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TELLURIUM, SELENIUM AND CADMIUM RESOURCES IN THE WASTE DUMPS OF SĂCĂRÂMB AREA (APUSENI MOUNTAINS), ROMANIA. A PRELIMINARY ESTIMATION

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Abstract: Since recently, tellurium was considered only from scientific – mineralogical point of view. No interest for resources estimation in Romania exists. Only in 2005 this element started to be considered as a useful component, when it was used in the construction of solar panels. A first estimation regarding tellurium resource in Săcărâmb ore deposit was made taking into consideration the Au: Te ratio from the most common tellurides - nagyágite and sylvanite, and the amount of gold extracted from Săcărâmb deposit (over 1746-1941), estimated as being approx. 30 t. Therefore, the amount of Te - mined and unprocessed, just dumped, would be of approx. 60 t. The base–metal ore veins are hosted into an andesitic stockwork generated by the Neogene calc-alkaline magmatic events in the Metaliferi Mountains. Over 100 mineral species have been identified in Săcărâmb ore deposit, of which a total of 14 minerals contain Au, Ag, Fe and Hg. Our paperwork presents the results of the explorations conducted over for years on the tellurium resources hosted into three waste dumps at Săcărâmb, and into the "Iazul Avariat / Damaged Tailings Pond" at Certej. Tellurium contents have been determined using ICP-MS method. The Au:Te ratio is approx. 0.25 in case of the damaged tailings pond, and it is averaging 0.35 in case of the three waste dumps. Regarding the correlation degree, tellurium is well, directly correlated with gold and silver, confirming that tellurium is related to gold and silver mineral compounds. Actually, the Au, Ag and Te distribution map into the tailings pond area and waste dumps area indicate overlapping of the enrichment zones for all those three elements. New metallogenic data reveal copper and silver selenides in the Săcărâmb area. Because of the relatively high content of Se and Cd in the analysed samples of the already mentioned three waste dumps and damaged tailings pond, it is possible to identify the association of these elements with other analysed elements. Mineralogical study confirmed eucairite and possible naumannite and klockmannite. There is a good correlation between cadmium and zinc in the analyzed samples of waste dumps and damaged tailings pond. But future mineralogical investigations are necessary for establishing if cadmium is a minor elements of sphalerite.

Keywords: tellurium, selenium, cadmium, resources, waste dumps, damaged tailingd pond, Săcărâmb.

1. INTRODUCTION

Telluride bearing gold and silver ore deposit from Săcărâmb is a part of the Neogene metallogenic subprovince, situated in the Metaliferi Mountains. It is the largest telluride mineral accumulation within Romania and Europe. More than 230 ore veins are known in this mineral occurrence documented from 1747. About 300 km of mineral shafts and tunnels are disposed on five main levels, in an area of approximately 1/1 km. A vertical zoning of ore deposit is mentioned, from the native gold significant presence in the upper position, to Au-Ag tellurides in the middle one and common sulphides with tellurium in the deeper part of it (Udubaşa et al., 2002). The base–metal ore veins are hosted into an andesitic stockwork, generated by the Neogene calc-alkaline magmatic events in the Metaliferi Mountains (Fig. 1).

There is no interest for tellurium resource estimation in Romania, since recently; this element is considered important only from scientific–mineralogical point of view.

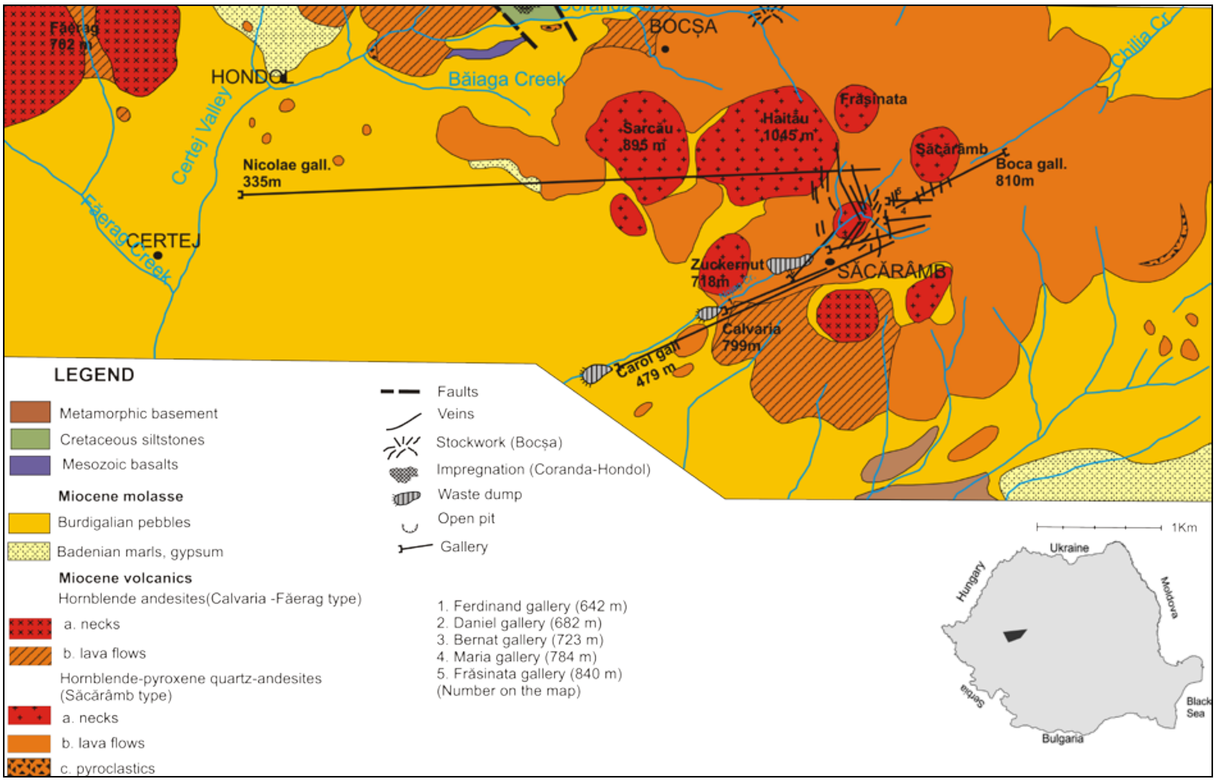


Figure 1. Geological sketh map of the Săcărâmb area, where the waste dumps are seen (redrawn after Udubaşa et al., 1992)

But, starting on 2005 tellurium was studied as a useful component when it was used in the construction of solar panels (Popescu & Neacşu, 2008, Buia & Lorinţ, 2011) using photovoltaic cells based on Cd-Te technology.

Tellurium is an emblematic element for Romania (Popescu & Şimon, 1992, Ciobanu et al., 2004). This is the place where it was described for the first time as a chemical element and a native mineral, back in 1798. It is also the place where many tellurium minerals have been discovered later to generate the expression „Romania – the country of tellurides", and where the most numerous telluride minerals in Europe occur, usually associated with gold-silver ore deposits. As a consequence, the research focused on the mineralogical features of this element is proven by the large number of minerals firstly described in Baia de Arieş (sylvanite), Faţa Băii (native tellurium and tellurite) and Săcărâmb.

Over 100 mineral species have been identified in the Săcărâmb ore deposit (Udubaşa et al., 2002 Ciobanu et al., 2004); some of them have been firstly described in the world (nagyágite, petzite, krennerite, stützite, muthmannite, museumite).

A first estimation regarding tellurium resource in the Săcărâmb ore deposit was made by Udubaşa & Udubaşa (2004), by assuming a Au:Te ratio of 1:2 in some of the most frequent gold tellurides occurring in the Te deposits - nagyágite and sylvanite. The average content for 250 years of gold extraction at Săcărâmb is estimated as 10 g/t. In 1941 Ghiţulescu and Socolescu estimated that the Săcărâmb mine produced approximately 30 t Au and 55 t Ag between 1747 and 1941.

The are no data looking the tellurium content in ore, so we are not able to realise the extracted tellurium amount. But we can estimate it, based on the Au:Te ratio. If this ratio is generalized to the entire Săcărâmb ore deposit, then the results will be a tellurium content of 20 g/t. Therefore, the amount of Te mined and unprocessed – just dumped, could be of approximately 60 t until 1941.

2. MATERIAL AND METHODS

Our aim is to present the results of the exploration activity conducted over two years (2008-2009) on the tellurium resources hosted into three waste dumps (I, II and III Sector) (Fig. 2) situated on the Nojag river Săcărâmb area (Fig. 1), and into the "Iazul Avariat / Damaged Tailings Pond" at Certej.

2.1. The microscopic study of the hosted-rocks of mineralization in the Săcărâmb ore deposit

The Au-Ag telluride mineralization is hosted within quartz andesite with hornblende and pyroxene, named *the Săcărâmb andesite.* It contains mainly plagioclase feldspar and hornblende. The microscopic investigations of the *Săcărâmb andesite* and also of ore samples of the three waste dumps described below have been marked up at the Department of Mineralogy, University of Bucharest, Faculty of Geology and Geophysics, Economic Geology & Metallogeny Laboratory, using a PANPHOT microscope, to which a Nikon Eclipse E-400, 40 W has been attached, being thus possible to obtain microscopically images. The thin and polished sections have been manufactured at the Sections Laboratory from the Mineralogy Department. This study reveals idiomorph oxihornblende partly or totally opacitized, zoned feldspar substitued by carbonate and micas, small biotite and augite crystals which are present subordinately, disseminated into fundamental mass and substituted by ilmenite. Accesory minerals are apatite, ilmenite and zircon. Andesite has been altered into propylite, consisting of chlorite-epidote-calcite±albite association, but also into argillaceous rock, resulting by feldspar alteration (Pl I). Cordierite has been altered to *pinite*, which is a fine- grained greenish or yellowish aggregate of chlorite, muscovite and other silicates (Nesse, 1986).

2.2. The mineralogical study of ore samples of the waste dumps of the I, II and III Sector, Certej

The microscopic study of the ore samples belonging to the waste dumps (Fig. 2, Pl. II) demonstrates that, in fact, they are fragments of the *Săcărâmb ore*. They are some textural-qualitative types of ore (Fig. 1, Pl. II):

I Sector: ore with parallel symmetrical texture, showing succesive deposition of alabandite (black), sulphides, sulphosalts and tellurides (grey),

Figure 2. The waste dumps of the I, II and III Sector, Săcărâmb area

Table 1. The comparative contents for Au, Ag, Te, Cd, Se in 62 samples from Au-Ag+Te mineralization of the waste dumps, Săcărâmb area. The values are in ppm.

Samples	Au	Ag	Te	Cd	Se	Samples	Au	Ag	Te	Cd	Se
1	1	5	4.1	3.8	11.3	32	1.11	4	1.6	4.3	4.9
2	1	5	4.4	4.2	10.3	33	1.91	4	3.7	3.9	11.5
3	1.04	6	3.9	4.3	11.7	34	1.43	5	3.1	4	5.7
4	1.04	6	3.8	4.1	10.9	35	1.52	8	3.4	7.4	7.9
5	1.16	7	4.8	5.8	16.8	36	1.06	7	3.4	8.3	11.3
6	1.2	6	4.9	6.7	11.1	37	1.15	6	2.9	6.9	7.8
7	1.27	4	4.1	1.4	12.8	38	1.03	4	2.4	3.8	6.8
8	5.1	11	13.3	13.3	13.4	39	1.36	2	2.4	1.4	6.1
9	1.24	4	4.2	3.1	10.4	40	1.17	3	2.5	2.5	5.6
10	1.03	7	3.9	2.9	11.3	41	1.62	4	3.1	4.3	6.8
11	1.04	12	3.6	6.2	12.6	42	1.19	3	3.2	2.6	6.7
12	1.17	13	4.4	4.9	12.3	43	1.63	6	4.8	5.6	6.4
13	1.04	3	3.1	0.9	8.7	44	1.51	6	3.8	3.1	7.3
14	1.04	4	3.3	4.1	10.2	45	1.5	4	2.9	5.4	6.1
15	10.7	2	2.9	0.9	8.9	46	1.42	7	3.9	4.4	7.3
16	1.04	4	3.3	2.9	8.8	47	1.83	4	4.2	4.5	6.5
17	1.26	5	2.9	1.5	9.2	48	2.04	6	4.6	9.3	7.2
18	1.35	5	3.1	4.1	9.5	49	1.09	7	2.4	3.3	8.7
19	1.18	9	4.1	3.9	8.3	50	1.22	3	2.7	2.1	7.9
20	1.13	3	3.6	3.6	8.2	51	1.33	4	2.8	2.9	6.7
21	1.34	6	2.9	7.8	9.3	52	1.51	4	3.1	3.6	5.4
22	1.46	9	4.6	7.5	7.5	53	1.3	3	2.9	3.1	15.8
23	1.97	6	5.4	4.5	6.8	54	1.04	2	1.6	1.2	10.1
24	1.06	3	2.7	1.4	6.9	55	1.65	5	3.7	3.3	9.1
25	2.01	6	5.5	9.7	9.7	56	1.77	5	3.3	4.3	11.9
26	1.59	7	4.5	7.2	8.1	57	1.49	4	2.5	4.7	10.3
27	1.42	2	2.5	0.6	5.6	58	1.64	3	2.1	0.8	9.4
28	1.46	11	2.9	4.3	5.5	59	1.55	3	2.8	3.1	10.3
29	1.37	2	2.5	2.1	5.7	60	1.16	4	3.2	1.1	10.1
30	12.53	6	4.1	4.8	5.1	61	1.59	5	3.3	8.9	9.2
31	1.86	7	3.2	6.1	6.4	62	1.11	1	1.3	0.5	9.3

and coarser spots of telluride assemblages within carbonates (white-pink).

II Sector: ore mainly consisting of alabandite and Mn carbonates dispersed within it.

III Sector: ore with symmetrical texture, presenting in central part of it tellurides and carbonates, marginally succeeded by Mn-carbonates and alabandite to the peripheria.

Tellurium, selenium and cadmium contents have been determined by the S.C. Prospecţiuni S.A. Bucharest, using ICP-MS method AAS-cold vapors, standard procedure PS-LAG-CAFCH-RM-009, 007, and by the S.C. Deva Gold S.A. respectively, for gold and silver, using ICP-MS method Au-AA26 (Table 1).

3. RESULTS AND DISCUSSION

There is a diference related to the contents of elements in the four studied regions. The Au:Te ratio is 0.25 into the damaged tailings pond, and varies from 0.32 to 0.38 into the three waste dumps (see Table 2). An explanation for 1:4 ratio of Au:Te existing at the level of the tailings pond, is that the material has been produced by the processing plant, therefore gold has been recovered. Tellurium has been discharged into the tailings pond. Consequently, the Au:Te ratio changes favourably for this element.

The waste dumps have interesting contents in Au and Te. Regarding the correlation degree, tellurium is well, directly correlated with gold and silver, and this confirms that tellurium is related to gold and silver mineral compounds.

Regarding the Au:Te ratio, our data indicated 1:3 ratio for Săcărâmb tailings pond and 1:2 to 1:3 ratio for each waste dump.

From the economic point of view, the recovery of tellurium from tailings ponds and waste dumps is much profitable, if we take into consideration a surface explotation and not a mining activity. The novelty and surprise of our 2008 and 2009 researches on the Certej I, II and III Sector perimeters is the notable presence of selenium and cadmium contents (Table 3).

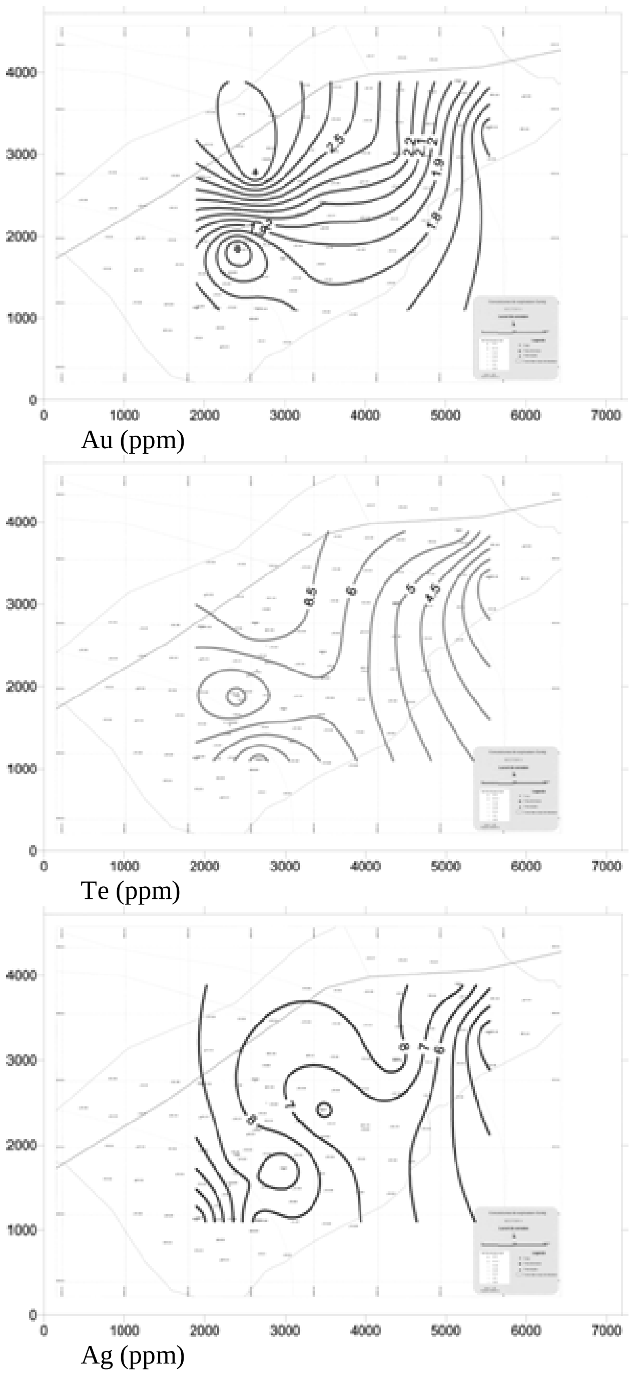


Plate III. The distribution of Au, Ag and Te in the waste dumps of the II Sector, Certej (unpublished data)

Until 2009 the presence of selenium in the Metaliferi Mts. was considered only from the geochemical point of view. As useful element, the selenium study has been made after geological survey of exploration waste dumps in Săcărâmb, when significant selenium contents have been evidentiated. The selenium values are constantly twice as much than tellurium.

Selenium forms often selenides with lead, silver, copper and iron, but its correlation is not good with any of the analyzed elements (R<0.30). A weak correlation tendency can be seen in the case of silver (R=0.28). This aspect is due to selenium produced in the Au-Ag ore deposit at Săcărâmb, such as those of copper and silver selenides. A larger value, but insignificant too, of the correlation degree (R=0.42) between selenium and antimony is obtained (Table 3).

Despite that eucairite (CuAgSe) is mentioned in 1853, it can not be confirmed until 2010. Eucairite is associated with an anisotropic mineral, possible naumannite (?) (Ag_2Se). The third selenide, probably klockmannite (CuSe), is found into a carbonate vein. To demonstrate the presence of selenium, a XRF investigation has been made, on a polish sample where the selenium minerals are associated with galena, alabandite and tetrahedrite (Popescu et al., 2010).

Cadmium is well correlated with zinc (R=0.78), which means that it could be a minor element of sphalerite. But there is not enough mineralogical analyses for sustaining this.

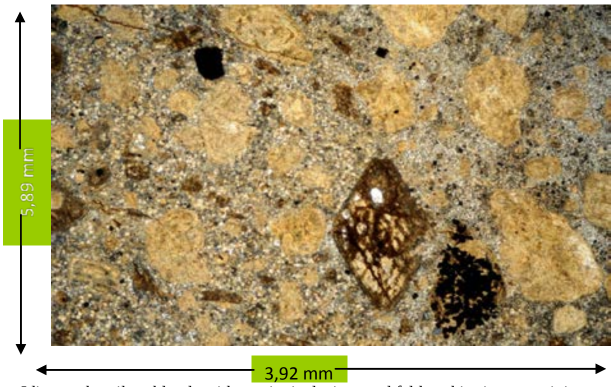
4. CONCLUSIONS

The exploration activity for developing the geological and qualitative data of gold-silver tellurides mineralization within the three waste dumps of the Săcărâmb area, represents a first stage in order to evidentiate the source of tellurium, selenium and cadmium. These elements are strategic for unconventional energy.

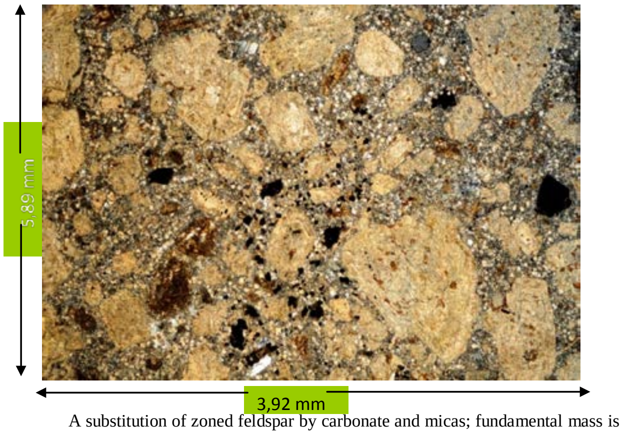
For the waste dumps area of Săcărâmb and also for the damaged tailings pond Certej the Au/Te ratio is different by the early 0.5, the estimated value for the primary ore deposit (Udubaşa & Udubaşa, 2004).

Table 2. The Au:Te ratio in the gold-silver+tellurium ore of the I, II and III Sector perimeters Certej, and of the tailings pond Cerej area

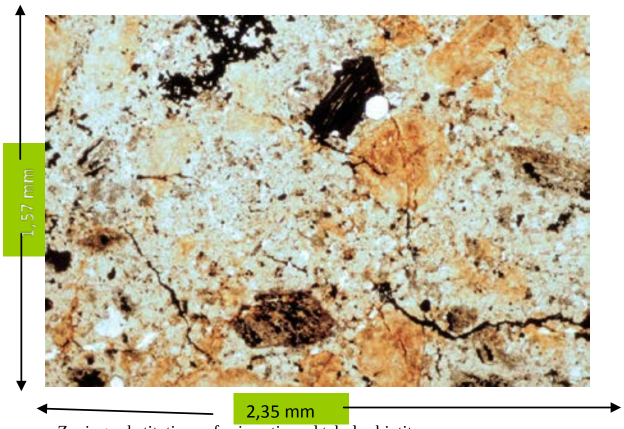
Perimeter	Average contents (ppm)		Au/Te Ratio
	Au	Te	
I Sector	2.49	7.62	0.32
II Sector	2.43	6.48	0.37
III Sector	2.57	7.37	0.38
Damaged tailings pond	1.12	4.51	0.25



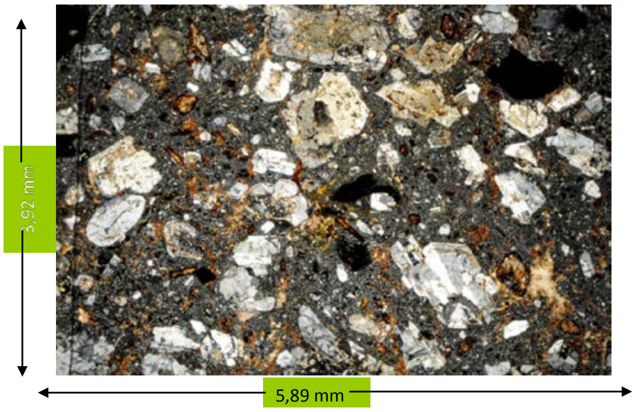
Idiomorph oxihornblende with apatite inclusions and feldspathic rims containing carbonates, sericite/ peripheral illite; fundamental mass - micas, carbonates, potassic feldspar. Nll



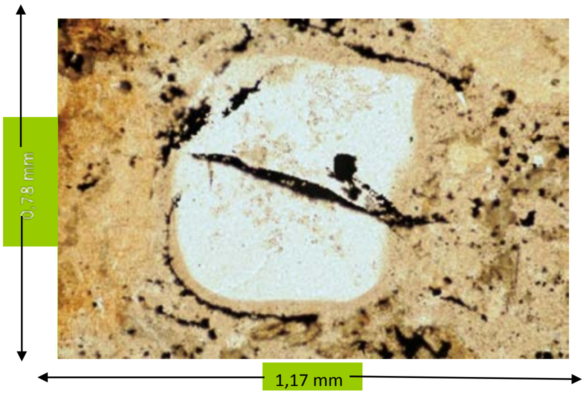
A substitution of zoned feldspar by carbonate and micas; fundamental mass is represented by micas, carbonate, potassic feldspar. Nll



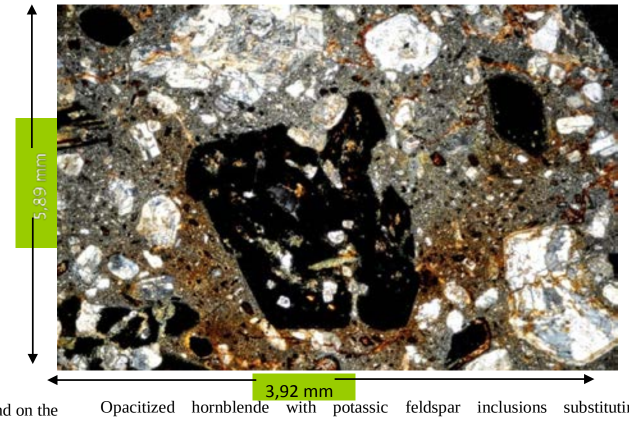
Zoning substitutions of prismatic and tabular biotite by illmenite. Fundamental mass: micas and potassic feldspar. Nll



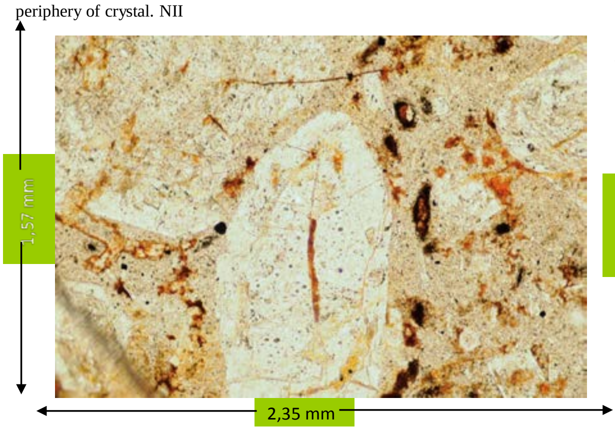
Partial substitution of the internal zones of plagioclase feldspar. There is a lot of siderite-ankerite grains, and also idiomorph prismatic oxihornblende, partly opacitized, into the microcrystalline fundamental mass . N+

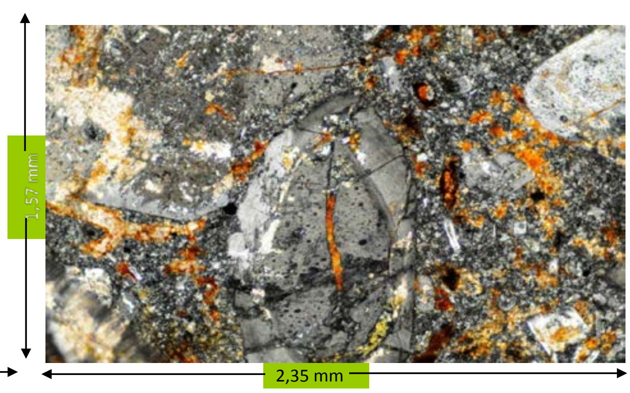


Cordierite porphyroblast rounded by pinite and opaque minerals within fissures and on the periphery of crystal. NII



Opacitized hornblende with potassic feldspar inclusions substituting plagioclase feldspar. Potassic feldspar is partly substituted by muscovite. On the inferior half a microlenticular chlorite is observed. N+





Zoned feldspar surrounded by plagioclase feldspar. There is a fissure within siderite on the central part, which is also found within the fundamental mass (NII on the left side and N+ on the right side).

Figure 1. The representative polished ore samples of the telluride, sulphide and sulphosalt associations in the waste dumps of the I, II and III Sector, Săcărâmb.

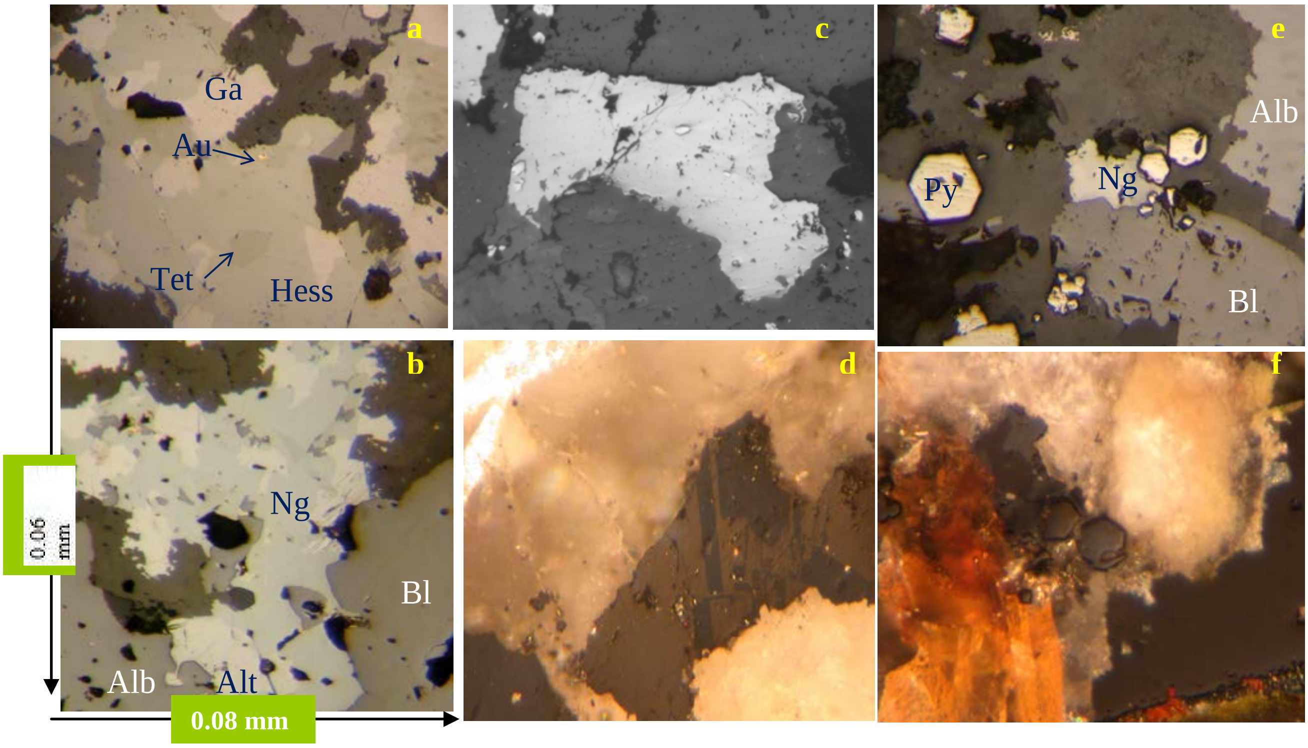


Figure 2. Microscopic images (reflected light) of the telluride association within the three waste dumps of the I, II and III Sector, Săcărâmb: a. Hessite (Hess) asociated with tetrahedrite (Tet), galena (Ga) and native gold (NII); b. Association of altaite (Alt), nagyágite (Ng), alabandite (Alb) and sphalerite (Bl) (NII); c. Lammelar twinning grain of hessite with pyrite inclusions (lighter) into a carbonate gangue (NII); d. Idem, N+; e. Sphalerite, pyrite (Py), nagyágite into a carbonate gangue (NII); f. Idem, N+: internal reflexes of sphalerite are evident.

Table 3. The values of the correlation degree between Se and other elements from the waste dumps of Săcărâmb area

	Au	Ag	Pb	Sb	Cu	Zn	Bi	As	Cd	Hg	Se
I Sector	0.68	0.77	0.76	0.76	0.65	0.70	0.32	0.63	0.92	0.52	0.28
II Sector	0.83	0.47	0.25	0.53	0.28	0.27	0.40	0.42	0.65	0.37	0.17
III Sector	0.78	0.44	0.18	0.74	0.13	0.12	0.74	0.63	0.45	0.54	0.26

Tellurium has been analysed from the damaged tailings pond Certej. Our data indicate an average content of 1.12 g/t Au and 4.51 g/t Te, meaning a 1:4 ratio for Au/Te.

In the waste dumps of I and II Sector of the Săcărâmb area, the average content is 2.73 g/t Au and 7.12 g/t Te, meaning a 1:2 ratio for Au/Te. The most increasing content of tellurium is for the III Sector, where an average of 7.62 g/t Te and a ratio of 1:3 for Au/Te are found. Therefore, the average ratio for Au/Te of the waste dumps are, in fact, more closer than those of the damaged tailings pond Săcărâmb ore deposit by the primary ore deposit.

Until 2009, in Romania selenium is disscused only of the geochemical point of view. One of the consequences of the Săcărâmb area investigation is the possibility to considerate selenium as an useful element. Significant contents of selenium in comparison with tellurium have been evidentiated, generally twice as much selenium than tellurium. This is an important evidence for the future investigations in order to discovery new selenium minerals, and to determine its economic potential in the Săcărâmb area. Three selenides have been already described there, confirmed by XRF investigtions.

There is a good correlation between cadmium and zinc in the analyzed samples of waste dumps and damaged tailings pond. New mineralogical investigations could show if cadmium is a minor element in sphalerite.

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