C., I.P.E.G., and authors' unpublished data). For legend, please see Fig. 1.

4.2.2 Disseminations and breccias

These mineralization styles occur locally, on Rodu shallow-dipping maar-diatreme polymictic breccias, the surrounding Cretaceous sediments, and in the shallow-dipping polymictic quartz-andesite breccias located along the eastern contact of the Frasin dacite dome. They appear as veins that usually contain angular blocks, especially near the vein margins. Adjacent to the veins there are interconnected irregular fissures, stockwork-like fissures up to 1 mm thick, which penetrate into veins and the host rocks.

In Rodu and Frasin area there are gradual transition zones from well-defined veins to breccia, then further, from stockwork zones to unmineralized breccia. In fact, the stockworks are ore dissemination zones, in some sections, which appeared as a result of intense deformation fissuring and brecciation, with mineralized breccias.

As a result of the gradual development of hydrothermal alteration and of the common fissuring and fragmented “jig-saw puzzle”, these breccias are distinctly different from volcanic polymictic breccias or volcanic conglomerates. Some parts of the breccias show evidence of multiple events of brecciation, cementation and reworking.

In Rodu area, from field observations, mining and drilling data, two zones of gold disseminations ± ore breccias can be outlined, namely the Meselor Hill-Radului Stream and Băișoara areas.

In Băișoara area, the disseminations and ore breccias exhibit features similar to those recorded in Meselor Hill and Radului Stream. However, they seem to be economically less important.

In Frasin area, the dissemination gold ore and the hydrothermal breccias occur in two zones related to the Frasin dacite dome: one in the eastern and northern contact zone of the Frasin andesite small dikes with volcaniclastic rocks and the other one, in the Frasin Hills central-south-west zone.

4.2.3 Au-Ag stockwork mineralizations

The eastern contact of the dacite dome with volcaniclastic rocks and Cretaceous sediments was the major pathway for ore fluids circulation. The southeastern extremity of this contact is one of the places where local conditions have been favourable to fluids circulation and ore deposition. Previously, the mineralization zone underwent an intense multi-stage deformation, consisting of high degree fissuring and brecciation, which can be observed in the drill cores.

The mineralization is situated at the intersection of E-W and NE-SW presumed faults with the dacite body. The host rocks, exhibiting high porosity and permeability, are represented by dacite and mono-/polymictic breccias. The dacite body underwent strong adularia, phyllic and carbonate alteration.

The stockwork with NNE direction reaches approximately 500 m in length, 250 m in width, and 350 m depths below surface. The westward and downward limits of the mineralization are unknown. Other NE and N-S promising zones remained untested (Leary et al., 2004).

5. Formation of the maar-diatreme complex

The maar-diatreme volcanoes have been addressed by a series of academic studies, many of which explained their genesis by means of phreatomagmatic eruptions (Wohletz 1986; Sheridan and Wohletz, 1983; Silitoe et al., 1984; Lorenz, 1986; Houghton and Smith, 1993; Büttner and Zimanowski, 1998; Zimanowski et al., 1997; Morrissey et al., 2001), and by hydromagmatic models (Lorenz, 2003). We favor the phreatomagmatic model, which takes into consideration the main role played by phreatic water joint aquifer, in magmatic eruptions and hard-rock environment. The interaction between cool meteoric water and dacitic magma has been manifested mainly as successive hydrovolcanic phreatic or phreatomagmatic explosions.

The maar-diatreme volcanoes of the Bucium Rodu-Frasin complex system are the result of lava interaction with groundwater, which led to brittle fragmentation of the magma volume quenched in this eruption process. The host-rocks fragmentation also took place (Zimanowski et al., 1997; Lorenz, 2003) because of the shock waves generated by the thermohydraulic explosions. The maximum explosive stage of these eruptions is reached when the water-to-magma ratios are especially low, approximately 0.3-0.5, and when the water and magma become well mixed and approach the thermal equilibrium (Sheridan and Wohletz, 1983). It is also known that the highly explosive conditions represent a transient eruptive phase, associated either with initially low contents of groundwater, or with the exhaustion of the available water supply during the eruption. With concern to the growth and the shape of the Rodu and Frasin-Şeasa craters, it is important to retain that the maar grows as a crater when walls collapse into successively deeper and wider conduits (Lorenz, 1986), and the pre- and sin-faulting and fracturing clearly played an important role in establishing the maar shape. Along its way to the surface, the groundwater, due to decompression, enters in condensation, fact which leads to the fallout of a large part of the pyroclastic-epiclastic products and their deposition on the crater floor. Such a succession of events results in the bedded distribution of the deposits inside the maar-diatreme. In general, the schematic diagram of Rodu volcano shows its cone-shaped diatreme with a lower level undeformed, and an upper level including pyroclastic beds interbedded with reworked pyroclastic beds with some unconformities due to collapse events, dikes, feeder vents and bedded diatreme facies; maar- post eruptive sediments are situated outside the cross-section line. Similar forming processes have been recognized at Roșia Montană and Truții Valley-Măgura Porcului (Vălișoara) areas. In comparison with Lorenz model (Lorenz, 2003), our model, chosen along the cross-section line, shows some differences, such as : 1) the Rodu diatreme consists of two parts separated by a Cretaceous block, one on the left slope of Abruzel River, composed of two feeder dikes, while the other one, on the right slope of Abruzel River, seems to be an apparently younger satellite structure, built up of black breccias and black shales, and 2) at the Rodu diatremes there is no root zone with explosion breccia rooms and un-bedded diatreme facies.

CONCLUSIONS

The most important observations and conclusions of this paper comprise: i) identification of the factors (tectonic, lithologic, petrographic, landform, etc.) controlling the location of the gold mineralizations, in direct correlation with associated structures - towards the outer boundaries of the maar-diatreme, and the central part of the flow dome; ii) explanation of the development and lithological variations in the evolutionary process of the maar structure; iii) for the first time, reports the presence of argillaceous rocks with blocks, and black breccias in Bucium Rodu maar-diatreme; iv) the development of a new structural image for Bucium Rodu-Frasin area.

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NEW SULFOSALT ASSOCIATIONS FROM SĂCĂRÂMB Au-Ag-Te ORE DEPOSIT. PRELIMINARY DATA

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Abstract: There are over 100 mineral species described at Săcărâmb Au-Ag-Te ore deposit, many found in connection with highly valued telluride mineralizations. The unusually diverse chemistry of the Săcărâmb ore deposit is also reflected in the compositions of the sulfosalt associations. By optical observation and chemical analyses on the the massive alabandite mineralization there has been identified a new mineral association Sb- As- Pb- and Mn- sulfosalts which comprises of famatinite-luzonite and benavidesite never described before at Săcărâmb. Further on there are Ag- bearing sulfosalts andorite and the Ag-Cd bearing quadratite which is described and documented for the first time in Romania and for the second time in the world.

Key words: sulfosalts, alabandite, famatinite-luzonite, andorite, quadratite, benavidesite, Săcărâmb.

Introduction - Geological setting

The Săcărâmb Au-Ag-Te ore deposit is located in the Metaliferi Mountains in Romania and it is best known for the famous Au-Ag tellurides; it is the largest telluride mineral accumulation in Europe with a total of 14 minerals containing Te, Au and Ag which some where first described at Săcărâmb: krennerite by vom Rath (1877), petzite by Haidinger (1845), nagyagite by Haidinger (1845), muthmannite by Zambonini (1911), museumite by Bindi and Cipriani (2004), etc. (Cook et al., 2004).

From the most recent studies, Săcărâmb is a calc-alkaline andesitic type structure with epithermal low-sulfidation-rich veins (Au, Ag, Pb, Zn), generated by the Neogene calc-alkaline volcanism (Vlad and Orlandea, 2004). Release of each batch of precipitate from the fluids is accompanied by partial replacement of previously formed phases. Shear assisted brecciation and syn-deformational deposition is characteristic of the veins at Săcărâmb (Ciobanu et al., 2004).

This ore deposit is a „mineralogical hot spot” not only because of the tellurides but for the large diversity of the described mineral species. Over 100 mineral species have been identified in the Săcărâmb ore deposit. One of the most recent mineral assemblages researched are selenides with three possible mineral species described: eucairite - CuAgSe (first described at Săcărâmb in 1853 by Kengott), naumannite - Ag_2Se and klockmannite - CuSe. (Popescu et al., 2013).

Despite its mineral diversity, from the last half of the 20th century the mineralogical studies, mainly focused on the Au-Ag telluride assemblages. This was caused by the economical necessities of Romania and because of the extensive exploitation in the 19th century of the base- metal sulfosalts ± tellurides mineralizations, situated in the upper zone of the andesitic neck.

This paper presents the results of a microscopic study of 27 polished sections taken from three waste dumps (Sector 1; Sector 2; Sector 3 at Săcărâmb). This paper manly focuses on three samples S3- sector 3; S6- sector 2 and C3-sector 3. The microscopic observations were carried out on a Leitz Wetzlar reflected light microscope. The microscopic images were taken using a PANPHOT microscope equipped with a Nikon Eclipse E - 400, 40 W camera. The chemical analysis where performed with a Zeiss Merlin GEMINI II column SEM-EDS with a working regime of: up to 300 nA; accelerating voltage 0 - 30 kV.

Results and Discussions

All of the discussed mineral assemblages are hosted by carbonate-quartz veins that formed after the precipitation of alabandite. This might indicate that the presence of massive alabandite created a perfect reducing environment hence the scarce presence of pyrite or arsenopyrite (frequently found in Săcărâmb ore deposit) and abundance of sulfosalts.

In the S3 sample the mineral association consists of: galena, sphalerite, alabandite, pyrite, tetrahedrite, tellurides and sulfosalts, famatinite-luzonite.

In sample S6 it was observed an alabandite, sphalerite, galena, sulphosalt and pyrite association. In this sample we have a larger concentration of sulfosalts, first of all has been observed an intergrowth texture between veenite (?) $Pb_2(Sb,As)_2S_5$ and galena; boulangerite ($Pb_5Sb_4S_{11}$) in quartz veins with geocronite ($Pb_{14}(Sb,As)_6S_{23}$) and dufrenoysite ($Pb_2As_2S_5$) in alabandite, famatinite-luzonite with galena, silver rich tetrahedrite, manganese rich sphalerite, pyrite, stibnite, chalcopyrite and silver suplhosalts.

In the sample C3 it was identified an alabandite, sphalerite, pyrite, galena, sulphosalt and telluride association. The optic determination of the specified mineral assemblages was confirmed by microprobe analyses.

Famatinite-luzonite series, (Cu_3SbS_4 to Cu_3AsS). It is the most widespread new Săcărâmb sulfosalt found in our samples. This series appears in association with galena, alabandite, sphalerite, pyrite, Ag rich tetrahedrite and in some assemblages it is found with chalcopyrite, geocronite-jordanite, silver sulfosalts, stibnite.

Optically it appears pinkish brown, with moderate anisotropism, widespread polysynthetic twins (Plate II 2c, 2d). We note the variable geometry of this assemblage; it can form borders on alabandite and tetrahedrite or it can form small patches in relationship with galena and sphalerite. Compositional variation (Table 1) is strongly related to the Sb-As ratio, highly influenced by the associated minerals, which is why it was not found a clear end member from this series. Furthermore it is noted that the rich stibium assemblage always appears with stibnite.

Table 1: Chemical composition of famatinite-luzonite from Săcărâmb, calculated formula in the basis of 3 Cu atoms

Element	P63	P67	P76	P80	P82	P89	P102	P103	Average
Ag	0.87	0.45	0.55	0.20	0.17	0.00	1.09	1.15	0.56
Fe	0.28	0.00	0.00	0.12	0.00	0.03	0.15	0.08	0.08
Pb	0.00	1.12	0.00	1.56	1.68	1.31	2.01	1.98	1.21
Zn	1.10	0.74	4.34	0.90	1.04	0.73	0.84	0.82	1.31
Cu	49.68	49.07	44.07	45.74	47.05	38.11	46.90	47.40	46.00
Sb	3.22	4.23	17.26	18.13	21.07	25.82	1.95	2.31	11.75
As	16.55	15.62	5.08	5.61	0.00	8.45	16.41	16.05	11.91
S	28.06	27.42	28.69	27.62	28.14	25.55	30.03	29.03	26.63
Total	99.76	98.65	99.99	99.88	99.15	100.0	99.38	98.82	99.45
Average Analyses Calculated Formula:									**$Cu_3As_{0.65}Sb_{0.4}S_{3.44}$**

Andorite, $PbAgSb_3S_6$ It was identified in the S6 sample in association with galena and famatinite-luzonite. Optically is light grey, moderate pleochroism, strong anisotropy with no distinct colors (Plate I 1b; II 2c) (Picot and Johan, 1982). Chemically it is very similar to andorite (Table 2) however because of the rich manganese environment, lead could be substituted by manganese, further studies are necessary to confirm if this is a manganese variety of andorite.

Table 2: Chemical composition of andorite from Săcărâmb, calculated formula in the basis of one Ag atom

Element	P6	P73	P74	P75	P82	P90	P91	Average
Ag	12.19	14.87	14.25	13.9	12.83	14.63	14.18	13.84
Mn	1.94	1.29	1.59	2.48	2.27	2.49	2.29	2.05
Sb	43.66	45.95	44.05	43	43.76	44.59	43.78	44.11
Pb	20.05	16.18	18.58	19.17	20.32	16.84	17.04	18.31
S	21.82	21.71	21.58	21.23	20.82	21.45	21.55	21.45
Total	99.66	100	100.05	99.78	100	100	98.84	99.76
Average Analyses Calculated Formula:								**$Ag(Pb_{0.69}Mn_{0.29})_{0.98}Sb_{2.83}S_{5.23}$**

Quadratite, $Ag(Cd,Pb)(As,Sb)S_3$. High cadmium concentrations were found in the waste dump samples from Săcărâmb and cadmium was correlated well with zinc which is a normal since cadmium rich sphalerite has been reported in Săcărâmb waste dumps (Popescu et al. 2013). However in the sample S6 it was found quadratite, $Ag(Cd,Pb)AsS_3$, a silver suplhosalt with a tetragonal crystal structure which has cadmium in its chemical structure. It appears as small subhedral grains in carbonate veins crosscuting alabandite. Optically it is grey-white, isotropic and it shows extensive red internal reflections (Plate I 1c and Plate II 2e,f), highly similar with the proustite-pyragyrite series. Quadratite is a rare mineral and it is only found in Lengenbach, Binnental (Switzerland) in cavities, in the white Lengenbach dolomite; it forms quadratic and orthogonal shaped crystals. Quadratite exclusively occurs together with low As phases, mainly in association with galena, jordanite, pyrite and sphalerite (Graeser et al., 1998).

The chemical composition of Săcărâmb quadratite (Table 3) is highly similar with the Lengenbach quadratite however manganese appears in its chemical structure. Recently in Uchucchacua, Peru it was discovered manganoquadratite, $AgMnAsS_3$ a manganese bearing sulfosalt with a similar crystal structure as quadratite, the authors presumed the possibility of Mn-Cd substitution (Bonazzi et al. 2012). It is highly probable that with further investigations of the newly discovered Săcărâmb quadratite to demonstrate an isomorphous series between quadratite and manganoquadratite.

Table 3: Chemical composition of quadratite from Săcărâmb, calculated formula in the basis of 3 cation atoms (Ag+As+Cd+Mn+Pb+Sb)

Element	P93	P97	P98	P94	Average
Ag	28.73	33.39	28.45	30.21	30.2
Mn	5.20	4.61	4.64	6.21	5.17
Cd	17.74	15.30	17.27	17.56	16.97
As	20.11	20.23	21.37	21.02	20.68
Sb	0.78	1.03	1.28	0.48	0.89
Pb	2.37	2.29	1.88	0.00	1.64
S	23.97	22.32	24.29	24.29	23.72
Total	98.90	99.17	99.18	99.77	99.26
Average Analyses Calculated Formula:					$\mathbf{Ag_{1.02}Cd_{0.55}Mn_{0.34}Pb_{0.029}As_{1.01}Sb_{0.027}S_{2.72}}$

Benavidesite, $Pb_4MnSb_6S_{14}$ In the sample C3 it was observed an alabandite, sphalerite, pyrite, galena, sulphosalt and telluride association. In this sample it was discovered, small vugs of neddle like sulphosalt (Plate I- II 1a,b; 2a,b), with all the optical characteristics of jamesonite ($Pb_4FeSb_6S_{14}$), grey color, blue to grey anisotropy (Picot and Johan, 1982), but what is interesting is that the vugs were formed in the massive alabandite. The chemical composition (Table 4) indicates the manganese end member of the jamesonite-benavidesite series and it is logic because benavidesite only occurs with alabandite and manganese sphalerite both present in our sample.

Table 4: Chemical composition of benavidesite from Săcărâmb, calculated formula in the basis of 11 cation atoms (Mn+ Sb+Pb)

Element	P16	P19	P21	P22	Average
Mn	2.69	2.86	2.78	3.8	3.03
Sb	34.5	34.09	33.7	33.67	33.9
Pb	42.9	43.06	41.99	42.43	42.5
S	19.83	19.57	19.88	20.09	19.8
Total	99.92	99.58	98.35	99.99	99.46
Average Analyses Calculated Formula:					$\mathbf{Pb_{4.1}Mn_{1.1}Sb_{5.68}S_{12.6}}$

Conclusions

It is evident that the Săcărâmb Au-Ag-Te ore deposit can still produce many mineralogical surprises. Despite its worldwide fame for the Au-Ag tellurides, a comprehensive description of the mineral assemblages which are found in the alabandite rich zones remains to be undertaken.

Săcărâmb ore deposit is known for its sulphosalt association especially Sb and As, it was found a new suplhosalt associations in the carbonate veins which crosscut alabandite.

It is evident that the reduced environment created by the presence of alabandite to permit the precipitation and formation of the identified sulphosalts in these samples. Based upon textural relationship it is interpreted that alabandite, galena, chalcopyrite and tetrahedrite represent the first mineralogical stage, followed by the second stage with sphalerite, second generation galena, bournonite-selligmanite, famatinite-luzonite and a last with geocronite-jordanite, dufrenoysite, benavidesite, stibnite, andorite and quadratite. This depositional sequence indicates a metal composition transition from Mn-Pb-Cu-Zn to Zn-Cu-Ag-Pb-Sb-As-Te and to Pb-As-Mn-Fe-Ag-Cd.

Furthermore it is confirmed the presence of Ag sulfosalts, the minerals are minor constituents of the ore but indicate the diverse chemistry of the Săcărâmb ore deposit.

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Plate I

SEM-SE images of : (a) benavidesite (Ben) vug in alabandite ; (b) andorite (And) with galena (Gal) and stibnite (Stb) in luzonite-famatinite (Luz-Fam); (c) quadratite (Qdt) developed on a euhedral pyrite (Py) in carbonate (Cbt) vein;”(d) luzonite-famatinite with stibnite (Stb) and alabandite (Alb)

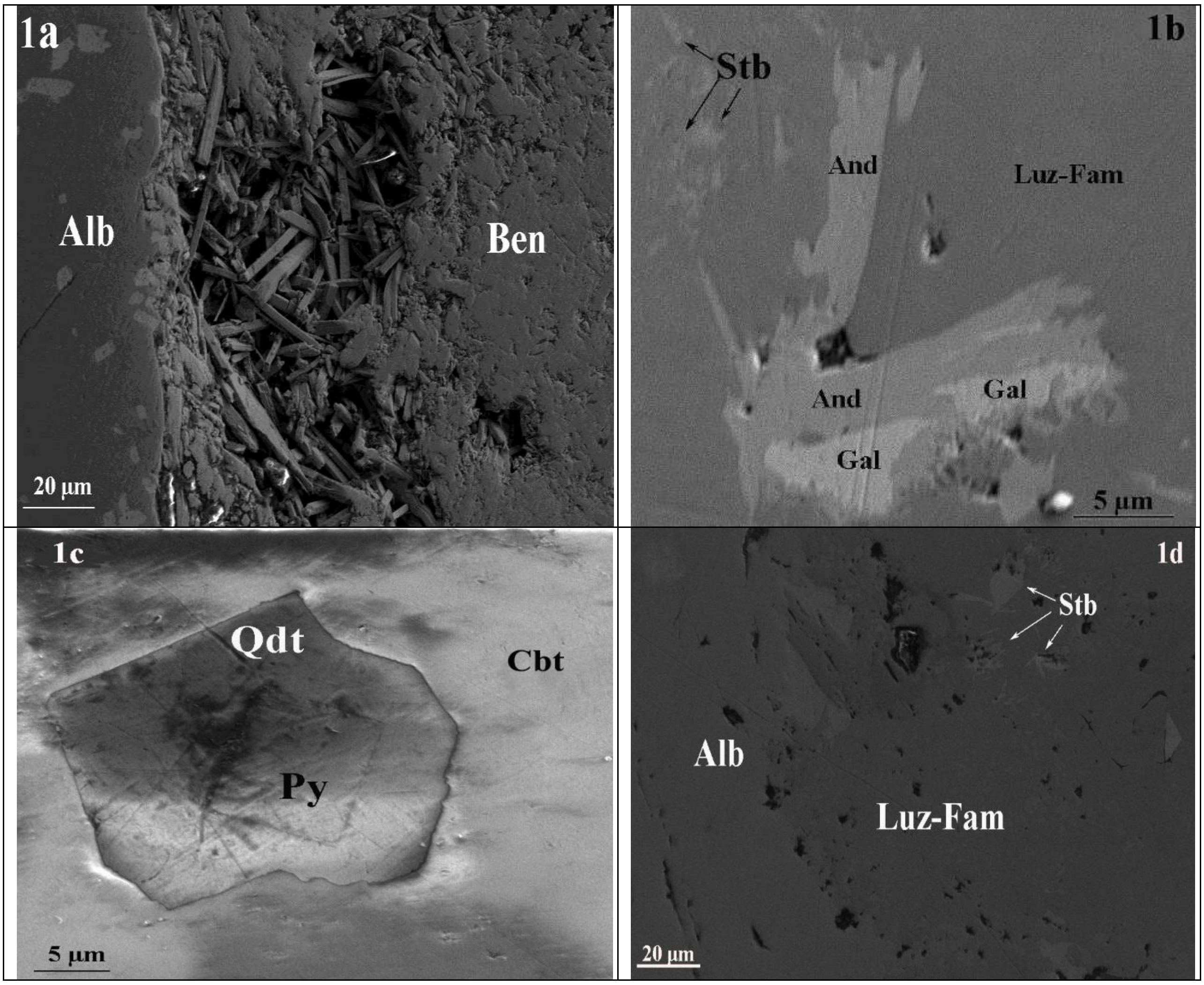
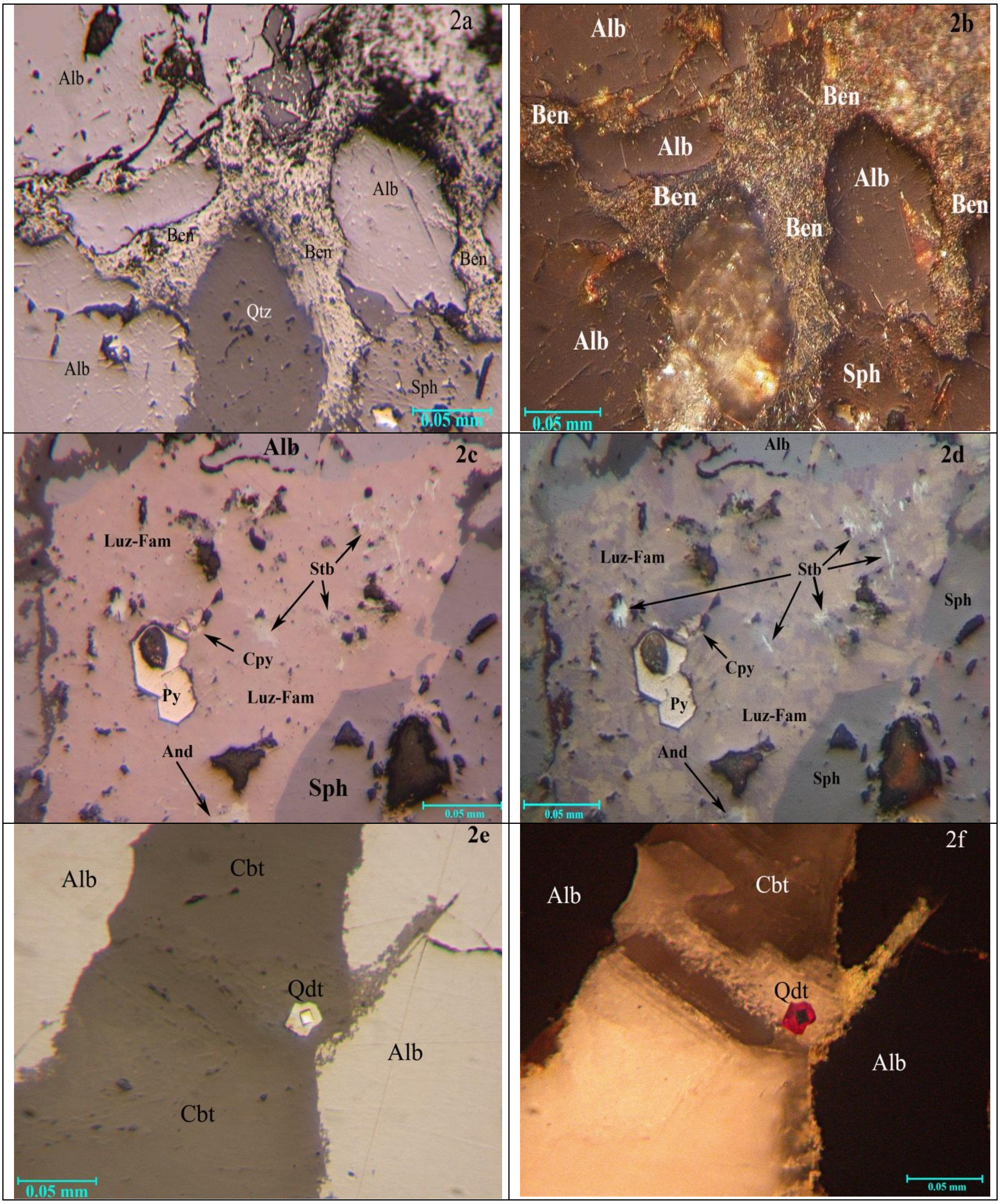


Plate II

Photomicrographs (reflected light) illustrating the sulphosalts identified in the Săcărâmb samples: (a,b) benavidesite (Ben) vug associated with sphalerite(Sph) in alabandite (Alb) in parallel and crossed polarized light; (c,d) mineral assemblage of luzonite-famatinite (Luz-Fam), Pyrite (Py), alabandite (Alb) sphalerite (Sph), stibnite (Stb), chalcopyrite (Cpy) and andorite (And) in parallel and crossed polarized light; (e,f) quadratite (Qdt) cristal in carbonate (Cbt) vein that cross-cuts alabandite (Alb) in parallel and crossed polarized light.



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THE EFFECTS OF MINING ACTIVITIES FROM CAMPU LUI NEAG AND IDENTIFICATION OF AFFECTED AREAS

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Abstract: The presence of coal deposit in Petrosani Depression has been the reason of the economic and social development in the area. But in time, the mining activity has created a landscape of bad land which oppose with the natural one. Campu lui Neag area has been affected by the mining activity which has created anthropogenic landforms, both positive (dumps) and negative (coal pit), which evolution over time is unpredictable. The paper aims to present the affected geomorphologic resources and to propose a rehabilitation method wherewith the area will revive in terms of economic development.

Key words: mining activity, coal, coal pit, sterile dump, rehabilitation, economic development

1. Introduction

Social and economical developments of Petroşani depression has accelerated the transformations of environmental components, and the answer may be noticed by highlighting the conflicting relations on the field. As technological development and spatial extension of anthropic areas, was an amplification of the conflicting relationships with the natural environment (Bradshaw, 1997, Filip, 2008).

The landscape of Petrosani Basin is transformed by summed actions and processes of the past through the present and continue into the future. This amount of processes is present and constant, even if in time, the content and proportions of the different elements change and adjust sometimes approaching to balance, but never really touching it (Buia, Rădulescu, 2002). Anthropic landforms resulted from coal mining activities give a discordant note in the natural landscape of the depression, but hidden potential that it holds can bring economic benefits by exploiting it by the local communities for tourism or recreation.

A specific of Petroşani mountain valley mining activity is the existence of derelict coal pits and sterile dumps due to the profitless exploitation and Câmpu lui Neag area is a part of it.

2. Regional setting

Petroşani Depression is a lowered region in the Carpathian mountains (Romania), but is considered a high mountain depression with a hilly bottom, with the lowest altitude of 556 m (at the confluence of the two Jiu rivers) and highest among 800-900 m on the periphery in the contact area with the mountain frame (Ardeiu, 2004, Badea, 1971, Lupu, 1967, Mutihac, 1990, Geography of Romania III, 1987).

Câmpu lui Neag is a mining area located in the western part of this depression (Figure 1), where the mining activity has stopped in the late 90's. The coal pit from here was the first one closed from the entirely mining basin. The terrain morphology is hilly, the alluvium bent of the Western Jiu is a flat area having a minimum height of 785 m, and the maximum of 1005 m to the contact of sedimentary area with Northern crystalline frame.

Maximum absolute altitudes are in the mountain area, where the Păroasa Hill has an altitude of 1436 m and dominates the whole area. There are small differences in level between the Jiu Valley alluvium bent and the contact with the mountain frame, so the region is presented in the form of a small hills area. General orientation of these small hills is North-West or South-West.

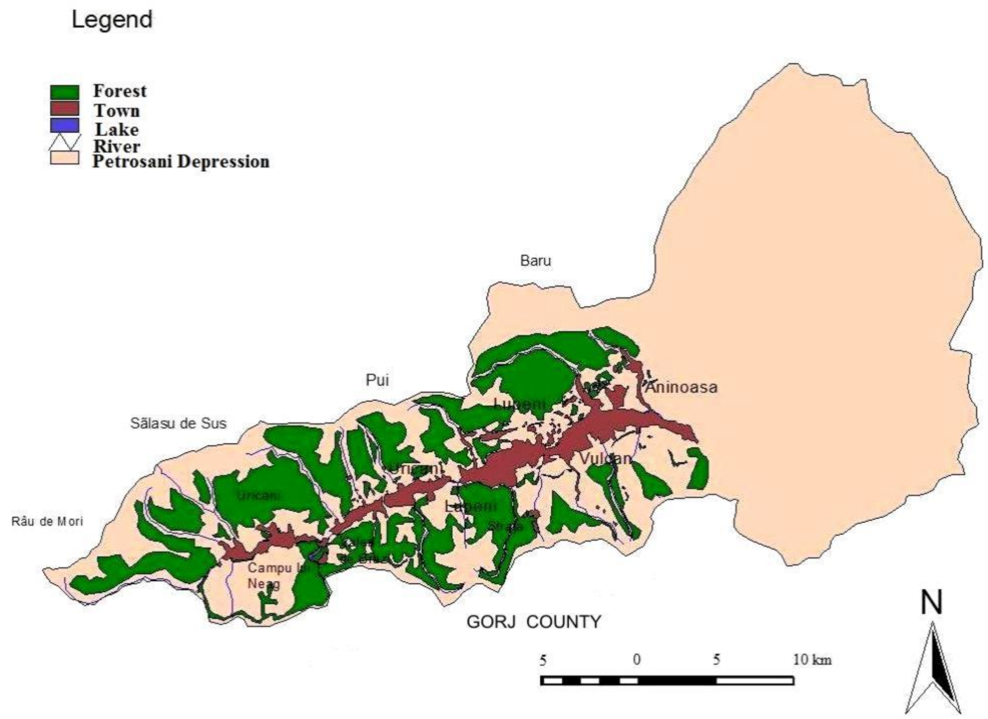


Figure 1. Localization of Câmpu lui Neag area in the western part of Petroşani Depression

3. Geology of the study area

Petroşani basin looks like a large synclinal elongated on NE-SW direction, with asymmetrical profile and angled at 75º-90º on the northern flank, or even inverted and rode on the crystalline-Mesozoic rim. Southern flank has a lower inclination of between 30º-70º-60º to 70º eastern half and in the west. Faults of particular importance are: the northern marginal fault and southern marginal fault, largely flanking the basin. In addition to the two major faults were identified a number of faults, which, by their direction on the synclinal axis can be: longitudinal, transverse or oblique. Oscillatory movements and subsidence movements have played an important role in the conduct of sedimentation. Subsidence movements influenced thickness of layers, layer composition of rocks, structure and texture of rocks, sedimentation rate and accumulation of sediment and position in space complexes sediments. Sedimentary fill of Petrosani Basin has in its constitution, six units grouped into five litho-stratigraphic formations (Mutihac, 1990).

Sandstones are found in a ratio of 55-60% in the western part of the basin, is present in all lithostratigraphic horizons. They are generally gray, from pale whitish to dark black. From the point of view of graininess, it is frequently found in sandstone fine grain (<0.05 mm), coarse (0.05-2 mm) and less the average grain size (0.05-0.5 mm).

Clays are found in a high proportion in the whole basin, are present in all lithostratigraphic horizons. The most important varieties encountered are clays, clay marl, shale clays. It shows a dark gray, red or greenish-purple and productive horizons are usually located in the roof layer of coal when their color is gray.

Marls are presented in the basin, but in much lower proportion than the other two types of rocks. Marls are found in basal horizon of red or greenish-purplish color in a rate of about 5%, in the productive horizon are found in a ratio of 7%, with the higher rate in the western part.

A mix of *lime stones and marls*, micro conglomerates are present in a small proportion compared with marl.

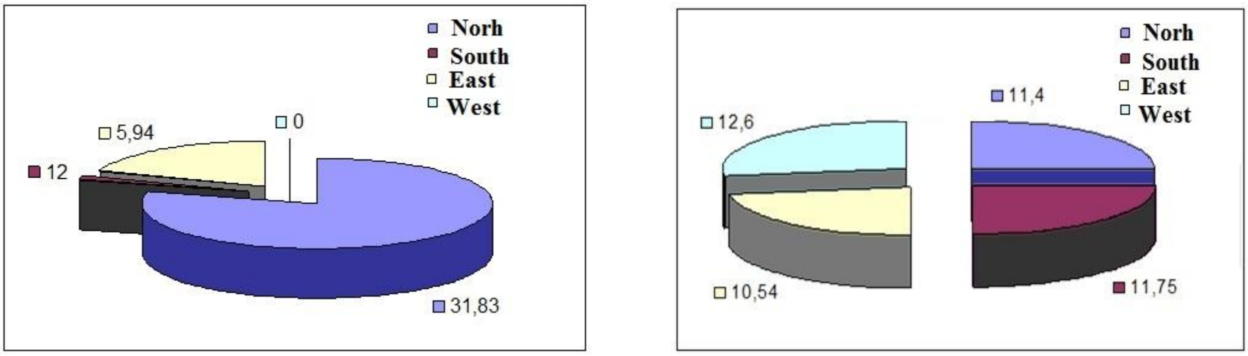
4. Discussion

There are lots of man made landforms in the western part of Petroşani depression, but the most important are: Câmpu lui Neag coal pit (Figure 2) and Poiana Mare and Șesul Șerbanilor sterile dumps.

Figure 2. Câmpu lui Neag coal pit

In the Câmpu lui Neag area, the land exhibition was originally predominantly northern, totaling an area of 31.83 ha. After human intervention, these surfaces takes a new configuration and exhibition with a western exhibition areas of 12.6 ha. It can be said that changes to the original land were significant in quantitative terms, given that the fact that the west exhibition areas did not really exist (Nimară, 2010).

The coal pit exploitation from Câmpu lui Neag area that has affected the Păroasa Hill, worked until 1997, being the first enclosed within the deprivation processes in the Petroşani Mining Basin. The occupied area by the former mining activity from Câmpu lui Neag represent approximately 7.5 hectares (758442 m^2) currently being flooded (figure 3), (Nimară, Buia, 2013, Development map of Jiu Valley, 2010).



a. b.

Figure 3. Land exhibition
a. initial land, b. anthropic land

Coal extraction activity started in coal pits such as:

- coal pit area A + C is located to the west of the main building and to the North of DN 66A road (figure 2);
- coal pit area E is located to the North of Western Jiu river and to the East of the main building;
- the small coal pit Buta is located on the left bank of Western Jiu river, downstream of Buta brook;
- the small coal pit Galbena is located on the right bank of Western Jiu river, în close to Mandeşti brook;
- the small coal pit, is located to the North-West of Poiana Mare sterile dump;

5. Conclusions

The affected areas by the mining activities from Câmpu lui Neag areas are the Păroasa Hill (the southern part). The rehabilitation works of the mining area were completed in 2002, and in 2006 was found out that in the mining precinct there are buildings which need to be demolished, are damaged or have not been used appropriately. Rehabilitation of pit slope assumed strengthening both current lake shore (in the South and Southeast) and creating a flat surface approximately 400 m long and 100 m wide, located near the 66A national road. This area of land has been consolidated and leveled using material from Poiana Mare sterile dump. In the Câmpu lui Neag area, the land exhibition was originally predominantly northern, totaling an area of 31.83 ha. After human intervention, these surfaces takes a new configuration and exhibition with a western exhibition areas of 12.6 ha.

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INFRAPROTEROZOIC „MINERALIZED BACTERIA” IN LETEA LEVEE SAND – DANUBE DELTA

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Abstract. Among the heavy minerals present in the finest granular fraction of the sands from Letea levee it has been discovered a grain composed by goethite and marcasite. At a closer look (analyzed with an electronic microscope) this grain presented a particular framboidal structure that raised some question marks. After looking up through the related literature the conclusion was that this structure mimed a bacterial one composed, as revealed by the optical observations and confirmed by SEM analyzes, of goethite, marcasite, silica and relicts from organic matter. The most accessible and closer source of origin for this in the Kryvyi Rih/ Krivoi Rog (Ukrainian: Кривий Ріг) Paleoproterozoic BIF’s (banded iron formations).

Key words: mineralized bacteria, Letea, Danube Delta, Krivoi Rog, BIF

1. Introduction - Localisation and geological context

The Delta formation assumed a combination of several conditions without which this relatively young unit would not have been generated in its current form if it had not been initially a golf Liman type (triangular), where the deepening of the self is done gradually (up to 180-200m over a distance of 180 km), the tides have a low amplitude (not contribute significantly to the process of removing the deposited sediment) - 9-11 cm, and the transportation of sedimentary material by the coastal currents resulted in large amounts of sediments brought by the Danube (Gâștescu and Știucă, 2008).

The sampling spot is located in the Letea Levee near the Buna Vestire Delta Monastery just under the surface in the sand dunes (Fig. 1).

Figure 1: The Letea Levee map with the position of the P4 sample near the Buna Vestire Delta Monastery

2. Analytical methods

The sample was obtained during a sampling campaign in 2012 that tried to make a general overview of the sand from the Letea levee. A number of 15 samples (P1-P15) have been collected, each in a separate plastic bag and transported to the laboratory where they have been separated on grain size fractions. The results of the X-ray fluorescence, microscopic and granulometric investigations are presented in Negrea et al (2014). Of interest for the present paperwork was P4 sample represented by the finest grain size fraction: 125-56 µm. It has been first observed under the binocular magnifier loupe (Stemi 2000-C Zeiss), X-ray diffraction analyzes was conducted after that and, finally, a small amount of sand was embedded in acrylic resin and resulted in a polished section and in a thin section (to be observed in polarized light with a Carl Zeiss Jena Amplival Microscope). The microscopic images were taken under a PANPHOT microscope equipped with a Nikon Eclipse E - 400, 40 W camera (Fig. 2b). All the optical analyses were made in the Department of Mineralogy, at the Faculty of Geology and Geophysics, University of Bucharest.

A small mineral grain (50 µm width and 100 µm long) was microscopically identified and more detailed analyzes were made with a scanning electron microscope (SEM, Hitachi S-2600 N,5 kV) with energy-dispersive X-ray (EDAX/2001) at the Faculty of Applied Chemistry and Material Science, The National Centre in Applied Chemistry and Material Sciences (BCUM), Polytechnic University of Bucharest (Fig. 2 and Table 1). Image analysis was performed with the backscattered electrons (BSE) with 5.0 nm resolution (at 25kV in the variable pressure), the pressure domain was of 1-270 Pa; the magnification ranged from 15x to 300.000x brought by METAV and qualitative and quantitative microanalysis by dispersive X-ray spectrometry energy.

Table 1: The results of the SEM analyzes presented in Fig. 2: spot 1- goethite, silica and relicts from organic matter, spot 2 – marcasite and relicts from organic matter, spot 3 – goethite and relicts from organic matter.

The analyzed spot	Element	Wt %	At %	K-Ratio	Z	A	F	Net Inte.	Bkgd Inte.	Inte. Error	P/B
1	C K	27.54	45.51	0.0624	1.0588	0.2139	1.0004	29.14	0.5	3.84	58.58
	O K	28.63	35.52	0.0702	1.0426	0.2349	1.0011	98.11	0.75	2.07	131.5
	AlK	0.5	0.37	0.002	0.974	0.4154	1.0033	7.21	4.14	11.11	1.74
	SiK	7.24	5.12	0.0397	1.0029	0.5458	1.0018	132.84	5.93	1.84	22.41
	P K	0.55	0.36	0.0032	0.9702	0.6018	1.0027	10.28	7.21	9.84	1.43
	S K	1.31	0.81	0.0093	0.9959	0.7094	1.0034	28.97	9.41	4.86	3.08
	CaK	1.07	0.53	0.0102	0.9762	0.9493	1.027	25.2	8.66	5.27	2.91
	FeK	33.16	11.79	0.3014	0.8952	1.0151	1	394.66	7.13	1.04	55.36
	Total	100	100								
2	C K	34.77	55.56	0.0566	1.0519	0.1548	1.0003	31.92	1.69	4.42	18.9
	O K	19.27	23.12	0.0366	1.0359	0.1832	1.0009	61.75	1.35	3.08	45.71
	SiK	5.05	3.45	0.0311	0.9965	0.6131	1.0071	125.59	6.08	2.22	20.66
	P K	0.54	0.33	0.0036	0.964	0.6781	1.0117	13.57	7.09	9.21	1.91
	S K	14.07	8.42	0.1084	0.9895	0.777	1.0026	409.37	8.67	1.2	47.22
	CaK	0.6	0.28	0.0054	0.9694	0.9126	1.0175	16.04	8.84	8.59	1.82
	FeK	25.71	8.83	0.2302	0.889	1.0073	1	363.94	6.42	1.27	56.71
	Total	100	100								
3	C K	34.77	55.56	0.0566	1.0519	0.1548	1.0003	31.92	1.69	4.42	18.9
	O K	19.27	23.12	0.0366	1.0359	0.1832	1.0009	61.75	1.35	3.08	45.71
	SiK	5.05	3.45	0.0311	0.9965	0.6131	1.0071	125.59	6.08	2.22	20.66
	P K	0.54	0.33	0.0036	0.964	0.6781	1.0117	13.57	7.09	9.21	1.91
	S K	14.07	8.42	0.1084	0.9895	0.777	1.0026	409.37	8.67	1.2	47.22
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	FeK	25.71	8.83	0.2302	0.889	1.0073	1	363.94	6.42	1.27	56.71
	Total	100	100								

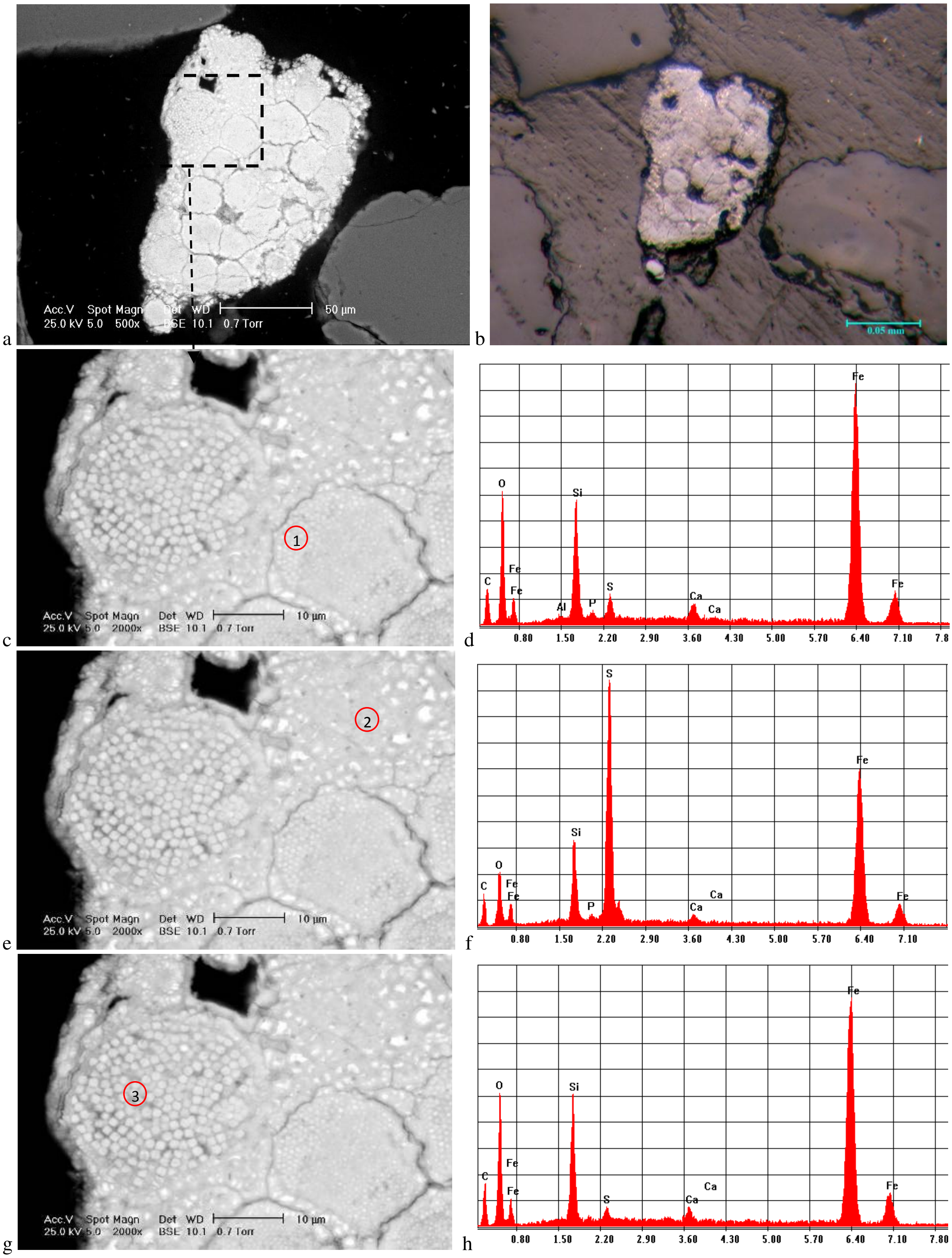

Figure 2: Microscopic images of the analyzed sample (P4) in polished section: a – on electronic microscope (SEM); b – on chalcographic microscope (N//); c, e, g – detail showing the analyzed spot; d, f, h – diagrams presenting the results detailed in Table 1

3. Results

The observation made under the binocular loupe showed that the fraction (125-56 μm.) of the sand sample P4 was composed by 60% quartz, 20% feldspar, 5% opaque minerals, 15% other minerals (especially heavy minerals).

The X-ray diffraction confirmed that the principal minerals present in the fine fraction of P4 are: anatase, calcite, clinochlore, quartz, dolomite, feldspar, muscovite, rutile and spinel. The observations made under the polarized light microscope lead to the identification of garnet, sericitized feldspar, hornblende and chlorite.

The results of the SEM analyzes confirmed that the particles composing the grain were goethite ($FeO(OH)$), marcasite (FeS_2) and silica (SiO_2). Some traces of organic compounds were also present.

4. Conclusions

Similar structures, called „mineralized bacteria" are presented in Ramdohr (1969) and they are clearly related to the sulphur bacteria. Ramdohr also stipulates that these grains are also very resistant to recristalizations. The mechanism of banded iron formation (BIF) has been interpreted to reflect ferrous iron (Fe^{2+}) oxidation, under anoxic conditions by molecular oxygen after cyanobacteria evolved on Earth (Kapple et al., 2005). Cloud and Licari (1968) analyzed the microbiotas that can be found in the BIFs and they are very similar to the images of goethite and marcasite presented in this paperwork. Panin (2005) interpreted (by studding the marine currents and analyzing the drill samples) the considered area as a fluvial-maritime levee and the continental sediments are provided by the: Danube, Dnister, Dniper and Southern Bug. Our results confirm the sedimentological interpretation of Panin (2005). Our mineralogical investigation on the relict found in the sedimentary sand from Letea Levee points toward an origin in the Krivoi Rog giant iron deposit - where BIFs occur. The age of the Krivoi Rog BIFs is Paleoproterozoic (Ilyin, 2009). The transportation agent was the Dniper River by its tributary stream, Ingulet.

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HEAVY METALS IN VEREDA'S SOIL OF THE FORMOSO RIVER BASIN, BURITIZEIRO, MINAS GERAIS, BRAZIL

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Abstract: This paper presents the geochemical data distribution of Cr, Cd, Cu, Co, Ni, Pb, Zn and Ba heavy metals in Vereda soils, located in the Rio Formoso basin, using a sampling network of vertical profiles, in order to assess the current condition of these environments. Considering that it comes to areas located near agroforestry activities, these elements were selected because they are present in pesticides and fertilizers and represents the major sources of contamination. The heavy metal content found in soils requires attention considering that many of them are beyond the limits of prevention set by CONAMA Resolution 420/2009. Geo-accumulation Index and Contamination Factor calculations revealed that these Veredas have high soil contamination by metals, particularly with Ni, Zn and Ba. Thus, the implementation mechanisms are necessary conducive to the protection of these environments as they are important to the region. It is suggested to create protected areas of sustainable use modality, specifically areas of ecological interest for the protection of Veredas, this being considered strategic to the conservation of soil and water.

Keywords: Vereda, Heavy metals, Soil contamination, Geo-accumulation Index, Contamination Factor

Introduction

Vereda is an ecosystem that is formed under well-defined conditions and moisture, and they are limited to the region of the Cerrado (Savannah). They normally form springs or spring galleries, which supply the major drainage basins of Brazil (Viana, 2006). The Formoso River basin, one of them, is an important tributary of the São Francisco River, and it is located in the North of the State of Minas Gerais. It hosts innumerous different Vereda types. Vereda is also considered a natural ecological corridor in the Cerrado area (Melo, 1992) because the alignments of its Buritis palms serve as trail for animals to loco move, feed and breed. According to the same author, these areas also have an important function in water distribution towards rivers as retaining it in wet seasons and liberating it in dry periods, maintaining perenity (continuity) of creeks and rivers. The aquifer exudes forming wetland in the drench very close to the surface, while the top of the steep-sided sandstone plateaus, works as a recharge area for the aquifers.

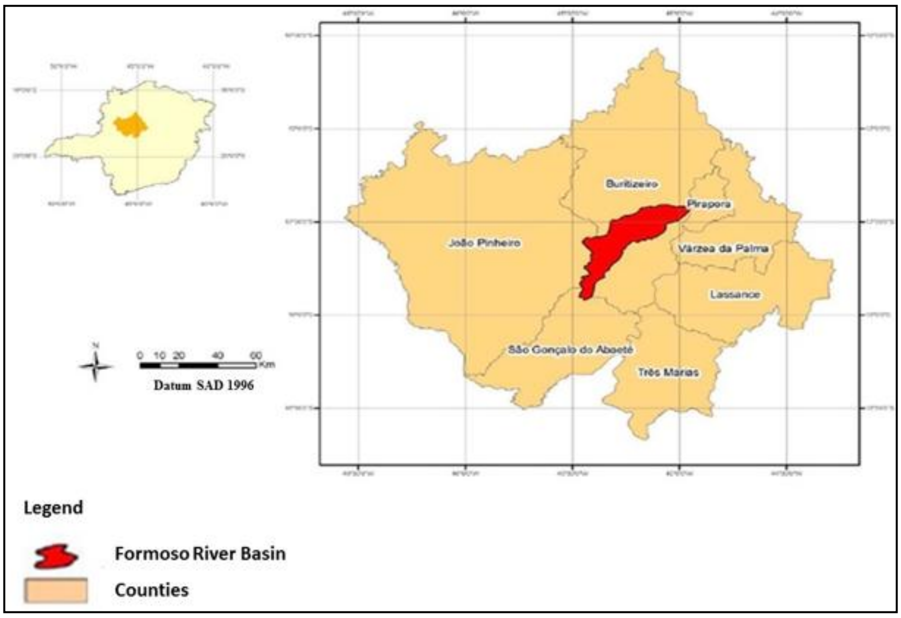
Another important aspect of Vereda, in relation to local communities, is their economic value due to the large potential of the Buriti palm in supplying the various local products, like oil, charcoal, leaves and construction material.

The soils of the Vereda are permanently saturated with water, in this way forming islands in arid regions. Due to this fact, agricultural activities are attracted and concentrated in this part of the Cerrado area, influencing the highly sensible equilibrium in the Cerrado biome. These activities may also alterate the quality of water and soil and they have an influence over the whole water support and quality of the connected basins.

The Vereda were classified due to their environmental, geological and morphological features and three representatives were selected. The aim of this work is to characterize the soil of the three selected Vereda and show the changes caused by human activities.

Localization

The studied area, Formoso River basin, is located in the Buritizeiro County, in the northern part of Minas Gerais State - Brazil. It is situated in the southwest portion of the Buritizeiro Municipality (Fig. 1).



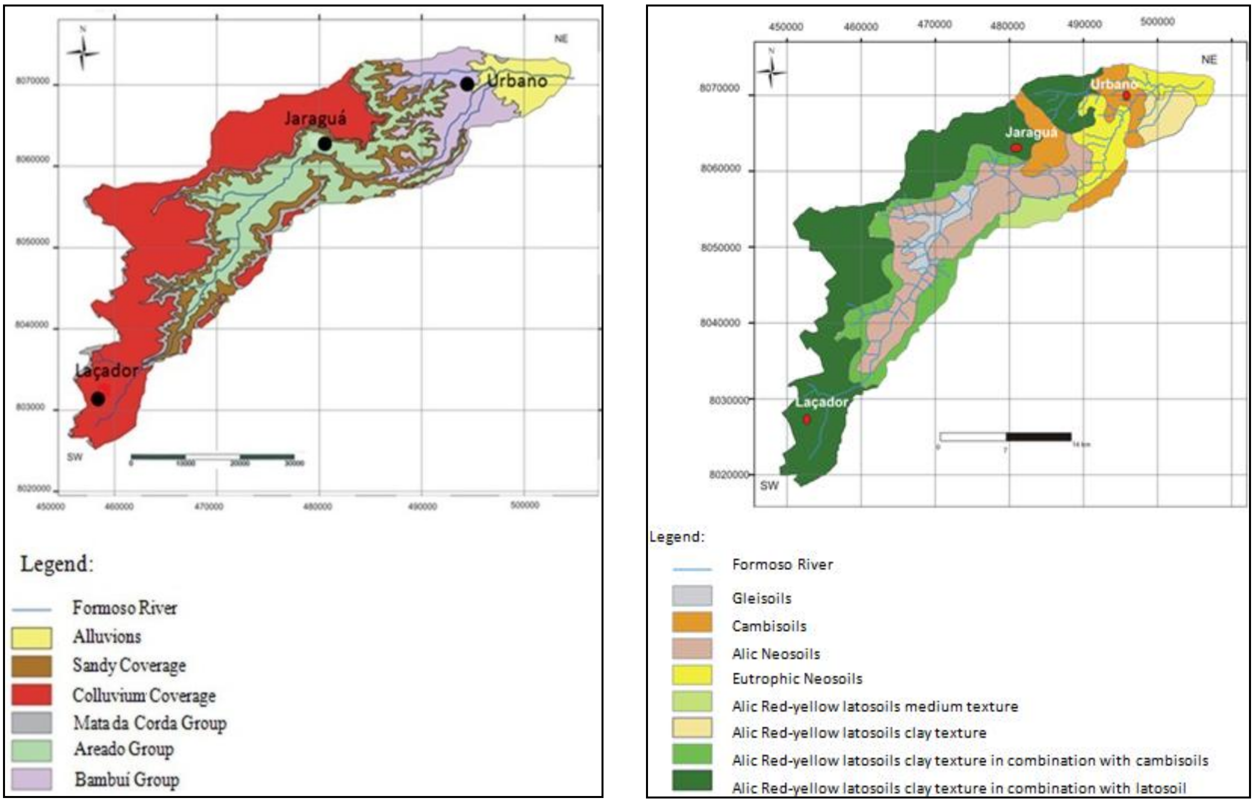


Fig. 1: Localization map of the investigated basin. The Formoso river basin situated in Buritizeiro County, in the State of Minas Gerais (Viana, 2006). Geological sketch map of the Formoso Basin. The map shows the distribution of the geological units in the investigated basin and the localization of all the Veredas (Baggio, 2008). 01: Vereda Urbana; 09: Vereda Jaraguá; 42: Vereda Laçador. Distribution of soils and soil use (agriculture; cattle; forests) activities in the basin (Baggio, 2008).

Geological setting

The Formoso River basin is located in the southern portion of the Sanfranciscana Basin, within the limits of the São Francisco Craton, in the eastern part of the Cretaceous area, covering the Minas Gerais State.

The rocks that characterize the studied area belong to the geological units of Areado e Mata da Corda Groups and their corresponding formations (Fig. 1). The Três Marias Formation, the upper unit of Bambuí Group, is located in the northern part of the basin (Melo, 1992). The Areado Group located in the central part of the basin, is represented by the Abaeté and Três Barras formations. The Abaeté formation constitutes the basal lithostratigraphic unit of the Sanfranciscana Basin and is represented in some places along the Formoso River basin, being consisted of fluvial conglomerates containing wind canter (Sgarbi, 2001). The Três Barras formation is composed of fine to medium sandstones from deposition in dry windy environments and fluvial-deltaic systems, cemented by limestone. The Mata da Corda Group is composed of volcanic and volcanoclastic rocks, discordantly covering the terrigenous Areado Group. It is divided into the Patos and Capacete Formations. The later, forms vast plateaus within the investigated area (Sgarbi, 2001). These plateaus are covered by more recent deposits, mostly of alluvio-colluvial and alluvial origin.

Pedology

Regarding the soil evolution and its occurrence in the studied area, it can be shown that in the median segment have principally formed Gleysols with humic-alic affinity, usually associated with the Vereda type (Melo, 1992). Indiscriminate hydromorphic soils (Gleysols and Organossolos) are typical for Vereda formation, extendedly occurring in the surrounding and underlying latosoils and quartz rich sands and micro conglomerates, showing the known dark grey to black colors for gleys (Melo, 1992). These soils (Fig. 1) are imperfectly to poorly drained, chemically very poor, strongly acidic (4<pH< 5.4) with very low base saturation values and a high saturation in aluminum. The gleisols possess a profile with an ACg horizons sequence, in which the A appears much darker given by the organic matter and C, sometimes can be subdivided into C1g and C2g (Melo, 1992). The gleisols profile contains Ao - A/Go – Gr horizons.

Methodology

The samples were collected from the selected Vereda, in horizontal and vertical profiles. Vertically, a 5 kg sample was taken every 20 m and from the upper 20 cm of soils. In selected positions, vertical sampling was executed taken 2-3 kg samples every 20 cm down to a maximum depth of 2 m. The samples were obtained with a sampler of “Wolf mouth” type and for deeper samples a normal soil sampler was used.

The samples were placed in paper trays and dried at room temperature for a period of 15 to 20 days. After drying, 500 g of each soil samples were submitted to particle size separation as the technical standard ABNT NBR 7181/1982 (ABNT, 1984). For chemical analysis of the selected elements, the finer fractions of the sieved samples (< 0.074 mm) were used.

We used the methodology of the Environmental Protection Agency of the United States of America – US -EPA 3051-16 (2007). The samples were analyzed using Optical Emission Spectrometry with Inductively Coupled Plasma (ICP-OES). We measured the soil pH in water and the cationic exchange capacity (CEC), using Embrapa procedure (EMBRAPA, 1997), the organic matter content, by colorimetric method and the color of the soil, using Soil Color Charts (Munsell, 1975).

Results and Discussion

The samples of Laçador, Jaraguá and Urbano Vereda show acidic to strong acidic soil, the pH values between 1.21 and 6.97 indicating favorable conditions to heavy metals liberation and transport. The pH values (2.5 -3) are the effect of the presence of humic and fulvic acids in the organic matter of the soil samples.

The samples of the Vereda Urbano have the highest organic matter content due to the permanent water presence and therefore, the chemical conditions (Fig. 2). The CEC, show the exchange capacity of cations in natural soil pH conditions and indicates the amount that the soil clay fraction components can adsorb due to its superficial negative charges.

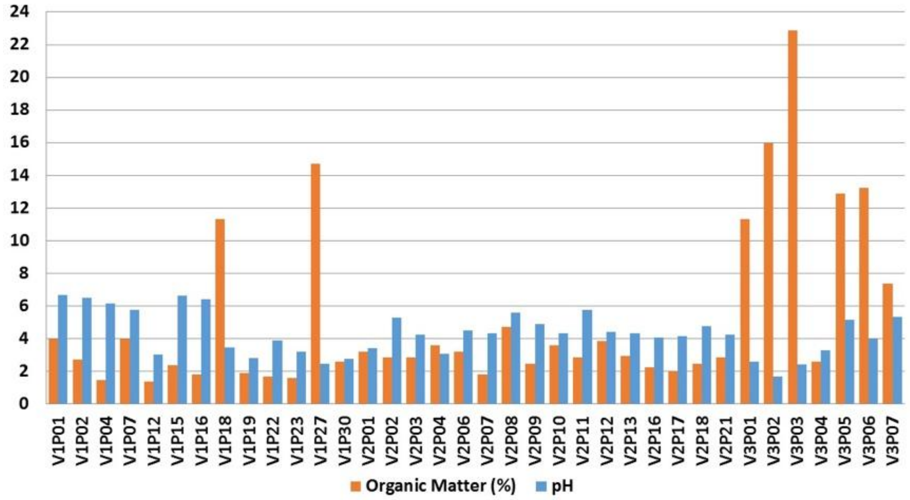


Fig. 2: The pH values versus organic matter. The lowest pH values have highest organic matter concentration.

The CEC-values ranged from 0.79 (Jaraguá Vereda) to 5.33 (Urbano Vereda).

In the Laçador Vereda samples, the color ranges from 5Y (light grey) to 2.5 N (black), in Jaraguá Vereda from 2.5 Y (light gray) to 2.5 YR (brown grayed) and for the samples of Urbano Vereda the colors are distributed from 10 YR 7/3 (brown with very slightly clear-greyed touch) to 10 YR 2/1 (black).

The color distribution is typical for very poorly drained soils with high organic content and formed under reduced conditions.

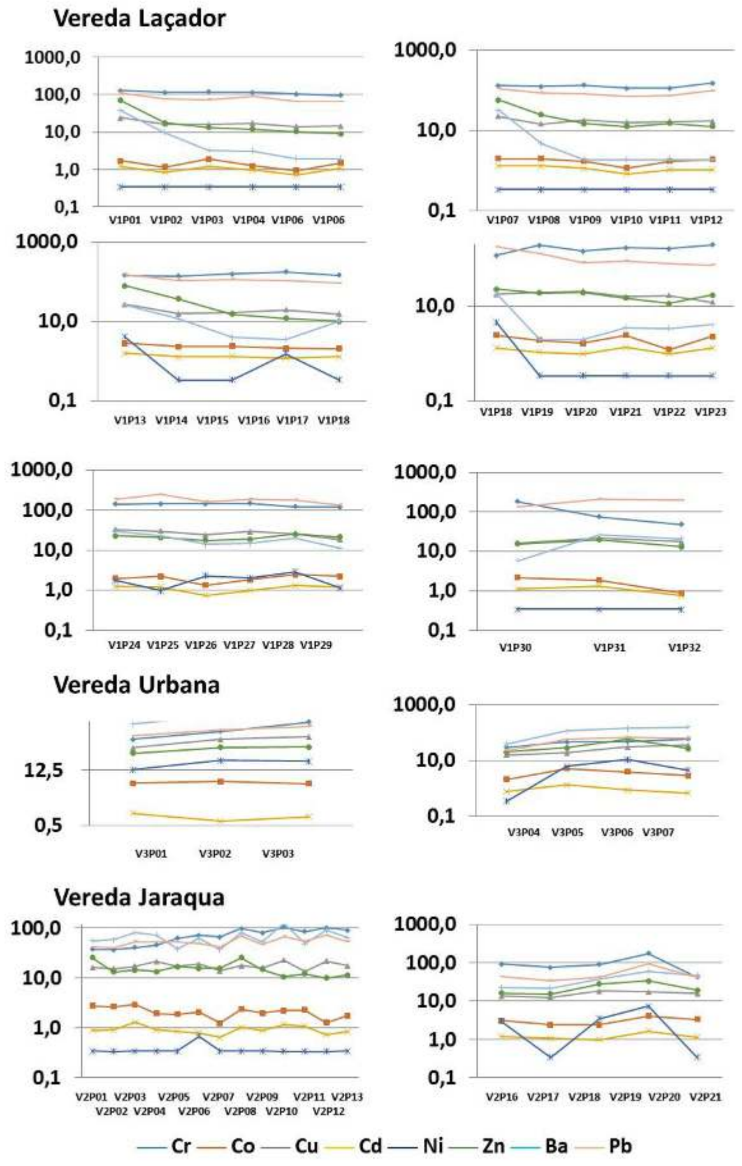


Fig. 3: Element distribution in the sampled profiles.

The results obtained by X-Rays diffraction indicate a predominance of quartz, kaolinite, gibbsite and subordinate of Vanadium-rich muscovite as important mineralogical constituents of the soil samples.

The analytical results show a wide variety of concentrations due to the lithological situation as also due to the anthropogenic activities in the basin (Fig. 3).

The Ni content present in sandstones and clays lithotypes of the substrate, analyzed for the Formoso River basin rocks (Baggio, 2008) demonstrate that these values are above the reference values for Medium Sandstone described by Bowen (1979) and Krauskopf (1976), causing a possible primary enrichment of this metal in basin's soils. But the extremely high contamination by Ni observed in soil and water samples (Baggio, 2008) is explicable only by anthropogenic contribution like agro-toxics, and defensives, principally. Zn shows similar behavior. The concentrations in the substrate are also higher than normally described (Bowen, 1979) probably caused also by the use of local limestone in agriculture. Contributions of the highways passing through the area are also possible.

How the primary concentrations of Co in the substrate are low, the enrichment of soils by Co can be related to involvement of one of its main salts, cobalt sulfate ($CoSO_4$) used with fertilization of pasture. The enrichment of the samples by Ba may be associated with its presence in pesticides from agricultural usage. Figure 3 shows the distribution of available elements for the selected Vereda.

From the three investigated selected Vereda ecosystems, each one represents the Vereda allocated in a specific geological, morphological and environmental compartment of the basin. In this way the problems show similarities and also specific differences in the form of contaminations, expressed by the calculated IGeo and FC-values (Fig. 4).

Jaraguá Vereda

The calculation of IGeo of Jaraguá Vereda revealed that soils are moderately to heavily polluted by Cr and Ba and stronger to very heavily polluted by Ni (Fig. 4). However, calculated CF shows that soils were enriched by Co, Zn and Pb, indicating considerable contamination, and for Cr, Ni and Ba, indicating high contamination (Fig. 4). The enrichment of soils of this Vereda with Ni has lithological source (natural origin), as well as for the Zn and Co, due to contamination sources cited previously.

Laçador Vereda

The calculation of IGeo for assessing the intensity of contamination by heavy metals in Vereda Laçador showed that soils are moderately to heavily pollute by Zn and heavily polluted by Ni and Ba (Fig. 4). However, CF shows that soils were enriched with Cr, Pb and Co, indicating considerable contamination. Also the presence of Ni, Zn and Ba show high contamination (Fig. 4). Zn, Cr and Pb metals may be associated with the intense use and occupation of the soil for farming activities in this portion of the basin.

Urbano Vereda

The IGeo on Urbano Vereda revealed that soils are moderately to heavily pollute by Ba and Pb, and very heavily polluted by Ni (Fig. 4). However, applying the CF, we conclude that soils were enriched by Cr, Ni, Ba and Pb, indicating high contamination (Fig. 4). The enrichment of soils of this Vereda by Ni has lithological and natural origin as explained to the previous Vereda. The Urbano Vereda presented the worst level of contamination (heavily polluted by Ni, CF = 73.59).

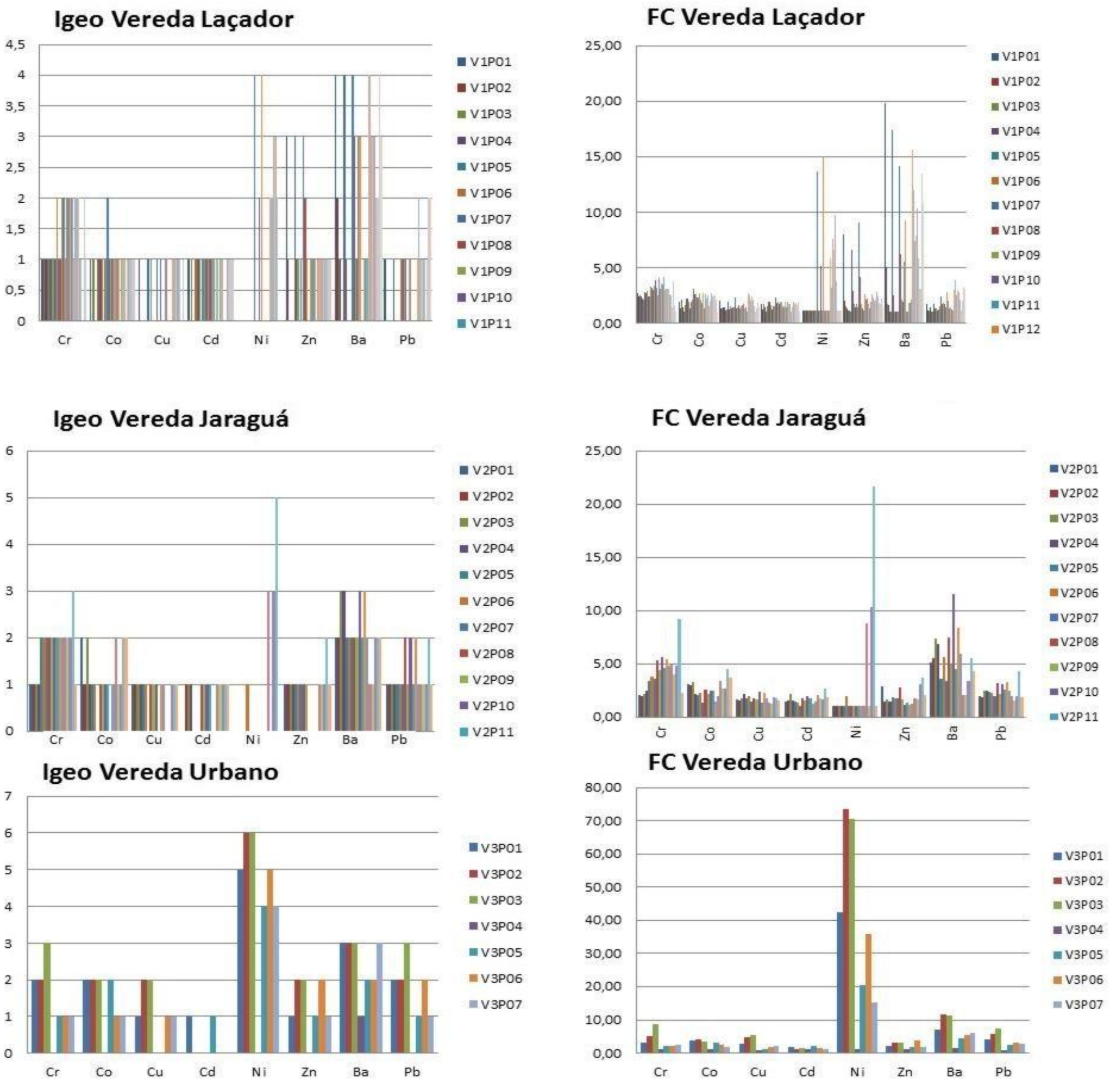


Fig. 4: IGeo and FC values for Vereda Laçador, Vereda Jaraguá and Vereda Urbano

Conclusions

The heavy metals levels found in Vereda's soils demand attention considering that a good portion of the concentrations surpasses the limits of prevention established by CETESB (2009) and intervention limits described by the CONAMA resolution 420/2009 (2009).

The proximity of these Vereda with areas of intense agricultural use (agriculture, cattle breathing and forests) suggests that a big amount of the found metal concentrations belong to them.

As a possible mechanism of the protection and preservation of the Vereda and in this way the water support for the big Brazilian river basins protection, may be the creation of specific conservation Units called Areas of Relevant Ecological Interest (Portuguese: Áreas de Relevante Interesse Ecológico – ARIE) and an intense control of environmental relative activities in their neighborhood.

In this way, the discharge to the rivers and recharge from rainfalls can be adequately maintained and this will permit the preservation of endemic species and plants of socio-cultural importance like the Buritis palms.

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GEOCHEMICAL ASPECTS OF THE MOHOŞ PEATLAND FROM HARGHITA MOUNTAINS

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Abstract: Geochemical analysis of samples peat bog collected from Mohoş area to allow determination of potential pollution sources. The elemental analysis shows a high content in carbon and a low content in oxygen and nitrogen. The pH lower, from 3.18 to 4.77, with low ash content, indicates us a low degree of decomposition of peat samples. The mineral assemblage found from XRD analyses of peat samples shows the presence of the following minerals: quartz, followed by clay minerals, feldspars, and minerals associated with the presence of organic matter. Additionally, the samples contain iron and titanium oxides such as hematite, goethite and rutile. For elemental analysis CHNS-O was used a EuroEa 3000 EuroVector and for examination of the mineralogy of peat samples was used X-ray diffraction.

Keywords: ombrotrophic bog, Mohoş, TOC, X-ray diffraction, pH, redox potential

1. INTRODUCTION

Peat covers approximately 4 % of the land area of the world, and 95 % of this peatland is in the cold and temperate zones from the northern hemisphere (Deboucha et al., 2008). One third of European peatlands are present in Finland, in Romania the peatland are distributed on the 39 km^2 (Montanarella et al., 2006).

Peat deposits are formed when organic matter accumulates more rapidly than it decays over thousands of years. The microbial degradation of plant residues is regarded as a result of poor aeration and acidic conditions below a high water table. The peat deposit often consists of more than 75 % organic substances (Andriesse, 1988).

Ash remaining after the burning of peat at 550° C is important in the characterization of peatland type. In ombrotrophic bogs, ash contents that reflect atmospheric-dust deposition are generally very low, between 1 and 3 % (Steinman and Shotyk, 1997). The mineral composition of ombrotrophic peat is homogeneous with depth. The ombrotrophic peat contains mainly quartz (60-90 %) and opaline silica (30-70 %) with less amounts of feldspar (5-15 %) and muscovite (5-15 %) (Steinmann and Shotyk, 1997).

The aim of the present paper is to describe the structural properties of peat samples which were collected from Mohoş peatland located in the southern part of Harghita Mountains, in Ciomadul crater, using the analysis of physic-chemical parameters, organic matter content, elemental analysis (CHNS-O) and X-ray diffraction, using the powder method.

2. GEOLOGICAL FRAMEWORK

With its over 160 km length, the Călimani-Gurghiu-Harghita (CGH) chain is the longest continuous volcanic range in the Carpatho-Pannonian Region. The Harghita Mountains represent the largest and most complex volcanic structure at the southern part of the CGH range in Romania, Neogen/Quaternary andesite and dacite (Szakács and Seghedi, 1995).

The Ciomadul is the main chain-ending volcano in the South of the Harghita Mountains, which is the southern segment of the CGH volcanic range in the East Carpathians, Romania (Fig. 1) (Szakács et al., 2015) and is composed of about 8-14 km^3 dacitic eruptives (Karátson and Timár, 2005; Szakács et al., 2015). The Ciomadul is the youngest volcano of the Carpathian–Pannonian region, which erupted last time at 32 ka. It produced high-K dacitic lava domes and pumiceous pyroclastic rocks. The dacite contains plagioclase, amphibole in addition to biotite, titanite, apatite, zircon and occasionally quartz, K-feldspar, olivine, clinopyroxene and orthopyroxene (Harangi et al., 2015).

The Mohoş peatland formed in the northern crater of Ciomadul massif, at an altitude of 1050 m in Harghita Mountains. The depth of the Mohoş caldera is estimated to be approximately 60 m, but his value is constantly changing due to sedimentation processes that take place (Diaconu and Mailat, 2007).

3. MATERIALS AND METHODS

The studied peat samples were collected from Mohoş peatland in August 2015, up to 30 cm deep under vegetation cover (Fig. 1), dried in an electric oven at 50° C and sieved at 0.63 mm. Redox and pH measurements were determined on all 50 samples, used an portable kit HACH HQ 40d. Ash content was determined by burning the peat samples at 550° C for 4 h expressing the results as percentage of the dry weight of the samples.

For elemental geochemical analysis was used a EuroEa 3000 EuroVector elemental analyzer to measure % TOC, H, N, S and O from Department of Geology, "Al. I. Cuza" University, Iaşi. Samples were crushed, followed by a 4 N HCl treatment for 24 h to remove inorganic carbon. The remaining material was washed with distilled water several times to remove the acid, and then dried at 50° C (Ortiz and Gentzis, 2015).

For the X-ray diffraction analyses, the samples were homogenized manually in an agate mortar to obtain the optimum particle size and to ensure the random orientations of the crystals in the samples (Tyni et al., 2014). XRD measurements were performed on representative powdered peat samples using a Shimadzu LabX XRD-6000 diffractometer (Cu Kα radiation $\lambda = 1.5406$Å), operating at 40 KV, with a beam current of 30 mA. Scans were recorded from 5 to 80º 2θ, with a scan steed of 1 deg/min and a sampling pitch of 0.02 deg.

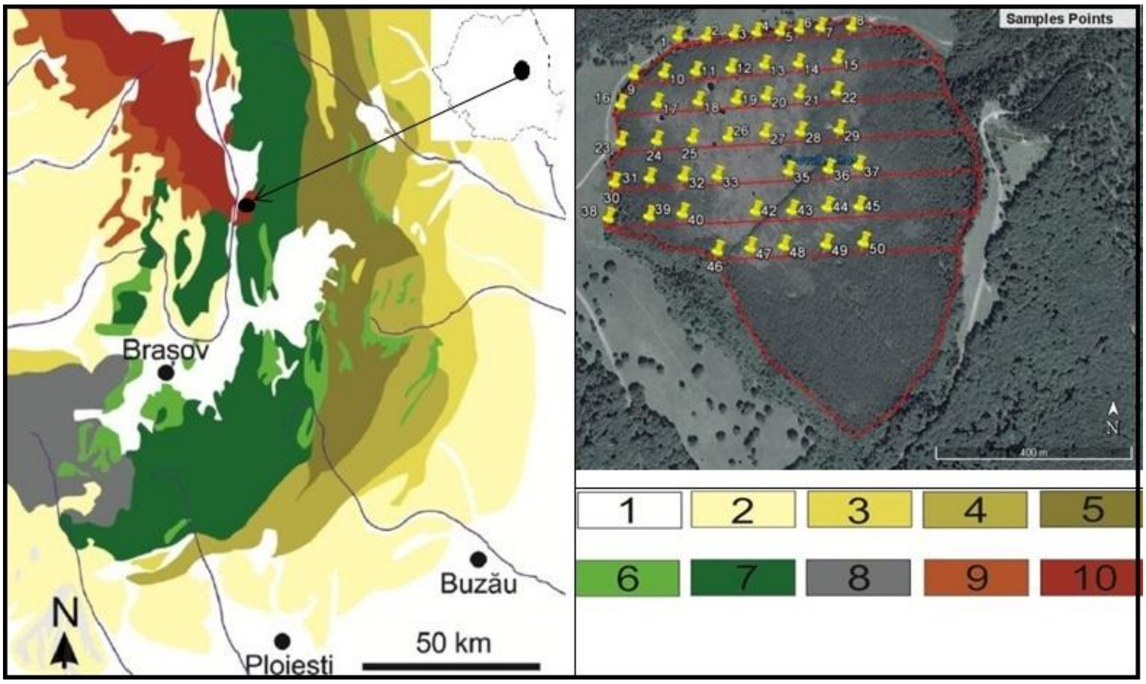

Fig. 1. Geological map and the samples points: 1 – Quaternary, 2 - Pannonian-Sarmatian, 3 - Paleozoic, 4 - Paleocene-Miocene, 5 - Oligocene, 6 - Neocomian, 7 - Tithonian-neocomian, 8 - Paleogene, 9 - Vucanogene Neogene deposits, 10 - Neogene volcanic (after Frunzeti, 2013)

4. RESULTS

Since the peat samples containing between 80-98% organic matter, pH is acidic, from 3.18 to 4.7 and the redox potential from 135.2 to 225.4 mV, Mohoş peatland can be classified as a ombrotrophic peatland. The degree of decomposition, according to von Post humification test, is between H1-H3 with high fiber content, partially decomposed, in brown colored.

The elemental composition, atomic ratios (H/C and C/N) of the studied peat samples are shown in Table 1. Because of the absence of carbonates, total carbon was assumed to be Total Organic Carbon (TOC) (Delarue et al., 2011). From the samples which were analysed, T_1 had higher percentages of carbon (46.09 %) and nitrogen (2.50 %), while T_{29} had a greater concentration in hydrogen (5.37 %) and T_{29} in oxygen (54.61 %). The H/C ratio is indicators for the percentage saturation of the C atoms within the organic molecule and of the carbohydrate content respectively. Lower H/C ratios indicate higher aromaticity in the samples (Fernandes et al., 2012).

The C/N ratio has been considered an index of the possible microbial activity because these communities need at least a C/N ratio of 30 to carry out the organic material decomposition. A decrease C/N ratio below 30 shows the increased of rate decomposition of organic matter (Kuhry and Vitt, 1996). C/N ratio confirms that the samples analyzed shows a close decomposition rate. The data in Table 1 confirm that the T_{12} sample is more decomposed, the nitrogen enrichment in T_{12} being related to a greater incidence of microorganisms, including bacteria, fungi, and actinomycetes, at this stage of decomposition

(Kuhry and Vitt, 1996). Another reason for which samples T_{12} and T_1 are more decomposed is that they were under incidence of water.

Table 1. Samples with the highest content in CHHS-O and atomic ratios.

Sample	N (%)	C (%)	H (%)	S (%)	O (%)[a]	H/C[b]	C/N[c]
T_{29}	2.09	44.43	5.37	0	48.09	1.44	24.71
T_{12}	2.12	38.43	4.82	0	54.61	1.49	21.13
T_1	2.50	46.09	5.25	0	46.14	1.35	21.45

[a] By difference of mean values.
[b] H/C=[(%H/1.008) / (%C/12.01)].
[c] C/N=[(%C/12.01) / (%N/14.00)].

Detailed examination of the mineralogy of the peat samples using XRD is shown in the Fig. 2a and Fig. 2b. The XRD diffractogram shows a hump, between 10° and 30°, highlight the amorphous matter that includes vitreous phases and gels (Tiainen et al., 2002). Analyzing the processes involved in peat formation, we recognized an anaerobic thick structural layer, which is formed of residual material from the original plant structure, decay products and new substances produced mainly by bacteria. At this level peat is amorphous and highly humified (Bozkurt et al., 2001).

Mineral phases consist of detrital minerals such as silicates, mainly quartz. They are followed by clay minerals (illite, kaolinite and dickite) and feldspar (anorthite and albite). There were small amounts of carbonates such as calcite and dolomite, and phosphate such as calcosiderite. It was observed the presence of the heavy minerals, dominated by iron and titanium oxides: hematite, goethite and rutile. Additionally, occurring minerals associated with the presence of organic matter (efremovite, simonellite) or coals (alunogen) and with the carbonification of wood (rorosite).

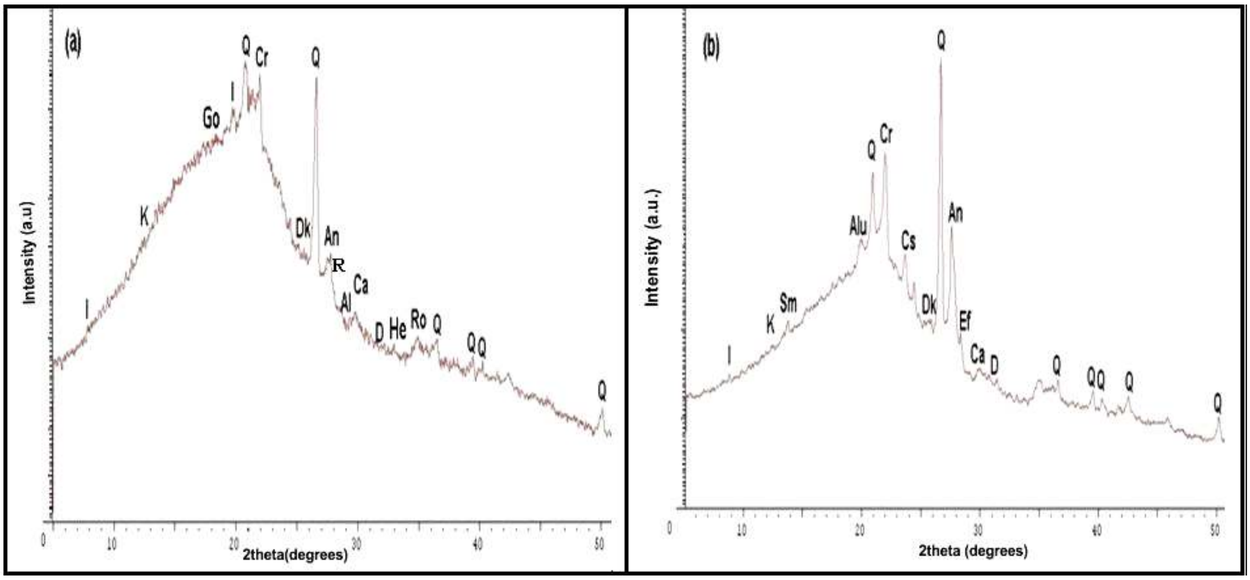

Fig. 2. XRD diffractograms of the peat samples (where Q=quartz, Cr=cristobalite, I=illite, K=kaolinite, Dk=dickite, An=anorthite , Al=albite, Ca=calcite, D=dolomite, Cs=calcosiderite, Ef=efremovite, Sm=simonellite, Ro=rorosite, Alu=alunogene, He=hematite, Go=goethite, R=rutile

5. CONCLUSIONS

The ombrotrophic nature of Mohoş peatland is given by low ash content, acid pH and low redox potential. The high content of organic material indicates the early stage of decomposition of plant materials due to the different areas of training and accumulation of inorganic materials, especially silicon dioxide, in the top layer of peat bogs.

The critical factors influencing the mineralogy of peatland are distance from pollution source and water conditions within the peatland. The minerals that dominate the inorganic fraction are detrital minerals such as quartz, clay and feldspars. The heavy minerals are represented by iron and titanium oxides: hematite, goethite and rutile. Mohoş peatland receive mineral particles from soil dust supplied by the atmosphere, resulting from the operation of quarries (andesites from Bixad, dolomite from Voşlobeni, kaolin in Harghita Bai or from Balan mine, followed by the construction of dumps close to it).

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ASSESSMENT OF SOME USEFUL ROCKS DEPOSITS IN TERMS OF ROCKS MECHANIC

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Abstract: If in the case of useful minerals deposits, the primary indicator of quality is the exploitable content, in the case of useful rocks deposits, the main quality indicator is given by the mechanical characteristics.
The aim of this paper is the assessment of some useful rocks deposits by the mechanical features (petrography-mineralogical, physical, mechanical, chemical).
For the use of rocks to the different engineering works it must meet certain characteristics required by the standards.

Key words: mineral deposit, useful rocks, assessment, quality indicators, mechanical features

1. Introduction

Rocks were used as construction material since ancient times. Over time, their use in various forms all over the world grew larger and larger, varying according to culture and time period.

In our country the rock deposits are widely distributed in the vorland structures, but especially in the Carpathian structures. They have many uses in construction, as well as in various other industries (Danciu, 2010 a).

This wide range of uses (especially in terrestrial communication ways) increases the interest in investigating new deposits and perspective areas that are not in exploitation or those for whom the reserves allow an extension, in order to capitalize useful rocks (Danciu, 2010 b).

Rocks and aggregates used in construction and construction materials industry require a detailed knowledge of their geo-mechanical characteristics.

Rocks and aggregates resulting from them can be used to manufacture various engineering works (housing, industrial facilities and a wide variety of public infrastructure works) only if they have a certain quality. In this context, in the Rock Mechanics Laboratory of the University of Petrosani, there were determined the physical-mechanical properties of some magmatic rocks taken from the Apuseni Mountains and the obtained results were compared with the conditions of admissibility of rocks used for railways and roads construction.

2. Methods And Results

Knowing the physical characteristics of the rocks can be used to obtain a quantitative description and an estimate on the influence on the resistance characteristics. For this purpose the following characteristics were determined: specific density (ρ), volumetric density (ρ_a), porosity (n), water absorption (a_i).

The determination of the physical and mechanical properties was carried out according to current standards (STAS SR EN, FR). Methods of determination and calculation relations are found in scientific literature (Toderaş, 2008), (Todorescu, 1984).

By determining the physical parameters according to specific procedures there were recorded the following average values for the analyzed samples (Table 1).

According to the pursued objective there were determined the following mechanical characteristics (Toderaş, 2008), (Todorescu, 1984): uniaxial compressive strength in dry state and after 25 freeze-thaw cycles, crushing strength by compression in dry state, abrasion resistance using the Los Angeles method and freeze-thaw resistance. Average values of the strength characteristics of analyzed rocks are shown in Table 2.

Table 1. Average values of the physical characteristics of rocks.

Sample no.	Type of rock/ Sampling point	Physical characteristics					
		Specific density (real) ρ x 10^4 [kg/m^3]	Volumetric density ρ_a x 10^3 [kg/m^3]	Total porosity n [%]	Open porosity n_a [%]	Compactness c [%]	Water absorption at normal pressure a_i [%]
1.	Granite/Şoimoş	2.635	2.619	0.588	0.361	99.411	0.138
2.	Granite/Săvârşin	2.645	2.625	0.759	0.496	99.240	0.189
3.	Andesite/Criscior	2.655	2.639	0.606	0.530	99.393	0.201
4.	Basalt/Brănişca	2.728	2.704	0.891	0.516	99.108	0.191
5.	Basalt/Dobra	2.724	2.699	0.930	0.423	99.068	0.157

Table 2. Average values of the resistance characteristics.

Sample no.	Type of rock/ Sampling point	Resistance characteristics					
		Uniaxial compressive strength σ_{rc} [MPa]		Freeze-thaw sensitivity η_{d25} [%]	Crushing strength by compression in dry state R_c [%]	Abrasion resistance using the Los Angeles method [%]	Gelivity coefficient μ_{25}[%]
		Dry	After 25 freeze-thaw cycles				
1.	Granite/Şoimoş	212.220	192.615	9.154	78.176	11.820	0.008
2.	Granite/Săvârşin	168.488	156.272	7.237	75.530	10.161	0.011
3.	Andesite/Criscior	143.538	125.297	12.715	72.014	16.369	0.127
4.	Basalt/Brănişca	170.839	157.856	7.619	74.061	13.724	0.057
5.	Basalt/Dobra	179.586	166.613	7.187	72.885	14.825	0.075

3. Discussions

Rocks (magmatic, metamorphic and sedimentary) used for road construction must be homogeneous in terms of structure and mineralogical and petrographic composition, without any physical or chemical alteration. They must be free of pyrite, limonite or soluble salts and contain no microcrystalline or amorphous silica, which react with alkali from cement (SR 667/2001).

In the case of natural aggregates used in construction of roads and railways there is accepted a proportion of 10% for crushed stone and 5% for chippings to be composed of altered rocks, soft, brittle, porous and vacuolar (SR 667/2001).

Based mainly on physical and mechanical characteristics, the rocks used in the production of natural stone products are classified into five admissibility classes, shown in Table 3.

The rocks that do not meet all the conditions of admissibility from Table 3 can be classified depending on the open porosity or on abrasion resistance using the Los Angeles method, the decisive one is that indicating the lower class.

The rocks that do not comply with the conditions of admissibility for resistance to freeze - thaw should not be used on road works (SR 667/2001).

Based on the average values of the main physical and mechanical characteristics obtained for analyzed rocks and compared with the conditions of admissibility, each rock is classified into one of the 5 classes of admissibility (Table 3).

Table 3. Conditions for admissibility of rocks used in rail and road works.

Characteristics	ROCK CLASS									
	A	B	C	D	E	A	A	B	A	A
	Admissibility conditions (SR 667/2001)					Rock type				
						Granite/ Şoimoş	Granite/ Săvârşin	Andesite/ Criscior	Basalt/ Brănişca	Basalt/ Dobra
Open porosity at normal pressure, %, max.	1	3	5	8	10	0.822	0.754	0.606	0.891	0.930
Uniaxial compressive strength in dry state, [MPa], min.	160	140	120	100	80	212.220	168.488	143.538	170.839	179.586
Abrasion resistance using the Los Angeles method, %, max.	16	18	22	25	30	11.820	10.161	16.369	13.724	14.825
Crushing strength by compression in dry state, %, min.	70	67	65	60	50	78.176	75.530	72.014	74.061	72.885
Freeze-thaw resistance: - frost cleftness coefficient (μ_{25}) ,%, max. - freeze sensitivity (η_{d25}), %, max.	3					0.008	0.011	0.127	0.057	0.075
	25					9.154	7.237	12.715	7.619	7.187

4. Conclusions

After determining the physical and mechanical characteristics and by comparing them with the admissibility conditions, the following conclusions can be drawn:

- the analyzed rocks are compact, with a high density (which results from a comparison between specific and volumetric densities). The porosity is quite small, characteristic to magmatic rocks, proving once again their qualities;
- uniaxial compressive strength of analyzed rocks, is quite high, ranging between 140-215 MPa (admissibility class between A and B);
- abrasion resistance using the Los Angeles method is low, and the crushing strength by compression in dry state has values that are above the set point of the admissibility class A (rocks recommended for rail and road construction);
- depending on the values obtained for gelivity coefficient and sensitivity to freeze-thaw cycle, it is considered that these rocks are weatherproof;
- after comparing the obtained results of analyzed rocks with the admissibility conditions, they can be divided into two classes: admissibility class A (Şoimoş Granite, Săvârşin Granite, Brănişca basalt and Dobra basalt) and admissibility class B (Criscior andesite).

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 93-98

A NEW OCCURRENCE OF ARSENIAN ALBURNITE, ITS ASSOCIATED PHASES AND ERRATUM TO A PREVIOUS REPORT

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Abstract: Alburnite, $Ag_8Ge(S,Te)_6$, hitherto known only from the type locality, was recognized in the Măgura epithermal veins, a second occurrence also in the Golden Quadrilateral. The veins contain chalcopyrite, sulfoarsenides-sulfoantimonides and tellurides. Alburnite, identified according to its optical properties and EDS, postdates the chalcopyrite-fahlore main-stage association and accommodates essential As. The coexisting telluride assemblage contains hessite, usually accompanied by petzite, and stützite associated with sylvanite. The late stage assemblage succeeding chalcopyrite is enriched in precious metals (especially Ag), Te and Ge, containing also pearceite-polybasite intergrown with argentian fahlore and benleonardite. Benleonardite displays an unusual composition as well, indicating notable Ge substitution for As. Cu, Fe - bearing silver and gold sulfotellurides we previously reported at Măgura resulted from instrumental artefacts, representing in truth plain Ag-Au tellurides.

Keywords: alburnite, tellurides, germanium, epithermal veins, Golden Quadrilateral

Introduction

The Golden Quadrilateral in the South Apuseni Mountains represents a remarkable metallogenetic province associated to extensional Neogene magmatism (Roşu *et al*., 2004), where massive development of hydrothermal deposits occurred within a relative small area (ca. 900 km^2) in a large number of prospects (64 altogether), with a vast diversity of mineral phases. In this very prolific mining province, somewhere near 1750 metric tons of gold metal have been extracted over the past two millennia (Vlad & Orlandea, 2004), while it is re-emerging again as a world class mining province. Most of the deposits are associated to subvolcanic bodies emplaced in penecontemporaneous lava flows, as well as in mid-Miocene basin deposits overlying a Late Cretaceous tectonic sequence consisting of a Jurassic ocean-derived units (ocean floor and island arc), Cretaceous flysch nappes and metamorphic basement units (Berbeleac *et al*., 2014). Among the typical features of the province, mention should be made of the close association of porphyry copper systems with epithermal veins and the constant appearance of Au-Ag tellurides in the ore associations. The Golden Quadrilateral hosts type localities for many mineral phases, comprising 12 tellurium minerals, of which alburnite has been only recently discovered (Tămaş *et al*., 2014) in the epithermal veins associated to the Roșia Montană mining district. Here we report the second occurrence of this new phase, in the Măgura epithermal vein system, and give a brief account of its position in the vein assemblage.

Geologic setting

The Măgura vein system is one of the satellite vein and stockwork orefields around the Bolcana porphyry structure. The mineralization is related to the Măgura-Făerag group of subvolcanic bodies, emplaced in the SE-part of the Brad-Săcărâmb extensional basin, along the southern magmatic lineament (also known as Brad-Săcărâmb) of the Golden Quadrilateral, represented by Barza-type Badenian-Sarmatian andesites (14.6-12.4 Ma, according to Pécskay *et al*., 1995). The Măgura vein system is known as a historical orefield mined for mostly native gold; a reappraisal of the valuation process was started by exploration works extending discontinuously since the late fifties to present (Orlandea & Velciov, 1996).

Tellurium or germanium-bearing phases have been mentioned in the surrounding areas, and tellurides in the Măgura vein assemblage itself (Cioacă *et al*., 2014). Socolescu *et al*. (1963) report optically determined argyrodite inclusions in chalcopyrite in ore from the Livia Mine near Hondol, while Au and Ag tellurides are described in the mineralization of the Coranda-Hondol open pit (Apopei *et al*., 2014).

Materials and methods

We identified alburnite in a polished section from the collection of the Faculty of Geology, University of Bucharest, namely chalcopyrite-rich vein material sampled from the exploration adits of Măgura. The sample was studied optically and by a BSE/EDS combination. Mineral X-ray spectra and compositions were recorded on a Merlin FE-SEM equipped with a high-resolution Schottky-type electron gun and a sensitive 50 mm^2 X-MaxN silicon drift detector, at an accelerating voltage of 15 kV and a beam current ranging between 0.2-0.5 nA, with live times oscillating around 10 s.

The abundance of chalcopyrite and its associations indicate provenance of the sample from the upper level of the western part of the Măgura orefield, according to the description of the mineralization types given in Orlandea & Velciov (1996).

Mineralogy and microtextures

The studied sample consists of a cm-sized vein filling with vuggy quartz cemented by chalcopyrite. Chalcopyrite includes coarser-grained pyrite, but often contains also mineral phases (pyrite, fahlore, tellurides), which apparently deposited in open cavities inside the host, as indicated by concentric textures (Fig. 1 A,B), central voids in aggregates (Fig. 1 A,D), and recurrent zonality abutting on chalcopyrite host and developing away from it (Fig. 1 C). The assemblage contains fahlore, enargite, stützite, hessite, petzite, electrum, pearceite-polybasite, rare benleonardite, and alburnite (Fig. 1,2).

The tellurides tend to appear in a regular association, sylvanite being associated with stützite (Fig. 2) and hessite with petzite.

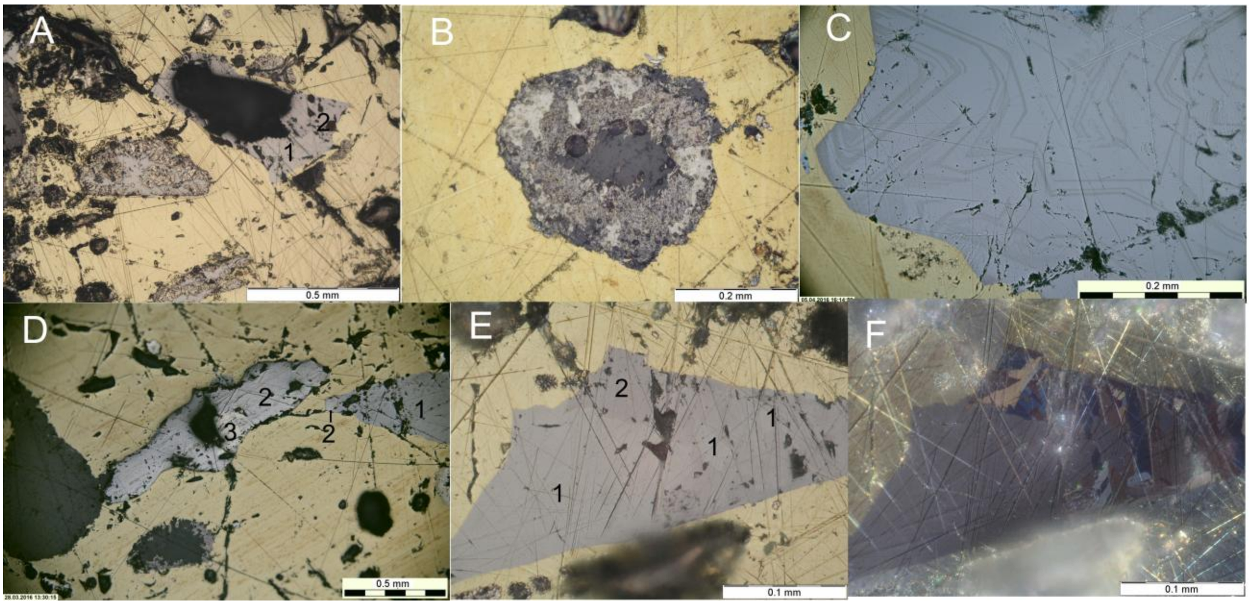

Fig. 1. Reflected light microphotographs of assemblages in chalcopyrite-dominated vein filling. A: Concentric pyrite-fahlore intergrowth (centre-left) and fahlore (1) replaced by enargite (2) in chalcopyrite aggregates; B: Concentric fahlore – enargite – quartz pseudo-inclusion in chalcopyrite, C: Recurrently zoned fahlore, structural attack with Ar ion beam. D: Composite pseudoinclusions containing fahlore (1) stützite (2) and sylvanite (3). E: Fahlore (1) engulfed, corroded and replaced by enargite (2). F: the same image under crossed polarizer, displaying the anisotropy of enargite and the fahlore rounded relics inside it.

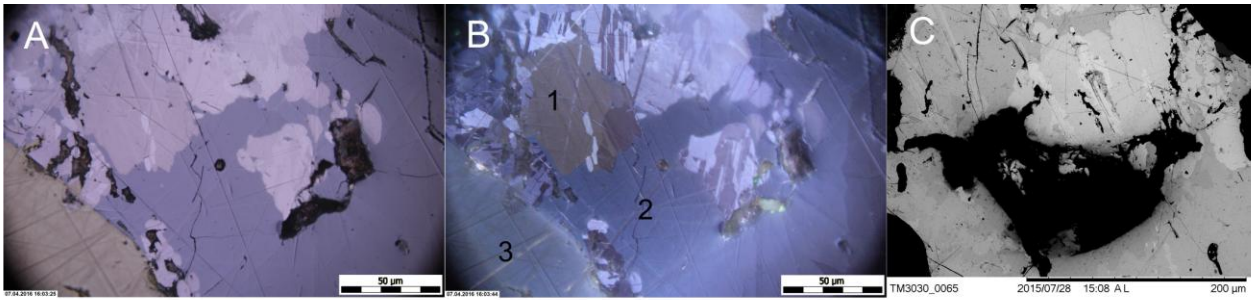

Fig. 2. Stützite-sylvanite composite pseudoinclusion in chalcopyrite. A: Plane polarized reflected light, oil immersion. B: Crossed polars, oil immersion, 1- sylvanite, 2-stützite, 3- chalcopyrite. C: BSE image

Remarkable are subhedral aggregates containing both hessite and stützite in irregular intergrowths, possibly formed by breakdown of the homogeneous $Ag_{1.9}Te$ phase (Fig. 3). The aggregates also contain minor Au-Ag tellurides, and apparently represent genuine inclusions in chalcopyrite. The two Ag tellurides display slight differences in bireflexion and anisotropy, more intense in oil immersion: stützite remains grey in any orientation, while hessite has a slight bireflexion in pinkish and cream hues; stützite has dark russet-brown to cobalt-blue anisotropy colours, while hessite appears more orange-brownish.

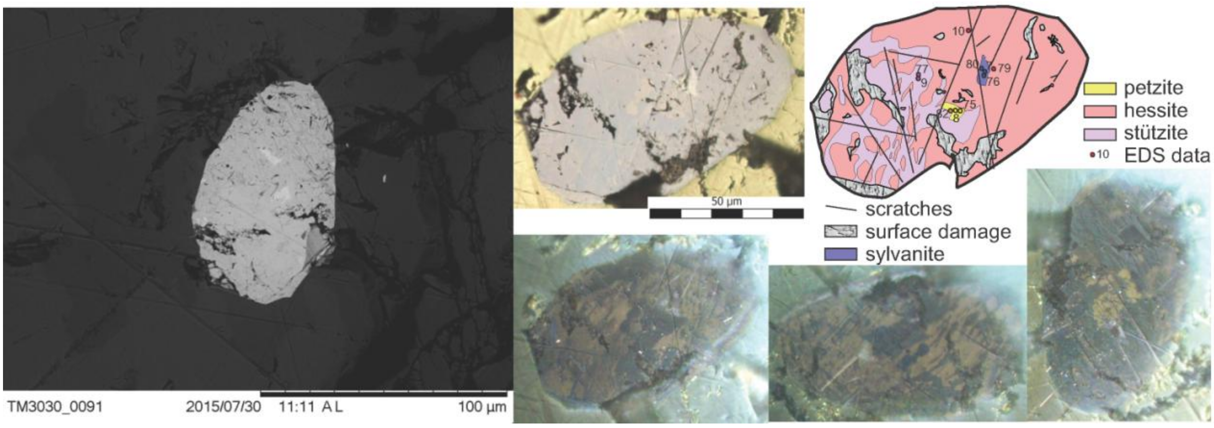

Fig. 3. Composite hessite – stützite inclusion containing minor sylvanite and petzite. Left – BSE image; upper row right – reflected light microphotograph of the same grain in oil immersion, and sketch showing the mineral composition and location of the EDS analyses; lower row left – reflected light microphotographs of the same grain rotated at different angles, in oil immersion and crossed polarizers

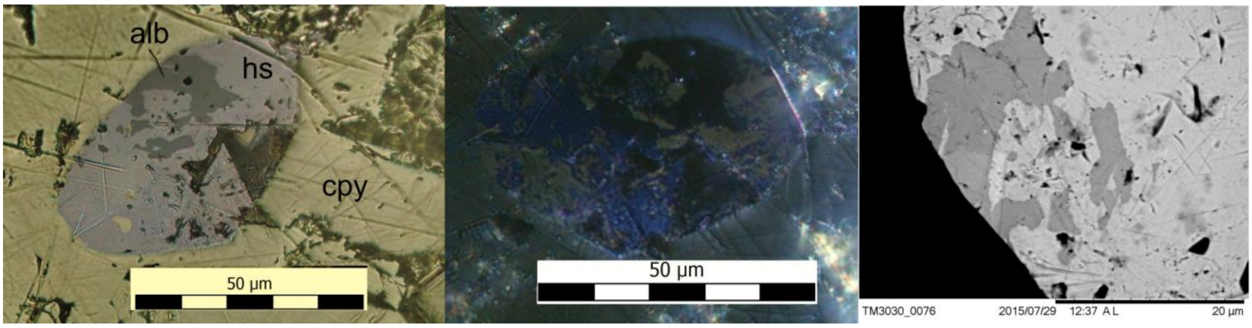

Fig. 4. Alburnite (alb - isotropic) intergrown with hessite (hs - bireflective, anisotropic) also possibly containing stützite, in a subhedral inclusion in chalcopyrite (cpy). Left – plane-polarized reflected light, oil immersion; centre – the same grain under crossed polarizers, rotated position; right – BSE image of a detail containing the alburnite grains.

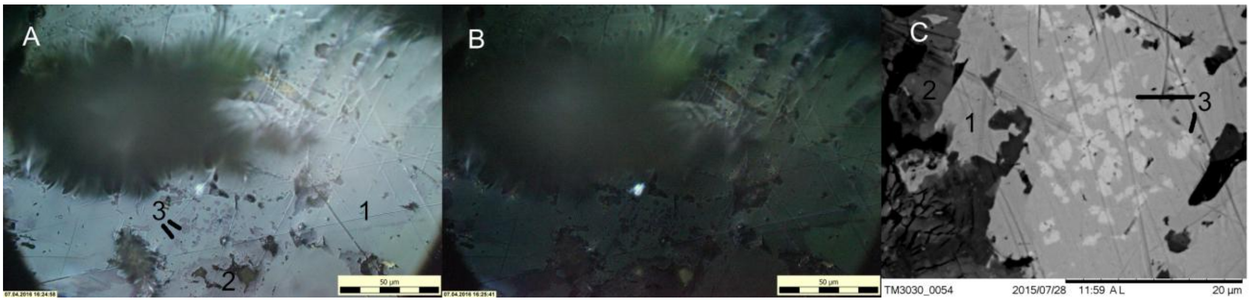

Fig. 5. Pearceite-polybasite (1) containing argentian fahlore (2) inclusions and overgrowths, as well as benleonardite blebs (3). A. Polarized reflected light, oil immersion; B. Crossed polarizers; C. Enlarged BSE image of a detail of the same field.

Alburnite laths and irregular patches up to 20 µ in size appear intergrown with hessite (Fig 4), in subhedral grains with outlines similar to the hessite-stützite composite grains in fig. 3. The diagnostic properties that allowed the identification of alburnite were: moderate reflectivity, slightly lower than that of tetrahedrite, a pure neutral grey hue, optical isotropy, and the EDS spectrum yielding a chemical composition consisting of Ag, S, Te, Ge, apart from which also significant and variable As was recorded.
Pearceite-polybasite aggregates displaying patchy compositional zonation overgrow chalcopyrite (Fig. 5). Ag-bearing tetrahedrite-tennantite forms inclusions as well as overgrowth in relationship with pearceite group minerals. Benleonardite of arsenian composition appears as isometric blebs only a few microns

across in Sb-richer pearceite-polybasite, displaying also a higher Ag/Cu ratio and containing essential Ge apparently substituting for As, reversely to the substitution identified in alburnite.

Chemical compositions

Alburnite was diagnosed by a combined optical and EDS study, in an assemblage of tellurides (Săbău et al., 2015). However, due to the equipment and working conditions used, systematic and high Fe, Cu and S contents were recorded in the tellurides, which were then tentatively identified as Cu and Fe-bearing sulfotellurides. The error was caused by using the charge compensation system of the Hitachi TM3030Plus tabletop SEM, which resulted in scattering of the incident beam outside the nominal scanning field and generation of a spurious XR signal coming from the neighbouring chalcopyrite. The sample was reinvestigated for semiquantitative and quantitative compositions of the phases on a Zeiss Merlin FE-SEM equipped with a high-resolution Schottky-type electron gun and a sensitive 50 mm^2 X-MaxN silicon drift detector. The EDS spectra obtained allowed a good stoichiometric recalculation of minerals of simple compositions (Tab. 1), yielding only diagnostic and informative data for more complex phases. Hessite and petzite may contain small amounts of Cu and Fe; Hg is habitual in stützite.

Table 1. Representative EDS telluride analyses.

wt. %	sylvanite			petzite			stützite			hessite	
ID	04C-80	01-59	04C-76	w-21	w-26	w-22	01-141	01-145	04C-9	v-192	u-115
Au	25.07	24.28	24.29	25.03	23.9	24.36			1.23		
Ag	13.27	13	12.84	40.97	40.53	40.74	55.24	55.16	56.14	61.22	61.14
Cu				0.53	1.21	0.96				0.82	0.85
Fe				0.67	0.78	0.46				0.65	0.63
Hg							2.79	2.35			
Te	61.66	62.72	62.87	32.8	33.58	33.48	41.89	42.33	42.07	37.32	37.37
S							0.08	0.15	0.14		
p. f. u.	Σ = 6			Σ = 6			Te+S = 3			Σ = 3	
Au	1.04	1.01	1.01	0.97	0.92	0.94			0.06		
Ag	1.01	0.98	0.97	2.91	2.84	2.88	4.64	4.56	4.67	1.92	1.92
Cu				0.06	0.14	0.12				0.04	0.05
Fe				0.09	0.11	0.06				0.04	0.04
Hg							0.13	0.10			
Te	3.95	4.01	4.02	1.97	1.99	2	2.98	2.96	2.96	0.99	0.99
S							0.02	0.04	0.04		

Alburnite failed to yield a stoichiometric formula; the EDS analyses indicate an Ag excess corresponding to the formula $(Ag_{8.589}Cu_{0.313}Fe_{0.093})_{=8.995}(Ge,As)_{1.014}(Te_{2.392}S_{3.599})_{=5.991}$ (average of 10 EDS analyses). Remarkable is the As/(As+Ge) ratio, ranging between 0.2-0.47. Benleonardite formula recalculation after the available EDS analyses also results in Ag excess. It is characterized by the absence of Sb, the presence of Ge as major substituent of As and the following elemental ratios: Cu/(Cu+Ag) = 0.1, Te/(S+Te) = 0.18. The Ge/(Ge+As) ratio amounts as much as 0.45. In comparison, pearceite-polybasite has variable As/Sb ratio and a Cu/(Ag+Cu) of 0.23-0.25.

Conclusions and interpretations

Besides the better-known pyrite – marcasite – arsenopyrite vein assemblage concentrating native gold (Orlandea & Velciov, 1996), we identified in the epithermal vein system at Măgura a chalcopyrite – fahlore association, in which precious metals are related to a telluride assemblage. In this assemblage, a second occurrence of alburnite was identified, in addition to another compound containing Ge and Te, Ge-bearing benleonardite.

Alburnite was diagnosed according to its optical properties and EDS-determined composition. The optical properties correspond to the argyrodite group and match those described at *locus typicus* (Tămaș *et al.*, 2014). Optical isotropy is indicative for the high-temperature polymorph of cubic symmetry, with essential As substituting for Ge. Electron backscatter diffraction and selected area electron diffraction patterns of alburnite from Roșia Montană (Tămaș *et al.*, 2014) are consistent with space group $F\bar{4}3m$, which represents the critical indication of a new phase rather than simply Te-substituted argyrodite (Tămaș *et al.*, 2006): natural argyrodite is the polymorph α", space group $Pna2_1$. The same holds true for Te-substitution in the related Te-bearing canfieldite (Gu *et al.*, 2012; Bindi *et al.*, 2012) leading to a cubic face-centred symmetry. Despite the absence of structural determinations on natural canfieldite, synthetic Ag_8SnS_6 also displays the α" structure ($Pna2_1$) at room temperature (Pistorius & Gorochov, 1970).

The argyrodite supergroup minerals have a structural pattern containing a rigid framework of chalcogenide tetrahedra, one sixth of which coordinate a metalloid cation. Inside this framework, silver distribution is highly disordered along diffusion paths inside icosahedral clusters of tetrahedra and connecting them (Boucher *et al.*, 1993), thus enabling ionic conductivity properties. The high-temperature (HT, γ) polymorph is characterized by highly disordered Ag along diffusion pathways, whereas 1-2 lower temperature polymorphs appear for each compound through cation localization, sometimes accompanied by tetrahedra distortion. A total of 7 polymorphs are cited by Pistorius & Gorochov (1970) in the supergroup, namely γ (HT), β, β', β", α, α', α", where β and α polymorphs record symmetry lowering from face-centred to primitive by cation ordering (Boucher *et al.*, 1992), and prime symbols indicate concurrent tetrahedral distortions. The inversions are fully reversible and the higher temperature phases unquenchable (Gorochov & Flahaut, 1967).

The chemical composition of the argyrodite supergroup may be summarized as $A^{m+}_{(12-n-x)}B^{n+}X^{2-}_{6-x}Y^{-}_{x}$ (Kuhs *et al.*, 1979), where A is a low-charge transitional cation with a d^{10} electronic structure (Cu^{+}, Ag^{+}, Cd^{2+}, Hg^{2+}), B a highly-charged, tetrahedrally-coordinated, usually metalloid cation (Ga^{3+}, Si^{4+}, Ge^{4+}, Sn^{4+}, P^{5+}, As^{5+}, but also Ti^{4+}, Nb^{5+}, Ta^{5+}), X a chalcogenide element, and Y a halogen.

Despite the large number of synthetized compounds and wide range of potential substitutions in the supergroup, only five natural phases have been so far identified, the argyrodite-alburnite pair, their Sn equivalent canfieldite-"tellurocanfieldite", and putzite $(Cu, Ag)_8GeS_6$. The substitutions reported, though extensive, are restricted to elements of the same subgroup on the same site, such as CuAg_, SnGe_ (Prior & Spencer, 1898), TeS_ and SeS_ (Wang *et al.*, 1984). The effect of Se and Te substitution consists in the stabilization of the HT-phase to lower temperatures, also surprisingly achieved by the CuAg_ substitution, as putzite is a γ phase (Paar *et al.*, 2006). The compositions found in the present investigation indicate extensive As substitution on the B site, implying solid solution towards billingsleyite (Ag_7AsTe_6), though the preliminary stoichiometry obtained by EDS is not consistent with this assumption, since Ag is apparently in excess. Considering also that billingsleyite represents the β polymorph ($P2_13$) at ambient temperature, it is not certain whether the actual space group of the reported phase is $F\bar{4}3m$, implying identity with alburnite, or a distinct phase with $P2_13$ symmetry.

The second sulfotelluride identified is the studied material is Ge-bearing benleonardite forming unmixed blebs in pearceite-polybasite. Benleonardite belongs to the pearceite group (Bindi *et al.*, 2015), containing sulfosalt-specific $[(As,Sb)S_3]^{3-}$ pyramids in the module A, $[(Ag, Cu)_6(As, Sb)_2S_7]^{2-}$, in contrast with the thiogermanate tetrahedra $[AsS_4]^{3-}$ in argyrodites. Yet a possible substitution mechanism for germanium is the replacement of two facing $[AsS_3]^{3-}$ pyramids by the thiodigermanate group $[Ge_2S_6]^{4-}$.

The subhedral Ag telluride (hessite-stützite) intergrowths included in chalcopyrite and associating with alburnite strongly suggest breakdown of a pre-existing homogeneous silver telluride. The phase relationships in the Ag-Te join (Karakaya & Thompson, 1991) indicate that between 33 and 38 per cent Te an $Ag_{1.9}Te$ compound would coexist with either stützite or hessite, from 460 °C down to 120 °C, temperature at which it decomposes spontaneously to stützite and hessite, presenting no natural occurrence. Fine intergrowths similar with those described above were interpreted also by Kelly & Goddard (1969) as $Ag_{1.9}Te$ breakdown textures in the Boulder County ore.

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LOCAL NATURAL RESOURCES USED BY THE EARLY NEOLITHIC COMMUNITIES FROM SOUTH-WESTERN TRANSYLVANIA IN GROUND STONE TOOLS

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Abstract: The natural resources of a geographical area start to be systematically exploited from the immigration of the first populations in a region. In time, this type of activity leads to the specialization of some settlements in the exploitation and transmission of raw materials to the other human communities. Our approach takes into account the first concerns about exploiting of the mineral resources by the prehistoric communities, more exactly by the Early Neolithic ones, in south-western Transylvania. One activity less common is the manufacture of polished stone tools. The first farming communities from the above mentioned area, also known as Starčevo-Criş populations, inhabited these region eight millennia ago, and they started exploiting gradually the local rocks for the needs of the new type of the Neolithic economy, based on the agriculture and livestock. Thus, after recent or past petro-graphic determinations results, we have a clearer picture on acquiring different types of raw materials which were used for the production of specific tools for Neolithic communities, such as: grinders, querns, hammers, axes, chisels etc.
After the analyzing of the petrographical results, we can conclude that the first Neolithic communities from south-western Transylvania exploited different types of rocks for the ground stone industry, most often sandstones, quartzites and andesites, the majority with occurrences in South of Apuseni Mountains or in North of Poiana Ruscă Mountains, other ones coming from the riverbeds of Mureş, Sebeş, Orăştie, Strei and Cerna rivers.

Keywords: south-western Transylvania, Starčevo-Criş settlements, local natural resources, ground stone industries, petrographic determinations

Introduction

The settling of the first farmers in the south-western Transylvania (more exactly in the region located between Sibiu and Deva) involved not only a good knowledge of the agricultural potential of the region, but also a good evaluation of the natural resources, so useful for the Neolithic communities in different stone tools manufacturing (chipping or polishing) processes. As a general observation we can say that, for chipped stone tools, the citations in Romanian bibliography are relatively numerous compared to references about raw materials for ground stone tools, almost unknown for local resources.

Starting from the archaeological and geological evidence considered at the moment, we can say that certain categories of local raw materials used by the first Neolithic population groups (Starčevo-Criş) from the South-West of Transylvania can be located, some of them being directly connected with the geological processes of a region over time.

An archaeological discussion

The polished stone tools are frequently found in the Middle Mureş Basin, but the number of the published pieces is limited. From the point of view of the polished stone tools, we can categorize them in this way: with sharp edge (axes and other version of them), hammerstones/strikers, grinders, querns or whetstones for pottery, stone, bone etc.

From all these artefacts, only the axes have received more attention over time; this statement can be substantiated by older studies published in the last decades. The axes discovered at Ocna Sibiului-*Triguri* (Paul, 1989; Paul, 1995; Ciută, 2005), Şeuşa-*La Cărarea Morii* (Ciută, 1997; Ciută, 2000; Ciută, 2005; Ciută, 2009), Călanul Nou-*La Podină* (Ciută and Andrei, 1999), Haţeg-*Câmpul Mare* (Roman and Diaconescu, 2002), Tărtăria-*Gura Luncii* (Lazarovici et al., 2011) and, recently, at Cristian I (Luca, 2015; Niţu et al., 2015) can be found among them.

On the other hand, the information about the raw materials geology is more less known for the south-western Transylvania. Even so, the geo-archaeological aspects of ground stone tools recently were approached differently (Lorinţ, Bărbat, 2012; Lorinţ, Bărbat, 2013; Lorinţ, Bărbat, 2014; Lorinţ, Bărbat, 2015), thereby, more than 30 samples from different archaeological sites were chemically and petrographically analyzed. In this way were reconstituted, even just partially, some possible exploitation points of local raw material in the Early Neolithic by the Starčevo-Criş cultural complex communities.

The recent geo-archaeological results

The newest geo-archaeological approaches provided the opportunity to outline some raw materials sources, some of them like andesites, unknown until now (Lorinţ and Bărbat, 2014; Lorinţ and Bărbat, 2015). To verify the local nature of andesites and other types of rocks like quartzites, sandstones and schists, petrographical and geochemical analysis were performed on some thin sections from the stone tools. The geo-archaeological information was added to those contributions, mostly of them provided by bibliography, outlining in this way a picture of the main natural resources available to the first farmers from the south-western Transylvania.

Classifying the polished stone tools made from local rocks (Table 1), we can promote several working versions of the use of the certain raw materials types. Also, some of the useful rocks for the Neolithic communities were near settlements, which shows that population groups usually know the mineral resources in a particular area, probably the locating process of a settlement being a consequence of raw materials occurrences in that territory.

For a more objective image about the raw materials sources, the local natural rocks will be presented according to their importance in the lithic inventory of Starčevo-Criş communities from south-western Transylvania, so that in future, new geo-archaeological research could be completed.

Table 1. The main local raw materials identified in the Early Neolithic sites from the south-western Transylvania utilized in production of ground stone tools

Raw material	Stone tool	Archaeological Site	Number of artefacts	Total
Andesite	Quern	Şoimuş-*Teleghi*	5	7
	Grinder		1	
	Splinter		1	
Sandstone	Quern	Şoimuş-*Teleghi*	2	9
		Şeuşa-*La Cărarea Morii*	4	
	Axe	Subcetate-*Halta Covragiu*	1	
		Şeuşa-*La Cărarea Morii*	1	
	Whetstone	Haţeg-*Câmpul Mare*	1	
Quartzite	Hammerstone/ Striker	Şoimuş-*Teleghi*	2	5
		Orăştie-*Fares*	1	
		Cerişor-*Peştera Cauce*	1	
		Cristian I	1	
Schist	Axe	Orăştie-*Dealul Pemilor* X_8	4	4
Chert	Striker/Grinder	Cristian I	4	4
Gneiss	Hammerstone/ Striker	Şoimuş-*Teleghi*	1	2
		Râpaş-*Fermă/Grivoni*	1	
Jasper	Hammerstone/ Striker	Şoimuş-*Teleghi*	1	7
		Cristian I	1	
Argilit/Silicolite	Striker/Grinder	Cristian	2	2
Diabase	Grinder	Şoimuş-*Teleghi*	1	1
Volcanic riolitic tuff	Axe	Călanul Nou-*La Podină*	1	1
Limestone	Axe (?)	Şeuşa-*La Cărarea Morii*	1	1
Local flint	Striker/Grinder	Cristian I	1	1
Unknown (I) „river stones”	Hammerstone/ Striker	Călanul Nou-*La Podină*	1	1
Unknown (II) „volcanic/hard rocks”	Hammerstone/ Striker	Şeuşa-*La Cărarea Morii*	4	14
		Haţeg-*Câmpul Mare*	1	
	Chisel		1	
	Striker/Grinder	Cristian I	1	
	Axe	Ocna Sibiului-*Triguri*	7	
Unknown (III)	Axe	Cristian I	1	7
	Grinder	Ghirbom-*La Ghezuini*	1	
	Hammerstone/ Striker	Cristian I	2	
		Geoagiu de Sus-*La Craia*	1	
		Tărtăria-*Gura Luncii*	1	
	Hammerstone/ Grinder	Cristian I	1	

The sandstones (Tables 1, 2, 4) are the most common materials found in the lithic inventory of the Early Neolithic settlements, which are used for different purposes; from these types of rock, querns, grinders or whetstones were manufactured. The querns, manufactured from sandstones found in terrace deposits, were discovered in the Early Neolithic settlement from Şoimuş-*Teleghi*; some of these Upper Cretaceous sandstones are visible even today at the surface, in the proximity of the area where was disposed this site (Lorinţ and Bărbat, 2015; Bărbat, 2015). From the Haţeg area we mention the presence of sandstones in the manufacturing of polished stone tools, as the discoveries made at Subcetate-*Halta Covragiu* (Lorinţ and Bărbat, 2013) and Haţeg-*Câmpul Mare* indicate (Roman and Diaconescu, 2002). In the case of the archaeological piece from Subcetate-*Halta Covragiu*, representing a massive axe from a polished stone, the petrographic studies of the thin sections led to the conclusion that it was made from siliceous sandstone (Lorinţ and Bărbat, 2013). Regarding the origins of the raw materials, for the both pieces cited in the Haţeg area, it is presumed that the raw materials were collected from Strei and Galbena river beds; either the stone axe from Subcetate-*Halta Covragiu* was brought in the Neolithic settlement through exchanges with other communities from different geographical region, such as Banat area. A type of sandy or micro-conglomeratic sandstone, possible collected from the nearby river beds, was identified during the archaeological investigations at Şoimuş-*Teleghi* (Lorinţ and Bărbat, 2015) and Şeuşa-*La Cărarea Morii* (Ciută, 2000, Ciută, 2005, Ciută, 2009).

The quartzite (Tables 1, 2, 5) is a raw material very easy to find and especially frequent in the studied area riverbeds (Mureş, Sebeş, Orăştie, Strei, Cerna), hence the preference of the first Neolithic communities for these boulders of quartzites suitable for using such as hammerstones and useful, for example, in wheat milling. These kind of pieces were often found in archaeological discoveries belonging to the Early Neolithic from Şoimuş-*Teleghi* (Lorinţ and Bărbat, 2012; Lorinţ and Bărbat, 2015), Cerişor-*Peştera Cauce* (Luca et al., 2004), from the Orăştie area (Lorinţ and Bărbat, 2012), or, recently, from Cristian I (Niţu et al., 2015, Luca, 2015). Unfortunately, it is very difficult to determine the source of raw material for each settlement in part, knowing that the quartzites, as well as sandstones, had a large distribution; that's why, we believe that these types of rocks (quartzites) were acquired from river valleys nearby the Neolithic settlements.

In south-western Transylvania, the andesites (Tables 1, 3) are known due to the geo-archaeological research on the chipped and polished stone tools artefacts discovered in the Early Neolithic settlement from Şoimuş-*Teleghi.* The mineralogical determinations for the ground stone tools showed that andesites present similar features as those existing in the North of Poiana Ruscă Mountains, near Deva; one of the possible sources can be *Dealul Cetăţii* deposits, located to 2 km South of the Şoimuş-*Teleghi* site (Lorinţ and Bărbat, 2014; Lorinţ and Bărbat, 2015; Bărbat, 2015).

The schists (Tables 1, 4) were used as raw material for manufacturing some axes from the Early Neolithic settlement Orăştie-*Dealul Pemilor* X_8. Petrographic analysis performed on four axes fragments, revealed that the quartz-feldspathic (with biotite) and amphibolic schists (with Tremolite and Actinolite) were sought to achieve the axes. Related to the raw material could be considered the local appurtenance of rocks, from the Orăştie river valley, but at the same time the native stones from the Southern and Oriental Carpathian Mountains should not be excluded, certainly, having as working hypothesis the importation possibility of finished parts from the neighbouring or from far away Neolithic communities (Lorinţ and Bărbat, 2013).

The gneisses (Tables 1, 2, 5) occur in the Neolithic settlements only as some ovoid boulders with wear traces at the ends or sides of the rock. As well as quartzites, gneisses were procured mostly from riverbeds. In case of the Şoimuş-*Teleghi* and Râpaş-*Fermă/Grivoni* sites may we could presumed the occurrence of such raw materials from the Mureş riverbed, a watercourse easily approached by Neolithic communities from the points mentioned, due to the proximity of the source of raw material (Lorinţ and Bărbat, 2012, Lorinţ and Bărbat, 2015).

The jasper (Table 1) is also met in the manufacturing of lithic stone tools with polishing traces, often this type of artefacts like hammerstones, being present in the Şoimuş-*Teleghi* site. The jasper boulders as a raw material could be provided from the Mureş River or on its nearby tributaries such as Boholtului, Certejului and Căianului Valleys. For this type of raw material, other sources known for surface occurrance can be located in the South of the Apuseni Mountains or North of Poiana Ruscă Mountains (Luca et. al., 2004).

The diabase (Tables 1, 2) is archaeological certified as a raw material in one of the earliest feature from Şoimuş-*Teleghi*, respectively in C18a pit-house. A grinder is made from this kind of rock (Lorinţ and Bărbat, 2015). Regarding the raw material source, we believe it is still a local one, most likely tributary to the southern Apuseni Mountains.

Other possible categories of local rocks, which were analyzed only macroscopically (Table 1), can be mentioned also: limestones, siliceous clay, granodiorite and rhyolitic volcanic tuffs (Ciută and Andrei, 1999; Ciută, 2000; Roman and Diaconescu, 2002; Ciută, 2005; Ciută, 2009).

Table 2. Fragmentary hammerstones (1-2), grinder (3) and querns (4-5) found at Şoimuş-*Teleghi*; Macroscopic and microscopic view – X40 Magnif (1-5) /cross and plane polarized light (XPL/PPL)

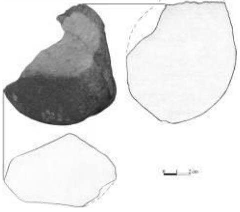
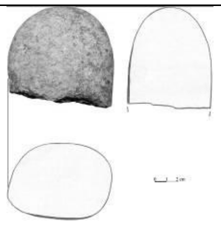
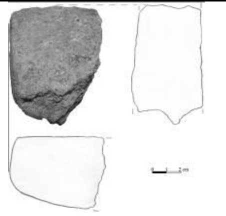
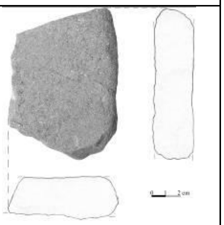
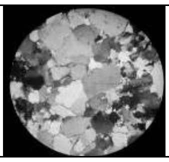
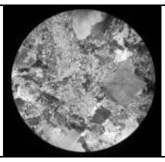
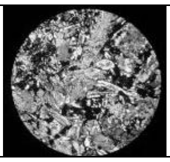
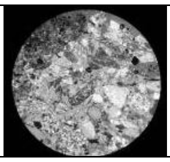
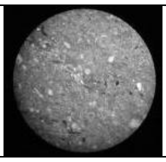
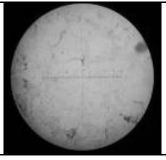
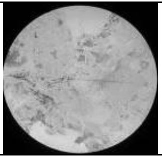
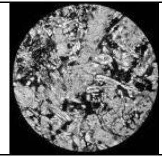
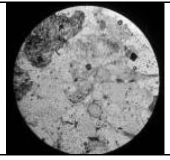
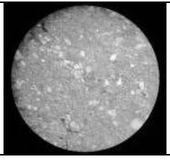
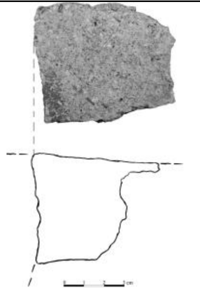
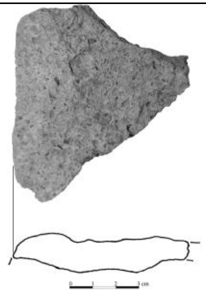
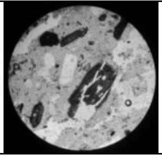
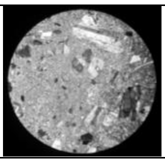
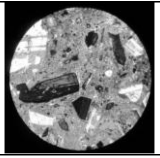
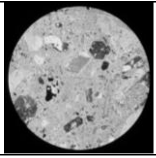
1	2	3	4	5
white-yellow pale quartzite	white-pink to gray gneiss.	dark to gray diabase	Micro-conglomeratic sandstone	sandstone
				
				
1a (N+)	2a(XPL)	3a(XPL)	4a(XPL)	5a(XPL)
				
1b (N//)	2b(PPL)	3b(PPL)	4b(PPL)	5b(PPL)

Table 3. Fragmentary querns (1, 3, 5), grinder (4) and splinter (2) found at Şoimuş – *Teleghi*; Macroscopic and microscopic view – X40 Magnif (1-5)) /cross and plane polarized light (XPL/PPL).

1	2	3	4	5
Light to dark gray colour andesites varieties				
				
				
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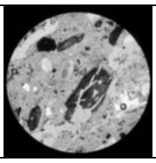
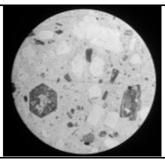
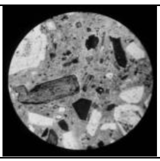
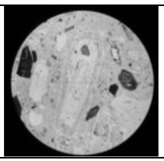
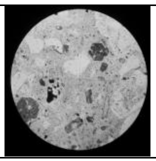
				
1b (PPL)	2b(PPL)	3b(PPL)	4b(PPL)	5b(PPL)

Table 4. Fragmentary axes (1-5), found at Orăştie-*Dealul Pemilor* (1-4) and Subcetate-*Halta/Canton Covragiu* (5); Macroscopic and microscopic view – X40 Magnif (1-5) /cross and plane polarized light (XPL/PPL)

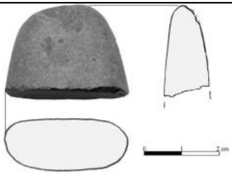
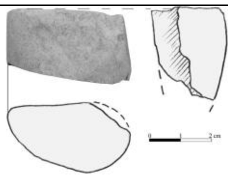
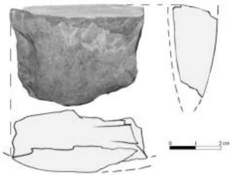
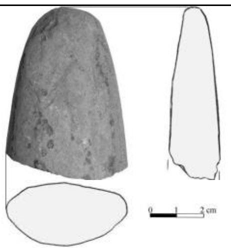
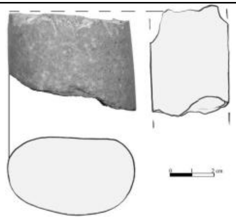
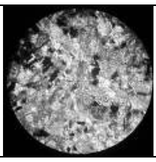
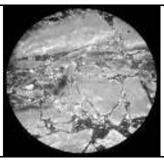
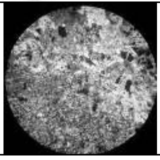
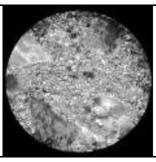
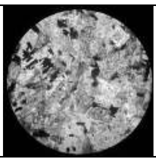
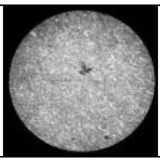
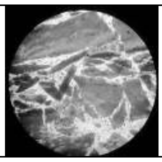
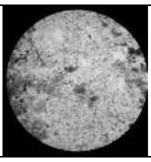
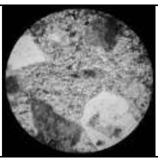
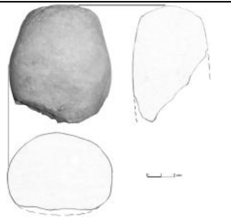
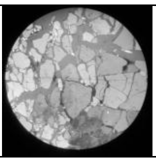
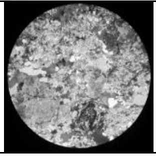
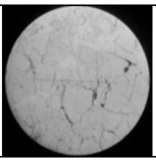
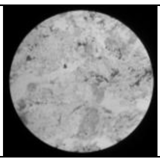
1	2	3	4	5
quartz-feldspathic schist	quartz-feldspathic schist with biotite	amphibolic schist with tremolite and actinolite	quartz- feldspathic schist	siliceous sandstone
				
				
1a (XPL)	2a(XPL)	3a(XPL)	4a(XPL)	5a(XPL)
				
1b (PPL)	2b(PPL)	3b(PPL)	4b(PPL)	5b(PPL)

Table 5. Fragmentary hammers (crusher / striker), found at: Orăştie-*Fares* (1) and Râpaş-*Fermă/Grivoni* (2); Macroscopic and microscopic view – X40 Magnif (1-2) /cross and plane polarized light (XPL/PPL)

1	2
quartzite	gneiss/orthogenesis
	
	
1a (XPL)	2a(XPL)
	
1b (PPL)	2b(PPL)

Conclusions

Although still in its beginning, the recent geo-archaeological studies undertaken on the ground stone tools from the Early Neolithic settlements in the south-western Transylvania indicates the preference of the Starčevo-Criş communities for the local rocks, with the sandstones and quartz rocks being the most common raw materials. However, interest in andesites, schists, gneisses and jaspers would have been second to this group of useful rocks, being accessible to the Neolithic population groups from the studied area. A less documented volcanic rock is the diabase; its presence probably indicate a possible source of raw material at a distance much greater, hence the rock scarcity in the lithic inventory of the Early Neolithic sites from south-western Transylvania.

Still little known, the raw materials used by the Early Neolithic communities from the south-western Transylvania begin, gradually, to be recognized by these geo-archaeological studies. Unfortunately, the lithic materials published so far for the geographical area mentioned are still restricted in terms of number, which still leaves open the problem of using local rocks in ground stone tools production but especially the knowledge of the areas from where the Neolithic farmers exploited the raw materials.

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Rom. J. Mineral Deposits, vol. 89 (2016), nr. 1-2, p. 105-110

PRELIMINARY DATA OF HEAVY MINERAL PLACERS DEPOSITS FROM PETITE COTE, SENEGAL

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Abstract. The purpose of this paper is the study of heavy minerals placers deposits from SW Senegal (Petite Côte), West Africa which covers an area of 1599 km^2. Petite Côte is represented by fluvial deposits of heavy minerals which are spatially and genetically associated with coastal deposits of heavy mineral sands. Alluvial deposits containing economic or potentially economic concentrations of heavy minerals are traditionally referred to as "placer deposits". The main products are zircon, ilmenite, rutile accompanied by small amounts of tourmaline and leucoxene. The igneous rocks represent by the main source of the heavy minerals and in a lesser extent other secondary deposits that form the heavy-mineral sands in coastal settings.

Keywords: West Africa, Petite Côte, heavy minerals, placers deposits, fluvial deposits, source rocks

1. Introduction

Heavy minerals deposits from Senegal had an economic interest for the first time in the 1990ies. In the present paper we deal with the placers formed as a combined result of the fluvial erosion, transport and accumulation of the Somone, Casamance, Saloum, Gambia, and Senegal rivers and the influence of marine currents, which transported the unconsolidated sediments derived from the Precambrian inland basement area composed of granites, granodiorites, andesites, basalts and shales etc. The marine currents supsequently processed the unconsolidated sediments and reshaped the beach deposits in Senegalo - Mauritanian basin. The placers deposits from south - weastern Senegal are recent accumulations of heavy minerals (Holocene) and they represent one of the largest deposits of this (Diara, 1999).

2. Geological mapping of the studied area

Senegal is located in West Africa, roughly at the intersection 14º N latitude and 14º W longitude. Regarding the geological setting, the territory of Senegal is dominated by two major units: the Precambrian basement located in the eastern part of the country and the so-called Senegal Basin composed of sedimentary deposits (Upper Cretaceous - Quaternary) in the west - central part of the country (Gaina et al. 2013). The Precambrian formations are made of volcano-sedimentary deposits which belong to the tectonic window Kédougou-Kenieba, and represent the main source area for the heavy mineral deposits. The age of the sediments is Hercynic and they form one of the moving areas of West African craton (Gaina et al.2013) craton.

The study area, Petite Côte, is situated in the western part of Senegal, in Senegalo-Mauritanian sedimentary Basin and covers 1599 m^2 (Fig. 1). The investigated area is crossed by the Saloum river which forms a delta and brings 665.000 tons of sediments per year (Sakho, 2011).

The entire perimeter is covered by Tertiary sedimentary formations, represented by laterite deposits, fluvial alluvium, marine sand banks, eolian mobile dunes, continental fixed dunes and marine sands situated at the entrance of Saloum Delta. Marine sand deposits contain heavy minerals, mainly ilmenite and zircon and subordinately rutile and leucoxene (Diara, 1999). In the northern part of the Petite Cote perimeter between M'Boudiene - Nianing and Ndiagania the Lower Ypresian deposits belongs to Thies Formation and are represented by marls, phosphate and glauconitic limestones, clays and sands.

In the central part of the perimeter, in the area between Saloum delta - Djifere - Palmarin, the basement is represented by the Lam Lam Formation (Lutetian) which consists of an alternance of marls with *Discocyclina* and limestones with shellfish and algae. In Saloum Delta area Holocene old coastal cordons of 2-3 km width and metric heights made of sand banks, dunes and coastal sand which remained after the withdrawal of the sea are known (Diara, 1999).

The rock sources of heavy minerals deposits from Petite Côte are particularly those enriched in Ti-oxide minerals and it is supposed that they belong to Mako Grup (Precambrian Age) which contains mafic and ultramafic rocks (peridotite, diorite, granodiorite) and Saraya Grup (granite).

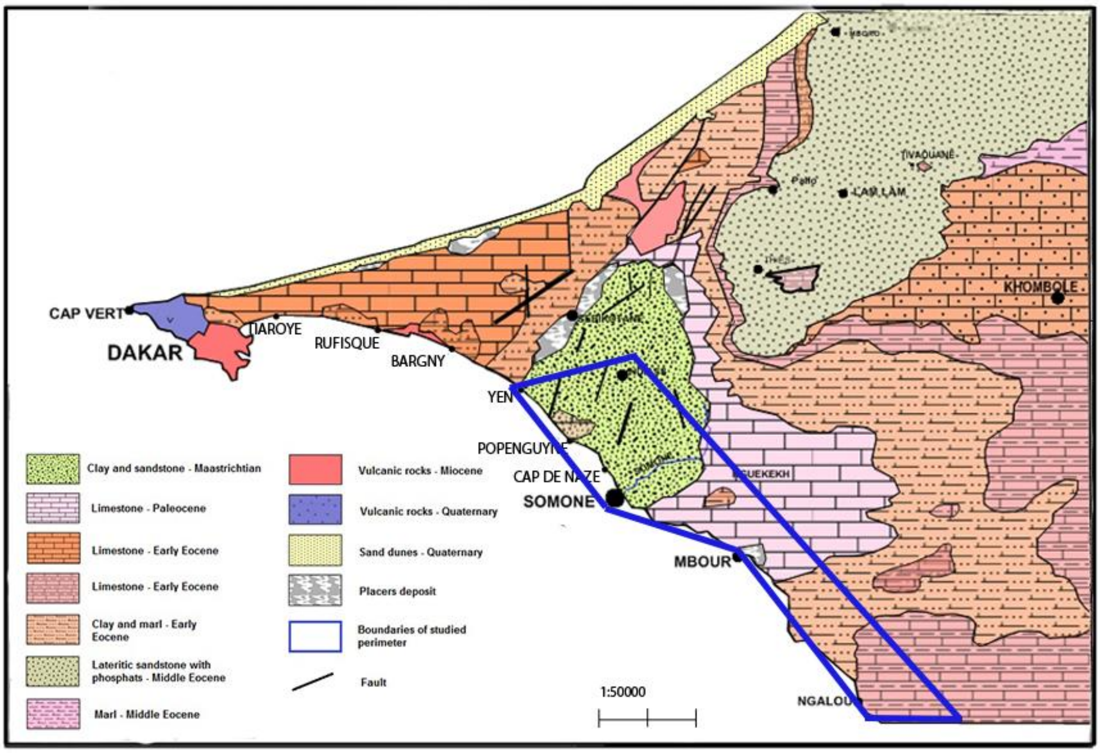

Figure 2: Simplified geology and boundaries of studied perimeter (Oprea, 2014)

3. Material and Methods

After all samples were collected from the Mbour-Ngalou area, 120 representative samples were analyzed. The first method used was mineral separation with sodium and lithium polytungstate liquid with a density of 3.0 g/cm^3. After separation of mineral grains were analysed by granulometric, morphometric and mineralogical studies. The particle size of the sand placers was measured by laser granulometry with a HORIBA LA-950 device, which uses the principle of laser light diffraction on the surface of the particles. Morphometric studies of samples consisted in a statistical assessment of a large number of grains. The assessment leads to the reconstitution of the origin and the genesis of the paleo-environment. Using a Krumbein and Sloss diagram, the sphericity and the roundness parameters were determined. For the final assessment 12 polished sections were analyzed with an AXIO IMAGER - Carl Zeiss microscope and binocular microscope. The microscope was equipped with a digital camera and the images were processed with Axio Vision software.

4. Mineralogy

The processes that form the heavy-mineral sands deposits in the coastal area begin inland, through the erosion of metamorphic and igneous rocks containing the heavy minerals. Streams and rivers transport the detritus to the coast, where it was accumulated in a variety of coastal environments. The sediments are reworked by waves, alongshore currents and wind, which are effective mechanisms for sorting the mineral grains, on the basis of their differences in size and density. The finest grained, most dense minerals are the most effectively sorted (Bradley et al., 2010).

Mineralogical analysis enabled the identification of heavy minerals after separation with sodium and lithium polytungstate liquid. The following minerals were identified (Fig. 2): zircon, tourmaline, rutile, ilmenite, magnetite, hematite, anatase, goethite and highly mechanic - resistant minerals such staurolite and kyanite. From the above mentioned minerals the less frequent are garnet, titanite and lepidocrocite.

The microscopical study revealed several mineralogical characteristics as follows (Fig. 2). The zircon crystals show pleochroism in yellow-green tones, compositional zoning and rutile inclusions. Ilmenite contains exsolutions of rutile and around ilmenite grains were observed rutile and zircon wreaths. Magnetite usually contains exsolutions of hematite. Lepidocrocite appears on polished sections with red - yellow internal reflections.

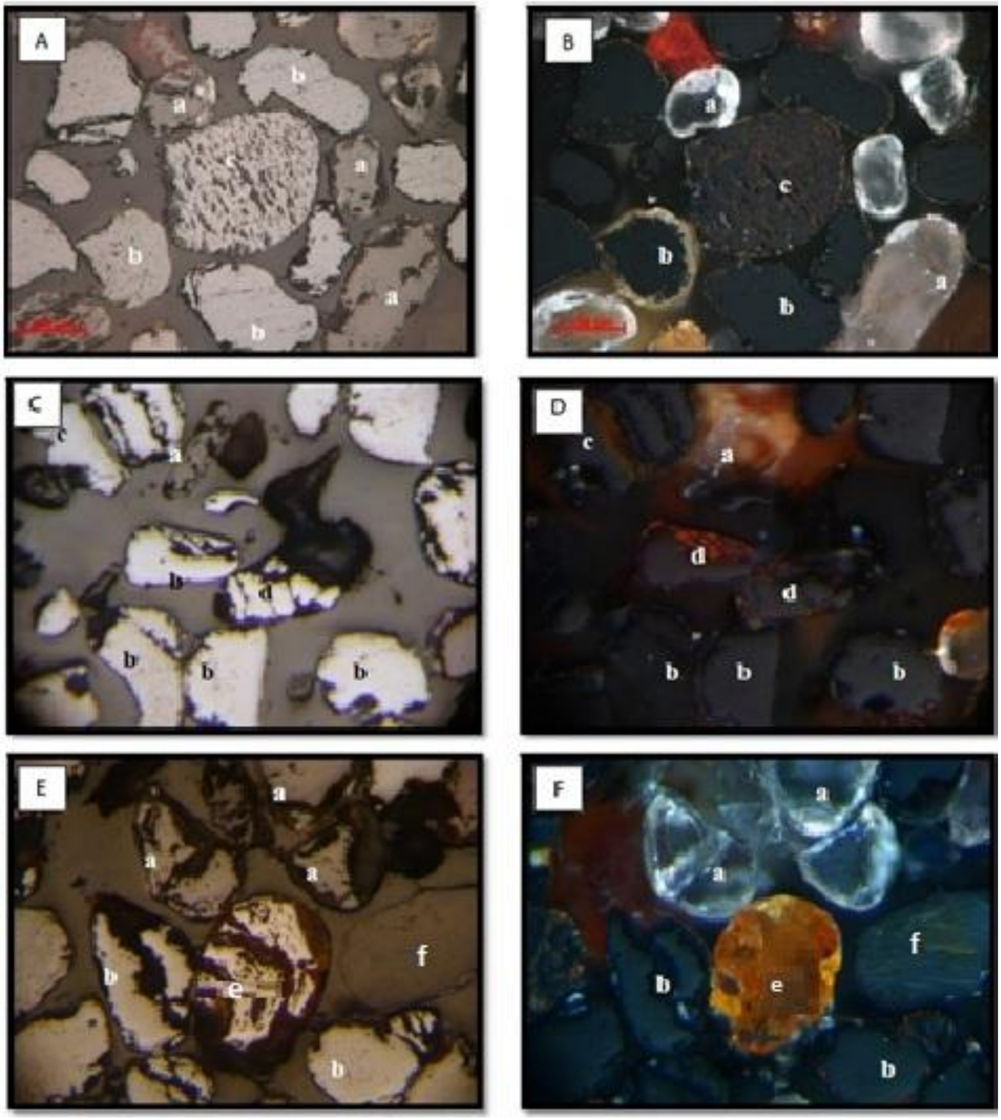

Figure 3: Microscopic views (left column - one polarizer, right column - two polarizers) of the heavy fraction: A and B - zircon, ilmenite, and exsolution of ilmenite within rutile; C and D - zircon, ilmenite, lepidocrocite with internal reflection, and ilmenite with rutile wreaths; E and F zircon, ilmenite, goethite, and hematite. Abbreviations: a - zircon, b - ilmenite, c - exsolution of ilmenite within rutile, d- lepidocrocite with internal reflection, e - goethite, f - hematite.

The mineralogical percentages were represented on graphs taking into account the depth of the drillings, for each meter (Figure 3). From the graphs below, it can be observed the predominance of ilmenite in the first two meters with a maximum of 23 %, followed by rutile + ilmenite (ilmenite with wreaths of rutile) and goethite. Zircon and leucoxene presents low concentrations from 0,40 % to a maximum of 3,25 %.

The distribution of mineral species present two trends: Saloum Delta barriers are rich in rutile, while beach barriers are richer in goethite. All other heavy minerals show a homogeneous distribution parallel to the shoreline.

5. Grain size

For the analyzed samples the particle size fraction is homogeneous throughout the study area. The median value ranges from 1.862 - 1.968 Φ, which suggests that the primary fraction is represented by medium grain sand.

The degree of keenness calculated by statistical method varies between 0.95 and 1.090 Φ. According to these values and scale variation keenness of Folk (KG = 0.67 very platykurtic; KG = 0.67 – 0.90 platykurtic, KG = 0.90 – 1.11 mesokurtic, KG = 1.11 – 1.50 leptokurtic, KG = 1.50 – 3.00 very leptokurtic, KG > 3 extreme leptokurtic) it is possible to sustain the mesokurtic representation type, demonstrating a moderate to well sorting of the analyzed material.

The cumulative curve (Figure 4) presents the segments C (sliding transport), B (suspension transport), and segment A (saltation transport), which indicates that the analysed materials supported the action of the waves and consequently these materials coming from the placer deposits are very well washed.

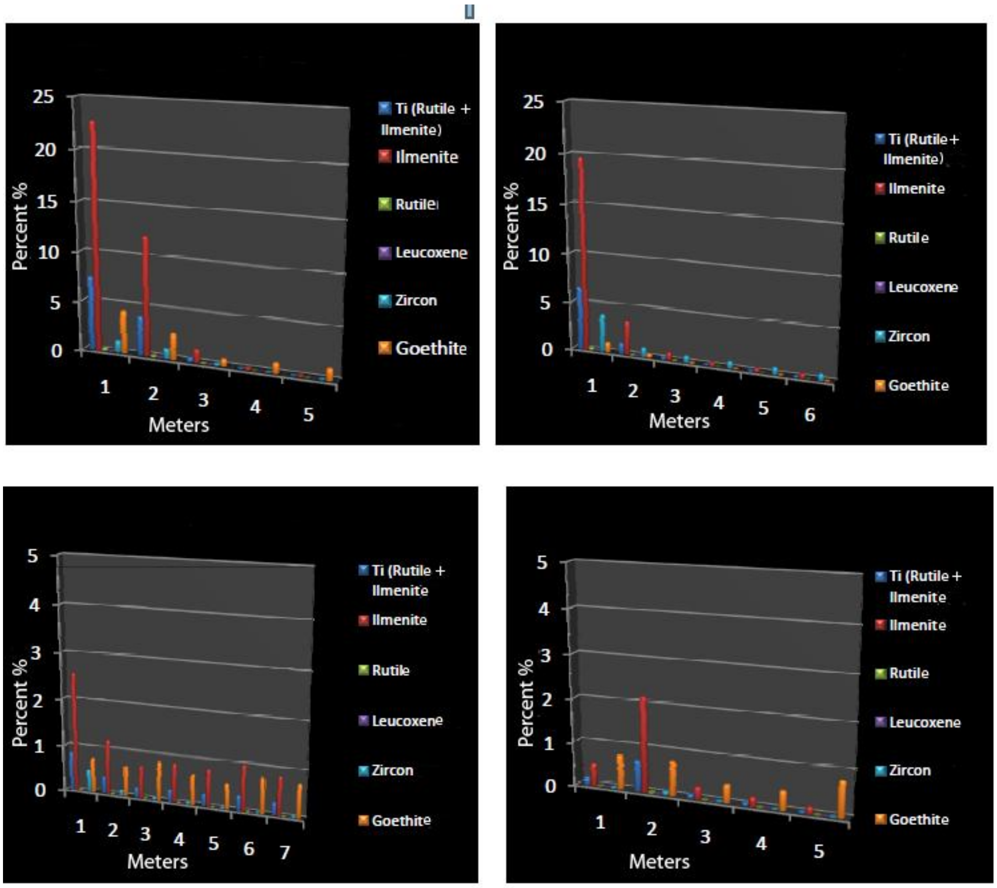

Figure 3: Distribution of heavy minerals in boreholes.

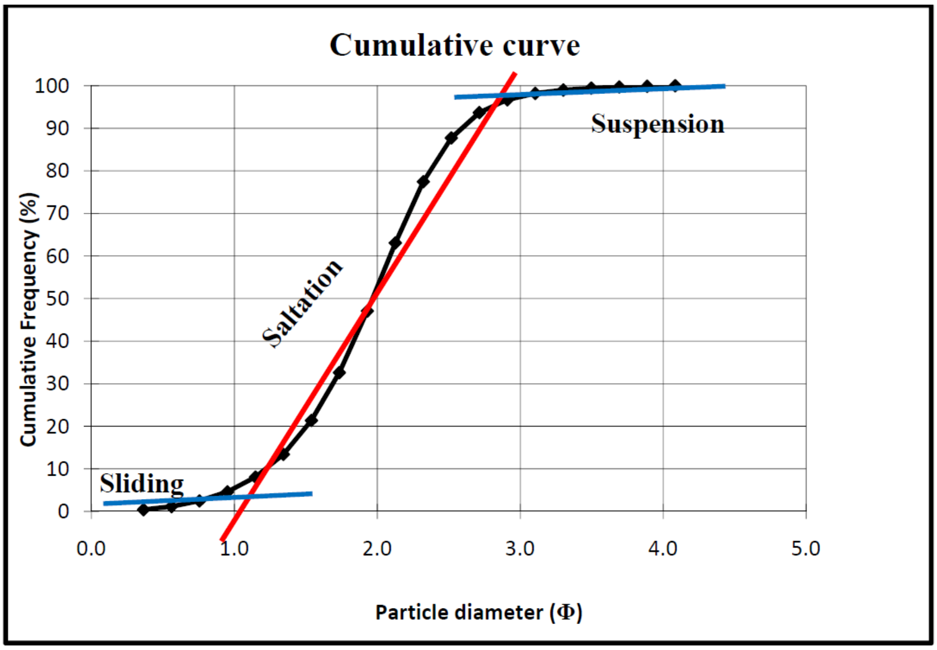

Figure 4: The cumulative curve of heavy minerals in the beach area

This distribution suggests the proximity to the shore area with the highest wave actions enabling thus the washing of the unconsolidated material, removal of very fine fraction and rolling of the particles. This is demonstrated by the sorting, granulometry and composition of the analyzed material. The absence of grains population transported by bottom sliding may be due to the existence of a very strong current enough to produce saltation ofall the coarser grains.

6. Morphometry

The identified minerals on the binocular microscope present the shape and contours as follows:

a) garnet (sperssartine - XRF analysis), rutile, ilmenite, magnetite, have isometric - spheroidal shapes and very well rounded contours;

b) staurolite, goethite, kyanite and zircon, have prismatic or columnar cylindrical shapes and various contours from angular (staurolite) to very well-rounded (zircon);

c) tourmaline crystals and anatase presents some planar - discoidal shapes and various contours from sub angular (anatase) to very well-rounded (tourmaline).

The shapes of the crystals may indicate the origin of country rock of the minerals. For example, garnet, kyanite, staurolite, rutile, leucoxene, anatase coming from metamorphic rocks (schists, gneisses, amphibolites) localized in eastern part of Senegal and zircon, magnetite, ilmenite, hematite and goethite come from magmatic origin possible from the tectonic window Kédougou-Kenieba.

Regarding the roundness degree most of the grains are sub-rounded which indicates a fluvial domain. The roundness is the degree of smoothing due to abrasion and it depends of the currents flow velocity.

7. Conclusion

According to the reference systems used, the dominant granulometric fraction of the analysed samples from La Petite Côte is included in the class of medium grained sand, with a good sorting and homogeneous distribution.The cumulative curve is well developed in its central segment, suggesting a dominant transport by saltation, in the beach area where wave action is maximized, making possible the washing of the sedimentary material with a good sorting and homogene compositional granulometry.

The morphometric analysis focused on the grain shape and extent of their contour. These parameters varies according to the mineralogy of the mineral grains. The shape of the grains is dominantly spheroidal - isometric, with rounded and subrounded contours, which indicates a long transport in a fluvial environment, where the level of rolling increases with the velocity of the flow or continuous running of the granules in the marine environment due to the wave action.

The mineralogical analysis revealed the following minerals: ilmenite, goethite, magnetite, garnet, rutile, leucoxene, zircon, anatas, staurolite, tourmaline, and lepidocrocite.

The correlation of the morphometric information with the particle size and the geology of the inland area indicates that the accessory minerals of the sands analyzed are transported by the network of rivers from the western Senegal towards a beach area where the sands are washed and sorted by ocean waves and redistributed in littoral placers.

Acknowledgements

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HEAVY MINERALS IN THE AREA SOUTH WESTERN IRAQ

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Abstract: This research includes a detailed study of the variation of heavy minerals in the recent sediment (sands) of the valley "Shib Huwami" south-west of Iraq. Grain size of sand is 0.250-0.063 mm. The heavy mineral analysis also showed different types, dominated by opaque (Hematite), non opaque minerals (Zircon, Tourmaline, Rutile, Pyroxenes, Hornblende, Garnet) and other heavy minerals (Titanite, Celestite and Chlorite) as a further indication of multiple source rocks. Heavy minerals have been identified and estimated using both polarizing and binocular microscopes.

Keywords: valley Shib Huwami, heavy minerals, sands, garnet, source rocks.

1. Introduction:

Iraq is part of the Arabian plate .The Arabian plate is located in the middle east of Asia and on the teritory of Kuwait Bahrain Qatar and United Arab Emirates, Oman, Yemen, Saudi Arabia, Syria, Jordan and Iraq (Konert et al., 2001). The rocks of Arabian plate range in age from the Precambrian to the present day, forming part of a larger unit that includes the Arabian Peninsula and is known as the Arabian Plate. Some Precambrian rocks in this region date back to the Archean (nearly 3 million years ago) but most are Neoproterozoic (1000-540 Ma*). They originated as volcanic islands or as chains of volcanoes along spreading centers and subduction zones in a Neoproterozoic ocean and against ancient continental margins, and were folded and uplifted toward the end of the Precambrian as a large belt of mountains. The mountains existed between about 680-540 Ma and were part of one of the largest mountain belts ever known to have existed on Earth (Fig 1.1).

Areas are situated in the stable platform in southern part of western desert between latitudes (31°) and longitude (44). Terrigenous and carbonate sediments of Miocene period covered the most part of western desert with appearance of Paleocene to Holocene sediments. Dibdibba sediments of upper Miocene are appear in southern part of desert while residual and terraces deposits are restricted in western side of alluvial plane (Al- Ani, 1979). The stratigraphic units according to (Buday, 1980, Jassim and Goff, 2006) are described to their age as Pre-Quaternary units and quaternary deposits

Heavy mineral analyses of Quaternary sediments in the south-west part of Iraq have been studied in 15 samples that were chosen from 15 full core boreholes within the study area (Fig. 1.1). The microscopic study included the identification and point counting of 300 detailed grains in the (0.250 – 0.063) mm fraction. A number of 25 detailed heavy mineral species identified in the Quaternary samples have been compared (using numerical method and their presence or the presence of particular assemblages of heavy minerals) to describe the occurrence, general abundance, and distribution of heavy minerals in Quaternary deposits moreover to indicate the original sources of the sand.

The color of the sand is dominantly brownish grey or greenish grey occasionally grayish brown, bluish brown, yellowish and pale grey to whitish colored bed of sands are also appeared in the sequence. The sands are generally fine to medium grained, friable to fairly compacted; compacted and cemented layers are rare. Coarse grained sandy layers are scarcely appears and if they exist, they are usually developed close to the margins of the basin. The sand sediments as thin layers of few centimeters inter bedded with other thin layers of silt and clay or deposited in a thick sequences reach seven of meters, well bedded laminated and banded sedimentary structures are quite common feature of the sand sequences.

1.1. Location

The project area is located in the southwest part of Iraq (Fig. 1.1). Longitude (44^{0} $52^{\backslash}$ $30^{\backslash\backslash}$- 44^{0} $30^{\backslash}$ $00^{\backslash\backslash}$) Latitude ($31^{0}$ $07^{\backslash}$ $30^{\backslash}$- 31^{0} $22^{\backslash}$ $30^{\backslash}$)

2. Sampling and techniques

A total of 15 core samples have been collected from 15 bore holes within the study area; the sampling interval varies from 10cm to 1m. Laboratory techniques were carried out to take 50 g from each sample and treat it with 10% HCL to remove the carbonate materials then dried in oven at 40 C and weighted.

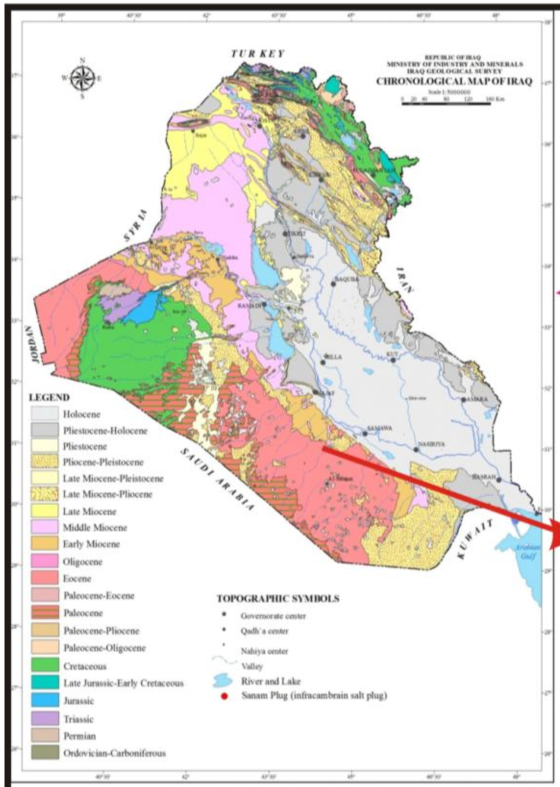
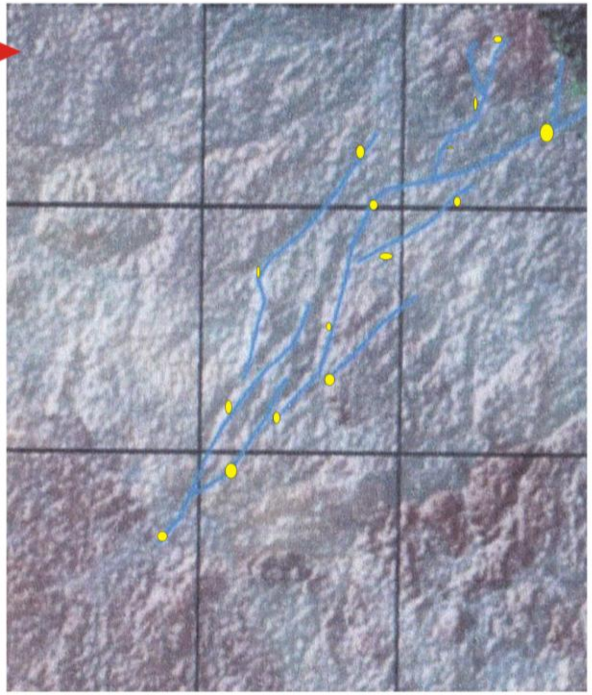
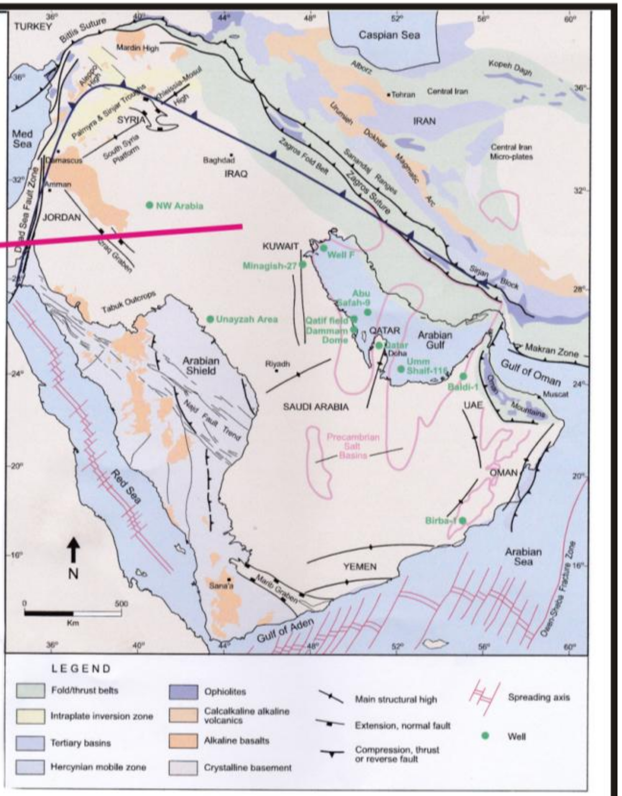


Fig 1.1: Location map of the study area.



Major tectonic elements of the Arabian Platform and peri-Platform Basins of Yemen, Oman, Arabian Gulf, Southern Iraq, Jordan and the Red Sea (after Konert et al ., 2001).



The samples were washed by water to remove the clay materials, heated in oven at 40 C, then sieved by screen of 0.250-0.063 mm size and weighted. The heavy minerals have been separated from the light minerals by using bromoform with specific gravity 2.89, and then the grains of heavy minerals have been mounted on glass slide using Canada balsam. Binocular and polarizing microscopes have been used to identify each mineral and about 300 grain had been counted in order to calculate the percentage of heavy minerals.

3. Identification of heavy minerals

Binocular and polarizing microscopes have been used to identify the heavy minerals and to separate them into two groups arranged in descending order of frequency: opaque group and non opaque group (see the average percentage of heavy minerals in figure 1.2).

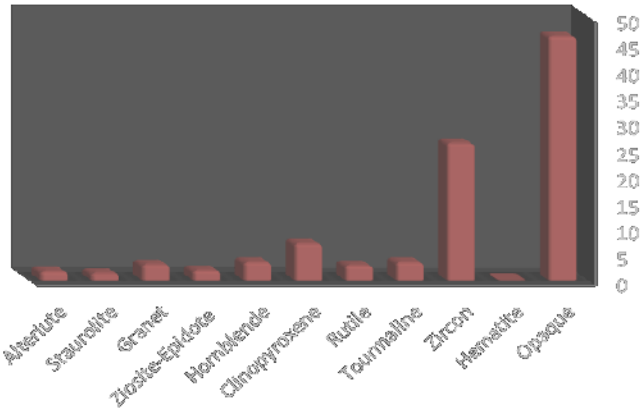


Fig 1.2: Average percentage of heavy minerals

3.1.1. The opaque group

This group includes brown grains represented by hematite, goethite (a few) and limonite. The shape of the three types of opaque minerals are subrounded, subangular and some of them subhedral. Their concentrations are indicated in Table 1.1 . The average percentage of opaque group in the studied area is 0.04% and their occurrences are usually in igneous, metamorphic and sedimentary rocks (Hamilton, 1976)

3.1.2. The non opaque group

The identified non opaque minerals are as follows:

3.1.2. 1. Zircon, TiO_2

Colorless, most of grains are rounded to sub rounded in shape and few subhedral (Plate 1). Some grains are with inclusion of opaque minerals or minute zircon. The average percent of zircon in the study area is (26.00%). Zircon is particularly ubiquitous in silicate and intermediate igneous rocks; it may reach high concentration in some beach sands and placers (Mange and Maurer, 1992). Consequently zircon may be recycled many times and represent multi cycles sand which may contain zircons from variety of source rocks, carbonates and mafic igneous rocks have little or no zircon (Berent et al., 2004).

3.1.2. 2. Tourmaline, $Na\ (Mg, Fe, Mn, Li, Al)_3AL_6\{Si_6O_{18}\}(BO_3)_3(OH,F)_4$

Tourmaline is present essentially as yellowish brown to brown and a few blue crystals. The shape of grains is mostly rounded or sometimes is long, see Plate 1). It is characterized by a strong pleochroism and its average percent is 3.36%, as shown in Table 1.1. Tourmaline occurs in some metamorphic schist, in metasomatic rocks and in certain basic igneous rocks (Mange and Maurer, 1992).

3.1.2. 3. Rutile, TiO_2

It is the most frequent of the three polymorphs of titania TiO_2; the other two polymorphs are brookite and anatase. The color is red, reddish brown and rarely yellow; the shape of the grains are mostly subrounded oblong forms, see Plate 1. The average percent of rutile in all study area is 2.77%. Rutile is widespread accessory mineral in metamorphic rocks, particularly in schist, gneiss and amphibolites; it is less significant in igneous rocks, where it occurs in hornblende- rich plutonic types and in pegmatite (Mange and Maurer, 1992).

Table 1.1: Heavy minerals in sediments stream of Shib Huwami

Sample Number	Heavy Fraction Wt%	Light Fraction Wt%	Opaque N.%	Hematite N.%	Zircon N.%	Tourmaline N.%	Rutile N.%	Cliopyroxene N.%	Orthopyroxene N.%	Hornblend N.%	Zoisite-Epidote N.%	Granet N.%	Staurolite N.%	Alterite N.%
P1	0.22	99.73	41.57	0.05	36.75	1.20	1.81	7.23	0.00	1.20	1.20	2.41	0.00	1.20
P2	0.65	99.23	50.47	0.12	30.84	0.93	1.40	3.74	1.86	3.27	0.00	0.93	0.47	1.40
P3	0.56	99.43	48.51	0.007	28.71	0.99	0.00	3.96	0.99	1.98	0.00	4.95	0.47	1.98
P4	0.78	99.21	58.95	0.01	24.21	2.63	3.68	2.63	1.05	0.53	1.58	0.53	1.98	1.58
P5	0.02	99.98	57.14	0.00	26.46	4.23	2.12	3.17	2.12	1.59	0.00	0.00	0.00	1.59
P6	0.28	99.67	56.34	0.05	27.46	5.28	2.11	1.76	1.76	1.06	0.35	1.06	0.00	1.41
P7	0.47	99.45	34.18	0.08	16.88	2.11	0.84	14.35	14.35	10.5	6.33	2.53	1.69	0.84
P8	0.14	99.84	33.18	0.02	18.89	3.23	2.76	14.29	14.29	8.76	2.30	7.37	1.84	2.30
P9	0.15	99.82	54.48	0.03	22.02	5.52	2.76	6.89	6.89	1.38	0.00	1.38	0.00	2.07
P10	0.20	99.78	33.73	0.02	15.87	2.78	2.78	16.27	16.27	4.37	4.37	4.76	3.17	2.38
P11	1.04	99.87	33.21	0.09	26.64	1.46	4.38	9.12	9.12	8.76	4.01	2.55	1.46	1.82
P12	0.16	99.83	44.56	0.01	29.53	2.07	5.18	5.18	5.18	1.04	0,52	5.69	2.59	2.59
P13	0.39	99.55	54.17	0.06	21.88	6.25	5.21	3.13	3.13	2.60	0.52	1.56	0.52	1.56
P14	0.13	99.8	52.23	0.07	28.03	9.55	1.27	8.28	8.28	1.27	5.73	3.18	3.82	1.27
P15	0.07	99.93	41.41	0.003	35.84	2.21	5.31	3.54	3.54	2.21	0.44	4.87	1.78	0.44
Average	0.35	99.61	46.27	0.04	26.00	3.36	2.77	6.90	5.92	3.37	1.82	2.92	1.28	1.63

3.1.2. 4. Pyroxenes

There are two principle subdivisions that exist: clinopyroxene with monoclinic and orthopyroxene with orthorhombic symmetry. Pyroxenes are colorless, green and brown. Grains are dominantly long or short stumpy prisms, irregularly terminated prismatic fragments, some grains are rounded edges and corners others are with cleavage and parting (Plate 1).

Orthopyroxenes are common constitutes of igneous rocks such as gabbro and pyroxenite while some enclaves of monopyroxene occur in igneous rocks such as basalt, gabbro and pyroxenite and others occur in metamorphic rocks (Hamilton, 1976). The average percent of orthopyroxene is 5.92% and for monopyroxene is 6.90% in all study area.

3.1.2. 5. Hornblende

The general formula can be given as $(Ca,Na)_{2\text{–}3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$.Hornblende is a common constituent of many igneous and metamorphic rocks such as granite, syenite, diorite, gabbro, basalt, andesite, gneiss and schist. Typically it has an opaque green, greenish-brown, brown or black color. The average percent of hornblende is 3.37% in all study area.

3.1.2. 6. Garnet

Colorless and light pale pink garnets with high relief, etch facets have been spoted; they are subrounded to subangular in shape; their isotropic character can be seen in Plate1. The average percentage of garnet in all study area is 2.29%. It is common in a variety of metamorphic rocks and is also present in plutonic igneous rocks, pegmatite, in ultramafic varieties and in some acid volcanoes (Mange and Maurer, 1992)

3.1.2. 7. Zoisite – Epidote

The predominant mineral recognized in this study is epidote and the dominant mineral is clinozoisite while zoisite is present as a trace mineral. They are colorless, almost always in shades of green, usually yellowish green (Plate 1). They occur mostly irregular, angular, equant forms more over clinozoisite occurs as short or long prisms and rounded grains. The occurrence of epidote mineral is in the green- schist regional metamorphism and is also present in contact metamorphic rocks and in hornfelses, epidote together with clinozoisite are common product of low to medium grade metamorphism (Mange and Maurer, 1992). The average percent of epidote group in all study area is 1.82%.

3.1.2. 8. Staurolite

Staurolite occurs as irregular, angular to sub angular in shape and has bright yellowish colors. High relief combined with shades of yellow or yellowish-brown and distinct pleochroism are diagnostic (Plate 1). The average percentage of staurolite in all study area is 1.28%. It is almost exclusively a product of medium-grade regional metamorphism and it forms in mica schist, derived from argillaceous sediments, and less frequently in gneisses (Mange and Maurer 1992).

3.1.2. 9. Alterite

It is difficult to differentiate only by polarizing microscope because it cannot have any character to be recognized. The average percentage of alterite in the study area is 1.63%. Other heavy minerals included celestite (0.35%), titanite(0.44%), sillimanite(T) , monazite(T) ,chromite(T) and anatase (0.53%) are present in some samples as traces. The sources of these minerals are igneous, metamorphic and sedimentary rocks (Hamilton, 1976).

4. Discussion and conclusions

- The studied samples taken from Shib Huwami were, mainly, similar in results the dominating sand grain sizes are fine and medium.
- The study of the heavy minerals shows the abundance of the heavy fraction in sands ranging in size from 36-125 mm
- The main silicates are represented by pyroxene and zircon.
- The study revealed the kind of parent rocks that probably generated the sands:
  - a- Acidic igneous indicated by the presence of euhedral to subhedral zircon, rutile, and tourmaline
  - b- Metamorphic rock indicated by the presence of garnet, chlorite, actinolite-tremolite, epidote and hornblende groups.
  - c- Basic igneous rock indicated by the presence of pyroxene and hematite.
- Source area of the sediments is the Arabian Shield.

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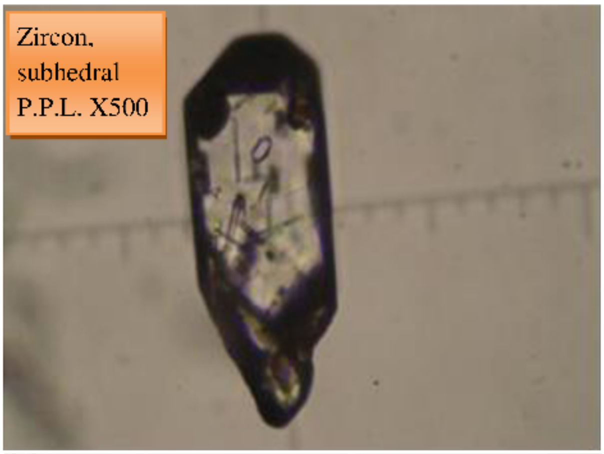
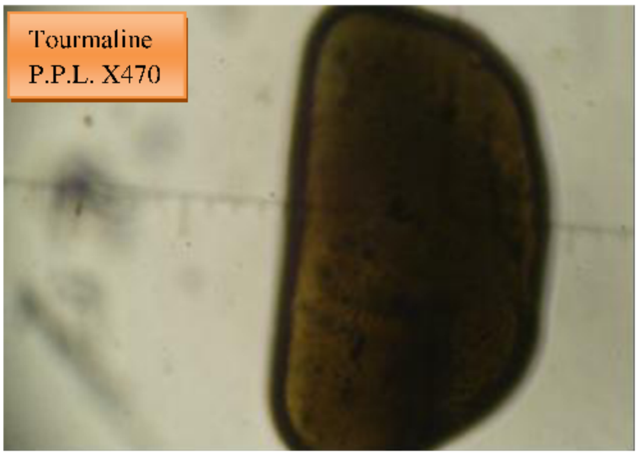
Plate 1

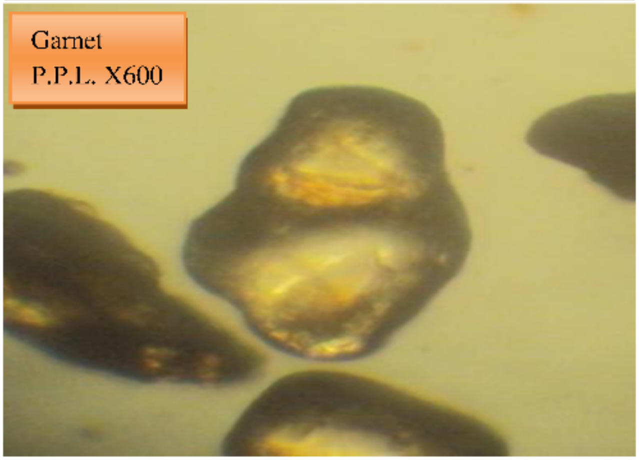

Zircon, subhedral
P.P.L. X500

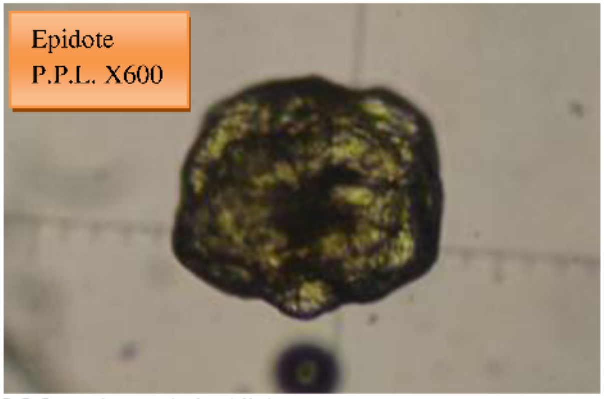

Tourmaline
P.P.L. X470

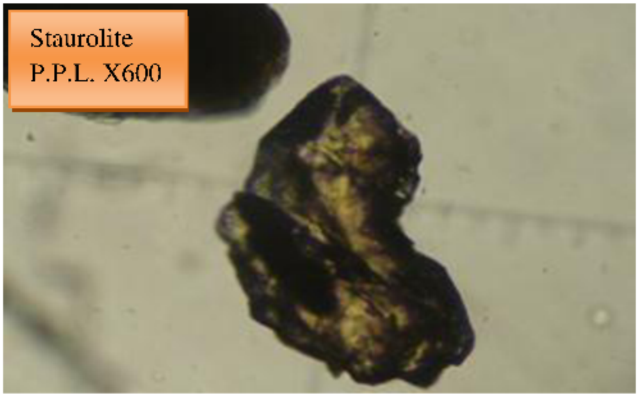

Rutile
P.P.L. X500


Clinopyroxene
P.P.L. X500


Hornblende
P.P.L. X430


Garnet
P.P.L. X600


Epidote
P.P.L. X600


Staurolite
P.P.L. X600

P.P.L. = plane polarized light

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NEW OPINION ON THE ORIGIN OF THE GOLD FROM ALLUVIAL PLACERS OF ROMANIA

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Abstract: The mechanical and chemical processes lead to the formation of the alluvial placersses: the grains are transported by gravity, running water, torrents, a.s.o., with the modification of the shape and dimensions; the chemical change is due to solution of silver within the natural Au-Ag alloy and formation of the gold enriched rims. The mode of concentration of the gold grains in the flood plains and selection of the enriched band, the „pay streaks", there are of interest for sampling and for evaluation regarding the potential gold and other heavy minerals. The geological and geotectonic context is revealed by traditional practice of alluvial matter selection: important amounts of gold proceed from the Neogene ore deposits in the Golden Quadrangle (Metaliferi Mts.); subordinate quantities of gold proceed from the polymetallic (Pb-Zn-Cu) and Au, Ag ore deposits, related to Gutâi Neogene volcanism; notable amounts of gold proceeds from the metamorphic terrains in the Southern Carpathians and Apuseni Mts. Four ore deposits are described in this paper - Valea lui Stan and Costești (Căpățânii Massif), Slătinicului (Semenic region) and Someșul Rece (Gilău Mts.) with the conclusion about the source/sources for the gold.

Keywords: alluvial placers, golden quartz enriched rims, gold in Neogene ore deposits, gold in the metamorphic terrains.

1. Introduction. From historical times, the alluvial placers represented an important source of gold. The method of recovery of the gold grains using wooly tissues in the sluices of the mountain torrent is known from Antiquity. It reminds the Legend of the Argonauts Expedition in the Colchis Country (Caucasus) to find the "Golden Fleece". Variants of this method "hurca" was used by the alluvial miners form Apuseni Mts. (Arieș and Crișul Alb rivers) (Brana, 1958), or "doska" – a gutter board – at Pianu de Sus (Strei Valley).

A quasi systematical research of the alluvial placers for gold and other heavy minerals was performed by V. Brana and his coworkers in the middle of the last century. The first practice in the field geology of the writer, integrated in this geologic company, in 1957, concern the research of the alluvial placers along the Someș and Bistrița Aurie rivers. For sampling the alluvia matter was used the traditional woody pan – "Șaitroc".

An interesting paper about these and similar investigations was published in 1963 by Lidia and V. Bârlea. In this paper may be found the assertion: "many rivers coming from Carpathians carry grains of gold". There is the first attempt to explain the source of the gold from the auriferous placers of Romania. New data on auriferous placers was published by I. Berbeleac and colab., in 1998. In the last decade of the 20-th Century a geologic company from "Prospecțiuni S.A." Bucharest tested the fine fraction processed in many gravel pits of Romania using shaking tables. In 1992 this company started extraction of the gold from these alluvia, processed in some of these gravel pits (Chivulescu et al., 1998).

2. A short overlook on the alluvial placers. The geologic conceives point out that the ore minerals, inclusive the native gold from primary outcrops, due to the weathering processes, pass into alluvial matter and then in alluvial placers. The formation of the "auriferous placers" is a combination of both mechanical and chemical processes. The mechanical agencies that concur to transport of the gold in alluvial placers are gravity and running water of the rivers, torrents a.s.o. (Boyle, 1979).

Nearly of primary are deposit the gold, in a rough material, preserve some of the original aspects. So, in the samples of the alluvia may be find dendrites, wire and intergrowths of euhedral crystals of native gold with pyrite, quartz or other minerals; to certain distance of primary source frequently there are the rounded grains, blades or spangle like. Far, to kilometers distance, the gold as fine grains is dispersed in the alluvial sediments of the flooded plains.

The richest bands of gold, so named by Boyle "pay streaks" may be find to meander course of the river, eventually to abandoned traces. The geologic practice revealed that the golden grains are concentrated on the bed-rocks, or to bottom of the layers of sand, gravels and above of the impermeable argillitic beds, mudstones a.s.o. This is more evidently to the sequences of the rocks from risen terraces ("terase"), as to the flood plain of the Olt River. Such observations may be of interest in the evaluation of the alluvial prospects for gold and other heavy minerals.

Many geochemical data reveal that the fineness of the gold from alluvial placers is higher than the primary (originally) "in situ" native fold. This is the case especially for the Neogene epithermal ore deposits of Romania, containing electrum (an argentiferous variety of gold). For example, the golden grains within the Sarmatian sedimentary deposits from Vârtop (originate from the Roșia Montană and Bucium gold deposits) have a fineness of 22-23 ct. (equiv. to 93% Au) ac. to Ghițulescu and Socolescu (1940), whereas the "in situ" gold display a fineness of 65-75% Au and 34-35% Ag, ac. to Posepny (1869) or 79.8% Au, ac. to G. Tămaș (2002). There are the gold containing sands and conglomerates in the "local siliciclastic sediment", covered by Panonian volcanoclastic – andesitic products of the Rotunda volcanic apparatus (9 Ma, Roșu et al., 2004). It is considered by I. Berbeleac and the other geologistes a "fossil golden placer"; a "modern golden placer" ac. to Boyle; the fossil placer, only for pre-Tertiary alluvial placers.

The enriched rims of the golden grains are due, ac. to Boyle, to solution of silver during transport as alluvial matter. Interesting aspects of enriched rims was proved by V. Popescu (1989) in his microscopic and electronooptic studies of alluvial gold from the Olt River.

3. The origin of the gold from Romanian alluvial placers

3.1. The Negone ore deposits. The geological reasons (thoughts) and traditional practice of select the valuable minerals from alluvial matter pointed out that an important amount of gold within Romanian alluvial placers proceed from the Neogene ore deposits of the Golden Quadrangle of Metaliferi Mts. (Apuseni Mts). There are mainly epithermal ore deposits of native and free gold, associated frequently with tellurides, silver minerals and/or sulfides, related to the Sarmatian and Badenian quarts-andesites and dacites; the famous ore deposits Roșia Montană, Bucium, Musariu – Brad, Săcărâmb, Almaș and Zlatna, some of which exploated (mined) from Antiquity, the source of the gold from Arieș, Crișu Alb and Ampoi rivers with their affluents.

According to the new geotectonic teories, the region of the Metaliferi Mts.belong to the Tisia block. In this idea the Miocene magmatism and the related metalofenesis of the Metaliferi Mts. Evolved in condition of an extensionary tectogenesis, marked by horst and graben structures. These uncomon ore deposits are generated in relation to a specific magmatism of calc-alkaline character, with some "adakite like" variety of rocks (Roșu et al., 2000). Only to some ore deposits, among the porphyry Cu-Py-Au, as Deva, Troița-Bolcana and Brad, the native gold occur as sizable, micronic, dimensions.

The polimetallic (Pb, Zn, Cu) and Au-Ag ore deposits from Baia Mare Mining Region are related to the Neogene vulcanism of the Gutâi Mts.

Together with Tokai (in Hungary), Vihorlat, Beregovo (in Ukraine), the Oaș and Gutâi Neogene volcanic rocks accupy the NE border of the Pannonian Basin and belong to the central (median) segment of the Charpathians volcanic chain (Seghedi et al., 2005), a subduction vulcanism of island arc type.

Characteristic to the Neogene magmatites of the Gutâi Mts. and the Oaș District (inclusive Vîshkovo area of Ukraine) there is the predominance of the two pyroxene andesites, basalt andesites, hyperstene andesites, even basalts, interposed or juxtaposed with intermediate and felsic ones: qtz-andesites, dacites and ryolites. All the volcanic products cover the interval from Badenian to Pontian (15 – 7 Ma) (Kovacs et al., 1998).

The Neogene mineral deposits. Southern of the Gutâi Mts. are distributed into an elevated (up risen) zone of pre-Neogene basement, marked by outcrops of Paleogene and Cretaceous sedimentary rocks under the Neogene sedimentary and volcanogenic formations. The ore deposits are connected to the magmatic intrusions of subvolcanic or hypabissal facies, the main argument (reasoning) for grouping the ore fields in three structural and metalogenetic districts: Ilba-Nistru metallogenetic district; Băița – Dealul Crucii and Herja – Băiuț District (Jude, 2010). The Ilba – Nistru metallogenetic district includes all the mineral deposits hosted by the Sarmatian pyroxenic andesites, Seini andesites (Rădulescu, 1958) of 12.1 – 13.4 Ma. The radiometric data of the ore minerals (adularia) point out an age around 11 Ma (Kovacs et al., 1998), indicating a Pannonian age.

Three types of hydrothermal paragenesis are characteristic for this district: Cu-py (chalcopyrite and pyrite) with a small proportion Pb+Zn sulphides lack or are insignificant (Jude and Popescu, 1997). New geological investigations point out a distinctive paragenesis sequence of Cu-Au-Bi minerals (Damian, anul).

The Băița – Dealul Crucii District comprises the Au-Ag ore deposits related to the Pannonian qz-andesites and dacites (10.5 – 11.3 Ma). The radiometric data show around 10 Ma for the adularia gangue mineral (Kovacs et al., 1998). The mineralogical studies revealed two stages of metallogenetic processes: the former generated gold, pyrite and Pb+Zn+Cu sulphides in silica mineral gangue (amethyst, chalcedony, opal); the second stage is marked by silver minerals, argentian gold (electrum), even native silver in carbonate minerals gangue. From the 4200 grains of gold from the veins X and XXV of the Săsar

Mine, 88.29% have dimension < 0.074 mm; 6.72% between 0.074 and 0.1 mm; 0.96% 0.01 – 0.15 mm and 4.91%, 0.15 – 0.25 mm (Petrulian et al., 1961).

Similar geologic and metallogenetic features are known for the Dealul Crucii Au-Ag deposit (Jude, 2010). There are low sulphidation epithermal styles of gold deposits.

The Herja – Băiuț District comprises the mineral deposits related to the Pannonian pyroxene and pyroxene – hornblende andesites (Jereapan type) of 10.1 – 10.9 M.y. The radiometric analyses of the adularia and illite samples of ore mineral, show 8.8 – 9.3 M.y., a good correlation with the host andesitic rocks (Kovacs et al., 1995).

The Herja mineral deposits, South of Igniș volcanic massif, comprise a group of aprox. 260 veins and veinlets of Pb+Zn+Ag and Sb minerals, connected to a subvolcanic intrusion of pyroxene – hornblende andesite. The mineralization is characterized by an excessive concentration of Pb+Zn sulphides, Sb and Ag minerals, but poor in gold, with quartz, carbonates, some fluorite and barite gangue (Petrulian, 1934; Damian, 1996).

The Baia Sprie mineral deposits, an important ore vein – „Filonul Principal", aprox. 2000 m long and E-W trend, with many branches at upper part, mined since Middle Age in the „Grosse Grube" from Mons Medius (Baia Sprie). It occupies the northern side of a Pannonian volcanic structure of pyroxene – hornblende andesites. Another vein, „Filonul Nou" is located on the southern part of the same andesitic body. Baia Sprie mineral deposit summarizes the main characteristiques of the Baia Mare mining district: Cu – py paragenesis with chlorite (pennine) as principal gangue, to deeper part of the mine, the former paragenetical sequence, fallowed by Pb+Zn+Cu paragensis and Au-Ag sequence of the mineralization, to upper part of the ore deposit. The last minerals are marked bu occurrences of barite and stibnite, telescoped into the Pb+Zn+Cu paragenesis; metacinabarite, cinabarite, realgar, in the cavities of the veins. Far, to the East, up to Văratic and Băiuț, the ore deposits exhibit similar features.

The Neogene ore deposits, related to the Gutâi magmatites, as well as of Oaș District, the gold occur mainly as native gold, associated with quartz, sulphides and/or silver minerals. The free gold is a rarity. Significant, in the Baia Mare Mineralogic Muzeum lack the samples of the free gold. The tellurides occur only as "accessory minerals", a different feature relative to the Metaliferi Neogene metallogenesis. But, may occur Bi minerals.

The geological literature mention some golden grains in the alluvial placers of the Handal, Moshuhaz and Cicârlău Valleis, afluents of the Ilba Valley, tributary to the Someșul Mare river (Bârlea and Bârlea, 1963). Very probable, some quantities of golden grains was drained by Borcutului Băiței, and Roșie Valleis and dispersed in the flood plain of the Someș River.

3.2 The Laramic – banatitic occurrences of gold. The geological literature mentions some occurrences of gold, generally associated with sulphides, as at the "Cracul cu Aur" nearly the Ocna de Fier and Oravița mineral deposits, in the Banat region (Petrulian, 1973). Other occurrences are related to the granitoidic pluton of Bihor Mts., in Ca-skarns and/or associated with the Bi minerals, at the Băița Bihorului mineral deposits (Petrulian, 1973; Cioflică, 1977) The native gold is known, also, in some sufidic veins of Pb-Zn-Cu, at Luncșoara (southward of Băița Bihorului) a.s.o. There are gold grains of micronic size, scarcely regarding the frequency and so insignificant for alluvial placers.

3.3 Gold in metamorphic terrains. Notable amounts of gold from the Romanian alluvial placers proceed of metamorphic terrains of southern Carpathians and Apuseni Mts. This auriferous placers, very probable, originate from the occurrences of gold bearing quartz±other minerals; as chalcopyrite, pyrite, arsenopyrite, a.s.o. and carbonates in tectonized areas. They were integrated by G. Udubașa, Gh. Popescu and I. Berbeleac in the category of "Gold mineralization related to shear zones". Generally, these mineralized lens and veins of quartz occur in strain fissures, adjacent to the S-Shearing plane or in the blasto-mylonitic matter, along the faults, in the dilatant zones. They are known in the Făgăraș group of metamorphites as well as in Sebeș - Lotru – Căpățânii and Mehedinți massifs, characterized, in some papers by Gh. Popescu and his colab. (1996, 1998). They are distributed mainly in the Preambrian Getic Domain of metamorphites of the Sebeș - Lotru series, the gold source for the alluvial placers of the Râul Doamnei, Topolog, Olt and Gilort rivers of Getic depression.

The Sebeș - Lotru series comprise a Barrovian facies of metamorphites and subordinate (partially) a Pirinian type of intermediate to low preasure metamorphism, in Mehedinți, Godeanu and into Căpățânii, the Ursu formation (I. Hârtopanu, 1982).

3.3.1 Gold in the Căpățânii metamorphites. Characteristic for this category of ore deposits there is the Valea lui Stan mineral deposit, 2 km West of Brezoi locality, in Căpățânii metamorphites, mined (exploited) at beginning of the last century (Haiduc, 1940).

The ore bodies as veins and lens like of quartz and subordinate carbonates consist of pyrite, arsenopyrite, chalcopyrite, occasionaly sphalerite, galena, pyrrhotite, tetrahedrite and magnetite. The gold, usualy of microscopic size occur in relation with the chalcopyrite and arsenopyrite (Petrulian, 1936, 1973). The ore grade may reach up to 16.5 g/t Au and 34.2 g/t Ag (Haiduc,1940).

The nature of the mineralization is a debate problem – N. Petrulian (1973) supposed a hydrothermal genesis, the mineralizing fluids proceeding from a deepseatinf granitoid pluton; the author admits, however, the presence of the metamorphic solutions in the genetic process.

G. Udubaşa (1976) promoted the concept of tectogenetic process in order to explain the origin of the Valea lui Stan mineral deposit. In other paper, G. Udubaşa discusses the origin of the gold in relation with the amphibolites of the Sibişel formation, a formation similat with the Green Stone Belt. In this idea, the sequences of the omphibolites have the role of protone in the genetic process (Udubaşa and Hann, 1988); a hypothessis plausible if we keep in mind the geochemical affinity of the gold for mafic rocks. It remindes of the old theory of lateral secretion.

Among another gold-bearing quartz and sulphides within Căpăţânii metamorphites, important there are those of the upper part of the Costeşti Valley, northern of the Horezu town.

The principal ore veins and lensoidal shape occur in the Netedu and Comarnici brooks, two affluents of the Costeşti Valley, in the Sebeş - Lotru Precambrian metamorphites.

The ore bodies consists of arsenopyrite, pyrite, chalcopyrite, sphalerite, Bi–minerals, tetrahedrite, gold and some time pyrhotite, galena and Ag minerals. The gold occurs, mainly, in relation with arsenopyrite, pyrite, quartz and Bi – minerals (Apostoloiu et al., 1990).

Interesting mineralogic and geochemical investigations are realized by S.S. Udubaşa (2004a), both on the Valea lui Stan and Costeşti mineral deposits. The golden grains from the Valea lui Stan ore deposit show a significant Ag content and „geochemical impurities” of Cu, Ni, Mn and Bi; the gold fineness varies from 246.61 to 835.92‰; for Costesteşti ore deposits the microprobe analysis performed by S.S. Udubaşa, reveal variable contents in Ag and „impurities” of Cu, Bi, Ni, Mn. The gold fineness varies between 448.29 and 743.42 ‰ (Udubaşa, 2004b).

The biotite blastomilonitic formation has been considered the protore for these Au-As mineralizations (Hârtopanu et al., 1991, in Udubaşa, 2004b).

3.3.2. Semenic region. In the Semenic region the alluvial gold was extratected episodic before of 18th Century until recent. The Nera river is known for it's richness in gold.

The geologic investigations from the last century found out some occurences of lens, veins and nests of „auriferous quartz” in the Sebeş - Lotru type of metamorphites, of Slătinicului Valley, to the border of the Badenian sedimentary basin. A lenticular vein, of 200 m long and 0.2 to 2 m thickness, was exploated from 1924 until 1950. It consists of gold and pyrite in white quartz subordinate carbonates and films of chlorite as gangue. The ore grade was around 5 g Au/t.

A clast (fragment) of aprox. 5 cm of white quartz with an euhedral crystal of gold of aprox. 3 mm in interstices was found, in 1993, in the basal conglomerates of the Badenian molasse; it displays a characteristic yellow colour; a sort of „old gold”. The mineralogic studies pointed out a fineness of 840-850‰ Au (Întorsureanu et al., 1985).

Some alluvial placers rich in gold of the Bistra and Bistra Mărului Valleys, afluents of the Timiş river (Bârlea and Bârlea, 1963) suggest another „in situ” occurences of mineralizations.

3.3.3. Gold in the Gilău Mountains. The gold mineralization occurs in the Someşul Rece river, at Băilor and Valea Seacă, aprox. 20 km WSW of Cluj Napoca town. The ore bodies have been exploated in the last century.

The lenticular ore bodies of 20-30 m lenght and about 1 m thickness lie concordant, as well as discordant to the shistozity of the quartz – sericite and quartz – chlorite rocks (Lucca, 1937), a metamorphized feature of the Precambrian Someş Series of metamorphites (Berbeleac, 1955). The mineral paragenesis consists of pyrite, chalcopyrite, gold, arsenopyrite, galena, sphalerite, tetrahedrite and rutile in quartz, chlorite and siderite gangue (Lucca, 1937; Berbeleac, 1995); the stibnite and molybdenite may be related to the Laramic – Banatitic magmatism. The ore is rich in chalcopyrite, the content of the gold varyes between 2.4 and 20 g/t Au (Lucca, 1937). Far, 25 km southward, the gold mineralizations occur again in the Erzului and Vadului Valleys (Berbeleac, 1995). In the upper part of the Iara Valley the petrographic data reveal a migmatitic facies of the gneiss and occurences of the granitic pegmatites (Giuşcă, 1974) – the field of pegmatites of Muntele Rece.

4. Discussions. The geological literature distinguishes two categories of gold ore deposits in metamorphic terranes: one in gneisses, another in migmatites (Deb and Goldfarb, 2009).

Some examples: in the Challenger Gold Deposits, South Australia, the gold and/or Cu, Bi, etc. originaly present in the country rocks, was mobilized in metamorphic processes. Spherical gold-sulphides inclusions in the peak – metamorphic garnet suggests that the gold was present durring garnet's formation, prior to or durring the granulite facies of metamorphism. Gold rich melt was trapped as liquid inclusions within and between crystallising minerals in the leucosome. The Challenger deposit represents a new class of deposits, „a migmatized gold deposit" (Tomkins and Mavrogenes, 2002, p. 1269).

A close relationship between migmatization and sulphide mineralization in known to south-eastern part of the Shinghbhum Shear Zone (Bihar, India) around of the Mosabow Cu Mine. The sulphide mineralizations of Cu – py and pyrhotite of this region are related to the soda – granites and epidiorites, in a variety of Na – migmatites (Talapatra, 1968). Trace – element analysis of the sulphides and adjiacent migmatized rocks indicates that Cu, Co, Ni and V, though present within these rocks, are highly concentrated within sulphides; probable they were added to the migmatitic solutions (Talapatra, 1968).

Field geologic observations, in the last two decades of the 20th Century, on the metamorphic rocks around of the Late Cretaceous – Banatitic intrusions at Tincova (South of the Poiana Ruscă Massif), Teregova, Mehadica (Semenic Mts.) as well as at Liubcova (Southern Banat) reveal interesting features.

Large areas of these territories the migmatites, a petrografic facies of peack metamorphism (Mehnert, 1968) have an excellent spread. „At the highest temperature of metamorphism regional anatexis and the formation of the migmatites are inevitable, if some H_2O is present" (Winkler, 1979). In the same areas the granitic pegmatites accompanyes the migmatites, frequently in the Sebeș - Lotru Series of metamorphites. In such geologic context, very probable the gold and related minerals were mobilized by the metamorphic processes. Many occurences of gold – quartz sulphides, even some of rare element minerals are hosted by migmatites, as it is at the Grădiștea de Munte – Sebeș Mts. (Hîrtopanu and Fairhurst, 2014).

May be mentioned, also, the gold occurence of Liubcova (Southern Banat), nearby the Lilieci banatitic intrusions with porphyry copper mineralization, hoasted by migmatized gneisses. There is a mineralization of gold and arsenopyrite with quartz gangue, of centimeters size, in brecciated gneisses. It was remobilized, from deeper levels, by the hydrothermal Laramic – Banatitic solutions (Cioflică et al., 1992). So, it is logical, reasonable to consider such gold bearing quartz mienralizations, sulphides of Cu-Zn-Pb, Bi minerals a.s.o. hosted by migmatites as products of mobilization in the metamorphic processes, by highgrade of metamorphism.

5. Some conclusions. Notable amounts of gold from Romanian alluvial placers proceed from the Neogene ore deposits of the Golden Quadrangle of Metaliferi Mts. Subordinate quantities came from the Neogene polimetalic Pb, Zn, Cu with Au, Ag ore deposits related to the Gutâi volcanites and similary magmatites of Eastern and SE Carpathians (Țibleș, Toroioaga, Gurghiu shallow magmatic intrusions). Animportant contribution has the Laramic – Banatitic metallogenesis of Bihor Mts. and Banat.

On the other hand, interesting quantities of alluvial golden grains proceed from the gold bearing quartz, gold and sulphide ore deposits or occurences, hosted by metamorphites, in shear zones of Southern Carpathians and Apuseni Mts. The origin of the gold may be in the metamorphic rocks (the femic minerals as amphibol, pyrozenes, biotite, magnetite) mobilized in the metamorphic processes as to the Valea lui Stan and Costești golden deposits within the Căpățânii metamorphites (acc. to Udubașa and Udubașa, 2002).

Some gold bearing quartz and/or sulphides in the migmatized gneisses, seem to be related to the high grade of metamorphism.

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CONTENT

– continued from the front cover –

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