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## 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.crystalmaker.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  $b$ .

















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### 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 staldelite).

### 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):



































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