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IN MEMORIAM Alexander von Humboldt (1769-1859)

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GEOCHEMICAL PATTERNS OF THE WASTE-TYPES ACROSS THE SURFACE OF THE TAILINGS PONDS FROM THE FUNDU MOLDOVEI MINING FIELD

Dan STUMBEA

University „Alexandru Ioan Cuza" of Iași, 20A Copou Bv., 700505 Iași, Romania
dan.stumbea@uaic.ro

Abstract: Data of descriptive and multivariate statistics, along with information on waste mineralogy and tailings ponds morphology, suggested three types of waste: (i) Waste type 1, from the slightly elevated sectors of the beach of the tailings ponds, temporarily having low and variable contents of secondary minerals (hydrated sulfates); (ii) Waste type 2, rich in hydrated sulfates, formed through evaporation of multi-element-rich water (leachate) accumulated as shallow pools on the slightly lower sectors of the beach; (iii) Waste type 3, from the flanks of the waste deposits, depleted of soluble fraction and most of major and minor elements. The statistical approach also pointed out to the following geochemical patterns of the waste: (i) Pattern 1: the abundance of Al, K, Zn, Pb, Co, Ni and soluble fraction in tailings increases following the next waste sequence: waste type 3 – waste type 1 – waste type 2; (ii) Pattern 2: Fe and As are quasi-uniformly distributed over the surface of the tailings ponds, only displaying a slight increase within the waste rich in hydrated sulfates; (iii) Pattern 3: the waste type 3 has higher contents of Ca, Mn and Cd, because of these elements accumulation within the cemented layers developed on the flanks of the waste deposits. The distribution of Cu content and pH values does not fit in with any of the three patterns.

Keywords: tailings, toxic elements, descriptive statistics, cluster analysis, Fundu Moldovei

1. Introduction

Exploitation of sulfides produces large amounts of wastes, including flotation slurry, which is deposited in tailings ponds. The presence of sulfides within the tailings explains the high concentration of potentially toxic metals and metalloids in the waste (Kossoff et al., 2011). Due to their long-term interaction with the atmosphere, sulfides (especially pyrite) within tailings are subject of oxidative weathering, often caused by oxygen dissolved in waters bathing the mineral surface. The process produces acid mine drainage (AMD), i.e., leachates, heavily charged with sulfates, toxic metals and metalloids (Rice and Herman, 2012). Consequently, AMD controls the toxic metals mobility and speciation (Lacal et al., 2003). Commonly, the AMD leachates occur as pore-water between the waste grains, but they can also accumulate as shallow pools on the beaches of the tailings ponds, during heavy rains. In either case, the evaporation of AMD leachates produces highly soluble efflorescent aggregates or crusts of hydrated oxides and sulfates (secondary minerals) (Sherriff et al., 2011); usually, the latter concentrate potentially toxic elements (Bea et al., 2010).

The ongoing processes at the surface of tailings ponds and their resulting products are diverse and frequently recurrent. This makes difficult the understanding of waste evolution and requires specific investigative approaches, meant to reduce the number of variables; for this purpose, statistical tools are a solution (Oyarzún et al., 2012; El Amari et al., 2014; Li et al., 2015). Given this context, the aim of the present study is to identify the main types of waste and their evolution on the surfaces of the two tailings ponds from the mining district of Fundu Moldovei, by using some statistical tools. The statistical data were confronted with the field observations and mineralogy of waste.

2. Geology and study area

2.1 Geological setting

In the mining field of Fundu Moldovei, two tailings ponds were built up in the late sixties, i.e., Dealul Negru – on the Moldova River valley and Pârâul Cailor – on the Pârâul Cailor creek. Both of them consist of waste resulted from the ore processing plant of Fundul Moldovei, which was extracting the Cu from the chalcopyrite and Cu-rich pyrite of the polymetallic ore bodies in the perimeter. The ore bodies are metallogenic subunits of the 200 km length Polymetallic Belt of Eastern Carpathians, which has a NNW-SSE orientation. The ores are hosted by the low-grade metamorphic rocks of Tulgheș Group, settled within the Putna Nappe, which is a subunit of the Alpine Bucovinian Nappe (Fig. 1). The Group of Tulgheș consists of the following four lithostratigraphic subunits (Balintoni, 2010): Căboaia, Holdița, Leşu Ursului and Arşiţa Rea. The main rock types described in the Group of Tulgheş are quartzites and quartz-feldspar rocks. However, the lithology is highly diverse, because of continuous variation of ratio between the most abundant minerals, such as quartz, feldspar, chlorite and sericite. Consequently, the most frequent rocks of the Group of Tulgheş are quartz-schists, sericite-schists, chlorite-schists and rhyolitic metatuffs (Kräutner et al., 1986).

The ore deposits are clustered in three districts, which are (from N to S): (1) Borşa-Vişeu, (2) Fundu Moldovei- Leşu Ursului, and (3) Bălan and Fagu Cetăţii. Ore appears as lenses or tabular bodies, consisting of either disseminated or massive sulfides. Cu-rich pyrite is the most common sulfide, being associated with sphalerite, galena and chalcopyrite; the latter prevails over sphalerite and galena, in the mining field of Fundu Moldovei. In the massive ores, pyrite appears as submillimetric crystals; when disseminated, pyrite has millimetric size. Within the ore bodies, pyrite and chalcopyrite are frequently associated either as irregular mineral aggregates or subcentimetric veinlets.

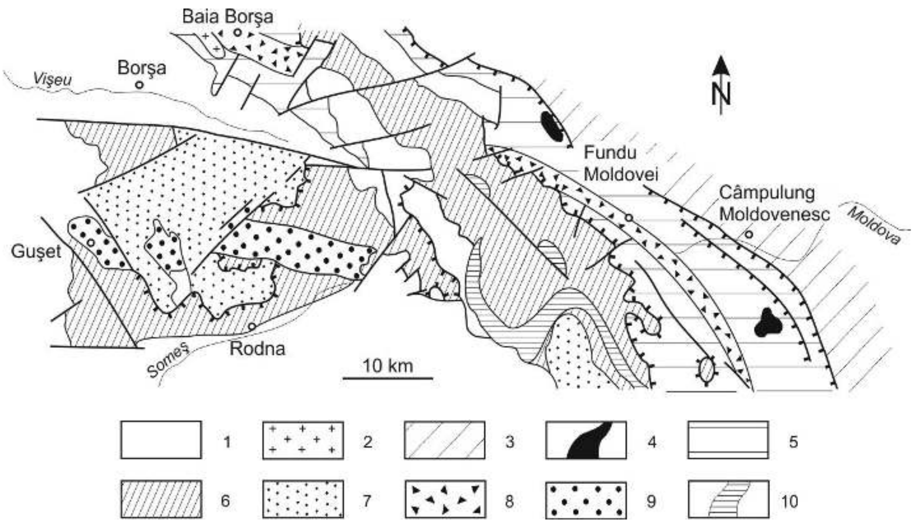

Figure 1. Geological setting of the middle sector of the Polymetallic Belt of Eastern Carpathians (from Kräutner et al., 1986, modified). 1-post meso-Cretaceous sedimentary cover; 2-Neogene volcanic rocks; 3-flysch nappes; 4-Transylvanian Nappes; 5-Bucovinian Nappe; 6-Subbucovinian Nappe; 7-Infrabucovinian Nappes; 8-Cu-Zn-Pb-rich pyrite (Burloaia-Fundu Moldovei-Leşu Ursului-Bălan type); 9-Pb-Zn ores (Valea Blaznei-Guşet type); 10-Mn-Fe-barite ores (Iacobeni type, Holdiţa-Broşteni type).

2.2 Study area

The two tailings ponds, which are the subjects of the study, are located in the neighborhood of Fundu Moldovei village, as follows: (i) Dealul Negru tailings pond (DN) is a hill-type waste deposit, which lies on the right bank of Moldova River, at the west end of the Fundu Moldovei village; (ii) tailings pond of Pârâul Cailor (PC) is a valley-type waste deposit, located northeast of village, about 1.5 km upstream from the confluence of Pârâul Cailor creek with Moldova River (Fig. 2). Both waste deposits use to accumulate the slurry from the ore preparation plant of Fundu Moldovei, which has ended the activity in 2004.

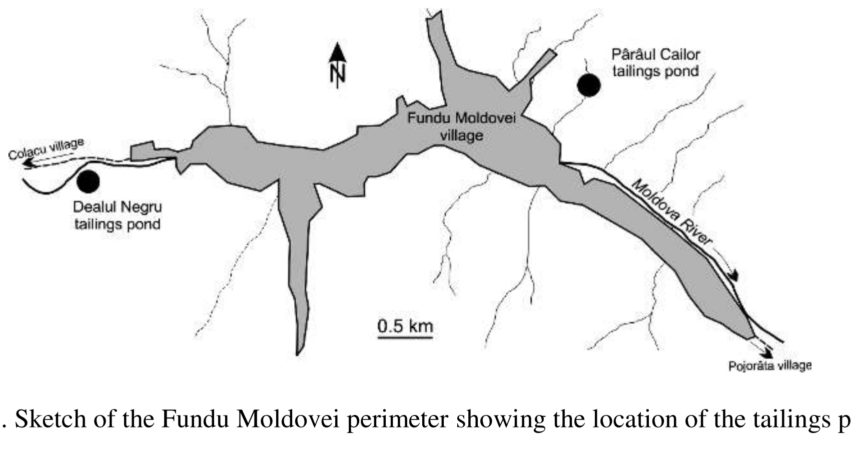

Figure 2. Sketch of the Fundu Moldovei perimeter showing the location of the tailings ponds.

The tailings dam of DN is 45 m height, displaying a 200 m long and 120 m wide horizontal surface (beach); the total volume of waste is about 0.70 mil. m^3. The tailings pond of PC is only 30 m high at the southern end and contains around 0.90 mil. m^3 of waste. The beach has a length of 350 m and a width of 280 m; the northern flank is only 8-10 m high. The flanks of both waste deposits are heavily affected by erosion, as the rain gullies dug on their surface suggest. The limit between the beach of each tailings pond and its flank is given by a 80-100 cm high ridge, which prevent the surface runoff during heavy rains. The northern sector of the PC beach is around 40 cm lower than the rest of the surface. The tailings of both waste deposits are mainly sandy, but areas with silty and clayey appearance can also be noticed on the beaches. The main color of the detritus is yellow, ranging to deep-yellow and ochre on the flanks; the beach of DN is mainly grayish. During heavy rains, shallow pools of deep-brown water use to accumulate in the slightly lower areas of the beach of the waste deposits. They are highly acidic leachates, heavily charged with toxic metals, which turn by evaporation into highly soluble, hydrated sulfates.

The tailings ponds are located at 750 m altitude (DN) and 850 m altitude (PC), the weather parameters being specific to low-altitude mountain regions from the temperate climate zone. During summer, the average temperature is around 16 ºC and the humidity is over 80 %. The rainfall regime is moderate (83 mm/year) and the average speed of wind is 4 m/s. The wind blows mainly from NW, affecting especially the DN tailings pond, which is, by its position, the most exposed.

3. Materials and methods

3.1 Sampling

The field works took place during the autumns of 2010 (DN) and 2013 (DN and PC). The sampling procedure was chosen so as to meet the following requirements: (i) to collect samples from the entire surface of the tailings ponds (both beach and flanks); (ii) the number of samples to represent a reliable statistical population, i.e., at least 30. In this respect, the waste samples were collected following rectangular grids of 25×25 m (flank of DN), 30×40 m (beach of DN) and 30×50 m (beach and flanks of PC). Consequently, the number of samples collected from the two waste deposits were 30 (DN) and 30 (PC). All samples were collected with the help of a plastic paddle and stored in sealed plastic bags. Once brought in the laboratory, preliminary mineralogical observations were performed with help of a Meiji 9400 ML stereomicroscope.

3.2 Particle size analysis

The assessment of particle size distribution was performed by the sieving method. To this purpose, the samples were dried at 50 °C for 24 h and weighed afterwards. Further, the samples were passed through three sieves of known size, i.e., 1 mm, 0.25 mm and 0.063 mm. Eventually, each grain fraction was weighed and its percentage calculated.

3.3 X-ray diffraction

XRD analyses were performed on samples previously grounded using a mechanic mill. Then, the samples were analysed with help of a Philips PW 1739 X-ray diffractometer equipped with monochromatic CuKα (1=1.54056 Å); the scan setting were 5–65° 2θ, 0.5° step size and 2 s counting time per step.

3.4 X-ray fluorescence

The abundance of major and potentially toxic elements was determined by energy-dispersive X-ray fluorescence (EDXRF), with help of an Epsylon 5 XRF-spectrometer. For this, the samples were previously grounded, mixed with Hoechst wax and pressed to pellets. Data available for reference materials such as river and lake sediments, as well as soil samples, were used to calibrate the spectrometer.

3.5 Leaching tests

To determine pH and the abundance of water-soluble fraction, 10 g aliquot of each sample was mixed with 100 mL of deionized within a beaker. Then, the latter was stirred for 2 h at 100 rpm and left for 1 h so as the solid to decant. Using a Corning M555 pH-meter, the pH of leachates were measured. After this, the leachates were filtered through a 0.2 µm cellulose filter; then, the cellulose filter was dried and weight to calculate the percentage of the soluble phases.

3.6 Statistical analyses

The data of descriptive statistics (mean, median, standard deviation, type of statistical distribution) and multivariate statistics (k-means clustering) were determined with help of XL Stat Pro 7.5 software.

4. Results and discussion

4.1 Grain size

The grain size analyses performed on the tailings collected from the beaches of the two waste deposits show that detritus consists mostly of fine and very fine mineral particles. Thus, the fine and very fine sand-particles represent about 53 wt% (DN) and 57 wt% (PC) of the waste, while the mean abundance of silt + clay fractions is around 40 wt% (DN) and 38 wt% (PC), respectively. On the other hand, the grain size distribution across the flanks of the waste deposits shows an increase of the smallest particles abundance, from the upper levels of flanks, towards the lowest. Hence, the abundance of the mineral grains smaller than the medium sand-size fraction increases from over 76 wt% in the waste from the upper levels, to around 90 wt% in the waste from the bottom levels. This is because the fine waste particles are highly susceptible to be removed and transported from the upper levels of the tailings ponds, towards the lower ones, either by runoff waters during rainfalls or by wind. Moreover, the lowest levels are less steep than the upper ones, favoring thus the accumulation of fine detritus.

4.2 Mineralogy

Microscopic examination and XRD analyses revealed that the waste of the two tailings ponds consists of primary and secondary minerals. The primary minerals come from the low-grade metamorphic rocks of Tulgheş Group and the associated polymetallic sulfides. This category of minerals can be identified using either stereomicroscope or XRD patterns and consists of both silicates (quartz – often limonitized, sericite, chlorite, rarely biotite) and sulfides (especially pyrite, but also sphalerite and galena).

The secondary minerals appear as products of the weathering of primary minerals in the waste. Under microscope, they appear mostly as tabular or needle-like, translucent, white or ochre crystals, attached on the surface of the primary minerals. The secondary minerals can only be identified by XRD analyses. Within the study tailings, two categories of secondary minerals were identified, i.e., clay minerals and hydrated oxides and sulfates. Illite and kaolinite are the clay minerals identified by XRD analysis. Thus, illite may appear by the weathering of sericite (Chen et al., 2012), while kaolinite may come from the weathering of either chlorite (Raigemborn et al. (2014) or biotite (Girty et al. (2013). The hydrated oxides and sulfates result from the weathering of primary silicates and sulfides, which provide the major elements of the secondary minerals (Al, Fe and SO_4^{2-}). The secondary minerals identified by XRD analyses are goethite, limonite, alunogen, halotrichite, apjohnite, jarosite, butlerite, römerite and coquimbite.

4.3 pH and soluble fraction

The pH of the waste is low and constant; the mean pH is around 3.1 in each of the two waste deposits and shows the high acidity of tailings. On the contrary, the abundance of soluble fraction is much larger in the waste of DN (about 13 wt%), than in the tailings of PC (around 3.5 wt%). This is because of the far higher exposure of DN waste to wind, which increases the evaporation rate and causes a more intense precipitation of highly soluble hydrated sulfates.

4.4 Geochemistry. Statistical approach

The first step of the statistical approach regarding the chemical data specific to the study tailings is the descriptive statistics (Table 1). The chemical properties are closely related to the mineralogy of the waste. Thus, the content of major elements can be explained as follows: (i) Al comes from the primary minerals (sericite, chlorite), but also accumulates within the structure of some secondary minerals, formed through weathering, such as alunogen, halotrichite and apjohnite; (ii) the main source of Fe is pyrite, but also hydrated salts (i.e., halotrichite, jarosite, butlerite, römerite and coquimbite) and more or less hydrated oxide-hydroxides (i.e., goethite, limonite); (iii) together with Al, Mn accumulates in the secondary sulfate apjohnite; (iv) the K content results from sericite, but it also accumulates in secondary minerals, i.e., jarosite; (v) Ca may result from the treatment of the slurry with $Ca(OH)_2$ in order to neutralize it, at the time the tailings pond was operational.

The amount of potentially toxic, minor elements is explained by the presence of sulfides within the tailings (especially, pyrite, but also sphalerite and galena), which are known as sources of heavy metals (Yurkevich et al., 2012; Bempah et al., 2013). Moreover, the concentration level of potentially toxic elements is highly increased by the sulfide exposure to process of chemical weathering (Ogola, 2010) and the addition of chemicals during the extraction process in the preparation plants.

Table 1. Descriptive statistics of the chemical properties of all tailings samples (n = 60)

	Al_2O_3	**FeO***	**MnO**	**CaO**	**K_2O**	**Cu**	**Zn**	**Pb**	**Co**	**Ni**	**Cd**	**As**	**pH**	**SF**
Min.	2.58	3.24	0.02	0.11	0.72	38	45	40	9	0.3	0.0	65	2.3	0.02
Med.	8.42	8.04	0.03	0.21	1.94	318	142	909	33	3.0	0.1	154	3.1	1.98
Max.	19.33	14.05	0.07	1.37	4.68	1982	1112	2674	72	6.2	1.9	304	4.7	27.51
Mean	9.58	8.45	0.03	0.37	2.29	499	192	1039	36	2.9	0.3	157	3.1	5.26
St. Dev.	4.89	2.38	0.01	0.32	1.06	449	170	650	14	1.3	0.3	60	0.5	5.21

FeO* = FeO + Fe_2O_3; SF-soluble fraction. The amounts of Al_2O_3, FeO, MnO, CaO, K_2O and soluble fraction (SF) are expressed as (wt%); the amounts of Cu, Zn, Pb, Co, Ni, Cd and As are expressed as (ppm).

The normality tests show non-normal data concerning the content of most of the major elements (Al, Mn, Ca and K) and minor elements (Cu, Zn, Pb and Cd); the amounts of soluble fraction (SF), as well, show a non-normal distribution. This, together with a high standard deviation compared to the mean of some elements (Cu, Zn, but especially Cd and SF) (Table 1), may be considered as an overlap of two or more processes/factors involved in the tailings evolution under subaerial conditions. In terms of statistics, the presumed overlap of processes or factors consists in a mixture of two ore more statistical populations of data. On the other hand, data regarding the abundance of Fe, Co, Ni, As and pH follow a normal distribution, which suggest a homogeneity of the waste with reference to these chemical properties. The normal distribution of Fe, Co, Ni and As amounts may be ascribed to a constant presence of pyrite in the waste. The pH also seems to vary little from one sector to another of the waste deposit.

To identify the statistical populations suggested by the descriptive statistics, the k-means clustering method was used; the cluster composition is summarized in table 2. The analysis of all information regarding the study tailings has allowed to associate a waste type to each of the three clusters: (i) Waste-type 1, associated to cluster (statistical population) 1, consists of samples collected from slightly elevated areas of the tailings ponds beaches, where rain water does not accumulate; (ii) Waste-type 2, associated to cluster (statistical population) 2, gathers samples from areas where rain water accumulates as shallow pools, on the beaches of the waste deposits; (iii) Waste-type 3, associated to cluster (statistical population) 3, consists of samples collected from the flanks of the tailings ponds.

Table 2. Clusters composition

Cluster	1	2	3
Minimum distance from centroid	171.245	129.917	210.856
Average distance from centroid	533.064	648.274	406.322
Maximum distance from centroid	1357.608	1868.358	681.632
Size	21	19	20

Table 3 contains some of the descriptive statistic parameters specific to each of the three populations identified through the clustering method. The comparison of means with standard deviations confirms the accuracy of k-means clustering method in identifying the three statistical populations. As a result, the comparison between the means of the three populations is reasonable and suggests some geochemical patterns of the waste, which will be discussed in the following paragraphs.

Table 3. Descriptive statistics of the chemical properties of the three statistical populations

	Al_2O_3	FeO*	MnO	CaO	K_2O	Cu	Zn	Pb	Co	Ni	Cd	As	pH	FS
			(wt%)					(ppm)						(wt%)
Population 1 (*n* = 21)														
Min.	2.58	4.22	0.02	0.11	0.76	151	80	471	17	2	0.0	74	2.6	0.5
Med.	14.19	10.20	0.04	0.36	3.49	1850	659	1830	53	6	0.3	196	3.7	10.5
Max.	6.10	6.97	0.03	0.18	1.81	345	135	851	32	3	0.1	113	2.9	2.3
Mean	6.93	6.94	0.03	0.19	1.90	599	182	929	33	3	0.1	124	3.0	3.6
St. Dev.	3.02	1.40	0.01	0.05	0.68	465	126	331	8	1	0.1	35	0.3	2.8
Population 2 (*n* = 19)														
Min.	5.79	7.01	0.02	0.11	1.30	226	124	925	32	2	0.0	146	2.6	0.9
Med.	19.33	14.05	0.04	0.24	4.68	1982	1112	2674	72	5	0.5	304	3.9	27.5
Max.	16.45	10.03	0.03	0.19	3.73	345	168	1554	49	3	0.1	196	3.2	7.4
Mean	14.50	9.97	0.03	0.18	3.30	550	235	1668	49	3	0.1	206	3.2	10.7
St. Dev.	4.18	1.82	0.01	0.04	0.90	474	219	518	10	1	0.1	44	0.3	9.4
Population 3 (*n* = 20)														
Min.	3.74	3.24	0.03	0.79	0.72	38	45	40	9	0	0.6	65	2.3	0.0
Med.	10.21	12.39	0.07	1.37	2.90	934	609	893	37	5	1.9	293	4.7	1.6
Max.	6.93	9.50	0.04	0.81	1.51	222	108	242	22	1	0.8	116	3.0	0.3
Mean	6.87	8.79	0.05	0.88	1.54	277	150	384	22	2	0.8	146	3.2	0.4
St. Dev.	1.98	2.72	0.01	0.18	0.54	278	129	288	7	2	0.3	66	0.7	0.4

FeO* = FeO + Fe_2O_3. The amounts of Al_2O_3, FeO, MnO, CaO, K_2O and soluble fraction (SF) are expressed as (wt%); the amounts of Cu, Zn, Pb, Co, Ni, Cd and As are expressed as (ppm).

Pattern 1. The amounts of Al, K, Zn, Pb, Co, Ni and soluble fraction increase in the following sequence of waste-types (Fig. 3): tailings from the flanks of the waste deposit (waste-type 3) – waste from areas of the beach where rain water does not accumulate as shallow pools (waste-type 1) – tailings from the sectors where the shallow pools of rain water usually accumulate (waste-type 2). This pattern may be in relation with the ratio of soluble fraction in each of the three types of waste and some of its properties. Thus, the soluble fraction consists of more or less hydrated sulfates of Al and K, identified through XRD analyses, i.e., alunogen, halotrichite, jarosite and apjohnite, which are highly soluble. Moreover, the hydrated sulfates are well known as minerals that concentrate potentially toxic elements, such as Zn, Pb, Co and Ni (Kovács et al., 2006; Bea et al., 2010; Kossoff et al., 2011).

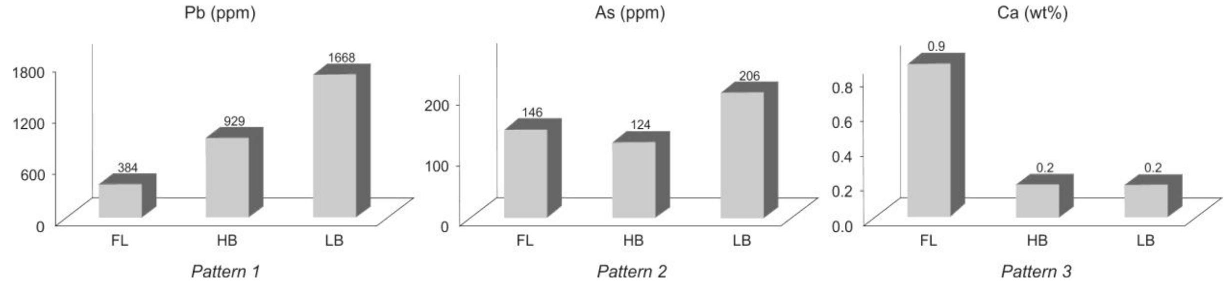

Figure 3. Examples of geochemical patterns of the tailings. FL-tailings from the flanks (stat. pop. 3); HB-tailings from the slightly higher areas of the beach, where rain water does not accumulate (stat. pop. 1); LB- tailings from the slightly lower areas of the beach, where rain water accumulates as shallow pools (stat. pop. 2).

Considering the context described in the previous paragraph, the pattern 1 can be explained as following: because of the steepness, after rainfalls, the waste of the flanks of the tailings ponds retains smaller quantities of water within pores, compared to the beaches. Therefore, during dry periods, only little hydrated sulfates can precipitate on the flanks surface, through evaporation. Besides, the highly soluble hydrated sulfates formed that way are readily dissolved and removed by the surface runoff, when medium and heavy rains occur. Therefore, the waste from the flanks is generally depleted in soluble fraction and, consequently, in the major and minor elements associated to the soluble fraction. The surface of the beach of the tailings ponds usually displays slightly lower, a few centimeters-deep, sectors, where the rain water accumulates and, as a result, slightly elevated areas. On the latter, the runoff is much less intense than on the flanks of the waste deposit, so as the water infiltrate within the detritus, accumulating as pore-water. By interacting with the grain minerals, the water becomes a leachate enriched in SO_4^{2-}, Al, K and also potentially toxic elements. During the long dry periods, the evaporation of this leachate leads to the formation of efflorescent hydrated sulfates, which appear either as very thin crusts or as small aggregates coating the grain of primary minerals (especially quartz and chlorite). These secondary minerals are short-living appearances, because, when rainfall occurs, the salts are dissolved and transported towards the lower areas of the tailings pond beach, where the leachates are accumulated as shallow pools. The evaporation of these highly acidic leachates (pH between 2.5 and 3.5), which also are rich in SO_4^{2-}, Al, K and minor elements, lead to the formation of about 0.5 cm thick crusts of hydrated sulfates. The recurrence of these processes makes the low sectors of the waste deposit beach the most enriched areas in Al, K, potentially toxic elements and soluble fraction.

Pattern 2. The contents of Fe and As are somewhat higher in the samples rich in hydrated sulfates (waste-type 2), compared with the samples collected from the flanks of the waste deposit (waste-type 3) and the elevated sectors of the beach (waste-type 1), where the abundance of the two elements is quasi-equal. This geochemical pattern is explained by the higher abundance of Fe-rich hydrated sulfates (i.e., halotrichite, butlerite, coquimbite, jarosite and römerite) within the samples of waste-type 2; the latter minerals can act as temporary hosts for As (Buckby et al., 2003; Hammarstrom et al., 2005; Khorasanipour, 2015). On the other hand, Fe and As data show normal statistical distributions, suggesting that the difference between the slightly richer and slightly poorer waste is rather minor. This may indicate a quasi-uniform spatial distribution of pyrite over the surfaces of the waste deposits, regardless their morphological features. The presence of arsenopyrite within the tailings can be considered as well.

Pattern 3. The samples collected from the flanks of the tailings pond (waste-type 3) show a much higher content of Ca, Mn and Cd, than the samples collected from the beaches (waste-types 1 and 2); the latter display an almost equal abundance of the three elements. This is because of the cemented layers of waste, formed on the lower, less steeper levels of the flanks of especially Dealul Negru tailings pond; these layers are known as concentrator of Ca, Mn and Cd, among other elements (Lottermoser and Ashley, 2006; Graupner et al., 2007).

The spatial distribution of the Cu does not fit in any of the patterns described above. The content of Cu is two times smaller in the waste from the flanks of the waste dams, in comparison with the tailings from the beaches (waste-types 1 and 2). The explanation may consist in the capacity of some of the clay minerals (especially illite) to concentrate Cu (Chen et al., 2012). In the two tailings ponds under study, the clay fraction was only identified on the beach sectors, where it was not removed and transported by the rain waters, as is expected to have happened on the flanks of the waste deposits. The hypothesis is also supported by the non-normal distribution of Cu data.

The mean of pH values is practically the same for each of the three types of waste (Table 3) and it is equal to the general mean and median as well (Table 1). Statistically, the pH data display a normal distribution, which supports the presumption of an uniform acidity of the entire amount of tailings contained by the two waste deposits under study.

5. Conclusions

Data released by some of the descriptive and multivariate statistics performed on the study waste have resulted in the following three types of tailings: (i) Waste-type 1, which consists of detritus from the slightly elevated areas of the beaches of the tailings pond, more or less poor in secondary minerals (hydrated sulfates); (ii) Waste-type 2, from the slightly lower sectors of the beaches of the waste pond, where secondary hydrated sulfates (soluble fraction) usually occur through evaporation; (iii) Waste-type 3, located on the flanks of the tailings ponds, highly depleted of soluble fraction and most of major and minor elements.

Statistical tools also indicated three main geochemical patterns of the study waste: (i) Pattern 1 consists in the increase of Al, K, Zn, Pb, Co, Ni and soluble fraction abundance, following the sequence:

waste-type 3 – waste-type 1 – waste type-2; (ii) Pattern 2 refers to Fe and As, which display rather constant amounts across the waste deposits; the slightly higher contents within the waste-type 2 are due to their affinity for hydrated sulfates; (iii) Pattern 3 consists in higher contents of Ca, Mn and Cd within the waste-type 3, because of their accumulation within the cemented layers developed on the lower and less steeper levels of the tailings ponds. The distribution of Cu content and pH does not fit in any of the three patterns. Cu seems to be in relation with the clay minerals formed through the weathering of some silicates from the waste of the tailings ponds beaches. The acidity is constant all over the surface of the waste deposits.

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MINERALS FROM RAZOARE Mn-Fe DEPOSIT, PRELUCA MOUNTAINS, EAST CARPATHIANS, ROMANIA: NEW DATA

Paulina HIRTOPANU*, Gheorghe UDUBASA

University of Bucharest, Faculty of Geology and Geophysics, 1, N. Balcescu Blv., 010041, Bucharest, Romania
**paulinahirtopanu@hotmail.com*

Abstract. The Razoare manganese-iron deposit, Preluca Mts, Romania is a stratiform concentration of manganese, manganese-iron and iron minerals, showing evidences of regional metamorphism in the upper almandine amphibolite facies. The deposit is enclosed in a sequence of kyanite-bearing micaschists, paragneisses, amphibolites and carbonates rocks, interpreted to be Precambrian age. At least three metamorphic events have been recognized in the host metamorphic rocks and in the ores as well. The repeated changes of metamorphic facies is the main cause of a great number of mineral. The change from one facies of metamorphism into an other is accompanied by a change of mineralogy with new mineral appearances. The retrograde metamorphic evolution during the Caledonian and Hercynian events led a complicated mineralogy. The manganoan ferrosilite-enstatite was transformed in manganoan fayalite, the manganoan fayalite was changed in mangangrunerite, the tephroite has been transformed in manganese humites, the pyroxmangite was transformed in mangangrunerite, etc. The appearances of many varieties of Ni-Co sulfide, telluride, arsenide, sulfarsenide and bismuthinide minerals, may be attributable to the a late locally developed hydrothermal system. The mineral changes were continued with the appearances of some manganese arsenates at the expense of arsenides, the secondary manganese carbonates, phosphates and Fe-Mn oxides/hydroxides. The ores consist (in predominance order), of 12 carbonates+borates, 43 silicates, 21 oxides/hydroxides, 15 phosphates+arsenates, 30 sulfides/arsenides/tellurides/bismuthinides, 6 sulphates and 3 native elements. Only about 20 minerals are common for first stage metamorphic constituients that characterize the original deposit in a genetic sense. Most of the over 130 different minerals that have been identified at Razoare are either weathering products or are associated with low temperature hydrothermal activity and altered areas. The locally hydrothermal mineralization derived probably from the reworking and leaching of the mineral of the primary ore, by a later regional metamorphism and of lower grade than the original recrystallization.

Key words: Fe-minerals, Mn-minerals, Fe-Mn/Mn-Fe minerals, polyphase metamorphic evolution of deposit.

I. Introduction. The Razoare Mn-Fe deposit is located in the Preluca Mts, an ‘island’ of Precambrian metamorphic rocks in a Tertiary sedimentary environment. The ores form lenses up to 60m thick. The lenses are invariable enveloped by nearly continuous bands of black quartzites reaching a maximum thickness of about 2m. More details about geological setting and host rocks have been presented previously by Udubasa et al., (1996). The deposit was originally described by Kossmat and von John (1905), who reported the general geology and the relationship of the ores with the host rocks, concluding that the deposit was undoubtedly regionally metamorphosed. They recognized the knebelite and dannemorite as the main minerals occuring together with variable amount of magnetite, spessartine, apatite and pyrite. Giusca (1962) reported the presence of the rhodonite and manganoan hissingerite. Radulescu and Dimitrescu (1966) have shown the presence of pyroxmangite. Kalmar (1972) made a general approach concerning the “crystalline islands” of North Romania including an overview on the associated mineral deposits. Gotz et al. (1977) gave important data on mineralogy and geochemistry of the ores. Kalmar and Lelkes-Felvari (1991) summarized old and new data about the Preluca Mts and gave also a list of minerals so far identified in the Razoare deposit. Hirtopanu et al. (1992) described manganoan fayalite and its association in Razoare deposit. Hirtopanu et al (1993) recognized five mineral assemblages, which differ in their position in the lithostratigraphical column of the ore sequence belonging to the different metamorphic events and consequently in their mineralogical composition. The leading minerals of the six assemblages are: (1) manganoan fayalite (old name knebelite); (2) tephroite-manganese bearing humites; (3) pyroxmangite; (4) mangangrunerite; (5) spessartine (6) rhodochrosite. The first three assemblages are undersaturated in silica, they are not associated with quartz, rhodochrosite being omnipresent in associations. The two following assemblages (4) and (5) are saturated in silica having associated quartz. Rhodochrosite and quartz coexist only at very low grades of metamorphism. There have been presented physical/optical properties, X-ray and chemical data about tephroite and manganese humites. All these analyses showed the presence of tephroite, sonolite, leucophoenicite, alleghanyite and ribbeite, formed during a later, retrograde metamorphic phase. Udubasa et al (1996) described geological setting, host rocks and ore mineralogy of the Razoare deposit. The last authors have been mentioned three distinct assemblages at Razoare deposit, all having a constant position within the ore lenses (Fig. 1). At the bottom there is a rhodochrosite-rich assemblage, followed by an assemblage consisting mainly of tephroite and manganese humite minerals. At the top of the sequence there is a mangangrunerite-dominated assemblage with a definite enrichment in quartz towards the hanging wall. Udubasa et al (1996) have been identified following minerals: tephroite, nearly the whole morphotropic series of manganese humites (sonolite, leucophoenicite, alleghanyite, jerrygibbsite), carbonate-fluorapatite, orthopyroxene, pyrophanite, suggesting a very complex mineralogical composition and metamorphic evolution of the ore. Also, they gave a list of 72 minerals so far identified in the Razoare Mn-Fe deposit. The ratio Mn:Fe is here near unity. Correspondingly, there exist both Mn-Fe minerals with varying Mn:Fe rations induced by repeated metamorphic events and Fe minerals (magnetite, siderite, pyrrhotite) or Mn-minerals (tephroite, manganese humites, rhodochrosite), the presence of which seems to reflect the primary "layering" of the protolith (Udubasa et al,1996, Hirtopanu, 1997) presented the oldest association manganoan ferrosilite-enstatite /fayalite and its metamorphic evolution. Hirtopanu (2006) described the manganese minerals in Romania, many of them being from Razoare Mn-Fe deposit. Hirtopanu et al. (2015) described the sonolite, many sulphides, arsenides, some tellurides, bismuthinides, arsenates, and their associations and genesis.

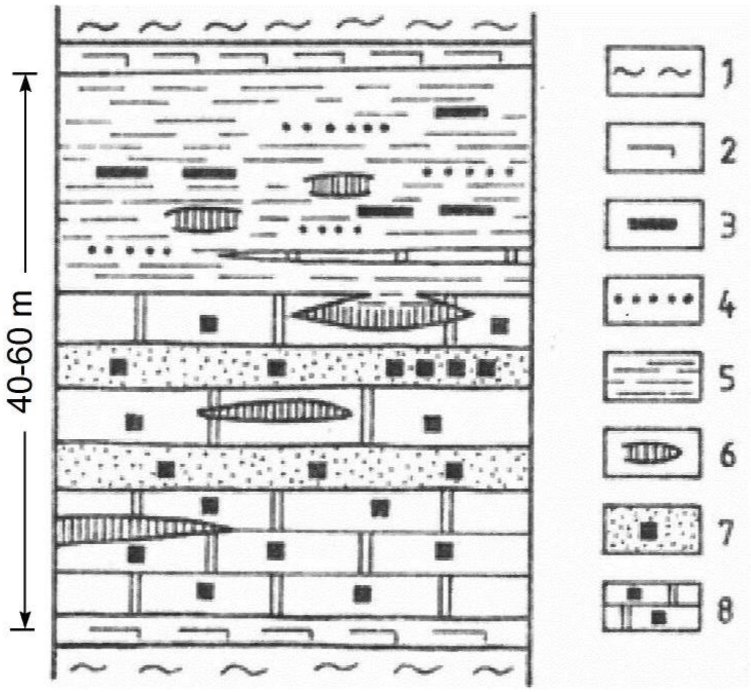

Fig. 1. A generalized column of lithologies of the ore lenses (thickness up to 60-70m), showing the lower, carbonate rich part, silica subsaturated and the upper, mangangrunerite-rich part, silica saturated. 1, gneisses and micaschists; 2, black quartzites: 3, magnetite beds or lenses; 4, manganoan fayalite/manganoan ferrosilite rich lenses and pods; 5, mangangrunerite; 6, pyrrhotite/magnetite bands; 7, massive aggregates of tephroite/manganese bearing humites/jacobsite /fluorapatite/rhodochrosite with many arsenides/sulfoarsenides; 8, rhodochrosite matrix with jacobsite dissemination (Udubasa et al., 1996).

Mineralogy of the ore deposit

The mineralogical composition of the Razoare ores is quite complex, including about 130 mineral species (Table 10), comprising almost the all mineral classes. They have been described in predominance order: I. Carbonates and Borates (12), II. Silicates (43), III. Oxides and Hydroxides (21), IV. Phosphates and Arsenates (15), V. Sulfides-Tellurides-Arsenides-Bismuthinides (30), VI. Sulphates (6), VII. Native elements (3). Many of these minerals were determined recently and are presented in this study (Table 11).

I.a. The carbonates. The rhodochrosite is the most widespread mineral the ore being undersaturated in silica. The carbonate rich assemblage forms the lowest part of the Mn-bearing sequence, with the rather sharp boundary to the host quartzites and/or paragneisses and micaschists. The rhodochrosite constitutes the matrix of the manganoan fayalite rich patches or alternates with its assemblages. Analyses of carbonate matrix indicate compositions near the rhodochrosite. The rhodochrosite is ubiquitous up to amphibolites facies, however it does not survive in granulite facies. The oldest association from Razoare, the aggregates of manganoan orthopyroxene/manganoan fayalite is almost rhodochrosite free. Sometimes, the bottom of a lens begins with a pure rhodochrosite sequence in which jacobsite aggregates gradually develop as well as manganoan fayalite dominated lenses (Fig 1). The composition of the rhodochrosite associated to manganese ore have little some variations. Generally, in the manganoan fayalite assemblages occurs a slightly ferroan rhodochrosite and in the the tephroite-manganese humites assemblages the rhodochrosite is slightly magnesian. The rhodochrosite associated to manganese humites has following composition (mol %): $FeCO_3$=0.4, $MnCO_3$=88.1, $MgCO_3$=5.0, $CaCO_3$=6.5. Rhodochrosite is only one carbonate type present in each assemblages. Other carbonates, like siderite and ankerite occur secondary, in mangangrunerite-magnetite-pyrrhotite-quartz association. The kutnahorite and Mn-calcite occur rarely, as veins. The secondary carbonates holdawayite, aragonite and calcite form veins in primary ores. At low temperature and high P_{O2}, typical of oxidized zones, the rhodochrosite transforms in pyrolusite and other higher Mn-Fe oxides.

I.b. Borates. The borates at Razoare (Table 11) are not enough determined. The presence of boron was determined in manganese humites by means of emission spectrography. It shows a large variation interval, i.e. between 80 and 2,500 ppm, and belongs most probably to another boron bearing associated mineral, because the IR spectroscopy did not confirm its presence in Razoare sonolite structure. These minerals may have been derived their boron content by the local hydrothermal reworking and leaching of the preexisting earlier boron bearing minerals in the ore body.

II. Silicates, are represented by pyroxene, olivine, manganese humite, garnet, mangangrunerite, pyroxenoide, epidote, amphibole, tourmaline, phyllosilicate, chlorite and one of other silicates groups.

Pyroxenes group. Manganoan ferrosilite-enstatite, is the oldest mineral in the pyroxene-olivine parageneses, almost without rhodochrosite. It was determined optically, with X-ray and electron microprobe analyses (Table 2). The big crystals of manganoan ferrosilite-enstatite, of about a few mm and more, are substituted by manganoan fayalite and mangangrunerite (Figs. 2A, 2B). It is not associated with pyroxmangite, no rhodonite, but some microscopic pyroxferroite grains were determined with electron microprobe.Manganoan ferrosilite was reported in granulite facies rocks in Sweden (Krogh, 1977). There this pyroxene coexists with a pyroxferroite which limits the iron content of the pyroxmangite structure to less than 70mol percent $FeSiO_3$ for the conditions of granulite facies of metamorphism (T=750^0 and P=9Kb).

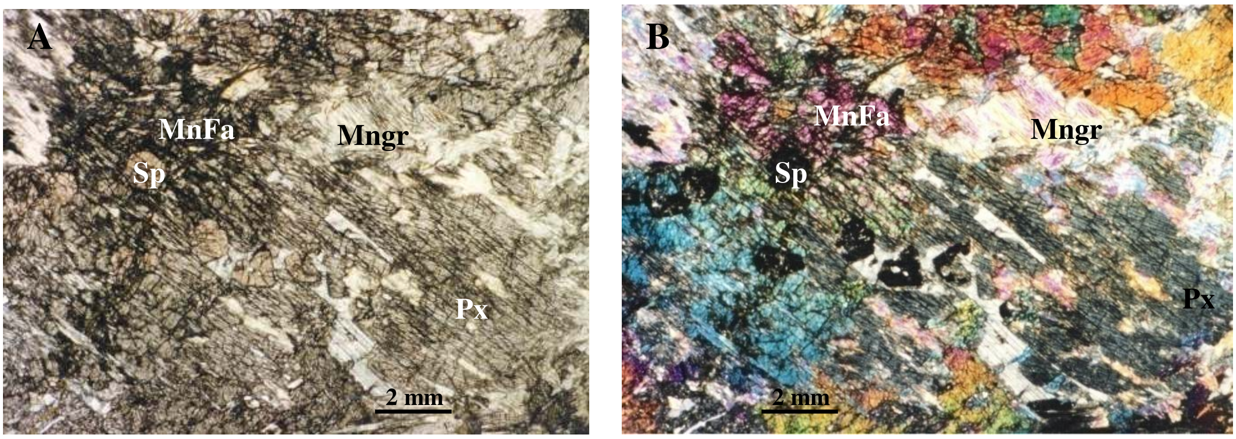

Fig. 2.A. Mnanganoan ferrosilite-enstatite (Px), elongated, grey grains with cleavages, low birefringence), manganoan fayalite (MnFa, high birefringence), mangangrunerite (Mngr, white, white-red), spessartine (Sp, isotrop), N+, sample Rz600; B. Manganoan fayalite (MnFa,) (imperfect cleavage (001) high birefringence), N+, sample Rz102.

The phase diagrams on the $MnSiO_3/FeSiO_3/CaSiO_3$ showed the compositional limits of $R SiO_3$ phases in the upper amphibolites/granulite facies, and the extent of solid solutions between them in amphibolite facies (Brown et al, 1980). For this system there are compositional gaps between bustamite/hedenbergite, bustamite rhodonite, rhodonite/pyroxmangite and manganoan ferrosilite/pyroxmangite. The chemical composition of Razoare pyroxene and pyroxenoids plotted in this diagram form different compositional fields: manganoan ferrosilite does not coexists with pyroxenoids, and pyroxmangite does not coexists with rhodonite. Manganese orthopyroxene is a mineral restricted only to upper amphibolites-granulite facies conditions (Dasgupta et al, 1990). Bohlen and Boettcher (1980) demonstrated that 5 to 10%$MgSiO_3$, solid solution is sufficient to stabilize ferrosilite at 6-7Kbar for temperatures of 750^0, although ferrosilite is unstable below about 11Kb at 750^0 with respect to fayalite and quartz.

Olivines group. One of the most typical features of the Razoare deposit are the presence of three olivines, i.e., **tephroite, ferroan tephroite and manganoan fayalite** (labeled knebelite in the earlier papers), but in different paragenesses. However, the three olivines show distinct positions within the Mn-

Fe ore sequence and different associations. The manganoan fayalite is a feature characteristic of both main parts of the layered Mn-Fe sequences as a result of better preservation it may now be observed more frequently in the lower, rhodochrosite-rich part; in the upper silicate part, the manganoan fayalite was largely transformed into mangangrunerite, occurring only as relics (Fig 3B). Lenses and thin beds rich in manganoan fayalite, locally reaching several dm in size, typically occur in a rhodochrosite-rich matrix. The manganoan fayalite aggregates displays big prismatic crystals up to 10 cm in length. In transmitted light, the manganoan fayalite is slightly green, has a imperfect cleavages and a high birefringence (Figs 3A, 3B). The fayalite-rich parts contain abundant apatite, spessartine, as well as magnetite and/or pyrrhotite, forming alternating bands of metamorphic origin; the banding is locally enhanced by the development of mangangrunerite at the expense of manganoan fayalite (Figs 3B, 5A, 5B). The paragenesis manganoan fayalite-orthopyroxene-calderite garnet (Figs 2A, 2B) represents the oldest and highest grade assemblages of the Razoare ores. Within the banded tephroite-manganese humites, lens-shaped aggregates of pegmatoid appearance with manganoan fayalite prisms up to 8 cm in length, of ball-shaped aggregates, as relics, occur. The first stage of gradual transformation of manganoan fayalite is marked by fine intergrowths of mangangrunerite and magnetite, forming fine veinlets within the manganoan fayalite. Further evolution of this replacement leads to quasitotal conversion of manganoan fayalite in mangangrunerite and to the appearance of quartz in assemblages. The manganoan fayalite is preserved as relics having the same optical orientation within the mangangrunerite aggregates. The Razoare manganoan fayalite is associated with rhodochrosite, being an undersaturated association. In other occurrences of higher grade metamorphism than the Razoare ore, manganoan fayalite coexists with quartz. The wet chemical analyses of manganoan fayalite on can see in Table 1 and with the electron microprobe in Table 2. The manganoan fayalite has high Fe:Mn ratio, showing the dominance iron over manganese; the same is shown by the end members procentage (fay=50-60, teph=35-38, fors=5-10% mol) as well as by cell parameters (Hirtopanu et al., 1992). All the analysed manganoan fayalites have fayalite rich and forsterite poor end members. This type of fayalite appears in other occurrences in granulite facies (Dasgupta et al., 1990).

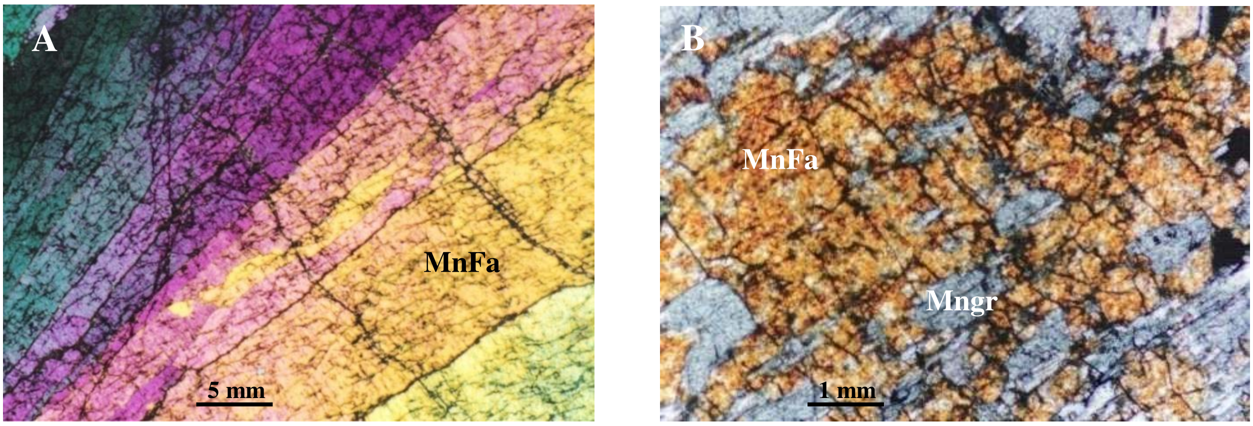

Fig. 3.A. Manganoan fayalite (MnFa,) (high birefringence), N+, sample Rz102; B. Manganoan fayalite (MnFa, high refringence) substituted by mangangrunerite (MnGr, low birefringence), sample Rz110.

Tabel 1. Wet chemical analyses of Mn-fayalite.

%wt	Rz207	Rz208	Rz204	Rz206	Rz6	Rz56	Rz149	Rz156	Rz50A	Rz90	Rz132	Rz138	Rz83	Rz2A	Rz95	Rz110
SiO_2	26.38	25.89	29.55	26.75	24.71	27.34	27.36	25.76	21.70	28.75	26.95	26.82	25.49	25.01	27.62	27.76
TiO_2	0.12	0.14	0.13	0.16	0	0.04	0	0	0.04	0	0	0.04	0.30	0.28	0.25	0.25
Al_2O_3	0.43	0.43	0.48	0.49	0.30	0.10	0.20	0.42	0.42	0	0.04	0.17	0.50	0.37	0.67	0.29
Fe_2O_3	7.33	10.42	8.73	5.52	4.57	3.90	5.47	3.42	3.73	0.44	1.81	1.89	3.87	4.29	3.86	2.48
FeO	30.54	28.36	31.04	31.10	28.88	32.82	33.20	30.49	35.36	39.49	36.18	36.73	35.19	34.50	34.40	31.07
MnO	23.02	24.38	22.67	26.44	24.12	24.31	25.41	26.96	21.66	21.93	23.22	22.52	22.50	19.86	23.44	25.67
MgO	3.74	3.87	2.39	2.05	5.23	3.74	3.50	2.19	3.28	2.60	3.24	3.27	3.62	4.58	3.60	3.74
CaO	2.62	1.21	2.10	3.15	2.50	2.74	0.64	3.16	1.70	0.63	1.58	1.69	1.69	2.71	0.74	2.24
K_2O	0.15	0.04	0	0	0.07	0.06	0.05	0.06	0.03	0	0	0	0.06	0.03	0.03	0.03
Na_2O	0	0	0	0	0.06	0.04	0.03	0.03	0	0	0	0	0	0	0	0
P_2O_5	1.82	0.66	1.63	2.60	0.85	1.57	0.19	0.90	1.23	0.44	0.86	1.01	0.24	1.21	0.29	1.35
H_2O^+	0.38	0.55	0.83	0.75	-	-	-	-	-	-	-	-	-	-	-	-
CO_2	-	-	-	-	-	1.63	-	-	-	-	-	-	-	-	-	-
Total	99.92	99.10	99.55	99.01	100.14	98.29	96.05	98.90	100.06	100.19	99.51	99.74	98.93	98.06	100.36	100.13
Fe_2O_3	41.26	41.93	43.21	40.07	36.65	40.36	42.35	37.29	43.01	56.49	41.30	41.9	42.97	42.62	42.08	37.00

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Some analyses of manganoan fayalite show little amounts of Al, which is due to some inclusions of garnets, and Fe^{3+} is due to some magnetite inclusions. Some analyses of “knebelite” in Table 2 include small amounts of H_2O^+ and CO_2. The latter is due to carbonate impurity and it is possible that some of the impurity with apatite.

The **ferroan tephroite** is associated/banded with pyroxmangite (Figs 7A and 7B) while the pure **tephroite** is closely associated with rhodochrosite, manganese humites or rhodonite. The tephroite occurs with quartz only in low grade metamorphic rocks. The chemical composition of ferroan tephroite one can see in Table 3 and that of tephroite in Table 4. Infiltration of fluids along the later veins led to the decomposition of tephroite/ferroan tephroite to form bementite and divers secondary Mn-carbonates, Mn-arsenates. The destabilization of ferroan tephroite appears to occur at increasing X_{CO2} in the fluid, but also decreasing temperatures and give rise to bementite/Mn secondary carbonates bearing assemblages and secondary Mn-Fe oxides and hydroxides.

Tabel 2. Electron microprobe analyses of manganoan fayalite (A) and manganoan ferrosilite (B).

	A. Mn fayalite Rz100, points 17, 19, 31, 38				B. FeMnMg Pyroxene, sample Rz100, points 21-34			
	from core to rim				from core to rim			
	17	19	31	38	21	25	28	34
SiO_2	30.89	31.22	31.09	31.00	52.14	52.16	51.31	53.07
Al_2O_3	-	-	-	-	0.07	0.06	0.03	0.04
TiO_2	-	-	-	-	0.05	0.03	0.05	0.02
FeO	42.49	42.00	42.78	41.83	28.45	28.20	28.10	27.65
MnO	25.48	24.02	25.11	25.64	10.78	10.60	10.71	10.91
MgO	1.82	1.40	1.53	1.91	7.86	8.13	8.79	7.93
CaO	0.01	0.02	0.02	0.04	0.32	0.27	0.14	0.27
NiO	0.07	0.15	0.16	-	-	-	0.01	-
Na_2O	-	-	-	-	-	0.01	0.02	-
K_2O	-	-	-	-	0.02	-	0.03	0.01
total	100.66	99.45	101.01	100.78	96.69	99.46	99.19	99.90

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Table 3. Electron microprobe analyses of ferroan tephroite.

	Sample Rz561, points 148-155 and 168-171, sample Rz562/48										
	From rim to core						From core to rim				
	148	150	151	153	154	155	168	169	170	171	48
SiO_2	30.97	30.65	30.69	30.92	30.85	30	30.74	31.06	30.48	30.68	30.76
Al_2O_3	-	0.04	-	-	-	0.02	0.05	-	-	-	-
TiO_2	0.01	-	-	0.02	-	-	0.02	0.01	0.01	-	-
FeO	13.95	13.29	14.43	13.37	13.54	13.27	14.61	14.66	14.11	13.37	17.81
MnO	54.03	54.46	54.55	54.00	53.62	54.09	53.88	53.32	54.06	53.76	50.98
MgO	1.06	1.03	1.00	1.15	1.10	1.01	0.91	0.75	0.73	0.84	0.96
CaO	0.15	0.17	0.13	0.13	0.18	0.19	0.29	0.31	0.31	0.36	0.09
Na_2O	0.02	-	-	0.03	-	-	-	0.03	-	0.05	-
K_2O	-	-	0.01	-	0.01	0.01	-	-	-	-	-
NiO	0.03	-	0.01	0.02	-	-	0.04	-	0.08	0.02	0.07
BaO	-	0.03	0.03	-	-	0.05	-	-	-	-	-
Total	100.22	99.67	100.85	99.64	99.30	99.58	100.54	100.14	99.78	99.08	100.67

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Table 4. Electron microprobe analyses of tephroite, sample Rz14.

	from core to rim				from rim to core				
	2	3	4	5	12	13	14	15	16
SiO_2	30.89	31.22	31.09	31.00	31.18	31.64	31.18	31.14	31.23
Al_2O_3	-	-	-	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-	-	-	-
FeO	1.83	1.74	1.89	1.83	1.68	1.79	1.90	2.16	2.01
MnO	62.45	63.04	62.78	62.62	61.92	61.24	62.26	63.16	62.10
MgO	4.31	4.31	4.38	4.45	4.32	4.38	3.68	4.40	4.22
CaO	0.06	0.04	0.06	0.16	0.07	0.10	0.07	0.04	0.06
NiO	-	-	0.02	-	0.07	-	-	0.05	-
Total	99.54	100.35	100.19	100.06	99.24	99.15	99.09	100.95	99.62

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Manganese humites form one the most typical assemblage of the Razoare ores, beside that of the olivines. The assemblage **tephroite-manganese humites** forms bands and lenses up to 1.5m thick, especially within the middle part of the ore-bearing sequence, rich in Mn and are silica undersaturated (Fig 1). The most striking feature of this assemblage is it restrictive mineralogical composition. Beside tephroite and manganese humites, the assemblage contains rhodochrosite, jacobsite, fluorapatite and less chlorapatite. The presence of Fe, Co, Bi and Ni sulphides/arsenides/bismuthinides as inclusions in jacobsite and tephroite-manganese humites, like arsenopyrite, cobaltite, gersdorffite etc (Tabel no 11) is another feature of this assemblage. The manganese terms determinated previously at Razoare, sonolite, leucophoenicite and probably alleghanyite, are intimately intergrown with tephroite (Hirtopanu et al., 1993, Udubasa et al. 1996).

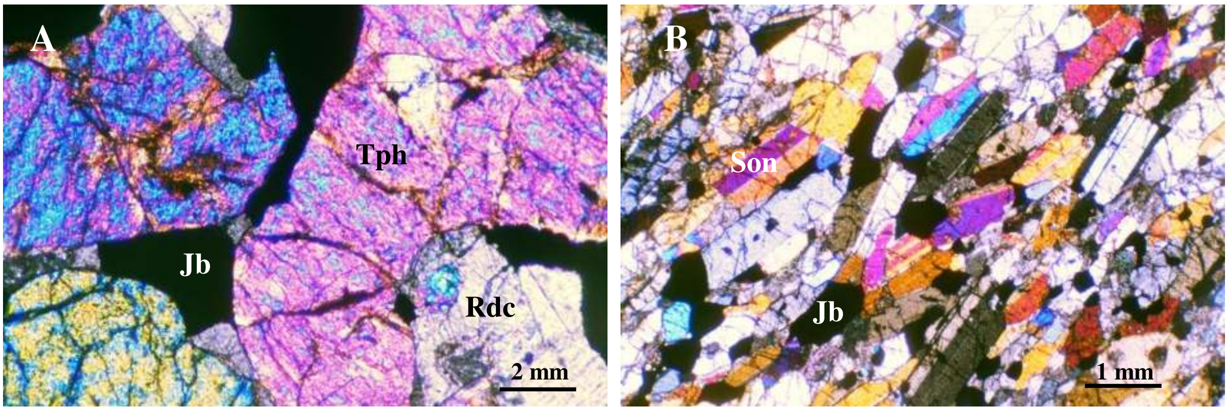

Fig. 4. A.Tephroite (Tph, big grains), jacobsite (Jb, black), rhodochrosite (Rdc), N+, sample Rz14; B. Sonolite monominerals (Son, twinned), N+, sample Rz522.

The Razoare humites coexist with tephroite, the tephroite coexists with rhodonite (Figs 8A and 8B) in rhodochrosite environment, but the humites are not stable relative to rhodonite. Qualitative phase equilibria suggest that the humites assemblages require water-rich conditions to form in silica undersaturated rocks during regional metamorphism and that variations in $X_{H2O}/(X_{H2O}+X_{CO2})$ may account for their formation. Also, the effect of F could be considered as a diluents in humites, extending their stability somewhat with respect to rhodonite and tephroite (Winter et al, 1983).

Table 5. Electron microprobe analyses of sonolite.

	Sample Rz550, points 100-104; points 115, 117-123										
	From rim to core			from rim to core			from rim to core				
wt%	102	103	104;	115	117	118	119	120	121	122	123
SiO_2	27.17	26.59	27.51	27.12	27.45	27.45	27.25	27.32	27.54	27.55	27.71
Al_2O_3	-	0.01	0.02	0.02	-	-	-	-	-	0.03	-
TiO_2	0.03	0.01	0.04	-	-	0.02	-	-	0.05	0.01	0.03
FeO	0.39	0.51	0.55	0.44	0.51	0.52	0.55	0.62	0.75	0.64	0.50
MnO	68.28	68.02	66.69	65.76	68.11	68.11	67.47	67.30	66.55	66.94	65.89
MgO	1.64	1.66	1.59	1.58	1.53	1.68	1.72	1.79	1.58	1.83	1.99
CaO	0.07	0.05	0.06	0.06	0.03	-	0.06	0.08	0.09	0.05	0.05
Cl	-	-	0.24	-	-	0.67	0.14	-	1.02	-	-
F	-	0.04	-	0.46	-	0.67	0.14	-	1.02	-	-
total	97.58	94.89	96.70	95.44	97.63	98.47	97.19	97.11	97.58	97.05	96.29

-continued from rim to core-

wt%	124	125	126	127	128	129	130	131	132	133	134	135	136	137
SiO_2	27.70	27.83	27.53	27.68	27.54	27.70	27.51	27.46	27.56	27.75	27.31	27.49	27.52	27.19
Al_2O_3	-	0.02	0.07	-	0.02	-	-	-	-	-	0.04	-	0.03	-
TiO_2	0.03	0.08	0.04	-	-	-	0.01	-	0.04	-	0.03	0.01	-	-
FeO	0.56	0.75	0.60	0.74	0.66	0.73	0.61	0.68	0.79	0.68	0.60	0.73	0.59	0.74
MnO	67.49	67.75	67.53	67.84	66.30	66.91	66.99	66.54	66.10	66.68	66.18	66.62	66.34	66.47
MgO	1.53	1.73	1.58	1.63	1.44	1.62	1.64	1.68	1.72	1.96	1.76	1.73	1.49	1.82
CaO	0.04	0.05	0.06	0.04	0.04	0.05	0.03	0.04	0.04	0.06	0.07	0.03	0.04	0.06
Cl	-	0.05	-	0.06	0.03	-	-	-	-	-	-	0.11	-	0.05
F	0.06	0.30	-	-	-	-	0.12	0.16	0.38	-	0.55	-	0.03	-
total	97.41	98.56	96.41	97.99	96.03	96.59	96.89	96.56	96.73	97.13	96.54	96.72	95.54	96.33

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The electron microprobe analyses (Table 5) show that the sonolite has a near $Mn_9(SiO_4)_4(OH)_2$ pure end member composition (%wt): SiO_2 = 26.59- 27.19, MnO = 65.89-68.28, FeO = 0.39-0.79, MgO = 1.36-1.99, CaO = 0.03-0.07, F = 0-1, Cl = 0-0.26, (OH) was calculated by difference (Hirtopanu et al., 2015). Compared with most of the previously published data of analyses of Mn-humites (Winter et al., 1983), the sonolite at Razoare is impoverished in F substituting for OH. When the F is present, its content rarely reaches 0.55 and very rarely 1%wt. The chlorine is present in very low content (0-0.26 %wt). The elements, Ti, Al and Ca are present only as minor elements. The iron is less than magnesium, varying between 0.39-0.79. The sonolite shows euhedral prismatic red pink, bright, transparent crystals with a glassy luster and of up to 0.5cm (and more) in size. Under the microscope they are colourless/light pink, sometimes exhibiting a slightly developed cleavage. The birefringence is relatively high and the optical angle (-2V) has high values. Polysynthetic twins may be always observed (Fig 4B), sometimes with a symmetrical development. The tephroite are in places mantled by sonolite but they seem to be also in direct contact, having the substitution relations. The electron microprobe analyses of tephroite show a slightly magnesian term. Being an almost pure term, with very low forsterite content, the Razoare tephroite prevailing up to amphibolites facies (Dasgupta, 1990). The components of rhodochrosite associated to tephroite are: $FeCO_3$=0.4, $MnCO_3$=88.1, $MgCO_3$=5, $CaCO_3$=6.5 (mol%). Very localized conditions might be needed for the formation of the sonolite at the expense of tephroite: a nearly closed system rich in Mn and silica undersaturated, water rich conditions, variations in X_{H2O}/X_{CO2} and $a(SiO_2)$. Other terms of manganese humites determined previously in Razoare ores are: manganhumite, alleganyite, ribbeite leucophoenicite, jerrygibbsite (Hirtopanu et al, 1993).

Garnets. Altough relatively frequent being present in almost all assemblages of ores, but with different chemical composition, corresponding to that of the each metamorphism types. The rich calderite spessartine is associated with manganoan orthopyroxene and manganoan fayalite (Figs 2A, 2B). The experimental data show that the calderite content of garnet is a function of pressure, or, alternatively, is dependent on the Ca content of the bulk composition.The spessartine garnet is commonly intergrown with manganoan fayalite-mangangrunerite±magnetite-apatite±quartz and less with pyroxmangite. The spessartine-andradite/grossular is noncubic and anisotrop (Fig 6B). This is a last type of garnets appearance, occurring with the change metamorphism conditions, especially that of the f_{O2}, beside the lowering of T and P and as well as with some changes in mineralogical environment. The old spessartine sometimes is corroded by quartz and substituted by manganoan actinolite (Fig. 6A). The wet chemical analyses of garnets have shown that they range into calcian and ferrian varieties of spessartine (Table 6). The variations of the garnets components are (mol%): 39-64 spessartine, 7-17 andradite, 3-13 grossular, 13-20 calderite, 11-27 almandine and 1-4 pyrop. The Razoare garnets are essentially spessartine rich, but may contain appreciable calderite, andradite, almandine and grossular component, and is poor in pyrop. The calderite component is present in garnet of manganoan fayalite while the andradite/grossular component is present in garnet of mangangrunerite/pyroxmangite associations.

The main term of **amphiboles group** is the **mangangrunerite** (former dannemorite). It is frequently associated with garnets, apatite, magnetite and relics of manganoan fayalite (Figs 5A and 5B). When the manganoan fayalite relics disappear from assemblage, the quartz occurs. The Razoare

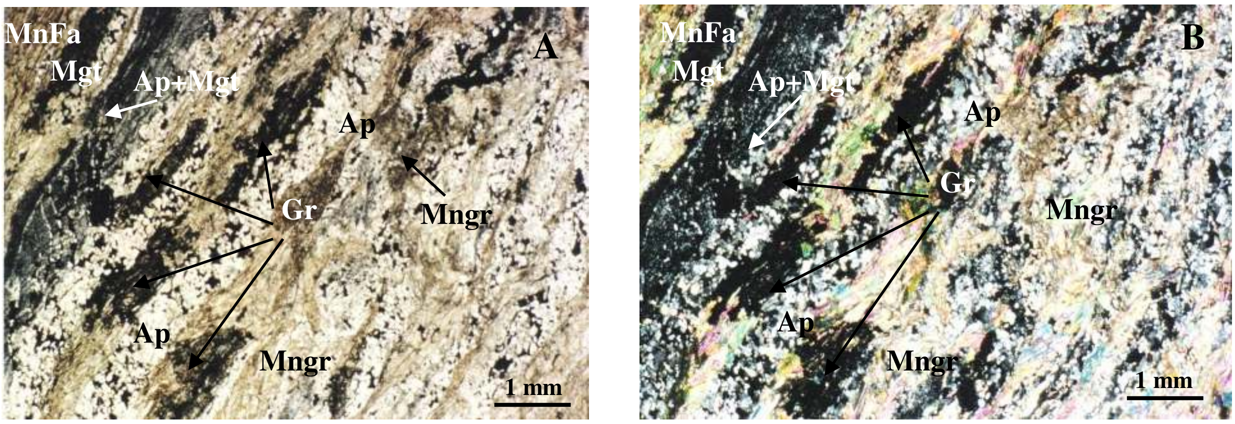

Fig. 5.A. Banding of mangangrunerite (Mngr)+garnet (Gr), apatite (Ap), (apatite+magnetite) manganoan fayalite (MnFa), NII; B. The same image in N+, sample Rz 167.

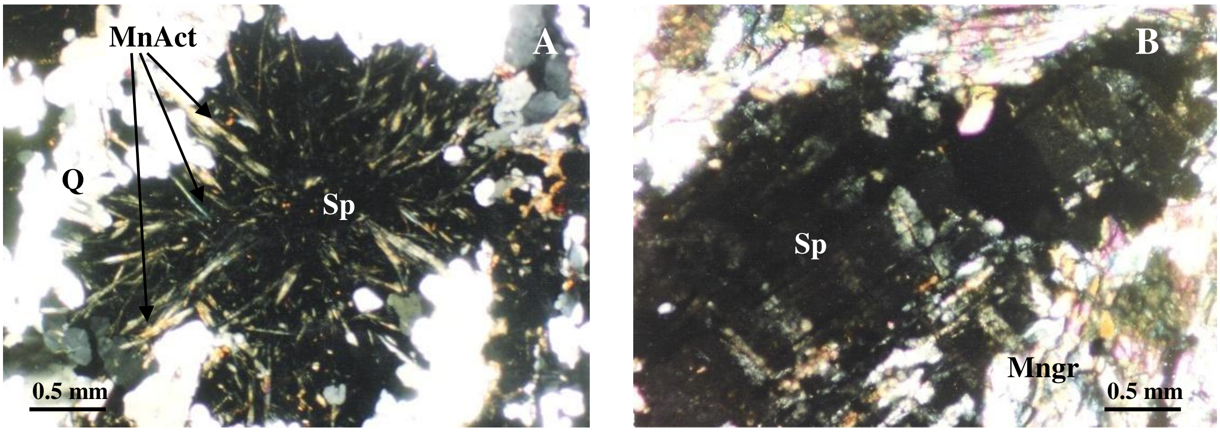

Fig. 6.A. Spessartine corodated by quartz and substituted by needles of manganoan actinolite, N+, sample Rz189b; B. Spessartine-andradite, partially anisotrop enclosed in mangangrunerite, N+, sample Rz5863.

Table 6. Wet chemical analyses of spessartine.

%wt	Rz32A	Rz29	Rz129;	Rz40	Rz145	Rz146	Rz45
SiO_2	34.69	36.18	35.91	33.70	34.00	33.47	35.30
Al_2O_3	18.39	19.17	19.06	18.82	17.95	18.62	19.48
TiO_2	0.35	0.76	0.65	0.29	0.26	0.38	0.89
Fe_2O_3	6.89	5.62	1.78	9.79	4.00	3.37	7.52
FeO	10.54	4.59	8.20	8.94	3.15	3.65	6.19
MnO	22.72	26.50	26.54	23.86	37.06	36.31	25.62
MgO	0.78	0.72	0.62	0.57	0.53	0.60	0.50
CaO	2.80	6.54	7.27	2.71	1.68	1.54	4.46
Na_2O	0	0	0.03	0	0	0.02	0
K_2O	0	0	0.10	0	0	0	0.04
P_2O_5	0	0	0	0.30	0.04	0.05	0.04
H_2O+	0	0	0	0.39	0.28	1.76	0
Total	99.92	100.20	100.16	99.37	98.95	99.77	100.04

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mangangrunerite is retrograde after orthopyroxene, coexisting with manganoan fayalite in assemblage, as the temperature is lowered. The replacement of manganoan fayalite and manganoan ferrosilite-enstatite by mangangrunerite depends of the availability of water as the temperature and pressure are lowered, and of the T-f_{O2} conditions of the original assemblages. The mangangrunerite has FeO higher than MnO and less MgO contents (Table 7). The other iron rich mangangrunerite occurrences reported in the world belong to upper amphibolites-granulite facies conditions. **Manganoan actinolite** was formed at the expence of garnets (Fig 6A), as secondary mineral.

Table 7. Wet chemical composition of mangangrunerite.

%wt	Rz137	Rz169	Rz32A	Rz47	Rz198	Rz56	Rz128	Rz130	Rz175
SiO_2	46.56	49.04	48.49	49.84	45.51	47.45	43.82	50.21	42.97
TiO_2	0.15	0.17	0.17	0.20	0	0.08	0.02	0.12	0.08
Al_2O_3	0.37	0.11	0.62	0.40	0	0.20	0.40	0	0.16
Fe_2O_3	4.34	5.10	3.69	5.09	10.66	5.25	4.77	4.83	4.62
FeO	21.93	23.93	22.50	23.81	16.56	19.33	18.41	18.13	19.11
MnO	18.12	12.40	12.96	11.04	21.42	12.65	21.05	11.05	21.30
MgO	6.79	7.12	7.83	7.12	2.67	9.45	4.39	10.05	7.80
CaO	1.35	0.47	0.90	0.38	1.81	0.72	2.25	1.12	1.31
K_2O	0	0	0.04	0.06	0.0	1	0.04	0.01	0.04
Na_2O	0	0	0.07	0.07	0.05	0.06	0.07	0.04	0
P_2O_5	0.37	0.02	0.11	0	0	0.15	0.88	0.59	0.36
H_2O^+	0.20	1.01	1.17	1.44	0.31	2.02	1.75	0.83	0.58
P.C.	-	-	-	-	-	2.14	2.04	2.01	0
Total	100.18	99.40	99.56	99.45	99.00	99.54	99.86	99.63	98.30

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The mangangrunerite has FeO higher than MnO and less MgO contents (Table 7). The other iron rich mangangrunerite occurrences reported in the world belong to upper amphibolites-granulite facies conditions. **Manganoan actinolite** was formed at the expence of garnets (Fig 6A), as secondary mineral.

Pyroxenoids group. The **pyroxmangite** generally forms almost monomineral lens, which are banding with fluorapatite/apatite, ferroan tephroite (Figs 7A, 7B), mangangrunerite and rhodochrosite. It is is a major component of ore, occurring in three generations, which differ in grain size, mineral assosiations and chemical composition: a) the oldest fine grained pyroxmangite form intergrowths/alterning bands with ferroan tephroite (Figs 7A, 7B) ; b) euhedral pyroxmangite as well as well developed crystals up to 5cm in size in some pegmatoid lenses within the ores; it is closely associated with coarse grained manganoan fayalite, spessartine and mangangrunerite; c) pyroxmangite of the vein, cutting across the bedded ores. Their chemical composition has a degree of FeO content from the oldest to the last generations, from 18.33 to 7.36, respectively (Table 8). Some very little grains showing some Ca content, besides high Fe and Mn, with Fe>Mn, determined with electron microprobe, could be pyroxferroite or at least a term of pyroxmangite-pyroxferroite series. A wide range of solid solution exists between $MnSiO_3$ and $FeSiO_3$ in pyroxmangite, while rhodonite shows complete solid solution between $MnSiO_3$ and $CaSiO_3$. The synthesis works have shown that pyroxmangite of $MnSiO_3$ composition is the high pressure, low temperature polymorph with respect to rhodonite of the same composition (Maresh and Mottana, 1976). In Razoare deposit the pyroxmangite does not coexists with rhodonite. The Razoare rhodonite belongs to tephroite assemblages and the pyroxmangite is associated with ferroan tephroite, manganoan magnetite, less with mangangrunerite and rarely with relics of manganoan fayalite. The compositions of coexisting pyroxmangite and rhodonite from other occurrences define the miscibility gaps at the ambient physical conditions of metamorphism (Winter et al., 1981). The low Mg content (Table 8) of pyroxmangite is a composition restricted at high T (Brown et al., 1980).

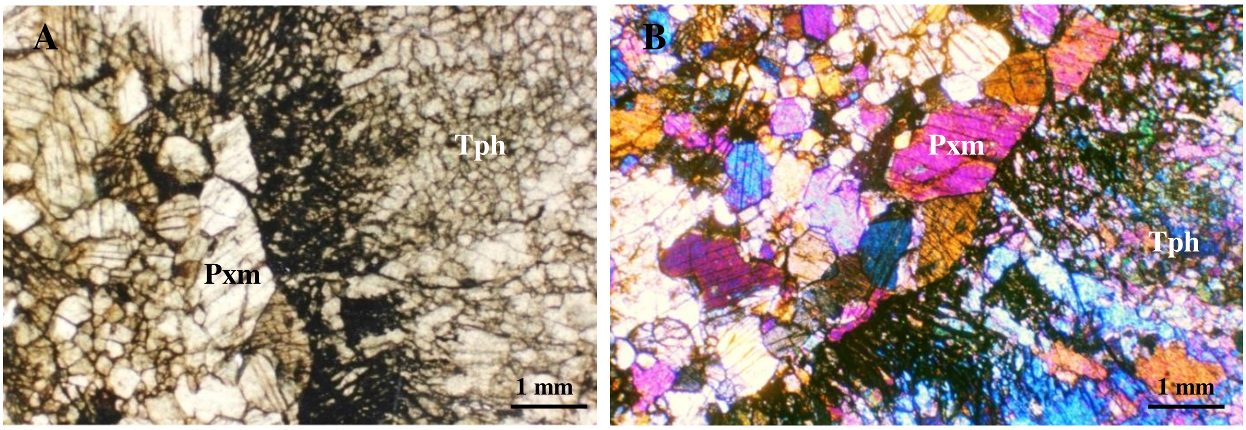

Fig. 7. Contact pyroxmangite (Pxm) band with ferroan tephroite (Tph) band, NII (A), N+ (B), sample Rz516.

Table 8. Wet chemical analyses (wt%) of Razoare pyroxmangite.

	Rz516	Rz516A	Rz49	Rz145	Rz44	Rz26	58B	Rz65	Rz113	Rz129A	Rz196B	Rz212	Rz214	Rz60C	Rz92	Rz20	Rz162
SiO_2	41.65	45.42	42.76	46.00	44.32	45.27	44.83	46.36	46.03	44.00	46.92	46.30	46.0	45.16	44.18	45.56	45.42
Al_2O_3	1.95	0.14	0.02	0.66	0.11	0.27	0.04	0	0	0.19	0	0	0	0	0.50	0	0.27
TiO_2	0.02	0.09	0.12	0.04	0.05	0.04	0.06	0.16	0.14	0.04	0.10	0.27	0.13	0.01	0.04	0.02	0.14
Fe_2O_3	1.67	0.80	1.48	2.82	1.62	2.15	1.77	1.87	1.1	1.73	1.17	0	2.34	3.19	2.07	6.51	1.54
FeO	8.92	6.84	9.07	2.63	8.38	17.82	17.97	14.68	7.36	14.32	15.79	18.00	14.73	18.57	18.33	16.57	13.77
MnO	40.69	41.38	42.22	44.52	39.37	28.32	29.45	33.37	41.26	29.44	29.78	31.60	32.28	28.73	29.67	27.23	30.11
MgO	0.78	0.88	1.32	1.79	2.74	3.00	3.33	1.54	2.20	2.40	2.56	2.47	2.02	1.83	2.60	1.49	5.28
CaO	2.82	4.05	1.06	1.17	1.30	2.17	1.80	1.63	1.05	6.10	2.87	1.26	1.55	1.79	1.68	1.95	2.14
Na_2O	0.02	0.01	0	0.01	0	0	0	0	0	0.87	0	0	0	0.15	0	0.17	0
K_2O	0	0	0	0.02	0.01	0.01	0	0.01	0.02	0	0.02	0.02	0.01	0	0.02	0	0.02
P_2O_5	-	-	0.22	0.06	0.06	0.65	0.25	0.10	0.12	0.48	0.05	0.05	0.04	0.07	0.22	0.06	0.42
H_2O^+	0.59	0.39	-	-	-	-	-	0	0.18	0	0.30	0	0	0	0	0	0
Total	99.34	100.04	98.27	99.72	99.96	99.70	99.50	99.72	99.59	99.61	99.56	100.83	99.48	99.5	99.31	99.56	99.11

Analyst Erna Calinescu

The pyroxmangite aggregates/grains display different colors and/or colors shades (roz, pink, reddish, brown, grey-yellowish as depending of the grain size and environment. Under the microscope it shows (010) and (001) cleavagesas as well as partings. The 2V angle is positive and has values around 30^0, suggesting relatively high FeO contents, a fact confirmed by chemical analyses (Table 8). **Rhodonite** occurs rarely by comparison with pyroxmangite. Because of the close similarity to pyroxmangite in appearance, some of its occurrences may have been overlooked. The formation of this mineral was favored by the scarcity of iron and the presence of Ca in place of crystallization. The chemical composition of the environment plays a more significant role in appearance of rhodonite relative to pyroxmangite, than does the surrounding condition of formation. The experimental data and natural assemblages, discussed by various authors, indicate that the stability of rhodonite with respect to that of pyroxmangite is favored by the presence of Ca, whereas the stability field of pyroxmangite is enlarged by incorporation of Fe^{2+} and Mg. The rhodonite substitutes tephroite (Figs 8A and 8B), the last one occuring as relics. This substitution is caused by local increase of f_{CO2} in ore, and the formation of rhodonite is due to the reaction: $Mn_2SiO_4+CO_2=MnSiO_3+MnCO_3$. The chemical composition of Razoare rhodonites (Table 9) are rich in Ca and poor in Fe, while the pyroxmangites are rich in Fe and poor in Ca, thus the two minerals differ in composition, which conform with their formation environment, between them being a compositional gap. This compositional gap between rhodonite and pyroxmangite is constrained for middle-upper amphibolites facies conditions (Brown et al., 1980). The associated minerals to rhodonite include rhodochrosite, tephroite, fluorapatite. The Razoare rhodonite never appears with pyroxmangite, each of them forming distinct associations/ore types. Rhodonite shows complet solid solutions with $CaSiO_3$ component and pyroxmangite shows a rather limited content of $CaSiO_3$, but higher $FeSiO_3$ in solid solution. By contrast, a wide range of solid solution exists between $MnSiO_3$ and $FeSiO_3$. In granulite facies rocks, the $FeSiO_3$ content of pyroxmangite may be appreciable reaching Mn/Fe<1 (Dasgupta et al., 1990). The Razoare pyroxmangite $FeSiO_3$ contents corresponds to its genesis under the amphibolte facies conditions, this being typical when the pyroxmangite coexists with manganese carbonate.

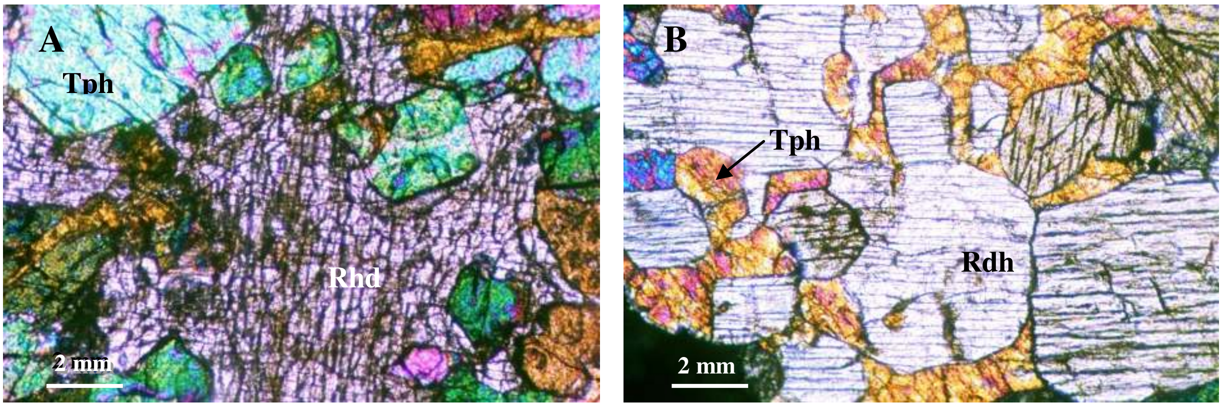

Fig. 8.A. Rhodonite (Rhd, two cleavages, low birefringence), tephroite (Tph, high birefringence), N+, sample Rz561
B. tephroite (Tph, high birefringence) relics in rhodonite (Rhd, cleavages, low birefringence), N+, sample Rz565.

Table 9. Electron micoprobe analyses (A) and wet chemical analyses (B) of rhodonite from core
A. points 138-145, sample 561; points 14-15, 18, sample Rz561A; B. wet analyses: sample Rz561B, C, D, P, Rz516.

	A										B				
	138	139	140	141	143	144	145	14	15	18	561B	561C	561D	Rz561P	Rz516
SiO_2	48.19	47.97	47.99	48.25	47.83	47.90	47.55	48.08	46.97	47.74	48.00	48.03	47.70	45.22	45.42
Al_2O_3	0.06	-	0.01	-	-	0.02	0.02	-	-	-	0	0	0	0.17	0.14
TiO_2	-	0.03	-	-	-	0.02	0.03	-	-	-	0	0	0	0.04	0.09
Fe_2O_3	-	-	-	-	-	-	-	-	-	-	0.19	0.10	0.34	1.64	0.80
FeO	3.24	3.38	3.57	3.35	3.33	3.30	3.35	5.89	6.10	4.94	5.00	3.00	3.30	5.53	6.84
MnO	39.86	40.04	40.59	40.26	41.24	43.26	43.44	41.87	42.30	42.36	41.80	40.30	41.36	40.84	41.38
MgO	0.64	0.73	0.67	0.58	0.70	0.67	0.74	0.50	0.47	0.53	0.50	0.64	0.70	0.78	0.88
CaO	7.75	7.94	7.24	7.70	6.82	5.62	4.32	4.53	4.41	4.50	4.50	7.40	6.80	4.57	4.05
Na_2O	0.05	-	0.08	-	-	-	0.01	-	-	-	0.05	0.05	0	0.02	0.01
K_2O	-	-	-	0.01	-	-	-	-	-	-	0	0	0	0	0
NiO	0.01	-	0.16	0.03	-	0.02	0.01	-	-	-	-	-	-	0	0
BaO	0.14	0.03	-	-	0.01	0.04	-	-	-	-	-	-	-	0	0
Total	99.94	100.12	100.31	100.18	99.93	100.85	99.47	100.87	100.25	100.07	100.08	99.52	100.2	99.26	99.61

Analyst Masaaki Shimizu

Analyst Erna Calinescu

Tourmaline group, is represented by **dravite**. It occurs in manganese humites/ jacobsite /fluor-apatite/ rhodochrosite assemblages as accessory mineral in grains of a few mm in size. Dravite have been formed mainly in recrystallized and hydrothermally altered areas and in hydrothermal veinlets. The boron of dravite, as well as of other borates, have been derived by the local hydrothermal reworking and leaching of earlier boron bearing minerals of the deposit.

Epidote group contains two minerals: **piemontite** and **allanite-(La)** (Table 11). In the ferroan tephroite assemblage appears as accessory mineral allanite-(La) with the following composition (wt %): SiO_2 =32.50, TiO_2=1.10, Al_2O_3=11.50, CaO=7.90, Fe_2O_3=1.40, FeO=5.43, MgO=2.20, MnO=20.10, La_2O_3=17.70 Ce_2O_3=6.50, Pr_2O_3=0.45, Nd_2O_3=0.90, Sm_2O_3=0, Gd_2O_3=0, ThO_2=0, F=0.

Phyllosilicates group is present rarely as primary mineral, occuring as **manganoan biotite**, in the mangangrunerite assemblage. In the manganese humites assemblage was determined, **caryopilite** and **friedelite,** phyllosilicates with chlorine, as secondary minerals. Their formation is due to the reaction of rhodonite with HCl and H_2O. The caryopilite, determined with X-ray analysis is associated with pennantite and diverse manganese arsenates, secondary carbonates and phosphates. The **kellyite,** manganese analogue of amesite, belongs to undersaturated assemblages. It is associated with tephroite, sonolite, jacobsite and manganese chlorites. The **manganoan hissingerite** is associated with pyrrhotite.

Chlorites group belong to series **penanntite-clinochlore** with more development of the manganese term, penanntite. It is lamellar, micaceous, with orange yellow, reddish brown color. In transmitted light, the pennantite is orange, pinkish red, yellow orange, with clearly pleochroism and perfect cleavage. It is formed during hydrothermal alteration of tephroite and manganese humites (Fig 9A). The pennantite occurs as small veins in association with manganese arsenates and secondary manganese carbonates. Other chlorites determined in Razoatre deposit one can see in Table 11.

Other silicates are showed in Table 11. Between them, **yoshimuraitete, zircon** and **ericssonite** are newly determined in Razoare deposit. The ericssonite is a rare Ba silicate mineral, determined with scanning electron microscop. It occurs accessory in the tephroite+manganese humites assemblages.

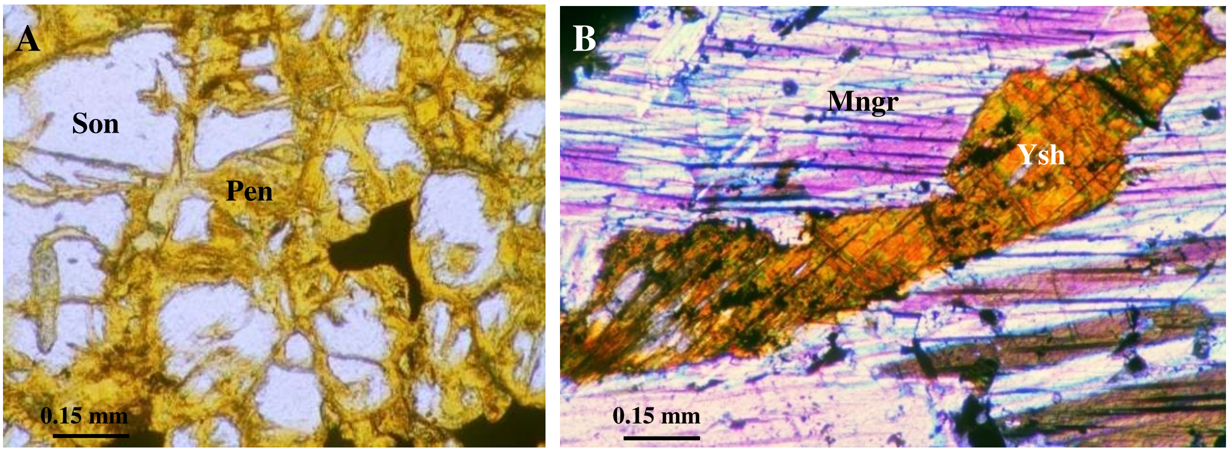

Fig. 9. A. Pennantite (Pen, yellow-orange) substitutes sonolite (Son, white), sample Rz524. B. Yoshimuraite (Ysh) in twinned mangangrunerite (Mngr), N+, sample Rz5912; B.

Yoshimuraite, $Ba_2TiMn_2(SiO_4)_2(SO_4,PO_4)(OH,Cl)$, is a complex barium-titanium-manganese sulphate-phosphate-silicate. The X-ray data powder pattern: 3.4(100), 2.9(100), 3.25(60), 2.72(60), 4.9 (60), 4.11(40), 3.14(40); cell parameters (Å): a=5.386, b=6.999, c=14.748, α=89.980, β=93.620, γ=95.500, Z=2, v=552.28, Density=4.395. In transmitted light it is brown, orange, yellow, yellow green, with weak pleochroism, perfect cleavage, biaxial (+2V≈85). Yoshimuraite occurs associated with tephroite and mangangrunerite (Fig. 9B).

III. Oxides, hydroxides

The most frequently encountered oxides are **magnetite** and **jacobsite**. Magnetite belongs to manganoan fayalite asemblage, while jacobsite belongs to manganese humites assemblage. They do not occur together. Three generation of magnetite have been identified, i.e., magnetite I, associated to manganoan fayalite, magnetite II, associated to mangangrunerite and magnetite III, which appears as a product of pyrrhotite decomposition, being closely intergrown with secondary pyrite. This transformation is related to the introduction of water in system which seems to cause also the transformation of magnetite into **maghemite.** It is presumed that the pyritization of pyrrhotite and the maghemitization of magnetite represent simultaneous processes. The jacobsite shows reaction texture with rhodochrosite. The **manganoan magnetite** (6%MnO) is associated with pyroxmangite. Generally, the jacobsite grains are euhedral, but sometimes, anhedral grains tend to cement the tephroite (Figs 10A and 10B) or the manganese humites. Accessory **pyrophanite** was determined microscopically in some sulfide rich samples and with electron microprobe in pyroxmangite dominated assemblages, as very little veins. The pyrophanite chemical composition, determined with electron microprobe has the following variations (wt%): TiO_2= 53.0-54.8, FeO=17.89-18.30, MnO=28.0-29.55. In some grains of jacobsite, was determinated the **hausmannite**, as discrete independent grains, that could be a exsolution from jacobsite. It was formed during cooling from a common solid solution with jacobsite. Jacobsite occurs in thin bands parallel to the general ore trend, alternating with tephroite-manganese humites bands. It is not in direct contact with quartz, pyroxmangite, rhodonite and spessartine. Chemically, the Razoare jacobsite contains about 60%Fe_2O_3 and 30%MnO. Some S contents in its chemical composition are due to the sulfides inclusions (Table 10). The Razoare jacobsite shows no considerable variation in Fe_2O_3 and MnO contents (Table 10). The content of Al_2O_3 belongs most probably to some accessories minerals, like **galaxite** and kellyite. In reflected light some grains with an intermediate color between magnetite and jacobsite, could be probably **iwakiite**.The Fe-Mn lower oxides were formed through prograde decarbonation-oxidation with unbuffered X_{CO2}, from a carbonatic precursor or Mn-Fe oxides admixed with carbonates one.

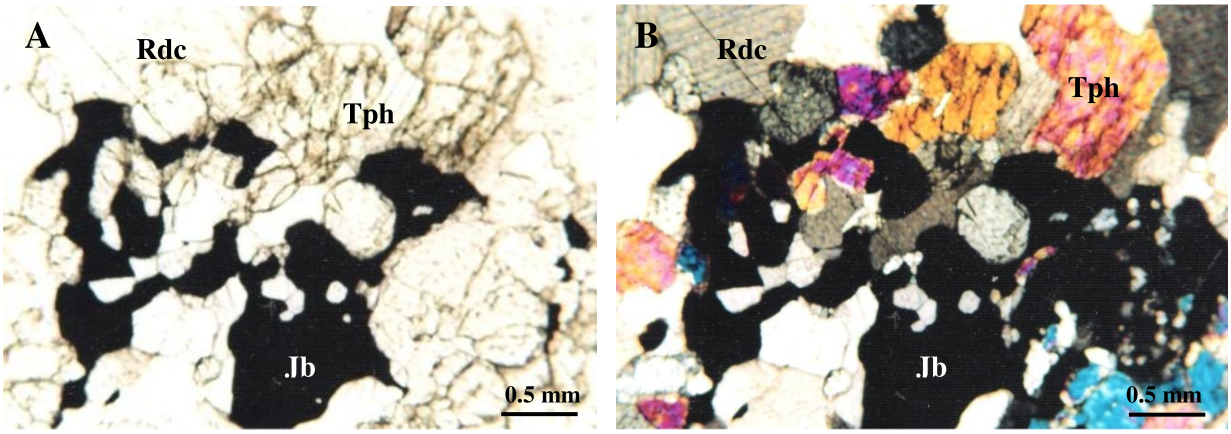

Fig 10. Tephroite (Tph, white), jacobsite (Jb, black), rhodochrosite (Rdc), NII (A) and N+ (B), sample Rz14.

Table 10. Wet chemical composition of magnetite (A)and jacobsite (B).

	A. Magnetite						**B.** Jacobsite		
Samples	Rz50B	Rz53D	Rz53	Rz50	Rz47	Rz562	Rz102	Rz191	Rz530
SiO_2	-	-	2.09	0.97	1.69	0	0.29	0.24	0
TiO_2	0.22	0.22	0.20	0.22	0.20	0.18	0.21	0.20	0
Al_2O_3	0.20	0.27	0.20	0.19	0.16	0.07	2.37	2.37	2.37
Fe_2O_3	66.74	62.42	64.22	64.56	65.08	68.20	59.58	60.86	60.23
FeO	23.57	24.53	23.21	24.51	25.40	26.21	1.55	1.97	4.20
MnO	1.54	1.20	1.88	1.63	1.25	5.05	31.12	28.93	32.12
MgO	0.18	0.11	0.39	0.21	0.34	0.10	0.48	0.83	0.40
CaO	2.34	4.14	4.21	4.25	2.84	0	0.37	0.42	0.37
K_2O	-	0.04	0.02	0.05	0.01	0	0.02	0.02	0
Na_2O	0.33	0.	36	0	0.01	0	0.04	0.04	0
P_2O_5	2.24	3.56	3.65	2.82	2.65	-	0.05	-	0.30
S	-	-	-	-	-	-	2.34	2.24	0
Total	99.97	99.57	100.07	99.42	99.62	-	98.42	100.09	99.99

Analyst Erna Calinescu

IV. Sulphides, tellurides, arsenides, bismuthinides

Sulphides. The **pyrrhotite** is the most frequent sulfide, especially in mangangrunerite dominated assemblage. Sometimes, the pyrrhotite is accompanied by **chalcopyrite,** and accidentally it contains minute grains of gold. Locally, it is completely altered to a lamellar intermediary product and/or fine aggregates of pyrite-magnetite-marcasite. Globular grains of pyrrhotite enclosed in silicates have been observed as well. Some grains of pyrrhotite are oxidized and replaced by Fe-oxyhydroxides, Fe-sulfates, Fe-silicates (hissingerite). The **pyrite** aggregates or crystals up to 4cm in size, were formed either by substitution of pyrrhotite or by direct deposition in some breccias surrounding fractures. The rare **molybdenite** grains have been observed within the mangangrunerite rich aggregates. The **sphalerite** is iron rich composition: ZnO=45.0, FeO=11.0, MnO=1.5, S=50.5. Other sulfides recognized at Razoare (galena, marcasite, etc) one can see in Table 11. A big variation of many terms of **arsenides, sulfoarsenides** (**Co, Ni arsenides) and bismthinides** (Table 11) were determined in in tephroite-manganese humites association. All these minerals, have been determined in reflected light and with electron microprobe and their chemical composition have been established. Bi minerals with mm/micronic size like native bismuth, **Bi-tellurides** (Figs 10A and 10B), **Bi-Te sulfides**,**bismuthinite**, were formed genetically associated with locally hydrothermal activity accompanying a later lower grade metamorphism. Their metal contents have derived from the local hydrothermal reworking and leaching of the preexisting minerals in the ore body. Some zoned rammelsbergite and gersdorfitte grains have chlorine contents (3-5%wt): Ni,As,Cl in centre, Ni,As,S in the midlle and Ni,As,S,Cl in the marginal parts. Other grains have Ni,As, Cl in centre and Ni,As, S, Cl marginal. Some zoned grains have Ni arsenides in centre and sulfides-arsenides on the edges. The mineralizing process was multistages, with the fluctuations in the composition of the hydrothermal fluid.

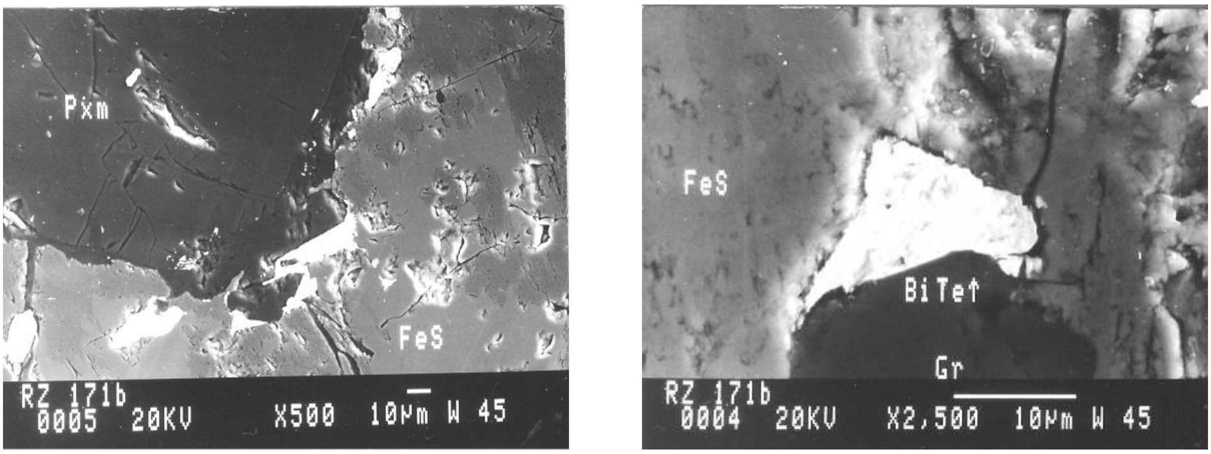

Fig 10 A. Bi-tellurides (white, microveinlets), in pyroxmangite (Pxm) and pyrrhotite (FeS); B. Bi-tellurides at pyrrhotite (FeS)/garnet (Gr) contact, sample Rz171.

V. Phosphates, arsenates

V.a. Phosphates are abundant in all mineral assemblages. The apatite is frequent in the old association, where it form monomineralic bands, alternating with manganoan fayalite-manganoan ferrosilite (Fig. 4A, 4B) The **fluorapatite** and less **chlorapatite** are typical for tephroite-manganese humites assemblages. Some of secondary phosphates like switzerite, vivianite, etc. (Table 10), have appeared at the expense of primary phosphates. Worth of mention is the presence of yttrium phosphates, **xenotime-(Y**), as accessory mineral in pyroxmangite association. In the same association, the xenotime-(Y) occurs with other accessory minerals, like **monazite-(Ce),** zircon, and manganoan barite. In the one microprobe analysis of xenotime-(Y) were determined europium (Eu_2O_3=1.79%wt) and gadolinium (Gd_2O_3=1.8%wt). The monazite-(Ce) are rich in Ce, La and Nd.

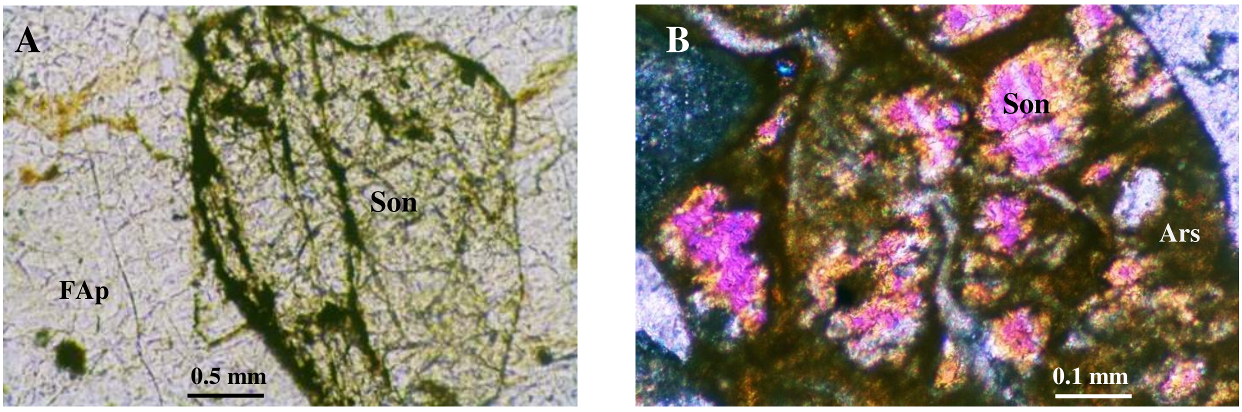

Fig. 11. Fluorapatite (FAp) (pink) with enclosed sonolite (Son) grain, NII, Rz100; B. Arsenoclasite (Ars) substituted twinned sonolite (Son), N+, sample Rz525.

V.b.Arsenates present a wide variety containing Mn, Fe and less Mg as the main cations. The most of them are of low temperature affiliation. The manganese arsenates **(arsenoclasite, sarkinite, eveite,** etc.) were formed at the expense of arsenide/sulphoarsenide (arsenopyrite, lollingite, cobaltite, rammelsbergite, skutterudite etc) (Table 11). The arsenoclasite from sample Rz100P has cell data: a=9.31, b=5.75, c=18.29, Z=4, volume=979.11, Density=4.16. It substituts manganese humites (Fig. 11B). The arsenates are associated with many secondary Mn-carbonates and Mn-chlorites, also formed on the primary minerals (tephroite, sonolite, old rhodochrosite). All these minerals represent the latest retromorphic parageneses.

VI. Native elements

The **graphite** are always present in the ores as small amounts. Rounded graphite aggregates, sometimes with radially disposed lamellae enclosed either in silicates or in sulfides (pyrrhotite and pyrite) are very typical of the Razoare ores. It is not associated with magnetite. Presence of graphite in these assemblages demonstrates that a low f_{O2} was maintained throughout the high grade metamorphic regime. The experimental data show that the stability of graphite decrease with rising T, and increase with rising of P. The **native gold** was determined in reflected light (oil immersion), as minute grains enclosed in chalcopyrite and in jacobsite. The **native bismuth** occur in manganoan fayalite /mangangrunerite assemblages in close association with Bi-tellurides and bismuthinite. Also, some small Bi native grains were determined by electron microprobe in pyroxmangite and pyrrhotite.

Table 11. Mineral list at Razoare Mn-Fe.

Minerals	Sources													
Ia. Carbonates class														
1. Rhodochrosite $MnCO_3$	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(X*)
2. Rhodochrosite ferroan (Mn, Fe), CO_3														
3. Siderite $FeCO_3$			(3)						(9)	(10)		(12)	(13)	
4. Mn-calcite $(Ca,Mn)(CO_3)$								(8)						
5. Aragonite $CaCO_3$								(8)						(X*)
6. Witherite $BaCO_3$								(8)						(X*)
7. Witherite, manganoan $(Mn,Ba)CO_3$								(8)						(X*)
8. Holdawayite $Mn_6(CO_3)_2(OH)_7(OH,Cl)$							(7)	(8)					(13)	(X*)
9. Calcite $CaCO_3$							(7)	(8)					(13)	
Ib. Borates class														
10. Jimboite $Mn_3(BO_3)_2$ (?)														(X*)
11.Wiserite $Mn_4(B_2O_5)(OH,Cl)_4$ (?)														(X*)
12. Sussexite $MnBO_3$ (?)														(X*)
II. Silicates class														
Pyroxene groupe														
1.Manganoan ferrosilite-enstatite $(MnMgFe)_2(SiO_3)_2$					(5)		(7)	(8)					(13)	(X*)
Olivine group														
2. Mn-Fayalite $(Mn,Fe)SiO_4$				(4)	(5)	(6)	(7)							
3. Tephroite, ferroan $(Fe,Mn)SiO_4$				(4)			(7)							(X*)
4. Tephroite $MnSiO_4$					(5)		(7)	(8)					(13)	(X*)
5. Forsterite $MgSiO_4$			(3)											
Manganese humites group														
6. Sonolite $Mn_9(SiO_4)_4(OH)_2$					(5)		(7)	(8)					(13)	(X*)
7. Leucophoenicite $Mn_7(SiO_4)_3(OH)_2$					(5)		(7)	(8)					(13)	
8. Alleghanyite $n_5(SiO_4)_3(OH)_2$					(5)		(7)	(8)					(13)	
9. Ribbeite $Mn_5(SiO_4)_3(OH)_2$					(5)		(7)							
10. Manganhumite $(Mn,Mg)_7(SiO_4)_3(OH)_2$					(5)		(7)							
11. Jerrygibbsite $Mn_9(SiO_4)_4(OH)_2$					(5)		(7)						(13	
Pyroxenoides group														
12. Pyroxmangite $MnSiO_3$	(1)		(3)			(6)	(7)		(9)			(12)	(13)	
13. Ferroan pyroxmangite $(Fe,Mn)SiO_4$				(4)		(6)	(7)							(X*)
14. Pyroxferroite $(Fe,Mn,Ca)SiO_3$						(6)	(7)							
15. Rhodonite $(Mn,Fe,Mg,Ca)SiO_3$		(2)							(9)	(10)		(12)		(X*)
16. Bustamite $CaMn(SiO_3)$			(3)											
17. Wollastonite $CaSiO_3$			(3)											
Garnets group														
18. Spessartine $Mn_3Al_2(SiO_4)_3$			(3)		(5)				(9)	(10)	(11)	(12)	(13)	

19. Spessartine-calderite $(Mn,Ca)_3(Fe,Al)_2(SiO_4)_3$				(4)		(6)							(13)	(X*)
20. Spessartine-grossular/andradite $(MnFeCa)_3(AlFe)_2(SiO_4)_3$														(X*)
21. Almandine manganoan $(MnFe)_3Al_2(SiO_4)_3$														(X*)
Amphiboles group														
22. Mangangrunerite $Mn_2(Fe,Mg)_5Si_8O_{22}(OH)_2$	(1)	(2)	(3)	(4)		(6)	(7)		(9)	(10)	(11)	(12)	(13)	
23.Manganoan actinolite $Ca_2(Mg,Fe,Mn)_5Si_8O_{22}(OH)_2$														(X*)
24. Actinolite $Ca_2(MgFe)_5Si_8O_{22}(OH)_2$													(13)	
Epidote group														
25. Allanite-(La) $Ca(Ce,La)(Al,Fe)_3(SiO4)_3(OH)_{l2}$								(8)						(X*)
26. Piemontite $Ca_2(MnFe)Al_2(Si_2O_7)(SiO_4)(OH)_2$										(10)				
Tourmaline group														
27. Dravite $NaMg_3Al_6(BO_3)Si_6O_{18}(OH)_4$								(8)						(X*)
Phillosilicates/phyllosilicate with Cl														
28. Mn-biotite $K(Mg,Fe,Mn)_3(Si_3Al)O_{10}(OH,F)_2$													(13)	
29. Caryopilite $(Mn,Mg)_3Si_2O_5(OH, Cl)_4$								(8)						(X*)
30. Friedelite Mn8Si6O15(OH,Cl)10														(X*)
31. Hissingerite $Fe_2Si_2O_5(OH)_4.2H_2O$		(2)												(X*)
32. Bementite $Mn_5Si_4O_{10}(OH)_1$								(8)					(13)	(X*)
33. Neotocite $(Mn,Fe)SiO_3.H_2O$									(9)	(10)			(13)	
Chlorites group														
34. Pennantite $(Mn,Al)_6Si,Al)_4O_{10}(OH)_8$					(5)		(7)	(8)						(X*)
35. Greenalite $Fe_{2-3}Si_2O_5(OH)_4$			(3)					(8)						
36. Clinochlore $(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$								(8)					(13)	(X*)
37. Kellyite $(Mn,Mg,Al)_3(Si,Al)_2O_5(OH)_4$							(7)							(X*)
38. Ni-Chlorites														(X*)
Other silicates														
39. Yoshimuraite $Ba_2TiMn_2(SiO_4)_2(SO_4,PO_4)(OH,Cl)$								(8)						(X*)
40. Staurolite $(Fe,Mg)_4 Al_{17}(Si,Al)_8O_{44}(OH)_4$											(11)			
41. Zircon $ZrSiO_4$								(8)						(X*)
42. Ericssonite $BaFeMn_2O(Si_2O_7)(OH)$														(X*)
43. Adularia											(11)			
III. Oxides class														
1. Magnetite Fe_3O_4	(1)	(2)	(3)	(4)		(6)	(7)		(9)	(10)	(11)		(13)	(X*)
2. Manganoan magnetite $(MnFe)_3O_4$														(X*)
3. Jacobsite $(Mn,Fe)(Fe,Mn)_2O_4$					(5)		(7)	(8)	(9)	(10)	(11)		(13)	(X*)
4. Pyrophanite $MnTiO_3$													(13)	(X*)
5. Braunite Mn_7SiO_{12}									(9)	(10)				
6. Iwakiite $Mn(Fe,Mn)_2O_4$													(13)	
7. Maghemite $Fe_{2.67}O_4$													(13)	
8. Wustite FeO							(7)							
9. Manganite γ-MnO(OH)											(11)	(12)	(13)	
10. Lepidocrocite γ–FeO(OH)							(7)							(X*)
11. Hematite α-Fe_2O_3										(10)	(11)	(12)		
12. Braunite Mn_7SiO_{12}									(9)	(10)				(X*)
13. Hausmannite Mn_3O_4			(3)											
14. Franklinite $(Zn,Mn,Fe)(Fe,Mn)_2O_4$														

15. Galaxite $MnAl_2O_4$														(X*)
16. Goethite α-FeO(OH)		(2)	(3)								(11)	(12)		
17. Anatase TiO_2											(11)			
18. Quartz SiO_2										(10)			(13)	
19. Opal $SiO_2.nH_2O$								(8)	(9)	(10)				(X*)
20. Psilomelane	(1)		(3)						(9)	(10)		(12)		
21. Pyrolusite	(1)		(3)						(9)	(10)	(11)	(12)		
IV. Phosphates, arsenates class														
1. Apatite $Ca_5(PO_4)_3(F,OH,Cl)$	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)		(13)	
2. Carbonate-fluorapatite $Ca_5(PO_4,CO_3)_3F$													(13)	
3. Fluorapatite $Ca_5(PO_4)_3F$								(8)						(X*)
4. Chlorapatite $Ca_5(PO_4)$														
7. Arsenoclasite $Mn_5(AsO_4)_2(OH)_4$								(8)						(X*)
8. Sarkinite $Mn_2(AsO_4)(OH)$								(8)						(X*)
9. Eveite $Mn_2AsO_4(OH)$								(8)						(X*)
10. Schallerite $(Mn,Fe)_{16}(As_3Si_{12}O_{36}(OH)_{17}$														(X*)
11. Johnbaumite $Ca_5(AsO_4)_3(OH)$														(X*)
12. Switzerite $(Mn,Fe)_3(PO_4)_2.7H_2O$														(X*)
13. Triplite $(Mn,Fe,Mg,Ca)_2(PO_4)(F,OH)$			(3)											
14. Wolfeite $(Fe,Mn)_2PO_4(OH)$			(3)											
15. Vivianite $Fe_3(PO_4)_2.8H_2O$										(10)				
V.Sulfides, tellurides, arsenides, bismuthinides class														
1. Pyrite FeS_2	(1)		(3)						(9)	(10)	(11)	(12)	(13)	(X*)
2. Pyrhotite $Fe_{1-x}S$			(3)						(9)	(10)			(13)	
3. Galena PbS									(9)	(10)				(X*)
4. Sphalerite ZnS			(3)							(10)				(X*)
5. Chalcopyrite $CuFeS_2$			(3)						(9)	(10)			(13)	(X*)
6. Covellite CuS										(10)				(X*)
7. Chalcocite Cu_2S										(10)				
8.Marcasite FeS_2			(3)							(10)			(13)	
9. Molybdenite MoS_2													(13)	
10.Cattierite CoS_2														(X*)
11.Pentlandite $(Ni,Fe)_9S_8$														(X*)
12. Tellurobismuthite Bi_2Te_3														(X*)
13. Joseite Bi_4TeS_4														(X*)
14.Tetradymite $Bi_{14}Te_{13}S_8$														(X*)
15. Arsenopyrite FeAsS														(X*)
16.Glaucodot (Co,Fe)AsS														(X*)
17.Nickelscutterudite $(Ni,Co)As_{2-3}$														(X*)
18. Skutterudite $CoAs_3$														(X*)
19. Safflorite $CoAs_2$														(X*)
20. Nickeline NiAs														(X*)
21. Linnaeite Co_3As_4														(X*)
22. Cobaltite CoAs														(X*)
23. Gersdorffite NiAsS														(X*)
24. Rammelsbergite $NiAs_2$														(X*)
25. Modderite (Co,Fe)As														(X*)
26. Rammelsbergite, cobaltian $(Ni,Co)As_2$														(X*)
27. Nickeline NiAs														(X*)
28. Smaltite $(Co,Ni)As_{3-x}$														(X*)
29. Lollingite $FeAs_2$														(X*)
30. Bismuthinite Bi_2S_3														(X*)
VI. Sulphates class														
1. Barite $BaSO_4$								(8)			(11)	(12)	(13)	(X*)
2. Manganoan barite $(Mn,Ba)SO_4$														(X*)
3. Gypsum $CaSO_4.2H_2O$										(10)				
4. Melanterite $FeSO_4.7H_2O$									(9)					
5. Szmikite $MnSO_4.H_2O$									(9)	(10)				
6. Chalcanthite $CuSO_4$										(10)				

VII. Native elements class														
1. Graphite C													(13)	
2. Bismuth Bi								(8)						(X*)
3. Gold Au													(13)	

(1) Ianovici et al. (1968); (2) Giusca (1962); (3) Gotz et al. (1977); (4) Hirtopanu et al. (1992); (5) Hirtopanu et al. (1993); (6) Hirtopanu (1997); (7) Hirtopanu (2006); (8) Hirtopanu et al. (2015); (9) Kalmar (1972); (10) Kalmar, Lelkes-Felvari (1991); (11) Kosmat, von John (1905); (12) Radulescu, Dimitrescu (1966); (13) Udubasa et al (1996); X*=this study.

Conclusions

The Razoare deposit is of Fe-Mn carbonate silicate oxide type ores (Dasgupta, 1990) which have the characteristic presence of the crucial phases carbonate and olivine. The Razoare deposit contains manganese and iron minerals relatively separated within the ore-bearing sequence. The minerals have formed during repeated metamorphism at the expense of a primary protolith, presumably of sedimentary carbonate (admixed with silica and alumina) origin (Udubasa, Hirtopanu, 1992). The Mn-Fe silicate-carbonates type derived from carbonate precursors show the most diverse assemblages. The variety of assemblages reflects the wide range in bulk composition of the precursors, particularly Mn:Fe:Mg:Ca ratios and variation in the composition of the metamorphic fluid (X_{CO2}). The whole metamorphic pile underwent an initial regional metamorphism of upper almandine amphibolites facies, resulting (1) the manganoan ferrosilite/manganoan fayalite/spessartine slightly rich in calderite. Later metamorphic events of essentially retrograde character involving high activity of water and other volatile components led to the formation of several parageneses showing a slight separation in space. The most important are (2) pyroxmangite-mangangrunerite-spessartine and (3) tephroite-manganese humites-jacobsite. Thus, from the lower rhodochrosite assemblage rich in iron and undersaturated in silica (Mn-orthopyroxenes-manganoan fayalite), the ore sequence passes through a Mn-dominanted assemblages, very poor in iron, undersaturated in silice, represented by tephroite-manganese humites-arsenides/ sulfoarsenide/sulfoarsenides /bismuthinides/tellurides to an upper silicate rich part, saturated in silica, represented by mangangrunerite-spessartine-quartz-sulfides.The metamorphic evolution of the assemblages have been from the subsaturated to the saturated one. The presence of some arsenides, sulfoarsenides and bismuthinides is linked with a locally hydrothermal mineralization process. The Mn-arsenates were formed at the expense of arsenides, simultaneous with the appearances of secondary manganese carbonates and diverse secondary phosphates. The whole mineral associations of the Razoare ores are rather complex, consisting of about 120 minerals. Some new minerals first cited in this paper, especially the silicates, tellurides, arsenides and arsenates, are now under study and will be later published in separate papers.

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THE NONMETALLIC MINERAL RESOURCES IN CONSTANTA COUNTY – FROM TRADITION TO UNIQUENESS

Gabriela-Silviana MARICA[1]*, Mihai MARINESCU[2]

[1] Geological Institute of Romania, Bucharest, Romania
[2] University of Bucharest, Faculty of Geology and Geophysics, Bucharest, Romania
**silviana.marica@gmail.com*

Abstract: Constanta county is one of the rich county in mineral resources for buldings with famous fortresses and monuments made up of limestones. The basement of the Central Dobrogea Massif is the main source of these resources. Mining in this county has a long tradition for clay resources as well as for products for ceramics, green schists, ornamental limestone, dolomite, chalk, sand for bulding, sand and gravel. In 2014 the situation of exploitable resources included 14 types of rocks and 32 deposits of nonmetallic minerals.

Keywords: limestones, Constanta county, nonmetallic resources, mineral deposits, heritage

1. Constanța County- between cultural heritage and stone tradition

Constanța County lies in the Southern part of Dobrogea region and is limited to the north by Tulcea county, to the east by the Black Sea, to the South by Bulgaria and to the west by the Danube, which forms a natural border with the Călărași and Ialomița counties. It is one of the most important counties in Romania being ranked 8th by size and 5th by population, inhabited since ancient times with obvious traces of Roman colonies (Fig.1 and Fig.2). The history of the county is linked also to that of the Dobrogea region and important archaeological stone sites are spread all over its territory.

The Dacian king Burebista took possesion of Dobrogea. Roma domination extended up to the seventh century and during these times they built cities, fortresses and monuments from local calcareous stones, evidence of a briliant civilization : Carsium (Harșova), Cius (Gârliciu), Capidava (Capidava-Topalu), Axiopolis (Cernavoda), Sacidava (Dunăreni), Ulmetum (Pantelimonu) and Tropaeum Traiani (Adamclisi). At the seaside there are the ruins at Histria (Istria), Ovidiu fortification (on the bank of Siutghiol lake), Tomis (Constanța) and Callatis (Mangalia).

2. Geographical and geological aspects regarding Constanta County

Physical and geographical peculiarities, location and especially history give Constanta county various riches, many still unused.

The Danube River – Black Sea Chanel in the middle of the county separates Casimcea Plateau from Southern Dobrogea Plateau (Fig. 3). The relief has between 0m and 200m in altitude, rarely exceeding 200 m, especialy in the north. In particular Crucea – Băltăgești area, in the Allah Bair Nature Reserve has a higher relief, the highest altitude being Stupina peak (235m).

"Canaralele Dunarii" represent one of the most beautiful specific relief from North of Constanta County and are geological monument (Fig. 4).

There are lakes that are strung along the Danube: Bugeac, Oltina, Dunareni, Vederoasa, Baciului; Hasarlak lake in the west and Tașaul and Sinoe lakes in the east.The Danube – Black Sea Channel has four locks and represents an important link and a segment of the European corridor Number 7 Danube.

From the geological point of view, Constanta county has two major geological units: Central Dobrogea Massif and Southern Dobrogea Platform. The Central Dobrogea Massif occupies the middle third of Dobrogea and is bordered to the south by Palazu Fault and to the north by Peceneaga Camena Fault The Southern Dobrogea Platform located south of the Danube and occupies the southern third of Dobrogea.

The basement of the Central Dobrogea Massif contains mesometamorphic crystalline schists and greenschists formation. The sedimentary cover contains Cretaceous and Jurassic deposits. The Southern Dobrogea Platform is represented by granitic gneisses and migmatites in the base levels and by crystalline schists, described as the Palazu lens, at the top. The sedimentary cover contains Paleozoic, Mezozoic and Neozoic deposits.

Fig. 1. Reconstruction of Tropaeum Traiani monument using Deleni limestone, Constanta county.

Fig. 2. Stone ruins of the largest Roman civil cities from Dobrogea, city of Adamclisi.

Fig. 3. Specific relief of limestone from Southern Dobrogea, Constanta county.

Fig. 4. Image of Canaralele Dunării from Hârşova.

3. Mining of mineral resources in the course of time in Constanța County

In the course of time in Constanta county several of the most important and unique nonmetallic resources from Romania have been exploited - like greenschists and chalk (Table 1).

Table 1. Number of surface mining activities known in the main ten counties in Romania (acc. to Marinescu et al., 2012).

No.	**County**	**Quarries and pits over time**
1	Hunedoara	235
2	Tulcea	202
3	Constanta	182
4	Maramures	162
5	Cluj	151
6	Arad	148
7	Covasna	134
8	Suceava	127
9	Brasov	123
10	Bihor	120

Table 2. Number and types of mineral resources exploited at the surface by counties of Romania in 2014 (Source: *www.namr.ro*).

No.	**County**	**Exploited deposits in 2014**	**Type of resouces**
1	Arad	22	6
2	Cluj	21	11
3	Constanta	17	14
4	Satu Mare	17	9
5	Bihor	16	10
6	Caras Severin	15	7
7	Dambovita	14	7
8	Salaj	13	9
9	Buzau	11	4
10	Arges	10	7

With a number of 182 of known surface mining activities and 14 in exploitation in 2014 (Table 2), Constanța is the third county from Romania as importance for exploiting mineral resouces over time and the first by the type of mineral resources point of view.

In Constanta county there are 14 types of solid non-metalliferous and non-combustible substances which have been extracted in the course of time, by means of 52 known (Marica, 2001) surface mining activities (Figs. 5-8).

Fig. 5. Exploitation of kaolinitic clays at Țibrinu, Medgidia.

Fig. 6. Limestone quarry from Celea Mare - Hârșova.

Fig. 7. View from Canaraua Fetei.

Fig. 8. Relief in chalk from Basarabi, Constanța conty.

4 Curent situation of mining and use of non-ferous mineral resourses from Constanta County

An inventory situation made in the last decade in Romania have counted 52 deposits for building materials: aggregates and crushed stone, dimension stones, clayey resources for ceramic industry, stones for binders and chalk (Marica et. al., 2008).

The list of the deposits from Constanta county and licenced perimeters in 2014 is presented in Table 3.

Table 3. List of the deposits with non-metallic mineral resources from Constanta County and the situation of mining licenses in 2014 (*)

No.	Substance (Nonmetallic resource)	Deposits /Perimeters	Uses
1	Green shists	Cheia; Morii Hill-Palazu Mic; Sibioara (Sibioara-Cotu lui Cergău*, Valley with spring, Piatra Lată, South Sibioara Peninsula, Sibioara –Năvodari*)	Aggregates (crushed stone)
2	Ornamental limestone	Deleni (Roman quarry)	Ornamental stone (tiles and plates)
3	Industrial and building limestone	Corbu*; Celea Lac –Hârșova*; Celea Mare; Celea Mică; Tabia; Canaraua fetii- Băneasa*; Deleni; Dumbrăveni-Independența; Luminița-Tașaul*; Medgidia*; Piatra-Tașaul; Plopeni; Remus Opreanu*, Nicolae Bălcescu*; Sitorman*; Șipote	Limestone for cement and building
4	Chalk	Basarabi-Valea Seacă (Murfatlar-Hălzi)	Animal husbandry, agriculture, filler, paints, polishing paste
5	Dolomite	Ovidiu*;	Buildings
6	Loess	Medgidia; Remus Opreanu	Raw ceramics
7	Common clays	Cobadin; Mamaia Sat ; Medgidia, Luminița-Tașaul; Siminoc	Raw ceramic industry

Table 3 - continued.

No.	Substance (Nonmetallic resource)	Deposits /Perimeters	Uses
8	Kaolinitic clay	Cuza-Vodă*; Defcea*; Țibrinu* (Gherghina, Satu Nou); Tortoman	Fine ceramic industry
9	Bentonite	Adâncata; Urluta	Drilling fluids, oil and chemical industry ,
10	Diatomite	Adamclisi; Adancata; Rașova- Hațeg (Șipote, Văleni, Padu); Urluta	Filtration, filling, insulating products
11	Phosphatic rocks	Ivrinezu Cave	Fertilizers
12	Siliceous sand	Remus Opreanu; Ciobănița; Plopeni	Glass
13	Sand for buildings	Peștera	Houses and buildings
14	Sand and gravel	Cochirleni (Cochirleni-Ostrovu Hinog-Cernavodă; Cochirleni II; Cochirleni – Danube km 306-307 *, Cochirleni km308-309*); Hârșova (km 250-252)	Buildings

5. Conclusions

Constanta county have a long tradition in exploiting and uses of non-metallic resources: limestone for historical buildings, clays for ceramics, chalk , green shists, some of them uniqe in this territory.

The updated inventory of non-metallic resources from Constanța county presented in this paper intends to contribute to the geological and economical knowledge of this county and those that promote territorial and national analyses and development : Prefecture, agencies, investors or different users.

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THE Au/Ag RATIO IN SAMPLES OF ROMANIAN NATIVE GOLD FROM THE GOLD MUSEUM OF BRAD, ROMANIA

Gheorghe C. POPESCU, Gheorghe ILINCA, Antonela NEACŞU

University of Bucharest, Faculty of Geology and Geophisics, Department of Mineralogy, 1, N. Bălcescu Blvd., 010041, Bucharest, Romania
ghpop@geo.edu.ro; ilinca@gg.unibuc.ro; antonela.neacsu@gmail.com

Abstract: The Gold Museum of Brad includes gold specimens from ore deposits of Romania and from all around the world. In order to achieve aspects related to the revaluation and classification of the gold heritage of the museum, several non-distructive procedures have been used to verify the gold content of each sample, and also the Ag content in native gold. Despite old analyzes which have identified the variation of silver content in native gold of the Romanian metallogenic units, no such data on gold samples in the Museum were avaible. The use of X-Ray fluorescence spectrometry, together with classical mineralogical investigation, could be helpful for the Au/Ag ratio investigation, and further for genetic conditions assumption.

Keywords: Au:Ag ratio native gold, gold-bearing minerals, X-Ray Fluorescence, type localities, morphological types of native gold, Romanian Carpathians, volcanic structures, alluvial gold.

1. Introduction

The Gold Museum of Brad (Hunedoara) is unique among other museums in Romania and even in Europe. It includes samples collected in Romania and around the world, with a special look to the mineral species described for the first time in Romania, such as in *Golden Quadrilateral* of the Metaliferi Mts and Baia Mare metallogenic district.

2. Brief History

The Museum hosted minerals, rocks and mining tools. At the beginning, the majority was represented by samples donated by the researchers involved in the geologic activity around Brad, starting with the end of the 19th century. Native gold and telluride gold-bearing minerals originate in the Metaliferi Mts, especially in the Brad region, and Musariu and Brădişor deposits.

In a report written in 1910-1911 by Friedrich Schumacher on the ore deposits owned by the *Ruda 12 Apostoli* Ass., a mineral collection with 200 specimens of gold is mentioned, but the author will add over 160 samples. The collection could be visited from 4th of July 1912, which should be considered the birth date of the Gold Museum of Brad. Under the administration of the *Mica Co.* (1920-1948) new gold specimens from Romania and all around the world have enriched the Museum, including exchanges and donations. On the 14th of June 1948, when *Mica Co.* was nationalized, the mineralogical and geological collection included 1000 samples of native gold aproximatelly, but their number has continued to grow. Our days the Museum includes 1305 samples of native gold from the Brad-Săcărâmb metallogenic district especially, but also from the Baia de Arieş, Căinel-Băiţa-Hărţăgani and Trestia-Măgura-Hondol metallogenic nodes, and from the metallogenic districts of Roşia-Bucium, Almaş-Stănija. The museum samples with native gold from Baia Mare come from Săsar and Dealu Crucii ore deposits. There are also specimens from Bozovici, South Carpathians, and alluvial gold samples from Pianu, Olt Valley, Ţebei Valley and Serbia occurences.

3. Overview of the metallogenic context of native gold and Au-Ag –mineral samples in the Gold Museum of Brad

Most of the gold deposits and occurences in Romania are associated with the Neogene volcanism from the southern part of the Apuseni Mts. (Metaliferi Mts) (Fig. 1), and the from the East Carpathians (Baia Mare metallogenic district) (Fig. 2). They are epithermal and porphyry copper systems. The banatitic magmatism had a subordinate role in the formation of gold deposits, which is limited to the Banat and Apuseni zones. Areas of mineralization associated with shear zones – which are occurrences from the economic point of view – are known in the South Carpathians and Apuseni Mts (Fig. 4). Areas with recent or fossil alluvial gold deposits were also an important source of gold (Fig. 3).

The metallogenic classification of gold samples in the Gold Museum of Brad is based on their original metallogenic units, almost all of them related to the Carpathian Neogene magmatism. The Neogene metallogenesis of the Apuseni Mts (Fig. 1) is characterized by Au-Ag veins and stockworks associated with volcanic structures and followed by porphyry copper type deposits. A geodynamic regime of subduction characterized this period, which could influenced the Badenian-Pliocene volcanic activity. The NW-SE Pre-Tertiary oriented fractures were reactivated in Neogene, allowind the formation of intracontinental basins, *i.e.* Brad-Săcărâmb, Zlatna-Stănija, Roşia Montană-Bucium and Mureşului Valley.

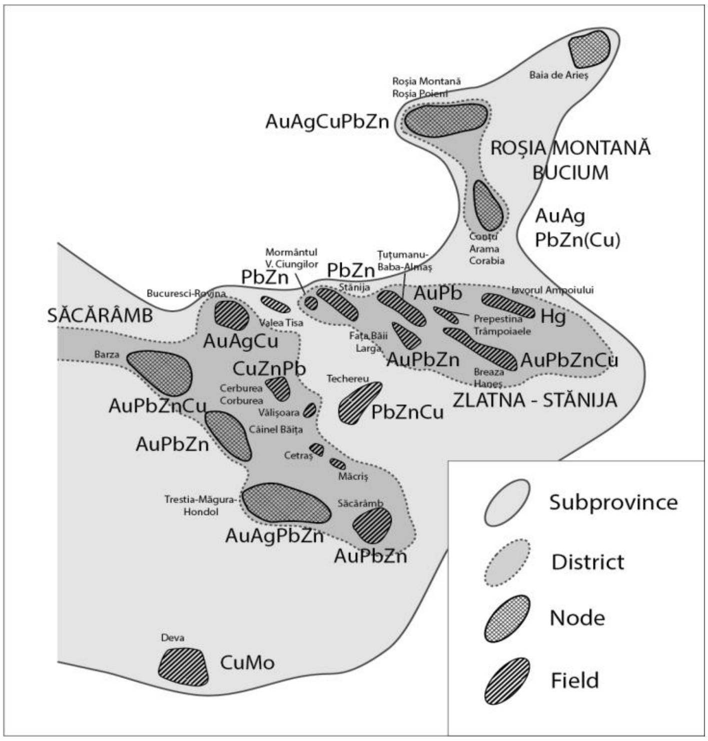

Fig.1. The Neogene metallogenic subprovince of Southern Apuseni Mountains (Popescu, 1986)

The Baia de Arieş metallogenic node is the *locus tipicus* for sylvanite $AuAgTe_4$, holding an important polymetallic and gold metallogenesis, concentrated in two metallogenic fields: Afiniş and Ambru. A particular feature in the context of the Apuseni Mts characterizes the Afiniş mineralization, where the presence of the gold-bearing arsenopyrite, and subordinately of gold and sulfides, could be evidentiated.

The Roşia-Bucium district hosts one of the most important metallogenic concentrations of the Metaliferi Mts, represented by the Roşia Montană-Roşia Poieni metallogenic node (NW), with two mineralized structures, Roşia Montană and Roşia Poieni, and Bucium-Conţu-Arama-Corabia node (SE). The first node is a heterochronous porphyry copper and gold-silver structure. Roşia Montană metallogenic field represents a significant gold-silver accumulations into the breccified structures Cetate and Cârnic. Roşia Montană is the *locus tipicus* for alburnite $Ag_8GeTe_2S_4$ (Tămaş et al., 2013). Metallogenesis was developed in two phases in the Bucium metallogenic node, first with a predominant Cu-py character in the andesitic structure of Arama, and the second, with a gold-polymetallic character, as the vein groups Arama, Vâlcoi (Vulcoi)-Boteş and Corabia. Boteş is the *locus typicus* for hessite Ag_2Te.

The linear metallogenesis of Almaş-Stănija district is hosted by volcanic structures disposed along tectono-volcanic alignments (Popescu, 1986): Haneş-Breaza, Prepeştenia-Trâmpoiele, Ţuţumanu-Baba-Almaş, Neagra-Dealul Ungurului-Stănija. Some of gold deposits belonging to this district present scientific significance, because there are *locus tipicus* for minerals and even elements, as Faţa Băii gold and sulfide veins field (Prepeştenia-Trâmpoiele metallogenic alignment) for native tellurium and tellurite. Almaş metallogenic field is the most important gold occurrence of the Ţuţumanu-Baba-Almaş metallogenic alignment, as Stănija (Popa) metallogenic field is for Neagra-Dealul Ungurului-Stănija metallogenic alignment. It is a famous group of veins hosted by the main andesitic body in the Ungurului hill, mined in the old times for gold in their upper parts, and subsequently for polymetallic-gold ore in depth.

The metallogenic district of Brad-Săcărâmb is the largest unit of the metallogenic Neogene subprovince in the Apuseni Mts. This is a post-tectonic basin which fragments the eastern part of the Drocea-Techereu ophiolitic massif and the Mesozoic sedimentary formations. The present configuration is determined by the newer NW-SE dominant fracture system, which intersected the older WSW-ENE or E-W systems, thus resulting in areas of minimum resistance in the crust. There are complex volcanic systems developed in relationship with these areas (Barza, Caraci, Corburea-Cerburea, Vălişoara, Cetraş, Măcriş, Săcărâmb and Căinel) where gold mineralization is located. An important aspect is the existance of metallogenic nodes into the Brad-Săcărâmb district, the most famous being Barza node, where auriferous and subordinately polymetallic vein groups and porphyry copper mineralization are evidentiated. As a part of this metallogenic node, Barza vein field is the place where gold veins have been mined for hundred of years (Ruda-Barza, Măgura-Brădişor, Valea Morii Veche), and the porphyry copper mineralization was discovered in the 1970's (Musariu Nou and Valea Morii Nouă). The most famous is Ruda-Barza vein group, located in the upper part of the Barza structure.

The Caraci (Căraciu) metallogenic field hosts the Caraci gold ore deposits, a famous vein system.

The Brădişor ore deposit is located westwards of Ruda and consists of the Brădişor vein group, where quartz is associated with gold-bearing sulfides.

The Musariu mineralized structure locates on the territory of Ruda village and includes old mines related to the intrusive andesitic body. The well-known NW area (Musariu Vechi) develops upwards until under the tree roots, and towards SE (Musariu Nou). Native gold occurs as impregnations, nests and sometimes as kilogram size concentrations (Popescu, 1986). Free gold occurs as leafs, threads or moss-like aggregates (Brana, 1958). At Musariu Nou the Cu-Au mineralization forms stockworks and impregnations (Vlad, 1983).

The Valea Morii metallogenic field consists of the Valea Morii ore deposit, including two vein groups: Valea Morii Veche - on the eastern and south-eastern fringes of Barza neck, in Sarmatian quartz andesites, breccia and Lower Miocene sedimentary, and Valea Morii Nouă. The Valea Morii Veche vein group consists of Au-Ag±Pb, Zn veins and their ramifications. The Valea Morii Nouă vein group represents the southward extension of the Valea Morii Veche vein group. Gold and sulfide veins have been known since a long time, and include *free* gold and gold associated with sulfides. The northern half of the valea Morii Nouă vein group contains a porphyry copper mineralized column.

The Căinel-Băiţa-Hărţăgani metallogenic node contains the mineralized structures of the Băiţa Valley, aligned along a NW-SE fracture system located on the SW limit of the Brad-Săcărâmb Basin. Three major mineralized fields are found: Căinel, Băiţa and Draica.

The Căinel Ag-Au metallogenic field is hosted by Căinel volcano. The Museum includes both native gold and native silver.

The Băiţa Au-Ag metallogenic field consists of mineralized veins and breccia controlled by a NW-SE fracture system located in the rooting area of Băiţa volcano. Mineralization is rich in sulfides, silver minerals and native gold (Popescu, 1986).

The Trestia-Măgura-Hondol metallogenic node is an ample metallogenic episode, favored by the tectonic and structural environment developed at the intersection of NW-SE and E-W fracture systems, where a significant magmatic activity took place. There are two metallogenic fields, as a consequence of the association of mineralization with volcanic structures within this metallogenic node: Troiţa-Măgura and Hondol-Băiaga-Bocşa (Popescu, 1986).

The Troiţa-Măgura metallogenic field includes gold-silver and subordinately gold-polymetallic and copper mineralization. Three vein groups are parts of this metallogenic fied, *i.e.*Trestia, Troiţa and Hondol.

The Baia Mare metallogenic district is the most important polymetallic metallogenic district of Romania (Fig. 2), but the vertical zonning of the mineralized structures often presents an upper gold-silver rich level. Săsar and Dealul Crucii have a marked gold character.

Alluvial gold occurences are over 125, because the gold extraction from alluvia has been widespread across Romania, starting in pre-Roman period until the dawn of the 20th century (Tămaş-Bădescu, 2010). Only five areas with alluvial gold resouces are mentioned on the Map of Mineral Substances of Romania, also indicated in Fig. 3: Pianu – on the northern boundary of Sebeş Mts; Cibin Olt - on the northern boundary of South Carpathians; Râureni - on the southern limit of the South Carpathians; Arieş Valley - in Apuseni Mts; Nera-Bozovici zone - in Banat Mts (Fig. 4).

4. Materials and methods

Experts from University of Bucharest and MINVEST Deva SA worked together in order to achieve aspects related to the revaluation and classification of the gold heritage of the Museum. Several non-distructive procedures have been used to verify the gold content of each sample, *e.g.* magnifiers, microscopes, electronic scale. Detailed mineralogical investigation of samples, such as X-Ray fluorescence spectrometry, allowed the evaluation of gold and silver content, as well as the identification of gold in samples where its presence is less evident. Another useful information is the Ag content in native gold. Non-destructive analyzes of Au/Ag ratio were performed by dr. Bogdan Constantinescu and dr. Daniela Cristea-Stan (National Institute of Nuclear Physics and Engineering Horia Hulubei) on more than 200 samples, using a portable X-MET 3000 TX X-Ray Fluorescence spectrometer.

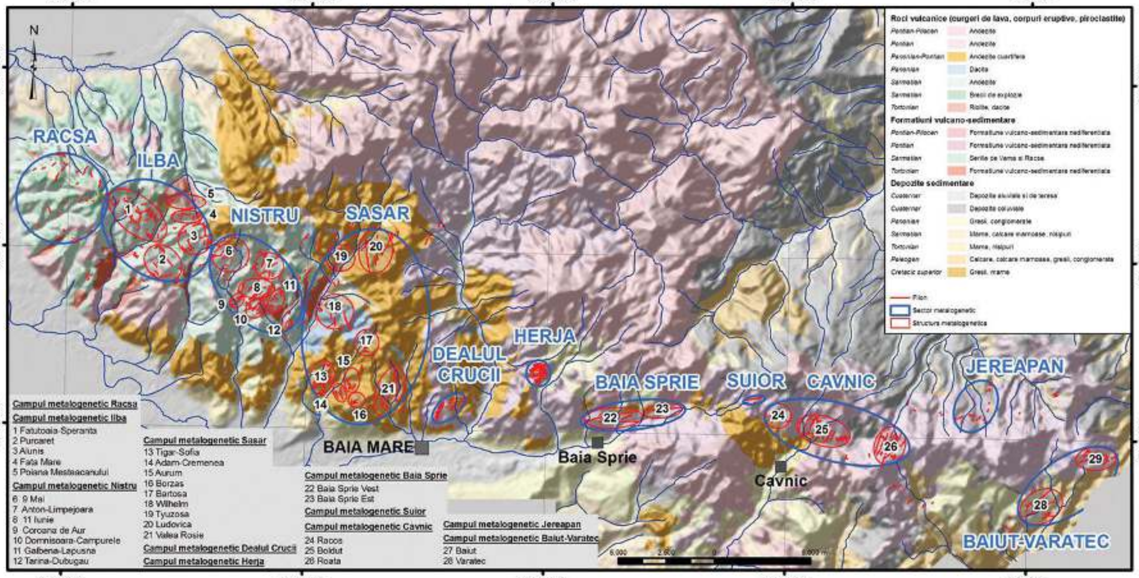

Fig. 2. Vein metallogenic fields of Baia Mare metallogenic district (Tămaş – Bădescu, 2010)

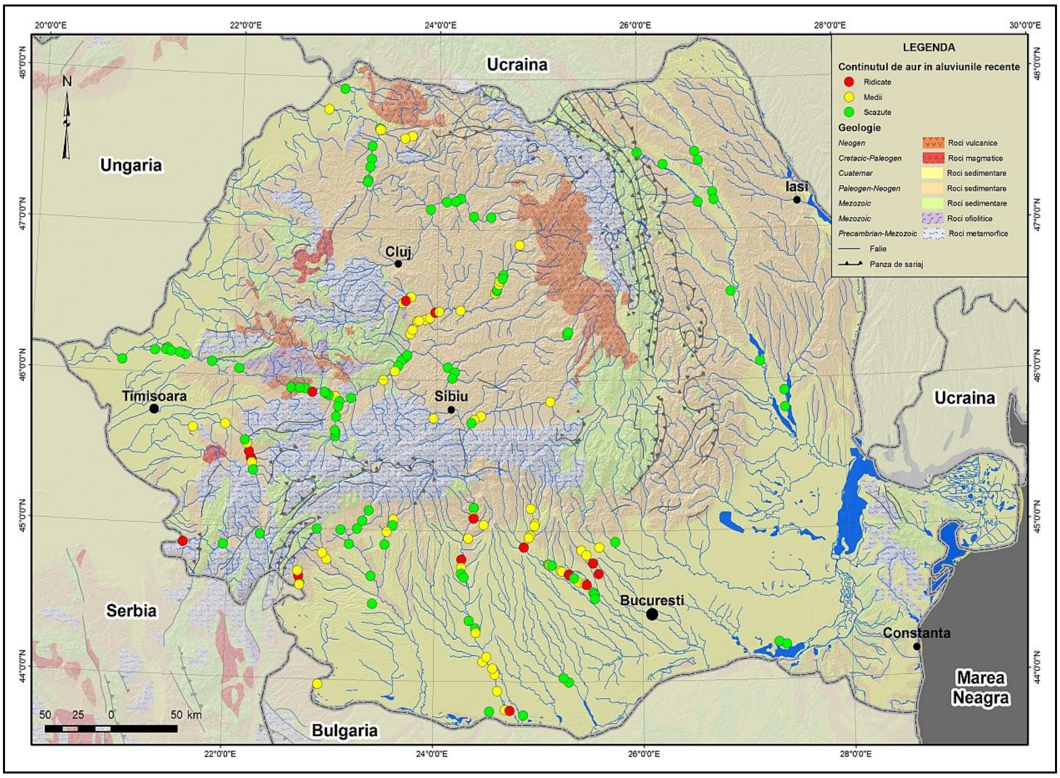

Fig. 3. Alluvial gold occurences historically exploited on the Romanian territory (Tămaş-Bădescu, 2010)

The X-Ray Fluorescence requires no sample preparation, providing a sensitive and rapid measurement on sample areas of 1 cm^2. The portable X-Ray tube can be used in any location. The exciting X-Ray beam is generated by a 40 KV tube with Rh-anode. A PIN silicon diode detector with Peltier cooling forms the detection system. The resolution of the detector is 270 eV for the K_α line of Mn (5.89 keV). The measurement spor size is about 30 mm^2. The X-MET XRF analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage. The Au-Ag composition was normalized to 100% in order to compare the Au/Ag variation in some metallogenic units of the Romanian Carpathians. Because there are gold-silver-bearing compounds, *e.g.* tellurides, sulfides, sulfosalts, and antimony minerals, many of them described for the first time in occurrences of the Metaliferi Mts, some measurement data have been influenced for sure.

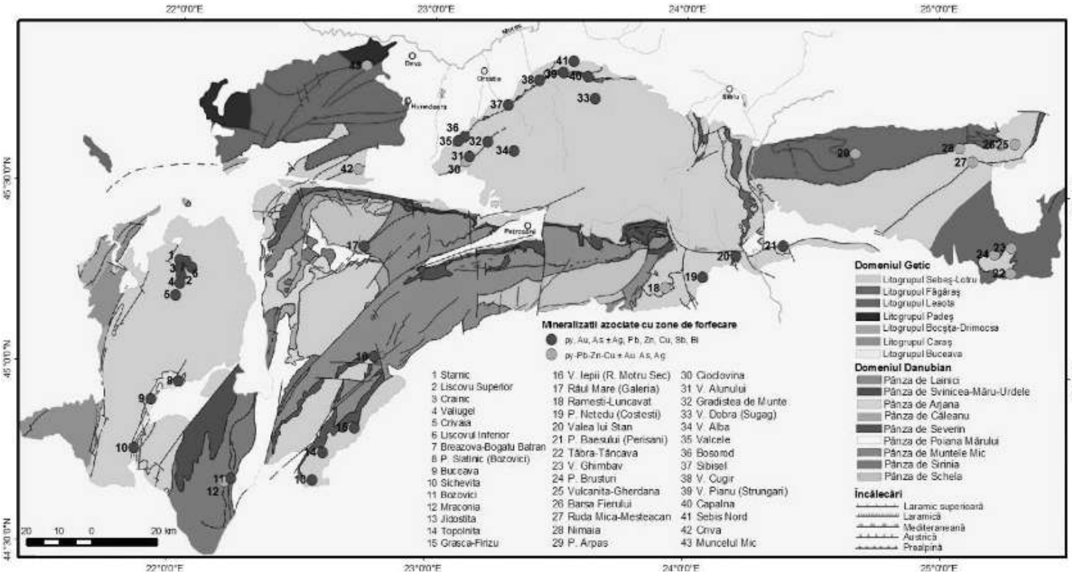

Fig. 4. Mineralization asociated with shear zones of the South Carpathians (Tămaş-Bădescu, 2010)

There are a lot of morphologic types of gold samples in the Museum. The gold samples from Baia de Arieş are characterized by lamellar or skeletal gold, frequently associated with quartz. Several specimens with native gold from Roşia Montană can be seen in the Museum, *i.e.* lamellar intergrowth of skeletal gold, cryptographic gold with reticulated structure, aggregates of gold crystals, lamellae and dendrites, microgranular gold intergrown with quartz, also gold intergrown with carbonates. The morfology of native gold in samples from Faţa Băii is skeletal-dendritic, with crystals of gold often covered by secondary Fe hydroxides. In samples from Almaş, gold morphology is diverse, from fibrous to granular isometric gold in carbonates within breccia, microgranular gold with quartz in sphalerite, microgranular gold in quartz, microgranular gold with sulfides, sphalerite and galena on quartz, and carbonate geodes. The morphology of native gold from Stănija goes from quasi-lamellar gold associated with quartz and clay minerals to dendritic gold in small nests, and finaly grained gold with sulfides and tellurides. The gold samples consist of gold lamellae on carbonates, lamellar gold with pellicles of Fe hydroxides, and dendritic gold. Gold are microgranular, skeletal, lamellar or dendritic in samples from Ruda-Barza vein group.Various morphological types of Brădişor gold samples are found, such as microgranular, dendritic-lamellar, skeletal, moss-like and thread-like gold, sometimes with pellicles of Fe hydroxides. The almost all the famous sample of the Gold Museum come from Musariu, an unique and remarcable between gold deposits of Romania. The predominant morphological feature of native gold from Musariu is the lamellar habit, and subordonately skeletal-dendritic and granular-isometric habits. The unique gold specimens have often been compared with natural forms, or have inspired metaphoric names: *the Polar Bear, Eminescu's Writing Plume, the Salamander, Horea's Spear, the Sitting Hen, Snake Head, the Stegosaurus, the Leopard, the Rhino, the Nicest Gold, the Map of Romania, the Dragon, the Feathered Helmet, the Duck, the Dog, the Lizard, the Cannon of Avram Iancu, the V Sign, the Great Romania, the Discobolos, the Ballerina, the Dragonfly.* Many of the samples of native gold from Valea Morii have a predominant lamellar morphology, so less dendritic and fibrous. Some of them are famous: *the Little Boat, Victory (the Eagle), the Cobra*. The Museum hosts native gold and silver from Căinel metallogenic field. This is the most silver-rich occurrence in the entire *Golden Quadrilateral*, so silver threads, silver wires, fibrous silver, felt-like silver are exhibited in the Museum. Also gold is present as microgranular skeletal forms with pellicles of Fe hydroxides, and lamellar-like shapes. Specimens of native gold from Băiţa are from lamellar crystals to microgranular gold, sometimes disposed as nests. Samples from Troiţa present microgranular to dendritic lamellar gold, sometimes organized as nests. The samples from Hondol are with lamellar gold and gold macrolamellae with pyramidal excrescences of variable sizes. The Museum holds samples with native gold from Baia Mare, *i.e.* dendritic, lamellar-dendritic, thread-like and invisible gold. And finally, several milimetric to maximim 1 cm alluvial gold samples from Pianu and Valea Oltului were investigated with X-Ray Fluorescence spectrometer.

5. Results and discussion

Few native gold samples from every mentioned metallogenic unit were analzyed with the X-MET 3000TX portable spectrometer. Correlation diagrams were drafted for each investigated metallogenic unit, because the Au/Ag ratio is not only an index of native gold quality, but also of genetic conditions. Two native gold samples from Baia de Arieş were analyzed, yielding 66.4% and 74.7% Au, and 16.1% and 18.1% Ag respectively.

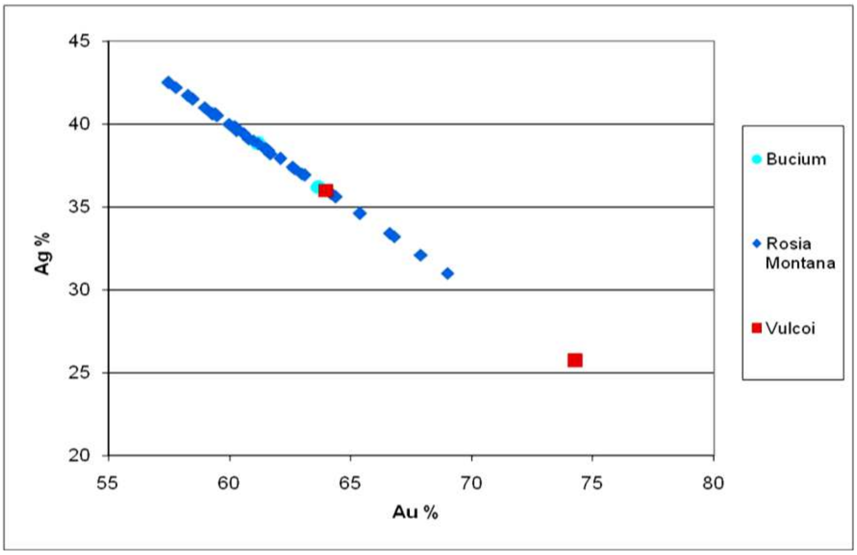

Fig. 5. The Au/Ag ratio in samples with native gold of the Roşia-Bucium metallogenic district

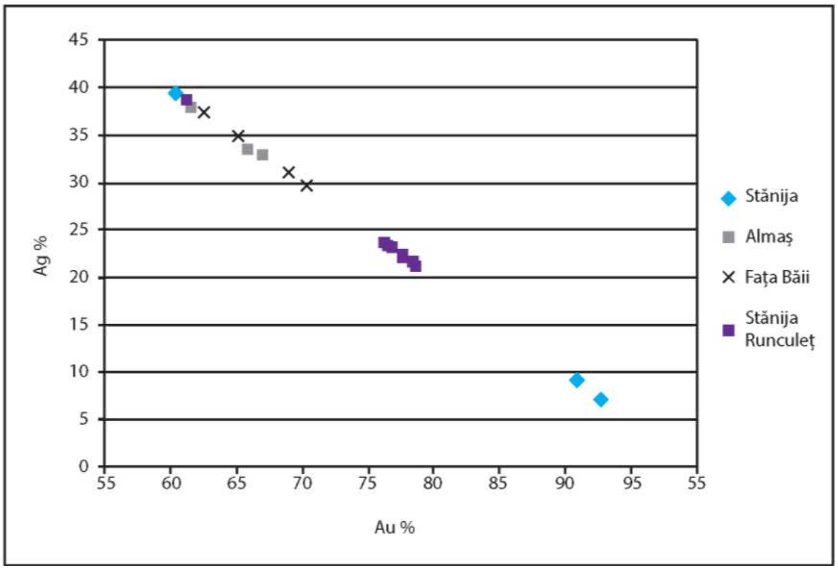

Fig. 6. The Au/Ag ratio in samples with native gold of the Almaş-Stănija metallogenic district

40 samples of native gold from Roşia Montană were analyzed. Results show relatively low contents of gold in comparison with the main ore deposits of the Barza metallogenic node, meaning Valea Morii and Musariu. The Roşia Montană ore deposit has the most large range of variation in these contents, between 57% to 68% Au (Fig. 5). At Vulcoi the Au/Ag ratio is either higher than in other metallogenic units of the Roşia-Bucium district, or falls in the middle of the Roşia Montană range, thus meaning similar

characteristics. However, the Au/Ag ratio measurements in only two samples of native gold from Bucium and Vulcoi are very few to be significant.

At Faţa Băii the Au/Ag ratio ranges between 62.5% and 68.9% (Fig. 6), which is higher than Stănija, but lower than Stănija Runculeţi. The Au/Ag ratio at Almaş is relatively low, ranging between 61.6% and 65.9%, near by the Faţa Băii values. Stănija Runculeţi samples gave the highest Au/Ag ratio from the Almaş-Stănija district (75-78%), as the older data indicated. But there are also very low gold percent which characterizes other samples from Stănija (60%), giving to this metallogenic field a particular note.

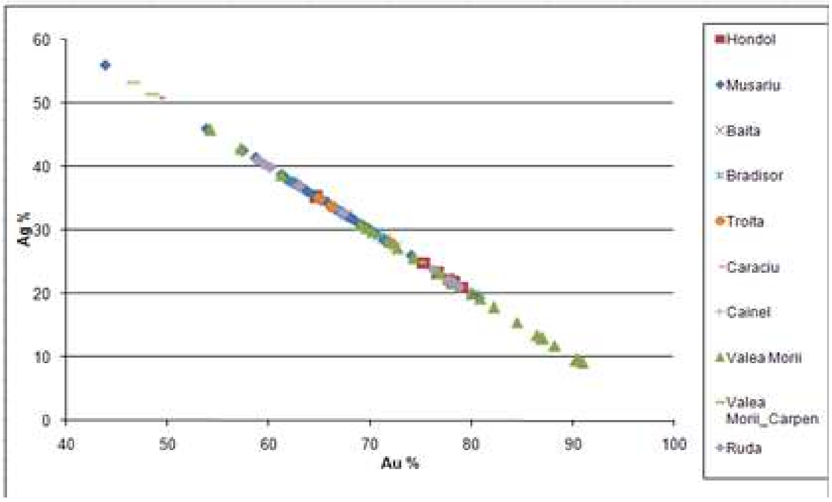

Fig. 7. The Au/Ag ratio in samples with native gold of the Brad-Săcărâmb metallogenic district

Going to the metallogenic district of Brad-Săcărâmb (Fig. 7), the Au/Ag ratio for Caraci (Căraciu) is the lowest recorded for this unit, with values ranging from 48.8% to 57.4%. Gold samples of Căinel metallogenic field indicate the Au/Ag ratio which falls in the middle regime of the Brad-Săcărâmb district, with values of 65-70%. The gold content in the native gold of Hondol is higher in comparison with that of Troiţa, *i.e.* 75-80% *vs.* 60-70%.

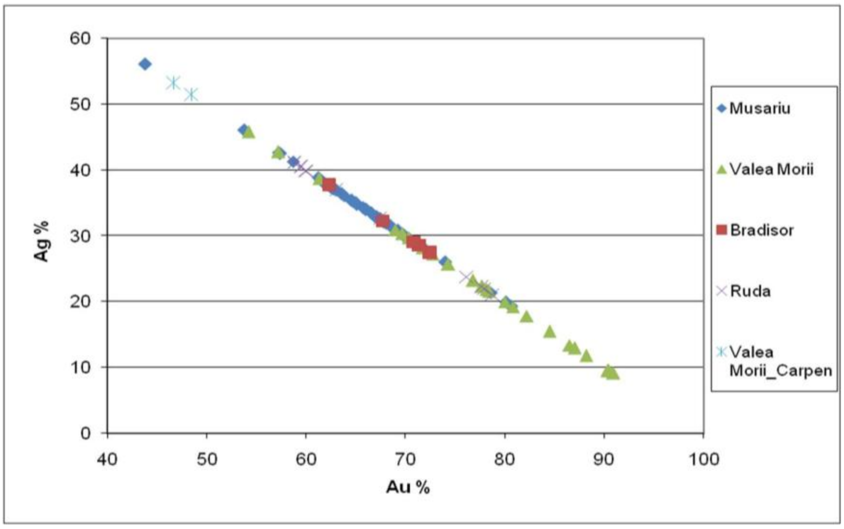

Fig. 8. The Au/Ag ratio in samples with native gold of the Barza metallogenic node

Ratios of approximately 55% to 80% (Ruda, Brădişor and especially Musariu) occupy the middle range of the Barza metallogenic node (Fig. 8), between the highest of Valea Morii, and the lowest of Valea Morii Carpen. The Au-Ag ratio for Brădişor also locates in the middle area of the Barza metallogenic node, with values ranging of 60% to mostly over 70%. The Au/Ag ratio at Musariu lies in the middle of the interval described for the Barza metallogenic node (60-70%), but there are several values which tend to be very low (<60% or even < 50%). For the Valea Morii metallogenic field the Au/Ag ratio of the

majority of gold samples is located towards the rich-end of the variation range for the Barza metallogenic node (75-90%), but there are few in the poor zone of graphic (50-60%).
Looking to the diagram in Fig. 9, the native gold from Baia Mare is among the richest in silver, only native gold from Bozovici exceeded it.

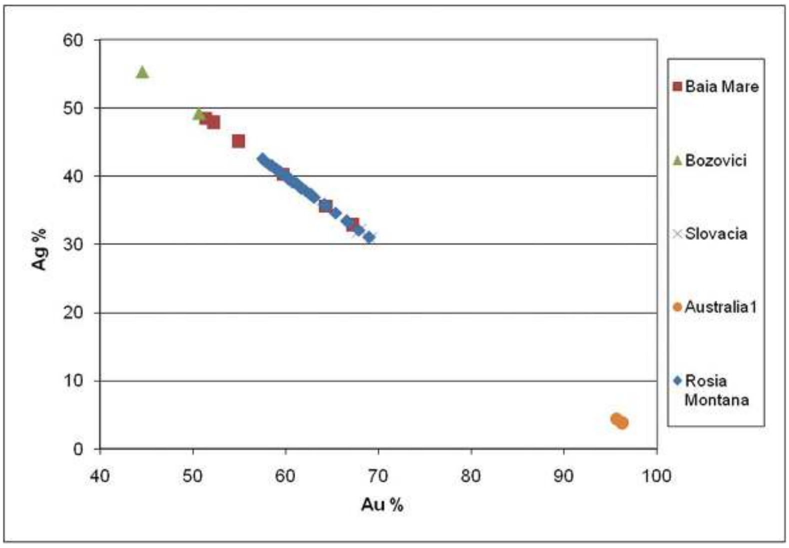

Fig. 9. The Au/Ag ratio in samples with native gold of the Baia Mare metallogenic district, in comparison with Roşia Montană and Bozovici occurences

The diagram in Fig. 10 suggests that the higher gold content of the samples from Pianu and Valea Oltului (>90%), in comparison with Valea Ţebei and Serbia. The first two have the same source (Getic shear zones), whereas the other two are of Alpine hydrothermal origin. Gold from Valea Ţebei indicates similar values with gold from Musariu (Fig. 7), so a common source of gold could be possible. Anyway, smaller gold contents were found at Pianu, meaning that at least two genetic types of gold could be assumed. Samples from Serbia have similar values of gold content with gold from shear zones.

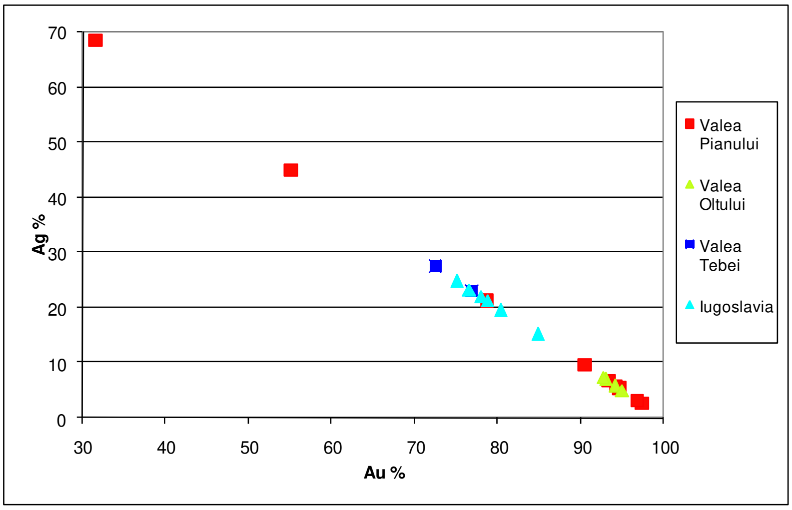

Fig. 10. The Au/Ag ratio in alluvial gold samples of Romania and in samples with native gold from shear zones of Serbia

6. Conclusions

- The use of X-Ray based analytical techniques allows the Au/Ag ratio investigation, which is an index of gold quality and genetic conditions assumption.
- The individual values of the Au/Ag ratio particularize every ore deposit and even the mineralization phases *e.g.* Roşia Montană (Cristea-Stan et al., 2010).

- The most extensive value spectra belong to the metallogenic units with the biggest ore deposits (*e.g.* the metallogenic node Barza and Roșia Montană).
- Alluvial gold has the highest gold content, probably because silver has been removed by the transport process.
- The assignment of gold sources from artefacts could be carefully made based only the gold content, because this is very different in some of the most important metallogenic units *e.g*. Roșia Montană (there is the largest range of variation in these contents, between 57% and 68% Au) and Barza.

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NOTE ON "ELATERITE", THE ORGANIC COMPOUND DISCOVERED IN 1958 IN SĂSAR GOLD ORE DEPOSIT (BAIA MARE)

Ioan MÂRZA[1*], Alexandru OTEA

[1] Babeş-Bolyai University, Department of Geology, Kogălniceanu Str., 1, 400084, Cluj-Napoca, Romania
* *marza.ioan@gmail.com.*

Abstract: The paper approaches, for the first time in the Romanian geological literature, the issue of the organic substance discovered in the epithermal vein mineralization (low sulphidation gold) from Săsar (Baia Mare). Taking advantage of personal observations performed by the authors within the described ore deposit, when the mentioned organic substance was discovered (1958), as well as of later performed analyses, the paper brings contributions to locating, describing the in situ appearance and genesis of the "Săsar gum", named *elaterite* by Tokody (1965). Having an ephemeral apparition and on a limited area, the organic substance described at Sasar did not offer the geologists enough samples to be collected in time. Therefore samples to be analyzed by using modern techniques are lacking, and there are no samples in none of the museums in Romania.

Keywords: elaterite, epithermal gold deposits, Săsar, Baia Mare, Romania

In memoriam of distinguished
Professor of Ore deposits Valeriu Lucca (1901-1969)

Introduction

The epithermal gold ore deposit from Săsar (Baia Mare), a low sulphidation (quartz-adularia) deposit, and the adjacent mining perimeters (Fig. 1) have been intensively studied by geologists such as Petrulian et. al. (1961), Savul and Pomârleanu (1961), Butucescu et al. (1963), Gurău et al. (1970), Borcoş et al. (1972, 1974), Petreuş and Kovacs (1978). Moreover, the famous Săsar petrometallogenic area was referred to by several authors in the frame of general metallogenic approaches. Nevertheless, very few modern studies mention elaterite as a component, while the older monographs often contain such a reference (Chisholm, 1911).

In 1958, the news on the discovery of a "chewing-gum"-like organic matter in the gold ore deposit from Săsar (Baia Mare) had rapidly spread among the local miners and then all over, from Baia Mare mining region further. By chance, in April 1958 - soon after this discovery, Prof. Valeriu Lucca accompanied by his assistants, Ioan Mârza and Virgil Ghiurcă, took part in a geological field trip with the students from the „Victor Babeş" University in Cluj.

The "elaterite"

The first location the group requested to see when visiting the Săsar mine on April 29, 1958, was the one where the new organic phase for the hydrothermal ores in Baia Mare region had been originally discovered. Topographically, this corresponded to the Speranţa (Rhodochrosite) Vein at the Research directional mine work along the 24 N Vein (the eastern wall and the eastern niche) (Fig. 1, the north-western sector). At the date of our visit, the whole underground environment was very hot – as a result of the heat resulted from the ore oxidation. Locally it was so hot that we could hardly handle the samples we had collected. The organic compound hosted by the Au-ore was associated by common sulphides (pyrite, marcasite, sphalerite, galena, stibnite etc.) and an abundant quartz, chalcedony and rhodochrosite gangue. Even at the dim light of the mine lamp it was easy to identify this phase, due to its brownish color and its elastic and soft touch. The author and his colleague assistant were excited about the scientific potential of this unique novelty, and thus extremely interested in collecting samples to be examined at day light, and then into the laboratory.

In the literature, the presence of organic compounds in primary ores of various metals and genetic types is mentioned as a curiosity. Among the names used to describe such compounds we can mention: elastic bitumen or elaterite, cerite, hatcetine, antracolite, pendlentonite, aeonite, coorongite etc. Their unusual occurrence is related to hydrothermal ores, from hypo- to epithermal, associated with diverse inorganic (metallic- and non-metallic) minerals.

Similar organic compounds were occasionally also noticed in metamorphic, sedimentary and magmatic rocks of various ages. As a rule, in all these cases the source is represented by hydrocarbon-type organic matter (and possibly organic matter of endogenous origin?) hosted by sedimentary rocks. These were chemically-structurally modified via polymerization, then they migrated into exotic geological contexts where they were redeposited. Starting with the 19th century, such organic compounds were described from a wide range of rocks and ores, e.g. USA, Ural Mountains, Transcarpathia, Uzbekistan, Caucasus, Ukraine (elaterite at Borislav), Canada, Australia, and the Republic of South-Africa. In Romania, only a few occurrences are known among which most famous are the ones in the Baia Mare ore district: Săsar (elaterite) and Trestia (black bituminous matter associated with blue chalcedony) (Ghergari et al., 1973). In the same region, organic matter was identified in andesites at Cavnic (Matias Fr., unpubl. pers. comm.) Another type of organic matter documented in the literature is present as inclusions in various petrogenous, endogenic minerals.

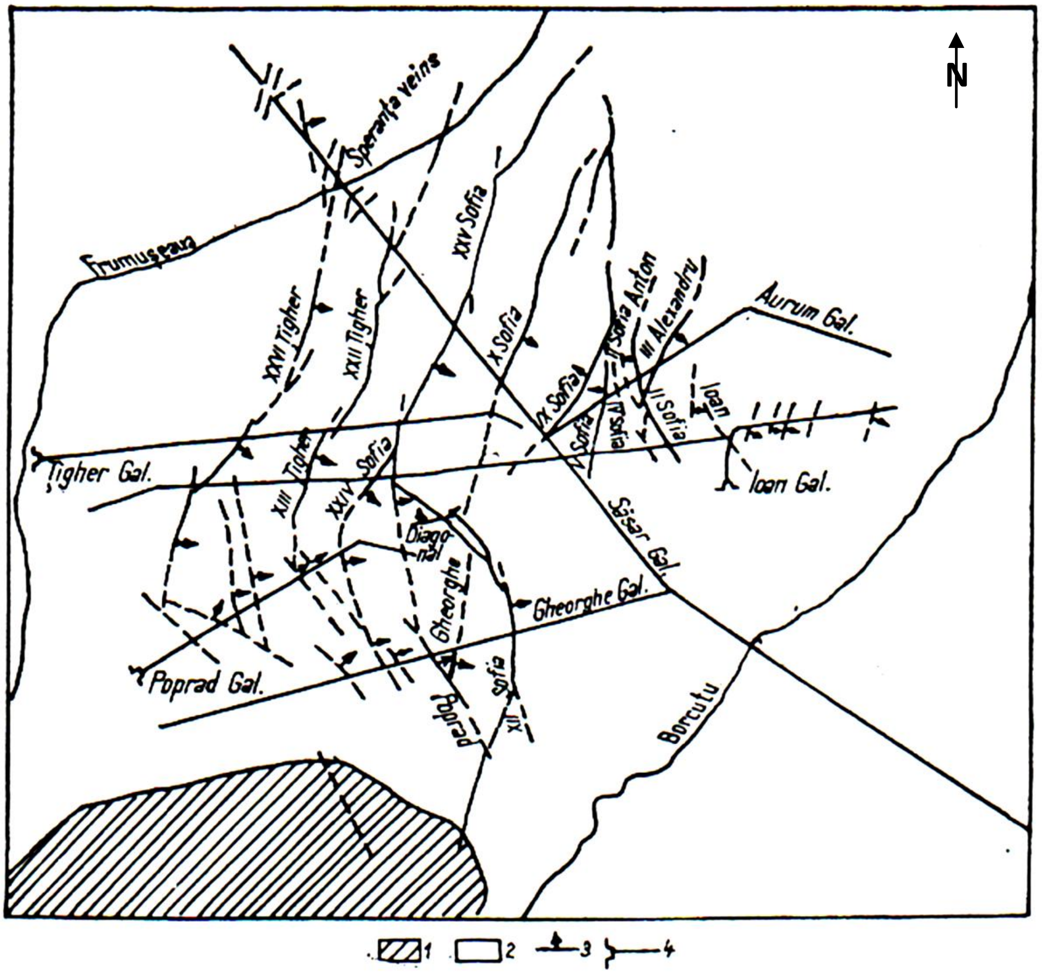

Fig. 1. Săsar vein system (according to Bocoş et al. 1972).
1. Pannonian sedimentary rocks; 2. Pannonian quartz andesite; 3. Vein; 4. Gallery.

The organic compound from Săsar consists of a spongy-like, microvacuolar brown-reddish elastic polymer. In general, it covers the last generation of concretionary and microstalactitic marcasite. It is also present along the walls of microgeodes in the gold ore, originally covered with fine (< 1 cm long) stibnite needle-crystals. Often the surface of this organic compound is sprayed with a white-yellowish powder of (exogenous) melanterite. In thin sections in plane polarized light this organic phase is brown-yellowish in color with red spots while under crossed polars it is isotropic showing slightly local anisotropy. Apparently, the investigated phase is amorphous: nevertheless the XRD pattern (Debye-diagram) evidences marcasite (as mineral inclusions) peaks of poor intensity as well as two other peaks attributed to a quasi-crystalline organic phase: d=10.8 and d=5.0 (Tokody, 1965) that we assume belongs to the investigated organic compound. The vacuolar structure is imprinted by the presence of ovoid-shaped (80.04 x 0.10 to 0.50 x 0.80 mm), sub-rounded (0.035 x 0.050 to 0.15 x 0.18 mm), and only rarely irregular voids.

The investigation under the ore microscope evidenced the presence of powder-like marcasite within the elaterite (< 1 %). When fired, the elaterite turns into a black, coal-like matter with remnant vacuolar structure.

Briefly after its discovery, the new mineral phase was already transported, via "unorthodox" ways (in those times, mineral matter could cross the border only with special, legal approval) to Hungary: here Tokody (1965) had then first described it as "*elaterite*". The Romanian geologists were not aware of the scientific value of this discoverythat was mainly locally spread. It was Mârza (1977 – p. 424; and 1999 – p. 402) in his ore deposit books who briefly mentioned its presence and listed its optical properties.

In our opinion, the organic compound from Săsar does not totally correspond to the classical elaterite description in the references. The typical occurrence for elaterite is Borislav mine (Ukraine), where the extremely elastic fresh material turns into a crumbling, fragile "solid resin" after longer exposure to air (Loevinson-Lessing and Struve, 1963). On the contrary, the matter from Săsar preserves its elasticity also long after its removal from the ore. Most frequently, the chemical formula used for elaterite is that of "ozokerite" (C_nH_{2n+2}), see also (Tokody, 1965).

After a brief chemical investigation, our co-author - the organic chemist Al. Otea, stated that the organic compound from Săsar did not compositionally overlap ozokerite. Accordingly, we concluded that various organic minerals, with distinctive compositions and probably structures had been described under the same umbrella-name, as elaterite. This is also the reason why elaterite and its synonyms are not officially-approved mineral species names by IMA (the International Mineralogical Association). Nevertheless, investigating the elaterite composition and genesis represented a challenge for mineralogists, in particular for us - the generation who witnessed the discovery of the "chewing gum" from Săsar.

The first physical and chemical tests on elaterite in Romania were performed at the University in Cluj by a research group consisting of I. Mârza, Lucreţia Ghergari and A. Moţiu. Unfortunately, because they failed to fully dissolve the phase they could not reach a final conclusion about its composition. As mentioned previously, a second round of investigations was performed by I. Mârza and the organic chemist Al. Otea at the Faculty of Chemistry of the „Victor Babeş" University in Cluj. The first results of this study were promising: they were presented at the scientific meeting of the Chair of Mineralogy in 1979 (Marza et al., 1979). However, again a final composition of the new compound could have not been unequivocally defined. The reason was that after eight months of investigations, the compound failed again to fully dissolve in any of the tested reagents: alcohol, benzene, carbon disulfide, paraffin oil, or olive oil; for shorter times, also dichlorethane, carbon tetrachloride, ethylacetate, tetralene and nitrobenzene were also tested. By using any of these reagents, the final result was always a solid organic skeleton rest. A similar behavior was noticed also by other authors (Kerr and Kelley, 1956), who mentioned that: „the asphalt pyrobituminous matter (such as elaterite, wurtzilite, or albertite) are only partly soluble in common organic reagents".

Accordingly, we did not publish our results right away, with the intention to solve the issue of the incomplete dissolution first. Tragically, soon after we presented our first results, Al. Otea died unexpectedly and the data he obtained could have not been retrieved. This succession of unresolved attempts motivates us now to present, for the record, the remaining information regarding the history of discovery, the occurrence, presentation and some physiographic and mineralogical features of the organic compound identified more than half a century ago at Săsar. Unfortunately, it is impossible to start again this investigation by using modern equipment, given the absence of samples.

Conclusions

From genetic point of view, we consider that the organic compound from the Săsar (epithermal) gold-vein ore represents basically the original hydrocarbon matter of sedimentary origin that was then intruded by Neogene metallogenic magmatites. As a result of the hydrothermal/magmatic solutions, this original matter was remobilized and transformed into gases. The latter were polymerized under the thermodynamic conditions of the hydrothermal environment and deposited as a new compound following the deposition of the fine-acicular stibnite on the walls of elaterite-filled microgeodes. The formation of the organic compound was also subsequent to the deposition of the stalactitic, mammillary-reniform marcasite which it covers. By taking all these considerations into account, we interpret the organic compound as a late/final phase of the low sulphidation hydrothermal gold-silver vein mineralization.

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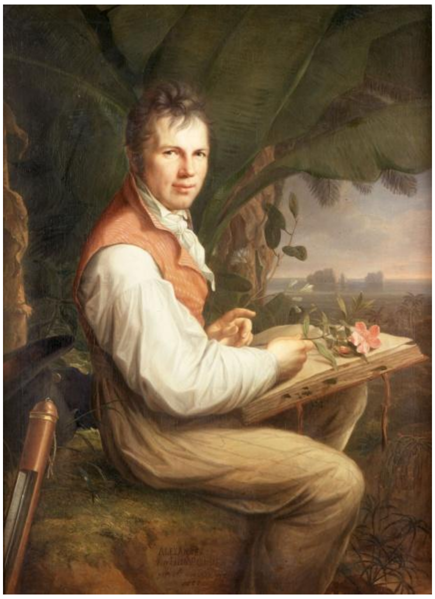
IN MEMORIAM

Alexander von Humboldt (1769-1859),

the great German naturalist, explorer and scientist



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ALEXANDER VON HUMBOLDT AND THE DEVELOPMENT OF NATURAL SCIENCES

Gheorghe UDUBASA

University of Bucharest, 1, Nicolae Balcescu Blv., 010041 Bucharest, Romania
udubasa@geo.edu.ro

Abstract: This is an attempt to make known (more) facts about the great scientist and explorer, perhaps the last scientist of enciclopedic knowledge in the XVIIIth and XIXth centuries, Alexander von Humboldt (1769-1859). In addition to his scientific trips in three continents with numerous new observations and first order discoveries, Alexander von Humboldt promoted freedom of research in being patron of excellent research talent. The "Alexander von Humboldt" Foundation, the final establishment of which was in 1953, continues the tradition of the man Alexander von Humboldt.
This is a small homage for the man Alexander von Humboldt at 246 years since his birth and 156 years since his death as well as for the "Alexander von Humboldt" Foundation at 62 years since its re-establishment.

Keywords: Humboldt, Humboldt-Foundation, Humboldt-heritage, Humboldt-names and -terms.

Alexander von Humboldt (1769-1859) was a scientist covering two centuries and many branches of science, in a manner typical of a man with encyclopedic thoroughness. He lived contemporary with Goethe, Schiller, Gauss etc, with which Humboldt has had many contacts and opinion exchanges.

A. His work – direct influence on the science

Known as a universal scholar, Alexander von Humboldt (AvH) has been concerned especially with plant geography, Earth magnetism, marine geology as well as with the languages and their origin in the countries he travelled during his trip to South and Central America (1799-1804). However, he wrote also several papers on geology (the basalts on the Rhine), mining geology and on volcanoes in general, as he studied many of them in America. His friends were wondered how deep the thinking of Alexander von Humboldt was, how large his knowledge in the scientific matter and how uncommon his memory was. In written form , this opinion belongs to Goethe. More recently, Heisenberg, the first president of the Alexander von Humboldt Stiftung (Foundation), recognised that Alexander von Humboldt was the last scientist of encyclopedic knowledge (Heisenberg, 1969). However, Heisenberg continued: "today is hardly possible that a scientist could have such a science coverage".

The work of Alexander von Humboldt is enormous. The results of his scientific work are widespread in numerous journals, even in the letters on his friends. This is why he decided to collect all the knowledge in a comprehensive work with a great title "Kosmos. Entwurf einer physischen Weltbeschreibung", 5 Bände, Cotta Verlag Stuttgart (1845-1862) ("Cosmos. Proposal for a physical description of the world", 5 volumes, Cotta Publishing House Stuttgart). This work grew from the nature research during the time of Renaissance (Hard, 1969) and influenced the scientific thinking for more than one century. Humboldt wrote more than 630 books (Safonov, 1962) and hundreds of papers and letters to the friends containing numerous scientific data and considerations (Meyer-Abich, 1967).

In recognition of his extensive work on 3 continents (Europe, South America and Asia – the last one as a part of his visit in Russia) the name Humboldt has been given to numerous items not only in the three continents visited and investigated but also in Australia, New Zealand and the neighboring countries. His name (partly of his brother Wilhelm too) paralleled and perhaps slightly exceeded the properly work. As thoroughfully investigated by Oppitz (1969) nearly 1100 items have been baptized by adding Humboldt and/or by replacing the old names.

1. By far the most numerous are the names of animals and plants, subordinately minerals (375) according to one of the most important fields of investigations of Alexander von Humboldt especially during the trip in South America. Among the minerals the name humboldtine, a hydrated ferrous oxalate

($FeC_2O_4 \cdot 2H_2O$), is the most significant. Worth of mentioning is the fact that the naming of majority of plants and animals baptized with Humboldt name were given in the XIXth century, i.e. during the life of Alexander von Humboldt.

2. The names related to geotopography are also numerous (240) and include localities (many in the USA), rivers, glaciers, geysers, falls as well as mountains (one even in Antarctica) and streets (many in cities from Germany). In the Canary island there is a “Humboldt- Blick” (Humboldt-Panorama); Alexander von Humboldt itself couldn’t help admiring the view from this place.

3. Some Publishing Houses (e.g. *Acta Humboldtiana* in Hamburg), hotels and restaurants, mines (especially in Germany), various houses of business and even ships, totalizing 207 items, bear the name of Alexander von Humboldt. One example: the luxurious hotel “Humboldt” in Caracas, Venezuela, on the Mt. Avila at 2250 m altitude.

4. Houses (for guests or students) belonging to different universities in Germany and abroad, foundations (a special mention deserves the Alexander von Humboldt Foundation in Bad Godesberg, a place well known by the former “Humboldt-Stipendiaten” all over the world), medals, scientific institutions and museums, clubs for foreign students in Germany and from former Humboldt scholar abroad (in 1930 existed already such clubs in Bulgaria, England, Finland, former Yugoslavia, Luxemburg and Latvia; nowadays there are some 60 Humboldt-clubs worldwide, Romania included), schools, the Humboldt University in Berlin, named after the both Humboldt brothers, they having statues in front of the building. Some 110 such items there exist in Germany and abroad.

5. Other items: Humboldt-cantata by Mendelssohn-Bartholdy, a crater on the Moon (for Wilhelm), even pseudonyms of some American writers (total 24).

Although Alexander von Humboldt visited Russia too (Urals, Altai), minutely described by Safanov (1962), apparently no names have been given there after Humboldt.

B. The Alexander von Humboldt Foundation – indirect influence on the science

The history of the Alexander von Humboldt Foundation is quite long. It was first established in 1860, one year after the death of Alexander von Humboldt, and re-established in 1925, ceasing the activity in 1945. Unfavourable historical events effaced the intentions of his friends (1860) and of the foreign minister at that time, Stressmann (1925), to honour the greatest discoverer and scientist Germany had during the 18th and 19th centuries.

Nevertheless, it was Konrad Adenauer, Foreign Minister at that time, who succeeded in 1953 to finaly re-establish the Alexander von Humboldt Foundation in the present form, in order to revive the external policy and international academic cooperation of the Federal Republic of Germany after the World War II. Ity was a good fortune that Werner Heisenberg one of the greatest physicists of the 20th century, accepted to act as President of the Foundation (1953-1975). Heisenberg vouched for integrity, academic quality and unerringness in human and political judgement in accepting young scientists form all over the world to undertake academic research in Germany as Humboldt scholars (Pfeiffer, 1993).

In this way, in the last 62 years since the final re-establishing, the Alexander von Humboldt Foundation sponsored nearly 25,000 young scientists from some 130 countries from Europe, Asia, the both Americas, Africa and Australia). The policy of the Alexander von Humboldt Foundation to maintain the scientific liaisons to the former “Humboldtianer” (even the re-invitation of former scholar to the guest institutes in Germany), as well as the establishment of some 60 Humboldt clubs all over the world is the best way to spread and multiply the Humboldt trace and name in the world. Romania followed this way. Between 1963 and1993 some 250 Romanian young scientists were active in Germany. It is to underline the good proportion of success (about 30%) in obtaining the Humboldt Stiftung sponsorship. In Romania the Humboldt-Club appeared in 1990 with some 180 members. Unfortunately and difficult to undestand is the diminishing of applications from Romania in the last decades. The initial difficulty for applicants with German language knowledge was also surpassed in the last year: English language knowledge is sufficient (except of course the applicants for “Germanistik”).

The alumni network of the Humboldt Foundation includes now nearly 25,000 “Humboldtianer” in more than 130 countries. This was and is a good opportunity to enlarge, stabilize and continue the work made by the great discoverer and scientist Alexander von Humboldt some 200 years ago. “He was a discoverer and cosmopolitan, an universal genius and fighter for the freedom of research. An humanist and patron of excellent research talent” (Scholl, 2007). The last sentence can be applied for the Alexander von Humboldt Foundation too as concerns the services provided for the young scientists.

C. What happened after beeing a Humboldt scholar?

The author has had the chance to win a Humboldt scholarship and so he was active at the Heidelberg University for two years (1970-1972). Mineralogy, synthesis and genesis of ore minerals have been investigated under guidance of Professors Paul Ramdohr, Günther Moh and Christian Amstutz, respectively. Finally, the stay in Heidelberg ended with a PhD thesis (*summa cum laude*) involving a comparative study of two base metal ore deposits, one in Romania, the other in Germany. Syngenesis has been documented for both the deposits (Udubasa, 1972, 1996), i.e. Blazna Valley in Romania and Ramsbeck in Germany.

The Humboldt scholarship at the Heidelberg University was followed by a series of scientific papers. My PhD thesis has been published later (1996) in the *Abhandlungen der Universität Heidelberg*, being printed due to a sponsorship of the late Professor Albert Streckeisen (Bern, Switzerland). The scholarship was a quite successful one, with significant follow-ups to my scientific activity.

In addition, with the occasion of the 50th Anniversary of the A v Humboldt Foundation I organised in the Museum of Geology of the Geological Institute of Romania a 3 week exposition "Minerals and rocks from 7 continents: a life collection". Noteworthy, the exposition has been visited by H.E. Wilfried Gruber, Ambassador of Germany in Romania; for H.E. the exposition was a pleasant surprise.

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REVERENTIAL REGARD WITH THE OCCASION OF 246 YEARS FROM THE BIRTH OF ALEXANDER VON HUMBOLDT (September 14, 1769)

Ovidiu DRAGASTAN

University of Bucharest, Department of Geology, Bd. N. Bălcescu No. 1, 010041, Bucharest, Romania

First and foremost, we will begin with a brief history of some important moments from Alexander von Humboldt's life and opera. Originating from a Huguenot family and son of an ennobled major, he was born on the 14th of September 1769 near Berlin, two years after his brother Wilhelm, spending their childhood at the parental castle from Tegel. At the beggining, he was home educated by different proffesors, and later he became a student at the universities from Frankfurt Oder (1787 – 1788), Berlin (1788 – 1789) and Göttingen (1789 – 1790) (Isbășescu, 1992).

His great affinity for field trips in different areas of Germany such as Heidelberg, Mainz, Düsseldorf, Münster, will be the base for all future expeditions and new worlds discoveries. In 1790, as a student he published his first book, "***Mineralogic Observations on Several Basalts on the River Rhine***" marking, among others, his preoccupations as a geologist and mineralogist. In 1791, he returns to Berlin where he carries botanical studies at Wildenow, and in 1793 he is named "Oberbergmeister", in other words, director of Franconia mines.

From April untill October he prepares for and organizes in Paris the expedition in South America, together with French naturalist Bonpland, who will became one of his friends for the rest of his life.

In 1805, a major change took place in his life when he was elected as a member of Science Academy from Berlin, followed by his addmision as a member into the National Institute or French Academy in Paris, and then at the Royal Society in London, Philosophical Society in Philadelphia, but also at the Russian Academy from Petersburg. At the same time, he became friend with important political figures: Th. Jefferson, Napoleon, kings of Prussia, Wilhelm III, Wilhelm IV, Simon Bolivar (whom he considered as the rightful discoverer of America), Metternich, Nicholas the First Tsar of Russia, but he also made connections with important scientific and cultural figures such as the physicist Arago, or with Berthelot, Gauss, Volta, Faraday, Cuvier, Goethe and Schiller (Isbășescu, 1992).

After the Christmas of 1829, Humboldt returns to Berlin at the age of 60, and after a trip among Russia he will not make any scientific expedition.

In the year of 1830, Humboldt will start his great scientific and encyclopaedic paper, a physical description of the world entitled: "***Kosmos, Entwurf einer physichen Weltbeschreinbung***". After some time, while he arranged his annonations and scientific data, the first volume from Kosmos will be published in 1845, at the age of 76, and the second volume will follow the next year, and after that the third volume in 1850 and the forth one in 1858, with a year before his death at the age of 90 due to a heart attack on the 6th of May 1859.

The fifth volume, which was the last one, was published posthumous in 1862. Although a magnificent work, written at an old age, you can still feel in it "*the gigantism that exceeded a one man's powers*", and a part of his theories and hypotheses, in respect of a "*world description and not an explanation of it*" does not correspond absolutely, considering the fact that, in the theory of the origin of species published by Darwin in 1859, the year of Humboldt's death, followed by the general morphology of Haeckel, in 1866, will be contributing to the genealogy of species concept within the animal kingdom and to the validation of darwinism until present.

The topics of the different chapters published within the five volumes of Kosmos, shows the wide purview of Humboldt's preoccupations and acquaintances, not only in the natural sciences field: geology, paleontology, mineralogy, geography, meteorology, mathematics, optics but also in aesthetics, philosophy and universal history.

After the scientist and researcher's death, the Alexander von Humboldt Foundation was brought into existence in 1860 by the friends in Berlin in order to remind his **maecenas** activity developed through the years of his entire life. The capital of the foundation was acquired from donations and grants from London's Royal Society, Academy of Sciences from Petersburg, from king of Prussia, Prussian Academy of Sciences and many other donations from different persons.

Along with the loss of the entire fortune because of the inflation from 1923, the foundation could only gave field trip scholarships to some German researchers in the Natural Sciences curriculum. In 1925, the Humboldt Foundation was re-established by the German Empire and then established again in 1953 as a foundation for community benefit to private right, which offers scholarships to young scientists with a PhD in Sciences. Beginning with 1979, within the foundation, there was the Feodor Lynen Scholarship (a biochemist and Nobel Prize laureate) for young German scientists who already had a PhD diploma (Pfeiffer, 1992).

His affinity for geology, even for mining geology, was crystallized during the confrontations between two geological schools or theories:

- **The school or plutonism theory**, promoted by Hutton since the XVIIIth century, explaining the Earth's birth as a result of the solidification of melting masses or magmas that came from depths and
- **The school or neptunism theory**, advocated and developed by Werner, saying that the Earth's crust rocks were formed by accumulating sequentially material in water.

In other words, if the "plutonism supporters" absolutized the volcanic fenomenon (magmatic), the "neptunism supporters" considered that the rocks were formed by sedimention processes in different water basins, marines or other type, basalt being a neptunian product developed through sedimentation in water.

The perfection in geological knowledge began with the enrollment at the Academy of Mines in Frelberg (Saxony), founded in 1766 by baron von Heinitz, Officer of state of Prussian Ministry for Industry and Mines. At that time, this Academy was not only the first school of this type in the world, but one of the most advanced institutes from Europe, where students from around the world came in order to prepare in this practical field, driven by the illustrious figure, a magister, professor Abraham Gottlob Werner. Considered the founder of Geology in Germany, he was one of the most endowed professors in the European academic world. At Freiberg, Humboldt sought to enrich his knowledge of general geology, paleontology, stratigraphy and mineralogy. Through his paper "***Basalts on the River Rhine – Mineralogische Beobachtungen über einige Basalte am Rhein***" from 1790, he received his first consecration in geology and, at the same time, he was praised by professor Werner. At Freiberg, the academic schedule was pretty busy. During the day they were studying the mining, geological and mineralogical practical problems in the mine, and in the afternoon it was followed by acquiring theoretical knowledge: geology, rock classification, mathematics, stratigraphy, especially for Jurassic, and many other laboratory experiments regarding different types of coals. The young student's other passions were paleontology, botany and chemistry. After graduating the Freiburg Academy in 1792, he was named inspector at the Prussian Center for Mine and Metallurgy.

In the stratigraphical geology, Humboldt had a well - known priority, because in 1795 he was the first that used the term of Jurassic in a paperwork, in order to designate some white limestones from Franconia (southern Germany), limestones that were lito – and biofacial similar to those of the same age described from Jura Mountains (Switzerland); for that matter, the region or type – locality for that geological period. We mention that the Jurassic subdivisions (in three substages), lower or the black Jura, middle or the brown Jura and upper or the white Jura were introduced by Leopold von Buch, late in 1837.

The time that Humboldt has lived, was characterized by "race" or collecting for "deeds", especially rocks and fossils to explain the evolution and geological history of the Earth. During the field trip in South America, Humboldt discovers in Colombia (in 1801), fossil bones of mastodons, coal "fields" and salt deposits, and in Mexico (1803 – 1804) he describes the first geological profile from this area, in which he mentions the sedimentary and eruptive deposits, using conventional signs for every type of rock (Fig. 1).

The science for the conventional signs or the pasigraphy, in Humboldt's vision, was the writing language through "signs", for map reading or interpretation and for geological profiles, an integrant part of the research program regarding the geological sciences progress.

In the name and memory of the great scientist Alexander von Humboldt, name of minerals or genres and new species for the science were dedicated to him even during his lifetime: the "humboldtine" mineral, a hydrated iron oxalate, frequently encountered in brown coal, but also in black shales. (Dragastan, 1992).

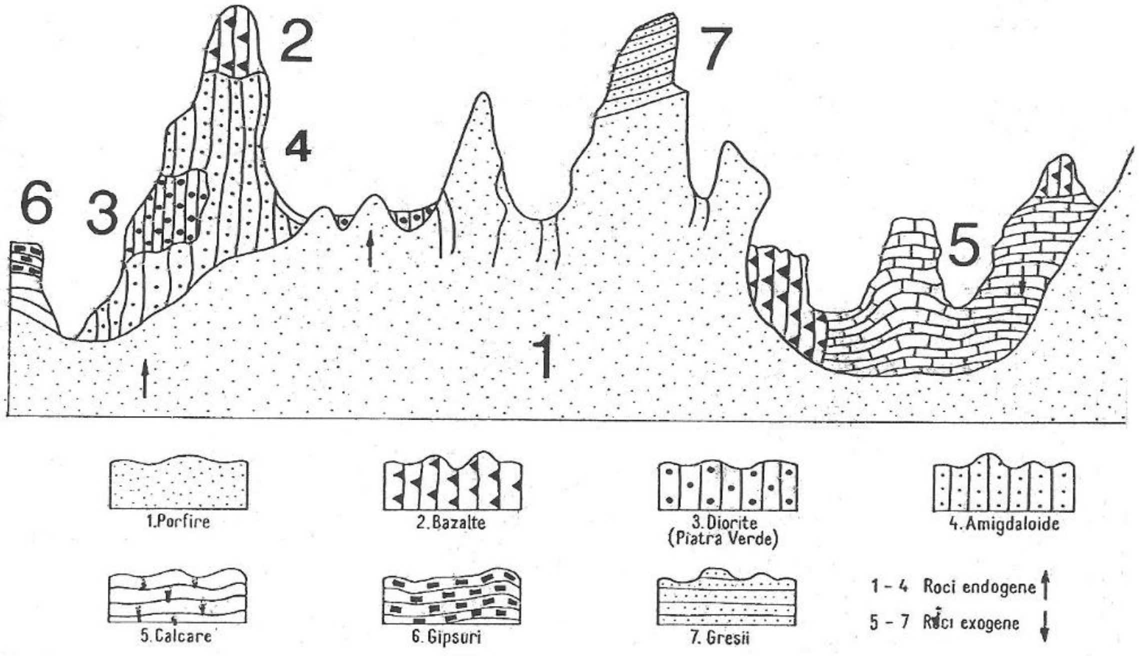

Fig. 1 – Geological profile or geognostic sketch of eruptive and sedimentary deposits that cross the Meran Valley and Totonilec Valley from Mexico. 1. Porphyry; 2. Basalts; 3. Diorites; 4. Amygdaloids; 5. Limestones; 6. Gypsum; 7. Sandstones; 1 - 4 –Endogenous rocks; 5 -7 - Exogenous rocks (after Humboldt).

My colleague from the Mineralogy Department, Prof. Dr. Gheorghe C. Popescu, in his paper „Geology and Mining Relationship", published in 2002 by the Society of Economic Geology of Romania, has mentioned that Alexander von Humboldt was the first to observe the links between metallic concentrations and igneous rocks, a concept assumed and mentioned also by Antonela Neacsu and Gheorghe C. Popescu in their book „Applied Metallogeny and Geological Prognosis".

In 1851, when Humboldt was still alive, the geologist and micropaleontologist E. Reuss dedicated to him a microfossil, a genus and a new species of Foraminiferida, naming it ***Sabellovoluta humboldti*** (Reuss, 1851), revised afterwards by Loeblich and Tappan in 1985 as a "***Spirolina***", which has been found in the Häringer schists, in Oligocene deposits from Tirol, Austria.

Afterwards, in 1957, in the Brasilian Atlantic Ocean's shelf it was described a trochospiral foraminifer in Holocene deposits, named ***Eggerella humboldti***, a new species dedicated to Humboldt by micropaleontologists Todd and Brönnimann.

The Romanian micropaleontology and microfacies school also brought a well – deserved tribute to Alexander von Humboldt by describing and dedicating a genus and new species in 1988, ***Alexanderella stricta* Dragastan, 1988**, an algae from the Chlorphyceae group encountered in the white limestones of Upper Jurassic age (Weisse Jura), from Mateiaș Mountain (Rucăr), Southern Carpathians (Dragastan, 1992).

Because the author of these pages received the Humboldt Foundation scholarship in 1980 and also has had the privilege to meet and work in collaboration with many professors, PhD scientists and PhD students from different universities or institutes from Germany, I cannot pass by in mentioning a series of opportunities of working in well – equiped laboratories, libraries for every departments subjects, but also with professors and doctors in sciences well - known and recognized by the international scientific world, pioneers in the fields of sedimentary petrography, micropaleontology, paleontology, paleoalgalogy, microfacies and paleoenvironments reconstruction and sedimentology, from which I mention **Prof. Erik Flügel** from University of Erlangen (Institute of Paleontology), the one who organized the **First International Symposium on Fossil Algae**, in Erlangen in October 1975, the one who wrote one of the most important books for studying the different carbonaceous rocks: "**Microfacies analysis of limestones**", published in 1982, in Springer, Berlin, Heidelberg, New York, with 633 pages.

I also must mention **Prof. Hans Füchtbauer** from Ruhr Universität Bochum, a prestigious representant of sedimentology school and President of International Association of Sedimentology, who wrote the book "**Sedimente und Sedimentgesteine**" that has been published in several editions, beginning with 1969.

Another professor to be mentioned is **Prof. Hans Mensink**, a paleontologist that had numerous PhD students from around the world under his lead and with whom I published a series of papers regarding the Jurassic – Cretaceous limestones from Asturias provence, Spain.

I also had and still have a long collaboration with **Prof. Dr. Detlev Richter**, a sedimentologist, a specialist in reefs and in different types of facies and we have published together with his PhD students a series of papers, as well a recent one which is to be published in 2015 or 2016, together with **Prof. Dr. Rolf Neuser**, both of them representing the team from Ruhr Universität Bochum, and from Department for Geology, Mineralogy and Geophysics – Microanalytical Labs.

I have also had a series of collaborations with **Prof. Dr. Dorothee Mertmann** from Frei Universität Berlin, as well as with **Prof. Dr. Hans Herbig** from University of Köln, with whom I published a series of papers regarding the Palaeogene deposits from Maroc.

This list could continue with many other colleagues from universities in Germany, doctors of sciences from different institutes or museums with whom I have published numerous scientific papers of regional interest for the European and Asian continents.

I cannot conclude without the words of a colleague professor from a German university who pleaded strongly that "*if you do not publish your research results, you do not exist*", a fact proven for years by many colleagues from universities from Romania and around the world.

Finally, as a tribute to the scientist **Alexander von Humboldt** and **Humboldt Foundation**, I shall mention a series of genres and new species described, published and dedicated to some colleagues, professors, doctors in sciences from universities and institutes from Germany, to whom I collaborate with over the years, as follows:

1. ***Suppiluliumaella erikfluegeli* (Dragastan, 1989) Dragastan & Richter 2003**, a new species dedicated to **Prof. Erik Flügel**, Erlangen University, Revista Espanola de Micropaleontologia (Rev. Esp. Micro., 1989), vol. XXI, No. 1, p. 18, Pl. 10, Figs. 1-4, redescribed by Dragastan & Richter, 2003, in Analele Universității București, Geology, Special Publication No. 1, 2003, p. 79, Pl. 3, Fig. 5, Pl. 4, Figs. 4-6;
2. ***Hansiella fibrata* Dragastan 1990**, new genus dedicated to **Prof. Hans Mensink**, Ruhr Univ. Bochum, published in Revista Espanola de Micropaleontologia (Rev. Esp. Micro., 1990), vol. XXII, No. 1, p. 13-14, Pl. 7, Figs. 1-2;
3. ***Franconiella polyfurcata* Dragastan 1990**, new genus and new species discovered with colleagues from Erlangen University, in a field trip at Kapfelberg, Franconia, Rev. Esp. Micro., 1990, vol. XXII, No. 1, p. 7-8, Pl. 3, Figs. 1-3, Pl. 4, Figs. 1-2;
4. ***Paraortonella richteri* Dragastan 1985**, new genus and new species dedicated to **Prof. Dr. Detlev Richter**, Ruhr Univ. Bochum, published in special volume: Palaeoalgology, Contemporary Research and Applications, Springer Verlag, 1985, p. 116-117, Pl. XVII, Figs. 4-5;
5. ***Garwoodia fluegeli* Dragastan 1985**, new species dedicated to **Prof. Erik Flügel**, Erlangen University, published in a special volume: Palaeoalgology, Contemporary Research and Applications, Springer Verlag, 1985, p. 119-120, Text – Fig. 3, Pl. XIX, Figs. 1-8;
6. ***Hedstroemia hansi* Dragastan 1989**, new species dedicated to **Prof. Hans Füchtbauer**, Ruhr Univ. Bochum, published in Rev. Esp. Micro., 1989, vol. XXI, No. 3, p. 419-421, Pl. 1, Figs. 4-6;
7. ***Hedstroemia klausi* Dragastan 1989**, new species dedicated to **Prof. Klaus Malmsheimer**, Ruhr Univ. Bochum, published in Rev. Esp. Micro., 1989, vol. XXI, No. 3, p. 424-427, Pl. 6, Figs. 1-2;
8. ***Erikiella ramosa* Dragastan 1990**, new genus and new species dedicated to **Prof. Erik Flügel**, Erlangen University, published in Rev. Esp. Micro., 1990, vol. XXII, No. 1, p. 8-9, Pl. 5, Fig. 1;
9. ***Cupasiella juberiae* Dragastan 1990**, new genus and new species dedicated to **Dr. Eleonore Juber–Wuendt**, Ruhr Univ. Bochum, Rev. Esp. Micro., 1990, vol. XXII, No. 1, p. 10-12, Pl. 6, Figs. 5-6;
10. ***Harlanjohnsonella fuechtbaueri* Dragastan & Richter 2003**, new genus dedicated to **Prof. Harlan Johnson**, father of American Palaeoalgology, Colorado School of Mines and new species dedicated to **Prof. Hans Füchtbauer**, from Ruhr Univ. Bochum, Analele Universității București, Seria Geologie, Special Publication, 2003, No. 1, p. 69, Pl. 4, Figs. 3-4;
11. ***Arabicodium hansi* Dragastan 1985**, new species dedicated to **Prof. Hans Mensink**, Ruhr Univ. Bochum, in Palaeoalgology, Contemporary Research and Applications, Springer Verlag volume, 1985, p. 125, Pl. XXV, Figs. 5-6, taxon *transferred* to *new genus Pseudopencillus with species*

hansi Dragastan & Richter 2003(Dragastan, 1985), in Analele Univeristății București, Seria Geologie, Special Publication, 2003, No. 1, p. 85, Pl. 8, Fig. 4;

12. ***Felixporidium*** **Dragastan, 1999**, new genus, dedicated to **Dr. Felix Schlagintweit** from Munich, publishe in Rev. Esp. Micro., Vol. 31, No. 2, p. 212 and ***Felixporidium renatae*** **Dragastan & Richter, 2003,** new species dedicated to **Mrs. Renate Richter**, Analele Univeristății București, Seria Geologie, Special Publication, 2003, No. 1, p. 82, Pl. 7, Figs. 2-5;
13. ***Suppiluliumaella riedeli*** **Dragastan 1989**, new species dedicated to **Prof. Dirk Riedel**, Ruhr Univ. Bochum, published in Rev. Esp. Micro., vol. XXI, No. 1, p. 18, Pl. 9, Figs. 7-9;
14. ***Megaporella fluegeli*** **(Dragastan 1978) Dragastan 1989**, new species dedicated to **Prof. Erik Flügel**, Erlangen University, redescribed in Rev. Esp. Micro., 1989, vol. XXI, No. 1, p. 10, Pl. 7, Figs. 1-4;
15. ***Halimeda erikfluegeli*** **Dragastan & Herbig 2007**, new species dedicated to **Prof. Erik Flügel** from Erlangen University, published in Micropaleontology, Vol. 53, No. 1-2, p. 20, Pl. 6, Figs. 6-7, New York, and this new species was transferred to ***Atlasinium*** **Dragastan, 2008**, new genus, published in Acta Palaeontologica Romaniae, vol. 6, p. 90, Pl. 2, Figs. 2-3.

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