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Mossbauer, TEM/SAED and XRD investigation on waste dumps of the Valea lui Stan gold mines

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ABSTRACT: *The complementary investigation techniques, Mossbauer spectroscopy, transmission electron microscopy with selected area electron diffraction (TEM/SAED), X-ray diffraction (XRD) have been used to investigate the fate of the Valea lui Stan, Romania, gold-ore nanoscale-minerals during the long time of residence in the waste dumps. The preliminary investigations showed such waste dumps to contain significant amount of metals which cannot be identified by conventional methods. An intense research activity started up in order to evaluate the possibilities to recycle Valea lui Stan waste dumps and to recover metals by chemical or phytoextraction procedures. The waste dumps naturally show different mineral constituents with clay minerals as major phases, observed by XRD-technique. Although the waste dumps materials have whitish-yellowish colours, MOSSBAUER technique evidences the presence of the finely dispersed iron bearing minerals. The authors are focusing to inspect and analyze Fe-compounds in the samples collected from Valea lui Stan's waste dumps in order to identify the magnetic phases by Mossbauer technique.*
Keywords*: Mossbauer; TEM/SED; XRD; Waste dump; Iron oxides;*

1. Introduction

The geological structure of Valea lui Stan area (South Carpathians, Romania) is extremely complicated involving several metamorphic groups of Precambrian age and sedimentary formations of Permian and Cretaceous ages. The dominant rocks are micaschists, orthoclase-bearing gneisses, amphibolites. migmatite& limestones and scarcely developed ultramafics. The sedimentary formations are represented mainly by conglomerates. The ores are shear-zone related and display a typical association of Au-As-Cu (1, 2). Arsenopyrite, pyrite, pyrrhotite etc. are the major gold bearing sulphides and MOssbauer investigations have pointed out the presence of iron minerals very finely dispersed, mainly at nanometric scale.

A set of k = 3 samples VS-k has been selected from the waste dumps of Valea lui Stan for detailed investigations. The low temperature inspection of VS-k samples by MOssbauer technique evidenced the Fe-phases.

The present work intends to inspect the iron phases in powdered VS samples by MOssbauer technique in T e (300 K-4.2 Kb taking into account the iron (ferric/ferrous. magnetic/nonmagnetic) phases' powerful diagnose of this technique. The RT spectra of samples are similar, but the inspection at liquid nitrogen temperature (LNT) VS-3 sample (as collected from waste dump) evidenced the magnetic phases. So, the authors are focussing to inspect and analyze the magnetic phases of Fe-oxides in this sample and its magnetically separated sample, VS-3m.

2. Experimental aspects

Some 25 samples (weighting about 0.5 kg each) have been collected from the waste dump of the former gold mine at Valea lui Stan, near the town of Brezoi, South Carpathians. The samples VS (Vain lui Stan) - -2 and -3 were chosen as they showed the highest metals contents. All the samples are similar, being intensely altered during quartz) and micas (-25%-52%, muscovite, biotite, etc.), hydrous ferric oxides, iron hydroxides and/or hydrated ferric sulphate (-14%-40%) and other phases (-6% for VS-1 up to 42% for VS-3). One can remark the contribution of phases with assumed amount of Fe (44% up to 90% for VS-3 and VS-2 respectively). On the other hand, TEM/SAED did not find trace amounts of hydrated ferric sulphate and the preliminary

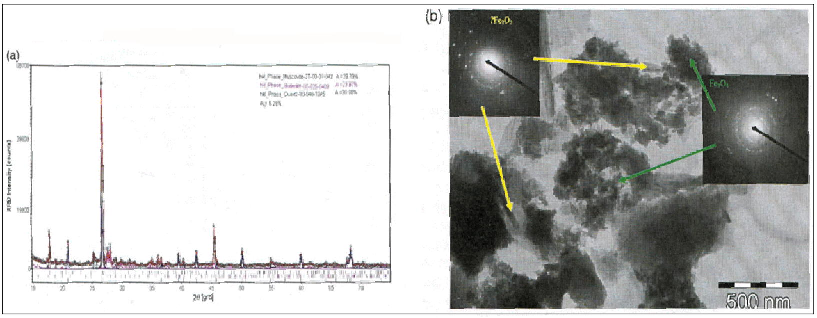

Fig. 1. The XRD patterns of VS-1 samples with the determined areas of the phase components, using the Rietveld fit procedure (a); TEM/SAED images of VS-3 sample (b)

the 50 years of waste residence. The samples have been inspected and analysed by the following techniques: XRD (Broker-D8 ADVANCE spectrometer). TEM/SAED (JEOL-JEM 200Cx transmission electron microscope) and MOSSBAUER (standard AM50 Promeda and Wissel-SeeCo) spectrometers in transmission geometry, using a "Co: Rh source and the velocity range up ±12 mm/s. The MOssbauer spectra have been obtained in the temperature range from 4.5 K (LHeT - liquid helium temperature) up to 300 K (RT - room temperature).

3. Results and discussion

The XRD (see Fig. la) patterns of all VS-samples are similar as concerns the presence of magnetic phases. The VS-samples showed to be the most complex. The analysis of them by Rietveld fit procedure evidenced silicate phases (>58%-100%) containing SiO_2 (-10%-30% EDX techniques evidences low traces (3-4% ±1.7) of S.

The analysis of TEM/SAED images evidenced the main phase of SiO_2 with ferric oxides (see Fig. lb). The observed iron-oxides phases are hematite. maghemite and magnetite.

In Fig. 2 Mossbauer spectra of samples VS-3 (Fig. 2a, 2c1) and VS-3m (Fig. 2b, 2c2) obtained at different temperatures are plotted. The analysis of spectra was carried out using standard fit and magnetic field distribution procedures. The presence of two elementary quadrupolar patterns is easy distinguished in the spectra, for T > LNT for all VS samples. VS-3 and VS-3m hyperfine parameters are AO [ram's] = 2.67, 0.72, 8Fe [mm/s] = 1.13, 0.70, weights w[%] = 31, 66, and aQ[mm/s] = 1.60, 0 60, SFe [mm/s] = 0.57 and 0.37, w[%] = 7, 23, respectively. It is expected that the difference between the ferric nonmagnetic phases of the two samples, is due to the magnetically separation of VS-3m samples from as

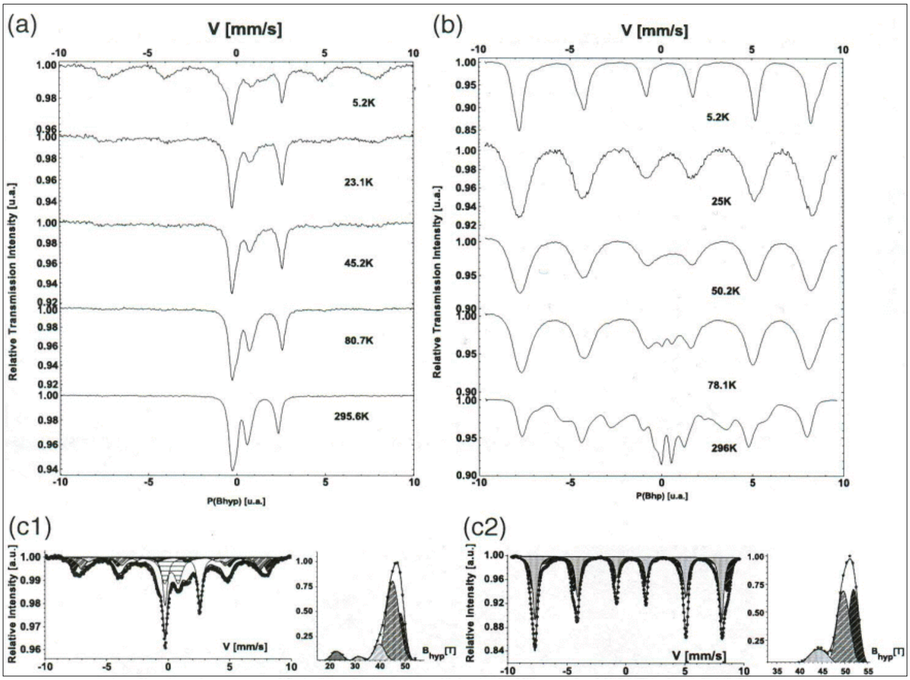

Fig. 2. The experimental MOssbauer spectra of the sample VS-3 (a) and VS-3m (b) for T E 296K-5K, and the fit of LHeT magnetic field distribution (ci) and (c2) respectively

extracted VS-3 sample.

The lack of magnetic patterns in VS-3 RT spectra could be explained by phases with magnetic transitions below RT or/and the low concentration of the magnetic phases in the as extracted VS-3 global sample. The magnetic and nonmagnetic patterns of VS-3m RT spectrum, are revealing a bimodal magnetic field distribution in the ranges B[T] E (20-39);(39-52), with probabilities, Pi (B,RT) > P2(B,RT). All these suggest the presence of ferric nonmagnetic /magnetic phases in VS-3m and VS-3 and the presence of a ferrous phase at least in VS-3. The values of the VS-3 quadrupolar elementary patterns could indicate the muscovite phases containing Fe2+ and Fe3+, [3]. The deconvolution of VS-3 LHeT spectra show magnetic phases only at T < LNT, but the nonmagnetic ones is still exists. The hyperfine parameters values of nonmagnetic and magnetic phases are in the Table 1. One can remark the large values of half linewidths (I" (mm/s] E [0.65-0.77) of Fe3÷ elementary magnetic patterns, which could suggest more magnetic phases. The values of B suggest a mixture of Fe3+-oxides, -hydroxides with cation substitution (probably Mn, Co, Ti, more surely Al), [4-6] and even trace of copper iron sulphides. The VS-3m paramagnetic phases are less and less intense under at T < LNT and at LHeT only a spectrum of elementary magnetic phases remained, the bimodal magnetic field distribution becomes B[T] E 140-501;[45-551, Pi (B, LHeT) < P2(B, LHeT). The deconvolution of spectra reveals five magnetic elementary patterns (see Table 1) suggesting for the first four patterns the mixture of hematite with maghemite phases with the most probably Al—cation substitution.

The bimodal magnetic fields and the temperature dependences of VS-3m spectra could be explained by the presence of the bimodal distribution of the grain sizes D

Table 1. The Mössbauer hyperfine parameters for LHeT

VS-3 sample				VS-3m sample			
w[%]	δ_{Fe} [mm/s]	ε_Q /* Δ_Q [mm/s]	B [T]	w [%]	δ_{Fe} [mm/s]	ε_Q /Δ_Q [mm/s]	B [T]
25	0.2	0.02	48.71	18	0.49	0.07	52.07
3	0.46	0.03	45.12	20	0.45	−0.08	51.86
18	0.44	0.3	34.50	44	0.48	−0.13	49.68
23	1.29	2.81	–	12	0.35	0.00	48.58
21	0.41	2.26	–	6	0.62	0.12	44.84
9	0.38	1.10	–	–			
±2	±0.04	±0.08	±0.31	±2	±0.03	±0.06	±0.52

suggesting a superpara-magnetic transition. One could consider the limit between two sorts of particles is under 15 nm, taking into account the low T (<LNT) under which the paramagnetic pattern disappears. That is true for VS-sample, but it is possible both a magnetic ordering phase transition of some VS-3 constituent compounds and a hidden super paramagnetic transition of an invisible magnetic pattern at RT.

4. Conclusions

The aim of this paper is to present the results of complex investigations carried out on the waste dump material which are resulting from Valea lui Stan's mining of gold ore, hosted by metamorphic rocks.

The main results by applying the above mentioned structural techniques consist in identification of several minerals not known in the primary ores of Valea lui Stan gold deposit, such as maghemite associated with other mineral grains (gold, silver etc.) at the nanometric scale.

The native gold forms spheroidal grains up to 50 nm in size either isolated or as coalescent coral-like aggregates, included in different minerals.

These analytical procedures were followed by experiments concerning metal uptake by plants, as a contribution to decontamination of old mining areas. In addition, gold recovery by plants has been partly successful. Such data will be published elsewhere.

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