

## Sulfosalt systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy

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**Abstract:** This report deals with a general reexamination of the systematics of sulfosalts. It represents an update of the activity of the Sulfosalt Sub-Committee within the Commission on Ore Mineralogy of the International Mineralogical Association, in connection with the Commission on New Minerals, Nomenclature and Classification (CNMNC-IMA). Part I presents generalities of sulfosalt definition and nomenclature. After an extended chemical definition of sulfosalts, attention is focused on “classic” sulfosalts with  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$  or  $\text{Te}^{4+}$  as cations, corresponding to the general formula  $(\text{Me}^+, \text{Me}'^{2+}, \text{etc.})_x [(\text{Bi}, \text{Sb}, \text{As})^{3+}, \text{Te}^{4+}]_y [(\text{S}, \text{Se}, \text{Te})^{2-}]_z$  ( $\text{Me}, \text{Me}'$ : various metals). General aspects of their chemistry and classification principles are summarized, especially with regard to chemical substitutions and modular analysis of complex crystal structures. On this basis, Part II presents a review of sulfosalt systematics. Six main crystal-chemical sub-groups are distinguished (plus some unclassified species), concerning more than 220 valid mineral species. Among others whose status is questioned are those considered to be varieties of well-defined species; minerals with ill-defined X-ray data; those that are possibly identical species; and those that represent the potential revalidation of old species. More than 50 crystal structures still remain unsolved, among which about a half probably corresponds to new structure types.

**Key-words:** sulfosalt, nomenclature, crystal chemistry, systematics.

## Preamble

Y. MOËLO and E. MAKOVICKY

The International Mineralogical Association (IMA) was founded in 1958. To coordinate its regular activity between general meetings (held every two years initially, and every four years since 1982), the IMA organized different specialized commissions, the best known being the Commission on New Minerals and Mineral Names (CNMMN – now Commission on New Minerals, Nomenclature and Classification, CNMNC). The Commission on Ore Microscopy (COM), since renamed the Commission on Ore Mineralogy, was originally created to establish quantitative data on the optical properties of opaque minerals. The data were subsequently published as *Quantitative Data File* volumes (see the Web-site of the IMA-COM). Within this Commission, the aim of the Sulfosalt Sub-Committee, under the direction of late Dr Roy Phillips, Chairman, was primarily to collect data for a complex group of ore minerals which, at the time, were poorly characterised. During the 13th General Meeting of IMA at Varna, Bulgaria (1982), Dr N. Mozgova succeeded R. Phillips as the new chair, with Dr. Y. Moëlo as secretary and the active collaboration of D.C. Harris (CANMET, Ottawa). Since the 15th IMA meeting at Beijing, China (1990), the activity of the Sulfosalt Sub-Committee has been carried on by us (Moëlo & Makovicky), primarily by compiling the internal reports and disseminating these among the committee members and specialists.

During the last four decades there has been a tremendous evolution of knowledge in the field of mineral systematics. More than 60 % of the mineral species known today were described since the foundation of the IMA-CNMMN. The percentage is even higher in the field of ore minerals, especially the complex groups of sulfosalts and the minerals of the platinum-group elements (Cabri, 1981, 2002). Together with the classic procedures to define the ore minerals, the increasing number of crystal-structure studies has permitted a general deciphering of the crystal chemistry of sulfosalts, which is the basis for a precise definition of mineral species and an understanding of their limits of validity.

This report is an update of the systematics of sulfosalts, reflecting a fruitful collaboration, past and present, of many specialists of sulfosalt mineralogy. Part I presents generalities concerning the definition and chemistry of sulfosalts, as well as some basic principles relevant to sulfosalt crystal-chemical classification. Part II is a detailed presentation of all known sulfosalts species, with selected references about their definition (if recent) and crystal structure

(if solved). Problems concerning the definition and nomenclature of some species are discussed on the basis of published data.

The choice of the crystal-chemical scheme used for the classification in Part II is a development of the modular approach to crystal structures. This choice does not necessarily reflect that of all the contributors and committee members, who may have adopted other points of view; above all, the choice is intended to promote the use of crystal-structure analysis as a basis for understanding the complex chemistry of sulfosalts in nature.

A draft version of this report was presented by E. Makovicky during the 19th General Meeting of the IMA at Kobe, Japan (July 23–28, 2006). A copy of this internal report was sent to the national representatives of the COM and CNMNC, for information and critical reading. This circulation led to significant improvements in the preparation of the final manuscript. The report has been approved as a whole by the CNMNC, through the direction of its Secretary, W.D. Birch. Nevertheless, due to the complexity of the sulfosalt group, this final version may contain errors and imperfections, for which we (Y.M. & E.M.) accept sole responsibility. Above all, this report must be considered as a guide for specialists interested in the field of ore mineralogy, and as help for the discovery and description of new mineral species. Without any excessive pretention, we hope that the report will be considered as the “state of the art” in sulfosalt systematics; however, the details of the classification of these species are considered as a basis for further work rather than a definitive scheme. The review of sulfosalt systematics may also be useful in the field of solid-state chemistry and material sciences, as sulfosalts today have aroused increasing attention in the search for new materials with interesting physical properties, such as in thermoelectricity, photovoltaic conversions, and magnetism.

All participating members are sincerely thanked for their contribution. We mention especially Dr N. Mozgova, past President of the Sulfosalt Sub-Committee, as well as Drs J.L. Jambor, N. Cook (Chairman of the IMA-COM) and E.H. Nickel (former Vice-Chairman of the CNMMN), for their careful reading of the text. We also thank E.A.J. Burke and W.D. Birch (Chairman and Secretary of the CNMNC, respectively), and anonymous members of this commission, as well as Prof. Y. Takéuchi (University of Tokyo) and Dr. Y. Matsushita (National Institute for Materials Science), for their useful comments and corrections.

## Part I. Revision of sulfosalt definition and nomenclature: generalities

Y. MOËLO and E. MAKOVICKY

### 1. Definition and general formula

#### 1.1. What is a sulfosalt?

The term “sulfosalt” (or “thiosalt”) was created by chemists during the XIXth century, by analogy to complex salts of oxygen, such as sulfate, phosphate, arsenate, antimonate, arsenite and antimonite. Oxysalts generally correspond to the combination of a simple cation with a complex anion  $(\text{MeO}_m)^{n-}$ ; this has been confirmed by crystal-structure studies and bond-valence calculations. In sulfosalts, S is considered to play the role of oxygen to similarly form complex anions. Although the configurations found in most modern studies of sulfosalts are more complicated than those encountered in similar oxysalts (*e.g.*, oxyarsenites), the term “sulfosalt” has been preserved as a practical, working category in the field of ore mineralogy. The main reason is that sulfosalt minerals form a genetically well-defined group encountered in specific conditions of ore formation, usually referred to as hydrothermal processes.

#### 1.2. Chemical nomenclature: an extended definition

In the literature, the definition of sulfosalts takes either formal chemistry or structural considerations as the starting point. According to the chemical definition, most sulfosalts are thioarsenites, thioantimonites, thiobismuthites and their combinations, *i.e.*, sulfosalts in which As, Sb and Bi have the same oxidation state +3. Goldfieldite is the only natural example of a thiotellurite (*i.e.*, with  $\text{Te}^{4+}$ ).

*Remark: In the chemical literature, elements of group 15 of the periodic system, P, As, Sb and Bi (but not N, chemically very different) are designated as “pnictogens” (like “chalcogens” for S, Se and Te). Compounds in which pnictogens act as anions correspond to pnictides (see “sulfosalt-pnictides” below).*

If the bond-valence concept is accepted as a basis for classification, the sulfosalts of both the lower- or higher valence elements [with groups such as  $(\text{As}^{3+}\text{S}_3)^{3-}$  or  $(\text{As}^{5+}\text{S}_4)^{3-}$ ] represent classification categories equally well justified as those of oxyarsenites  $(\text{As}^{3+}\text{O}_3)^{3-}$  or oxyarsenates  $(\text{As}^{5+}\text{O}_4)^{3-}$ . This aspect was first considered by Nowacki (1968, 1969). Any problem encountered for some sulfosalts using this concept will have a near-mirror image in the oxy-realm as well, with somewhat diminished covalence.

A very limited number of natural sulfosalts correspond to thioarsenates ( $\text{As}^{5+}$  – enargite, luzonite) or thioantimonates ( $\text{Sb}^{5+}$  – famatinite). There are about 15 thiostannates ( $\text{Sn}^{4+}$ ), mainly related to the ZnS archetypes (sphalerite and wurtzite), and a few thiogermanates ( $\text{Ge}^{4+}$ ). Similarly, sulvanite could be considered as a thiovanadate ( $\text{V}^{4+}$ ), whereas thio tungstates ( $\text{W}^{6+}$ ), and thio molybdates

Table 1. Different chemical types of thiosalts/sulfosalts and related chalcogenides.

| Anion            | Cation                             | Chemical name             | Example        | Frequency in nature |
|------------------|------------------------------------|---------------------------|----------------|---------------------|
| $\text{S}^{2-}$  | <b><math>\text{As}^{3+}</math></b> | <b>thioarsenite</b>       | tennantite     | numerous species    |
|                  | <b><math>\text{Sb}^{3+}</math></b> | <b>thioantimonite</b>     | boulangerite   | numerous species    |
|                  | <b><math>\text{Bi}^{3+}</math></b> | <b>thiobismuthite</b>     | cosalite       | numerous species    |
|                  | <b><math>\text{Te}^{4+}</math></b> | <b>thiotellurite</b>      | goldfieldite   | exceptional         |
|                  | $(\text{P}^{5+})$                  | thiophosphate             | none           | unknown in nature   |
|                  | $\text{As}^{5+}$                   | thioarsenate              | enargite       | rare                |
|                  | $\text{Sb}^{5+}$                   | thioantimonate            | famatinite     | very rare           |
|                  | $(\text{Bi}^{5+})$                 | unknown with S            |                |                     |
|                  | $(\text{Te}^{6+})$                 | unknown with S            |                |                     |
|                  | $\text{Sn}^{4+}$                   | thiostannate              | stannite       | a few               |
| $\text{Ge}^{4+}$ | thiogermanate                      | briartite                 | very rare      |                     |
| $\text{V}^{5+}$  | thiovanadate                       | sulvanite                 | very rare      |                     |
| $\text{Mo}^{6+}$ | thiomolybdate                      | hemusite                  | exceptional    |                     |
| $\text{W}^{6+}$  | thiotungstate                      | kiddcreekite              | exceptional    |                     |
| $\text{Se}^{2-}$ | <b><math>\text{As}^{3+}</math></b> | <b>selenio-arsenite</b>   | giraudite      | exceptional         |
|                  | <b><math>\text{Sb}^{3+}</math></b> | <b>selenio-antimonite</b> | hakite         | exceptional         |
|                  | <b><math>\text{Bi}^{3+}</math></b> | <b>selenio-bismuthite</b> | bohdanowiczite | exceptional         |
|                  | $\text{Sb}^{5+}$                   | selenio-antimonate        | permingeatite  | exceptional         |
| $\text{Te}^{2-}$ | <b><math>\text{Bi}^{3+}</math></b> | <b>telluro-bismuthite</b> | volynskite     | exceptional         |

In bold type: chalcogeno-salts dealt with in the detailed report (Part II).

( $\text{Mo}^{6+}$ ) are exceptional. Thiophosphates ( $\text{P}^{5+}$ ) are as yet unknown in nature. Minerals corresponding to selenio- and telluro-salts, with trivalent As, Sb or Bi, or, exceptionally,  $\text{Sb}^{5+}$  (permingeatite) are uncommon.

Table 1 enumerates these different types of chalcogeno-salts. The present report deals only with the definition and nomenclature of chalcogeno-salts with  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Te}^{4+}$ , having lone-pair electrons with generally a strong stereochemical activity, that enhances the complexity of crystal structures. However, Table 2 summarizes all mineral species corresponding to other chemical types of chalcogeno-salts.

In **morozeviczite**,  $(\text{Pb}, \text{Fe})_3\text{Ge}_{1-x}\text{S}_4$ , **polkovicite**,  $(\text{Fe}, \text{Pb})_3\text{Ge}_{1-x}\text{S}_4$ , and **florensovite**,  $\text{Cu}(\text{Cr}, \text{Sb})_2\text{S}_4$ , structural data are insufficient to decide whether these minerals are sulfosalts.

In **cylindrite** and related compounds (its homeotype **lévyclauidite** and its homologue **franckeite**), the composite crystal structure is built on the regular alternation of two types of layers (Makovicky, 1976; Evain *et al.*, 2006a), one pseudo-tetragonal (“Q” type), probably containing the bulk of  $\text{Sb}^{3+}$  or  $\text{Bi}^{3+}$ , the other pseudo-hexagonal (“H” type), containing principally  $\text{Sn}^{4+}$ . This series is thus of the thioantimonite/stannate type.

In **schlemaite**,  $(\text{Cu}, \nabla)_6(\text{Pb}, \text{Bi})\text{Se}_4$  ( $\nabla$  = vacancy), a crystal-structure study (Förster *et al.*, 2003) gave the

Table 2. List of minerals of the chalcogeno-salt types not considered in Part II.

| Type                                | Species                             | Formula   |                                   |
|-------------------------------------|-------------------------------------|---|-----------------------------------|
| Thioarsenates (As <sup>5+</sup> )   | Billingsleyite                      | Ag <sub>7</sub> AsS <sub>6</sub>  |                                   |
|                                     | Enargite                            | Cu <sub>3</sub> AsS <sub>4</sub>  |                                   |
|                                     | Fangite                             | Tl <sub>3</sub> AsS <sub>4</sub>  |                                   |
|                                     | Luzonite                            | Cu <sub>3</sub> AsS <sub>4</sub>  |                                   |
| Thioantimonates (Sb <sup>5+</sup> ) | Famatinite                          | Cu <sub>3</sub> SbS <sub>4</sub>  |                                   |
| Thiostannates (Sn <sup>4+</sup> )   | Canfieldite                         | Ag <sub>8</sub> SnS <sub>6</sub>  |                                   |
|                                     | Černýite                            | Cu <sub>2</sub> CdSnS <sub>4</sub>  |                                   |
|                                     | Chatkalite                          | Cu <sub>6</sub> FeSn <sub>2</sub> S <sub>8</sub>  |                                   |
|                                     | Ferrokesterite                      | Cu <sub>2</sub> (Fe, Zn)SnS <sub>4</sub>  |                                   |
|                                     | Hocartite                           | Ag <sub>2</sub> FeSnS <sub>4</sub>  |                                   |
|                                     | Kesterite                           | Cu <sub>2</sub> (Zn, Fe)SnS <sub>4</sub>  |                                   |
|                                     | Kuramite                            | Cu <sub>3</sub> SnS <sub>4</sub>  |                                   |
|                                     | Mawsonite                           | Cu <sub>6</sub> Fe <sub>2</sub> SnS <sub>8</sub>  |                                   |
|                                     | Mohite                              | Cu <sub>2</sub> SnS <sub>3</sub>  |                                   |
|                                     | Petrukite                           | (Cu, Ag) <sub>2</sub> (Fe, Zn)(Sn, In)S <sub>4</sub>                                      |                                   |
|                                     | Pirquitasite                        | Ag <sub>2</sub> ZnSnS <sub>4</sub>  |                                   |
|                                     | Stannite                            | Cu <sub>2</sub> FeSnS <sub>4</sub>  |                                   |
|                                     | Stannoidite                         | Cu <sub>8</sub> (Fe, Zn) <sub>3</sub> Sn <sub>2</sub> S <sub>12</sub>                     |                                   |
|                                     | Velikite                            | Cu <sub>2</sub> HgSnS <sub>4</sub>  |                                   |
|                                     | Thioindates (In <sup>3+</sup> )     | Cadmoidite  | CdIn <sub>2</sub> S <sub>4</sub>  |
|                                     |                                     | Indite  | FeIn <sub>2</sub> S <sub>4</sub>  |
|                                     | Thio germanates (Ge <sup>4+</sup> ) | Argyrodite  | Ag <sub>8</sub> GeS <sub>6</sub>  |
| Barquillite                         |                                     | Cu <sub>2</sub> (Cd, Zn)GeS <sub>4</sub>  |                                   |
| Briartite                           |                                     | Cu <sub>2</sub> (Fe, Zn)GeS <sub>4</sub>  |                                   |
| Calvertite                          |                                     | Cu <sub>5</sub> Ge <sub>0.5</sub> S <sub>4</sub>  |                                   |
| Germanite                           |                                     | Cu <sub>13</sub> Fe <sub>2</sub> Ge <sub>2</sub> S <sub>16</sub>                          |                                   |
| Putzite                             |                                     | (Cu <sub>4.7</sub> Ag <sub>3.3</sub> ) <sub>Σ=8</sub> GeS <sub>6</sub>                    |                                   |
| Sulvanite                           |                                     | Cu <sub>3</sub> VS <sub>4</sub>   |                                   |
| Thio-molybdate/stannate             | Hemusite                            | Cu <sub>6</sub> SnMoS <sub>8</sub>  |                                   |
| Thio-tungstate/stannate             | Kiddcreekite                        | Cu <sub>6</sub> SnWS <sub>8</sub>   |                                   |
| Thio-molybdate/germanate            | Maikainite                          | Cu <sub>20</sub> (Fe, Cu) <sub>6</sub> Mo <sub>2</sub> Ge <sub>6</sub> S <sub>32</sub>    |                                   |
| Thio-tungstate/germanate            | Catamarcaite                        | Cu <sub>6</sub> GeWS <sub>8</sub>   |                                   |
| Other mixed types                   | Ovamboite                           | Cu <sub>20</sub> (Fe, Cu, Zn) <sub>6</sub> W <sub>2</sub> Ge <sub>6</sub> S <sub>32</sub> |                                   |
|                                     | Colusite                            | (Cu <sub>12</sub> V(Sb, As, Sn) <sub>3</sub> ) <sub>Σ=16</sub> S <sub>16</sub>            |                                   |
|                                     | Germanocolusite                     | Cu <sub>13</sub> V(Ge, As) <sub>3</sub> S <sub>16</sub>                                   |                                   |
|                                     | Nekrasovite                         | Cu <sub>13</sub> V(Sn, As, Sb) <sub>3</sub> S <sub>16</sub>                               |                                   |
|                                     | Renierite                           | (Cu, Zn) <sub>11</sub> Fe <sub>4</sub> (Ge, As) <sub>2</sub> S <sub>16</sub>              |                                   |
|                                     | Stibiocolusite                      | Cu <sub>13</sub> V(As, Sb, Sn) <sub>3</sub> S <sub>16</sub>                               |                                   |
|                                     | Vinciennite                         | (Cu <sub>10</sub> Fe <sub>4</sub> SnAs) <sub>Σ=16</sub> S <sub>16</sub>                   |                                   |
|                                     | Selenio-antimonate                  | Permingeatite   | Cu <sub>3</sub> SbSe <sub>4</sub> |

general formula (Cu<sub>6-x</sub>∇<sub>x</sub>)(Pb<sub>1-x</sub>Bi<sub>x</sub>)Se<sub>4</sub> (with  $x$  close to 0.4), with identical coordinates for Pb and Bi. This species ought to be considered as a Bi-rich selenide of Pb, whereas the Bi-dominant derivative ( $x > 0.5$ ), if it exists, would be a selenio-salt.

### 1.3. General formula of the principal sulfosalt category with As<sup>3+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup> or Te<sup>4+</sup>

#### 1.3.1. Basic structural formula

As the bulk of natural thioarsenites, thiostannates, *etc.* corresponds structurally to homeotypes of simple sulfides, the term “sulfosalt” is usually limited to the vast group of chalcogeno-salts containing trivalent As, Sb or Bi, as well as (exceptionally) Te<sup>4+</sup>. They correspond to complex sulfides (more generally chalcogenides) wherein one or more of the cations As<sup>3+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup> or Te<sup>4+</sup> is associated with one or more metallic cation(s), *Me*, as essential (intrinsic) constituents. The S<sup>2-</sup> anion may be replaced by Se<sup>2-</sup> or

Te<sup>2-</sup> (chalcogeno-salts). Thus, the general chemical formula can be given as:

$$(Me^+, Me'^{2+}, etc.)_x [(Bi, Sb, As)^{3+}, Te^{4+}]_y \times [(S, Se, Te)^{2-}]_z. \quad (1)$$

From a structural point of view, atoms of the metals and atoms of the metalloids are not bonded to one another, and are bonded only to anions. Thus, compounds such as arsenopyrite, FeAsS, löllingite, FeAs<sub>2</sub>, or gudmundite, FeSbS, are not sulfosalts, as As or Sb are directly bonded to Fe, and act as anions relative to the metal. In sulfosalts, it is the lone-electron-pair activity of As<sup>3+</sup>, *etc.* and, as a consequence, a nearly universally present asymmetric coordination of these metalloids, that causes the structural complexity and specificity of these compounds, setting them apart from nearly all other chalcogenides.

#### 1.3.2. Borderline compounds

Several mineral species combine the structural properties of sulfides (chalcogenides) with those of the other chemical groups, and can be considered as borderline cases.

#### Sulfur-excess compounds

Sulfur (chalcogen) excess corresponds to S–S bonds in the crystal structure. These occur alongside the metal–sulfur bonds. Such compounds may be qualified as “*persulfides*” (“*perchalcogenides*” – the words “*polysulfides*” and “*polychalcogenides*” are also convenient). A well-known example among sulfosalts is **livingstonite**, HgSb<sub>4</sub>S<sub>6</sub>(S<sub>2</sub>) (Srikrishnan & Nowacki, 1975). It is also the case for **moëloite**, Pb<sub>6</sub>Sb<sub>6</sub>S<sub>14</sub>(S<sub>3</sub>) (Orlandi *et al.*, 2002), and of the synthetic sulfosalts Cu<sub>4</sub>Bi<sub>4</sub>X<sub>9</sub> ( $X = S, Se$  – Bente & Kupčik, 1984; Makovicky *et al.*, 2002). Another possible example is that of **museumite**, Pb<sub>2</sub>(Pb, Sb)<sub>2</sub>S<sub>8</sub>[Te, Au]<sub>2</sub> (Bindi & Cipriani, 2004a).

#### Subsulfides/subchalcogenides

In this case, the compounds have a sulfur (chalcogen) deficiency relative to those with ‘normal’ valences. Cations in their crystal structure show metal–metal or metalloid–metalloid bonding alongside the metal–chalcogen bonding. The name of “subsulfides” (“subchalcogenides”) has been used for such cases.

As the first example, within the tetradymite homologous series of layered structures, all compounds having a chalcogen deficit display pairs of Bi atomic layers, implying Bi–Bi bonding. Such is the case for the thioibismutite **babkinitite**, Pb<sub>2</sub>Bi<sub>2</sub>(S, Se)<sub>3</sub>.

In **gabrielite**, Cu<sub>2</sub>AgTl<sub>2</sub>As<sub>3</sub>S<sub>7</sub>, the valence balance is respected. Nevertheless, examination of the crystal structure (Balić-Žunić *et al.*, 2006) showed that Tl atoms form Tl–Tl pairs with a short distance (3.09 Å) corresponding to the sum of covalent radii, that indicates a metal–metal interaction. This is similar to the interaction in the Hg–Hg pairs (2.535 Å) in deane-smithite, (Hg<sub>2</sub>)Hg<sub>3</sub>CrO<sub>5</sub>S<sub>2</sub> (Szymański & Groat, 1997). In **staldelite**, Cu(Zn, Fe, Hg)<sub>2</sub>TlAs<sub>2</sub>S<sub>6</sub> (Graeser *et al.*, 1995),



and its isotype **routhierite**,  $\text{CuHg}_2\text{TlAs}_2\text{S}_6$ , Tl–Tl pairs, with a somewhat longer bond, are also present.

**Dervillite**,  $\text{Ag}_2\text{AsS}_2$ , **vaughanite**,  $\text{HgTlSb}_4\text{S}_7$ , and **fettelite**,  $\text{Ag}_{24}\text{HgAs}_5\text{S}_{20}$ , all with unknown crystal structures, apparently have a small excess of positive charges with respect to the charge balance, thus probably indicating some cation–cation bonding. The “excess” of positive charges is more pronounced in **criddleite**,  $\text{Ag}_2\text{Au}_3\text{TlSb}_{10}\text{S}_{10}$ , and **tvalchrelidzeite**,  $\text{Hg}_3\text{SbAsS}_3$  (Yang *et al.*, accept.). In all of these structures either metalloid–metalloid or metal–metalloid bonds are probably present, or even entire antimonide portions exist. Analogies to these situations are päakkonenite  $\text{Sb}_2\text{AsS}_2$  (Bonazzi *et al.*, 1995) and chalcocothallite (a sulfide–antimonide of Tl and Cu) (Makovicky *et al.*, 1980).

The same situation is encountered in two PGE (Platinum Group Elements)-bearing chalcogenides, **borovskite**,  $\text{Pd}_3\text{SbTe}_4$ , and **crerarite**,  $(\text{Pt,Pb})\text{Bi}_3(\text{S,Se})_{4-x}$ , for which the valence state of the metalloid is unknown.

#### Sulfosalt-pnictides

In the crystal structure of **hauchecornite**,  $\text{Ni}_9\text{Bi}(\text{Bi, Sb})\text{S}_8$ , the pure Bi atom position is preferentially bound to four S atoms (together with two Ni atoms) and acts partly as a cation, whereas the mixed (Bi, Sb) atom is exclusively bound to Ni atoms, and acts as an anion (Kocman & Nuffield, 1974). The same duality can be observed in other species isotypic with hauchecornite: **arsenohauchecornite**, **bismutohauchecornite**, **tellurohauchecornite** and **tucekite**. All these minerals are transition compounds between sulfosalts and pnictides.

#### Halide-sulfides (or halogeno-sulfides)

**Ardaite**,  $\text{Pb}_{17}\text{Sb}_{15}\text{S}_{35}\text{Cl}_9$ , **dadsonite**,  $\text{Pb}_{23}\text{Sb}_{25}\text{S}_{60}\text{Cl}$ , and **playfairite**,  $\text{Pb}_{16}(\text{Sb, As})_{19}\text{S}_{44}\text{Cl}$ , are three examples of natural chloro-sulfosalts. Only the crystal structure of dadsonite is known (Makovicky *et al.*, 2006b), but here, despite the very low Cl/S ratio, the Cl atom is fixed in a specific atomic position. Consequently Cl is essential for the formation of the mineral species.

#### Oxide (hydroxide)-sulfides

In **scainiite**,  $\text{Pb}_{14}\text{Sb}_{30}\text{S}_{54}\text{O}_5$  (Moëlo *et al.*, 2000), the O atoms are bound preferentially to Sb atoms, in a way analogous to that in kermesite  $\text{Sb}_2\text{S}_2\text{O}$ . Scainiite can be considered as an oxy-sulfosalt.

In **cetinite**,  $\sim \text{NaK}_5\text{Sb}_{14}\text{S}_6\text{O}_{18}(\text{H}_2\text{O})_6$ , both the  $\text{SbS}_3$  and  $\text{SbO}_3$  groups are present, and K is bound almost exclusively, and Na completely, to O atoms (Sabelli *et al.*, 1988; Wang & Liebau, 1999), with additional  $\text{H}_2\text{O}$  molecules bound only to Na. This compound is thus a hydrated thio-oxysalt, like its Na-pure end-member, **attensite** (Sejkora & Hyrsl, 2007).

In **sarabauite**,  $(\text{Sb}_4\text{S}_6)(\text{CaSb}_6\text{O}_{10})$ , Sb atoms again bind both to S and O atoms, whereas Ca atoms are exclusively bound to O atoms (Nakai *et al.*, 1978). This compound could be considered to be a “thio-oxysalt”.

**Apuanite** and **versiliaite** are two Sb-containing oxy-sulfides, derived from the oxide schafarzikite (Mellini &

Merlino, 1979). In apuanite, ideally  $\text{Fe}^{2+}\text{Fe}_3^{3+}\text{Sb}_4^{3+}\text{O}_{12}\text{S}$ , the Sb is bound only to O; thus the mineral cannot be considered to be an oxy-sulfosalt. In versiliaite,  $\text{Fe}_2^{2+}(\text{Fe}_3^{3+}\text{Sb}_{0.5}^{7+}\text{Zn}_{0.5}^{2+})_{\Sigma=4}\text{Sb}_6^{3+}\text{O}_{16}\text{S}$ , the situation is more complicated, as some Sb partly replaces Fe in a tetrahedral site, coordinated by 1 S and 3 O atoms. The Sb should correspond to  $\text{Sb}^{5+}$ , which suggests that versiliaite is a combination of antimonite-antimonate with thio-antimonate.

#### Hydrated sulfosalts

In **gerstleyite**,  $\text{Na}_2(\text{Sb, As})_8\text{S}_{13}\cdot 2\text{H}_2\text{O}$  (Nakai & Appleman, 1981), Sb is bound only to S atoms, whereas Na is bound to S atoms and  $\text{H}_2\text{O}$  molecules; the mineral corresponds to a hydrated sulfosalt. Numerous synthetic hydrated sulfosalts have been synthesized.

#### Oxy-chloro-sulfides

Minor contents of O and Cl have been recently discovered in two new Pb–Sb sulfosalts, **pillaite**,  $\text{Pb}_9\text{Sb}_{10}\text{S}_{23}\text{ClO}_{0.5}$ , and **pellouxite**,  $(\text{Cu, Ag})_2\text{Pb}_{21}\text{Sb}_{23}\text{S}_{55}\text{ClO}$ . Crystal-structure studies proved the O and Cl to be intrinsic components (Meerschaut *et al.*, 2001; Palvadeau *et al.*, 2004). These two minerals correspond to oxy-chloro-sulfosalts.

### 1.4. Conclusion

Taking into account the mineral species listed in Table 2 (more than 40 compounds) and those corresponding to the general formula [1] above (see the alphabetical index), as well as the borderline compounds, more than 260 mineral species belong to the “sulfosalt group” (sulfosalts and other chalcogeno-salts). There are also about 200 incompletely defined minerals (so-called “UM” – unnamed minerals) in the literature related to this vast group (Smith & Nickel, 2007), mainly because the chemical composition alone was determined by EPMA, which is generally easier to obtain than crystallographic data.

The “sulfosalt group” is as heterogeneous from a crystal-chemical point of view as, *e.g.*, the silicate group. Consequently, a rigorous classification and nomenclature of sulfosalts is much more complicated than that of more restricted mineral groups which have been reexamined in the past by specific committees of the IMA (amphiboles, micas, zeolites...). As already mentioned, some sulfosalts fit perfectly in specific sulfide groups; for instance, most of the sulfostannates belong structurally within the sphalerite group. Only the vast group of sulfosalts with  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$  or  $\text{Te}^{4+}$  stands structurally as an almost separate family – this group is the topic of the present report. At the present stage of research, some groups of these sulfosalts can already be neatly classified on a crystal-chemical basis, whereas others await further discoveries for achieving the same depth of classification. The latter are grouped on purely chemical principles. The intention of the report is to assist further development of mineralogical studies in the field of complex sulfides.

Table 3. Classification hierarchy within the present sulfosalts report.

|  | Level of classification                                  | Example |
|--|--|---------|
| Class  | Chalcogenides  |         |
| Chemical sub-type  | Sulfosalts   |         |
| Large structural family (plesiotypic and merotypic series, other groups) | Boulangerite plesiotypic family                          |         |
| Homologous series  | Lillianite homologous series                             |         |
|  | Plagionite homologous series                             |         |
| Iso- and homeotypic series   | Tetrahedrite isotypic series; aikinite homeotypic series |         |
| Species  |  |         |
| Sub-species: Polytypes   | Pearceite and polybasite polytypes                       |         |

## 2. Sulfosalts with As<sup>3+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup> or Te<sup>4+</sup>: chemistry and classification principles

### 2.1. General outline

There are various ways of classifying minerals. Some classifications are extrinsic (*i.e.*, a paragenetic classification), but intrinsic ones are the best for development of the scientific field of mineralogy. Today, the deeper level of knowledge about minerals is that of their crystal structure (their “genetic code”); thus, the best classification ought to be a crystal-chemical classification. The first general crystal-chemical approach for sulfide minerals and related species was presented by Hellner (1958). Since the end of the 1960s, several mineralogical crystallographers have paid special attention to the sulfosalts group: Makovicky (1967), Nowacki (1969), Takéuchi & Sadanaga (1969), Povarennykh (1971), Wuensch (1974) and Edenharter (1976). In the following decade, some important aspects of the systematics of sulfosalts were emphasized: polymerization of complex anions and comparison with the classification of silicates (Ramdohr & Strunz, 1978; Kostov & Minčeva-Stefanova, 1981; Nakai & Nagashima, 1983), problems of non-stoichiometry (Mozgova, 1984), modular analysis of the crystal structures (Makovicky, 1981, 1985a, 1989). Noteworthy is also the more recent work of Takéuchi (1997) on topochemical cell-twinning (Remark: ‘cell-twinning’, defined by Takéuchi *et al.* (1979), differs from ordinary twinning – see Nespolo *et al.*, 2004).

Table 3 presents the hierarchical structure of the system chosen for this review. Whenever possible, the system is based on the level of structural relationships among mineral species. Thus, for a large number of species the system is essentially a *modular* classification. The general definition of isotypic, homeotypic, and homologous series is given in “Nomenclature of Inorganic Structure Types” (Lima-de-Faria *et al.*, 1990). The best known example of homeotypic series is certainly the aikinite–bismuthinite series (Topa *et al.*, 2002a). A clear example of homologous series is that of the plagionite series, Pb<sub>3+2n</sub>Sb<sub>8</sub>S<sub>15+2n</sub> (with  $n = 0, 1, 2,$  or 3). The lillianite series is more complex, with numerous homeotypic and homologous phases. Dimorphism has been recognized in several, relatively rare cases, *e.g.* for proustite *versus* xanthoconite, Ag<sub>3</sub>AsS<sub>3</sub>, for pyrargyrite *versus* pyrostilpnite, Ag<sub>3</sub>SbS<sub>3</sub>, or for clerite *versus* synthetic monoclinic MnSb<sub>2</sub>S<sub>4</sub>.

The notion of family is less rigorous and corresponds to the “plesiotypic” and “merotypic” series of Makovicky (1997), or to more complex groups which may include such series. As detailed in Ferraris *et al.* (2004), within “plesiotypic” and “merotypic” series are grouped complex crystal structures showing a lower degree of topologic similarities than homologous series. For instance, in the zinkenite family, crystal structures consist of rods with simpler internal structure that are organized in different ways around pseudo-trigonal columns with Pb atoms in mono- or bi-capped prismatic coordination. This zinkenite family belongs to the supergroup of Pb sulfosalts with rod-type building blocks.

Definition of many of these series is fortified by data for a number of synthetic sulfosalts that do not have natural equivalents (*e.g.*, especially in Makovicky 1989, 1997, and Ferraris *et al.*, 2004). The current presentation, which in many aspects is distinct from the general classification of Strunz & Nickel (2001), is not intended to be an overall crystal-chemical classification; rather, the presentation is a review of sulfosalts species, organized on the basis of chemistry and, where possible, on the basis of crystal chemistry. In the future, discovery of new sulfosalts species, as well as the resolution of up to now unknown crystal structures, will permit the development and improvement of this sulfosalts systematization.

### 2.2. Chemistry

The formula indicated is the ideal formula derived from a crystal-structure study or, if the species is poorly characterised, it is the simplified formula given for the type sample. For non-commensurate composite structures (for instance cylindrite), a reduced formula is given, which is always an approximation of the true formula.

Many sulfosalts have a complex chemistry, and frequently a minor chemical component appears to be essential for the stabilization of a mineral species (*e.g.*, Cu in natural meneghinite, Cl in dadsonite). For a given species, the choice of the structural formula must indicate such minor components, whereas other elements, which are verifiably not essential (solid solution), can be excluded from the ideal formula as much as possible.

For the derivation of simplified formulae, it is important to know the principal substitution rules encountered among sulfosalts. For instance, if there is minor As together with

major Sb, in many cases As can be totally substituted by Sb, and thus will disappear from the final structural formula. On the contrary, Cl even in low concentration (some tenths of a percent – see dadsonite), is expected to play a specific role and therefore, generally, must be retained in the formula. The avoidance or retention of a minor component necessitates a precise knowledge of the crystal structure, particularly of the specific atomic positions at which this minor component is located. Experimental studies are often the only way to obtain the compound without the minor component, and to verify that this pure compound has the same crystallographic characteristics. For instance, natural geocronite always contains minor amounts of As, but synthetic As-free geocronite is known (Jambor, 1968).

Table 4 presents a non-exhaustive list of various substitution rules encountered in sulfosalts. It represents a first step in the examination of new EPMA data, in order to correlate them more or less precisely with a chemical group of sulfosalts or a definite mineral species.

*Remark: A one-for-one atom substitution does not necessarily imply that one element substitutes another on the same position in the crystal structure. Sometimes, it may imply distinct sub-sites within a polyhedron, or quite distinct sites. The mechanism may be more complex for heterovalent substitution rules.*

The role of temperature can be important in controlling the substitution. Extended solid solutions at high temperature (in hydrothermal conditions: 300 to 400 °C) may be drastically restricted at low temperature (epithermal conditions). For instance this aspect is particularly important in the aikinite–bismuthinite series (Topa *et al.*, 2002a). The substitution rules in Table 4 generally correspond to solid solutions, but the rules may also describe the homeotypic derivation of a species of complex chemistry, from another species that has a very close structure but a simpler composition (*e.g.*, all Pb- and Cu-containing derivatives of bismuthinite in the aikinite–bismuthinite homeotypic series).

Careful EPMA of sulfosalts in routine conditions (for instance, 20 kV, 20 nA, counting time 10 s, compositionally close secondary standards) permits a very good mineral identification, if no minor element is omitted (down to 0.1 wt.%). When such minor elements are present, and are not essential constituents (contrary to the 0.4 wt.% Cl in dadsonite,  $Pb_{23}Sb_{25}S_{60}Cl$ ), their subtraction using the substitution rules from Table 4 gives a simplified chemical formula that generally results in only one mineral species.

*Remark: Exceptionally, some sulfosalts have a very low content of oxygen (0.1 wt.%), which is nevertheless essential for their stability, as their crystal structure reveals a specific position for oxygen atoms (pillaite, pellouxite). EPMA would not be sufficient to prove the presence of oxygen within the structure, due to the easy formation of an oxidation film at the polished surface of the sample.*

The search for minor elements is important both for mineral identification and for ore geochemistry and regional metallogeny, as is well known especially for the tetrahedrite series. Another example is the andorite series, which contains small amounts of Sn, Cd, and In in the Potosi district (Bolivia), whereas in Romania the characteristic minor elements are Mn and Fe.

### 2.3. Crystal structure and modular analysis

Knowledge of the crystal structure is not necessary for the validation of a new mineral species by the CNMNC of the IMA. Nevertheless, for sulfosalts having a large unit cell (*e.g.*, most of the Pb sulfosalts), a solution of the crystal structure is today strongly recommended in order to prove the uniqueness of a new mineral species, and to reveal the role of minor components in the structure and composition. For these large structures it is also the only way to obtain a precise structural formula, and in some cases to decide whether a solid solution exceeds the 50 % limit in a characteristic site of the crystal structure, thereby giving a new isotopic mineral species.

Differences between the bonding strength and character of the metalloids (As, Sb, Bi) and metals, especially Pb, are less pronounced in sulfosalts than those between the bonding character in tetrahedral/triangular coordinations of Si, B, P, *etc.* and the associated cations in the relevant oxyalts. This difference, together with the variable types of coordination polyhedra of As, Sb and Bi and other crystal-chemical phenomena connected with the covalent character of bonding in the majority of sulfosalts, makes a polyhedral classification ineffective for most sulfosalt families. The approach at a higher level of organization in accordance with the principles of modular analysis seems to be the most efficient way to obtain a crystal-chemical classification of sulfosalts. Modular analysis of a crystal structure is based on the discrimination of sub-units called *building blocks*. This does not signify that interatomic bonding between constitutive building blocks is weaker than inside these blocks (they can be as strong, indeed stronger).

Typical for the combined arrays of metalloids and Pb and some other metals (*e.g.*, Ag), as well as for some fairly pure Bi or Sb arrays, are extensive building blocks. The blocks approximate the topology of the PbS structure (cases with low activity of lone electron pairs) or of the SnS structure (TII, TISbS<sub>2</sub> are also approximations) for arrays that have well-expressed activity of lone electron pairs. lone electron pairs of metalloids are accommodated by the archetypal motif (often congregating in common spaces, so-called “lone electron pair micelles”) whereas the contact between blocks takes place via mutually non-commensurate surfaces or by means of unit-cell twinning (details in Makovicky 1989, 1997). Structures with low contents of metalloids tend to follow the topologies dictated by the principal metals, eventually modified to satisfy the metalloid requirements as well.

The structural principles outlined in the preceding paragraph commonly lead to the presence of homologous series differing in the size of blocks but not in the principles of their recombination into one structure, or to more general families of related structures when the simple homologous expansion is hindered on structural grounds. Increase in the block size alters the Pb(Sn)/metalloid ratio in favour of divalent metals; the same may happen in favour of combined AgBi or, rarely, even CuBi arrays. More extensive arrays and less expressed lone-electron-pair character may be favoured by elevated temperatures and by the substitution of S by Se or even Te.

Table 4. Principal chemical substitution rules observed in natural sulfosalts.

| Anions  | Comments/Examples   |
|---|---|
| $S^{2-} \leftrightarrow Se^{2-}$  | cannizzarite $\leftrightarrow$ wittite ( <i>e</i> – see abbreviations at the bottom of the table)   |
| $(Se, S)^{2-} \rightarrow Te^{2-}$  | watkinsonite ( <i>I</i> )   |
| $Cl^- \leftrightarrow S^{2-}$   | pellouxite, dadsonite ( <i>I</i> ), coupled with cation substitutions   |
| Cations   | Comments/ Examples  |
| $Bi^{3+} \leftrightarrow Sb^{3+}$   | easy and frequent   |
| $Sb^{3+} \leftrightarrow As^{3+}$   | easy and frequent (especially: tetrahedrite–tennantite isoserries)  |
| $As^{3+} \rightarrow Bi^{3+}$   | jordanite ( <i>I</i> ); tennantite ( <i>e</i> – but rare)   |
| $Pb^{2+} \rightarrow Sn^{2+}$   | cylindrite, franckeite ( <i>e</i> )   |
| $Pb^{2+} \rightarrow (Mn, Fe, Cd)^{2+}$   | andorite series ( <i>I</i> )  |
| $Cd^{2+} \rightarrow Pb^{2+}$   | kudriavite ( <i>I</i> )   |
| $3 Pb^{2+} \rightarrow 2 Bi^{3+} + \nabla$  | easy in galena, but difficult to prove in Pb sulfosalts (Ag-free lillianite – <i>I</i> )  |
| $3 Pb^{2+} \rightarrow 2 Sb^{3+} + \nabla$  | limited in galena, possible but not proved in Pb sulfosalts   |
| $2 Pb^{2+} \leftrightarrow Ag^+ + Bi^{3+}$  | lillianite series ( <i>e</i> )  |
| $2 Pb^{2+} \leftrightarrow Ag^+ + Sb^{3+}$  | andorite series ( <i>e</i> )  |
| $2Pb^{2+} \rightarrow (Ag, Tl)^+ + As^{3+}$   | sartorite series  |
| $Bi^{3+} + \nabla \leftrightarrow Pb^{2+} + Cu^+$   | bismuthinite–aikinite series ( <i>e</i> – ordered compounds (homeotypes) with decreasing <i>T</i> ); cosalite, nuffieldite ( <i>I</i> )   |
| $Sb^{3+} + \nabla \leftrightarrow Pb^{2+} + Cu^+$   | rare (zinkenite – <i>I</i> ; meneghinite)   |
| $Fe^{2+} + Pb^{2+} \rightarrow Cu^+ + Bi^{3+}$  | kobellite homologous series ( <i>I</i> )  |
| $Bi^{3+} \rightarrow 3 Cu^+$<br>(distinct sites)  | pavonite series ( <i>I</i> ). In this series and in some other sulfosalts, Cu may enter various interstitial sites, and the exact substitution rule needs accurate studies (first of all, precise crystal-structure data) |
| $2 Bi^{3+} \rightarrow 2 Ag^+ + 4 Cu^+$<br>(distinct sites)   | angelaite   |
| $Bi^{3+} \rightarrow In^{3+}$   | kudriavite  |
| $Sb^{3+} + Ag^+ \leftrightarrow Pb^{2+} + Mn^{2+}$  | at high temperature; ordering at low <i>T</i> : uchucchacuaite  |
| $Tl^+ \leftrightarrow Ag^+$   | never in the same atomic position! Limited at low <i>T</i> (rathite?); in the sartorite homologous series, Tl and Ag are apparently distributed in distinct sites, or in distinct sulfosalts (Lengenbach deposit)         |
| $Fe^{2+} \leftrightarrow Mn^{2+}$   | jamesonite–benavidesite ( <i>e</i> )  |
| $Hg^{2+} \leftrightarrow Zn^{2+}, (Fe^{2+})$  | routhierite–stalderite ( <i>e</i> )   |
| Mutual substitution among<br>$Fe^{2+} \leftrightarrow Zn^{2+} \leftrightarrow Mn^{2+} \leftrightarrow$<br>$Cd^{2+} \leftrightarrow Hg^{2+}$ | easy, up to 2 metal atoms among 12 in the tetrahedrite series (some Sn or Pb also possible)   |
| $Ag^+ \leftrightarrow Cu^+$   | tetrahedrite series ( <i>e</i> ); lengenbachite ( <i>I</i> ); pearceite–polybasite series ( <i>I</i> )  |
| $2 Fe^{2+} \leftrightarrow Fe^{3+} + Cu^+$  | tetrahedrite series (up to 1 atom in the structural formula)  |
| $Fe^{3+} + Cu^+ \leftrightarrow 2 Cu^{2+}$  | tetrahedrite series (remark: the presence of divalent Cu in sulfides <i>etc.</i> may be a purely formal expression of the true situation; this is discussed by the specialists of chalcogenide solid chemistry)           |
| $(Fe^{2+}, Zn^{2+} \dots) + (As, Sb)^{3+}$<br>$\leftrightarrow Cu^+ + Te^{4+}$  | tetrahedrite–goldfieldite series (up to 2 atoms in the structural formula)  |
| $Cu^+ + (Sb, As)^{3+} \leftrightarrow \nabla + Te^{4+}$   | tetrahedrite–goldfieldite series (when Te > 2 atoms in the structural formula)  |
| $Fe^{2+} \leftrightarrow 2 Cu^+$  | cylindrite–lévyclaudeite ( <i>e</i> )   |
| $Cs^+ \leftrightarrow Tl^+$   | exceptional (galkhaite – <i>e</i> )   |
| $Cu^+ (Ag^+?) \rightarrow Au^+$   | exceptional (goldfieldite – <i>I</i> ; needs crystal-structure study)   |
| $Ag^+ \rightarrow Au^+$   | exceptional (polybasite)  |
| Solid solutions with unknown substitution rules   |   |
| $S^{2-} \rightarrow \nabla^0$   | with increasing Ag content in freibergite (and decreasing unit cell)  |
| $In^{3+}$ in ramdohrite ( <i>I</i> )  |   |
| $Tl^+$ in owyheeite ( <i>I</i> )  |   |

Abbreviations: *e* = easy/extended substitution; *I* = limited;  $\nabla$  = vacancy;  $\leftrightarrow$  = reciprocal;  $\rightarrow$  = unidirectional.



Blocks of these archetypal structures can be, according to the general vocabulary:

- 0-dimensional (0D): fragments; clusters; molecules
- 1D: chains, rods, ribbons, columns (= complex rods)
- 2D: layers (generally plane, sometimes undulated); sheets (= layers with weaker interlayer bonding); slabs (= thick, complex layers)
- 3D: cases where the entire structure approximates an archetype (= 3-dimensional; no blocks distinguished) are rarer.

Numerous Pb sulfosalts, among them the boulangerite pleiotypic series, have been described using an intermediate category between 2D- and 1D blocks. The intermediate category is the “rod-layer” type, which results from the connection of rods along one direction (Makovicky, 1993).

The description of the general organization of a crystal structure involves the discrimination of the constitutive building blocks, and how they are interconnected. The description thus permits definition of the type of architecture of the crystal structure. The main part of the architectural types is based on a single type of building block. A significant part results in the combination of two types of blocks, as in some homologous series. The most complex architectural type is the boxwork type, a combination of three distinct blocks, as exemplified by the crystal structure of neyite (Makovicky *et al.*, 2001a).

#### 2.4. Non-stoichiometry in sulfosalts

The concept of non-stoichiometry in sulfosalts has been promoted especially by Mozgova (1984, 2000), and is discussed briefly here by using both a general approach and specific examples. The most common case of non-stoichiometry corresponds to various solid solutions, as presented in Table 4. Some substitution rules, isovalent or heterovalent, do not change the total number of atoms in the structural formula (= in the unit cell); other substitutions imply filling, or creating vacancies, which changes the total number of atoms present.

At the opposite end of the scale, syntactic intergrowths correspond to a mixture, at the (pseudo-)crystal level, of

3D domains of (at least) two species with similar crystal structures. Such intergrowths have various origins and present various textures (exsolution process, myrmekites by decomposition or substitution, simultaneous precipitation... ). When the size of domains decreases to a micrometer scale, it becomes difficult to recognize the domains even at the highest magnification with a metallographic microscope, and microprobe analysis typically shows analytical dispersion around theoretical stoichiometric formulae; examples are the plagionite (Mozgova & Borodaev, 1972) and andorite–fizélyite (Moëlo *et al.*, 1989) homologous series.

Intergrowths of the aforementioned type may be present even at a nanometric scale, and are visible with high-resolution techniques such as electron microscopy. SEM may give good images, which generally reveal a strong geometrical anisotropy of intergrowths, towards 2D domains with more or less pronounced stacking disorder. One of the best approaches is HRTEM, which permits a precise crystallographic characterisation of associated sulfosalts. These species correspond to two closely related members of a homologous series (Pring *et al.*, 1999), exceptionally even to more distinct species (Pring & Etschmann, 2002; Ciobanu *et al.*, 2004).

The most complex cases encountered in the sulfosalt group are exsolution aggregates of the bismuthinite series, wherein some samples correspond to a nanometric association of two or three members, some of them with their own deviations from a simple stoichiometry, which are related to a solid-solution mechanism (Topa *et al.*, 2002b).

Of course, these various types of non-stoichiometric members will give different X-ray signatures in powder diagrams or by single-crystal study.

A special example of non-stoichiometry is that of sulfosalts with layered composite non-commensurate structure (cylindrite and related compounds – Makovicky & Hyde, 1981, 1992). In these sulfosalts, each of the two constituent layers may have a stoichiometric formula, but the non-commensurate (non-integer) ratio between one or two pairs of in-plane parameters results in a “non-stoichiometric” (*i.e.*, complex) structural formula.

## Part II. Review of sulfosalt systematics

IMA-COM Sulfosalt Sub-Committee

### Introduction: general presentation of sulfosalt species

This general presentation takes into account the sulfosalt species given by “Fleischer’s Glossary of Mineral Species” (Mandarino & Back, 2004) (see also Blackburn & Dennen, 1997; Martin & Blackburn, 1999, 2001; Martin, 2003), plus the new species published or approved recently by the CNMNC-IMA (see its website). The presentation is concerned with more than 220 sulfosalt species, for which an alphabetical list is given at the end of the text, together with an appendix that lists discredited species.

As the crystal-chemical classification of sulfosalts is incomplete at present, the following general presentation of sulfosalt mineral species is subdivided into large chemical groups. Within each group, subdivisions are generally based on well-defined structure types.

Sulfosalt species whose specific crystal structure does not have a close relationship to those of other species are indicated separately as “*Single type*”. If the crystal structure of a species is not known, this species is classified, as much as possible, with sulfosalts that have a similar chemistry.

#### About the references

To reduce as much as possible the number of references cited in this review, only the following have been included:

- systematically, the studies presenting the crystal structures of the sulfosalt species (noted “STR” afterwards), but also taking into account data obtained on synthetic compounds (“synth.” afterwards);
- recent papers that define sulfosalt species (since 1990, or older, when necessary);
- all references needed for the presentation and discussion of problems of definition and nomenclature.

Crystallographic data (unit-cell parameters, symmetry, space group) have been avoided, except when a change in symmetry or space group appears crucial for the distinction between two very close species (*e.g.*, giessenite *versus* izoklakeite).

All other references and basic data are available in fundamental books on systematic mineralogy (*e.g.*, Strunz & Nickel, 2001; Mandarino & Back, 2004), as well as in PDF (JCPDF) or ICSD (FIZ – Karlsruhe) databases. Concerning the crystal structures, especially noteworthy is the extensive work of Dr Y. Matsushita, who has compiled systematically all chalcogenide and related structures, both of natural and synthetic phases. Access to the data-library is free at <http://www.crystallmaker.co.uk/library/chalcogenides.html>.

Where problems are present regarding the definition of a species, relevant comments are given after the presentation of each species or group. The aim is to present the current status of sulfosalt definition, nomenclature and classification for all specialists interested in this field of research,

thereby pointing out various unsolved questions and facilitating the discovery of new mineral species.

### 1. Sulfosalts with atom ratio of cation/chalcogen = 1

#### 1.1. Binary sulfosalts ( $MPnCh_2$ ), where $M$ = univalent cation (Cu, Ag, Tl); $Pn$ = pnictogen (As, Sb, Bi); $Ch$ = chalcogen

These sulfosalts are presented according to the organisation of pnictogen polyhedra.

##### 1. Matildite isotypic series (trigonal derivatives of $PbS$ , according to $(PbS)_{111}$ slices)

###### Matildite, $AgBiS_2$

STR (synth.): Geller & Wernick (1959).

###### Bohdanowiczite, $AgBiSe_2$

STR (synth.): Geller & Wernick (1959).

###### Volynskite, $AgBiTe_2$

STR (synth.): Pinsker & Imamov (1964).

All these structures could also be considered as derivatives of the  $CdI_2$  archetype (single layer of  $BiCh_6$  octahedra), with Ag atoms intercalated between the layers (so-called “intercalation compounds”). However, these old structure determinations appear to be (pseudo)cubic approximations, as it is unrealistic to consider regular  $BiCh_6$  octahedra because of the lone-electron-pair of  $Bi^{3+}$ .

##### 2. Aramayoite isotypes

###### Aramayoite, $Ag_3Sb_2(Bi, Sb)S_6$

###### Baumstarkite, $Ag_3Sb_3S_6$

Definition of baumstarkite and STR of aramayoite and baumstarkite are given by Effenberger *et al.* (2002).

##### 3. (Single type)

###### Cuboargyrite, $AgSbS_2$

Defined by Walenta (1998).

STR (synth.): Geller & Wernick (1959).

##### 4. (Single type) (sheared derivative of $SnS$ archetype)

###### Miargyrite, $AgSbS_2$

STR: Smith *et al.* (1997).

##### 5. (Single type)

###### Smithite, $AgAsS_2$

STR: Hellner & Burzlaff (1964). In the structure, As in triangular pyramidal coordination forms  $As_3S_6$  trimers arranged in columns parallel to  $b$ .

## 6. (Single type) Cyclic trigonal

### **Trechmannite**, AgAsS<sub>2</sub>

STR: Matsumoto & Nowacki (1969). Arsenic in triangular pyramidal coordination forms As<sub>3</sub>S<sub>6</sub> trimers that have trigonal symmetry.

## 7. Emplectite isotypic series

### **Emplectite**, CuBiS<sub>2</sub>

STR: Portheine & Nowacki (1975a).

### **Chalcostibite**, CuSbS<sub>2</sub>

STR: Razmara *et al.* (1997).

## 8. Weissbergite homeotypic pair

### **Weissbergite**, TlSbS<sub>2</sub>

STR: Rey *et al.* (1983).

### **Lorandite**, TlAsS<sub>2</sub>

STR: Balić-Žunić *et al.* (1995).

Weissbergite is a direct substitution derivative of the SnS archetype, whereas lorandite is a stacking variant related to this archetype with a double-layer periodicity.

## 1.2. Ternary sulfosalts ( $M1^+M2^{2+}PnS_3$ )

### 1. *Freieslebenite family (3-dimensional PbS-like arrays)*

#### *Freieslebenite (isotypic) series*

##### **Freieslebenite**, AgPbSbS<sub>3</sub>

STR: Ito & Nowacki (1974a).

##### **Marrite**, AgPbAsS<sub>3</sub>

STR: Wuensch & Nowacki (1967).

#### *Related*

##### **Diaphorite**, Ag<sub>3</sub>Pb<sub>2</sub>Sb<sub>3</sub>S<sub>8</sub>

STR: Armbruster *et al.* (2003).

##### **Quadratite**, Ag(Cd, Pb)(As, Sb)S<sub>3</sub>

STR: Berlepsch *et al.* (1999).

##### **Schapbachite**, Ag<sub>0.4</sub>Pb<sub>0.2</sub>Bi<sub>0.4</sub>S

Redefinition: Walenta *et al.* (2004).

##### **Schirmerite (Type 1)**, Ag<sub>4</sub>PbBi<sub>4</sub>S<sub>9</sub>

### **Schapbachite and schirmerite (Type 1): the same compound?**

Schapbachite, initially defined as the cubic form of AgBiS<sub>2</sub>, was subsequently discredited because it is a high-temperature form that always decomposes at low *T* to its trigonal dimorph, matildite. Schapbachite, was recently redefined by Walenta *et al.* (2004) through the study of a sample containing a significant amount of Pb (~ 20 % of the cation sum). This Pb content seems necessary for the stabilization of schapbachite, and ought to appear in the chemical formula.

Previously, Bortnikov *et al.* (1987) discovered a mineral ("Phase I") that has the composition originally assigned to schirmerite (Type I), Ag<sub>4</sub>PbBi<sub>4</sub>S<sub>9</sub> (that is, strictly in the AgBiS<sub>2</sub>-PbS pseudo-binary system), but without X-ray data. This schirmerite is very close to the stable form of schapbachite (Ag<sub>4</sub>PbBi<sub>4</sub>S<sub>9</sub> = Ag<sub>0.445</sub>Pb<sub>0.11</sub>Bi<sub>0.445</sub>S); however, in the absence of crystallographic data, it is not possible to conclude whether schirmerite is equivalent to schapbachite or corresponds to an ordered dimorph.

## 2. Bournonite isotypic series

### **Bournonite**, CuPbSbS<sub>3</sub>

STR: Edenharter *et al.* (1970).

### **Seligmannite**, CuPbAsS<sub>3</sub>

STR: Edenharter *et al.* (1970).

### **Součekite**, CuPbBi(S, Se)<sub>3</sub>

## 3. Mückeite isotypic series

### **Mückeite**, CuNiBiS<sub>3</sub>

STR: Bente *et al.* (1990). Isolated BiS<sub>3+1</sub> polyhedra.

### **Lapieite**, CuNiSbS<sub>3</sub>

### **Malyshevite**, CuPdBiS<sub>3</sub>

Def.: Chernikov *et al.* (2006).

### **IMA 2007-003**, CuPtBiS<sub>3</sub>

## 4. (Single type)

### **Christite**, HgTlAsS<sub>3</sub>

STR: Brown & Dickson (1976). It is a layered structure where a HgS mono-atomic layer alternates with a di-atomic layer (TlAsS<sub>2</sub>) of the SnS archetype.

## 1.3. Quaternary sulfosalts ( $M1^+M2^+M3^{2+}Pn_2S_5$ )

### *Hatchite isotypes*

#### **Hatchite**, AgTlPbAs<sub>2</sub>S<sub>5</sub>

STR: Marumo & Nowacki (1967a); Boiocchi & Callegari (2003).

#### **Wallisite**, CuTlPbAs<sub>2</sub>S<sub>5</sub>

STR: Takéuchi *et al.* (1968); Boiocchi & Callegari (2003).

## 2. Lead sulfosalts with a pronounced 2D architecture, their derivatives with a composite structure, and related compounds

### 2.1. Layered sulfosalts related to the tetradymite archetype

Tetradymite is the archetype of a complex group of chalcogenides, composed of numerous natural and synthetic compounds, of a great interest in the field of thermoelectrics. All crystal structures are derivatives of a NaCl distorted close packing, generally with trigonal symmetry. Within this group, minerals can be classified according to two complementary homologous series:

- the first homologous series results from the combination of (Bi<sub>2</sub>) layers with tetradymite-type layers (Bi<sub>2</sub>Ch<sub>3</sub>) (Ch = Te, Se, S), giving the general formula **nBi<sub>2</sub>.mBi<sub>2</sub>Ch<sub>3</sub>**;
- the second homologous series ("aleksite series") corresponds to an expansion of the tetradymite layer, related to an incorporation of Pb in specific atom sheets, according to the general formula **Pb<sub>(n-1)</sub>Bi<sub>2</sub>Ch<sub>(n+2)</sub>**;
- an unique case (babkinite) results apparently from the combination of these two trends (see below).

Details concerning the crystal chemistry of minerals of this group, especially complex Pb–Te derivatives, are presented by Cook *et al.* (2007a, 2007b). These Pb derivatives relate to the chemical definition of sulfosalt; but one must point that, in all this group, Bi<sup>3+</sup> ought to present a fairly its octahedral coordination, indicating a weak stereochemical activity of lone electron pair. Within this group are six Pb–Bi sulfosalts, among which five belong to the aleksite homologous series.

*Aleksite homologous series, Pb<sub>(n-1)</sub>Bi<sub>2</sub>Ch<sub>(n+2)</sub>*

**Kochkarite**, PbBi<sub>4</sub>Te<sub>7</sub> ( $c = 72.09 \text{ \AA}$ ) ( $n = 1, 2$ )

STR (synth. –  $c = 23.6 \text{ \AA}$ ): Petrov & Imamov (1970); Shelimova *et al.* (2004). The structure has a regular alternation, along  $c$ , of two layers, the first of which is five atoms thick (Te–Bi–Te–Bi–Te), and the second seven atoms thick (Te–Bi–Te–Pb–Te–Bi–Te). It can thus be modelled as a 1/1 intergrowth of tellurobismuthite Bi<sub>2</sub>Te<sub>3</sub> with rucklidgeite.

Poubaite isotypic pair ( $n = 2$ )

In this series, the  $c$  periodicity corresponds to three seven-atoms-thick layers *Ch–Me–Ch–Me–Ch–Me–Ch*, with the central *Me* atom probably corresponding to Pb, and the two marginal ones to Bi.

**Poubaite**, PbBi<sub>2</sub>(Se,Te,S)<sub>4</sub> ( $c = 40.09 \text{ \AA}$ )

STR (synth. –  $c = 39.20 \text{ \AA}$ ): Agaev & Semiletov (1963). Only a simplified structural model, based on an electron-diffraction study, is available.

**Rucklidgeite**, PbBi<sub>2</sub>Te<sub>4</sub> ( $c = 41.49 \text{ \AA}$ )

STR (synth. –  $c = 41.531 \text{ \AA}$ ): Zhukova & Zaslavskii (1972). The structural model was proposed on the basis of X-ray powder diagrams (especially 00 $l$  reflections).

**Aleksite**, PbBi<sub>2</sub>S<sub>2</sub>Te<sub>2</sub> ( $c = 79.76 \text{ \AA}$ ) ( $n = 2$ )

STR: unknown. The  $c$  periodicity corresponds to (14 × 3) atom layers, and may correspond ideally to the stacking sequence (Te–Bi–S–Pb–S–Bi–Te) ( $Z = 6$ ).

**Saddlebackite**, Pb<sub>2</sub>Bi<sub>2</sub>Te<sub>2</sub>S<sub>3</sub> ( $c = 33.43 \text{ \AA}$ ) ( $n = 3$ )

Def.: Clarke (1997).  $c$  would correspond to an 18-atom sequence.

STR: unknown. Petrov & Imamov (1970) described the crystal structure of Pb<sub>2</sub>Bi<sub>2</sub>Te<sub>5</sub>, with  $c = 17.5 \text{ \AA}$ , and a nine-atoms-thick layer with the sequence –(Te–Pb–Te–Bi–Te–Bi–Te–Pb–Te)–.

*Complex derivative*

**Babkinite**, Pb<sub>2</sub>Bi<sub>2</sub>(S, Se)<sub>3</sub> ( $c = 39.60 \text{ \AA}$ )

Def.: Bryzgalov *et al.* (1996). STR: unknown. The *Me/Ch* ratio is > 1, and the formula is unbalanced, indicating a transitional compound of the subchalcogenide type. It can be modeled as 2Bi<sub>2</sub>.1Bi<sub>2</sub>Ch<sub>3</sub>.6PbCh, and may be the chief-member of a complex homologous series, **nBi<sub>2</sub>.mBi<sub>2</sub>Ch<sub>3</sub>.pPbCh** (Cook *et al.*, 2007b).

*Remarks: 1. Higher or combined members of the aleksite series require detailed X-ray structure determinations. 2. Cannizzarite (see 2.3) is a composite structure with one*

*of the two layers of the tetradymite type. 3. “Platynite”, commonly given as PbBi<sub>2</sub>(Se, S)<sub>7</sub> in the literature, has been discredited (Holstam & Söderhielm, 1999).*

## 2.2. Composite structures from alternating pseudohexagonal and PbS/SnS-like tetragonal layers

### 1. Commensurate structures

Nagyágite homologous series

**Buckhornite**, (Pb<sub>2</sub>BiS<sub>3</sub>)(AuTe<sub>2</sub>) ( $N = 1$ )

STR: Effenberger *et al.* (2000).

**Nagyágite**, [Pb<sub>3</sub>(Pb, Sb)<sub>3</sub>S<sub>6</sub>](Te, Au)<sub>3</sub> ( $N = 2$ )

STR: Effenberger *et al.* (1999).

*Related*

**Museumite**, [Pb<sub>2</sub>(Pb, Sb)<sub>2</sub>S<sub>8</sub>][Te, Au]<sub>2</sub>

Def.: Bindi & Cipriani (2004a).

**Berryite**, Cu<sub>3</sub>Ag<sub>2</sub>Pb<sub>3</sub>Bi<sub>7</sub>S<sub>16</sub>

STR: Topa *et al.* (2006a).

*Tentative assignment to this series*

**Watkinsonite**, Cu<sub>2</sub>PbBi<sub>4</sub>(Se, S)<sub>8</sub>

Def.: Johan *et al.* (1987).

STR: unknown. A structure model was recently proposed by Topa *et al.* (2006a), on the basis of crystallographic similarities with berryite.

### 2. Non-commensurate structures

Type 1: Cylindrite homologous series

*Cylindrite type*

**Cylindrite**, ~ FePb<sub>3</sub>Sn<sub>4</sub>Sb<sub>2</sub>S<sub>14</sub>

STR: Makovicky (1974) and Williams & Hyde (1988) (mean structure).

**Lévyclaudeite**, ~ Cu<sub>3</sub>Pb<sub>8</sub>Sn<sub>7</sub>(Bi, Sb)<sub>3</sub>S<sub>28</sub>

Def.: Moëlo *et al.* (1990).

STR: Evain *et al.* (2006a), for the synthetic Sb-pure isotype (“lévyclaudeite-(Sb)”).

**IMA 2006-016**, Pb<sub>2</sub>SnInBiS<sub>7</sub>

*Franckeite type*

**Franckeite**, ~ Fe(Pb, Sn<sup>2+</sup>)<sub>6</sub>Sn<sub>2</sub><sup>4+</sup>Sb<sub>2</sub>S<sub>14</sub>

STR: Williams & Hyde (1988) and Wang & Kuo (1991) (mean structure).

**“Potosiite”**, ~ FePb<sub>6</sub>Sn<sub>2</sub><sup>4+</sup>Sb<sub>2</sub>S<sub>14</sub>

**“Incaite”**, ~ FePb<sub>4</sub>Sn<sub>2</sub><sup>2+</sup>Sn<sub>2</sub><sup>4+</sup>Sb<sub>2</sub>S<sub>14</sub>

Isotype

**IMA 2005-024**, (Pb, Sn)<sub>12.5</sub>As<sub>3</sub>Sn<sub>5</sub>FeS<sub>28</sub>



**Potosiite and incaite: two varieties of franckeite**

Franckeite has a composite layered structure, with in-plane non-commensurability (Makovicky & Hyde, 1981). One layer “H” is of the CdI<sub>2</sub> type, (Sn, Fe, Sb)<sub>2</sub>S<sub>2</sub>, like in cylindrite (Makovicky, 1974); the second one “Q” is of the SnS/TII type, four atoms thick (twice that of cylindrite): (Pb, Sn, Sb, Fe?)<sub>4</sub>S<sub>4</sub>. Sn is tetravalent in H, divalent in Q, where it substitutes for divalent Pb. The synthetic composite compound [(Pb, Sb)S]<sub>2.28</sub>NbS<sub>2</sub> (Lafond *et al.*, 1997) has the same Q layer as franckeite; here Sb is exclusively in the two central atomic planes of this layer. Wolf *et al.* (1981 – definition of potosiite) and Mozgova *et al.* (1976) pointed out that franckeite is crystallographically similar to potosiite and incaite (defined by Makovicky, 1974 and 1976). On the basis of the crystal-chemical model, potosiite is Sn<sup>2+</sup>-poor franckeite (Makovicky & Hyde, 1992), and incaite is Sn<sup>2+</sup>-rich franckeite, always with Pb > Sn<sup>2+</sup> in natural samples. Thus, potosiite and incaite correspond to varietal compositions in the franckeite solid-solution field (Mozgova *et al.*, 1976) and should be taken off the list of mineral species.

In synthetic samples, Sn/Pb can surpass 1 (up to Pb-free franckeite and cylindrite – Moh, 1987). The discovery of such samples in nature would permit redefinition of incaite as a new mineral species.

Type 2

**Langenbachite**, ~ Cu<sub>2</sub>Ag<sub>4</sub>Pb<sub>18</sub>As<sub>12</sub>S<sub>39</sub>

STR: Williams & Pring (1988) (structural model through HRTEM study).

Crystal chemistry revised by Makovicky *et al.* (1994).

Type 3: Cannizzarite isotypic pair

**Cannizzarite**, ~ Pb<sub>8</sub>Bi<sub>10</sub>S<sub>23</sub>

STR: Matzat (1979).

**Wittite**, ~ Pb<sub>8</sub>Bi<sub>10</sub>(S, Se)<sub>23</sub>

*Remark: “Wittite B” of Large & Mumme (1975) corresponds to proudite (Mumme, 1976).*

**Wittite: original species, or Se-rich cannizzarite?**

Wittite and cannizzarite obey the same crystal-chemical model of composite, non-commensurate structure: a (Pb, Bi)<sub>2</sub>(S, Se)<sub>2</sub> layer “Q” alternating with a (Bi, Pb)<sub>2</sub>(S, Se)<sub>3</sub> layer of the tetradymite type (*i.e.*, a double-octahedral layer). The main difference in the structural formula is the high Se/S ratio of wittite (Mumme, 1980a). This Se/S atomic ratio never exceeds 1, but the tetradymite-type layer is very probably enriched in Se relative to the Q layer (Mozgova *et al.*, 1992). Precise knowledge of the Se partitioning between the two layers is necessary to validate wittite as a species, if Se/S > 1 in the tetradymite-type layer.

On the contrary, if in natural compounds the Se/S atomic ratio is always below 1 in the tetradymite-type layer, wittite would correspond to a Se-rich variety of cannizzarite. The pure Se derivative of cannizzarite has been synthesized recently, and its structure solved (Zhang *et al.*, 2005). This complete Se-for-S substitution enhances the possibility of validating wittite.

**2.3. Commensurate composite derivatives of cannizzarite**

In this group, all structures show an alternation of two types of ribbons or stepped layers resulting from the fragmentation of the two layers comprising the cannizzarite-like structure (one pseudo-quadratic, of the PbS archetype, the other pseudo-hexagonal, of the CdI<sub>2</sub> archetype). Three factors govern structural variations: 1) the thickness of each layer/ribbon; 2) the widths between consecutive planes of slip/shear and the width of their interface (according to a *mQ/nH* ratio); and 3) the spatial offset of ribbons of each type around planes of step (relative to the original layer).

*1. Cannizzarite plesiotypic derivatives*

This sub-group is described by Makovicky (1997).

## (a) Stepped layers

*Homologous pair*

**Junoite**, 3Q, <sup>4</sup>/<sub>2</sub>H – Cu<sub>2</sub>Pb<sub>3</sub>Bi<sub>8</sub>(S, Se)<sub>16</sub>

Def./STR: Mumme (1975a); Large & Mumme (1975).

**Felbortalite**, 3Q, <sup>4</sup>/<sub>2</sub>H – Cu<sub>2</sub>Pb<sub>6</sub>Bi<sub>8</sub>S<sub>19</sub>

Defined by Topa *et al.* (2001).

STR: Topa *et al.* (2000a).

**Nordströmite**, 4Q, <sup>5</sup>/<sub>2</sub>H – CuPb<sub>3</sub>Bi<sub>7</sub>(S, Se)<sub>14</sub>

STR: Mumme (1980b).

**Proudite**, 8Q, <sup>9</sup>/<sub>2</sub>H – Cu<sub>2</sub>Pb<sub>16</sub>Bi<sub>20</sub>(S, Se)<sub>47</sub>

Def./STR: Mumme (1976, and unpublished new revision). First description as “wittite B” in Large & Mumme (1975).

## (b) Sheared layers (chessboard type)

**Galenobismutite**, <sup>1</sup>/<sub>2</sub>Q, <sup>1</sup>/<sub>2</sub>H – PbBi<sub>2</sub>S<sub>4</sub>

STR: Iitaka & Nowacki (1962); Wulf (1990).

**Angelaite**, Cu<sub>2</sub>AgPbBiS<sub>4</sub>

(Remark: The *Me/S* ratio is > 1)

Def.: Brodtkorb & Paar (2004); (Topa *et al.*, in prep.).

STR: Topa *et al.* (2004 – abstract). It is a homeotype of galenobismutite.

**Nuffieldite**, 1Q, <sup>2</sup>/<sub>2</sub>H – Cu<sub>1.4</sub>Pb<sub>2.4</sub>Bi<sub>2.4</sub>Sb<sub>0.2</sub>S<sub>7</sub>

Redefinition: Moëlo (1989).

STR: Moëlo *et al.* (1997). The general structural formula is Cu<sub>1+x</sub>Pb<sub>2+x</sub>Bi<sub>3-x-y</sub>Sb<sub>y</sub>S<sub>7</sub>.

**Weibullite**, 6Q, <sup>7</sup>/<sub>2</sub>H – Ag<sub>0.33</sub>Pb<sub>5.33</sub>Bi<sub>8.33</sub>(S, Se)<sub>18</sub>

STR: Mumme (1980c).

*2. Boxwork derivatives of cannizzarite*

This boxwork type results from a combination of three types of building blocks. There are two types of ribbons (slab fragments) alternating to form complex slabs. These slabs are separated by a layer or ribbon-layer (here three atoms in thickness), giving the final boxwork architecture. One type of ribbons in the complex slabs and the latter layer (both with surfaces of pseudotetragonal character) form a boxwork system of partitions; the remaining type of fragments fills the boxes.

**Neyite**, 7Q, <sup>9</sup>/<sub>2</sub>H – Cu<sub>6</sub>Ag<sub>2</sub>Pb<sub>25</sub>Bi<sub>26</sub>S<sub>68</sub>

STR: Makovicky *et al.* (2001a).

**Rouxelite**, 5Q, <sup>7</sup>/<sub>2</sub>H – Cu<sub>2</sub>HgPb<sub>22</sub>Sb<sub>28</sub>S<sub>64</sub>(O, S)<sub>2</sub>

Def./STR: Orlandi *et al.* (2005).

*Remark: Complex Pb/Sb oxy-(chloro)-sulfosalts (scainite, pillaitite and pellouxite) belonging to the zinkenite pleiotypic series can also be described by a similar boxwork architecture.*

### 3. Lead sulfosalts based on large 2D fragments of PbS/SnS archetype

#### 3.1. Lillianite homologous series (PbS archetype)

The definition and crystal chemistry of this homologous series were presented by Makovicky (1977), and Makovicky & Karup-Møller (1977a, 1977b). Additional data were given in Makovicky & Balić-Žunić (1993). All structures are based on PbS-like slabs of various thickness (number  $N$  of octahedra). Each homologue type is symbolized as  $NL$ , or as  $N^1.N^2L$  (when there are two slabs of distinct thickness).

##### 1. Lillianite homeotypic series ( $^4L$ )

*Bi-rich members*

**Lillianite**,  $Ag_xPb_{3-2x}Bi_{2+x}S_6$

STR: Takagi & Takéuchi (1972); Ohsumi *et al.* (1984).

**Gustavite**,  $AgPbBi_3S_6$

STR (synth.): Bente *et al.* (1993).

*Sb-rich members*

General formula:  $Ag_xPb_{3-2x}Sb_{2+x}S_6$  ( $And_n$ :  $n = 100 \cdot x$ )

**Andorite VI\***,  $AgPbSb_3S_6$  ( $And_{100}$ )

\*Named “senandorite” by Moëlo *et al.* (1984a).

STR: Sawada *et al.* (1987).

**Nakaséite**,  $\sim (Ag_{0.93}Cu_{0.13})_{\Sigma=1.06}Pb_{0.88}Sb_{3.06}S_6$   
( $\sim And_{106}$ )

**Andorite IV\***,  $Ag_{15}Pb_{18}Sb_{47}S_96$  ( $And_{93.75}$ )

\*Named “quatrandorite” by Moëlo *et al.* (1984a).

**Ramdohrite**,  $(Cd, Mn, Fe)Ag_{5.5}Pb_{12}Sb_{21.5}S_{48}$  ( $And_{68.75}$ )

STR: Makovicky & Mumme (1983).

**Fizélyite**,  $Ag_5Pb_{14}Sb_{21}S_{48}$  ( $And_{62.5}$ )

**Uchucchacuaite**,  $MnAgPb_3Sb_5S_{12}$  ( $And_{50}$ )

**Roshchinite**,  $(Ag, Cu)_{19}Pb_{10}Sb_{51}S_{96}$  ( $And_{118.75}$ )

Def.: Spiridonov *et al.* (1990).

STR: Petrova *et al.* (1986).

*Lillianite dimorph ( $^4L$ )*

**Xilingolite**,  $Pb_3Bi_2S_6$

STR: Berlepsch *et al.* (2001a). In comparison with lillianite, the cations in the crystal structure are ordered in a monoclinic fashion.

*Doubtful*

“**Bursaite**”,  $Pb_{3-3x}Bi_{2+2x}S_6$  (?)

#### Andorites IV and VI: two distinct species

These two minerals have distinct symmetry, with very close but distinct chemistry, without solid solution, as they are frequently observed in close epitaxial intergrowth (Moëlo *et al.*, 1984a, 1989). Thus they correspond to two homeotypic species, with distinct superstructures ( $4c$  and  $6c$ , respectively) and not to two

polytypic forms of the same species. The study of Sawada *et al.* (1987) solved the true ( $6c$ ) crystal structure of andorite VI (or “senandorite”).

#### Nakaséite: a variety of andorite VI

Nakaséite, defined by Ito & Muraoka (1960) as a Cu-rich derivative of andorite with a superstructure of  $(c \times 24)$ , was considered by Fleischer (1960) to be a polytypic variety of andorite (andorite XXIV). A later detailed examination of minerals of the andorite–fizélyite series (Moëlo *et al.*, 1989) confirmed that nakaséite is an oversubstituted, Cu-rich ( $\sim 1$  wt.%) variety of andorite VI, with a formula close to  $(Ag_{0.93}Cu_{0.13})_{\Sigma=1.06}Pb_{0.88}Sb_{3.06}S_6$ .

#### Ramdohrite: species, or variety of fizélyite?

Ramdohrite from the type deposit has a significant Cd content (Moëlo *et al.*, 1989) and is compositionally close to fizélyite (ideally  $And_{68.75}$  and  $And_{62.5}$ , respectively), but it is not known if there is a solid solution (ramdohrite = Cd-rich variety of fizélyite?) or an immiscibility gap (ramdohrite = specific species?). Fizélyite from Kisbánya (Romania) shows exsolutions of a (Mn, Fe)-rich variety of ramdohrite; such exsolutions correspond to a specific species (same study). A crystal-structure study of fizélyite from the type deposit is necessary to confirm the distinction between these two species.

#### “Bursaite”

Bursaite from the type deposit corresponds to Ag-poor lillianite (Makovicky & Karup-Møller, 1977b). A new occurrence (Shumilovskoe, West Transbaikal) studied by Mozgova *et al.* (1988) was found by X-ray powder and electron-microdiffraction data to be an intergrowth of two lillianite-related phases, each with a distinct unit cell. The electron-microprobe composition, which represents a composite from the two phases, indicates a Pb deficit ( $N \sim 3.83$ ). Bursaite would correspond to the Pb-poor phase, with cation vacancies.

( $^4L$ ) homologue

**Vikingite**,  $Ag_5Pb_8Bi_{13}S_{30}$

STR: Makovicky *et al.* (1992).

( $^4L$ ) homologue

**Treasurite**,  $Ag_7Pb_6Bi_{15}S_{30}$

*Remark: Borodaevite (see 3.2) may correspond to a homeotypic derivative of treasuresite (Ilinca & Makovicky, 1997).*

##### 2. Heyrovskýite homeotypic series ( $^7L$ )

*Orthorhombic, disordered (with minor Ag)*

**Heyrovskýite**,  $Pb_6Bi_2S_9$

STR: Otto & Strunz (1968 – synth.); Takéuchi & Takagi (1974). The structure of an (Ag, Bi)-rich derivative was solved by Makovicky *et al.* (1991). Its structural formula is  $Pb_{3.36}Ag_{1.32}Bi_{3.32}S_9$ , and one of the cation sites has major Ag (s.o.f.  $\sim 0.657$ ), that could justify (Ag, Bi)-rich heyrovskýite as a specific mineral species.

*Homeotype (monoclinic, ordered)*

**Aschamalmite**,  $Pb_{6-3x}Bi_{2+x}S_9$

STR: Mumme *et al.* (1983).

Related ( $^{5,9}L$  dimorph)

**Eskimoite**,  $\text{Ag}_7\text{Pb}_{10}\text{Bi}_{15}\text{S}_{36}$

### 3. Ourayite homeotypic pair ( $^{11,11}L$ )

**Ourayite** (*B*-centered),  $\text{Ag}_3\text{Pb}_4\text{Bi}_5\text{S}_{13}$

**Ourayite-P** (primitive unit cell),  $\sim \text{Ag}_{3,6}\text{Pb}_{2,8}\text{Bi}_{5,6}\text{S}_{13}$  (empirical formula)

### 4. Disordered phase

**“Schirmerite” (Type 2)**,  $\text{Ag}_3\text{Pb}_3\text{Bi}_9\text{S}_{18}$  to  $\text{Ag}_3\text{Pb}_6\text{Bi}_7\text{S}_{18}$

### 5. Related?

**Ustarasite**,  $\text{Pb}(\text{Bi}, \text{Sb})_6\text{S}_{10}$

#### Ourayite and ourayite-P: close, but distinct species

An exsolution pair of major ourayite with minor ourayite-*P* has been described by Makovicky & Karup-Møller (1984). Ourayite-*P*, poorer in Pb than ourayite, is clearly a distinct species (probably an ordering variant of ourayite), but it needs further data that include an exact chemical formula and crystal structure.

#### Schirmerite: two “schirmerites”, and two questions

Reexamination of schirmerite (Type 2) from the type deposit (Karup-Møller, 1977; Makovicky & Karup-Møller, 1977b) proved it to be a disordered intergrowth of different proportions of slabs  $^4L$  and  $^7L$ , with a composition between those of gustavite and (Ag, Bi)-rich heyrovskýite. Such a disordered intergrowth is not a valid species.

On the other hand, in another deposit, Bortnikov *et al.* (1987) discovered a new phase (Type 1 – see schapbachite) with the original composition of schirmerite (that is, strictly in the  $\text{AgBiS}_2$ – $\text{PbS}$  pseudo-binary system).

#### Ustarasite: needs unit-cell data

Ustarasite was defined by Sakharova (1955) on the basis of chemical analysis and X-ray powder data. The mineral is compositionally close to synthetic Phase V of Otto & Strunz (1968), which is  $\sim \text{PbBi}_4\text{S}_7$  (lillianite–pavonite super-family). Unit-cell data are needed to validate ustarasite.

## 3.2. Pavonite homologous series

The pavonite homologous series was defined by Makovicky *et al.* (1977) ( $^N P$  = homologue number), and additional structural data were presented by Mumme (1990).

**Grumiplucite**,  $\text{HgBi}_2\text{S}_4$  ( $^3 P$ )

Def.: Orlandi *et al.* (1998).

STR (synth.): Mumme & Watts (1980).

**Kudriavite**,  $(\text{Cd}, \text{Pb})\text{Bi}_2\text{S}_4$  ( $^3 P$ )

Def.: Chaplygin *et al.* (2005).

STR: Balić-Žunić & Makovicky (2007). About 1/10 Bi is substituted by In.

**Makovickyite**,  $\text{Cu}_{1,12}\text{Ag}_{0,81}\text{Pb}_{0,27}\text{Bi}_{5,35}\text{S}_9$  ( $^4 P$ )

Def.: Žák *et al.* (1994).

STR: Mumme (1990); Topa *et al.* (2007).

Homeotype

**Cupromakovickyite**,  $\text{Cu}_4\text{AgPb}_2\text{Bi}_9\text{S}_{18}$  ( $^4 P$ )

Def.: (Topa & Paar, accept.).

The name of this new species was first given in the definition paper of kupčikite (Topa *et al.*, 2003a).

STR: Topa *et al.* (2007).

**Pavonite**,  $\text{AgBi}_3\text{S}_5$  ( $^5 P$ )

STR (synth.): Makovicky *et al.* (1977).

Homeotype

**Cupropavonite**,  $\text{Cu}_{0,9}\text{Ag}_{0,5}\text{Pb}_{0,6}\text{Bi}_{2,5}\text{S}_5$  ( $^5 P$ )

**Benjaminite**,  $\text{Ag}_3\text{Bi}_7\text{S}_{12}$  ( $^7 P$ )

STR: Makovicky & Mumme (1979).

**Mummeite**,  $\text{Cu}_{0,58}\text{Ag}_{3,11}\text{Pb}_{1,10}\text{Bi}_{6,65}\text{S}_{13}$  ( $^8 P$ )

Def.: Karup-Møller & Makovicky (1992).

STR: Mumme (1990).

**Borodaevite**,  $\text{Ag}_{4,83}\text{Fe}_{0,21}\text{Pb}_{0,45}(\text{Bi}, \text{Sb})_{8,84}\text{S}_{16}$  ( $^{11} P$ )

Def.: Nenasheva *et al.* (1992), who considered this species as  $^{12} P$ . Borodaevite is questionable as a pavonite homologue (see *treasurite* (3.1.1) – Iinca & Makovicky, 1997).

IMA 2005-036,  $\text{Cu}_8\text{Ag}_3\text{Pb}_4\text{Bi}_{19}\text{S}_{38}$

Derivatives

**Mozgovaite**,  $\text{PbBi}_4(\text{S}, \text{Se})_7$

Def.: Vurro *et al.* (1999). According to the unit-cell parameter (with  $b = 37.4 \text{ \AA}$ , derived from powder data), this mineral probably corresponds to synthetic Phase V2 (Takéuchi, 1997), giving the ideal formula  $\text{Pb}_{3,19}\nabla_{0,27}\text{Bi}_{12,54}\text{S}_{22}$  ( $\nabla$  = cationic vacancy). The structure would be a composite of lillianite- and pavonite-type layers ( $m^2 P + n^2 L$ ).

**Livingstonite**,  $\text{HgSb}_4\text{S}_6(\text{S}_2)$

STR: Srikrishnan & Nowacki (1975). It is a composite structure formed of two rod-layers, one of which is equivalent to a component of the rod-layer structure of grumiplucite. Homeotype of  $^2 P$ .

## 3.3. Cuprobismutite homologous series

A general review of this series is given by Topa *et al.* (2003b).

**Kupčikite**,  $\text{Cu}_{3,4}\text{Fe}_{0,6}\text{Bi}_5\text{S}_{10}$  (Type 1,1,1)

Definition and STR: Topa *et al.* (2003a).

**Hodrushite**,  $\text{Cu}_8\text{Bi}_{12}\text{S}_{22}$  (Type 1, 2, 1, 2)

STR: Topa *et al.* (2003b). It explains chemical shifts relative to the ideal formula given here, analogous to those in kupčikite and cuprobismutite.

**Cuprobismutite**,  $\text{Cu}_8\text{AgBi}_{13}\text{S}_{24}$  (Type 2, 2, 2)

STR: Topa *et al.* (2003b).

Related:

**Pizgrischite**,  $(\text{Cu}, \text{Fe})\text{Cu}_{14}\text{PbBi}_{17}\text{S}_{34}$

Definition and STR: Meisser *et al.* (2007).

It is further twinning of a kupčikite-like structure.



*Related (unit-cell-intergrowth derivative of kupčikite)*

**Paděraite**,  $\text{Cu}_7[(\text{Cu}, \text{Ag})_{0.33}\text{Pb}_{1.33}\text{Bi}_{11.33}]_{\Sigma 13}\text{S}_{22}$   
STR: Mumme (1986); Topa & Makovicky (2006).

### 3.4. Meneghinite homologous series (SnS archetype)

This series, defined by Makovicky (1985a), was reexamined by Berlepsch *et al.* (2001b). It also includes the aikinite–bismuthinite homeotypic series ( $N = 2$ ), placed in section 4.5 of the present report.

**Meneghinite**,  $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$  ( $N = 5$ )

STR: Euler & Hellner (1960). Moëlo *et al.* (2002) for a Cu-poor variety.

**Jaskolskiite**,  $\text{Cu}_x\text{Pb}_{2+x}(\text{Sb}, \text{Bi})_{2-x}\text{S}_5$  ( $x$  close to 0.2) ( $N = 4$ )

STR: Makovicky & Nørrestam (1985).

### 3.5. Jordanite homologous series

1. *Jordanite isotypic pair* ( $N = 4$ )

**Jordanite**,  $\text{Pb}_{14}(\text{As}, \text{Sb})_6\text{S}_{23}$

STR: Ito & Nowacki (1974b).

**Geocronite**,  $\text{Pb}_{14}(\text{Sb}, \text{As})_6\text{S}_{23}$

STR: Birnie & Burnham (1976).

There is a continuous solid solution between jordanite and geocronite. In nature, geocronite always contains some As, but the pure Sb member has been synthesized (Jambor, 1968).

2. *Kirkiite homologue* ( $N = 3$ )

**Kirkiite**,  $\text{Pb}_{10}\text{Bi}_3\text{As}_3\text{S}_{19}$

STR: Makovicky *et al.* (2006a).

3. *Related?*

**Tsugaruite**,  $\text{Pb}_4\text{As}_2\text{S}_7$

Def.: Shimizu *et al.* (1998).

The crystal structure of tsugaruite is unknown, but is probably complex as is indicated by the large unit cell ( $V = 4678 \text{ \AA}^3$ ).

### 3.6. (Single type) PbS hexagonal derivative

**Gratonite**,  $\text{Pb}_9\text{As}_4\text{S}_{15}$

STR: Ribár & Nowacki (1969).

### 3.7. Plagionite homologous series

The crystal chemistry of this homologous series was characterised by Kohatsu & Wuensch (1974), and was reexamined by Takéuchi (1997). General formula:  $\text{Pb}(\text{Pb}_N\text{Sb}_4)_2\text{S}_{13+2N}$  ( $N = 1$  to 4).

**Fülöppite**,  $\text{Pb}_3\text{Sb}_8\text{S}_{15}$  ( $N = 1$ )

STR: Nuffield (1975), and Edenharter & Nowacki (1975).

**Plagionite**,  $\text{Pb}_5\text{Sb}_8\text{S}_{17}$  ( $N = 2$ )

STR: Cho & Wuensch (1974).

**Heteromorphite**,  $\text{Pb}_7\text{Sb}_8\text{S}_{19}$  ( $N = 3$ )

STR: Edenharter (1980).

*Semseyite isotypic pair* ( $N = 4$ )

**Semseyite**,  $\text{Pb}_9\text{Sb}_8\text{S}_{21}$

STR: Kohatsu & Wuensch (1974); Matsushita *et al.* (1997).

**Rayite**,  $(\text{Ag}, \text{Tl})_2\text{Pb}_8\text{Sb}_8\text{S}_{21}$

#### Rayite: true unit cell?

Rayite (Basu *et al.*, 1983) was related to semseyite on the basis of the powder diagram, but this choice was disputed by Roy Choudury *et al.* (1989), who could only synthesize (Ag, Tl)-rich boulangerite with a composition close to that of rayite. This result was confirmed by Bente & Meier-Salimi (1991). Rayite needs a single-crystal study (X-ray or electron diffraction) of the type sample to confirm the unit cell and the relationship of rayite to the plagionite series.

### 3.8. Sartorite homologous series

General building principles for structures of this series were described by Le Bihan (1962); the homologous series itself was defined by Makovicky (1985a) and was completed by Berlepsch *et al.* (2001c). Only two types of homologous slabs are known ( $N = 3$  or 4), and each homologue type corresponds to a regular stacking of these slabs.

1. *Sartorite homeotypes* ( $N = 3$ )

**Sartorite**,  $\text{PbAs}_2\text{S}_4$  (or  $\text{Pb}_{1+2x}\text{As}_{2-2x}\text{S}_{4-x}$ ?)

STR (subcell): Nowacki *et al.* (1961); Iitaka & Nowacki (1961).

**Sartorite-9c**,  $\text{Tl}_{1.5}\text{Pb}_8\text{As}_{17.5}\text{S}_{35}$

STR: Berlepsch *et al.* (2003).

**Twinnite**,  $\text{Pb}(\text{Sb}_{0.63}\text{As}_{0.37})_2\text{S}_4$

**Guettardite**,  $\text{Pb}_8(\text{Sb}_{0.56}\text{As}_{0.44})_{16}\text{S}_{32}$

2. *Baumhauerite homeotypes* ( $N = 3, 4, 3, 4$ )

**Baumhauerite**,  $\text{Pb}_{12}\text{As}_{16}\text{S}_{36}$

**Baumhauerite-2a**,  $\sim \text{Ag}_{1.5}\text{Pb}_{22}\text{As}_{33.5}\text{S}_{72}$

Def.: Pring *et al.* (1990). Remark: The proposed chemical formula, which with a  $2a$  periodicity is  $\text{Ag}_{1.4}\text{Pb}_{22}(\text{As}, \text{Sb})_{35.2}\text{S}_{72}$ , is not charge balanced. A simplified formula is proposed above on the basis of EPMA by Laroussi *et al.* (1989).

STR: according to Laroussi *et al.* (1989), the crystal structure of “baumhauerite” published by Engel & Nowacki (1969) corresponds to baumhauerite-2a, and not to baumhauerite.

**Baumhauerite- $\psi$ O3abc**,  $\text{Ag}_3\text{Pb}_{38.1}(\text{As}, \text{Sb})_{52.8}\text{S}_{96}$

Def.: Pring & Graeser (1994).

3. *Homologue*  $N = 4, 3, 4$

**Liveingite**,  $\text{Pb}_{20}\text{As}_{24}\text{S}_{56}$

STR: Engel & Nowacki (1970) (“Rathit II”).



#### 4. *Dufrénoysite* homeotypes ( $N = 4$ )

**Dufrénoysite**,  $\text{Pb}_2\text{As}_2\text{S}_5$

STR: Marumo & Nowacki (1967b).

**Veenite**,  $\text{Pb}_2(\text{Sb}, \text{As})_2\text{S}_5$

**Rathite**,  $\text{Ag}_2\text{Pb}_{12-x}\text{Tl}_{x/2}\text{As}_{18+x/2}\text{S}_{40}$

STR: Marumo & Nowacki (1965); Berlepsch *et al.* (2002). The developed structural formula is  $\text{Pb}_8\text{Pb}_{4-x}(\text{Tl}_2\text{As}_2)_x(\text{Ag}_2\text{As}_2)\text{As}_{16}\text{S}_{40}$ .

#### 5. *Homologues with long-range periodicity*

**Marumoite** (IMA 1998-004),  $\text{Pb}_{32}\text{As}_{40}\text{S}_{92}$

This mineral species was approved by the CNMNC, but the description has not as yet been published. Preliminary data were given by Ozawa & Takéuchi (1983). The composition and unit-cell parameters indicate that the mineral belongs to the sartorite series. The long periodicity (115 Å) corresponds to  $2 \times (4, 3, 4, 3, 4)$  stacking sequences. Recently, the name marumoite was used in the study of another occurrence of the mineral (Shimizu *et al.*, 2005).

**Rathite-IV** (unknown formula)

This **rathite-IV** (Ozawa & Nowacki, 1974) is the re-named **rathite-V** of Nowacki *et al.* (1964); its periodicity of 138 Å corresponds to the stacking sequence (4, 3, 4, 3, 4, 4, 3, 4, 3, 4, 3, 4) (see Berlepsch *et al.*, 2003). The mineral is an insufficiently described homologue, more complicated and quantitatively different from liveingite. The chemical composition is unknown; without additional cations, the stacking sequence would give the formula  $\text{Pb}_{19}\text{As}_{24}\text{S}_{55}$ .

#### 6. *Unit-cell-intergrowth derivative of dufrénoysite*

**Chabournéite**,  $\text{Tl}_5(\text{Sb}, \text{As})_{21}\text{S}_{34}$

Def.: Mantiene (1974); Johan *et al.* (1981).

STR: Nagl (1979).

The structural formula proposed by Nagl (1979) for a  $b/2$  subcell is  $\text{Tl}_8\text{Pb}_4\text{Sb}_{21}\text{As}_{19}\text{S}_{68}$ . This formula is questioned by Johan *et al.* (1981), who proposed the formula  $\text{Tl}_{21}(\text{Sb}, \text{As})_{91}\text{S}_{147}$  for the unit cell of the Pb-free member, but this formula shows clearly a S excess, incompatible with the modular organisation of the crystal structure. According to the substitution  $\text{Tl}^+ + (\text{Sb}, \text{As})^{3+} \rightarrow 2\text{Pb}^{2+}$ , demonstrated by Johan *et al.* (1981), the general simplified formula is  $\text{Tl}_{5-x}\text{Pb}_{2x}(\text{Sb}, \text{As})_{21-x}\text{S}_{34}$ . The Pb-free pole ( $x = 0$ ) corresponds to  $\text{Tl}_5(\text{Sb}, \text{As})_{21}\text{S}_{34}$ , while the Pb-rich composition studied by Nagl ( $x \sim 1$ ) is close to  $\text{Tl}_4\text{Pb}_2(\text{Sb}, \text{As})_{20}\text{S}_{34}$ .

#### 7. *Pierrotite* homeotypic pair ( $N = 3, 3$ )

**Pierrotite**,  $\text{Tl}_2(\text{Sb}, \text{As})_{10}\text{S}_{16}$  (ortho.)

STR: Engel *et al.* (1983).

**Parapierrotite**,  $\text{TlSb}_5\text{S}_8$  (monocl.)

STR (synth.): Engel (1980).

#### **Sartorite: chemical formula?**

The crystal chemistry of sartorite is very complex, and has been recently reviewed by Berlepsch *et al.* (2003). Various supercells and non-commensurate superstructures seem common (Pring *et al.*, 1993). According to Berlepsch *et al.* (2003) different chemical and crystallographic varieties of sartorite ought to be considered as polytypoids, and not as distinct mineral species.

The classic stoichiometric formula,  $\text{PbAs}_2\text{S}_4$ , is doubtful, and has never been encountered in modern EPMA. There is always some Tl, which is up to 6.4 wt.% in sartorite-9c, whose structural formula is  $\text{Tl}_{1.5}\text{Pb}_8\text{As}_{17.5}\text{S}_{35}$ . A Tl-poor variety ("Mineral A" of Laroussi *et al.*, 1989) is close to  $\text{Tl}_{0.02}\text{Pb}_{1.11}\text{As}_{1.87}\text{S}_{3.96}$  ( $\Sigma_{\text{cations}} = 3$  at.), but its crystal structure is unknown. Tentatively, Tl-free sartorite may correspond to the formula  $\text{Pb}_{1+2x}\text{As}_{2-2x}\text{S}_{4-x}$ , with  $x$  close to 0.07.

#### **Twinnite and guettardite: one or two species?**

Twinnite and guettardite, defined by Jambor (1967b), and re-analyzed by Jambor *et al.* (1982), are very close, chemically and structurally. Original twinnite has a slightly higher Sb/As ratio than guettardite ( $\sim 1.7$  against  $\sim 1.3$ , respectively), but this ratio may reach 3.1 (Moëlo *et al.*, 1983). Guettardite is defined as a monoclinic dimorph of twinnite, but Z. Johan (unpublished – see Mantiene, 1974), on the basis of the examination of twinnite from another deposit, considered twinnite and guettardite as identical. Reexamination of the type samples, including structure data, would be necessary to understand the exact structural relationships.

#### **Baumhauerite varieties: polytypes or homeotypes?**

Baumhauerite-2a and baumhauerite- $\psi O3abc$  were considered by Pring & Graeser (1994) as polytypes of baumhauerite, but they differ chemically because of the presence of Ag. Thus, it seems better to consider them as homeotypes. Whereas baumhauerite-2a is a well-defined species, approved by the IMA-CNMNC, the validation of baumhauerite- $\psi O3abc$  would need a crystal-structure study.

Baumhauerite II of Rösch & Hellner (1959) was first obtained by hydrothermal synthesis, and was subsequently recognized by those authors in a natural sample. Pring & Graeser (1994) considered baumhauerite II as identical to baumhauerite-2a. However, baumhauerite II does not contain Ag. See also Pring (2001).

#### **Rathite varieties**

Numerous rathite varieties from the deposit of Lengenbach, Switzerland, have been described. A critical review of these rathites has been given by Makovicky (1985a), and, more recently, by Berlepsch *et al.* (2002), through the reexamination of the crystal structure of rathite. According to these authors and some previous works, the following is concluded:

- " **$\alpha$ -Rathite**" = rathite;
- "**Rathite-I**" = rathite or dufrénoysite;
- "**Rathite-1a**" = dufrénoysite;
- "**Rathite II**" is liveingite (Nowacki, 1967);
- "**Rathite III**" is most probably a misidentified compound;
- "**Rathite-IV**" (of Nowacki *et al.*, 1964) = sartorite.

### 3.9. Unclassified

**Mutnovskite**,  $\text{Pb}_2\text{AsS}_3(\text{I}, \text{Cl}, \text{Br})$

Def./STR: Zelenski *et al.* (2006).

The crystal structure of this halogeno-sulfosalt is very specific, with a layered organisation, but there is no clear relationship with any other Pb sulfosalt.

## 4. Sulfosalts based on 1D derivatives of PbS/SnS archetype, *i.e.*, on rod-type building blocks

A general review of this vast group of Pb sulfosalts and related synthetic compounds has been presented by Makovicky (1993). The main geometric factors that are used for the description and comparison of the various crystal structures and their hierarchy are:

- the size of the rod component(s);
- the number of different rod-types coexisting in a structure (generally only one; exceptionally up to four);
- their general organisation, giving principally the “rod-layer”, “cyclic” and “chessboard” sub-types.

### 4.1. Rod-layer sub-type (boulangerite plesiotypic family)

**Cosalite**,  $\text{Pb}_2\text{Bi}_2\text{S}_5$

STR: Srikrishnan & Nowacki (1974).

**Falkmanite**,  $\text{Pb}_3\text{Sb}_2\text{S}_6$  (or  $\text{Pb}_{5.4}\text{Sb}_{3.6}\text{S}_{10.8}?$ )

Redefinition: Mozgova *et al.* (1983).

**Boulangerite**,  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$

STR: Mumme (1989).

**Plumosite**,  $\text{Pb}_2\text{Sb}_2\text{S}_5$

Redefinition: Mozgova *et al.* (1984).

**Moëloite**,  $\text{Pb}_6\text{Sb}_6\text{S}_{14}(\text{S}_3)$

Definition & STR: Orlandi *et al.* (2002).

**Dadsonite**,  $\text{Pb}_{23}\text{Sb}_{25}\text{S}_{60}\text{Cl}$

STR: Makovicky & Mumme (1984 – abstract); Makovicky *et al.* (2006b).

**Robinsonite**,  $\text{Pb}_4\text{Sb}_6\text{S}_{13}$

STR: Skowron & Brown (1990 – synth.); Franzini *et al.* (1992); Makovicky *et al.* (2004).

#### *Jamesonite isotypic series*

**Jamesonite**,  $\text{FePb}_4\text{Sb}_6\text{S}_{14}$

STR: Niizeki & Buerger (1957); Léone *et al.* (2003); Matsushita & Ueda (2003 – synth.)

**Benavidesite**,  $\text{MnPb}_4\text{Sb}_6\text{S}_{14}$

STR: Léone *et al.* (2003 – synth.).

**Sakharovaite**,  $\text{FePb}_4(\text{Sb}, \text{Bi})_6\text{S}_{14}$

Def.: Kostov (1959).

#### **Sakharovaite: species, or jamesonite variety?**

In sakharovaite, the Bi-for-Sb substitution is close to the 50 % at. limit, but does not clearly exceed it (Sakharova, 1955; Kostov, 1959; Borodaev & Mozgova, 1975). Thus, unless there is strong partitioning in the substitution of Bi among the three Sb positions in the jamesonite crystal structure (see below for

the example of garavellite), sakharovaite is a Bi-rich variety of jamesonite. Confirmation of sakharovaite needs a crystal-structure study.

#### **Parajamesonite: reexamination of a specimen from the type deposit (Herja, Romania)**

Parajamesonite was defined by Zsivny & Naray-Szabo (1947) as a dimorph of jamesonite, with a distinct X-ray powder diagram. The unit cell was not determined, but the elongate crystals were reported to be up to 8 mm long and 2.8 mm wide, and would have easily permitted a single-crystal study. It was thought that the type sample was destroyed by fire during the conflict in Budapest in 1956, but rediscovery of the original samples studied by Zsivny permitted the discreditation (Papp, 2004; Papp *et al.*, 2007).

#### **Falkmanite: crystal structure relative to that of boulangerite?**

The validity of falkmanite was questioned for a long time. Re-examination of falkmanite from the type locality led Mozgova *et al.* (1983) to suggest its close relationship with boulangerite but with a higher Pb/Sb ratio and a different degree of structural ordering. McQueen (1987) studied a second occurrence of falkmanite, with a chemical composition very close to the ideal one,  $\text{Pb}_3\text{Sb}_2\text{S}_6$ , and with crystal data (X-ray powder pattern; unit cell) almost identical to those of boulangerite. Without cation excess, its formula could be  $\text{Pb}_{5.4}\text{Sb}_{3.6}\text{S}_{10.8}$ . A solution of the crystal structure of falkmanite is necessary for its definite classification.

#### **Plumosite: a specific, but incompletely defined mineral species**

Many old museum samples labelled “plumosite”,  $\text{Pb}_2\text{Sb}_2\text{S}_5$ , correspond to various Pb–Sb sulfosalts with a hair-like habit. Mozgova & Bortnikov (1980) identified a plumosite-type phase,  $\sim \text{Pb}_2\text{Sb}_2\text{S}_5$ , in symplectitic association with boulangerite. Later, Mozgova *et al.* (1984) and Vrublevskaya *et al.* (1985) described another occurrence of plumosite as lamellar exsolutions in boulangerite, with the same sub-cell, but with a distinct true unit cell. Like falkmanite, plumosite is considered as a homologous derivative of boulangerite (the term “homeotype” seems more appropriate). Mumme (1989) pointed out similarities between plumosite and jaskolskiite. Crystal-structure data are needed to classify this species.

#### *Berthierite isotypic series*

**Berthierite**,  $\text{FeSb}_2\text{S}_4$

STR: Lemoine *et al.* (1991).

**Garavellite**,  $\text{FeSbBiS}_4$

Def.: Gregorio *et al.* (1979).

STR: Bindi & Menchetti (2005).

**Clerite**,  $\text{MnSb}_2\text{S}_4$

Def.: Murzin *et al.* (1996).

STR (synth.): Bente & Edenharter (1989).

*Remark: A synthetic monoclinic dimorph of clerite is known; its crystal structure (Pfitzner & Kurowski, 2000) is isotypic with that of grumiplucite (Part III, § 3.2). Unnamed  $\text{MnSb}_2\text{S}_4$  described by Harris (1989) in the Hemlo*

gold deposit (Ontario) may correspond to this monoclinic dimorph.

#### Garavellite: a definite species

The recent study by Bindi & Menchetti (2005) of a new occurrence of garavellite has proved that Sb and Bi atoms, despite their close crystal-chemical affinity, are positioned on distinct sites in the crystal structure. As a consequence, garavellite is clearly a definite mineral species, and not a Bi-rich variety of berthierite. This aspect is considered for the discussion of the validity of sakharovaite.

## 4.2. “Cyclic” sub-type and chessboard derivatives (zinkenite family)

The fundamentals of the crystal chemistry of this family have been defined by Makovicky (1985b).

### 1. Zinkenite plesiotypic series (cyclic rod-type)

#### Zinkenite, $Pb_9Sb_{22}S_{42}$

STR: Portheine & Nowacki (1975b).

#### Pillaite, $Pb_9Sb_{10}S_{23}ClO_{0.5}$

Def.: Orlandi *et al.* (2001).

STR: Meerschaut *et al.* (2001).

*Remark: An iodine derivative of pillaite was recently synthesized (Kryukowa et al., 2005).*

#### Scainiite, $Pb_{14}Sb_{30}S_{54}O_5$

Def.: Orlandi *et al.* (1999).

STR: Moëlo *et al.* (2000).

#### Marrucciite, $Hg_3Pb_{16}Sb_{18}S_{46}$

Definition and STR: Orlandi *et al.* (2007); STR: Laufek *et al.* (2007).

#### Pellouxite, $(Cu, Ag)_2Pb_{21}Sb_{23}S_{55}ClO$

Def.: Orlandi *et al.* (2004).

STR: Palvadeau *et al.* (2004).

#### Vurroite, $Sn_2Pb_{20}(Bi, As)_{22}S_{54}Cl_6$

Def.: Garavelli *et al.* (2005).

STR: Pinto *et al.* (2004 – abstract; accept.).

#### Owyheeite, $Ag_3Pb_{10}Sb_{11}S_{28}$

The chemistry of owyheeite was reexamined by Moëlo *et al.* (1984b), giving the general structural formula:  $Ag_{3+x}Pb_{10-2x}Sb_{11+x}S_{28}$  ( $-0.13 < x < +0.20$ ).

STR: Laufek *et al.* (2007). The proposed structural formula,  $Ag_{1.5}Pb_{4.43}Sb_{6.07}S_{14}$ , is outside the compositional field established by Moëlo *et al.* (1984b).

*Remark: Pillaite, scainiite and pellouxite can also be described according to a “boxwork” principle (see neyite and rouxelite in Sect. 2.3).*

### 2. Chessboard derivatives (kobellite plesiotypic series)

#### Kobellite homologous series

The crystal chemistry of this series has been defined by Zakrzewski & Makovicky (1986) and Makovicky & Mumme (1986), and a general chemical formula was proposed by Moëlo *et al.* (1995).

*Kobellite isotypic pair*

#### Kobellite, $(Cu, Fe)_2Pb_{11}(Bi, Sb)_{15}S_{35}$

STR: Miede (1971).

#### Tintinaite, $Cu_2Pb_{10}Sb_{16}S_{35}$

The composition was redefined by Moëlo *et al.* (1984c).

#### Giessenite homeotypic pair

#### Giessenite, $(Cu, Fe)_2Pb_{26.4}(Bi, Sb)_{19.6}S_{57}$

#### Izoklakeite, $(Cu, Fe)_2Pb_{26.4}(Sb, Bi)_{19.6}S_{57}$

STR: Makovicky & Mumme (1986); Armbruster & Hummel (1987), for a Bi-rich variety.

#### Giessenite and izoklakeite: from monoclinic to orthorhombic symmetry with increasing Sb content

There is apparently a quasi-continuous solid solution from giessenite to izoklakeite with increasing Sb/Bi ratio, which is nevertheless always  $< 1$  except for izoklakeite of the type locality ( $\sim 1.04$ ). The main difference is that the monoclinic symmetry of giessenite (Bi-rich) changes to orthorhombic in izoklakeite (Sb-rich) (Makovicky & Karup-Møller, 1986). The exact Sb/Bi ratio at which the symmetry changes is unknown.

#### Related

#### Eclarite, $(Cu, Fe)Pb_9Bi_{12}S_{28}$

Def.: Paar *et al.* (1983).

STR: Kupčik (1984).

### 3. Related?

#### Zoubekite, $AgPb_4Sb_4S_{10}$

#### Zoubekite: needs single-crystal study

Zoubekite, defined by Megarskaya *et al.* (1986), was approved by the IMA-CNMNC, although the unit cell was calculated solely on the basis of a powder diagram with only six lines above 2.00 Å. Zoubekite is compositionally close to owyheeite; X-ray single-crystal study is needed to prove that the two are distinct species.

## 4.3. Aikinite–bismuthinite homeotypic series

This family constitutes the most complex and didactic series of homeotypes among the sulfosalts. The first sulfosalt member, aikinite, was defined by Chapman (1843), and the fundamental work of Johansson (1924) permitted definition of the series on the basis of the new descriptions of gladite, lindströmite and hammarite. Since the end of the 1960s, numerous papers have brought new chemical, crystallographic and crystal-structure data, and very recent works have presented a relatively advanced overview of this series.

Besides the end-member bismuthinite, there are ten homeotypic sulfosalt species. Three members, the two end-members bismuthinite ( $Bi_4S_6 = b$ ) and aikinite ( $Cu_2Pb_2Bi_2S_6 = a$ ), and the median one krupkaite ( $CuPbBi_3S_6 = k$ ), permit definition of structural formulae of the eight other members by a simple combination of *b* or *a* with *k*. This also leads to the idealized classical formulae given below.



Nevertheless, careful examination of various samples indicates that chemical shifts from the ideal compositions (Mozgova *et al.*, 1990) are common because of Cu over- or undersubstitution (Topa *et al.*, 2002b), or because of the presence of very fine exsolution or intergrowth textures (Topa *et al.*, 2002a) that extend to the nanometer scale (Pring & Hyde, 1987). As a consequence, it is dangerous to assign specific mineral names (the end-members excepted) on the basis of EPMA data alone, and the best way is to use a chemical notation, as proposed by Makovicky & Makovicky (1978), indicating the “aikinite substitution percentage”,  $n_{aik}$ , equal to  $[2Pb/(Pb + Bi)] \times 100$ . For instance, ideal hammarite,  $Cu_2Pb_2Bi_4S_9$ , corresponds to  $n_{aik} = 67$ .

*Remark: This homeotypic series is also the lowest known homologue of the meneghinite homologous series (see Part 3, Sect. 4).*

In the following list, the idealized substitution percentage is followed by the observed analytical values (in italics), when different. All species probably have narrow solid-solution fields (see for instance krupkaite and gladite – Topa *et al.*, 2002b), but the fields are difficult to delimit, all the more because they may vary with crystallization temperature.

- Aikinite**,  $CuPbBiS_3$  ( $a = Cu_2Pb_2Bi_2S_6 - n_{aik}$ : 100)  
STR: Ohmasa & Nowacki (1970).
- Friedrichite**,  $Cu_5Pb_5Bi_7S_{18}$  ( $2a + k - n_{aik}$ : 83; 80)  
Def.: Chen *et al.* (1978).  
STR: unknown.
- Hammarite**,  $Cu_2Pb_2Bi_4S_9$  ( $a + 2k - n_{aik}$ : 67; 68)  
STR: Horiuchi & Wuensch (1976).
- Emilite**,  $Cu_{10.7}Pb_{10.7}Bi_{21.3}S_{48}$  ( $a + 3k - n_{aik}$ : 63; 67)  
Def.: Topa *et al.* (2006b).  
STR: Balić-Žunić *et al.* (2002).
- Lindströmite**,  $Cu_3Pb_3Bi_7S_{15}$  ( $a + 4k - n_{aik}$ : 60)  
STR: Horiuchi & Wuensch (1977).
- Krupkaite**,  $CuPbBi_3S_6$  ( $k - n_{aik}$ : 50; 49 to 50 ?)  
STR: Mumme (1975b), and Syneček & Hybler (1975).
- Paarite**,  $Cu_{1.7}Pb_{1.7}Bi_{6.3}S_{12}$  ( $b + 4k - n_{aik}$ : 40; 42)  
Def.: Topa *et al.* (2005).  
STR: Makovicky *et al.* (2001b).
- Salzburgite**,  $Cu_{1.6}Pb_{1.6}Bi_{6.4}S_{12}$  ( $b + 3k - n_{aik}$ : 38; 41)  
Def.: Topa *et al.* (2005).  
STR: Topa *et al.* (2000b).
- Gladite**,  $CuPbBi_5S_9$  ( $b + 2k - n_{aik}$ : 33; below 33, up to 38)  
STR: Syneček & Hybler (1975), Kohatsu & Wuensch (1976), Topa *et al.* (2002b).
- Pekoite**,  $CuPbBi_{11}S_{18}$  ( $2b + k - n_{aik}$ : 17)  
STR: Mumme & Watts (1976).
- Bismuthinite**,  $Bi_2S_3$  ( $b = Bi_4S_6 - n_{aik}$ : 0)  
Ciobanu & Cook (2000) detected by ore microscopy and EPMA two new Bi-rich minerals, “Phase 70”, close to  $CuPbBi_7S_{12}$  ( $n_{aik} = 25$ ), and “Phase 88.6”, close to  $Cu_{0.33}Pb_{0.33}Bi_{7.67}S_{12}$  ( $n_{aik} = 8$ ), which could correspond to new homeotypes between gladite and pekoite (type “ $b + k$ ”?), and between pekoite and bismuthinite (type “ $5b + k$ ”?), respectively. Similar suggestions, with  $n_{aik} \sim 22$  and

27, appear in Topa *et al.* (2002b). All of these possible minerals need further study.

#### 4.4. Related sulfosalts?

The crystal structures of following species are unknown, which does not permit their classification among the groups within Sect. 4 (or in Sects. 2 or 3).

**Ardaite**,  $Pb_{17}Sb_{15}S_{35}Cl_9$   
Def.: Breskovska *et al.* (1982).

**Launayite**,  $CuPb_{10}(Sb, As)_{13}S_{30}$

**Madocite**,  $Pb_{19}(Sb, As)_{16}S_{43}$

**Playfairite**,  $Pb_{16}(Sb, As)_{19}S_{44}Cl$

**Sorbyite**,  $CuPb_9(Sb, As)_{11}S_{26}$

**Sterryite**,  $(Ag, Cu)_2Pb_{10}(Sb, As)_{12}S_{29}$

These five species have been defined in the same deposit of Madoc, Ontario (Jambor, 1967a, 1967b).

**IMA 2007-010**,  $PbHgAs_2S_6$

Considering As only at the trivalent state would indicate a S excess (“persulfosalts”?).

### 5. Specific Tl(Pb) and Hg sulfosalts: structures with SnS layers (with or without additional layers)

A first overview of the systematics of Tl sulfosalts has been presented by Balić-Žunić (1989).

#### 5.1. Hutchinsonite merotypic series

The general outline of this series is given in Makovicky (1997 – Table 5). The series consists principally of Tl sulfosalts and related compounds (natural or synthetic) with large monovalent cations ( $Na^+$ ,  $(NH_4)^+$ ,  $Cs^+$ ). All structures are based on the combination of two types of layers, one of which corresponds to an  $(010)_{SnS}$  slab of variable width (with the exception of gerstleyite, derived from the PbS archetype).

##### 1. Hutchinsonite–bernardite homologous pair

**Hutchinsonite**,  $TlPbAs_5S_9$

STR: Takéuchi *et al.* (1965); Matsushita & Takéuchi (1994).

**Bernardite**,  $TlAs_5S_8$

Definition and STR: Pasava *et al.* (1989).

##### 2. Edenharterite–jentschite pair

A detailed structural comparison of edenharterite and jentschite was given by Berlepsch *et al.* (2000).

**Edenharterite**,  $TlPbAs_3S_6$

Def.: Graeser & Schwander (1992).

STR: Balić-Žunić & Engel (1983 – synth.); Berlepsch (1996).

**Jentschite**,  $TlPbAs_2SbS_6$

Def.: Graeser & Edenharter (1997).

STR: Berlepsch (1996).



### 3. Other members

#### **Imhofite**, $\text{Ti}_{5.8}\text{As}_{15.4}\text{S}_{26}$

STR: Divjakovic & Nowacki (1976); Balić-Žunić & Makovicky (1993).

#### **Gillulyite**, $\text{Ti}_2\text{As}_{7.5}\text{Sb}_{0.3}\text{S}_{13}$

Def.: Wilson *et al.* (1991).

STR: Foit *et al.* (1995); Makovicky & Balić-Žunić (1999).

### 4. PbS archetype

#### **Gerstleyite**, $\text{Na}_2(\text{Sb}, \text{As})_8\text{S}_{13} \cdot 2\text{H}_2\text{O}$

STR: Nakai & Appleman (1981).

### 5.2. Rebulite plesiotypic pair

A comparative modular analysis of the crystal structures of rebulite and jankovičite has been presented by Makovicky & Balić-Žunić (1998).

#### **Rebulite**, $\text{Ti}_5\text{As}_8\text{Sb}_5\text{S}_{22}$

Def.: a complete description required for a definition is lacking.

STR: Balić-Žunić *et al.* (1982).

#### **Jankovičite**, $\text{Ti}_5\text{Sb}_9(\text{As}, \text{Sb})_4\text{S}_{22}$

Def.: Cvetkovic *et al.* (1995).

STR: Libowitzky *et al.* (1995).

### 5.3. Single type: sicherite

#### **Sicherite**, $\text{Ag}_2\text{Ti}(\text{As}, \text{Sb})_3\text{S}_6$

Definition and STR: Graeser *et al.* (2001).

### 5.4. Unclassified

#### **Erniggliite**, $\text{SnTi}_2\text{As}_2\text{S}_6$

Definition and STR: Graeser *et al.* (1992).

#### **Vrbaite**, $\text{Hg}_3\text{Ti}_4\text{As}_8\text{Sb}_2\text{S}_{20}$

STR: Ohmasa & Nowacki (1971).

#### **Simonite**, $\text{HgTiAs}_3\text{S}_6$

Def.: a complete description required for a definition is lacking.

STR: Engel *et al.* (1982).

#### **Vaughanite**, $\text{HgTiSb}_4\text{S}_7$

Def.: Harris *et al.* (1989).

#### **Gabrielite**, $\text{Cu}_2\text{AgTi}_2\text{As}_3\text{S}_7$

Def.: Graeser *et al.* (2006).

STR: Balić-Žunić *et al.* (2006). A 3-slab structure, with one of the layers related to cyclic sulfosalts.

#### **Rebulite: needs a mineralogical description**

Rebulite was defined on the basis of its crystal-structure study (Balić-Žunić *et al.*, 1982), but without a proposal submitted to the IMA-CNMNC. A complete mineralogical description is needed.

#### **Simonite: needs a mineralogical description**

Like rebulite, simonite is known only by its crystal-structure study (Engel *et al.*, 1982). It has been approved by the IMA-CNMNC, but a mineralogical description is lacking.

## 6. Sulfosalts with an excess of small (univalent) cations (Ag, Cu) relative to (As, Sb, Bi)

In the majority of these sulfosalts the ratio  $(\Sigma Me)/S$  is  $> 1$ ; however, in the presence of divalent metals (Zn, Hg, Fe), the ratio may equal 1 (galkhaite, laffittite, routhierite and stalderite).

### 6.1. Cu(Ag)-rich sulfosalts

#### 1. Wittichenite homeotypic pair

##### **Wittichenite**, $\text{Cu}_3\text{BiS}_3$

STR: Kocman & Nuffield (1973).

##### **Skinnerite**, $\text{Cu}_3\text{SbS}_3$

STR: Makovicky & Balić-Žunić (1995).

#### 2. Tetrahedrite isotypic series

Among sulfosalts, this is the most complex isotypic series, because of the multiplicity of iso- and heterovalent substitutions. Numerous crystal-structure studies have been performed since the early ones of Machatschki (1928) and Pauling & Neuman (1934). The simplified general formula is  $A_6(B, C)_6X_4Y_{12}Z$ , where  $A$  is Cu or Ag in triangular coordination,  $B$  is Cu or Ag in tetrahedral coordination,  $C$  is generally a divalent metal (typically Fe or Zn, but also Hg, Mn, Cd...) in the same tetrahedral coordination,  $X$  is Sb, As, Bi or Te in trigonal pyramidal coordination,  $Y$  is S or Se in tetrahedral coordination, and  $Z$  is S or Se in a special octahedral coordination. The presence of vacancies or interstitial atoms (*e.g.*, Cu), or heterovalent substitutions due to the incorporation of  $\text{Fe}^{3+}$  or  $\text{Te}^{4+}$ , have been confirmed by structural studies.

In tetrahedrite–tennantite, the amount of divalent metals is limited to 2 a.p.f.u. but, especially in synthetic samples, it may vary between 0 and 2, indicating the variable presence of (formal)  $\text{Cu}^{2+}$ .

There are seven well-defined species, but various data (EPMA, experimental studies, Mössbauer spectroscopy, X-ray) indicate that the crystal chemistry of this series is complex, and individual problems can require highly specialized research methods. As a consequence, limits between mineral species (for instance freibergite or goldfieldite relative to tetrahedrite) are still questionable.

Structural formulae presented below are simplified to ideal ones as much as possible (for instance, the  $B/C$  ratio is equal to  $4/2$ , and  $C$  is restricted generally to Fe and Zn). In other cases, the formula of the type sample is also given (for very rare species).

##### **Tetrahedrite**, $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{Sb}_4\text{S}_{13}$

STR: Wuensch (1964); Peterson & Miller (1986); Makovicky & Skinner (1979) and Pfitzner *et al.* (1997) for Cu-pure synthetic varieties,  $\text{Cu}_{12+x}\text{Sb}_4\text{S}_{13}$ .

##### **Tennantite**, $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{S}_{13}$

STR: Wuensch *et al.* (1966); Makovicky *et al.* (2005) for a Cu-rich unsubstituted composition,  $\text{Cu}_{12.5}\text{As}_4\text{S}_{13}$ .

##### **Freibergite**, $\text{Ag}_6[\text{Cu}_4\text{Fe}_2]\text{Sb}_4\text{S}_{13-x} (?)$

STR: Rozhdestvenskaya *et al.* (1993).

##### **Argentotennantite**, $\text{Ag}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{S}_{13}$

Type sample (Spiridonov *et al.*, 1986a):

$(\text{Ag}_{5.67}\text{Cu}_{4.48})_{\Sigma=10.15}(\text{Zn}_{1.52}\text{Fe}_{0.37})_{\Sigma=1.89}(\text{As}_{2.14}\text{Sb}_{1.89})_{\Sigma 4.03}\text{S}_{12.90}$

**Argentotetrahedrite**,  $\text{Ag}_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$

Formula according to Zhdanov *et al.* (1992):  $\text{Ag}_{10.9}(\text{Fe}, \text{Zn}, \text{Hg})_{1.9}(\text{Sb}_{3.9}\text{As}_{0.1})_{4.0}\text{S}_{12.2}$ .

**Goldfieldite**,  $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$

Relative to this ideal end-member, charge-balanced with  $\text{Cu}^+$  and  $\text{Te}^{4+}$ , natural compositions of goldfieldite with decreasing Te content agree with the two complementary formulae (see comments below):

- (1)  $\text{Cu}_{12-x}[\text{Te}_{2+x}(\text{Sb}, \text{As}, \text{Bi})_{2-x}]\text{S}_{13}$  ( $2 > x > 0$ ), and
- (2)  $\text{Cu}_{10+y}(\text{Fe}, \text{Zn}\dots)_{2-y}[\text{Te}_y(\text{Sb}, \text{As}, \text{Bi})_{4-y}]\text{S}_{13}$  ( $y < 2$ , and  $\text{Te} > \text{Sb}, \text{As}, \text{Bi}$ ).

Numerous EPMA data are given by Kovalenker & Rusinov (1986).

STR: Kalbskopf (1974), on the synthetic, pure Te end-member; Dmitrieva & Bojik (1988).

**Hakite**,  $\text{Cu}_6[\text{Cu}_4\text{Hg}_2]\text{Sb}_4\text{Se}_{13}$

Type sample (Johan & Kvaccek, 1971):

$(\text{Cu}_{10.2}\text{Hg}_{1.8})_{\Sigma 12}(\text{Sb}_{3.1}\text{As}_{1.0})_{\Sigma 4.1}(\text{Se}_{10.4}\text{S}_{2.6})_{\Sigma 13.0}$

**Giraudite**,  $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{Se}_{13}$

Type sample (Johan *et al.*, 1982):

$(\text{Cu}_{10.6}\text{Ag}_{0.3}\text{Zn}_{1.0}\text{Hg}_{0.1})_{\Sigma 12}(\text{As}, \text{Sb})_4(\text{Se}, \text{S})_{13}$

In giraudite (formal)  $\text{Cu}^{2+}$  is present.

“**Annivite**”,  $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2](\text{Bi}, \text{Sb}, \text{As})_4\text{S}_{13}$ .

### Related

**Galkhaite**,  $(\text{Cs}, \text{Tl}, \nabla)(\text{Hg}, \text{Cu}, \text{Zn}, \text{Tl})_6(\text{As}, \text{Sb})_4\text{S}_{12}$

This mineral species was initially defined as  $\text{HgAsS}_2$  by Gruzdev *et al.* (1972). The structural role of Tl was determined by Divjakovic & Nowacki (1975), but Chen & Szymański (1981, 1982) subsequently proved that Cs always exceeds Tl.

STR: Divjakovic & Nowacki (1975); Chen & Szymański (1981).

### Freibergite

The status of freibergite as a valid species is still discussed. The Ag-for-Cu substitution induces a regular increase of the parameter *a*, as exemplified by the tennantite–argentotennantite complete solid solution; this solid solution has been also observed to occur between tetrahedrite and its pure Ag derivative, argentotetrahedrite. However, when the Ag content is more than about 23 wt.% (~ 4 a.p.f.u.), an abnormal trend of decreasing *a* has been observed (Riley, 1974; Samusikov *et al.*, 1988; Balitskaya *et al.*, 1989). The decrease has been explained by Rozhdestvenskaya *et al.* (1993) as follows. In the metal site with planar triangular coordination, Cu is mainly or completely substituted by Ag. At the same time, the special S position (Z) with octahedral coordination is progressively emptied, thereby permitting the formation of  $\text{Ag}_6$  octahedral metallic clusters. For the highest Ag content, the crystal structural formula is:  $^{[3]}\text{Ag}_6^{[4]}\text{Cu}_{4.44}(\text{Fe}, \text{Zn})_{1.56}^{[3]}\text{Sb}_4^{[3]}\text{S}_{12}^{[6]}\text{S}_{0.09}$ .

Thus, this abnormal trend may be considered as belonging to a specific species, freibergite, which is distinct from Ag-rich tetrahedrite (improperly called “freibergite”). For the time being, the structural formula of this freibergite trend may be idea-

lised as:  $(\text{Ag}_{4+2x}\text{Cu}_{2-2x})[(\text{Cu}, \text{Ag})_4(\text{Fe}, \text{Zn})_2]_{\Sigma 6}\text{Sb}_4\text{S}_{12}\text{S}_{1-x}$  ( $0 < x < 1$ ). Varieties with Ag below 4 a.p.f.u. should be called Ag-rich tetrahedrite. The problem definitely needs further study.

### Argentotetrahedrite

This name was proposed by Spiridonov *et al.* (1986b) for a Sb-rich derivative of argentotennantite, on the basis of EPMA, but without X-ray data. Later, Zhdanov *et al.* (1992) analysed an Ag end-member without Cu, and gave the unit cell as 10.92 Å, but without submitting a formal proposal to the CNMNC. These data validate the existence in the tetrahedrite series of a mineral species with ideal formula  $\text{Ag}_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$ , in accordance with the experimental data of Patrick & Hall (1983). A (re)definition through a proposal to the CNMNC is highly desirable, with more complete data (X-ray powder pattern; reflectance data).

### Goldfieldite nomenclature

In goldfieldite  $\text{Te}^{4+}$  substitutes for  $\text{Sb}^{3+}$  in the tetrahedrite structure. For compositions with up to 2 Te a.p.f.u., the valence balance is maintained by an equivalent substitution of the divalent metals (Fe, Zn...) by monovalent Cu, as in structural formula (2) above. When Te is > 2 a.p.f.u., there are no more divalent metals; hence, the excess of Te above 2 at. is balanced by an equal number of vacancies among Cu sites that have three-fold coordination (structural formula (1) above). In these two consecutive solid-solution fields, the name goldfieldite is to be used when Te is predominant over each of Sb, As and Bi. Conversely, if for instance Te is minor together with major Sb, one has Te-rich tetrahedrite, and not goldfieldite.

### “Annivite”: potential revalidation

“Annivite” from the type deposit of Einfisch or Anniviers valley (Wallis, Switzerland) corresponds to a Bi-rich (~ 5 wt.%) variety of tennantite, according to the original analysis of Fellenberg (1854). On the basis of a total of 16 cations, its structural formula is  $(\text{Cu}_{9.93}\text{Fe}_{1.22}\text{Zn}_{0.55})_{\Sigma=11.70}(\text{As}_{2.60}\text{Sb}_{1.28}\text{Bi}_{0.42})_{\Sigma=4.30}\text{S}_{13.15}$ . Since this time, microprobe analyses have revealed in some deposits compositions in which the Bi atom concentration exceeds those of Sb or As (Kieft & Eriksson, 1984; Bortnikov *et al.*, 1979; Spiridonov *et al.*, 1986a). X-ray data from one of these occurrences could permit the validation of annivite as the Bi pole relatively to tetrahedrite and tennantite.

### 3. Nowackiite isotypic series

**Nowackiite**,  $\text{Cu}_6\text{Zn}_3\text{As}_4\text{S}_{12}$

STR: Marumo (1967).

**Aktashite**,  $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$

STR: Kaplunnik *et al.* (1980).

**Gruzdevite**,  $\text{Cu}_6\text{Hg}_3\text{Sb}_4\text{S}_{12}$

### Related

**Sinnerite**,  $\text{Cu}_6\text{As}_4\text{S}_9$

STR: Makovicky & Skinner (1975).

**Watanabeite**,  $\text{Cu}_4(\text{As}, \text{Sb})_2\text{S}_5$

Def.: Shimizu *et al.* (1993).

**Laffittite**,  $\text{AgHgAsS}_3$

STR: Nakai & Appleman (1983).

#### 4. *Routhierite isotypic pair*

**Routhierite**,  $\text{CuHg}_2\text{TlAs}_2\text{S}_6$   
**Stalderite**,  $\text{Cu}(\text{Zn}, \text{Fe}, \text{Hg})_2\text{TlAs}_2\text{S}_6$   
 Definition and STR: Graeser *et al.* (1995).

##### **Routhierite: new structural formula**

The formula of routhierite (Johan *et al.*, 1974) was revised by Graeser *et al.* (1995), together with the definition of stalderite: routhierite is the Hg isotype of stalderite (Zn-rich end-member).

#### 5. *Unclassified Cu sulfosalts*

**Miharaite**,  $\text{Cu}_4\text{FePbBiS}_6$   
 STR: Petrova *et al.* (1988).  
*Isotypic pair*  
**Petrovicite**,  $\text{Cu}_3\text{HgPbBiSe}_5$   
**Mazzettiite**,  $\text{Ag}_3\text{HgPbSbTe}_5$   
 Def.: Bindi & Cipriani (2004b).  
**Chaméanite**,  $(\text{Cu}, \text{Fe})_4\text{As}(\text{Se}, \text{S})_4$   
 Def.: Johan *et al.* (1982).  
**Mgriite**,  $(\text{Cu}, \text{Fe})_3\text{AsSe}_3$   
 Def.: Dymkov *et al.* (1982).  
**Larosite**,  $(\text{Cu}, \text{Ag})_{21}\text{PbBiS}_{13}$   
**Arcubisite**,  $\text{CuAg}_6\text{BiS}_4$

##### **Chaméanite and mgriite: the same species?**

Chaméanite (Johan *et al.*, 1982) and mgriite (Dymkov *et al.*, 1982) have very similar chemical compositions and X-ray powder diagrams; the *a* parameter of chaméanite is twice that of mgriite. They probably are the same species; in this case, chaméanite (IMA 1980-088) would have priority relatively to mgriite (IMA 1980-100), but reexamination of the type samples is needed.

In the Cu–As–Se ternary system (Cohen *et al.*, 1995), there are only two ternary phases,  $\text{CuAsSe}_2$  and  $\text{Cu}_3\text{AsSe}_4$ . According to Golovej *et al.* (1985),  $\text{Cu}_3\text{AsSe}_4$  has the same unit cell as mgriite (5.530 Å; chaméanite:  $5.519 \times 2$ ), and its crystal structure is given. Thus, the discrepancy between Cu/As/Se ratios of these three close compounds is difficult to explain.

### 6.2. Ag-rich sulfosalts

#### 1. (Single type)

**Samsonite**,  $\text{MnAg}_4\text{Sb}_2\text{S}_6$   
 STR: Edenharter & Nowacki (1974); Bindi & Evain (2007).

#### 2. *Pyrargyrite family*

*Pyrargyrite isotypic pair*

**Pyrargyrite**,  $\text{Ag}_3\text{SbS}_3$

**Proustite**,  $\text{Ag}_3\text{AsS}_3$

STR: the two structures were refined by Engel & Nowacki (1966).

*Related*

**Ellisite**,  $\text{Tl}_3\text{AsS}_3$

STR: Gostojic (1980 – synth.).

#### 3. *Pyrostilpnite isotypic pair*

**Pyrostilpnite**,  $\text{Ag}_3\text{SbS}_3$

STR: Kutoglu (1968).

**Xanthoconite**,  $\text{Ag}_3\text{AsS}_3$

STR: Engel & Nowacki (1968); Rosenstingl & Pertlik (1993).

#### 4. *Polybasite isotypic series*

The nomenclature of this series has now been clarified through the resolution of the crystal structures of various polytypes. Details are given by Bindi *et al.* (2007a).

**Polybasite**,  $\text{Cu}(\text{Ag}, \text{Cu})_6\text{Ag}_9\text{Sb}_2\text{S}_{11}$

STR: Evain *et al.* (2006b). The structural formula is  $[\text{Ag}_9\text{CuS}_4][(\text{Ag}, \text{Cu})_6(\text{Sb}, \text{As})_2\text{S}_7]$ .

**Pearceite**,  $\text{Cu}(\text{Ag}, \text{Cu})_6\text{Ag}_9\text{As}_2\text{S}_{11}$

STR: Bindi *et al.* (2006). The structural formula is  $[\text{Ag}_9\text{CuS}_4][(\text{Ag}, \text{Cu})_6(\text{As}, \text{Sb})_2\text{S}_7]$ .

Correspondence between old mineral names and related unit-cell types and new polytype nomenclature is given in Table 5.

**Selenopolybasite**,  $\text{Cu}(\text{Ag}, \text{Cu})_6\text{Ag}_9\text{Sb}_2(\text{S}, \text{Se})_9\text{Se}_2$

Def.: Bindi *et al.* (accept.). It is the Se-rich analogue of the polytype polybasite-*Tac*.

STR: Evain *et al.* (2006c). The structural formula is:  $[(\text{Ag}, \text{Cu})_6(\text{Sb}, \text{As})_2(\text{S}, \text{Se})_7][\text{Ag}_9\text{Cu}(\text{S}, \text{Se})_2\text{Se}_2]$ .

#### 5. *Stephanite isotypic pair*

**Stephanite**,  $\text{Ag}_5\text{SbS}_4$

STR: Ribár & Nowacki (1970).

**Selenostephanite**,  $\text{Ag}_5\text{Sb}(\text{Se}, \text{S})_4$

*Related?*

**Fettelite**,  $\text{Ag}_{24}\text{HgAs}_5\text{S}_{20}$

Def.: Wang & Paniagua (1996).

STR: abstract by Pérez-Priede *et al.* (2005), who indicate similarities with laffittite although in this species the (Ag, Hg)/Pn/S ratio is quite distinct, and is identical to that of stephanite (5/1/4).

#### 6. *Unclassified Ag sulfosalts*

**Benleonardite**,  $\text{Ag}_8(\text{Sb}, \text{As})\text{Te}_2\text{S}_3$

**Tsnigriite**,  $\text{Ag}_9\text{Sb}(\text{S}, \text{Se})_3\text{Te}_3$

Def.: Sandomirskaya *et al.* (1992). May be related to the argyrodite group.

**Dervillite**,  $\text{Ag}_2\text{AsS}_2$

Redefinition: Bari *et al.* (1983).

##### **Dervillite: As–As bonding? (subsulfosalt)**

As in tvalchrelidzeite (see below), the redefinition of dervillite (Bari *et al.*, 1983) indicates a sulfur deficit that may correspond to As–As bonding, as in realgar. A crystal-structure determination is needed.

### 7. Unclassified sulfosalts

#### 7.1. Oxysulfosalts

**Sarabauite**,  $\text{Sb}_4\text{S}_6 \cdot \text{CaSb}_6\text{O}_{10}$

Table 5. Polytype nomenclature in the polybasite-pearceite series (Bindi *et al.*, 2007a).

| Name                       | As/Sb ratio | Unit-cell | Old name         | Structure                   |
|----------------------------|-------------|-----------|------------------|-----------------------------|
| Pearceite- <i>Tac</i>      | As > Sb     | Type 111  | Pearceite        | Bindi <i>et al.</i> (2006)  |
| Pearceite- <i>T2ac</i>     | As > Sb     | Type 221  | Arsenopolybasite | Bindi <i>et al.</i> (2007b) |
| Pearceite- <i>M2a2b2c</i>  | As > Sb     | Type 222  | Arsenopolybasite | – – –                       |
| Polybasite- <i>Tac</i>     | Sb > As     | Type 111  | Antimonpearceite | – – –                       |
| Polybasite- <i>T2ac</i>    | Sb > As     | Type 221  | Polybasite       | Evain <i>et al.</i> (2006b) |
| Polybasite- <i>M2a2b2c</i> | Sb > As     | Type 222  | Polybasite       | – – –                       |

STR: Nakai *et al.* (1978).

**Cetineite**,  $\sim \text{NaK}_5\text{Sb}_{14}\text{S}_6\text{O}_{18}(\text{H}_2\text{O})_6$

STR: Sabelli *et al.* (1988).

*Isotype*:

**Ottensite**,  $\text{Na}_3(\text{Sb}_2\text{O}_3)_3(\text{SbS}_3)\cdot 3\text{H}_2\text{O}$

Def.: Sejkora & Hysrl (2007).

## 7.2. “Subsulfosalts”

**Tvalchrelidzeite**,  $\text{Hg}_3\text{SbAsS}_3$

STR: Yang *et al.* (2007).

**Criddleite**,  $\text{Ag}_2\text{Au}_3\text{TlSb}_{10}\text{S}_{10}$

**Jonassonite**,  $\text{Au}(\text{Bi}, \text{Pb})_5\text{S}_4$

Def.: Paar *et al.* (2006). There are two varieties of jonassonite. One variety, including that from the type deposit (Nagybörzsöny, Hungary) is Pb-rich (between 5 and 8 wt.%); the second one, which is more common, is Pb-free. Without crystal-structure data, one cannot say if the incorporation of Pb just corresponds to a solid solution, or if it induces structural changes.

### Sulfosalts, or not?

All these three minerals show a strong sulfur deficiency (“subsulfides”), indicating that As, Sb or Bi may also act as an anion (see also dervillite). Crystal-structure studies are needed to answer this question and to confirm that these minerals conform to the extended definition of a sulfosalt.

## 7.3. PGE sulfosalts?

**Borovskite**,  $\text{Pd}_3\text{SbTe}_4$

**Crerarite**,  $(\text{Pt}, \text{Pb})\text{Bi}_3(\text{S}, \text{Se})_{4-x}$

Def.: Cook *et al.* (1994).

Crystal-structure data are necessary to ascertain whether these minerals are sulfosalts.

## 8. Conclusion

This re-examination of sulfosalt systematics indicates that today there are more than 220 valid mineral species (see the alphabetical index). Together with the regular discovery of new species, as exemplified by the annual reports of the IMA-CNMNC and previous CNMMN, the progress in crystal-structure study will play a critical role for the resolution of some questions of systematics still in abeyance. More than 50 crystal structures remain unsolved, among which about half probably correspond to new structure types.

In addition to the sulfosalt minerals listed in this report, the published literature contains reports of about 200 unnamed minerals that can probably be regarded as sulfosalts, with compositions significantly different from those of known sulfosalt minerals. Data on these minerals are included in a report by the Sub-Committee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification (Smith & Nickel, 2007).

The still-outstanding questions of systematics encountered in this report are summarized below. The questions mainly concern the status of about twenty species. As a complement, the final appendix is an extract of discredited names of sulfosalt species.

### 1. Valid minerals without specific published definitions

- Approved by the IMA-CNMNC, but unpublished: marumoite (IMA 1998-004);
- approved by the IMA-CNMNC, but only the crystal structure has been published: simonite (IMA 1982-052) (Engel *et al.*, 1982);
- without approval of the IMA-CNMNC, with publication of only the crystal structure: rebulite (Balić-Žunić *et al.*, 1982).

### 2. Identical, or distinct species?

- Fizélyite – ramdohrite pair;
- twinnite – guettardite pair;
- chaméanite – mgriite pair.

### 3. “Sulfosalt limbo”

#### 3.1. Ill-defined or still questionable mineral species

- Falkmanite ( $\text{Pb}_3\text{Sb}_2\text{S}_6$ ) and plumosite ( $\text{Pb}_2\text{Sb}_2\text{S}_5$ ): relationship with boulangerite?
- Sakharovaite [ $\text{FePb}_4(\text{Sb}, \text{Bi})_6\text{S}_{14}$ ]: species, or Bi-rich jamesonite?
- Ustarasite [ $\text{Pb}(\text{Bi}, \text{Sb})_6\text{S}_{10}$ ]: no unit-cell determination.
- Wittite [ $\text{Pb}_8\text{Bi}_{10}(\text{S}, \text{Se})_{23}$ ]: species, or Se-rich variety of cannizzarite?
- Zoubekite ( $\text{AgPb}_4\text{Sb}_4\text{S}_{10}$ ): doubtful unit-cell data.

#### 3.2. Possible definition or redefinition as valid species

- Annivite [ $\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2](\text{Bi}, \text{Sb}, \text{As})_4\text{S}_{13}$ ]: possible revalidation for Bi > Sb, As (unit-cell data lacking);
- Baumhauerite- $\psi\text{O}3abc$  [ $\text{Ag}_3\text{Pb}_{38.1}(\text{As}, \text{Sb})_{52.8}\text{S}_{96}$ ]: homeotype of baumhauerite and baumhauerite-2a?
- Bursaitite [ $\text{Pb}_{3-3x}\text{Bi}_{2+2x}\text{S}_6(?)$ ]: needs crystal-structure data;



- *Incaite* ( $\sim \text{FePb}_4\text{Sn}_2\text{Sn}_2\text{Sb}_2\text{S}_{14}$ ): possible revalidation if  $\text{Sn}^{2+} > \text{Pb}^{2+}$  in a natural sample;
- *Ourayite-P* ( $\sim \text{Ag}_{3.6}\text{Pb}_{2.8}\text{Bi}_{5.6}\text{S}_{13}$ ): empirical formula;
- *Rathite-IV*: chemical formula unknown;
- *Schirmerite* (Type 1 –  $\text{Ag}_4\text{PbBi}_4\text{S}_9$ ): identical with schapbachite, or a dimorph?

Beyond, and complementary to the definition of each individual mineral species, is the question of relative limits of neighbouring sulfosalts in complex crystal-chemical systems. Four examples have been presented in this report:

- the aikinite–bismuthinite homeotypic series. Here numerous intermediate homeotypes have been defined, but the narrow solid-solution fields of all species have to be defined;
- the sartorite homologous series. In this group complex superstructures are present, especially for As-rich members, together with the presence of minor Tl or Ag. New resolutions of true structures in this system are necessary to understand the role of these chemical factors;

- tetrahedrite isotypic series. Contrary to the aikinite–bismuthinite series, in this series there are extended solid solutions, and the transitions between different poles must be defined (*e.g.*, the limits between tetrahedrite, freibergite and argentotetrahedrite);
- the lillianite–andorite homologous series. Here there are extended (but not complete) solid solutions on the one hand (*e.g.*,  $\text{Bi}^{3+} \leftrightarrow \text{Sb}^{3+}$ , or  $2 \text{Pb}^{2+} \leftrightarrow \text{Ag}^+ + \text{Bi}^{3+}$ ), and, on the other hand, stabilization of discrete compounds by metals with minor content (Mn, Cd, Fe).

In the years to come, progress in the field of the systematics of sulfosalts will be more and more dependent on crystal structure studies, that requires the availability of well-ordered natural or synthetic crystals, as well as a combination of various methods, taking into account modern approaches (*e.g.*, single crystal and powder synchrotron X-ray diffraction; application of non-harmonic approach to atomic displacement parameters for Cu- and Ag-rich sulfosalts; *ab initio* structure determinations).

### Alphabetical index of accepted species of sulfosalts with $\text{As}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Bi}^{3+}$ or $\text{Te}^{4+}$

CSU: Crystal structure unsolved.  $\nabla$ : vacancy. Q: Validity questionable (see Sect. 3.1 of the final conclusion)

| Species             | Chapter | Formula  | Remark                                |
|---------------------|---------|--|---------------------------------------|
| <b>A</b>            |         |  |                                       |
| Aikinite            | 4.3     | $\text{CuPbBiS}_3$   |                                       |
| Aktashite           | 6.1.3   | $\text{Cu}_6\text{Hg}_3\text{As}_4\text{S}_{12}$   |                                       |
| Aleksite            | 2.1     | $\text{PbBi}_2\text{S}_2\text{Te}_2$   | CSU                                   |
| Andorite IV         | 3.1.1   | $\text{Ag}_{15}\text{Pb}_{18}\text{Sb}_{47}\text{S}_{96}$                                    | CSU – also named “quatrandorite”      |
| Andorite VI         | 3.1.1   | $\text{AgPbSb}_3\text{S}_6$  | Also named “senandorite”              |
| Angelaite           | 2.3.1   | $\text{Cu}_2\text{AgPbBiS}_4$  |                                       |
| Aramayoite          | 1.1.2   | $\text{Ag}_3\text{Sb}_2(\text{Bi}, \text{Sb})\text{S}_6$                                     |                                       |
| Arcubisite          | 1.5     | $\text{CuAg}_6\text{BiS}_4$  | CSU                                   |
| Ardaite             | 4.4     | $\text{Pb}_{17}\text{Sb}_{15}\text{S}_{35}\text{Cl}_9$                                       | CSU                                   |
| Argentotennantite   | 6.1.2   | $\text{Ag}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{S}_{13}$                   | CSU                                   |
| Argentotetrahedrite | 6.1.2   | $\text{Ag}_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$                             | CSU. Published without CNMNC approval |
| Aschalmite          | 3.2     | $\text{Pb}_{6-3x}\text{Bi}_{2+x}\text{S}_9$  |                                       |
| <b>B</b>            |         |  |                                       |
| Babkinite           | 2.1     | $\text{Pb}_2\text{Bi}_2(\text{S}, \text{Se})_3$  | CSU                                   |
| Baumhauerite        | 3.8.2   | $\text{Pb}_{12}\text{As}_{16}\text{S}_{36}$  | CSU                                   |
| Baumhauerite-2a     | 3.8.2   | $\sim \text{Ag}_{1.5}\text{Pb}_{22}\text{As}_{33.5}\text{S}_{72}$                            |                                       |
| Baumstarkite        | 1.1.2   | $\text{Ag}_3\text{Sb}_3\text{S}_6$   |                                       |
| Benavidesite        | 4.1     | $\text{MnPb}_4\text{Sb}_6\text{S}_{14}$  |                                       |
| Benjaminite         | 3.2     | $\text{Ag}_3\text{Bi}_7\text{S}_{12}$  |                                       |
| Benleonardite       | 6.2.6   | $\text{Ag}_8(\text{Sb}, \text{As})\text{Te}_2\text{S}_3$                                     | CSU                                   |
| Bernardite          | 5.1.1   | $\text{TlAs}_5\text{S}_8$  |                                       |
| Berryite            | 2.2.1   | $\text{Cu}_3\text{Ag}_2\text{Pb}_3\text{Bi}_7\text{S}_{16}$                                  |                                       |
| Berthierite         | 4.1     | $\text{FeSb}_2\text{S}_4$  |                                       |
| Bohdanowiczite      | 1.1.1   | $\text{AgBiSe}_2$  | True crystal-structure unknown        |
| Borodaevite         | 3.2     | $\text{Ag}_{4.83}\text{Fe}_{0.21}\text{Pb}_{0.45}(\text{Bi}, \text{Sb})_{8.84}\text{S}_{16}$ | CSU                                   |
| Borovskite          | 7.3     | $\text{Pd}_3\text{SbTe}_4$   | CSU                                   |
| Boulangerite        | 4.1     | $\text{Pb}_5\text{Sb}_4\text{S}_{11}$  |                                       |
| Bournonite          | 1.2.2   | $\text{CuPbSbS}_3$   |                                       |
| Buckhornite         | 2.2.1   | $(\text{Pb}_2\text{BiS}_3)(\text{AuTe}_2)$   |                                       |

| Species           | Chapter | Formula  | Remark                                   |
|-------------------|---------|--|--|
| <b>C</b>          |         |  |  |
| Cannizzarite      | 2.2.2   | ~ Pb <sub>8</sub> Bi <sub>10</sub> S <sub>23</sub>   |  |
| Cetineite         | 7.1     | NaK <sub>5</sub> Sb <sub>14</sub> S <sub>6</sub> O <sub>18</sub> (H <sub>2</sub> O) <sub>6</sub> |  |
| Chabournéite      | 3.8.5   | Tl <sub>5</sub> (Sb, As) <sub>21</sub> S <sub>34</sub>   |  |
| Chalcostibite     | 1.1.7   | CuSbS <sub>2</sub>   |  |
| Chaméanite        | 6.1.5   | (Cu, Fe) <sub>4</sub> As(Se, S) <sub>4</sub>   | CSU – probably identical with mgriite    |
| Christite         | 1.2.4   | HgTlAsS <sub>3</sub>   |  |
| Clerite           | 4.1     | MnSb <sub>2</sub> S <sub>4</sub>   |  |
| Cosalite          | 4.1     | Pb <sub>2</sub> Bi <sub>2</sub> S <sub>5</sub>   |  |
| Crerarite         | 7.3     | (Pt,Pb)Bi <sub>3</sub> (S, Se) <sub>4-x</sub>  | CSU                                      |
| Criddleite        | 7.2     | Ag <sub>2</sub> Au <sub>3</sub> TlSb <sub>10</sub> S <sub>10</sub>                               | CSU                                      |
| Cuboaargyrite     | 1.1.3   | AgSbS <sub>2</sub>   |  |
| Cuprobismutite    | 3.3     | Cu <sub>8</sub> AgBi <sub>13</sub> S <sub>24</sub>   |  |
| Cupromakovickyite | 3.2     | Cu <sub>4</sub> AgPb <sub>2</sub> Bi <sub>9</sub> S <sub>18</sub>                                |  |
| Cupropavonite     | 3.2     | Cu <sub>0.9</sub> Ag <sub>0.5</sub> Pb <sub>0.6</sub> Bi <sub>2.5</sub> S <sub>5</sub>           | CSU                                      |
| Cylindrite        | 2.2.2   | ~ FePb <sub>3</sub> Sn <sub>4</sub> Sb <sub>2</sub> S <sub>14</sub>                              | (mean structure only)                    |
| <b>D</b>          |         |  |  |
| Dadsonite         | 4.1     | Pb <sub>23</sub> Sb <sub>25</sub> S <sub>60</sub> Cl   |  |
| Dervillite        | 6.2.6   | Ag <sub>2</sub> AsS <sub>2</sub>   | CSU                                      |
| Diaphorite        | 1.2.1   | Ag <sub>3</sub> Pb <sub>2</sub> Sb <sub>3</sub> S <sub>8</sub>                                   |  |
| Dufrénoysite      | 3.8.6   | Pb <sub>2</sub> As <sub>2</sub> S <sub>5</sub>   |  |
| <b>E</b>          |         |  |  |
| Edenharterite     | 5.1.2   | TlPbAs <sub>3</sub> S <sub>6</sub>   |  |
| Ellisite          | 6.2.2   | Tl <sub>3</sub> AsS <sub>3</sub>   |  |
| Emilite           | 4.3     | Cu <sub>10.7</sub> Pb <sub>10.7</sub> Bi <sub>21.3</sub> S <sub>48</sub>                         |  |
| Eclarite          | 4.2.2   | (Cu, Fe)Pb <sub>9</sub> Bi <sub>12</sub> S <sub>28</sub>   |  |
| Emplectite        | 1.1.7   | CuBiS <sub>2</sub>   |  |
| Erniggliite       | 5.4     | SnTl <sub>2</sub> As <sub>2</sub> S <sub>6</sub>   |  |
| Eskimoite         | 3.1.2   | Ag <sub>7</sub> Pb <sub>10</sub> Bi <sub>15</sub> S <sub>36</sub>                                | (CSU – structure model only)             |
| <b>F</b>          |         |  |  |
| Falkmanite        | 4.1     | Pb <sub>3</sub> Sb <sub>2</sub> S <sub>6</sub>   | Q – CSU. Relationship with boulangerite? |
| Felbertalite      | 2.3.1   | Cu <sub>2</sub> Pb <sub>6</sub> Bi <sub>8</sub> S <sub>19</sub>                                  |  |
| Fettelite         | 6.2.5   | Ag <sub>24</sub> HgAs <sub>5</sub> S <sub>20</sub>   | Crystal structure: abstract only         |
| Fizélyite         | 3.1.1   | Ag <sub>5</sub> Pb <sub>14</sub> Sb <sub>21</sub> S <sub>48</sub>                                | CSU                                      |
| Franckeite        | 2.2.2   | Fe(Pb, Sn) <sub>6</sub> Sn <sub>2</sub> Sb <sub>2</sub> S <sub>14</sub>                          | (mean structure only)                    |
| Freibergite       | 6.1.2   | Ag <sub>6</sub> [Cu <sub>4</sub> Fe <sub>2</sub> ]Sb <sub>4</sub> S <sub>13-x</sub> (?)          | Limit with Ag-rich tetrahedrite?         |
| Freieslebenite    | 1.2.1   | AgPbSbS <sub>3</sub>   |  |
| Friedrichite      | 4.3     | Cu <sub>5</sub> Pb <sub>5</sub> Bi <sub>7</sub> S <sub>18</sub>                                  | CSU                                      |
| Fülöppite         | 3.7     | Pb <sub>3</sub> Sb <sub>8</sub> S <sub>15</sub>  |  |
| <b>G</b>          |         |  |  |
| Gabrielite        | 5.4     | Cu <sub>2</sub> AgTl <sub>2</sub> As <sub>3</sub> S <sub>7</sub>                                 |  |
| Galenobismutite   | 2.3.1   | PbBi <sub>2</sub> S <sub>4</sub>   |  |
| Galkhaite         | 6.1.2   | (Cs, Tl, ∇)(Hg, Cu, Zn, Tl) <sub>6</sub> (As, Sb) <sub>4</sub> S <sub>12</sub>                   |  |
| Garavellite       | 4.1     | FeSbBiS <sub>4</sub>   |  |
| Geocronite        | 3.5.1   | Pb <sub>14</sub> (Sb, As) <sub>6</sub> S <sub>23</sub>   |  |
| Gerstleyite       | 5.1.4   | Na <sub>2</sub> (Sb, As) <sub>8</sub> S <sub>13</sub> ·2H <sub>2</sub> O                         |  |
| Giessenite        | 4.2.2   | (Cu, Fe) <sub>2</sub> Pb <sub>26.4</sub> (Bi, Sb) <sub>19.6</sub> S <sub>57</sub>                | CSU                                      |
| Gillulyite        | 5.1.3   | Tl <sub>2</sub> As <sub>7.5</sub> Sb <sub>0.3</sub> S <sub>13</sub>                              |  |
| Giraudite         | 6.1.2   | Cu <sub>6</sub> [Cu <sub>4</sub> (Fe, Zn) <sub>2</sub> ]As <sub>4</sub> Se <sub>13</sub>         | CSU                                      |
| Gladite           | 4.3     | CuPbBi <sub>5</sub> S <sub>9</sub>   |  |
| Goldfieldite      | 6.1.2   | Cu <sub>10</sub> Te <sub>4</sub> S <sub>13</sub>   |  |
| Gratonite         | 3.6     | Pb <sub>9</sub> As <sub>4</sub> S <sub>15</sub>  |  |
| Grumiplucite      | 3.2     | HgBi <sub>2</sub> S <sub>4</sub>   |  |
| Gruzdevite        | 6.1.3   | Cu <sub>6</sub> Hg <sub>3</sub> Sb <sub>4</sub> S <sub>12</sub>                                  | CSU                                      |
| Guettardite       | 3.8.1   | Pb <sub>8</sub> (Sb <sub>0.56</sub> As <sub>0.44</sub> ) <sub>16</sub> S <sub>32</sub>           | CSU – difference with twinnite?          |
| Gustavite         | 3.1.1   | AgPbBi <sub>3</sub> S <sub>6</sub>   |  |

| Species        | Chapter | Formula  | Remark                                      |
|----------------|---------|--|---|
| Hakite         | 6.1.2   | $\text{Cu}_6[\text{Cu}_4\text{Hg}_2]\text{Sb}_4\text{Se}_{13}$                       | CSU   |
| Hammarite      | 4.3     | $\text{Cu}_2\text{Pb}_2\text{Bi}_4\text{S}_9$  |   |
| Hatchite       | 1.3     | $\text{AgTlPbAs}_2\text{S}_5$  |   |
| Heteromorphite | 3.7     | $\text{Pb}_7\text{Sb}_8\text{S}_{19}$  |   |
| Heyrovskýite   | 3.1.2   | $\text{Pb}_6\text{Bi}_2\text{S}_9$   |   |
| Hodrushite     | 3.3     | $\text{Cu}_8\text{Bi}_{12}\text{S}_{22}$   |   |
| Hutchinsonite  | 5.1.1   | $\text{TlPbAs}_5\text{S}_9$  |   |
| I              |         |  |   |
| Imhofite       | 5.1.3   | $\text{Tl}_{5,8}\text{As}_{15,4}\text{S}_{26}$                                       |   |
| Izoklakeite    | 4.2.2   | $(\text{Cu}, \text{Fe})_2\text{Pb}_{26,4}(\text{Sb}, \text{Bi})_{19,6}\text{S}_{57}$ |   |
| J              |         |  |   |
| Jamesonite     | 4.1     | $\text{FePb}_4\text{Sb}_6\text{S}_{14}$  |   |
| Jankovičite    | 5.2     | $\text{Tl}_5\text{Sb}_9(\text{As}, \text{Sb})_4\text{S}_{22}$                        |   |
| Jaskólskiite   | 3.4     | $\text{Cu}_x\text{Pb}_{2+x}(\text{Sb}, \text{Bi})_{2-x}\text{S}_5$                   |   |
| Jentschite     | 5.1.2   | $\text{TlPbAs}_2\text{SbS}_6$  |   |
| Jonassonite    | 7.2     | $\text{Au}(\text{Bi}, \text{Pb})_5\text{S}_4$  | CSU   |
| Jordanite      | 3.5.1   | $\text{Pb}_{14}(\text{As}, \text{Sb})_6\text{S}_{23}$                                |   |
| Junoite        | 2.3.1   | $\text{Cu}_2\text{Pb}_3\text{Bi}_8(\text{S}, \text{Se})_{16}$                        |   |
| K              |         |  |   |
| Kirkiite       | 3.5.2   | $\text{Pb}_{10}\text{Bi}_3\text{As}_3\text{S}_{19}$                                  |   |
| Kobellite      | 4.2.2   | $(\text{Cu}, \text{Fe})_2\text{Pb}_{11}(\text{Bi}, \text{Sb})_{15}\text{S}_{35}$     |   |
| Kochkarite     | 2.1     | $\text{PbBi}_4\text{Te}_7$   |   |
| Krupkaite      | 4.3     | $\text{CuPbBi}_3\text{S}_6$  |   |
| Kudriavite     | 3.2     | $(\text{Cd}, \text{Pb})\text{Bi}_2\text{S}_4$  |   |
| Kupčfkitite    | 3.3     | $\text{Cu}_{3,4}\text{Fe}_{0,6}\text{Bi}_5\text{S}_{10}$                             |   |
| L              |         |  |   |
| Laffittite     | 6.1.3   | $\text{AgHgAsS}_3$   |   |
| Lapieite       | 1.2.3   | $\text{CuNiSbS}_3$   | CSU   |
| Larosite       | 6.1.5   | $(\text{Cu}, \text{Ag})_{21}\text{PbBiS}_{13}$                                       | CSU   |
| Launayite      | 4.4     | $\text{CuPb}_{10}(\text{Sb}, \text{As})_{13}\text{S}_{30}$                           | CSU   |
| Lengenbachite  | 2.2.2   | $\sim \text{Cu}_2\text{Ag}_4\text{Pb}_{18}\text{As}_{12}\text{S}_{39}$               | CSU – structural model                      |
| Lévyclauidite  | 2.2.2   | $\sim \text{Cu}_3\text{Pb}_8\text{Sn}_7(\text{Bi}, \text{Sb})_3\text{S}_{28}$        |   |
| Lillianite     | 3.1.1   | $\text{Ag}_x\text{Pb}_{3-2x}\text{Bi}_{2+x}\text{S}_6$                               |   |
| Lindströmite   | 4.3     | $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$                                     |   |
| Liveingite     | 3.8.3   | $\text{Pb}_{20}\text{As}_{24}\text{S}_{56}$  |   |
| Livingstonite  | 3.2     | $\text{HgSb}_4\text{S}_6(\text{S}_2)$  |   |
| Lorandite      | 1.1.7   | $\text{TlAsS}_2$   |   |
| M              |         |  |   |
| Madocite       | 4.4     | $\text{Pb}_{19}(\text{Sb}, \text{As})_{16}\text{S}_{43}$                             | CSU   |
| Makovickyite   | 3.2     | $\text{Cu}_{1,12}\text{Ag}_{0,81}\text{Pb}_{0,27}\text{Bi}_{5,35}\text{S}_9$         |   |
| Malyshevite    |         | $\text{CuPdBiS}_3$   | CSU   |
| Marrite        | 1.2.1   | $\text{AgPbAsS}_3$   |   |
| Marumoite      | 3.8.5   | $\text{Pb}_{32}\text{As}_{40}\text{S}_{92}$  | CSU – no mineral description (IMA 1998-004) |
| Marrucciite    | 4.2.1   | $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$                               |   |
| Matildite      | 1.1.1   | $\text{AgBiS}_2$   | True crystal-structure unknown              |
| Mazzettiite    | 6.1.5   | $\text{Ag}_3\text{HgPbSbTe}_5$   | CSU   |
| Meneghinite    | 3.4     | $\text{CuPb}_{13}\text{Sb}_7\text{S}_{24}$   |   |
| Mgriite        | 6.1.5   | $(\text{Cu}, \text{Fe})_3\text{AsSe}_3$  | CSU – probably identical with chaméanite    |
| Miargyrite     | 1.1.4   | $\text{AgSbS}_2$   |   |
| Miharaite      | 6.1.5   | $\text{Cu}_4\text{FePbBiS}_6$  |   |
| Moëloite       | 4.1     | $\text{Pb}_6\text{Sb}_6\text{S}_{14}(\text{S}_3)$                                    |   |
| Mozgovaite     | 3.2     | $\text{PbBi}_4(\text{S}, \text{Se})_7$   | CSU   |
| Mückeite       | 1.2.3   | $\text{CuNiBiS}_3$   |   |
| Mummeite       | 3.2     | $\text{Cu}_{0,58}\text{Ag}_{3,11}\text{Pb}_{1,10}\text{Bi}_{6,65}\text{S}_{13}$      |   |
| Museumite      | 2.2.1   | $\text{Pb}_2(\text{Pb}, \text{Sb})_2\text{S}_8[\text{Te}, \text{Au}]_2$              | CSU   |
| Mutnovskite    | 3.9     | $\text{Pb}_2\text{AsS}_3(\text{I}, \text{Cl}, \text{Br})$                            |   |

| Species          | Chapter | Formula   | Remark                                     |
|------------------|---------|---|--|
| <b>N</b>         |         |   |  |
| Nagyágite        | 2.2.1   | [Pb <sub>3</sub> (Pb, Sb) <sub>3</sub> S <sub>6</sub> ](Te, Au) <sub>3</sub>                                      |  |
| Neyite           | 2.3.2   | Cu <sub>6</sub> Ag <sub>2</sub> Pb <sub>25</sub> Bi <sub>26</sub> S <sub>68</sub>                                 |  |
| Nordströmite     | 2.3.1   | CuPb <sub>3</sub> Bi <sub>7</sub> (S, Se) <sub>14</sub>   |  |
| Nowackiite       | 6.1.3   | Cu <sub>6</sub> Zn <sub>3</sub> As <sub>4</sub> S <sub>12</sub>   |  |
| Nuffieldite      | 2.3.1   | Cu <sub>1.4</sub> Pb <sub>2.4</sub> Bi <sub>2.4</sub> Sb <sub>0.2</sub> S <sub>7</sub>                            |  |
| <b>O</b>         |         |   |  |
| Ottensite        | 7.1     | Na <sub>3</sub> (Sb <sub>2</sub> O <sub>3</sub> ) <sub>3</sub> (SbS <sub>3</sub> )·3H <sub>2</sub> O              | CSU  |
| Ourayite         | 3.1.3   | Ag <sub>3</sub> Pb <sub>4</sub> Bi <sub>5</sub> S <sub>13</sub>   | CSU  |
| Owyheeite        | 4.2.1   | Ag <sub>3</sub> Pb <sub>10</sub> Sb <sub>11</sub> S <sub>28</sub>   |  |
| <b>P</b>         |         |   |  |
| Paarite          | 4.3     | Cu <sub>1.7</sub> Pb <sub>1.7</sub> Bi <sub>6.3</sub> S <sub>12</sub>   |  |
| Padëraite        | 3.3     | Cu <sub>7</sub> [(Cu, Ag) <sub>0.33</sub> Pb <sub>1.33</sub> Bi <sub>11.33</sub> ] <sub>Σ13</sub> S <sub>22</sub> |  |
| Parapierröte     | 3.8.7   | TlSb <sub>5</sub> S <sub>8</sub>  |  |
| Pavonite         | 3.2     | AgBi <sub>3</sub> S <sub>5</sub>  |  |
| Pearceite        | 6.2.4   | Cu(Ag, Cu) <sub>6</sub> Ag <sub>9</sub> As <sub>2</sub> S <sub>11</sub>   |  |
| Pekoite          | 4.3     | CuPbBi <sub>11</sub> S <sub>18</sub>  |  |
| Pellouxite       | 4.2.1   | (Cu, Ag) <sub>2</sub> Pb <sub>21</sub> Sb <sub>23</sub> S <sub>55</sub> ClO                                       |  |
| Petrovicite      | 6.1.5   | Cu <sub>3</sub> HgPbBiSe <sub>5</sub>   | CSU  |
| Pierrotite       | 3.8.7   | Tl <sub>2</sub> (Sb, As) <sub>10</sub> S <sub>16</sub>  |  |
| Pillaite         | 4.2.1   | Pb <sub>9</sub> Sb <sub>10</sub> S <sub>23</sub> ClO <sub>0.5</sub>   |  |
| Pizgrischite     | 3.3     | (Cu, Fe)Cu <sub>14</sub> PbBi <sub>17</sub> S <sub>34</sub>   |  |
| Plagionite       | 3.7     | Pb <sub>5</sub> Sb <sub>8</sub> S <sub>17</sub>   |  |
| Playfairite      | 4.4     | Pb <sub>16</sub> (Sb, As) <sub>19</sub> S <sub>44</sub> Cl  | CSU  |
| Plumosite        | 4.1     | Pb <sub>2</sub> Sb <sub>2</sub> S <sub>5</sub>  | Q – CSU. Relationship with boulangerite?   |
| Polybasite       | 6.2.4   | Cu(Ag, Cu) <sub>6</sub> Ag <sub>9</sub> Sb <sub>2</sub> S <sub>11</sub>   |  |
| Poubaite         | 2.1     | PbBi <sub>2</sub> (Se, Te, S) <sub>4</sub>  |  |
| Proudite         | 2.3.1   | Cu <sub>2</sub> Pb <sub>16</sub> Bi <sub>20</sub> (S, Se) <sub>47</sub>   |  |
| Proustite        | 6.2.2   | Ag <sub>3</sub> AsS <sub>3</sub>  |  |
| Pyrargyrite      | 6.2.2   | Ag <sub>3</sub> SbS <sub>3</sub>  |  |
| Pyrostilpnite    | 6.2.3   | Ag <sub>3</sub> SbS <sub>3</sub>  |  |
| <b>Q</b>         |         |   |  |
| Quadratite       | 1.2.1   | Ag(Cd, Pb)(As, Sb)S <sub>3</sub>  |  |
| <b>R</b>         |         |   |  |
| Ramdohrite       | 3.1.1   | (Cd, Mn, Fe)Ag <sub>5.5</sub> Pb <sub>12</sub> Sb <sub>21.5</sub> S <sub>48</sub>                                 | Distinction from fizélyite?                |
| Rathite          | 3.8.4   | Ag <sub>2</sub> Pb <sub>12-x</sub> Tl <sub>x/2</sub> As <sub>18+x/2</sub> S <sub>40</sub>                         |  |
| Rayite           | 3.7     | (Ag, Tl) <sub>2</sub> Pb <sub>8</sub> Sb <sub>8</sub> S <sub>21</sub>   | CSU – needs an unit-cell redetermination   |
| Rebulite         | 5.2     | Tl <sub>5</sub> As <sub>8</sub> Sb <sub>5</sub> S <sub>22</sub>   | No mineral description, nor CNMNC approval |
| Robinsonite      | 4.1     | Pb <sub>4</sub> Sb <sub>6</sub> S <sub>13</sub>   |  |
| Roshchinite      | 3.1.1   | (Ag, Cu) <sub>19</sub> Pb <sub>10</sub> Sb <sub>51</sub> S <sub>96</sub>  |  |
| Routhierite      | 6.1.4   | CuHg <sub>2</sub> TlAs <sub>2</sub> S <sub>6</sub>  | CSU  |
| Rouxelite        | 2.3.2   | Cu <sub>2</sub> HgPb <sub>22</sub> Sb <sub>28</sub> S <sub>64</sub> (O, S) <sub>2</sub>                           |  |
| Rucklidgeite     | 2.1     | PbBi <sub>2</sub> Te <sub>4</sub>   |  |
| <b>S</b>         |         |   |  |
| Saddlebackite    | 2.1     | Pb <sub>2</sub> Bi <sub>2</sub> Te <sub>2</sub> S <sub>3</sub>  | CSU  |
| Salzburgite      | 4.3     | Cu <sub>1.6</sub> Pb <sub>1.6</sub> Bi <sub>6.4</sub> S <sub>12</sub>   |  |
| Sakharovaitite   | 4.1     | FePb <sub>4</sub> (Sb, Bi) <sub>6</sub> S <sub>14</sub>   | Q – CSU. unit cell not given               |
| Samsonite        | 6.2.1   | MnAg <sub>4</sub> Sb <sub>2</sub> S <sub>6</sub>  |  |
| Sarabauite       | 7.1     | Sb <sub>4</sub> S <sub>6</sub> ·CaSb <sub>6</sub> O <sub>10</sub>   |  |
| Sartorite        | 3.8.1   | PbAs <sub>2</sub> S <sub>4</sub>  |  |
| Scainiite        | 4.2.1   | Pb <sub>14</sub> Sb <sub>30</sub> S <sub>54</sub> O <sub>5</sub>  |  |
| Schapbachite     | 1.2.1   | Ag <sub>0.4</sub> Pb <sub>0.2</sub> Bi <sub>0.4</sub> S   | Redefinition                               |
| Selenopolybasite | 6.2.4   | Cu(Ag, Cu) <sub>6</sub> Ag <sub>9</sub> Sb <sub>2</sub> (S, Se) <sub>9</sub> Se <sub>2</sub>                      |  |
| Selenostephanite | 6.2.5   | Ag <sub>5</sub> Sb(Se, S) <sub>4</sub>  | CSU  |
| Seligmannite     | 1.2.2   | CuPbAsS <sub>3</sub>  |  |



| Species              | Chapter | Formula   | Remark                             |
|----------------------|---------|---|------------------------------------|
| Semseyite            | 3.7     | Pb <sub>9</sub> Sb <sub>8</sub> S <sub>21</sub>   |                                    |
| Sicherite            | 5.3     | Ag <sub>2</sub> Tl(As, Sb) <sub>3</sub> S <sub>6</sub>                                  |                                    |
| Simonite             | 5.4     | HgTlAs <sub>3</sub> S <sub>6</sub>  | No mineral description             |
| Sinnerite            | 6.1.3   | Cu <sub>6</sub> As <sub>4</sub> S <sub>9</sub>  |                                    |
| Skinnerite           | 6.1.1   | Cu <sub>3</sub> SbS <sub>3</sub>  |                                    |
| Smithite             | 1.1.5   | AgAsS <sub>2</sub>  |                                    |
| Sorbyite             | 4.4     | CuPb <sub>9</sub> (Sb, As) <sub>11</sub> S <sub>26</sub>                                | CSU                                |
| Součekite            | 1.2.2   | CuPbBi(S, Se) <sub>3</sub>  | CSU                                |
| Stalderite           | 6.1.4   | Cu(Zn, Fe, Hg) <sub>2</sub> TlAs <sub>2</sub> S <sub>6</sub>                            |                                    |
| Stephanite           | 6.2.5   | Ag <sub>5</sub> SbS <sub>4</sub>  |                                    |
| Sterryite            | 4.4     | (Ag, Cu) <sub>2</sub> Pb <sub>10</sub> (Sb, As) <sub>12</sub> S <sub>29</sub>           | CSU                                |
| <b>T</b>             |         |   |                                    |
| Tennantite           | 6.1.2   | Cu <sub>6</sub> [Cu <sub>4</sub> (Fe, Zn) <sub>2</sub> ]As <sub>4</sub> S <sub>13</sub> |                                    |
| Tetrahedrite         | 6.1.2   | Cu <sub>6</sub> [Cu <sub>4</sub> (Fe, Zn) <sub>2</sub> ]Sb <sub>4</sub> S <sub>13</sub> |                                    |
| Tintinaite           | 4.2.2   | Cu <sub>2</sub> Pb <sub>10</sub> Sb <sub>16</sub> S <sub>35</sub>                       | CSU                                |
| Treasurite           | 3.1.1   | Ag <sub>7</sub> Pb <sub>6</sub> Bi <sub>15</sub> S <sub>30</sub>                        | CSU                                |
| Trechmannite         | 1.1.6   | AgAsS <sub>2</sub>  |                                    |
| Tsnigriite           | 6.2.6   | Ag <sub>9</sub> Sb(S, Se) <sub>3</sub> Te <sub>3</sub>                                  | CSU                                |
| Tsugaruite           | 3.5.3   | Pb <sub>4</sub> As <sub>2</sub> S <sub>7</sub>  | CSU                                |
| Tvalchrelidzeite     | 7.2     | Hg <sub>3</sub> SbAsS <sub>3</sub>  |                                    |
| Twinnite             | 3.8.1   | Pb(Sb <sub>0.63</sub> As <sub>0.37</sub> ) <sub>2</sub> S <sub>4</sub>                  | CSU – difference with guettardite? |
| <b>U</b>             |         |   |                                    |
| Uchucchacuaite       | 3.1.1   | MnAgPb <sub>3</sub> Sb <sub>5</sub> S <sub>12</sub>                                     | CSU                                |
| Ustarasite           | 3.1.5   | Pb(Bi, Sb) <sub>6</sub> S <sub>10</sub>   | Q – CSU. No unit-cell data         |
| <b>V</b>             |         |   |                                    |
| Vaughanite           | 5.4     | HgTlSb <sub>4</sub> S <sub>7</sub>  | CSU                                |
| Veenite              | 3.8.4   | Pb <sub>2</sub> (Sb, As) <sub>2</sub> S <sub>5</sub>                                    | CSU                                |
| Vikingite            | 3.1.1   | Ag <sub>5</sub> Pb <sub>8</sub> Bi <sub>13</sub> S <sub>30</sub>                        |                                    |
| Volynskite           | 1.1.1   | AgBiTe <sub>2</sub>   | True crystal structure unknown     |
| Vrbaite              | 5.4     | Hg <sub>3</sub> Tl <sub>4</sub> As <sub>8</sub> Sb <sub>2</sub> S <sub>20</sub>         |                                    |
| Vurroite             | 4.2.1   | Sn <sub>2</sub> Pb <sub>20</sub> (Bi, As) <sub>22</sub> S <sub>54</sub> Cl <sub>6</sub> |                                    |
| <b>W</b>             |         |   |                                    |
| Wallisite            | 1.3     | CuTlPbAs <sub>2</sub> S <sub>5</sub>  |                                    |
| Watanabeite          | 6.1.3   | Cu <sub>4</sub> (As, Sb) <sub>2</sub> S <sub>5</sub>                                    | CSU                                |
| Watkinsonite         | 2.2.1   | Cu <sub>2</sub> PbBi <sub>4</sub> (Se, S) <sub>8</sub>                                  | CSU                                |
| Weibullite           | 2.3.1   | Ag <sub>0.33</sub> Pb <sub>5.33</sub> Bi <sub>18.33</sub> (S, Se) <sub>18</sub>         |                                    |
| Weissbergite         | 1.1.7   | TlSbS <sub>2</sub>  |                                    |
| Wittichenite         | 6.1.1   | Cu <sub>3</sub> BiS <sub>3</sub>  |                                    |
| Wittite              | 2.2.2   | Pb <sub>8</sub> Bi <sub>10</sub> (S, Se) <sub>23</sub>                                  | Q                                  |
| <b>X</b>             |         |   |                                    |
| Xanthoconite         | 6.2.3   | Ag <sub>3</sub> AsS <sub>3</sub>  |                                    |
| Xilingolite          | 3.1.1   | Pb <sub>3</sub> Bi <sub>2</sub> S <sub>6</sub>  |                                    |
| <b>Z</b>             |         |   |                                    |
| Zinkenite            | 4.2.1   | Pb <sub>9</sub> Sb <sub>22</sub> S <sub>42</sub>  |                                    |
| Zoubekite            | 4.2.3   | AgPb <sub>4</sub> Sb <sub>4</sub> S <sub>10</sub>                                       | Q                                  |
| <b>IMA approved*</b> |         |   |                                    |
| IMA 2005-024         | 2.2.2   | (Pb, Sn) <sub>12.5</sub> As <sub>3</sub> Sn <sub>5</sub> FeS <sub>28</sub>              | As-derivative of franckeite        |
| IMA 2005-036         | 3.2     | Cu <sub>8</sub> Ag <sub>3</sub> Pb <sub>4</sub> Bi <sub>19</sub> S <sub>38</sub>        | Pavonite series                    |
| IMA 2006-016         | 2.2.2   | Pb <sub>2</sub> SnInBiS <sub>7</sub>  | In-derivative of cylindrite        |
| IMA 2007-003         | 1.2.3   | CuPtBiS <sub>3</sub>  | Pt-isotype of lapieite             |
| IMA 2007-010         | 4.4     | PbHgAs <sub>2</sub> S <sub>6</sub>  |                                    |

Total: 223 sulfosalt species. \*Data source: IMA-CNMNC website.

## Appendix: Additional list of discredited species

This list represents a selection of abandoned names, which are found in modern publications. The great majority of these discredited names (noted \*) is compiled in the recent report on “Mass discreditation of GQN minerals” by E.A.J. Burke (2006), Chairman of the CNMNC-IMA. This report is of free access on the Net, at the CNMNC-IMA site.

\*\* : Possible revalidation (see 3.1 in the final conclusion).

*Alaskaite* = a mixture of various Bi sulfosalts (Karup-Møller, 1972).

*Annivite*\*\* = Bi-rich tennantite.

*Beegerite*\* = a mixture of “schirmerite” and matildite (Karup-Møller, 1973).

*Bonchevite*\*,  $\text{PbBi}_4\text{S}_7$ , defined by Kostov (1958), was formally discredited by the CNMNC (IMA 67-2a; Franz *et al.*, 1967; 1969), as a mixture of galenobismutite with a sulfosalt of the lillianite type. Through reexamination of new material from the type deposit, Birch & Mumme (1985) identified pekoite, and considered bonchevite as a mixture of pekoite and galenobismutite.

*Brongniardite/Brongniartite*\*,  $\text{PbAg}_2\text{Sb}_2\text{S}_5$  (Pb-poor diaphorite – Mozgova *et al.*, 1989) (retained in Strunz & Nickel, 2001).

*Bursaite*\* = an intergrowth of two phases (Mozgova *et al.*, 1988).

*Eichbergite* = a mixture of jaskolskiite and Bi-bearing meneghinite (Paur *et al.*, in prep.)

*Goongarrite*\*,  $\text{Pb}_6\text{Bi}_2\text{S}_9$  = a symplectitic mixture of galena and cosalite, from the decomposition of metastable heyrovskýite (Klominsky *et al.*, 1971). See also Rieder (1963).

*Gelnicite/Gelnicaite*\* = identical with marrucciite (Orlandi *et al.*, 2007).

*Incaite*\*\* :  $\text{Sn}^{2+}$ -rich franckeite (Mozgova *et al.*, 1976).

*Kitabelite*\* = Pb-containing pavonite (Weiszbürg *et al.*, 1992).

*Nakaséite*,  $\text{Ag}_3\text{CuPb}_4\text{Sb}_{12}\text{S}_{24}$  (Fleischer, 1960) = a disordered precursor of andorites IV and VI (Moëlo *et al.*, 1989).

*Parajamesonite*\*,  $\text{FePb}_4\text{Sb}_6\text{S}_{14}$  = a mixture of jamesonite and other sulfosalts (Papp, 2004; Papp *et al.*, 2007).

*Platynite*,  $\text{Pb}_4\text{Bi}_7\text{S}_4\text{Se}_7$  = a mixture of laitakarite and galena (Holtstam & Söderhielm, 1999) (retained in Strunz & Nickel, 2001).

*Potosiite* =  $\text{Sn}^{2+}$ -poor franckeite (Makovicky & Hyde, 1992).

*Rathite varieties*: see details in this report.

*Rézbányite* = a mixture of aikinite derivatives, padëraite and other sulfosalts (Žák *et al.*, 1992).

*Schirmerite (Type I)\*\**,  $\text{Ag}_4\text{PbBi}_4\text{S}_9$  = schaphachite.?

*Schirmerite (Type II)*,  $\sim \text{AgPbBi}_3\text{S}_6$  to  $\text{Ag}_{1.5}\text{Pb}_3\text{Bi}_{3.5}\text{S}_9$  = a disordered member of the lillianite homologous series (Makovicky & Karup-Møller, 1977b).

*Schulzite*,  $\text{Pb}_{14}\text{Sb}_6\text{S}_{23}$  (As-free geocronite).

*Scleroclase*,  $\text{PbAs}_2\text{S}_4$  (old name for sartorite).

*Teremkovite*,  $\text{Pb}_7\text{Ag}_2\text{Sb}_8\text{S}_{20}$  (CNMNC-IMA, 1971) (probable Ag-poor variety of owyheite – Moëlo *et al.*, 1984b).

*Wittite B* = proudite (Mumme, 1976).

## References

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