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# MINERALOGICAL AND STRUCTURAL FINGERPRINT METHODS OF NANOMINERALS IDENTIFICATION

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***Abstract:*** *The combined investigation techniques, electron probe microanalysis (EPMA), Mössbauer spectroscopy (NGR), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) evidenced the third level of the inclusions at nanosize scale for specific minerals of different Romanian metamorphic deposits. So, NGR technique reveals the contribution of the (Mn, Fe) oxides - small particles at standard (RT) and at very low temperature (LHeT) in the* $^{57}Fe$ *$\gamma$-ray signal of manganoan-fayalites (Razoare deposit). The EM analysis techniques confirmed the presence of the nanometric Fe and Mn oxides inclusions in manganoan fayalites, as well as of pyroxferroite (Razoare deposit). On the other hand, an extensive investigation of the gold ores in the South Carpathians (Costesti, Valea lui Stan and Jidostita) has been performed by using a fruitful combination among the above mentioned complementary mineralogical and structural methods. The investigation of the representative sulfide samples by the structural techniques relieved new minerals in the gold ores, the presence of submicroscopic inclusions of uytenbogaardtite, cobaltite and loellingite as well as the "coral like" aggregates of nanometric gold.*

***Keywords****: EPMA, NGR, TEM/SAED, XRD, Fe and Au compounds, manganoan-fayalite, wustite, uytenbogaardtite, cobaltite, loellingite, pyrite, pyrrhotite, chalcopyrite and arsenopyrite.*

## 1. Introduction

The about 4000 (now may be 4200) valid mineral species known worldwide, (including Moon and meteorites minerals) occur in very various environments and show extremely variable grain or crystal sizes. Some 500 or more mineral species were encountered only under the microscope and only few as inclusions in other minerals; they are commonly named microminerals.

Now, by using more powerful and refined methods, the possibilities of chemists, physicists and mineralogists to identify and analyze the microstructure and micro-chemistry of such inclusions, finally led to identify minerals at micrometer and nanometric scale.

Generally, the crystal/grain size of minerals can vary between $10^2$m and $10^{-9}$ m. The proposed classification ([1],[2]) includes the following categories (and the adequate methods of investigation):

A – macrominerals $10^5$ – $10^{-3}$ m (mineralogical methods)
B – microminerals $10^{-4}$ – $10^{-6}$ m (optical mineralogy)
C – inframinerals $10^{-7}$ – $10^{-8}$ m (EPMA, NGR, XRD)
D – nanominerals less than $10^{-8}$ m (TEM/SAED)

The category A, the macrominerals, includes the majority of the mineral species known worldwide (may be 3000 – 3500 in number).

The microminerals (category B) include a relatively large number of minerals, which can be detected under the microscope and occur mainly as inclusions in other minerals or form only fine to very fine grained aggregates, e.g. clay minerals. Exsolution bodies belong hitherto as well as the daughter minerals in the fluid inclusions.

The inframinerals (category C) cannot be seen or cannot reasonably good be identified under the optical microscope. They occur as ultrafine inclusions and/or as very fine intergrowths, a fact preventing a reliable identification as a result of interfering properties. The main and mostly used methods of identification are EPMA, NGR and XRD.

The nanominerals (category D) cannot be depicted by usual mineralogical/physical methods; even EPMA seems to be useless in many cases. However, their presence can be "seemed"/predicted (NGR) or visualized (TEM/SAED, HRTEM). Namely these nanominerals are the most interesting as they have unexpected properties (as the nanominerals generally do) and occur also in unexpected environments.

The main interest in such complex and complementary nanominerals investigation is given by the possibility to reveal and to extend the knowledge about the main steps in the metamorphic evolution of natural deposits.

## 2. Experimental aspects

The NGR spectra have obtained on sample powders at RT and LHeT in transmission geometry, using a $^{57}$Co:Rh source (intensity of 50mCi, $a_{57Fe}$= 2%, f(300K)=0.76, $\Gamma_{obs}$ = 0.22mm/s for metallic iron foil). The spectra are showing superposed signals of $^{57}$Fe in different local vicinities, characterized by electric field gradient (EFG) and/or internal magnetic field (B). They have been analyzed by the $\chi$2-criterium fit procedure.

The selected powder samples have been also investigated using JEM-200 CX installation. The principal characteristics are:

- Lattice fringes - 0.14 nm ;
- Resolution point-to-point – 0.25 nm;
- Accelerating voltage [kV] – 80, 100, 120, 160, 200
- Magnification –x 1000 to 750.000
- SEM attachment with accelerating voltage 40 kV with a possibility to apply also SAED technique.

All the samples studied were previously investigated by using high resolution optical microscopy and EPMA (Jeol Superprobe at the University of Sazburg, Austria and Ecole Superieure des Mines, St. Etienne, France). Inhomogeneities of mineral grains (especially of sulfides) and slightly unbalanced chemical analyses (especially of silicates) prompted the above mentioned structural methods to be applied. The expected results have finally been proved to be unexpectedly interesting and useful.

## 3. Results and discussions. Nano- and Inframinerals in the Mn-Fe Razoare Deposit

The RT-NGR spectra of the investigated samples carried out on the large velocity scale, have shown many sublattices, which correspond to nonmagnetic (the main contribution in $^{57}$Fe signal corresponds to Mn-Fe olivine) and magnetic phases of a small concentration corresponding to the Mn-Fe oxide. The relative ratio is 79.0%/14.2%. This ratio can be explained only by the presence of very small Mn-Fe oxides contribution to the Mössbauer signal. At LHeT, due to the increasing of recoilless fraction oxide phases are more evident in NGR-spectra, and an apparent decreasing ratio is shown (see figure 1). This above mentioned apparent decreasing ratio at low temperature could be explained only by the presence of nanometric Mn-Fe oxides inclusions, contributing to the magnetic phases. On the other hand, TEM/SAED analysis of the manganoan-fayalite has revealed the presence of pyroxferroite crystals as well as wustite and magnetite nano-precipitations [3]. The identification of wustite (as precipitations and/or micro- and nano-inclusions) and pyroxferroite (as single crystals with perfect geometrical shape) in the manganoan fayalite gives a deeper insight into metamorphic evolution of the Razoare Mn-Fe deposits, the largest of this kind in Romania, with a geological age of more than 550My. The PT estimations, based on the mineral assemblages, shows highest metamorphic peak to slightly exceed the upper amphibolite metamorphic facies (about 700$^{o}$C and 700MPa) entering the field of eclogite facies. After primary crystallization of manganoan orthoferrosilite, the manganoan fayalite has been transformed on it, being the first retrograde transformation; the second retrograde transformation was that of manganoan fayalite into mangangrünerite [4]. It is to note that abundant mangangrünerite is accompanied by development of magnetite by increasing oxygen fugacity during the late evolution of the deposit [4]. The Mössbauer spectra and the TEM/SAED images are given in Figs. 1 and 2, respectively.

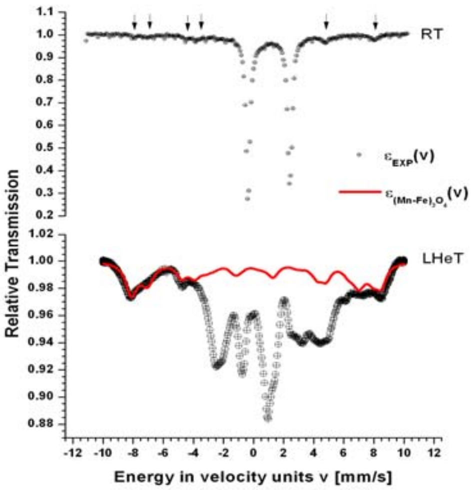


**Fig.1: The RT and LHeT spectra of the sample 088 from Razoare deposit. One observes the distinct elementary patterns of the non- ( Mn-Fe olivine) and magnetic (Mn-Fe oxides) phases**

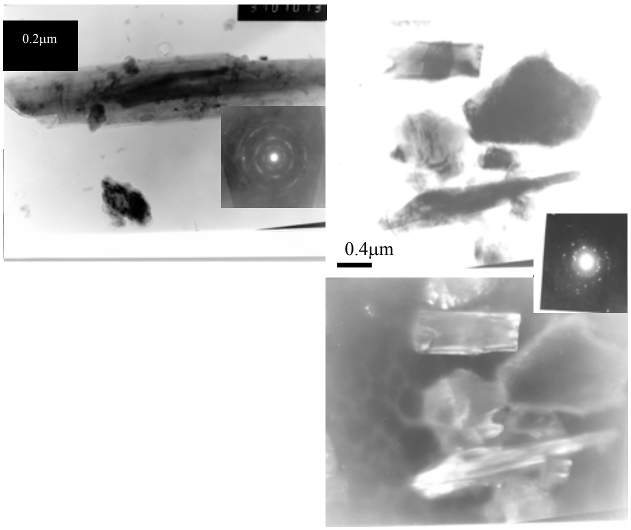


**Fig. 2 (a): TEM on mangangrünerite (with parallel cleavage) and wustite precipitation/inclusions;**

**(b): BFTEM, DFTEM, and SAED DFTEM, and SAED on a manganoan fayalite crystal with precipitations of wüstite and pyroxferroite.**

## Nano- And Inframinerals In Gold Ores From Southern Carpathians

Valea lui Stan (near Brezoi), Costeşti (near Horezu) and Jidoştiţa (near Drobeta-Turnu Severin) are shear-zone related gold ores/mineralizations hosted by the metamorphic rocks of the Getic Realm of the South Carpathians. Although similar, these occurrences are different in respect to the main geochemical association and related protores (Udubaşa, 2004; [7]). In all the occurrences the gold is present as inclusions mainly in arsenopyrite, pyrite, chalcopyrite, sphalerite, pyrrhotite and quartz. Previous work (Udubaşa S. *et al.*, 2005; [6]) emphasized the differences in chemical composition of gold as a function of the host sulphides.

Nearly all the sulphides of the shear-zone related gold ores contain gold, which is unequally distributed over the investigated sulphides, i.e. arsenopyrite, pyrite, chalcopyrite, sphalerite etc. (Udubasa S. *et al.,* 2005; [6]) emphasized also the preference of gold for a certain sulphide as function of the mineral association.

A first attempt to classify the solid inclusions (gold included) in different minerals has been made by (Udubaşa G. *et al.,* 2006; [5]). It has been shown that there exists micro-, infra- and nano-minerals or inclusions. Gold can occur at any of these levels and the methods of investigation are specific for each type of inclusions.

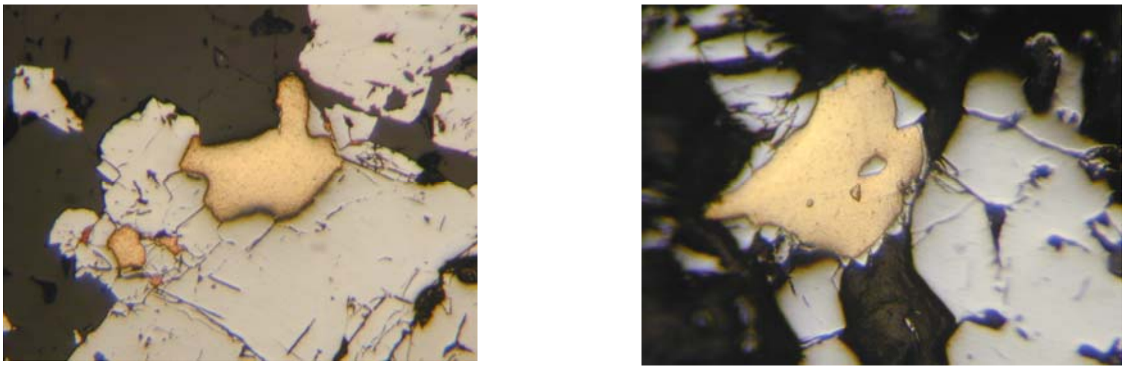
In the investigated ores the gold has been found to occur either at macroscopic level or at submicroscopic one (micro-, infra- and nano-inclusions). The macroscopic gold is rarely found in such ores, especially in the Valea lui Stan ores; at Costeşti the gold was seen with naked eyes only in some heavy mineral concentrates.

Microscopic inclusions of gold have been observed both in sulphides (arsenopyrite, pyrite, chalcopyrite, sphalerite) and quartz (Fig. 3). Their form and size greatly vary.

The best developed and most interesting are the gold inclusions in arsenopyrite; in some cases such inclusions are enveloped in bands of apparently gold-free arsenopyrite, non-visible under the optical microscope. Nevertheless, investigation with the electron microprobe shows the presence of gold (contents of about 0.2 ppm and less), which gradually disappears as the distance from the gold inclusion increases. This may be called “infra-gold”, which can be interpreted as a result of solid state diffusion in arsenopyrite. It is interesting to note that no cracks in arsenopyrite occur. Zoned arsenopyrite with gold inclusions and satellite fine gold inclusions were observed by Möller *et al.* (1997) [8], who suggested that electrochemical processes are responsible for such distribution patterns, in relation to varying As/S ratio in arsenopyrite. Grain boundaries with variable As/S ratios give rise to formation of *np*-junctions, i.e. favourable sites for gold deposition.

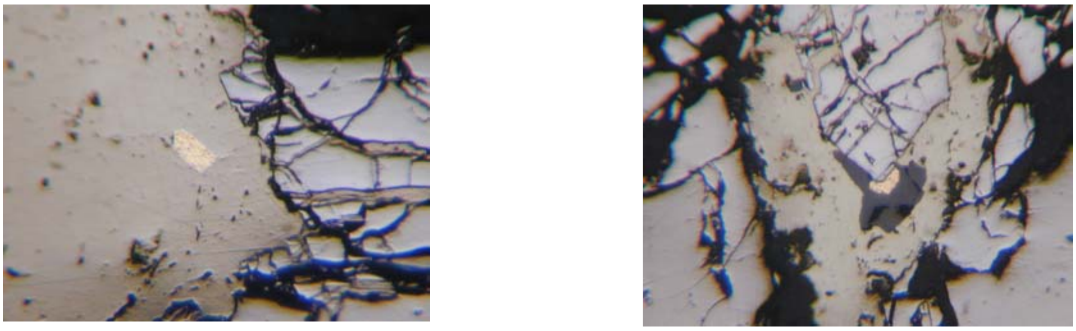
Perhaps the most interesting and at the same time most intriguing feature of gold occurrence pattern in sulphides from the studied ores was depicted by using TEM equipped with selected area electron diffraction (SAED). Coral-like aggregates up to 60-80 nm in size have been identified on the grain surface of sulphides (Fig. 4). This is the third level (the fourth if we take into consideration the macroscopic gold) of gold occurrence in sulphides, which cannot be depicted by any other methods of investigation.

Among sulphides the arsenopyrite is the most important gold-bearer. Therefore $^{57}$Fe Mössbauer spectra of arsenopyrite (and other sulphides too) have been registered and analysed [9]. Spectral parameters showed that the dominant FeAsS phase represents 74%, 70% and 47% for the investigated samples from Costeşti and Valea lui Stan, respectively.



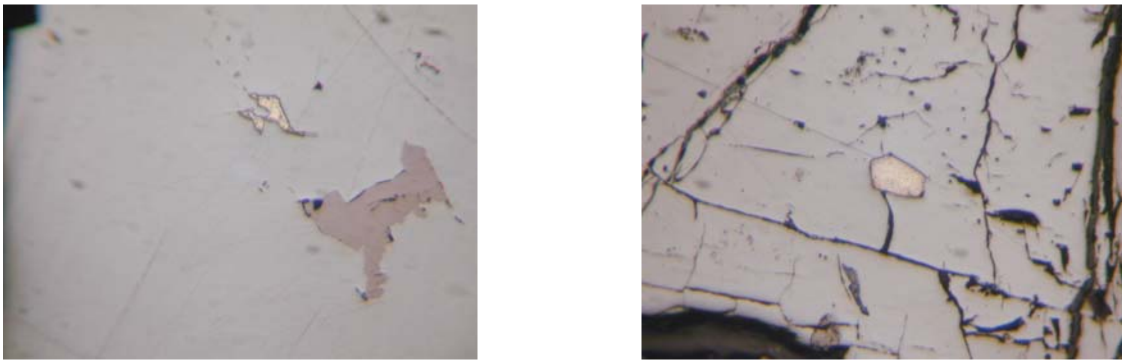
a) Gold inclusions in arsenopyrite. Valea lui Stan ores. N II, 120x magnification.

**b) Gold with arsenopyrite inclusions. Valea lui Stan ores. N II, 120x magnification.**



c) Gold in chalcopyrite. Valea lui Stan ores. N II, 190x magnification, oil imersion.

**d) Native gold at the boundary between quartz and arsenopyrite, in chalcopyrite. Valea lui Stan ores. N II, 190x magnification, oil imersion.**



**e) Native gold and pyrrhotite in arsenopyrite. Costeşti ores. N II, 190x magnification, oil imersion.**

**f) Native gold in pyrrhotite. Costeşti ores. N II, 120x magnification.**

**Fig. 3: Gold inclusions in sulphides and quartz.**

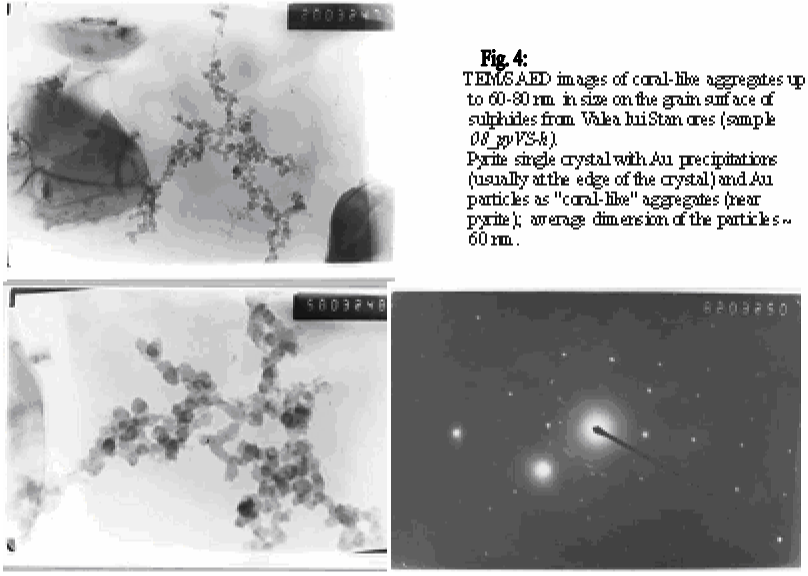


**Fig. 4:**
TEM/SAED images of coral-like aggregates up to 60-80 nm in size on the grain surface of sulphides from Valea lui Stan ores (sample *08_pyVS-h*).
Pyrite single crystal with Au precipitations (usually at the edge of the crystal) and Au particles as "coral-like" aggregates (near pyrite); average dimension of the particles ~ 60 nm.

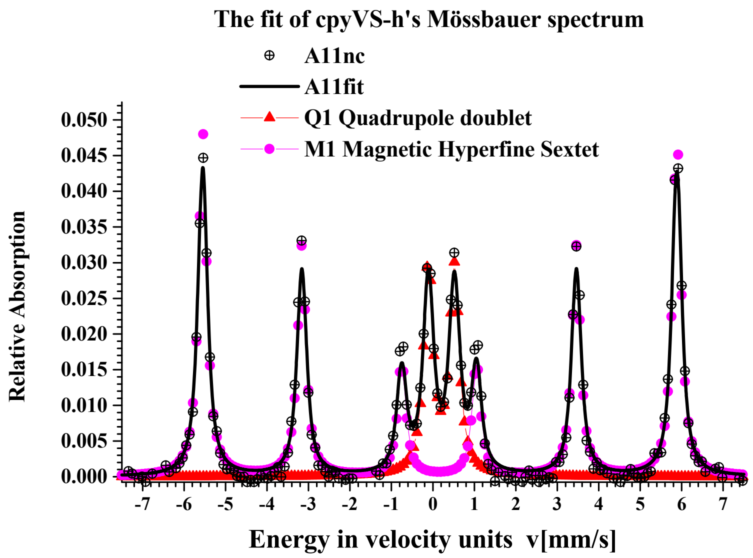


**Fig. 5: The fit of chalcopyrite Mössbauer spectrum at RT from a Valea lui Stan sample (*cpyVS-h*).**

The accompanying phases were identified in all the investigated samples. So, in the spectra of some samples at Valea lui Stan traces of (Co, Fe)AsS and $FeAs_2$ (~ 4%) have been detected. Pyrite and a larger quantity of löllingite (~ 28%) have been found in the sample of Jidoștița. In all the phases the Mössbauer spectra show octahedral arrangement and a fractional ionic valence (~ +2) of low spin. The Mössbauer spectra of some chalcopyrite and pyrrhotite exhibit the magnetic ordering and coexistence of the main phase with pyrite and/or marcasite (so for cpyVS-h sample, i.e. 25.32%/74.68 %; Fig. 5).

## 4. Conclusions

A combination of complementary investigation methods i.e. high-resolution optical microscopy, XRD, EPMA, NGR and TEM/SAED, was used in order to identify minerals at nanometric scale. The fruitful cooperation among mineralogists and physicists allowed to detect several dimensional categories of mineral inclusions, proving the used methods to be fingerprint of nanominerals identification. In Table 1, there are given the mineral categories observed and detected in the investigated samples of investigated deposits.

Successful efforts have been made to get a deeper insight into both the condition of the presence and the evolution of the nanominerals during the metamorphic processes of the given deposits.

**Table 1[2]: Size related mineral categories in the investigated samples.**

Investigated samples of gold ores from Southern Carpathians

| Category | Mineral species | Methods used |
|---|---|---|
| A - macrominerals | Pyrite, arsenopyrite, galena, chalcopyrite, sphalerite, GOLD | Observed by naked eyes and OM[3] |
| B - microminerals | Pyrrhotite, GOLD, Bi | OM |
| C - inframinerals | Greenockite, GOLD, schreibersite-like, Bi-sulphosalts | EPMA |
| | Uytenbogaardtite | XRD |
| | Cobaltite, löllingite | NGR |
| D- nanominerals | GOLD (coral–like aggregates) | TEM/SAED |

**Investigated samples from Mn-Fe Razoare deposit**

| Category | Mineral species | Methods used |
|---|---|---|
| A - macrominerals | Mn-fayalite - grains up to 20 cm long | OM |
| | Mangangrünerite, magnetite | |
| | Manganese humites | OM, XRD |
| | Pyroxmangite | |
| B - microminerals | Jacobsite,<br>Magnetite inclusions in fayalite | OM |
| C - inframinerals | Magnetite | OM ? |
| | Ferrosilite (Mn) | XRD |
| D- nanominerals | Magnetite, Mn-Fe oxides inclusions in fayalite | NGR |
| | Wüstite | TEM/SAED |
| | Pyroxferroite | |

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[2] Note: Macro- micro- and partially inframinerals (ferrosilite) as given in [3]; nanominerals – see [2].

[3] Optical microscopy.

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