## "ALEXANDRU IOAN CUZA" UNIVERSITY of IAȘI FACULTY OF GEOGRAPHY AND GEOLOGY

## THE "CHEMISTRY AND LIFE AND EARTH SCIENCES" DOCTORAL SCHOOL

## Mineralogy and geochemistry of polymetallic mineralization from Coranda-Hondol (Metaliferi Mts., ROMANIA)

ABSTRACT

Ph.D. supervisor:

Prof. Dr. Damian Gheorghe

Ph.D. Student:

Apopei Andrei Ionuț

#### Acknowledgements

I wish to express my deepest gratitude to my Ph.D. supervisor Prof. Dr. Gheorghe DAMIAN for the initiation in the field of Hydrothermal Ore Deposits; also, for the analytical support, trust, support and advice given throughout my Ph.D. thesis. The support to do an internship abroad and the opportunity to work with modern analytical technique, helped enormously in achieving of this thesis.

I am also deeply indebted to Prof. Dr. Nicolae BUZGAR for the initiation in the Mineralogy and Spectrometry fields, for all analytical support, and also for helping both in achieving of the thesis and other related activities.

I also want to thank to the committee members, to Mr. Conf. Dr. Dan STUMBEA and Mr. Lecturer Dr. Mitică PINTILEI, for the time and observations that contributed to the quality of this thesis. Here, I want to express my thanks to Mr. Conf. Dr. Dan STUMBEA for its willingness to provide binocular microscope and to Mr. Lecturer Dr. Mitică PINTILEI for the facilitating of the XRD analyzes and determinations of pH measurements.

Thanks goes to Mr. Prof. Dr. Peter Andráš from Matej Bel University, Banská Bystrica (Slovakia), for their help and guidance throughout the one month mobility in Banská Bystrica (August 2014).

In addition, I want to thank and acknowledge the staff (professors and auxiliarry staff) from the Department of Geology of the Faculty of Geography and Geology, "Alexandru Ioan Cuza" University of Iași, for the education, guidance and their help during my bachelor and master degrees.

I also gratefully acknowledge the Engr. Nicolae Stanca, geologists Engr. Paul Mircea Ivăşcanu, Engr. Dan Filipescu and Engr. Laurențiu Igna from S.C. DevaGold S.A., for access on the Coranda Hondol open pit and their support on the sampling site.

Finally, I wish to express my gratitude to my family for their support, understanding and sacrifice made.

## **TABLE OF CONTENTS**

Chapter 1.	Introduction	1
1.1	Objectives	1
1.2	Reasearch history	1
Chapter 2.	Materials and methods	2
Chapter 3.	Regional and local geology	3
3.1	Geological setting	3
3.2	Geology of the Certej area	4
3.2.1	Stratigraphic and petrographic considerations	4
3.2.2	Hydrothermal alteration	6
3.2.3	Mineralization and ore type	6
Chapter 4. Hondol	Mineralogy and geochemistry of mineralization from Coranda- 7	•
4.1	Gangue minerals	7
4.2	Common sulfides	8
4.2.1	Sphalerite and chalcopyrite	8
4.2.2	Pyrite	8
4.2.3	Galena	9
4.3	Sulfosalts	9
4.3.1 4.3.2 4.3.3 Slg an	Tetrahedrite-tennantite series Bournonite-seligmannite and geocronite-jordanite series The effect of As-Sb substitution in the Raman spectra of Td-Tn, Bnn- d Gcn-Jor series	9 13 17
4.4 4.5 Coranda	Tellurides Mineralogy and geochemistry of sediments and detritus material from i-Hondol perimeter	17 19
Chapter 5.	Supergene alteration	20
5.1	Secondary sulfates and their fotochemical degradation	20
5.2	Acidic waters	22
Chapter 6.	Conclusions	22

**Keywords:** Coranda-Hondol, Certej, polymetallic mineralization, Au-Ag ore deposits, hydrothermal, tellurides, sulfosalts, supergene alteration, Apuseni Mountains

## List of scientific papers published or under review during the period of the PhD thesis

- Apopei, A. I., Damian, G., Buzgar, N., Buzatu, A. (2014) Bournonite-seligmannite and geocronite-jordanite solid-solution series at Coranda-Hondol open pit and their compositional variation (Certej Au-Ag deposit, ROMANIA). Ore Geology Reviews, (under review).
- Apopei, A. I., Damian, G., Buzgar, N., Buzatu, A. (2014) Compositional variations of tetrahedrite-tennantite minerals from Coranda-Hondol open pit perimeter (Certej Au-Ag deposit, ROMANIA). *Mineralogical Magazine*, (under review).
- Apopei, A. I., Buzgar, N., Damian, G., şi Buzatu, A. (2014) The Raman study of weathering minerals from Coranda-Hondol open pit (Certej gold-silver deposit) and their photochemical degradation products under laser irradiation. *The Canadian Mineralogist, (under review).*
- Buzatu, A., Damian, G., Dill, H. G., Buzgar, N., Apopei, A. I. (2014) Mineralogy and geochemistry of sulfosalts from Baia Sprie ore deposit (Romania) – new bismuth minerals occurrence. Ore Geology Reviews, 65, 132–147. doi: 10.1016/j.oregeorev.2014.09.016. Factor de impact 3.383
- Apopei, A. I., Damian, G., Buzgar, N., Milovska, S., şi Buzatu, A. (2014) New occurrences of hessite, petzite and stützite at Coranda-Hondol open pit (Certej gold-silver deposit, ROMANIA). Carpathian Journal of Earth and Environmental, 9(2), 71-78. Factor de impact 0.727
- Buzgar, N., Buzatu, A., Apopei, A. I., Cotiugă, V. (2014) In situ Raman spectroscopy at the Voronet Monastery (16th century, Romania): New results for green and blue pigments. *Vibrational Spectroscopy*, 72, 142-148. doi: 10.1016/j.vibspec.2014.03.008. *Factor de impact 1.547*
- Buzatu, A., Buzgar, N., Damian, G., Vasilache, V., Apopei, A. I. (2013) The determination of the Fe content in natural sphalerites by means of Raman spectroscopy. *Vibrational Spectroscopy*, 68, 220-224. doi: 10.1016/j.vibspec.2013.08.007. *Factor de impact 1.547*
- Buzgar, N., Apopei, A. I., Buzatu, A. (2013) Characterization and source of Cucuteni black pigment (Romania): vibrational spectrometry and XRD study. *Journal of Archaeological Science*, 40(4), 2128-2135. doi: 10.1016/j.jas.2012.12.034. *Factor de impact 2.139*
- Buzgar, N., Apopei, A. I., Diaconu, V., Buzatu, A. (2013) The composition and source of the raw material of two stone axes of Late Bronze Age from Neamt County (Romania) - A Raman study. *Analele ştiințifice ale Universității "Al. I. Cuza" din Iași, Seria Geologie*, 59(1), 5-22.
- Apopei, A. I., Damian, G., şi Buzgar, N. (2012) A preliminary Raman and FT-IR spectroscopic study of secondary hydrated sulfate minerals from the Hondol open pit (Metaliferi Mts., ROMANIA). *Romanian Journal of Mineral Deposits*, 85(2), 1-6.

#### CHAPTER 1. INTRODUCTION

#### 1.1 Objectives

The present study, entitled "*Mineralogy and geochemistry of polymetallic mineralization from Coranda-Hondol (Metaliferi Mts., ROMANIA)*" has as the main objective the mineralogical and geochemical study of polymetallic mineralization from Coranda-Hondol.

Within this thesis, the main purpose was textural characterization of mineralised samples, identification of sulfides, sulfosalts and tellurides, which are present in the epithermal mineralization at Certej ore deposit. In addition, it was intended to identify the sulfosalts minerals by means of Raman spectrometry in order to establish a direct relationship with their chemistry.

Another objective of the present study was to identify the secondary sulfates from the surface of the studied perimeter, minerals precipitated as a result of acid mine drainage. In this context, have been pursued the change of mineralogical phases arising from the photochemical degradation (high intensity of the Raman laser) of the secondary sulfates samples. It was also aimed to study the acidic waters (temporary ponds and streams) and the sediments / detritus material from the studied perimeter.

The original contributions of this thesis can be found in Chapter 4, Chapter 5 and Chapter 6. Some of these original contributions have been materialized of are in progress to materilze in scientific papers which are published in international scientific journals (included in the database and ISI Web of Science).

#### 1.2 Reasearch history

Certej ore deposit is located in Hunedoara County, located from the geological point of view in the SE part of the Metaliferi Mountains (South Apuseni), part of the socalled "Golden Quadrilateral" (Brad - Deva - Zlatna - Baia de Arieş). The Certej ore deposit is located at about 12 km northeast of Deva.

Operating activities began approximately in 1774, being more the subject of an ad-hoc mining until 1960, when it began the explorations of the mine for lead and zinc. During the 80s', mining activity is concentrated on Coranda-Hondol open pit (CHOP). CHOP is located in the central part of the Certej ore deposit, and it was continued to be

1

operated until 2006 when the mine was closed (Ianovici *et al.*, 1976; Forward *et al.*, 2009). In this study, we use the expression "Coranda-Hondol open pit (CHOP)" referring to the perimeter of the open pit. Some authors use the name "Certej ore deposit" which refers to the entire area (including the CHOP). Further, will be used both terminologies with reference to the above explainations.

The perimeter from Coranda-Hondol has been studied since the 1940s, and a comprehensive summary of preliminary investigations are presented by Udubaşa *et al.* (1980). Uniform interpretations of the petrographic, mineralogical, geochemical and metallogenic data on the Certej ore deposit, which exist up to that time, are done in the same work.

Once the license for geological exploration was obtained, besides the fesability study (Forward *et al.*, 2009) and technical report (Alexander *et al.*, 2014), should be noted the following studies: hydrothermal alteration (Alderton *et al.*, 1998) and supergene alteration (Apopei *et al.*, 2012), radiometric dating (Rosu *et al.*, 1997), new occurrences of Au-Ag tellurides (Apopei *et al.*, 2014), and other studies related to geology of the Certej ore deposit (Pricopie *et al.*, 2004; Ageneau *et al.*, 2006).

#### CHAPTER 2. MATERIALS AND METHODS

This study aimed to study the mineralogy and geochemistry of polymetallic mineralization from the perimeter of Coranda-Hondol open pit (part of Certej ore deposit). To achieve this purpose, 112 polished sections were made from mineralized samples collected throughout the Coranda-Hondol open pit perimeter. Calcographic studies were undertaken for all polished sections.

Chemical analyses (EPMA, SEM-EDX and XRF) were performed on the most representative polished sections, with particular attention to sulphides and sulfosalts minerals.

Also, vibrational spectroscopy studies (Raman and infrared) were performed for routine mineralogical study (gangue minerals, common sulphides, supergene minerals). Another goal of this study was to establish thresholds of the photochemical degradation (in the case of hydrated sulfates at high intensities of the Raman laser). The  $\mu$ -Raman technique was used for semiquantitative analysis of some common sulfosalts. The analytical methods used for the mineralogical identification, were complemented by X-ray diffraction (XRD). Secondary alterations (mainly secondary sulfates) were affected the polymetallic sulphides of Fe, Cu, Zn and in a lesser extent of Pb.

Acidic water samples were taken (from temporary ponds and streams) in order to precipitate secondary minerals. These minerals being subsequently identified and correlated with pre-existing secondary minerals, which were found throughout the studied perimeter.

For a correlation with supergene alteration (secondary sulfates and acidic water samples) were taken samples of sediments and detritus material throughout the study area. The sampling was made in three different seasons, as follows: November 2011, July 2012 and October 2013.

#### CHAPTER 3. REGIONAL AND LOCAL GEOLOGY

#### 3.1 Geological setting

Based on different pre-Alpine geological evolution (Ianovici *et al.*, 1976; Balintoni, 1997), Apuseni Mountains are divided into two major structural units: North Apuseni Mountains (NAM) and the South Apuseni Mountains (SAM).

Neogene volcanism characteristic of SAM is associated with different intrusive and extrusive volcanic edifices. These volcanic edifices show a structural NW-SE trend and are divided into three alignments (figure 3-1): (i) Zarand-Brad-Săcărîmb; (ii) Zlatna-Stănija; and (iii) Roșia Montană-Bucium. The ore deposits from Baia de Arieş and Deva appear as isolated volcanic bodies of the three alignments (Rosu *et al.*, 1997).

Neogene magmatism in the SAM (14.7 - 7.4 Ma, Rosu et al. (1997)) is accompanied by a very important metallogenetic activity, particularly for Cu-Au (Mo) mineralization, togheter with Au-Ag±Te mineralization and common sulphides (Udubasa *et al.*, 2001).



Figure 3-1 Regional geological map of the South Apuseni Mountains, with a) structures and Neogene magmatic rocks; and b) major structural elements and main vein systems (modified after Neubauer *et al.* (2005))

#### 3.2 Geology of the Certej area

Certej epithermal Au-Ag deposit fall within metallogenetic province of the Apuseni Mountains, belonging to the SE area of the metallogenetic district "Brad-Săcărîmb" (figure 3-1), between localities Hondol, Bocşa Mare and Bocşa Mică. In figure 3-2 is presented the geology of the studied area.

#### 3.2.1 Stratigraphic and petrographic considerations

This metallogenetic district is strongly structural controlled, due to a fracture oriented E-W which is interpreted from geophysical data (Udubaşa *et al.*, 1980; Pricopie *et al.*, 2004; Forward *et al.*, 2009). This fracture is intersected by a major volcanic alignment oriented NE-SW. Most of the subvolcanic bodies, which occur on this alignment, are well defined. These are Bocşa and Băiaga. At the intersection of fracture and alignments, whose thickness exceeds 30 m, the breccias are widely developed and extensively mineralized (Udubaşa *et al.*, 1980). The main fault trends are approximately

NNW-SSE, NNE-SSW, NW-SE, NE-SW, ENE-WSW and WNW-ESE (Pricopie *et al.*, 2004; Forward *et al.*, 2009).



Figure 3-2 Geological map of the Coranda-Hondol perimeter (modified after Alexander *et al.* (2014) and Ivăşcanu *et al.* (2013)). At the bottom of the figure is represented a longitudinal section between points A and B (WNW-ESE). Longitudinal section was created using DEM data and geology modified after Alexander *et al.* (2014)

From the structural point of view, the basement in the area have been mapped as part of the Jurassic ophiolitic basalts and outcrop only in the southern part of CorandaHondol open pit. The Certej ore deposit is dominated by three bodies of andesitic composition. Therefore, from west to east: Hondol, Băiaga and Grozii Hill andesitic body. Cretaceous sediments are represented by sandstones and black shale, while the Neogene sediments overlie the Cretaceous sediments and consist in conglomerates, sandstones, marls and clays (Udubaşa *et al.*, 1980; Pricopie *et al.*, 2004; Forward *et al.*, 2009; Alexander *et al.*, 2014).

#### 3.2.2 Hydrothermal alteration

Generally, the clay alteration extends over a large area, followed by potassic and silicic alteration. Depending on the host lithologies were delineated the following types of alterations (Udubaşa *et al.*, 1980; Forward *et al.*, 2009; Alexander *et al.*, 2014):

- Cretaceous sediments: argillic alteration with associated quartz, adularia and barite;
- > Neogene sediments: quartz-adularia-pyrite and intense silicification;
- Hondol andesites: argilic and propylitic alteration with adularia, silica and clay minerals;
- Băiaga andesites: strong argillic alteration;
- > Dealul Grozii andesites: potassic alteration and locally silicic alteration.

#### 3.2.3 Mineralization and ore type

The neogene hydrothermal activity is responsible for precipitation of goldsilver mineralization in two ways: as impregnation and subordinate along two orthogonal vein systems (with NW-SE and NE-SW strikes respectively) (Udubaşa *et al.*, 1980; Pricopie *et al.*, 2004). The first type of mineralization had an intense role for the Grozii Hill and Hondol subvulcanic andesitic bodies. Băiaga subvolcanic andesitic body is less mineralized (in general only with pyrite).

Udubaşa *et al.* (1980) have found the evidence for some non-synchonicity of mineralization but does not regard distinct phases of mineralization and the poliascendent character of the hydrothermal activity cannot be accepted. Subsequently, Pricopie *et al.* (2004) argues that there is a second stage of mineralization which occur especially in the western part of the deposit, as a consequence of the intrusion of Băiaga subvolcano.

The presence of sphalerite and galena in a large amounts, and subordinate pyrite, As-Sb sulfosalts, arsenopyrite and locally tellurides and stibine suggests the

development of an *intermediate-sulfidation* (IS) type (Udubaşa *et al.*, 1980; Forward *et al.*, 2009; Gál *et al.*, 2010; Alexander *et al.*, 2014; Apopei *et al.*, 2014).

Gangue minerals present within Certej ore deposit are quartz, calcite and barite (in order of their abundance). The main metallic minerals within the Certej ore deposit are sphalerite, pyrite and galena. Locally were identified arsenopyrite, stibine and chalcopyrite. In the samples from the superficial levels, chalcopyrite is present as "chalcopyrite disease". In the samples from the lower levels, the chalcopyrite is more abundant, and appears as spherical particles included in sphalerite.

Minor amounts of tetrahedrite-tennantite, bournonite-seligmannite, geocronitejordanite and Au-Ag tellurides were identified at the microscope.

The dominant form of presentation of the mineralization is mainly of impregnation type, predominantly with pyrite, which occurs generally in Cretaceous sediments. In the Neogene sediments and polymictic breccias, the impregnative mineralization type is rich in galena and sphalerite. On this impregnative aspect, appear centimetric or decimetric veins and geodes rich in sphalerite and galena (Udubaşa *et al.*, 1980; Forward *et al.*, 2009; Alexander *et al.*, 2014).

#### CHAPTER 4. MINERALOGY AND GEOCHEMISTRY OF MINERALIZATION FROM CORANDA-HONDOL

#### 4.1 Gangue minerals

Gangue minerals present within Certej ore deposit are quartz, calcite and barite (in order of their abundance).

Quartz is the most common gangue mineral, which is found as euhedral crystals arranged in geodes or cracks and is frequently associated with the phenomenon of silicification. In general, it is milky white and subordinate semi-transparent, varying greatly in size (reaching up to 3-4 cm).

Calcite occurs, as in the case of quartz, along cracks and voids, being preferred by the entire suite of sedimentary rocks (Cretaceous and Miocene). It occurs as anhedral crystals, frequently encountered as vein in sandy clays, and locally it occurs as centimetric crystals.

Barite occurs as tabular crystals with dimensions that can reach up to 10 cm in length, which precipitate in the late stages of hydrothermal activity.

The chalcographic study conducted on all mineralized samples and based on the field observations, it was noted the presence of quartz on the entire paragenetic sequence. Regarding calcite and barite, they precipitated in the last stages of hydrothermal activity.

#### 4.2 Common sulfides

#### 4.2.1 Sphalerite and chalcopyrite

Sphalerite is the dominant mineral of the primary paragenesis. Macroscopic observations reflect a chromatic heterogenity of the sphalerite crystals (from a reddish brown to a light yellow tint color). Microscopically, the sphalerite from Coranda-Hondol shows chalcopyrite inclusions of two types: (i) in the form of *"chalcopyrite disease"*; and (ii) anhedral or subhedral crystals included in sphalerite, having dimensions of tens of  $\mu$ m. After Udubaşa *et al.* (1980) the Fe content in sphalerite is about 2-3 %. The same authors suggest that the manganese in sphalerite from Coranda-Hondol increases with depth.

The XRF analyses on sphalerite sample (sample from the superficial levels), revealed relatively low Fe content (0.53%), Cd (963 mg·kg<sup>-1</sup>) and Mn (528 mg·kg<sup>-1</sup>) compared with the results obtained by Udubaşa *et al.* (1980) on the sphalerites from the depth levels of Coranda-Hondol, or sphalerites from Săcărîmb and Măgura (Cook *et al.*, 2009). The very low contents of As (18.80 mg·kg<sup>-1</sup>) and Sb (2.74 mg·kg<sup>-1</sup>) on the sphalerite from the superficial levels suggest the presence of very small contents of sulfosalts inclusions (*e.g.*, tetrahedrite-tennantite).

#### 4.2.2 Pyrite

Following the field and chalcographic observations was pointed out that pyrite is commonly disseminated in Cretaceous sediments (especially in sandy clays), often associated with quartz. At the contact with volcanic bodies, the Cretaceous sediments have undergone pyritisation and silicification processes. In the polished sections, the pyrite commonly occurs as euhedral crystals included in sphalerite, galena and gangue minerals, since the beginning of the hydrothermal activity.

#### 4.2.3 Galena

Within the Certej ore deposit, galena is generally developed along cracks. From the chemical point of view, the electron microprobe analyses shows a stoichiometric compositions (PbS). XRF analyses on galena reveal high contents of Zn (1248.82 mg·kg<sup>-1</sup>) and As (6543.50 mg·kg<sup>-1</sup>). High content of Zn can be attributed to inclusions of sphalerite, whereas high contents of As can be due to the sulfosalts inclusions (*e.g.*, jordanite).

Udubaşa *et al.* (1980) revealed very low content of As (300 mg·kg<sup>-1</sup>) and high content of Sb (1600 mg·kg<sup>-1</sup>), whereas for the sample used in this study it was observed a high content of As (6543.5 mg·kg<sup>-1</sup>) and low content of Sb (22.73 mg·kg<sup>-1</sup>). Most likely, this variability can be due to the presence / absence of Sb-As sulfosalts.

#### 4.3 Sulfosalts

#### 4.3.1 Tetrahedrite-tennantite series

Minerals from tetrahedrite-tennantite series (TTS) are the most common and widespread of all sulfosalt minerals (Skinner *et al.*, 1972). Among sulfosalts, TTS is the most complex due to iso- and heterovalent substitutions (Moëlo *et al.*, 2008).

Based on optical observations, TTS minerals from CHOP perimeter usually appear either enclosed within sphalerite grains or at the contact between sphalerite and galena, sulfosalts or gangue minerals (mainly quartz). Anhedral crystals of TTS minerals occur predominantly as patches, generally smaller than 500  $\mu$ m, but can reach up to 1 mm across.

Following the last systematic classification of sulfosalts approved by IMA (Moëlo *et al.*, 2008) the general simplified formula of TTS minerals can be described as follow:  $A_6^{TRG}(B, C)_6^{TET}X_4^{TRGP}Y_{12}^{TET}Z^{OCT}$  (where A = Cu or Ag in triangular coordination (*TRG*), B = Cu or Ag in tetrahedral coordination (*TET*), C = Fe, Zn, Hg, Cd, Mn, Pb in the same tetrahedral coordination (*TET*) (generally occupied by a divalent metal), X = Sb, As, Bi or Te in trigonal pyramidal coordination (*TRGP*), Y = S or Se in tetrahedral coordination (*TCT*).

## 4.3.1.1 Compositional variations and substitutions in the tetrahedrite-tennantite series from Coranda-Hondol open pit perimeter

Microprobe analyses were performed on 7 mineralised samples. Major compositional variations occur in four structural positions (A, B, C and X). Thereofore, TTS minerals identified within Coranda-Hondol perimeter presents a wide range of variability in terms of antimony, arsenic, copper and silver contents, and to a lesser extent for zinc and iron.

The chemical composition for TTS minerals used in this study will be expressed as  $Td_x$  (tetrahedrite<sub>x</sub>) where  $x = Sb/(As+Sb) \times 100$ . So far, within Coranda-Hondol it was highlighted an intermediate member containing relatively low content of As (Td<sub>65</sub>) (Udubaşa *et al.*, 1980). In the present study, the electron microprobe analyses reveal the presence of a complete solid solution between end members (tetrahedrite-tennantite, Td<sub>97</sub>-Td<sub>0</sub>) (figure 4-1a). This situation being unique in the epithermal ore deposits from Romania.

Approximately 65% of all 106 analyses performed on TTS grains contain less than 10 Cu *a.p.f.u.* (the minimum content in the analysed samples being 8.38 Cu *a.p.f.u.*). In figure 4-1b, the contents (in *a.p.f.u.*) of Cu correlates almost linearly (r = 0.9772) with those of Ag. Therefore, the depletion of Cu is directly responsible for the enrichment of the samples in Ag (up to 1.68 Ag *a.p.f.u.*).

Taking into account the other substitutions that may occur in the structural position *C* generally occupied by divalent cations (Fe, Zn, Hg, Cd, etc.), the composition of TTS minerals from Coranda-Hondol ore deposit correspond to zincian varieties with low Fe content (*e.g.* sample CH550):

$$(Cu_{9.78}Ag_{0.22})_{10}(Zn_{1.48}Fe_{0.38}Cu_{0.06}Cd_{0.01}Pb_{0.01})_{1.94}(Sb_{2.57}As_{1.49})_{4.06}S_{13})$$



Figure 4-1 Binary diagrams showing the composition (expressed as *a.p.f.u.*) of TTS minerals from Certej ore deposit: a) As *vs.* Sb; b) Cu *vs.* Ag

This substitution between Sb and As is directly responsible for the partial substitution of  $Cu^+$  and Ag, influencing in a lesser extend the incorporation of  $Cu^{2+}$  in structural position *C* and hence the Zn:Fe ratio. These coupled substitutions can be synthesized, in order of importance, as follows:

$$(Sb \leftrightarrow As)^{TRGP} > (Ag^+ \leftrightarrow Cu^+)^{TRG} > (Zn \leftrightarrow Fe)^{TET} > (Cu^{2+} \leftrightarrow Fe^{2+})^{TET}$$

#### *4.3.1.2 Tetrahedrite-tennantite zonnation from Coranda-Hondol open pit perimeter*

The TTS minerals identified at Coranda-Hondol shows a *"saw tooth-*type" form that can be observed only in the BSE images. However, in the same sample are TTS crystals that do not show such a zonal pattern (*n.e.*, figure 4-2).



Figure 4-2 Back-scattered electron (BSE) image of a tennantite crystal with an oscillatory zonation. Five main precipitation stages can be distinguished, from which stages I-III can be considered as alternative precipitations and stages IV-V successive precipitations. The inset corresponds to the reflected light microphotograph (plane polarized light) corresponding to the electron microprobe studied area. Abbreviations: Tn = tennantite, Sph = sphalerite, Py = pyrite, Ccp = chalcopyrite

The zonality of TTS minerals suggests compositional variations due to successive or alternative precipitation of the hydrothermal solutions with different composition.

The results obtained by the electron microprobe analysis results obtained from 27 analytical points along a compositional profile (figure 4-2) reveals the presence of a tennantite crystal (Td<sub>23</sub>) with cristalo-chemical formulae calculated on the basis of the total number of *a.p.f.u.* (29) and presented as the average of all 28 analytical points, as follows:

$$(Cu_{9.94}Ag_{0.06})_{10}(Zn_{1.63}Fe_{0.41}Cu_{0.14}Pb_{0.01})_{2.19}(Sb_{0.94}As_{3.16})_{4.06}S_{12.71}$$

Variations in terms of intensity and width of this zoning is observed along the entire profile (core  $\rightarrow$  rim) of the tennantite grain (figure 4-2). In terms of Sb/(As+Sb)

ratio, the composition of this zonality varies between  $Td_{51}$  (the intermediate member of the tetrahedrite-tennantite series) and  $Td_0$  (the As end member).

### 4.3.1.3 The spatial trends of tetrahedrite-tennantite compositions from Coranda-Hondol open pit perimeter and metallogenic aspects

Taking into account the variability of the TTS minerals composition from CHOP perimeter and considering the possibility of a spatial distribution that may occur, three content ratios was considered (in order of importance), as follows: Sb/(As+Sb), Ag/(Ag+Cu) and Zn/(Zn+Fe). Highest variability in terms of chemical compositions is observed vertically, so that at the deepest level it was highlighted the As end-member (Td<sub>0</sub>) with high contents of Cu and Fe, and towards the upper levels it was highlighted the tetrahedrite almost pure (Sb member, Td<sub>97</sub>) with high contents in Ag and Zn.

Considering that the distribution of analysed samples, were observed a slightly lateral chemical variability. Therefore, the TTS minerals with low contents in Sb and Ag (*e.g.*, sample CH550 with Td<sub>63</sub> and Ag/(Ag+Cu)<sub>0.02</sub> respectively) were identified in the western part of the CHOP perimeter, while the high contents have been identified in the eastern part (*e.g.*, sample CH16 with Td<sub>81</sub> and Ag/(Ag+Cu)<sub>0.13</sub> respectively). This may suggest that in the western part, the source of hydrothermal solutions is closer to the surface than in the east. This WNW-ESE variability (observed in the TTS minerals composition) overlaps to the main structural corridor (*i.e.* Brad-Săcărîmb) which controls the mineralization in the Certej district.

Taking into account the above discussions and the correlations observed, it might be assumed the poliascendent character of the mineralization from Certej ore deposit, which reflects multiple hydrothermal events. Following these observations, it can be considered that the distribution of silver from the Coranda-Hondol open pit perimeter is controlled by the Sb content in TTS minerals, having a high affinity with the tetrahedrites. Although the silver is not present in a very high amounts in the TTS minerals from CHOP perimeter, they constitute an important source of silver in addition to the Au-Ag tellurides (*e.g.*, hessit, petzit and stützit, Apopei *et al.* (2014)).

#### 4.3.2 Bournonite-seligmannite and geocronite-jordanite series

In the Apuseni Mts., the occurrences of Bnn-Slg<sub>ss</sub> has been observed at Săcărîmb ore deposit (situated 3 kilometres southeast of the Certej ore deposit), ranging

between Bnn<sub>22</sub> to Bnn<sub>87</sub> (Ciobanu *et al.*, 2005). Other occurrences of Sb-rich members were reported in many deposits from Baia Mare district (Romania): Văratec, Breiner, Baia Sprie and Herja ore deposit (Damian and Costin, 1999; Damian and Damian, 2003).

In the case of geocronite-jordanite solid solution series (Gcn-Jor<sub>ss</sub>, Pb<sub>14</sub>(Sb, As)<sub>6</sub>S<sub>23</sub> - Pb<sub>14</sub>(As, Sb)<sub>6</sub>S<sub>23</sub>), few occurences has been reported previously on Romanian territory. Within Săcărîmb ore deposit have been reported members of the Gcn-Jor<sub>ss</sub> ranging between Gcn<sub>0</sub> to Gcn<sub>60</sub> (Ciobanu *et al.*, 2005). Intermediate members of Gcn-Jor<sub>ss</sub> have been reported at Baia de Arieş ore depost (Cook and Ciobanu, 2003). No other occurrences of Gcn-Jor<sub>ss</sub> have been reported yet on Romanian territory.

# 4.3.2.1 Compositional variations in the bournonite-seligmannite solid solution series (Bnn-Slg<sub>ss</sub>)

The minerals from Bnn-Slg<sub>ss</sub> were observed in all polished samples from the upper levels of the studied perimeter. The Sb-rich member (bournonite) from Coranda-Hondol perimeter was previously described based just on optical observations (Udubaşa *et al.*, 1980). Members of this series are the most abundant sulfosalts at the Certej ore deposit and usually appear at the contacts between pockets or veins of galena. The bournonite-seligmannite minerals also occur within the pyrite aggregates (disposed at the pyrite crystals boundaries) and less developed at the contact between sphalerite, quartz and tetrahedrite-tennantite. In plane-polarized incident light, the Bnn-Slg minerals have a clear greyish colour with a distinct bluish green tint especially at the contact or within galena. Bnn-Slg, which displays its characteristic *"parquet*-type" twinning, replaces galena, pyrite and tetrahedrite, forming crystal aggregates that occasionally can reach up to 1-2 centimeters in length.

The electron microprobe analyses obtained in this study reveal the presence of an almost complete series from the arsenic rich-member ( $Bnn_{25}$ , seligmannite) to antimonian end-member ( $Bnn_{96}$ ) (figure 4-3). The heterogeneity of  $Bnn-Slg_{ss}$  within a single grain, usually leads to a zonation with a random spatial arrangement and occasionally as concentric (figure 4-4a) or arched bands (figure 4-4b).

To the best of our knowledge, the concentric and arched bands-type zonalities of  $Bnn_{ss}$  has not been reported yet in the literature. In the case of concentric zonality, the

chemical variability ranges between  $Bnn_{37}$  to  $Bnn_{89}$ , and for the arched zonality, the chemical variability ranges between  $Bnn_{60}$  to  $Bnn_{93}$ .



Figure 4-3 Compositional variation of bournonite-seligmannite and geocronite-jordanite solidsolution series from the Certej ore deposit (horizontal axis), in terms of Sb/(As+Sb) ratio. The Yaxis of the chart displays the elevation for every sample (from the shallow to upper levels). Square symbols represent the mean values for every sample



Figure 4-4 BSE image of bournonite-seligmannite series from Certej ore deposit, showing the presence of (a) concentric zonality and (b) arched bands-type zonality

These oscillations of both types argue the dynamic character, especially for the second hydrothermal event. They may be attributed to multiple hydrothermal pulses, which are expressed as alternative precipitation due to Sb-As variability.

# 4.3.2.2 Compositional variations in the geocronite-jordanite solid solution series (Gcn-Jor<sub>ss</sub>)

So far, the occurrences of geocronite-jordanite have not been reported yet at Certej ore deposit. Minerals from Gcn-Jor<sub>ss</sub> usually appear as small patches (0.1-0.2 mm) within or at the contact with bournonite-seligmannite and galena crystalline aggregates. The Gcn-Jor<sub>ss</sub> patches rarely exceed 0.6 mm, and occur to a lesser extent than Bnn-Slg minerals. In plane-polarized incident light and up to  $20 \times$  magnification power, the Gcn-Jor minerals have the same color tint as Bnn-Slg minerals.

The microprobe analyses cover a wide range of the solid solution, ranging between  $Gcn_9$  to  $Gcn_{67}$  (figure 4-3).

In contrast to  $Bnn-Slg_{ss}$ , we could not detect specific zonation of the Gcn-Jor<sub>ss</sub> in the BSE images, which show a high heterogenity.

4.3.2.3 The spatial trends of bournonite-seligmannite and geocronite-jordanite compositions from Coranda-Hondol open pit perimeter and metallogenic aspects

The Sb/(As+Sb) ratios of Bnn-Slg and Gcn-Jor minerals from the Certej ore deposit suggest that the high content of Sb from hydrothermal fluids favor the precipitation of bournonite, while the high content of As favors the precipitation of jordanite (figure 4-3). Considering the compositional variability of both series from sample to sample, a spatial trend is observed (in terms of Sb/(As+Sb)) and represented in figure 4-3.

Taking into account the average values of Sb/(As+Sb) ratios of every sample which are displayed in figure 4-3 from the shallow to upper levels (y-axis, vertically), the following observations can be drawn: (i) the Sb content from Bnn-Slg<sub>ss</sub> tend to increase towards the upper levels from an intermediate member (Bnn<sub>59</sub>) to a Sb-rich member (Bnn<sub>76</sub>); and (ii) the same trend can be observed in the case of Gcn-Jor<sub>ss</sub>, with

the observation that it is ranging from an As-rich member  $(Gcn_{26})$  to an intermediate member  $(Gcn_{46})$ .

### 4.3.3 The effect of As-Sb substitution in the Raman spectra of Td-Tn, Bnn-Slg and Gcn-Jor series

Considering the high chemical variability within sulfosalts identified at Coranda-Hondol (Td-Tn, Bnn-Slg and Gen-Jor), µ-Raman analyses was performed in parallel with the microprobe analyses.

The existence of a complete solid solution between the final members has allowed the acquisition of Raman spectra across the entire domain of the solid solution. The substitution between As $\leftrightarrow$ Sb (within Td-Tn solid solution series) is reflected in the  $\mu$ -Raman spectra by shifting of the spectral bands from 383 cm<sup>-1</sup> (assigned to symmetric stretching vibration  $v_{1tn}$ , Td<sub>1</sub>) to 361 cm<sup>-1</sup> (assigned to symmetric stretching vibration  $v_{1td}$ , Td<sub>97</sub>), and from 140 cm<sup>-1</sup> (Td<sub>1</sub>) to 112 cm<sup>-1</sup> (Td<sub>97</sub>) (figure 4-5).

As in the case of tetrahedrite-tennantite series, the  $\mu$ -Raman spectra obtained on bournonite-seligmannite and geocronite-jordanite solid solution series can be used to accurately identify the member of the solid solution based only on the Raman spectra.

Taking into account the previous discussions, can be assumed that based on the Raman spectrum acquired on a sulfosalt member of tetrahedrite-tennantite, bournonite-seligmannitte and geocronite-jordanite series it may be deduced the exact member of the series (according to the Sb/(Sb+As) ratio).

#### 4.4 Tellurides

The "Golden Quadrilateral" (Metaliferi Mts., Romania) is well-known for the telluride-bearing epithermal ore deposits (Cook et al., 2004).

This sub-chapter presents new occurrences and compositional data of Au-Ag tellurides from Coranda-Hondol ore deposit. The hessite (Ag<sub>2</sub>Te), petzite (Ag<sub>3</sub>AuTe<sub>2</sub>) and stützite (Ag<sub>5-x</sub>Te<sub>3</sub>, where x = 0.24-0.36) were identified by means of EPMA (Electron Probe Microanalyzer) and  $\mu$ -Raman spectrometry technique (Apopei *et al.*, 2014).



Figure 4-5 µ-Raman spectra of the solid solution Td1-Td97

Electron microprobe analyses reveal the presence of hessite and petzite. Based on the results of the chemical composition, the content of Ag and Te in hessite is from 57.35 wt.% to 60.61 wt.% and from 35.77 wt.% to 38.35 wt.%, respectively (Apopei *et al.*, 2014).

For petzite, the content of Ag, Te and Au is 41.90 wt.% to 42.07 wt.%, 29.88 wt.% to 32.31 wt.% and 22.74 wt.% to 23.91 wt.%, respectively (Apopei *et al.*, 2014). The microanalytical data give the empirical mean composition Ag<sub>3.06</sub>Au<sub>0.93</sub>(Te<sub>1.92</sub>Se<sub>0.05</sub>S<sub>0.01</sub>) $\Sigma$ =1.98 for petzite, and Ag<sub>1.96</sub>Te<sub>1.02</sub> for hessite (Apopei *et al.*, 2014). The presence of stützite was identified by  $\mu$ -Raman spectrometry (Apopei *et al.*, 2014). 2014).

### 4.5 Mineralogy and geochemistry of sediments and detritus material from Coranda-Hondol perimeter

Taking into account that the studied area (Coranda-Hondol open pit) shows high contents of common sulphide minerals, in this chapter was aimed to study the mineralogy of the sediments / detritic material (material originated from mechanical disaggregation of preexisting rocks). In addition, 11 chemical elements (Cr, Mn, Fe<sub>2</sub>O<sub>3</sub>, Co, Ni, Cu, Zn, Cd, Pb, As, S) were determined in order to establish their abundance and distribution.

For the identification of the mineralogical components, the samples were analyzed by X-ray diffractometry (XRD) and studied at the binocular microscope. XRD analyzes performed on all samples showes the presence of quartz, feldpsars and carbonates as principal minerals, while clay minerals (sericite, illite, kaolinite) as accessory minerals. The gypsum is found in most of the samples.

The samples were washed in order to remove the clay minerals (process repeated for three times for each sample separately), afterthat the samples were dried and studied at binocular microscope in order to identify the other minerals. Thus, in addition to the minerals identified by XRD were highlighted the following minerals (in order of their abundance): oxy/oxyhydroxides, pyrite, galena, and sulfates precipitated after washing the sediments / detritus material. After drying, in all samples were precipitated (quantitatively significant) secondary sulfates (prevailing gypsum and minerals from copiapite group).

pH measurements on sediments and detritic material shows their high acidity, with values between 2.25 and 4.78. This acidity can be explained by the presence of sulphides (especially pyrite) in the composition of sediments and detritic material.

Geochemical study of sediments and detritic material from Coranda-Hondol perimeter revealed the following chemical contents (in order of average per element for all samples): S (80.27 %) > Fe<sub>tot</sub> (6.44 %) > Zn (6.25 %) > Pb (2.63 %) > As (1.81 %) > Mn (1.60 %) > Cr (0.44 %) > Cu (0.34 %) > Co (0.13 %) > Ni (0.06 %) > Cd (0.01 %).

The high contents of S, Fe<sub>tot</sub>, Zn, Pb and As are due to the presence of sulphides in sediments and detritic material, thus: pyrite, sphalerite, galena and subordinate amounts of chalcopyrite and other sulfosalts (*e.g.*, tetrahedrite-tennantite).

19

#### CHAPTER 5. SUPERGENE ALTERATION

#### 5.1 Secondary sulfates and their fotochemical degradation

Secondary minerals of supergene origin can be found in various environments, especially in areas of oxidation of metalliferous ore deposits containing sulfides. In some cases high and varied concentrations of sulfosalts. These supergene alteration minerals are mainly formed through oxidation of common sulfides (especially pyrite) and then through precipitation during the acid mine drainage (AMD).

However, there are some misunderstandings in the reported Raman spectra, as in some studies, the laser power is not provided in the experimental section (nominal or on the surface of the sample). Especially for *in-situ* and non-contact Raman measurements, these reference spectra are essential for the correct use of the information obtained by Raman spectroscopy in mineral identification.

Pyrite is the main sulfide mineral from the Coranda Hondol open pit which turns into secondary minerals through oxidation and hydration. It is followed by sphalerite with a low content of Fe (1-3% Fe, after (Udubaşa *et al.*, 1980)), and followed closely by chalcopyrite. The chalcopyrite, as pyrite, can easily oxidize and participate in a high amount to the formation of the acid mine drainage (AMD). However, at the superficial levels of the Coranda-Hondol, the chalcopyrite is found in a very low concentration.

Galena, although widespread, did not lead to the formation of secondary lead minerals (*e.g.*, anglesite). This can be explained by the fact that lead sulfates (especially anglesite) have very high solubility in acidic waters, and their precipitation is not possible under these circumstances (Dove and Czank, 1995).

Based on main sulfides which generate oxidation reactions, neutralization, hydration and/or dehydration and lead to the formation of supergene alteration, secondary minerals can be divided into the following categories (in order of abundance):

- Fe(III)-sulfates rhomboclse, copiapite, ferricopiapite, coquimbite and hidroniumjarosite; they are the most abundant secondary minerals, mainly minerals from the copiapite-group. They occur on the walls of benches;
- Fe(II)-sulfates melanterite and rozenite, found in high amount at the bottom of the open pit;

- Zn-sulfates gunningite generally occurs on the walls of benches, as a white powder, but only where sphalerite mineralizations are also present;
- o Cu-sulfates antlerite and brochantite;
- Ca-sulfate exclusively gypsum;
- o Mg-sulfates epsomite and hexahydrite;
- o MnAl-sulfates apjohnite.

For the identification of these secondary sulfates were performed XRD, Raman, infrared and SEM analyses (figure 5-1).



Figure 5-1 Representative SEM micrographs of weathering products found at Coranda-Hondol open pit. Abbreviations: Cop – copiapite; Cq – coquimbite; Gy – gypsum; Apj – apjohnite; Fe-cop – ferricopiapite; Roz – rozenite; Eps – epsomite

Following the identification of these secondary sulfates using Raman spectrometry technique were highlighted that some common secondary sulfates undergo changes in the laser beam if too high laser power is used (generally between 7 - 15 mW on the sample surface). Some of them turn into other minerals. This photochemical breakdown is generally linked to dehydration and oxidation of iron(II) to iron(III). Other minerals are unstable and suffer lattice destruction without turning into other minerals.

Hydroniumjarosite is the only one that turns into hematite at maximum laser power. In the case of  $Fe^{2+}$  sulfates, laser power is insufficient to cause  $Fe^{2+}$  oxydation and hematite formation.

#### 5.2 Acidic waters

Water samples collected from the entire perimeter of the Coranda-Hondol open pit (both from temporary ponds and streams) were analyzed in terms of basic chemical parameters (pH, Eh, TDS, etc.). In all water samples, the pH shows values rangging between 2.17 and 2.6, thus all samples have an acidic pH due to the acid mine drainage (AMD). Total dissolved salts (TDS) ranges from 1.21 g/L and 6.94 g/L, the values obtained for each sample is directly proportional to the amount (in grams) of the precipitated product after heating the water samples (in the oven at 60 °C).

Following the identification of the supergene alteration products (by Raman and XRD), it can be stated that: (i) in all water samples was identified the sulfate anion and hydrogen sulphate; (ii) for the precipitated minerals from each water sample were identified the following minerals (in order of abundance): copiapite > gypsum > apjohnite > epsomite > anhydrite.

#### CHAPTER 6. CONCLUSIONS

The electron microprobe analyses revealed the existence of a complete series between the final terms As-rich (tennantite) and Sb-rich (tetrahedrite)  $(Td_{97}-Td_0)$ . Also, on the basis of binary diagrams, it was observed linear correlations between Sb-As, Cu-Ag, and in a lesser extent between Zn-Fe. On the basis of the correlations obtained between Sb-As, Cu-Ag and Zn-Fe and between the ratios Sb/(As+Sb), Ag/(Ag+Cu) and Zn/(Zn+Fe), it was assumed the poliascendent character of the mineralization from Certej ore deposit during two hydrothermal events. The lithology has played an important role in the direction and evolution of the hydrothermal fluids, where faults and fractures (oriented to WNW-ESE direction) acted as pathways for the ascending mineralizing. The dynamic character which is given especially in the second stage of hydrothermal activity, led to the development of a vertical and lateral zonality of the contents of Sb/As, Ag/Cu and Zn/Fe in TTS minerals from Coranda-Hondol open pit perimeter. The geocronite-jordanite solid solution series have been identified within Certej ore deposit for the first time. The EMPA analyses revealed the existence of two extensive solid solution series, as follows: (i) between Bnn<sub>25</sub> to Bnn<sub>96</sub> in the case of bournonite-seligmannite solid solution series; and (ii) between Gcn<sub>9</sub> to Gcn<sub>67</sub> in the case of geocronite-jordanite solid solution series. The Sb-As variation between both series (Bnn-Slg and Gcn-Jor) reveals that high Sb from hydrothermal fluids favors bournonite, while the high As favors jordanite. Considering the chemical variations in terms of Sb/(As+Sb) ratio for the both series, a spatial trend can be observed. Vertically, the Sb content from both series tends to increase towards the upper levels. The heterogenity of both series, especially for bournonite-seligmannite series, suggests a high activity of As and Sb during the final stages of paragenetic sequence. For the bournonite-seligmannite series, the chemical variations within a single grain lead ocasionally to a concentric and arched-type zonalities, which were not described until now in literature. The zonalities suggest multiple hydrothermal pulses that are expressed as alternative precipitation due to Sb-As variability.

The presence of trace amounts of Se, Te and Bi in bournonite-seligmannite and geocronite-jordanite series observed for the sample from the shallow level may be related to the chemistry of magmatic intrusion (Băiaga andesitic subvolcano).

The chemical variations among the identified sulfosalts series (tetrahedritetennantite, bournonite-seligmannite and geocronite-jordanite) can be used to determine the main flow paths of the hydrothermal fluids, which are important in the exploration stage.

Optical and textural observations are accompanied by EPMA and  $\mu$ -Raman analysis for identification purpose. Ag- and/or Au-Ag-tellurides (hessite, petzite and stützite) are identified for the first time at the Coranda-Hondol open pit. Thus, the hessite (Ag<sub>2</sub>Te), petzite (Ag<sub>3</sub>AuTe<sub>2</sub>) and stützite (Ag<sub>5-x</sub>Te<sub>3</sub>, where x = 0.24-0.36) were identified for the first time within Certej ore deposit. The  $\mu$ -Raman spectrum of stützite shows a distinct fingerprint against hessite, petzite or other Ag- and/or Au-Ag-telluride. The broadness of the main Raman peak of stützite (147 cm<sup>-1</sup>) may be related to the non-homogeneous distribution. The idea is supported by the observations made at electronic microscope (BSE images), where is observed irregular intergrows of petzite and stützite in hessite. These tellurides usually occur as patches in galena, in bournonite-seligmannite

and at the contact between galena and bournonite-seligmannite  $\pm$  geocronite-jordanite series.

The microscopic observations and the presence of the intergrowths of hessite, petzite and stützite may be related to the breakdown of a mixture between  $\chi$ -phase and  $\gamma$ -phase of ternary Au-Ag-Te solution, bellow 120±15 °C. The observations of the hessite-petzite-stützite assemblage at the Coranda-Hondol open pit suggest that they have formed contemporaneously and that they can possibly be attributed to a later silver-rich telluride-bearing substage. Further investigations are however necessary to interpret the presence of other assemblages (?calaverite-?krennerite-?sylvanite, ?krennerite-petzite, ?sylvanite-hessite and/or ?sylvanite-petzite) which probably belong to a gold-rich telluride-bearing substage preceded by the later silver-rich telluride-bearing substage.

Regarding the supergene alteration study throughout the Coranda-Hondol open pit perimeter, were identified 14 secondary sulfates, which have not been described so far at Coranda-Hondol:

- Fe(III)-sulfates: rhomboclase, coquimbite, copiapite, ferricopiapite and hydroniumjarosite;
- ▶ Fe(II)-sulfates: melanterite and rozenite;
- Mg-, Al- and Ca-sulfates: epsomite, hexahydrite, gypsum and apjohnite;
- > Cu- and Zn-sulfates: antlerite, brochantite and gunningite.

Among common sulfides, pyrite is the main sulfide mineral from the Coranda-Hondol open pit that participates at the formation of secondary minerals through oxidation and hydration reactions. It is followed by sphalerite and subordinate amounts of chalcopyrite.

Based on the analyses performed on acidic water samples (temporary ponds and streams), identification of the minerals precipitated after heating the water samples at 60 °C and chemical analyses of sediments / detritic material, can be done a prediction of acid mine drainage.

Taking into account that all secondary sulfates identified for the first time at Coranda-Hondol were analyzed primarily by Raman spectrometry, mineralogical phase changes and thus spectral changes (Raman spectra) were observed at high laser powers. This photochemical breakdown is generally linked to dehydration and oxidation of iron(II) to iron(III). Following the photochemical degradation study, were established the laser intensity thresholds and optimum experimental conditions for the non-destructive identification of the sulfates by Raman spectrometry.

In general, at laser powers between 7 - 15 mW (on the sample surface) lead to a mineralogical phase transformation or the crystal structure break down without forming new minerals. This work will significantly improve the understanding of how the Raman spectra of sulfates are affected by differences in instrument parameters (in principal laser power on the surface of the sample). Also, the results of this paper contribute to improve decision making regarding the laser power used for analysis, which is important for suitable conservation interventions and also for a proper identification of mineralogical phases.

Following the  $\mu$ -Raman analyses on three solid solution series of sulfosalt minerals (tetrahedrite-tennantite, bournonite-seligmannite and geocronite-jordanite), major changes was observed in the spectral lines (in terms of wavelengths and intensity of the spectral bands). Thus, based on the Raman spectra obtained on any member of these series (Td-Tn, Bnn-Slg and Gcn-Jor) can accurately identify the member inferred by the effect of Sb/(Sb+As) ratio on Raman spectrum.

#### **Selective References**

- Ageneau, M., Mastrodicasa, L., Marton, I. (2006) Magmatism and metallogeny of the Certej-Săcărâmb District, Apuseni Mts. Romania Field Trip SEG Student Chapters Uni Geneva - ETH Zürich - Uni Budapest - Uni Cluj.
- Alderton, D. H. M., Thirlwall, M. F., Baker, J. A. (1998) Hydrothermal alteration associated with gold mineralization in the southern Apuseni mountains, Romania: preliminary Sr isotopic data. *Mineralium Deposita*, 33(5), 520-523.
- Alexander, R., Juras, S., Miller, R., Kalanchey, R. (2014) Technical Report for the Certej Project, Romania.
- Apopei, A. I., Damian, G., Buzgar, N. (2012) A preliminary Raman and FT-IR spectroscopic study of secondary hydrated sulfate minerals from the Hondol open pit (Metaliferi Mts., ROMANIA). *Romanian Journal of Mineral Deposits*, 85(2), 1-6.
- Apopei, A. I., Damian, G., Buzgar, N., Milovska, S., Buzatu, A. (2014) New occurrences of hessite, petzite and stützite at Coranda-Hondol open pit (Certej gold-silver deposit, ROMANIA). *Carpathian Journal of Earth and Environmental*, 9(2), 71-78.
- Balintoni, I. (1997) Geotectonica terenurilor metamorfice din România. *Editura Carpatica, Cluj-Napoca.*
- Ciobanu, C. L., Cook, N. J., Capraru, N., Damian, G., Cristea, P. (2005) Mineral assemblages from the vein salband at Sacarimb, Golden Quadrilateral, Romania: I. Sulphides and sulphosalts. *Geokhimiia, Mineralogiia i Petrologiia*, 43, 47-55.
- Cook, N. J., Ciobanu, C. L. (2003) Cervelleite, Ag<sub>4</sub>TeS, from three localities in Romania, substitution of Cu, and the occurrence of the associated phase, Ag<sub>2</sub>Cu<sub>2</sub>TeS. *Neues Jahrbuch für Mineralogie Monatshefte*, 2003(7), 321-336.
- Cook, N. J., Ciobanu, C. L., Damian, G., Damian, F. (2004) Tellurides and sulphosalts from deposits in the Golden Quadrilateral. In N. J. Cook, Ciobanu, C.L., Ed. Au-Ag-telluride Deposits of the Golden Quadrilateral, Apuseni Mts., Romania., Guidebook of the International Field Workshop of IGCP Project 486, IAGOD Guidebook Series, p. 111-144, Alba Iulia, Romania.
- Cook, N. J., Ciobanu, C. L., Pring, A., Skinner, W., Shimizu, M., Danyushevsky, L., Saini-Eidukat, B., Melcher, F. (2009) Trace and minor elements in sphalerite: A LA-ICPMS study. *Geochimica Et Cosmochimica Acta*, 73(16), 4761-4791.
- Damian, F., Damian, G. (2003) The Bournonite from Baia Sprie Ore Deposit. Series D Mining Mineral Processing Non-ferrous Metallurgy Geology, XVII, 193-202.
- Damian, G., Costin, D. (1999) Tetrahedrite bournonite in Breiner Băiuț mineralization (Gutâi Mts., Eastern Carpathians). Studia Universitatis Babeş-Bolyai, Geologia, 137-149.
- **Dove, P. M., Czank, C. A.** (1995) Crystal chemical controls on the dissolution kinetics of the isostructural sulfates: Celestite, anglesite, and barite. *Geochimica Et Cosmochimica Acta*, 59(10), 1907-1915.
- Forward, P., Liddell, N., Jackson, T. (2009) Certej Updated Definitive Feasibility Study Summary Technical Report. European Goldfields Limited.

- Gál, Á., Molnár, F., Szakács, A., Kristály, F., Weiszburg, T. G., Pécskay, Z. (2010) The Certej hydrothermal ore deposit (Apuseni Mts., Romania) : fluid inclusions, types and age of the related hydrothermal alteration. *Scientific Annals of the Department of Geology*, 39(1).
- Ianovici, V., Borcoş, M., Bleahu, M., Patrulius, D., Lupu, M., Dimitrescu, R., Savu, H. (1976) The Geology of Apuseni Mountains (Geologia Munților Apuseni). (In Romanian). Editura Academiei Republicii Socialiste România, Bucharest. 605 pp.
- Ivășcanu, P., Baker, T., Juras, S., Lewis, P., Bena, G., Igna, L. (2013) The Certej Epithermal Gold Deposit, Golden Quadrilateral, Romania.
- Moëlo, Y., Makovicky, E., Mozgova, N. N., Jambor, J. L., Cook, N., Pring, A., Paar, W., Nickel, E. H., Graeser, S., Karup-Møller, S., Balic-Žunic, T., Mumme, W. G., Vurro, F., Topa, D., Bindi, L., Bente, K., Shimizu, M. (2008) Sulfosalt systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy. *European Journal of Mineralogy*, 20(1), 7-62.
- Neubauer, F., Lips, A., Kouzmanov, K., Lexa, J., Ivăşcanu, P. (2005) 1: Subduction, slab detachment and mineralization: The Neogene in the Apuseni Mountains and Carpathians. *Ore Geology Reviews*, 27(1-4), 13-44.
- Pricopie, M., Tuşa, L., Cristea, P., Căpraru, N., Marton, I. (2004) Geology of the Certej project area and a new model for high-grade gold mineralisation hosted within the Dealul Grozii - Hondol Perimeter (Certej deposit). In C. Ciobanu, and N. J. Cook, Eds. Gold-Silver-Telluride Deposits of the Golden Quadrilateral, South Apuseni Mts., Romania. Guidebook of the International Field Workshop of IGCP project 486, Alba Iulia, Romania, 31<sup>st</sup> August - 7<sup>th</sup> September 2004.
- Rosu, E., Pecskay, Z., Stefan, A., Popescu, G., Panaiotu, C., Panaiotu, C. E. (1997) The evolution of the Neogene volcanism in the Apuseni Mountains (Rumania): Constraints from new K-Ar data. *Geologica Carpathica-Bratislava*, 48, 353-359.
- Skinner, B. J., Luce, F. D., Makovicky, E. (1972) Studies of the Sulfosalts of Copper III; Phases and Phase Relations in the System Cu-Sb-S. *Economic Geology*, 67(7), 924-938.
- Udubaşa, G., Istrate, G., Vălureanu, M. (1980) Metallogenesis of Coranda Hondol region, Metaliferi Mountains (Metalogeneza regiunii Coranda - Hondol, Munții Metaliferi). (In Romanian). D.S. Inst. Geol., LXVII(2), 197-232.
- Udubasa, G., Rosu, E., Seghedi, I., Ivascanu, P. M. (2001) The "Golden Quadrangle" of the Metaliferi Mts., Romania: What does this really mean? *Rom. Jour. Min Dep.79, Suppl. 2, Special Issue, Geodynamics and Ore Deposits Evolutions of the Alpine-Balkan-Carpathian-Dinaride province, ABCD-GEODE WORKSHOP 2001 Vata Bai, România, 8-12 June 2001, Abstract Volume, 24-34, Bucharest.*

"The [silicon-oxygen] structure is so rigid... that it decides the crystal form."

W. L. Bragg, 1937

