Mineralogy and geochemistry of Baia Sprie polymetallic ore deposit (Romania)
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Apopei, A.I., Damian, G., Buzgar, N., Milovska, S., BUZATU, A. (2014) – New occurrences of hessite, petzite and stutzite at Coranda-Hondol open pit (Certej gold-silver deposit, Romania). Carpathian Journal of Earth and Environmental Sciences 9, 2, 71-78. Impact factor 0.727; Relative influence score 0.179.


INTRODUCTION

The Baia Sprie ore deposit drew the attention of geologists since 1862. Several authors described chemically and crystallographically a number of minerals from the deposit. The minerals andorite, felsőbányaite, klebelsbergite, semseyite and szmikite have been described for the first time at Baia Sprie mineralization (Krenner, 1881). Other authors have shown interest in the geology of the area and in the relationship between geology and mineralization. Savul and Pomîrleanu (1961) determined the homogenization temperatures of liquid-gas phase inclusions of quartz crystals from Baia Sprie. The authors observed crystallization temperatures of quartz between 155-310 °C and concluded that the temperature increases with depth.

One of the most important and complex studies is the one conducted by Manilici et al. (1965), where the authors presented a very detailed microscopic description of the deposit, and also geochemical data and interpretations related to the ore genesis. Borcoș et al. (1973) also published an important study which presents mineralogical, geochemical and geothermometrical data on several major veins of Baia Sprie deposit. As a result, the authors suggested a single metallogenetic phase, but with two distinct sequences at short intervals. In the same year, Stanciu (1973b) studied the types of hydrothermal alteration associated with the mineralization, showing a zonal and symmetric distribution of the altered areas.

Studies on pyrite morphology, quartz fluid inclusions and isotopic compositions from Baia Sprie, have also provided valuable information about the genesis of mineralization (Nedelcu et al., 1992, Nedelcu and Pintea, 1993).

More recently, the studies have focused mainly on the upper part of the deposit. Iștovan et al. (1996) suggested different metallogenic conditions for the upper levels in the western and eastern side of Baia Sprie ore deposit. Damian et al. (2003) reported for the first time a new occurrence of several silver sulfosalts in the upper part, with direct implications on the zoning of the deposit. A more recent work presented a vibrational study of certain supergene alteration products from Dealul Minei open-pit (Buzatu et al., 2012).

The purpose of this paper is to present a detailed chemical and mineralogical study, together with the paragenetic relationships between common sulfides, sulfosalts and bismuth minerals from the Baia Sprie polymetallic deposit. The present work describes for the first time the presence of bismuth minerals within the deposit that have not been identified so far at Baia Sprie. New chemical electron microprobe results are presented for the common sulfides, pyrite, arsenopyrite, chalcopyrite, sphalerite and galena. Also, a new occurrence of geocronite-jordanite series and seligmannite
member was identified in the present study. Semseyite from the type locality was chemically described. The compositional results of tetrahedrite-tennantite series allowed an extensively discussion on the members distribution within the deposit. The results show a significant importance for epithermal deposits, Baia Sprie being accepted as a classic model for such mineralization. Another important objective was the vibrational study by means of Raman and Infra-red spectrometry, of secondary sulfates associated with supergene alteration, as well as of natural sphalerite for the iron determination.

I would like to express my gratitude to people who helped me in achieving these goals. First of all, I thank to my scientific adviser, prof. univ. dr. Gheorghe DAMIAN for guidance in writing the thesis and support offered in obtaining the analytical data. I also appreciate the help of prof. univ. dr. Nicolae BUZGAR in coordination with valuable suggestions during the doctoral studies.

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I. GEOLOGY AND METALLOGENY OF BAIA SPRIE ORE DEPOSIT

The deposition of Baia Sprie mineralization was determined by a series of major tectonic events and an intense volcanic activity. The three stages of volcanic activity took place since the Badenian-Sarmatian (acid character), followed by the Sarmatian – Pannonian (intermediate character) and the last phase in Pliocene with a basic character. The mineralization is spatially associated with the amphibole-pyroxene andesitic compartment and with subvolcanic intrusions and it consists predominantly of a vein system developed along the faults that are located at magmatic-sedimentary contacts or near the intrusions (Manilici et al., 1965, Borcoş et al., 1998).

A well-defined vertical zoning was observed for Baia Sprie ore deposit, especially within the Principal Vein: copper-rich mineralization in the deeper part of the deposit, lead-zinc mineralization within the intermediate levels, and gold-silver in the upper part. This kind of zoning was observed also for other deposits within Baia Mare: Nistru, Cavnic (Manilici et al., 1965, Borcoș et al., 1973, Udubașa, 1995, Iștvan et al., 1996, Mărza, 1999, Damian et al., 2003).

The Baia Sprie area (Figure 1) is characterized by Tertiary (Paleogene-Neogene) sedimentary deposits which were mostly covered by magmatic successions during Neogene intensive magmatic events (Manilici et al., 1965). The volcanic deposits are represented by lavas, pyroclastic products and explosion breccias (Figure 1). Manilici et al. (1965) separate them as follows: amphibole-pyroxene andesites, rhyolites, quartz-andesites, amphibole-pyroxene dacites, biotite-dacites, and augite-hypersthene basaltic andesites. The amphibole-pyroxene andesites have the greatest spreading and are the main rocks that compose Dealul Minei area as a 700-1200 meters wide compartment. The almost entirely andesitic body shows intensive hydrothermal alteration associated with the mineralization events (Manilici et al., 1965).

The amphibole-pyroxene andesitic compartment is considered to be a dyke with the northern side orientated E-W and the southern side as WNW-ESE, and with a north-orientated slope (Manilici et al., 1965, Borcoș et al., 1973). The volcanic activity with andesitic character from the Baia Mare district lasted 4-5 Ma from 13.4 to 9.0 Ma, with a final phase of basalt intrusions between 8.1-6.9 Ma (Lang et al., 1994, Pécskay et al., 1995).

The most important tectonic feature of the Baia Mare district is the W-E trending Bogdan Vodă- Dragoș Vodă fault system, located in the southern part of Gutăi Mountains (Popescu and Ștefănoiu, 1972, Borcoș et al., 1975, Lang, 1979, Măldărascu and Popescu, 1981, Popescu, 1994, Borcoș et al., 1998).

Hydrothermal alteration associated with Baia Sprie mineralization shows a very clear vertical and horizontal zoning. Four major types of alteration zones were observed: chlorite, carbonate, adularia and argillic (Stanciu, 1973a). The transformations have a selective, zoned and intensive character. The zonal character is observed along the fractures especially towards the deeper parts. Stanciu (1973a) indicate the following associations between mineralization and alteration zones:
cupriferous ore – chlorite zone; Pb-Zn ore – adularia and carbonate zone; Au-Ag ore – adularia zone.

The Baia Sprie ore deposit is of low-intermediate sulfidation type – LS-IS (Kouzmanov et al., 2005). Two metallogenetic stages were considered for the formation of Baia Sprie deposit (Figure 2). A first series of fractures appeared on contacts of amphibole-pyroxene andesite compartment, where the hydrothermal solutions deposited the cupriferous mineralization in the deeper levels. Subsequently, the tectonic activity created fractures also within the compartment especially in the upper parts. The hydrothermal fluids deposited the Pb-Zn and Au-Ag mineralizations while the andesite body was strongly hydrothermally altered almost entirely (Manilici et al., 1965).

Figure 1. a. Carpathian-Pannonian region with the location of Baia Mare district (Seghedi et al., 2004); b. Simplified geological map of Baia Sprie area (Iștvăn et al., 1996); c. Geological cross-section of Baia Sprie deposit – eastern part (Mariaș, 2005); (Buzatu et al., 2015)
Studies on the formation temperatures of quartz crystals showed homogenization temperatures of 261-268 °C for the cupriferous mineralization, and 255-277 °C for the polymetallic one (Manilici et al., 1965). Borcoș et al. (1973) determined the formation temperatures of quartz between 215 and 300 °C. Nedelcu et al. (1992) and Nedelcu and Pintea (1993) studied the pyrite morphology and fluid inclusions in quartz from the Principal Vein. The authors concluded that the hydrothermal fluids with low salinity (3.6-19.9 wt% NaCl) and with temperatures of 147-359 °C circulated from the lower east side towards the upper levels from the west (Dealul Minei).

The Baia Sprie ore deposit was subject to numerous research papers in the past century describing the mineralogy as well as discussing different hypotheses regarding the forming conditions (Savul and Pomirleanu, 1961, Manilici et al., 1965, Borcoș et al., 1973, Borcoș et al., 1998, Damian et al., 2003, Buzatu et al., 2015). The deposit has an impressive richness of mineralogical associations with almost 90 mineral species and it is the type locality for 6 minerals. The relationships established between the metallic and gangue minerals show the presence of two distinct metallogenic sequences. The first one is a cupriferous stage with a specific assemblage of pyrite, chalcopyrite, magnetite, hematite, scheelite, wolframite, while the second sequence with Pb-Zn character is characterized by pyrrhotite, sphalerite, chalcopyrite, galena,
tetrahedrite, stibnite, freislebenite, followed by sulfosalts and native elements. The gangue minerals are: cupriferous stage – chlorite, quartz, ankerite and barite; polymetallic – quartz, adularia, calcite, rhodochrosite and barite (Borcoș et al., 1973).

II. SAMPLES AND ANALYTICAL METHODS

1. Samples

In the present study, two types of samples were used: (1) ore samples, from the mineralized veins consisting of metallic and gangue minerals; and (2) efflorescent salt samples from Dealul Minei open-pit, represented by secondary minerals of supergene alteration.

The ore samples have been prepared as polished sections to be studied by reflected-light microscopy. A total number of 140 polished sections, realized at Technical University Cluj-Napoca, North University Center of Baia Mare, have been studied by ore microscopy in order to identify the minerals present and to establish textural relations among these. From the initial sections, were selected samples of sphalerite from all three main levels of the deposit (lower, intermediate, upper) and further analyzed by electron microscopy (SEM-EDX), Raman spectroscopy and X-ray diffraction, to determine the Fe content based only on Raman spectra.

Also, a number of polished sections were selected based on the content of sulfides and sulfosalts, in order to be analyzed by electron microprobe and micro-Raman spectroscopy (Figure 1).

The samples of efflorescent salts were collected from Minei Hill open pit during November 2011 and June 2012. The samples were collected in plastic containers and sealed in order to prevent any possible hydration/dehydration of the mineral phases. From the entire batch a number of 7 final subsamples were obtained by sorting the mineral phases using a binocular magnifier. The sorting was realized by hand-picking considering the color and morphology of crystals in order to achieve as much as possible monomineral samples. The final samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman and near-infrared (NIR) spectroscopy. The near-infrared measurements were carried out using a Portable Infrared Mineral Analyzer (PIMA) from Integrated Spectronics Pty Ltd. After an initial set of PIMA analyses was carried out the samples were treated at different temperatures in order to examine phase transformations and structure changes of every species. Each sample was heated in an electric oven in the 30-90°C interval of temperature for 4 hours for each 10°C step, and from 100 to 220°C for 2 hours with an
increment of 20°C. After every heating the samples were measured using the PIMA
device, therefore obtaining a spectrum for each temperature step showing the
dehydration degree and transformations of the mineral phases. X-ray diffraction
measurements were carried out on the final samples in order to identify the phases after
the heating process.

2. Analytical techniques

The ore samples were prepared as polished sections in order to be studied under
the reflected-light microscope. The mineralogical identification and description was
realized with a Meiji Techno model ML 9430 microscope.

The chemical compositions of sulfides and sulfosalts were determined using the
Cameca SX-100 Electron Probe Microanalyzer (EPMA). The analyses were carried out
at State Geological Institute of Dionyz Stur (Bratislava, Slovakia) and at Federal
Institute for Geosciences and Natural Resources (Hannover, Germany). The analysis
spots were selected using the back-scattered electron (BSE) images. The measurements
were performed on carbon coated polished sections.

Another series of chemical results was obtained by using the scanning electron
microscope VEGA II LSH with EDX Quantax QX2 detector, within the Arheoinvest
platform, Alexandru Ioan Cuza University of Iași. The morphology of secondary
minerals (supergene sulfates) was studied with the same model of electron microscope,
at the Faculty of Biology, Alexandru Ioan Cuza University of Iași.

The Raman spectra were acquired using a Horiba Jobin-Yvon RPA-HE 532
Raman Spectrograph with a multichannel air cooled CCD detector (-70°C) and Nd-
Yag laser at 532 nm with a nominal power of 100 mW. The measurements were
carried out at the Department of Geology of Alexandru Ioan Cuza University of Iași,
on the sphalerite samples and supergene sulfates. For the sulfosalts samples were
obtained micro-Raman spectra in the same measurement points of the electron
microprobe analysis. It was used a Raman Horiba-Jobin Yvon – LabRam HR 800
spectrometer, from the Geological Institute of Slovak Academy of Sciences, Banská
Bystrica, Slovakia.

Near-infrared spectra were obtained using a Portable Infrared Mineral Analyzer
(PIMA) from Integrated Spectronics Pty Ltd, at the Federal Institute of Geosciences
and Natural Resources, Hannover, Germany. The mid-infrared spectra were acquired
using a Fourier transform infrared spectrometer Bruker Vertex 70, within the
Department of Geology of Alexandru Ioan Cuza University of Iași.

The XRD measurements were carried out using a Shimadzu LabX XRD-6000
diffractometer, at the Faculty of Physics of Alexandru Ioan Cuza University of Iași,
and a PANalytical MPD Pro diffractometer at the Federal Institute of Geosciences and Natural Resources, Hannover, Germany.

III. MINERALOGY AND GEOCHEMISTRY OF BAIA SPRIE DEPOSIT

1. Sulfides

1.1. Pyrite

Arsenic has variable concentrations in the studied pyrite samples, ranging from 0 to 9.72 wt%. The BSE images show interesting zonal structures of pyrite crystals with different As contents (Figure 3a-d). The oscillatory As-pyrite zonings show concentrations that change significantly from \( \text{Fe}_{1.00} \text{S}_{1.99} \) to \( \text{Fe}_{0.98} \text{As}_{0.16} \text{S}_{1.85} \). The As-pyrite rims are observed at the outer zones of the pyrite crystals from the first stage of mineralization (Figure 3a-d). Very similar As-bearing pyrite with oscillatory zonings was observed also at Roudný gold deposit, Czech Republic, but with lower As content of 4.5 wt% (Zachariáš et al., 2004).

The As zonal structures of pyrites from Baia Sprie reflect chemical changes in ore-bearing fluids during the first stage of mineralization. The As-free core and As-rich rims suggest a relatively high S activity and low As in the early fluids of the depositional stage, followed by a sharp increase of As activity in the late fluids. The oscillatory zoning bands indicate multiple pulses of As-rich fluids which might reflect in changes in the As activity and temperature conditions (Buzatu et al., 2015).

The presence of a substantial fraction of Au within iron sulphides (mainly pyrite and arsenopyrite) is referred to as “invisible gold”. Studies on synthetic pyrite under Au-saturated conditions showed that up to 0.64 wt% Au may be incorporated into pyrite (Fleet and Mumin, 1997). The amount of Au that can be incorporated into pyrite is strongly dependent of As concentration (Cook and Chryssoulis, 1990, Reich et al., 2005, Deditius et al., 2014). The substitution of As into pyrite creates structural distortions which enhance the incorporation of Au. Gold substitutes for Fe in the distorted octahedral sites of pyrite (Deditius et al., 2014). At Baia Sprie, the high contents of As in pyrites with Fe deficiency might prove the presence of invisible gold (Buzatu et al., 2015). Further more sensitive analytical methods must be applied in order to determine Au concentrations. Other authors previously reported in the pyrite from Baia Sprie Au contents of 16.74 μg·g⁻¹, but in samples with low As content (1.25 wt%) (Nedelcu et al., 1992).
Figure 3. Back-scattered electron images showing specific oscillatory zoning of the main sulphides within Baia Sprie deposit. 

a-d. Several examples of pyrite (Py) crystals with zoning bands of arsenian pyrite; pyrite is surrounded by sphalerite (Sph) and tetrahedrite-tennantite (Td-Tn); e. Arsenopyrite (Apy) showing growth zones due to Sb content, associated with galena (Gn); f. Chalcopyrite (Cp) surrounding tetrahedrite-tennantite and presenting euhedral growth zoning (Buzatu et al., 2015)
1.2. Arsenopyrite

The As content from 29.58 to 30.51 at% (average of 30.34 at% As) of the analyzed arsenopyrite from the lower level of the deposit indicates temperatures of 320-360 °C according to the phase diagram Fe-As-S of Kretschmar and Scott (1976). The temperatures were estimated based on the arsenopyrite-pyrite-As assemblage (Buzatu et al., 2015). These temperature values are slightly higher than those reported previously of 300-330 °C based on fluid inclusions (Borcoș et al., 1973, Nedelcu and Pintea, 1993).

1.3. Sphalerite

1.3.1. The determination of Fe content in natural sphalerites

The purpose of this section is to estimate the iron content in natural sphalerites based on the Raman spectra exclusively (Buzatu et al., 2013). By using a fast and easy technique like Raman spectroscopy to determine the iron content in sphalerite, one can analyze a large number of samples across a shorter time span, as well as acquire valuable information.

The first-order Raman spectrum is split into two fundamental modes: the longitudinal optical (LO) mode at ~348 cm\(^{-1}\) (the vibrations are parallel to the exciting light), and the transverse optical (TO) mode at ~272 cm\(^{-1}\) (perpendicular vibrations) (Krauzman, 1968, Schneider and Kirby, 1972, Hope et al., 2001). Acoustic modes appear at lower wavenumbers, in longitudinal and transverse forms (LA at ~216 cm\(^{-1}\) and TA at ~177 cm\(^{-1}\)), as well. The Raman spectrum also displays combination modes based on the fundamental ones: TO+TA (396 cm\(^{-1}\)), TO+LA (419 cm\(^{-1}\)), LO+LA (449 cm\(^{-1}\)), and LO+TO (637 cm\(^{-1}\)). Less intense are the second-order modes at 613 and 668 cm\(^{-1}\) (Krauzman, 1968, Hope et al., 2001).

In synthetic low-iron sphalerites, the LO mode dominates the Raman spectra, while the TO and acoustic modes can also be observed, but with a smaller intensity and breadth. As the iron content increases, two other bands arise, at ~296 and ~331 cm\(^{-1}\). Their intensities increase with the Fe concentration, while that of the LO band from ~348 cm\(^{-1}\) decreases (Hope et al., 2001, Kharbish, 2007, Osadchii and Gorbaty, 2010). These changes in intensity of the three main bands can be used in estimating the Fe content in sphalerite samples, by using several ratios of these three peaks heights: \(h_1/h_3\), \(h_2/h_3\) and \((h_1+h_2)/h_3\).

Multiple Raman spectra were acquired on each sample (10-15). The Fe concentration was calculated based on the Raman spectra exclusively, using the method suggested by Osadchii and Gorbaty (2010). One important observation, which could prove beneficial to the method presented, was made in the present study. Based on the fact that Zn-S vibrations are responsible for the 350 cm\(^{-1}\) band, Fe-S vibrations are the source of the 331 and 300 cm\(^{-1}\) bands, and their intensities modify in relation to
the Fe content, a correlation should be made between the intensities of these three peaks. It was noticed that not only the \( h_1/h_3 \) ratio, but the \( h_2/h_3 \) and \( (h_1+h_2)/h_3 \) ratios as well, increase with the Fe concentration, the trend lines showing very high correlation coefficients (Figure 4). Therefore, by employing these new diagrams, which allow the lines to be used as calibration curves and all three ratios to be plotted, the accuracy of the results will improve considerably, since the intensities of all three main peaks will be taken into account (Buzatu et al., 2013).

Figure 4. Correlation between the iron content in sphalerite samples and the \( h_1/h_3 \), \( h_2/h_3 \) and \( (h_1+h_2)/h_3 \) ratios (Buzatu et al., 2013)
2. Sulfosalts

2.1. Bismuth minerals

The bismuth minerals were not identified so far at Baia Sprie, this study being the first mention of them (Buzatu et al., 2015), although in other deposits within the metallogenic district of Baia Mare several Bi-sulphosalts were reported recently. The bismuth minerals were observed in samples from the eastern part of Baia Sprie deposit near shaft no. 5 (Figure 1c), within the cupriferous level (lower) of Principal Vein. The following minerals within this group were identified: bismuthinite \((\text{Bi}_4\text{S}_6)\), lillianite-gustavite \((\text{Pb}_{N-1-2x}\text{Bi}_{2+x}\text{Ag}_x\text{S}_{N+2})\), disordered intergrowths of lillianite homologues, heyrovskyite \((\text{Pb}_{12}\text{Bi}_4\text{S}_{18})\) and cosalite \((\text{Cu}_{n}\text{Ag}_{i+j}\text{Pb}_{8-2x-0.5(x+i)}\text{Bi}_{8+x}\text{S}_{20})\) (Figures 5 and 6).

By plotting the chemical compositions from Baia Sprie on the \((\text{Bi}+\text{Sb})-(\text{Ag}+\text{Cu})-\text{Pb}\) diagram, most of the points can be observed situated somewhere between the lines \(N=4\) and \(N=7\) (Figure 6). This kind of non-ideal compositions for bismuth minerals are not uncommon, similar phases being reported also by other authors (Cook, 1997, Cook, 1998, Putz et al., 2003, Cook and Ciobanu, 2004, Voudouris et al., 2013). The authors interpreted these compositions quite differently suggesting to represent possible new unreported lillianite homologues or submicroscopic (below the scale of microprobe beam) disordered intergrowths of \(^4\text{L}\) and \(^7\text{L}\) homologues. In the case of Baia Sprie samples, the submicroscopic intergrowths of different homologues are considered more likely (Buzatu et al., 2015). This aspect is suggested also by the micro-Raman spectra obtained on this kind of compositions. The DI1 and DI2 spectra appear as intermediary between the compositions of lillianite and heyrovskyite. Only in the case of DI2 type it is observed a linear trend in the arrangement of the plotted compositions, due to similar \(N\) values (Figure 6) that might indicate a possible solid solution series between vikingite and the Ag-free member. However, a more accurate identification is difficult to provide based only on microprobe analyses. The small grain sizes and the intergrowths between different lillianite homologues preclude any available X-ray structural determination.

The described new occurrence of Bi-sulphosalts (Figure 1c) was expected at Baia Sprie, since these minerals were identified all over the segments of Neogene Carpathian Arc. In Baia Mare district the Bi-sulphosalts have been identified at Toroiaga, Băiuț, Nistru and Şuior (Cook, 1997, Cook, 1998, Damian, 1999, Damian et al., 2000, Damian et al., 2008), where the occurrences are similar with those from Baia Sprie. The Bi-minerals assemblage from Baia Sprie was observed only in the lower cupriferous level of the deposit belonging to the first event of mineralization (Buzatu et al., 2015). Based on their textural relations, Bi-minerals were deposited at the same time with galena, being intimately intergrown with, and before the second generation of chalcopyrite and quartz (Figure 2).
Figure 5. Back-scattered electron images showing the presence of bismuth minerals at Baia Sprie: a. Bismuthinite (Bmt), lillianite-gustavite (Lil) and cosalite (Cos) association at contact between quartz (Qtz), pyrite (Py) and chalcopyrite (Cp); b. Bismuthinite as inclusion in pyrite; c. Elongated lamellae of lillianite-gustavite included in chalcopyrite; d. Intergrowths of galena (Gn) and bismuth sulphosalts - lillianite-gustavite and disordered phases (Dis) – within chalcopyrite; e. Lamellae of heyrovskýite (Hey) and disordered phases intergrown with galena; f. Intergrowths of galena and disordered phases within chalcopyrite (Buzatu et al., 2015)
Figure 6. Ternary diagram (Bi+Sb)-(Ag+Cu)-Pb of lillianite homologues from Baia Sprie deposit showing intermediate members of lillianite-gustavite series, disordered intergrowths, heyrovskyite and cosalite.

Bismuth sulphosalts can be valuable indicators of physico-chemical forming conditions due to their sensitivity to changes in temperature, Eh-pH and oxygen and sulphur fugacities (Cook and Ciobanu, 2004). Experimental studies in Cu$_2$S-PbS-Bi$_2$S$_3$ system showed that galenobismutite decomposes to bismuthinite and lillianite at 375 °C (Chang and Hoda, 1977). Cook (1997) reported temperatures for Bi assemblages to be $>350$ °C. Moëlo et al. (1987) suggested formation of several lillianite homologues at temperatures of 350-400 °C and shown them to be unstable at lower temperatures. Significant contents of Sb can be incorporated in lillianite, heyrovskyite and cosalite only at temperatures higher than 350 °C (Chang et al., 1980). The presence at Baia Sprie of intermediate phases of solid solution among lillianite homologues, with high Sb content, may suggest temperatures of $\sim350$ °C (Buzatu et al., 2015), as proposed previously by Cook (1997) for Toroiaga deposit and Voudouris et al. (2013) for Stanos mineralization. These temperatures are also in good agreement with the ones extracted...
from arsenopyrite geothermometer of 320-360 °C, but still too high than the values reported previously (~300 °C) by Borcoş et al. (1973) and Nedelcu and Pintea (1993).

The Bi-sulphosalts may be also valuable indicators for gold mineralizations, since a strong geochemical and mineralogical correlation between these two was observed in other ore types (Cook, 1998, Damian et al., 2008, Voudouris et al., 2013). Experimental studies on the Au partitioning between hydrothermal solutions and liquid Bi in Au-undersaturated conditions showed that above its melting point (271 °C) liquid Bi is a powerful scavenger for Au (Douglas et al., 2000). Although incorporation of Au in such Bi-based melts was observed to be more likely in high-temperature conditions (>400 °C) it was argued that the process could operate also at lower temperatures (Ciobanu et al., 2006, Damian et al., 2008).

2.2. Tetrahedrite – Tennantite

At Baia Sprie, phases of tetrahedrite-tennantite series (Td-Tn - Cu_{10}(Fe,Zn)_{2}Sb_{4}S_{13} – Cu_{10}(Fe,Zn)_{2}As_{4}S_{13}) are observed within the entire depth of the deposit with an enrichment towards the deeper parts (cupriferous level), frequently associated with chalcopyrite. Most of the compositions were found to be very close either to As-member (tennantite) or to Sb-member (tetrahedrite). Intermediate compositions were also identified but with a lower frequency. It was observed that tennantite is more abundant in the samples from the cupriferous level, while tetrahedrite appears mostly within intermediate and upper parts of the deposit.

As for pyrite and arsenopyrite, the zoning bands of tetrahedrite-tennantite series indicates a high activity of As and Sb in hydrothermal solutions (Figure 7). The zoning structures of Td-Tn were observed only in the lower level of Baia Sprie and none in intermediate and upper parts of the deposit. The zonation pattern parallel to the crystallographic faces is consisting of compositional fluctuation of alternating zones from a tetrahedrite core, evolving towards tennantite composition and changing back to tetrahedrite (Figure 7). This kind of behavior is displayed as oscillatory zoning bands of different intermediate members of the series (As- or Sb-rich phases). Another type of chemical variation was observed as a smooth gradient shifting from a tetrahedrite-like composition towards tennantite member, without displaying zonal bands.

This chemical heterogeneity indicates small-scale fluctuations of As and Sb in ore fluids, due to growth rate kinetics of fahlore crystals, controlled by the concentrations of these elements in the reaction zone (Plotinskaya et al., 2005). The oscillatory zoning suggests multiple pulses of hydrothermal solutions with high As content, as in the case of pyrite crystals. The analyzed fahlores grains with gradient shifting from tetrahedrite towards tennantite composition suggest the crystallization in
a single sequence and a depletion of Sb during the deposition together with an As enrichment of the fluids (Buzatu et al., 2015).

**Figure 7.** Back-scattered electron images of tetrahedrite-tennantite series from Baia Sprie. **a.** Tennantite crystal showing euhedral growth zones with slightly different compositions; **b.** Tennantite core and outer zones with composition towards tetrahedrite; **c.** Fahlore with intermediate compositions and oscillatory zoning bands; **d-f.** Tetrahedrite-like compositions evolving towards tennantite members (Buzatu et al., 2015)
In the case of tetrahedrite-tennantite series from Baia Sprie it was observed that tennantite members were deposited at the first stages of mineralization being more abundant in the lower levels, with several chemical fluctuations reflecting the high As activity in the hydrothermal solutions. Towards the surface in the more recent depositional stages, the Sb-member (tetrahedrite) is more abundant. The Ag content of fahlores is very high in tetrahedrite members from intermediate and upper levels of the deposit. The correlation between Ag content and %Td shows that Ag concentrates mainly in tetrahedrites and its content is decreasing as the phases shift towards the As-member of the series. The incorporation of such significant concentrations of Ag in tetrahedrites is controlled by crystallochemical factors that enable Sb-rich tetrahedrite to accommodate more Ag than Sb-poor members (Vassileva et al., 2014).

2.3. Geocronite – Jordanite

Members of geocronite-jordanite solid solution series (Pb14(Sb,As)6S23) have not been identified so far at Baia Sprie. This series appears within the deposit in very low quantities as small anhedral grains and it was observed only in the intermediate level (Buzatu et al., 2015). It is associated with bournonite and sphalerite and often is surrounding and replacing galena and chalcopyrite formed previously. Microprobe data revealed only intermediate members of the series.

2.4. Bournonite – Seligmannite

The solid solution series bournonite-seligmannite – PbCu(Sb,As)S3 – was observed at Baia Sprie within the intermediate level of the deposit. Members of this series appear also in small quantities often associated with senseyite and tetrahedrite. The bournonite from Baia Sprie was previously identified but described based just on optical observations (Manilici et al., 1965). The present work reports the chemical compositions of this series and also confirms the presence of seligmannite member within the Baia Sprie deposit (Buzatu et al., 2015).

2.5. Senseyite

Baia Sprie is the type locality for senseyite (Pb9Sb8S21), samples from this deposit being first time studied by Krenner (1881). New EPMA compositional data are presented within this study for senseyite samples from the type locality Baia Sprie. Senseyite was identified only in samples within intermediate and upper level of the deposit. It was observed in polished sections as elongated lath-like grains associated with geocronite and bournonite. The EPMA data show an average chemical formula for senseyite of Pb8.88Sb8.02S20.92 which is very close to stoichiometric composition.
IV. SUPERGENE ALTERATION

1. The Raman and IR study of goslarite and rozenite

The mining activity that took place in the past at the Baia Sprie left behind at the surface the sulfide-bearing material which in atmospheric conditions can lead to the formation of secondary minerals, such as sulfates that concentrate metals. These minerals are very soluble and can release the metals in the environment, during the complex process of acid mine drainage. Thus, it is important to know the mineral species that form through weathering in such mining sites and how they can affect the environment.

A first set of samples of supergene products was studied by using Raman and infrared spectroscopy (Buzatu et al., 2012). The samples were collected from the Minei Hill open pit, in the eastern part of the Baia Sprie ore deposit. The weathering product is developed on the surface of mineralized ( sphalerite and galena) areas and occurs as a white fine deposition material.

The Raman spectra revealed two distinctive minerals. Under the laser excitation, the sample revealed one spectrum in the first seconds of exposure, and in less than two minutes, the spectrum was changed to a different one. The first type of Raman spectrum is characteristic to rozenite (FeSO$_4$ · 4H$_2$O), showing the typical Raman bands for sulfate minerals, namely the four fundamental vibration modes. The second type of Raman spectrum is showing the $\nu_1$ mode shifted at higher wavenumbers (1024 cm$^{-1}$), the vibrations assigned to $\nu_2$ are found at 427 and 506 cm$^{-1}$, $\nu_4$ mode at 626 cm$^{-1}$ and the $\nu_3$ modes at 1080 and 1191 cm$^{-1}$. These peaks were found to correspond to hydrated zinc sulfate, bianchite ((Zn,Fe)SO$_4$ · 6H$_2$O) or goslarite (ZnSO$_4$ · 7H$_2$O) (Chio et al., 2007, Buzgar et al., 2009). These two minerals have very similar Raman spectra due to the same type of structure, which makes the clear identification difficult.

The changes that take place during the Raman analysis were observed at laser intensity higher than 60% (7.37 mW). Thus it is possible that these changes are due to laser radiation which at 100% intensity gives a power on the sample surface of 53.6 mW. It is possible that rozenite is unstable under laser irradiation, due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$. Less Raman signal is received from rozenite during the lattice destruction, and thereby the hydrated zinc sulfate, which was masked by rozenite, dominates the Raman spectrum.

The IR spectrum confirms the presence of goslarite in the sample. The $\nu_1$ vibrational mode of SO$_4$ is observed at 1009 cm$^{-1}$, at 459 cm$^{-1}$ is present the $\nu_2$ mode, at 1108, 1157 and 1267 cm$^{-1}$ – $\nu_3$ modes, and the $\nu_4$ vibration modes are shown at 610, 632 and 655 cm$^{-1}$. 

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2. Thermal transformation of secondary sulfates

A second set of samples consisting in efflorescent salts was collected within Dealul Minei open-pit during June 2012 (Figure 8a-d). The newly-formed minerals were observed on the exposed walls of the open pit, on the mineralized veins outcrops, and on the ground surface along dried drainage paths.

From the entire batch a number of 7 final subsamples were obtained by sorting the mineral phases using a binocular magnifier. The final samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman and near-infrared (NIR) spectroscopy. The near-infrared measurements were carried out using a Portable Infrared Mineral Analyzer (PIMA). After acquiring the NIR spectra on the initial samples, a heating procedure combined with multiple PIMA analyses were applied, in order to observe the dehydration and structural changes in sulfates at different temperature steps.

2.1. X-ray diffraction

The identified phases represent mostly iron sulfates with different hydration degrees (szomolnokite - FeSO₄ . H₂O, rozenite - FeSO₄ . 4H₂O, melanterite - FeSO₄ . 7H₂O, coquimbite - Fe³⁺₂(SO₄)₃ . 9H₂O, ferricopiapite - Fe³⁺/²/³Fe³⁺₄(SO₄)₆(OH)₂ . 20H₂O), suggesting pyrite oxidation as the main source for AMD-precipitates. Other observed minerals are Zn and Al sulfates (gunningite - (Zn,Mn)SO₄ . H₂O, alunogen - Al₂(SO₄)₃ . 17H₂O, halotrichite - FeAl₂(SO₄)₄ . 22H₂O).

2.2. Crystals morphology

Melanterite was observed as massive granular crusts of bluish green color associated frequently with halotrichite (Figure 8c,e,g,h). Halotrichite can be easily recognized by its capillary-acciular habit (Figure 8f). Rozenite and szomolnokite appear commonly in association as cotton-like nodules (rozenite) and dipyramidal crystals (szomolnokite) evolved on the acicular halotrichite (Figure 8i-j). Ferricopiapite has an intense yellowish-brown color (Figure 8d) and the crystals form as thin plates intergrowths (Figure 8k). Coquimbite was observed associated with ferricopiapite and halotrichite showing a tabular-platy habit (Figure 8k-l).

2.3. Raman spectroscopy

The Raman measurements carried out on the selected subsamples confirmed the XRD results. The sulfate minerals can be easily identified in generally by comparison with reference spectra. The vibrational modes of sulfate minerals are generally classified into three types: (1) vibrations SO₄²⁻ group, (2) H₂O vibrations, and (3) vibrations of cation-oxygen bonds (Nakamoto, 2009). The free sulfate anion in
Figure 8. The presence of secondary sulfates in the field and crystal morphologies. a-b. Supergene products within Dealul Minei open-pit; c-e. Examples of collected samples consisting in complex assemblages of secondary sulfates; f. Acicular-capillary habit of halotrichite (Hlt); g-h. Melanterite (Mel) as massive granular crusts associated with halotrichite; i-j. Rozenite (Rzn) as spheroidal growths and dipyramidal crystals of szomolnokite (Sz); k-l. Ferricopiapite (Fe-Cop) and coquimbite (Coq) with tabular habit.
aqueous solution has four fundamental vibrational modes characterized by the following Raman bands: (a) nondegenerate $\nu_1$ symmetric stretching at 981 cm$^{-1}$, (b) doubly degenerate $\nu_2$ symmetric bending at 451 cm$^{-1}$, (c) triply degenerate $\nu_3$ antisymmetric stretching at 1104 cm$^{-1}$, and (d) triply degenerate $\nu_4$ antisymmetric bending at 613 cm$^{-1}$ (Omori, 1968, Lane, 2007, Buzgar et al., 2009, Nakamoto, 2009, Frost et al., 2014). If in solution the SO$_4^{2-}$ group vibrates freely, in minerals the atoms vibrate under additional influences from the cations, reduction in symmetry in the crystal structure causing the splitting of vibrational modes and variation of the bands wavenumber (Omori, 1968, Buzgar et al., 2009, Nakamoto, 2009).

### 2.4. NIR spectroscopy

The NIR reflectance spectra of sulfate minerals in the range 1.3-2.5 μm can be divided into two sections based on the characteristic bands assignment: (1) the bands between the wavelengths 1.30-1.52 μm are attributed to the first overtone of stretching modes of water (w), 2$\nu_1^w$ or 2$\nu_3^w$; and (2) the 1.52-2.50 μm region assigned to the combination modes of water $\nu_2^w + \nu_1^w$ (or $\nu_3^w$), and combination modes of water and SO$_4$ tetrahedra ($\nu_1 + \nu_3$)$_{SO_4}^+$ + $\nu_2^w$ (Cloutis et al., 2006, Ling and Wang, 2010).

After acquiring the NIR spectra on the initial samples, a heating procedure combined with multiple PIMA analyses were applied, in order to observe the dehydration and structural changes in sulfates at different temperature steps.

During the heating process the NIR spectra of melanterite (Figure 9), reveal changes in sample at the first temperature step (30 °C) where the melanterite changes to rozenite by dehydration with 3 water molecules. The crystal structure changes from isolated polyhedra to finite clusters. Rozenite spectrum shows one band assigned to water overtones at 1.45 μm and multiple ones attributed to the combinations modes at 1.73, 1.95, 1.98 and 2.41 μm. Rozenite structure remains stable up to 60 °C when szomolnokite marks its presence in the NIR spectra. After the heating at 60 °C the sample contains rozenite and szomolnokite, the quantity of rozenite decreasing as the temperature steps increase, as showed by the less and less intense bands of rozenite. At 80 °C rozenite is transformed totally in szomolnokite. The NIR reflectance spectrum of szomolnokite shows the characteristic bands of sulfates at 1.34, 1.44 and 1.52 μm assigned to the overtones of water stretching modes, and at 1.98, 2.09 and 2.40 μm for the combination modes. At 80-90 °C a new peak appears in the NIR spectra at 2.23 μm which increases the intensity towards higher temperature steps (Figure 9). At 140 °C other two new peaks are observed at 1.48 and 1.83 μm, while the main band of szomolnokite from 2.09 μm is getting less intense. The new peaks observed at 1.48,
1.83 and 2.23 μm belong to a new compound formed by the dehydration of melanterite, the iron hydroxide sulfate (Fe(OH)SO₄). After the final heating at 220 °C the NIR spectrum shows the total transformation of szomolnokite in Fe(OH)SO₄, as it was confirmed also by the XRD results.

Figure 9. Selected NIR spectra of samples 11909800, 11909804 și 11908802 at different temperature steps showing transformations during the heating procedure (melanterite – Mel, rozenite – Rzn, szomolnokite – Szm)
V. CONCLUSIONS

The mineralogical and chemical study on Baia Sprie samples provide important information about the ore forming conditions and chemical variations within the mineralogy of the deposit.

The present study describes for the first time the occurrence of bismuth minerals in Baia Sprie ore deposit. Also, a new occurrence of geocnite-jorndanite series and of the member seligmannite was identified within this work, and semseyeite from the index locality was chemically described. The obtained results are of great importance for epithermal base metal-gold ore deposits, Baia Sprie being accepted as classic model of this mineralization type.

The As zonal structures of pyrites from Baia Sprie reflect chemical changes in ore-bearing fluids during the first stage of mineralization. The As-free core and As-rich rims suggests a relatively high S activity and low As in the early fluids of the depositional stage, followed by a sharp increase of As activity in the late fluids. The presence of a substantial fraction of Au within iron sulphides (mainly pyrite and arsenopyrite) is referred to as “invisible gold”. The amount of Au that can be incorporated into pyrite is strongly dependent of As concentration. At Baia Sprie, the high contents of As in pyrites with Fe deficiency might prove the presence of invisible gold. The As content from 29.58 to 30.51 at% (average of 30.34 at% As) of the analyzed arsenopyrite from the lower level of the deposit indicates temperatures of 320-360 °C according to the phase diagram Fe-As-S of Kretschmar and Scott (1976).

Raman spectroscopy has proven both a time-saving and an efficient technique in the study of sphalerite structure and in the determination of the iron concentrations of this mineral, particularly when other methods are not available. The present study has revealed that, in natural sphalerites, the intensities of all three peaks are correlated with Fe content. The use of the $h_2/h_3$ and $(h_1+h_2)/h_3$ ratios, together with the newly-suggested calibration curves, also increases the accuracy of the results.

The bismuth minerals were not identified so far at Baia Sprie, this study being the first mention of them. Bismuth sulphosalts can be valuable indicators of physico-chemical forming conditions due to their sensitivity to changes in temperature, Eh-pH and oxygen and sulphur fugacities. The Bi-sulphosalts may be also valuable indicators for gold mineralizations, since a strong geochemical and mineralogical correlation between these two was observed in other ore types.

The presence at Baia Sprie of intermediate phases of solid solution among lillianite homologues, with high Sb content, may suggest temperatures of ~350 °C, in good agreement with the temperatures obtained from arsenopyrite geothermometer of 320-360 °C.
At Baia Sprie, phases of tetrahedrite-tennantite (Td-Tn) series are observed within the entire depth of the deposit with an enrichment towards the deeper parts (cupriferous level). The zoning bands indicate a high activity of As and Sb in hydrothermal solutions. The oscillatory zoning suggests multiple pulses of hydrothermal solutions with high As content, as in the case of pyrite crystals. The analyzed fahlores grains with gradient shifting from tetrahedrite towards tennantite composition suggest the crystallization in a single sequence and a depletion of Sb during the deposition together with an As enrichment of the fluids.

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