NGR, XRD and TEM/SAED investigations on waste dumps materials with a view to recover precious metals

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Abstract. Two types of ores were selected for the investigation of the fate of the ore minerals during relatively long time of residence in the waste dumps (active mining: 25 years ago in the Bâdeanca Valley and some 50 years ago in the Valea lui Stan area). The pentametallic ores (Co-Ni-Bi-Ag-U) in the Leaota Mts. contain a great number of primary minerals of Cu, As etc. Although the waste dumps materials have whitish-yellowish colors their NGR spectra show the presence of iron minerals very finely dispersed. In the gold ores of Valea lui Stan deposit numerous minerals were identified, such as arsenopyrite, pyrite, pyrrhotite, etc., as major gold bearing sulfides. The waste dumps materials naturally show different mineral constituents, with clay minerals as major phases. Detailed NGR investigations show however Mössbauer spectra pointing out the presence of finely dispersed iron or iron-bearing minerals. Under supergene conditions gold is commonly sequestrated by iron hydroxydes; further TEM/SAED and XRD investigations are contributing to localize the gold. In some samples Mössbauer spectra resembling those of greigite have been obtained. Greigite is also a principal concentrator of gold under supergene conditions.

1. Aim of the paper
Waste dumps are quite widespread in Romania, a country with a long history of mining activity. Preliminary investigations showed that such waste dumps material still contains significant amounts of metals which cannot be recovered by conventional methods. Detailed investigation of the waste dump material is the first step of an integrated research aiming to localize the metals (especially precious one) and then to find out methods to recover them using chemical and phytoextraction procedures, as shown by [1] and [2].

The methods used involve a combination of optical microscopy, EMPA, XRD, EDX, TEM/SAED and NGR (Mössbauer), in order to obtain as many as possible data at different observation scales.

2. Geological setting and petrography of the Valea lui Stan area
The Valea lui Stan area is located in the South Carpathians (Căpățâni Mts.) near the Olt river. The dominant rocks are micaschists, red, ortochlase-dominated gneisses, amphibolites, migmatites, limestones and scarcely developed ultramafics. The dominant sedimentary formations are represented

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by cretaceous conglomerates. The ores are shear-zone related and display a typical association of Au-As-Cu. The gold ores have been mined during the XX<sup>th</sup> century yielding significant waste dumps. The mines are now closed. More details are given in [3] and [4].

3. Geological setting and petrography of the Bădeanca Valley area
The Bădeanca Valley belongs to the Leaota Mts. in the South Carpathians. The rocks occurring in the area are mainly micaschists in which intercalations of quartzites, amphibolites, gneisses and scarcely developed eclogites and granites occur in places. Regional retromorphic changes are widespread, on which retrograde transformation on shear planes overlap. The ore occurrences contain a great number of metals, Au and U included. (For details see [5] and [4]).

4. Optical microscopy
The fine grained materials from waste dumps have been embedded in epoxy and thin and polished sections have been realized. The mineral observed in these thin sections are generally the same with those observed mainly in the host rocks from the two occurrences. Photos taken from the thin sections are presented in figures 1 and 2.

![Figure 1](image1.png)
**Figure 1.** Rock fragments with euhedral opaque minerals (black), muscovite (white) and chlorite (green). Left side: a “ghost” of garnet (spessartine?) with black rims, presumably consisting of a Mn-spinel. Badeanca Valley area. Transmitted light (TL), N //, x40.

![Figure 2](image2.png)
**Figure 2.** Fine opaque blades (ilmenite), euhedral grains (magnetite) and Fe-hydroxides (yellowish-brown spots). Left: a garnet (spessartine) “ghost” with opaque rims (similar to figure 1). Valea lui Stan area, TL, N //, x40.

5. TEM/SAED investigations
Electron microscopy investigations (transmission electron microscopy and selected area electron diffraction) on powder samples (2B1 – Badeanca Valley) have shown the followings:
- nanometric “precipitates” (average size ~ 9.8 nm) of Au, Ag or (Au, Ag) alloy in presence of maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) (figures 3, 4)
- nanometric particles of Au, Ag or (Au, Ag) alloy near β-cristobalite (agglomerates or monocrystals); it can be observed the mode of growth of the particles starting from the isolate spherical crystal → agglomerates (2 – 4 spheres) → monocrystals;
- the sample reveals a great diversity of morphologies: isolated spherical gold nanoparticles, between 24 – 75 nm in size, with average value of 42 - 0.412 nm up to monocrystals (average value 300 nm);
During the microstructural investigations, some minerals have been identified:
- α-quartz and β-quartz hexagonal - very small monocrystals about 140 – 350 nm in size (figure 4);
- maghemite, hematite (γ-Fe<sub>2</sub>O<sub>3</sub>, α-Fe<sub>2</sub>O<sub>3</sub>), (figure 4).
- pyrrhotite (Fe<sub>1-x</sub>S) – rarely
6. XRD and EDX investigations

The XRD spectrum has been obtained using a Bruker D8 Advance diffractometer and CuKα₁ radiation ($\lambda = 1.540598$ Å). The dominant (> 50%–80%) contribution is given by SiO₂ phases, different Si-Al – oxides and – oxihydrites (with alkali, alkaline earth metals, 3d-metals, etc.).

Generally, due to the high XRD intensity on 011 planes of quartz, other contributions are hardly to detect. One can remark low amount (<3%–5%) of Fe, Ti, Ni, Co oxides/silicates, in some of samples. It is notable that low detectable and/or no evidence of the sulfides, arsenides and/or arsено-sulfides are revealed by the XRD spectra. So, in the case of 2B-3m sample, the main contributions of SiO₂ phases and the non-Fe silicates, oxides and oxihydrites are about 76.63% and the minor (19.31%) one is given by sulfides and arsenides. The Fe-compound contribution is up 5%. The XRD data of 2B-3m sample are shown in the table 1.

The energy dispersive X-ray analysis (EDX) has been used, in order to identify the elemental composition of the specimens. The peak spectrum of the bombarded sample by electrons permits to identify the containing element and the type of X-ray. EDX analysis reveals the notable presence of iron.

| Sample | Phase          | XRD Line Intensity [ % ] | 2θ₉₄₄ [grd] | d₉₄₄ [Å] | Phase Contribution [ % ] | Miller Indices |
|--------|----------------|--------------------------|-------------|----------|---------------------------|----------------|
| 2B-3m  | Quartz         | 100.0                    | 26.64       | 3.343    | 21.971                    | 1 0 1          |
|        | 2B-3m          | 16.4                     | 20.86       | 4.255    | 3.603                     | 1 0 0          |
|        | 2B-3m          | 10.4                     | 50.14       | 1.818    | 2.285                     | 1 1 2          |
|        | 2B-3m          | 43.3                     | 27.96       | 3.188    | 6.928                     | 1 2 0          |
|        | 2B-3m          | 41.1                     | 26.96       | 3.304    | 6.576                     | 3 1 0          |
|        | 2B-3m          | 100.0                    | 35          | 2.562    | 4.631                     | 3 1 1          |
|        | 2B-3m          | 41.0                     | 42.52       | 2.124    | 1.899                     | 4 0 0          |
|        | 2B-3m          | 38.4                     | 61.7        | 1.502    | 1.778                     | 4 4 0          |
7. NGR / Mössbauer investigations

The Mössbauer spectra were obtained in transmission geometry on the velocity scale ± 15 mm/s, using a 57Co:Rh at room temperature (RT) [6]. 2B-3 and a spectrum at 77K (LNT) has been also recorded. All 2B spectra (from Badeanca Valley) are showing an intense magnetic-phase contribution and in their centres a non-magnetic one. The less intense magnetic contribution is shown by 2B-9 sample. The contribution of the paramagnetic signal (characterizing the ferrous and ferric valence states) has both different line shapes and intensities. Generally the sublattices of more/less intense magnetic fields are corresponding to ferric/ferrous ions in samples [7].

The fit of 2B RT-spectra reveals that some spinellic and pyrrhotite phases are responsible for the magnetic contribution and biotites, nonmagnetic spinel and ferrihydrites phases are responsible for the central signals in spectra. LNT-spectra are more complex (see table 2 and figure 5) due to paramagnetic to magnetic-ordering phase transition supported by some chemical Fe-compounds vs. decrease of the temperature [8]. The RT indexed phases are evidenced at LNT too, but with changed parameters.

Table 2. The RT and LNT Mössbauer parameters of 2B-3m sample spectrum

| Sample | $\delta_{Fe}$ | $A/\varepsilon$ | B [T] | A [%] | $\delta_{Fe}$ | $A/\varepsilon$ | B [T] | A [%] |
|--------|---------------|-----------------|------|-------|---------------|-----------------|------|-------|
| RT     |               |                 |      |       |               |                 |      |       |
| 2B-3m  | 0.24          | -0.13           | 48.09| 36.5  | 0.09          | 0.16            | 44.93| 8.0   |
|        | 0.97          | 2.74            | -    | 4.6   | 0.48          | 0.60            | 35.22| 3.8   |
|        | 0.89          | 2.26            | -    | 9.2   | 0.37          | -0.09           | 50.58| 42.3  |
|        | 0.25          | 0.72            | -    | 14.4  | 0.86          | 1.64            | -    | 1.2   |
|        | 0.38          | 0.32            | -    | 8.7   | 0.22          | 0.60            | -    | 10.9  |
| 2B-3m  | 0.21          | 0.42            | -    | 5.3   | 0.16          | 0.46            | 31.09| 6.4   |
|        | 0.34          | -0.06           | 47.93| 9.2   | 0.50          | 0.30            | -    | 8.3   |
|        | 0.74          | 2.06            | -    | 3.7   | 0.29          | 2.12            | -    | 1.0   |
|        | 0.64          | -0.42           | 27.69| 8.4   | 1.16          | 1.94            | -    | 5.0   |
|        |               |                 |      |       | 0.94          | 2.52            | -    | 6.5   |
|        |               |                 |      |       | 1.11          | 2.90            | 6.4   |       |
| Errors | ±0.05         | ±0.07           | ±0.05| ±2.5  | ±0.05         | ±0.07           | ±0.05| ±2.5  |

Figure 5. The fit of the B-3m RT-spectra (a) and LNT-spectra (b) and the corresponding hyperfine parameters. Abbreviations: sp = spinel; po = pyrrhotite; spm = magnetic spinel; ferhyd = ferrihydrite; sp/ol = spinel-olivine; bi = biotite; spmag = superparamagnetic.
8. Conclusions
The investigation of waste dump material can produce valuable results, provided that several methods are applied. Combination of optical and structural methods is in a way the key of obtaining information about the fate of the minerals down to the nanometric scale. The special properties of the nanominerals such as high(er) reactivity and probably the availability for the plants uptake are of interest in both theoretical and practical aspect.

The waste dump materials used in this study have been collected from two different occurrences located in metamorphic rocks of the South Carpathians: Valea lui Stan gold ores (Au-As-Cu) in the Capatana Mts. and Badeanca Valley pentametallic occurrence (Co-Ni-Bi-Ag-U) in the Leaota Mts.

The study material has been first investigated by using optical microscopy in order to locate the opaque minerals, some of them having magnetic properties and/or producing reasonably good Mössbauer spectra. Macroscopic examination of the material revealed whitish-yellowish colours, however at the microscopic scale a number of opaque minerals do occur, either euhedral (magnetite) or elongated (ilmenite), as well as irregular patches within silicates (Fe-hydroxides) and rutile and “leucoxene”; rounded grains showing opaque rims are reminiscent of intensely transformed spessartine garnet; the rims might host the Mn-bearing spinel evidenced by Mössbauer spectra.

In addition to the clay minerals which might adsorb gold or other metals, a lot of possibly gold-bearing minerals have been identified: magnetite, ferrihydrite, greigite, even “leucoxene” loose-aggregates.

The complementarity of the methods used was a good choice to follow up the distribution of minerals and metals (especially gold) down to the nanometric scale; the next step will be the investigation of specially grown plants on metal-enriched substratum and the role of nanominerals availability for plants.

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