RARE SULPHOSALT MINERALS IN ROMANIA

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Introduction

The territory of Romania contains a significant part of the Alpine–Carpathian chain and has witnessed complex geological and mineralogenetical cycles spanning from Precambrian to Neogene, with an expectedly comprehensive yield of rock forming and ore minerals. Sulphosalt minerals are constant accessories of various polymetallic ore deposits and mineralized bodies in Romania, *i.e.*: 1) deposits related to Upper Cretaceous – Paleocene magmatism in Southwestern Banat and Bihor Mts. 2) deposits related to Neogene volcanism in East Carpathians and Apuseni Mts. 3) Hercynian granites of Northern Dobrogea or Highiş Mts (Fig. 1).
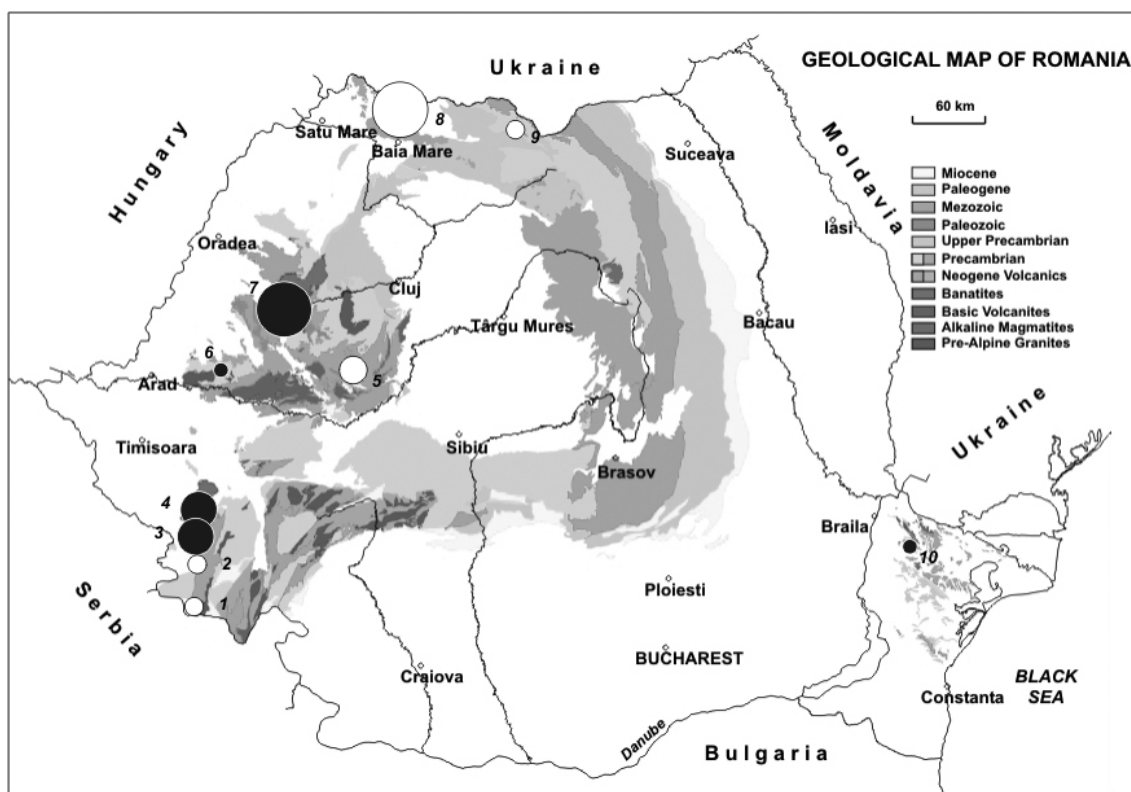

Fig. 1: Simplified geological map of Romania with the main areas of occurrence for sulphosalt minerals: (1) Moldova Nouă; (2) Sasca Montană; (3) Oravița – Ciclova; (4) Dognecea – Ocna de Fier; (5) Metaliferi Mts.; (6) Highiş Mts. (7) Băița Bihor – Valea Seaca; (8) Baia Mare; (9) Baia Borşa; (10) Pricopan – Greci. Black circles denote prevailing Bi sulphosalts; white circles, Sb(As) sulphosalts. Higher circle diameters correspond to higher frequency/diversity of sulphosalt species (base map after Geological Institute of Romania).

Many of the sulphosalt species in Romania – as mostly everywhere else – occur in minute grains or in very small quantities suggesting that they might not be of great importance in the ore forming processes. Different views might point to the fact that sulphosalt scarcity reflects very narrow genetical conditions, thus worth to be known and deciphered.

Another possible reason behind sulphosalts low esteem is the difficulty to build a long term research program, especially against today's widely accepted priorities. However, one of the main significance of sulphosalts arises from the fact that they represent the most general example of modern principles applied to mineral classification and crystal chemistry. Many of today's fundamental concepts, such as poly-

somatism, homology, plesiotypism, merotypism, hierarchical classification of crystal structures, the understanding of the role and constraints imposed by the atomic structure upon the chemical variability of minerals, find a good and relevant illustration in sulphosalts. Natural sulphosalts are of renowned significance for mineralogical, geological and material-science studies. Considerable interest has been raised during the last decades by this specific group of minerals, in connection with their potential benefits for modern technologies based on photovoltaic effects and superconductibility. The interest in sulphosalts as relevant materials is also driven by the lack of knowledge in the field of macroscopic physical properties, such as elastic, dielectric, Raman and infrared

behaviour, *etc*. to serve as constraints in *ab-initio* computer simulations. Detailed crystal structures, chemical variability data and physical measurements would be of highest relevance for such determinations.

Natural mineral occurrences are often singular and highly valued sources of sulphosalts for the study of crystal structures and material properties, as only a small proportion of such compounds may be obtained by synthetic methods. In spite of a considerable progress achieved by experimental mineralogy, many sulphosalts remain outside the actual possibilities of mineral synthesis. It is especially the case of sulphosalts with ordered supercells (*e.g.* ordered superstructure members of the bismuthinite-aikinite series, Bi_2S_3–$CuPbBiS_3$, involve reaction times in the order of 28-30 months, while maintaining a relatively high temperature of at least 175 °C (PRING, 1995). Another example is given by the 4th, 7th and 8th pavonite homologues, the 5th lillianite homologue as well as several fundamental phases in the cuprobismutite series (*e.g.*, paděraite), which could never be synthesized in laboratory. Crystallographic research on natural phases is often influenced by the discovery of new, less common or not yet known natural compounds. Therefore, entirely new opportunities to verify some of today's structural predictions or to initiate not yet foreseen directions in the complex study of this group can arise if new sulphosalt minerals are discovered and described.

Sulphosalt definition and features

Sulphosalts are a group of complex sulphides (rarely selenides and tellurides) with the general formula $A_xB_yC_z$ where *A* is commonly Pb, Ag, Cu and less commonly Hg, Tl, Fe, Mn, Cd, Sn^{2+}, Sn^{4+}, Na, K *etc*. *B* can be As, Sb or Bi (metalloids) with a conventional 3+ charge and a fundamental trigonal, non-planar [BS_3] coordination. *C* position is S^{2-} and or Se^{2-}, rarely Te^{2-}. Sulphosalt crystals are generally silvery grey in colour and are characterized by a fine needle-like morphology caused by a usually present 4 Å short cell axis. The extreme steric mobility of metalloids (Bi, As, Sb), the structural analogies between these elements and common sulphosalt metals (Pb, Ag, Cu) are the fundaments of an unmatched structural diversity and complexity in the mineral realm. Each sulphosalt phase has a well-defined crystal-chemical identity, requiring a specific definition and classification. While extremely numerous and diverse (Fig. 2), sulphosalt structures can be derived from just two major structural archetypes and include a limited range of chemical elements, to which most of the common indirect mineralogical determination methods fail, asking instead for complex quantitative determinations of chemical composition and crystal structure, or other parameters uniquely identifying the structural features.
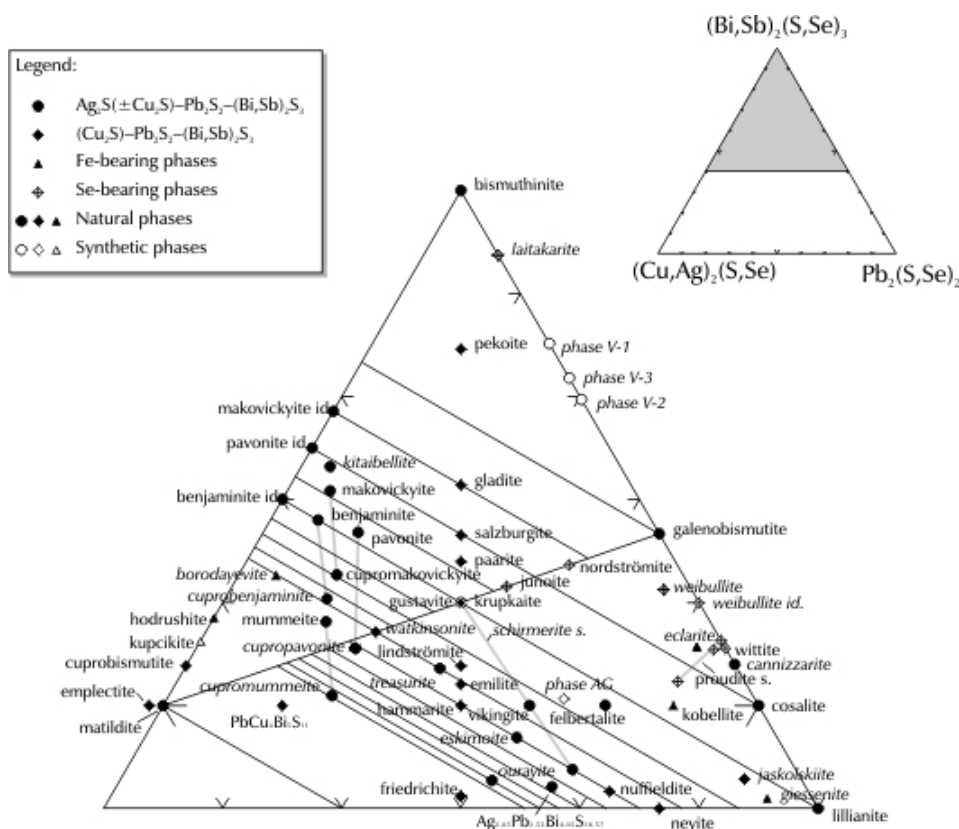

Fig. 2: Synoptic view of the upper part of the $(Bi,Sb)_2(S,Se)_3$–$(Cu,Ag)_2(S,Se)$–$Pb_2(S,Se)_2$ compositional diagram, showing several known natural and synthetic sulphosalt minerals. Phases still unknown in Romanian occurrences are in italics.

Important families of sulphosalt minerals in Romanian occurrences

Though rare, Bi-based sulphosalt minerals identified in Romanian occurrences are so diverse that to describe them in their entire complexity would be far beyond the reach of this lecture. Therefore, only the most remarkable examples will be mentioned and illustrated here.

The pavonite homologous series is represented by a family of crystal structures with two types of slabs parallel to (001): thinner slabs with single metal octahedra alternating with pairs of square pyramids [Bi(Pb)S$_5$], and thicker slabs composed of parallel chains of little deformed metal octahe-

dral in a galena-like pattern. Without significant amounts of Cu, the general formula of the series is Ag$_{(N-1)/2-x}$Pb$_{2x}$Bi$_{(N+7)/2-x}$S$_{N+5}$, where N is the number of octahedra in one octahedral chain across thicker, 'galena-like' slabs in the structure, and x is the degree of substitution for Pb (KARUP-MØLLER & MAKOVICKY, 1979).

The co-ordination requirements of Ag and Cu, as well as near-octahedral co-ordination of Bi play a decisive role in the layout of the series, and control – by still incompletely known mechanisms – the exsolution phenomena that are typical for pavonite homologues (Fig. 3).
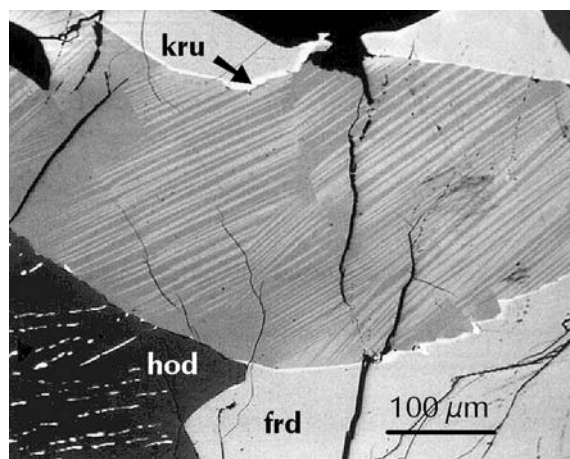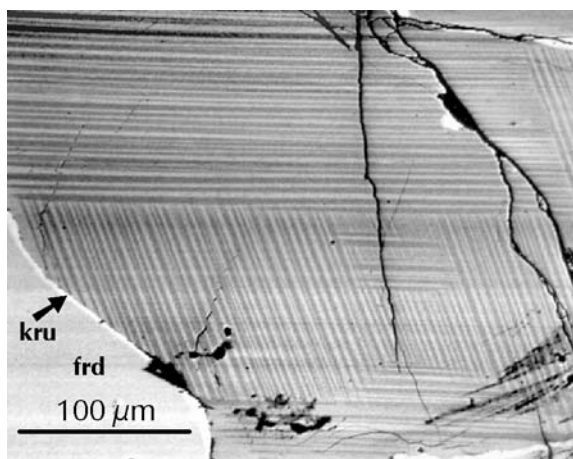

Fig. 3: Typical aspects of makovickyite–cupromakovickyite exsolutions from Băița Bihor; krupkaite, friedrichite and hodrushite are associated with the pavonite homologues. BSE image.

Several occurrences such as those at Băița Bihor, Valea Seacă, Ocna de Fier and Oravița are unique in holding an entire range of exsolved or homogeneous Cu-free and Cu-rich pavonite homologues, among which the presence of hitherto completely unknown 6th and 9th homologues and the presence of mummeite-cupromummeite pair (the 8th homologue, KARUP-MØLLER & MAKOVICKY, 1979) is assumed. Furthermore, new investigations are expected to clarify the background of the doubling of the c unit-cell dimension of cupropavonite (KARUP-MØLLER & MAKOVICKY, 1979), a copper-rich variety of the 5th homologue, in respect to the c axis of pavonite, and to observe a similar mechanism for Cu-rich 4th homologues, which are frequent in the above mentioned occurrences.

Due to their modular structure, the members of the pavonite series are also prone to developing intermediate homologues with mixed layers of N and $N + 1$ octahedra wide, already found in synthetic products such as Cd$_{2.8}$Bi$_{8.1}$S$_{15}$ (CHOE *et al.*, 1997).

The junoite-felbertalite-(neyite) series may be interpreted as an accretional homologous series, with the general formula Cu$_2$Pb$_{3N}$Bi$_8$S$_{3N+13}$, where junoite – Cu$_2$Pb$_6$Bi$_8$(S,Se)$_{16}$ (a = 26.4, b = 4.01, c = 16.6 Å, β = 126.5º, *C2/m*, *Z* = 2) is the N = 1 and felbertalite – Cu$_2$Pb$_3$Bi$_8$S$_{19}$(a = 27.6, b = 4.05, c = 20.7 Å, β = 131.3º, *C2/m*, *Z* = 2) is the N = 2 homologue (MAKOVICKY *et al.*, 2001). Both structures posess identical (100)$_{PbS}$ layers, which are two atomic layers thick and which

are periodically sheared, giving rise to tetrahedral Cu sites. The accretion takes place in the kinked and periodically sheared (111)$_{PbS}$ layers, which are single-octahedron in junoite and double-octahedron in felbertalite.

The crystal structure of neyite – Ag$_2$Cu$_6$Pb$_{25}$Bi$_{26}$(S,Se)$_{68}$ (a = 37.5, b = 4.07, c = 43.7 Å, β = 108.8º, *C2/m*, *Z* = 2; MAKOVICKY *et al.*, 2001) can be described as an alternation of triple-octahedra (111)$_{PbS}$-like layers with (100)$_{PbS}$-like layers, two atomic planes thick. Both sets of layers are sheared, giving rise to tetrahedral Cu sites, and truncated by complex PbS-like layers (001)$_{ney}$, three atom planes thick. The resulting structure can be described as a supercomplex structure, built up from three different elements. Neyite does not belong to the junoite homologous series, but it relates to it by containing elements of what should correspond to the hypothetical 3th homologue of the stepped layer structure of the junoite–felbertalite homologous series. A new occurrence of neyite in association with cosalite, has recently been identified at Dognecea (ILINCA & TOPA, 2005, unpublished data).

Recent investigations revealed the presence of junoite in the skarn deposits of Băița Bihor and of felbertalite at Ocna de Fier and Oravița (Fig. 4). Junoite from Băița Bihor is among the very few occurrences departing from the Se-bearing archetype described at Tennant Creek, Australia (MUMME, 1975) and requires new crystal structure determinations. Wider knowledge on the detailed crystal chemistry

of the extremely rare felbertalite and neyite is also likely to occur from these new findings.

The same stands for *proudite* – which has been recently identified in a Se-free form – $CuPb_{7.5}Bi_{9.3}(S)_{22}$ at Ocna de Fier, Southwestern Banat, where it associates with cosalite, felbertalite and bismuthinite derivatives (Fig. 4).
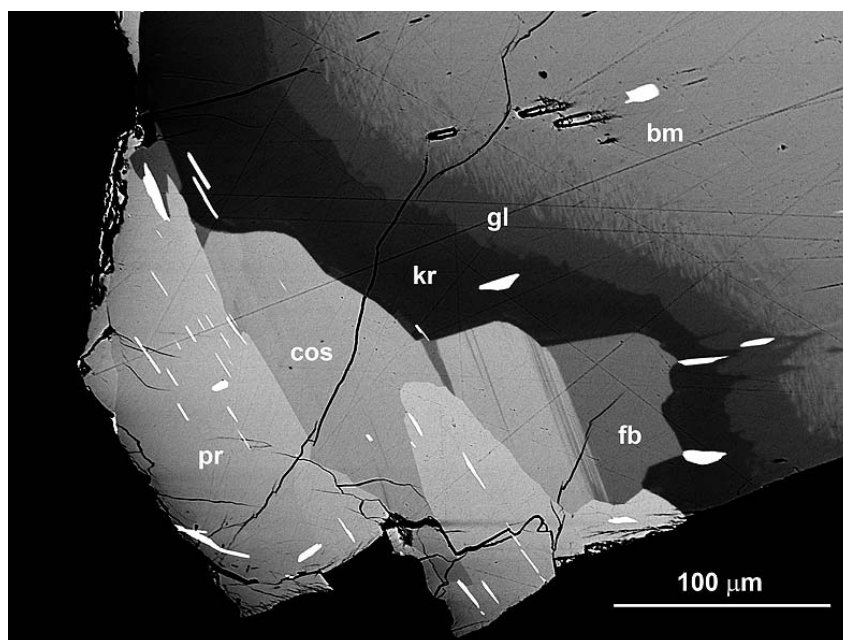

Fig. 4: Complex sulphosalt assemblage with bismuthinite (bm), gladite (gl), krupkaite (kr), proudite (pr), cosalite (cos) and felbertalite (fb) – Ocna de Fier, Southwestern Banat. White laths are Bi (sulpho-) tellurides (BSE image).

Some rare occurrences such as the one at Ciclova, potentially contain at least two new sulphosalt minerals with chemical compositions plotting in the felbertalite-nordströmite region: phase A: $\sim Cu_{0.6}Ag_{0.3}Pb_{3.1}Bi_{5.7}S_{12.3}$ and phase B: $\sim Cu_{0.4}Ag_{0.8}Pb_{3.4}Bi_{5.3}S_{11.9}$ (Fig. 5) and for which, crystal structure determinations are ongoing. Phase B displays a relic character due to widespread replacement by wittite and bismuthinite derivatives. Due to elevated Ag contents, phase B might be a false felbertalite plot in a combined Cu + Ag compositional diagram such as the one in Fig. 2.
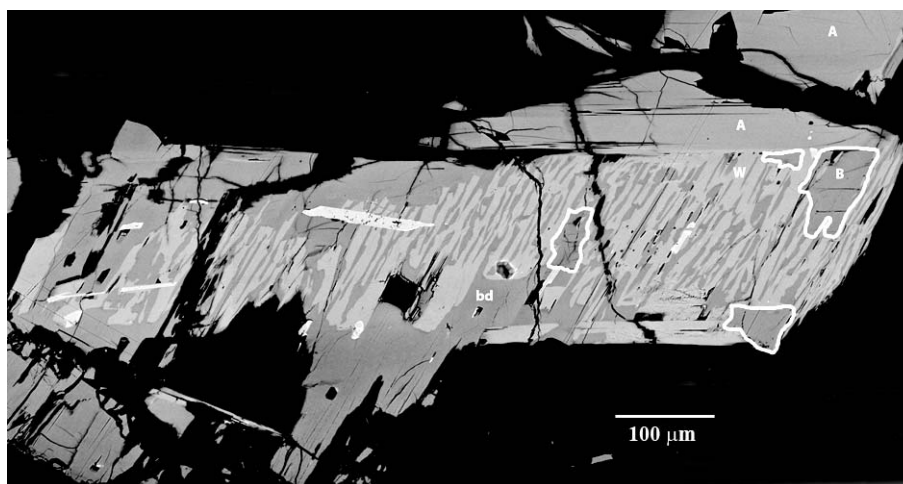

Fig. 5: BSE imaging of Bi-sulphosalt assemblage from Ciclova, Southwestern Banat: unknown phases A and B, wittite (W) and bismuthinite derivatives (bd). White needles are Bi tellurides.

All members of *the cuprobismutite family – i.e.*, cuprobismutite, hodrushite, padĕraite and the recently discovered kupčíkite are represented in Romanian occurrences. Such episodes are confined to ore-deposits related to contact-metamorphic aureoles of Upper Cretaceous–Palaeocene calcalkaline igneous rocks in the so-called Banatitic Belt.

Structural affinities of cuprobismutite members often reflects in coherent intergrowths of two or three different phases, such as hodrushite + kupčíkite ± padĕraite (Fig. 6). A similar case of intergrowths between cuprobismutite and padĕraite from Ocna de Fier has recently been discussed by CIOBANU *et al.* (2004). Typical assemblages include bismuthinite derivatives, makovickyite-cupromakovickyite, emplectite and various Bi tellurides.
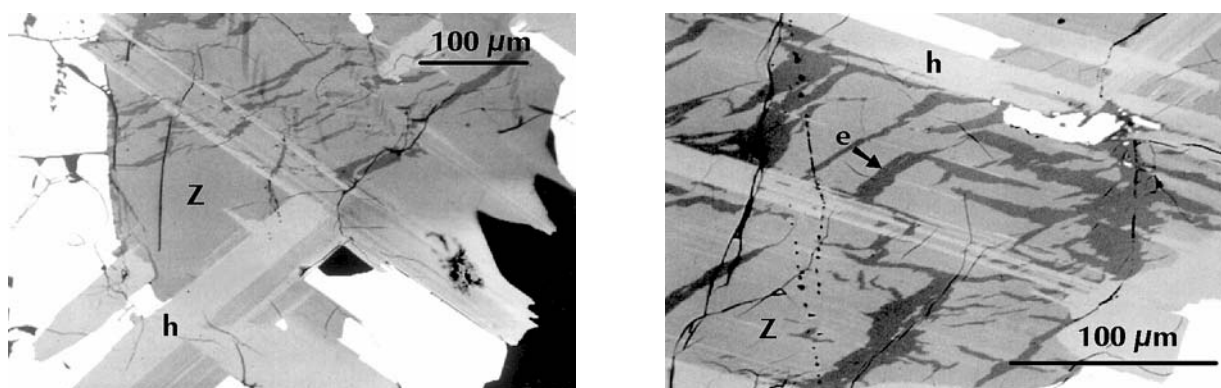

Fig. 6: Parallel intergrowths between hodrushite (h) and kupčíkite (Z) at Băița Bihor. Kupčíkite is preferentially altered by emplectite (e) BSE image.

Finally, not all sulphosalts may be considered rare, yet many of the more common species reveal very peculiar aspects of their crystal chemistry. It is the case of *the bismuthinite–aikinite series* (Bi_2S_3–$CuPbBiS_3$), a discrete family of sub- and supercell structures which seemed a closed case some ten years ago, but to which three more 4-fold and 5-fold superstructure members were added: salzburgite $Cu_{1.6}Pb_{1.6}Bi_{6.4}S_{12}$, paarite $Cu_{1.7}Pb_{1.7}Bi_{6.3}S_{12}$ and emilite $Cu_{10.7}Pb_{10.7}Bi_{21.3}S_{48}$ (BALIĆ-ZUNIĆ *et al.*, 2002; MAKOVICKY *et al.*, 2001; TOPA *et al.*, 2005). Compositional ranges pointing to these three phases have already been identified in several occurrences from Romania, but they will be in need of detailed crystal structure determinations.

Cosalite – ideally $Pb_2Bi_2S_5$ – is another example of a rather common sulphosalt species but with a complicated history in what concerns substitutional mechanisms involving Ag and Cu, *e.g.* $2Pb \Leftrightarrow Bi(+Sb) + Ag$; $Bi(+Sb) \Leftrightarrow Pb + Cu$; $Pb + \square \Leftrightarrow Me^+ + Me^+$; $Pb + \square \Leftrightarrow Cu^{2+}$ *etc*. Significant amounts of chemical and structural data are necessary to identify the relevant trends for such replacement schemes.

Acknowledgements

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