

**Zeitschrift:** Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie  
**Band:** 81 (2001)  
**Heft:** 1  
  
**Artikel:** The crystal chemistry of the sartorite group minerals from Lengenbach, Binntal, Switzerland : a HRTEM study  
**Autor:** Pring, Allan  
**DOI:** <https://doi.org/10.5169/seals-61681>

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*Dedicated to Prof. Dr. Stefan Graeser on his 65<sup>th</sup> anniversary*

## The crystal chemistry of the sartorite group minerals from Lengenbach, Binntal, Switzerland – a HRTEM study

by Allan Pring<sup>1,2</sup>

### Abstract

The crystal chemistry of the sartorite group of minerals is reviewed and structures are treated in terms of compositional modulations associated with Pb and As ordering. The minerals have modular structures based on the intergrowth  $N = 4$  and  $N = 3$  units, with  $N = 4$  units dominated the more Pb-rich minerals. High-resolution transmission electron microscopy was used to investigate the nature of long range order-disorder of structural modules. The more Pb-rich members of the group: dufrénoysite ( $N = 4$ ), rathite ( $N = 4$ ), and liveingite ( $N = 3.75$ ) were found to be perfectly ordered with no evidence of polytypism or polysomatic disorder. The compositional region between liveingite and baumhauerite is dominated by the occurrence of long period homologues with 10 and 12 units in the structural repeat. Disordered intergrowths of  $N = 4$  and  $N = 3$  units occur in this compositional region. Baumhauerite ( $N = 3.5$ ) exhibits extensive polytypism, both ordered and disordered and this is thought to be associated with periodic inversions of the Pb/As order about  $c$ . Sartorite ( $N = 3$ ) exhibits a complex modulated structure that is associated with the inherent mismatch of As and Pb polyhedra within the structural modules.

Critical evaluation of the structural data on rathite suggests that it is part of a complex solid solution between dufrénoysite and a hypothetical end-member  $Pb_8(Ag,Tl)_8As_{24}S_{40}$ . The existence of rathite III and its relationship to rathite are discussed. The paragenetic relationships between the sartorite minerals at the Lengenbach Quarry, Binntal, Switzerland are also discussed.

**Keywords:** sartorite, rathite, polytypism, polysomatism, Lengenbach, HRTEM.

### Introduction

The modular treatment of crystal structures has done much to simplify our understanding of the crystal chemistry of complex minerals, such as the sulfosalts (HYDE et al., 1979; TAKÉUCHI, 1970; TAKÉUCHI and TAKAGI, 1974; WUENSCH, 1979; MAKOVICKY, 1981, 1985, 1989, 1997 a, b; SKOWRON and BROWN, 1994). The ideas behind modular crystal chemistry have their roots in the work of BAUMHAUER (1915). He introduced the concept of polytypism in order to explain the many structural modifications of SiC, formed by different stacking sequences of structurally and stoichiometrically identical layers. Many minerals and other compounds exhibit polytypism.

MAGNÉLI (1953) introduced the concept of a homologous series to describe groups of com-

pounds that are characterized by a general formula and built upon a common structural principle. This concept is typified by the rare earth oxides and the sulfosalt minerals of the lillianite group (MAKOVICKY, 1981; PRING et al., 1999). The somewhat parallel idea of polysomatism was introduced by THOMPSON (1970, 1978) in order to explain the relationship between structures based on the ordered intergrowth of two or more structurally and stoichiometrically distinct types of units or modules, rather than identical units as required by polytypism, or common structural principles as required by homology. Perhaps the best known example of polysomatism is the biopyribole mineral group. The work of Veblen and others (see VEBLEN, 1991) on structural and paragenetic relationships in the biopyriboles has done much to clarify the nature of these minerals, and

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Tab. 1 Minerals of the sartorite group.

| Name                     | Composition   | Structure             | Cell*                        | Reference                  |
|--------------------------|---|-----------------------|------------------------------|----------------------------|
| Dufrenoyite              | Pb <sub>16</sub> As <sub>16</sub> S <sub>40</sub>   | 4,4                   | a 7.90<br>b 25.74<br>c 8.37  | MARUMO and NOWACKI (1967)  |
| Rathite                  | Pb <sub>11,1</sub> Tl <sub>0,9</sub> As <sub>16</sub> (As <sub>1,6</sub> Ag <sub>2,3</sub> )S <sub>40</sub> | 4,4                   | b 7.94<br>a 25.16<br>c 8.47  | MARUMO and NOWACKI (1965)  |
| Rathite-III              | Pb <sub>12</sub> As <sub>20</sub> S <sub>40</sub>   | 4,4                   | b 7.91<br>a 24.52<br>c 8.47  | LEBIHAN (1962)             |
| Liveingite               | Pb <sub>18,5</sub> As <sub>25</sub> S <sub>56</sub>   | 4,3,4                 | c 7.91<br>b 70.49<br>a 8.37  | ENGEL and NOWACKI (1970)   |
| 115 Å phase              | Pb <sub>32</sub> As <sub>40</sub> S <sub>92</sub>   | 4,3,4,3,4,4,3,4,3,4   | b 7.90<br>a 115.75<br>c 8.37 | OZAWA and TAKÉUCHI (1983)  |
| 138 Å phase (rathite-IV) | Pb <sub>38</sub> As <sub>48</sub> S <sub>110</sub>  | 4,3,4,3,4,4,3,4,3,4,4 | b 7.92<br>a 138.6<br>c 8.46  | OZAWA and TACHIKAWA (1996) |
| Baumhauerite             | Pb <sub>12</sub> As <sub>16</sub> S <sub>36</sub>   | 4,3                   | b 7.89<br>a 22.80<br>c 8.36  | ENGEL and NOWACKI (1969)   |
| Baumhauerite-2a          | Pb <sub>22</sub> Ag <sub>1,4</sub> As <sub>34,3</sub> S <sub>72</sub>                                       | 4,3,4,3               | b 7.89<br>a 44.75<br>c 8.48  | PRING and GRAESER (1994)   |
| Baumhauerite-ψO3abc      | Pb <sub>38,1</sub> Ag <sub>3</sub> (As,Sb) <sub>52,8</sub> S <sub>108</sub>                                 | 4,3,4,3,4,3           | b 7.89<br>a 68.3<br>c 8.48   | PRING and GRAESER (1994)   |
| Sartorite                | PbAs <sub>2</sub> S <sub>4</sub>  | 3,3                   | b 7.89<br>a 19.62<br>c 4.19  | PRING et al. (1993)        |

\* unit cell data rest to a common parent cell.

of the solid state reactions by which they are formed. A number of other polysomatic mineral systems have also been studied (see ALLEN (1992) for review).

In modular crystallography families of structures are generated by stacking units in different ways and the central requirement is that the energy of the interface between component units be relatively low; i.e. a requirement for structural coherence between units. The most extensive modular structural families are those where the individual modules have a very low residual electrostatic charge and low surface energies. Structural disorder due to errors in the stacking sequence have been observed in nearly all modular series and many polysomatic and homologous series also exhibit polytypic behaviour. The relationships between the structural concepts of polysomatism, homology and polytypism are clearly very close and ANGLE (1986) advocated treating polysomatic structures as a special case of polytypism. The contrary idea, of treating polytypism as a special case of polysomatism, would appear however to have equal validity.

The sartorite group (also known as the rathite group) of lead arsenic sulfide minerals are amongst the most studied of the sulfosalts despite their highly restricted occurrence in nature (Tab. 1). All of the members of this group occur together at the historic Lengenbach deposit in the Binntal, Wallis, Switzerland. This deposit has been worked spasmodically, since the 1850's, for specimens of these rare minerals (GRAESER, 1977; GRAESER and SCHWANDER, 1992; GRAESER et al., 1992, 1995a and b; STALDER et al., 1978; HOFMANN et al., 1993). The lead arsenic sulfide minerals not only occur as masses but also as sharp, well-formed crystals exhibiting complex arrays of forms. This feature attracted the attention of morphological crystallographers in the second half of the Nineteenth Century and the first two decades of the Twentieth Century. Despite the very close structural and chemical relationships between minerals within the group, the major members (dufrénoysite, liveingite, baumhauerite, rathite and sartorite) were, for the large part, distinguished, described and defined on the basis their morphological crystallography and chemistry (as determined by wet chemical analyses) (see STALDER et al., 1978 for compilation of early analyses). Unit cell and some space group data on the minerals were later obtained by BANNISTER et al. (1939) and BERRY (1953). LE BIHAN (1962) established the structural principles for the sartorite group, describing the structures in terms of units that she designated as S (for sartorite) and R (for rathite). Nowacki and his group (NOWACKI et al., 1961)

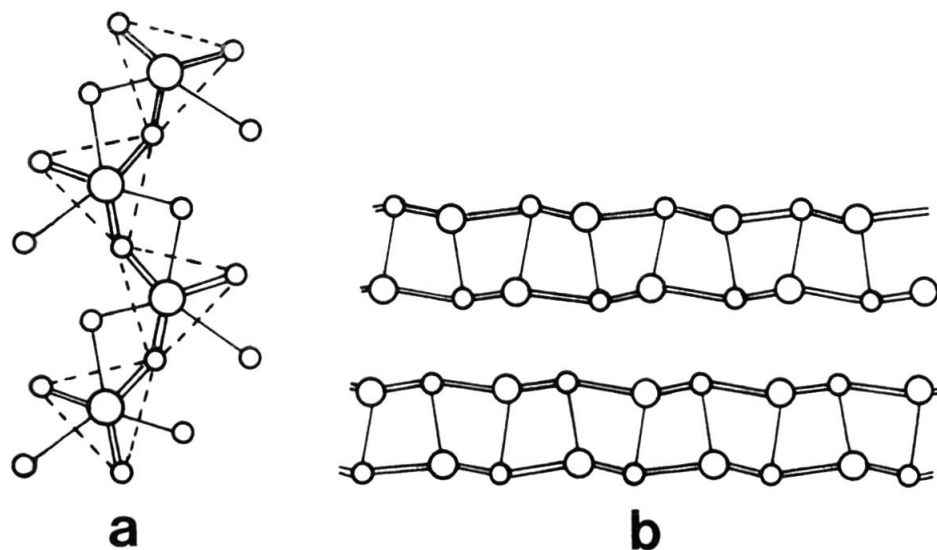


Fig. 1 Diagram showing the two structural elements which make up the structural modules in sartorite group minerals. (a) Infinite (100) planes of  $\text{PbS}_9$  tricapped trigonal prisms linked by edge-sharing in the **b** direction and face-sharing along the **c** direction. The repeat distance in the *ab*-plane is 7.9 Å and along *c* is 4.2 Å. (b) (100) slabs consisting of strips of  $(\text{Pb,As})\text{S}_{3(+2)}$  square pyramids of variable composition.

determined in detail many of the structures in the period 1961 to 1976 (see Tab. 1), and the basic structural features of the sartorite group are firmly established.<sup>1</sup> TAKÉUCHI (1970) also used a description based on R- and S- type slabs and showed how symmetry operators could be employed to generate members of the series from these basic modules. The structures of the sartorite homologues can be visualized as composed of slices of  $\text{SnS}$ -like structure cut parallel to the planes (301) and  $(30\bar{1})_{\text{SnS}}$ . These include polyhedra from both the walls and the slab and they are  $N = 3$  and  $N = 4$  polyhedra thick (MAKOVICKY, 1985).

Systematic high-resolution transmission electron microscope (HRTEM) studies of the lead arsenic sulfide mineralisation at Lengenbach were undertaken with the aim of clarifying structural and paragenetic relationships between members of the sartorite group and within the deposit (PRING, 1990; PRING et al., 1990, 1993; PRING and GRAESER, 1994; OZAWA and TAKÉUCHI, 1983, 1993; OZAWA and TACHIKAWA, 1996). This paper presents an overview of the crystal chemistry of the group and the results of recent detailed HRTEM studies. The focus is on the topological and chemical relationships between these structures without considering many of the fine-scale details of site occupancies. A number of the reported structure refinements show fractional occupancy and splitting of sites and while these are in part due to Ag or Tl substitution it should be remembered that many of these minerals are highly absorbing and the structures were determined and

refined using film methods. An element of uncertainty therefore remains about some of the occupancy factors and the positions of some of the split sites associated with cation substitutions.

### Structural relationships within the sartorite group

Compositional and structural data for the sartorite group minerals is summarized in table 1. The idealized "parent module" underlying these minerals consists of the intergrowth of two elements: infinite (100) planes of  $\text{PbS}_9$  tricapped trigonal prisms linked by edge-sharing approximately along the **b** direction and face-sharing along the **c** direction. These planes of  $\text{PbS}_9$  are linked by the second structural element, strips of edge-sharing  $(\text{Pb,As})\text{S}_{3(+2)}$  square pyramids of variable composition (Fig. 1). These two elements together constitute the basic structural modules of the sartorite group as defined by MAKOVICKY (1985). The  $\text{PbS}_9$  planes are similar to  $\text{PbCl}_9$  planes in  $\text{PbCl}_2$  (C23 structure) while the strips of  $(\text{Pb,As})\text{S}_{3(+2)}$  can be considered as (301) and  $(30\bar{1})$  slabs of distorted  $\text{GeS}/\alpha\text{-SnS}$ -like structure (B16/

<sup>1</sup> ITO and NOWACKI (1974) and RIBAR and NOWACKI (1969) reported the structures of jordanite and gratonite respectively. These two lead arsenic sulfide minerals are not members of the sartorite structural group; their structures are related to  $\text{PbS}$  by ordered substitution on the {111} planes.



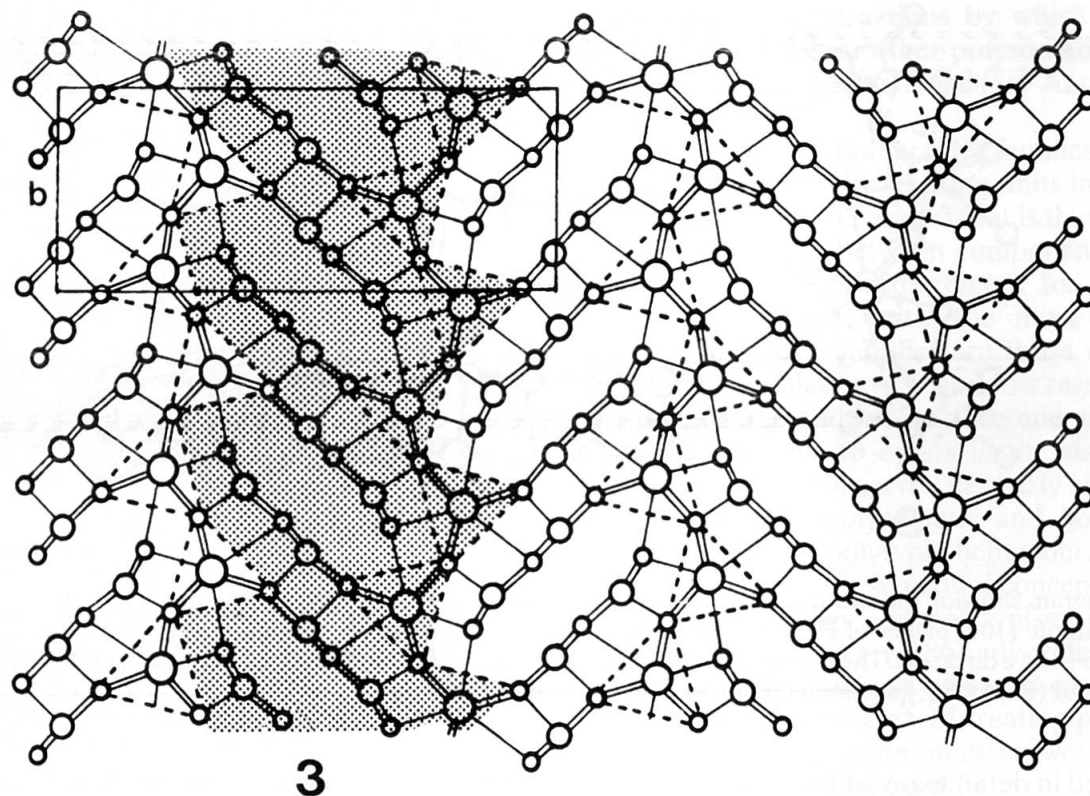


Fig. 2 Schematic diagram of the structure of sartorite down [001] (after NOWACKI et al., 1961). Note the herring bone arrangement of the  $(\text{Pb,As})\text{S}_{3(+2)}$  strips about the  $\text{PbS}_9$  planes. In sartorite the structural modules have 3 metal sites along the slab ( $N = 3$ ). Large circles Pb, medium circles As, small circles S.

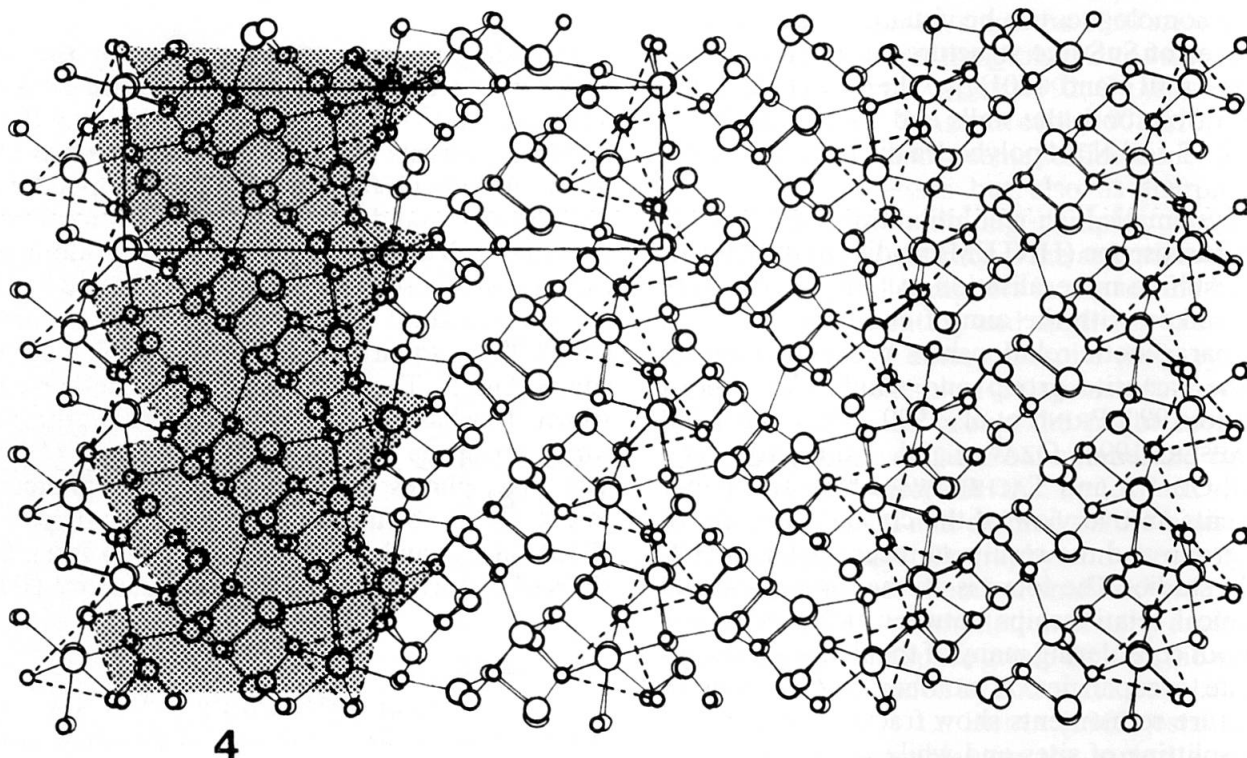


Fig. 3 The crystal structure of dufrénoysite,  $\text{Pb}_{16}\text{As}_{16}\text{S}_{40}$  (after RIBAR et al., 1969), homologue  $N = 4$  of the sartorite group down [001]. Large circles Pb, medium circles As, small circles S.

B29 structure) (SMITH and HYDE, 1983; MAKOVICKY, 1985). Two widths of the distorted  $\text{GeS}/\alpha\text{-SnS}$ -like strips are observed, thus there are two modules of different widths. These have been described by various authors as S and R units (LE BIHAN, 1962), B and C units (NOWACKI, 1969), S and D units (PRING, 1990). As noted above MAKOVICKY (1985) treats units formed by the intergrowth of the  $\text{PbS}_9$  planes and  $(\text{Pb,As})\text{S}_{3(+2)}$  strips as single units which he denotes as N = 3 and N = 4 units. This notation system, treating the two element of the structure together, will be used here as it gives the order number of the homologue (or polysome) N and can be used to calculate the number of cation sites in the structural formula (MAKOVICKY, 1985).

In general terms the formula is:



and for di- and trivalent cations it reads:



With partial  $\text{Me}^+ + \text{Me}^{3+} \rightleftharpoons 2 \text{Me}^{2+}$  substitution the formula becomes:



with  $\text{Me}^+ = \text{Ag}$  or  $\text{Tl}$ ,  $\text{Me}^{2+} = \text{Pb}$ ,  $\text{Me}^{3+} = \text{As}$ ,  $\text{Sb}$ .

There are modules three polyhedral wide (two  $(\text{Pb,As})\text{S}_{3(+2)}$  'square pyramids' and a  $\text{PbS}_9$  tricapped trigonal prism) (N = 3) (Fig. 2) as in sartorite, or four polyhedral wide (three  $(\text{Pb,As})\text{S}_{3(+2)}$  'square pyramids' and a  $\text{PbS}_9$  tricapped trigonal prism), as in dufrénoysite (N = 4) (Fig. 3). In the case of baumhauerite, the module width alternates 3 and 4 polyhedral in an ordered manner leading to a monoclinic parent structure. This homologue can be denoted 3,4. In all the above cases, the unit cells contains only two such slabs. Liveingite, by contrast, has a 6 slab repeat, 4,3,4,4,3,4; "the 115 Å mineral" has a 10 slab repeat, 4,3,4,3,4,4,3,4,3,4 and "the 138 Å mineral" has a 12 slab repeat: 4,3,4,3,4,4,3,4,3,4,3,4.

The related structural architecture of this group imposes certain common underlying structural parameters – the  $\sim 7.9$  Å repeat length of the planes of  $\text{PbS}_9$  tricapped trigonal prisms along **b** and the  $\sim 4.2$  Å repeat length of the height of the  $\text{PbS}_9$  tricapped trigonal prisms along **c**. The repeat length of the underlying parent structure along **a**,  $a_p$  ( $p$  for parent), depends upon the widths (and, to some extent, the composition) of the  $\text{GeS}/\alpha\text{-SnS}$ -like strips. The 3 polyhedral module is approximately 9.8 Å wide while the 4 polyhedral module is approximately 12.8 Å wide. In rathite the 4 module is only 12.3 Å wide ( $\sim 0.5$  Å less than in dufrénoysite, due to the partial replacement of Pb

by As in the  $(\text{Pb,As})\text{S}_{3(+2)}$  strip). In the case of baumhauerite, with its 3,4 sequence the parent **a** axis dimension is  $\sim 22.8$  Å (i.e.  $\sim 9.8 + 12.8$  Å). In all members of the group the underlying parent structures with cell dimensions  $a_p, b_p \sim 7.9$  Å,  $c_p \sim 4.2$  Å are displacively and compositionally modulated (PRING et al., 1993) (see Tab. 1). The nature of these modulations is discussed below.

## Experimental

### MATERIAL EXAMINED

Crystals and massive patches of the sartorite group minerals from the Lengenbach deposit were obtained from the collections of the South Australian Museum, Adelaide; the Museum of Victoria, Melbourne; the Department of Earth Sciences, University of Cambridge; and the Natural History Museums in Bern, Basel and London. The minerals were identified by powder X-ray diffraction (Guinier-Hägg patterns) and electron diffraction. The close chemical and structural similarities between the minerals in the group make it impossible to identify the individual minerals based on their physical properties or appearance. Not surprisingly, many of the museum specimens examined in this study were found to be incorrectly labeled. This problem is particularly so in the case of dufrénoysite and rathite. It is also clear from the results of this study that the rathite minerals (rathite, rathite III and rathite-IV) and "the 115 Å mineral" are very rare at Lengenbach. Baumhauerite, liveingite and sartorite were the most frequently encountered members of the series, whereas dufrénoysite and baumhauerite-2a were uncommon to rare.

### ELECTRON MICROSCOPY

For examination in the electron microscope, crystals or crystal fragments were generally prepared by grinding under an organic solvent in an agate mortar and then dispersed on Cu grids coated with holly carbon support films. The specimens were examined in several different transmission microscopes but mainly a specially modified JEOL 200 CX, 200 kV with theoretical point-to-point resolutions in the range 1.8–2.8 Å (depending on the goniometer and pole-pieces in use).

A large number of specimens of the various minerals were examined with a view to confirming their identification and to assess their structural state.

## Results

### SARTORITE GROUP

#### Dufrénoysite

Dufrénoysite was one of the first of the lead arsenic sulfide species to be described from Lengenbach; it was described by Damour in 1845 (see PALACHE et al., 1944) but his crystallographic measurements corresponded to tennantite. The mineral was redefined by von Rath in 1864 and later by Solly in 1902 (see PALACHE et al. (1944) for summary of early work). An antimony dominant analogue, veenite,  $\text{Pb}_2(\text{Sb,As})_2\text{S}_5$  occurs at Madoc, Ontario, Canada (JAMBOR, 1967a). The structure of dufrénoysite was determined by MARUMO and NOWACKI (1967) and a more detailed refinement was published by RIBAR et al. (1969). Dufrénoysite is a 4,4 homologue and the unit cell contains  $\text{Pb}_{16}\text{As}_{16}\text{S}_{40}$ , and the GeS/ $\alpha$ -SnS-like slabs have a cation composition  $\text{Pb}_4\text{As}_8$ . The structure is shown in figure 3. The mineral is compositionally modulated leading to a doubling of  $c_p$  to 8.4 Å. The structure effectively consists of two layers (the height of two face-sharing  $\text{PbS}_9$  tri-capped trigonal prisms) and the cations sites in the GeS/ $\alpha$ -SnS-like strips are paired over  $c$ . One pair of sites contains only Pb, two others contain a

Pb and an As (a Pb/As pair) and three sites contain As pairs (see Fig. 3). Figure 4a shows a [100] zone electron diffraction pattern, note intensity distribution of the subcell reflections, the absences due to the  $2_1$  screw are evident but very weak reflections are present due to multiple scattering. A high-resolution image shows the two layer nature of the structure (Fig. 4b). The crystal shown is well ordered and no defects were observed. All crystals of dufrénoysite examined in the HRTEM studies reviewed here were found to be well ordered, polysomatic disorder was absent.

Analyses of dufrénoysite show it to be generally close to ideal composition with little Ag, Sb or Tl substitution (see STALDER et al., 1978). Burri (in MARUMO and NOWACKI, 1967) reported a "dufrénoysite" containing 4% Tl intergrown with Tl-free dufrénoysite, but the mineral was in all probability rathite (see below). Veenite from Madoc shows significant As substitution for Sb (ratio Sb:As 1.5:1) (JAMBOR et al., 1982). NOWACKI et al. (1961) reported a fibrous sulfosalt that appeared to be an oriented intergrowth of dufrénoysite crystals on (001) or (010). A number of samples of the "fibrous sulfosalt" were examined by powder X-ray diffraction and the majority were found to be dufrénoysite. A fibrous form of baumhauerite was also found growing on the surface of some massive baumhauerite.

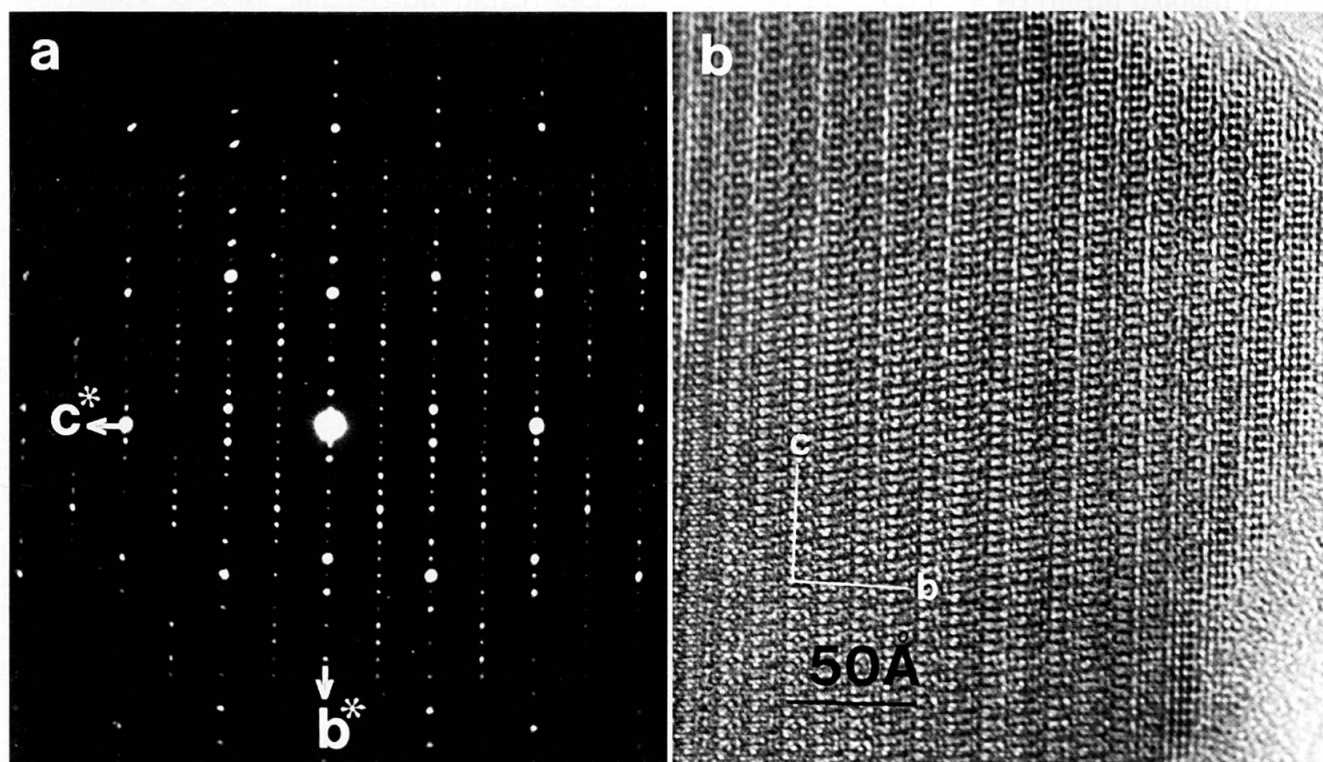


Fig. 4 (a) and (b). [100] zone electron diffraction pattern and image for dufrénoysite. Note the sharp spots in the diffraction pattern and the lack of disorder in the image.



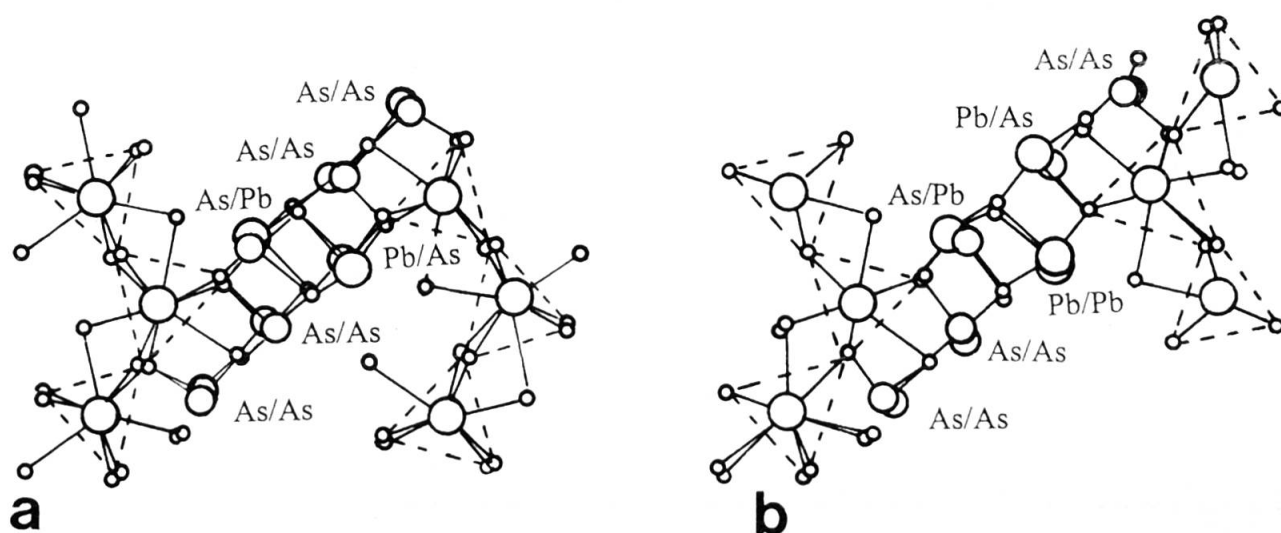


Fig. 5 Schematic diagram highlighting the similarities and differences between elements in the rathite and dufrénoysite structures. Both are  $N = 4$  homologues. (a) The  $(\text{Pb},\text{As})\text{S}_{3(+2)}$  strips in rathite contain four As/As pairs and two Pb/As pair. (b) The  $(\text{Pb},\text{As})\text{S}_{3(+2)}$  strips in dufrénoysite contain three As/As pairs, two Pb/As pairs and a Pb/Pb pair. Large circles Pb, medium circles As, small circles S.

### The Rathite problem

Rathite was described from Lengenbach by BAUMHAUER (1896) and as far as can be ascertained the mineral has not been found elsewhere. Crystals of rathite are usually twinned (MARUMO and NOWACKI, 1965) and when in the early part of the Twentieth Century morphological crystallographers encountered untwinned crystal a number of "new minerals" were described which were later shown to be "rathite" (LEWIS, 1912; SOLLY, 1911). This trend did not end at the turn of the century as modern crystallographers have also described a number of varieties of rathite. BERRY (1953) attempted to determine the cell parameters of rathite using part of a crystal originally analyzed by SOLLY and JACKSON (1901) and found the mineral to be a homologue with a 70 Å repeat which he called rathite II. Berry's rathite II was later shown to be liveingite (NOWACKI, 1967). In fact, all of the early analyses for rathite summarized in STALDER et al. (1978) correspond to liveingite.

LE BIHAN (1962) described three rathites which she designated rathite I, rathite II and rathite III. Her rathite II corresponded to Berry's mineral of the same name and is liveingite. The rathite I of Le Bihan was later shown to be dufrénoysite and in the literature it also figures as rathite 1a (MARUMO and NOWACKI, 1967). Rathite III is discussed below. NOWACKI and BAHEZRE (1963) published an analysis for rathite which gave the formula  $\text{Pb}_{11.1}\text{Ti}_{0.9}\text{As}_{16}(\text{As}_{1.6}\text{Ag}_{2.4})\text{S}_{40}$ . The crystal structure of this rathite was determined by MARUMO and NOWACKI (1965) and thus

the mineral was effectively redefined based on this compositional and structural data. The rathite structure is similar to dufrénoysite; both are 4,4 homologues and rathite can be derived from dufrénoysite by replacing one of Pb atoms in the Pb pair with As and Ag (split occupancy on one site) and the Pb in an Pb/As string linked to the  $\text{PbS}_9$  layers with As (Fig. 5). The arrangement (ordering) of Pb and As atoms in the  $(\text{Pb},\text{As})\text{S}_{3(+2)}$  strip leads to a doubling of both  $c_p$  and  $a_p$  axis. The resultant  $2a_p \times b_p \times 2c_p$  supercell is B-centred and hence can be reset into the conventional monoclinic cell  $a' = a_p - c_p$ ,  $b' = b_p$ ,  $c' = 2c_p$ .

Figure 6a shows a [010] zone electron diffraction pattern, note intensity distribution of the strong subcell reflections. A high-resolution image shows the two layer nature of the structure (Fig. 6b). The zig-zag nature of the structure down the [001] is illustrated in figure 7. The crystal is well ordered and no defects were observed. Although MARUMO and NOWACKI (1965) reported that rathite was usually polysynthetically twinned, no evidence of twinning or disorder was noted in the electron diffraction patterns or images.

Rathite and dufrénoysite, which are both 4,4 homologues, may be members of a complex "compositional series". As noted above Burri (in MARUMO and NOWACKI, 1967) a "dufrénoysite" containing 4% Tl was found to host lamella of Tl-free dufrénoysite. It has been postulated that it may represent a rathite-dufrénoysite intergrowth (MAKOVICKY, 1985). The analysis by NOWACKI and BAHEZRE (1963) is the only published analysis of rathite. A second set of elec-

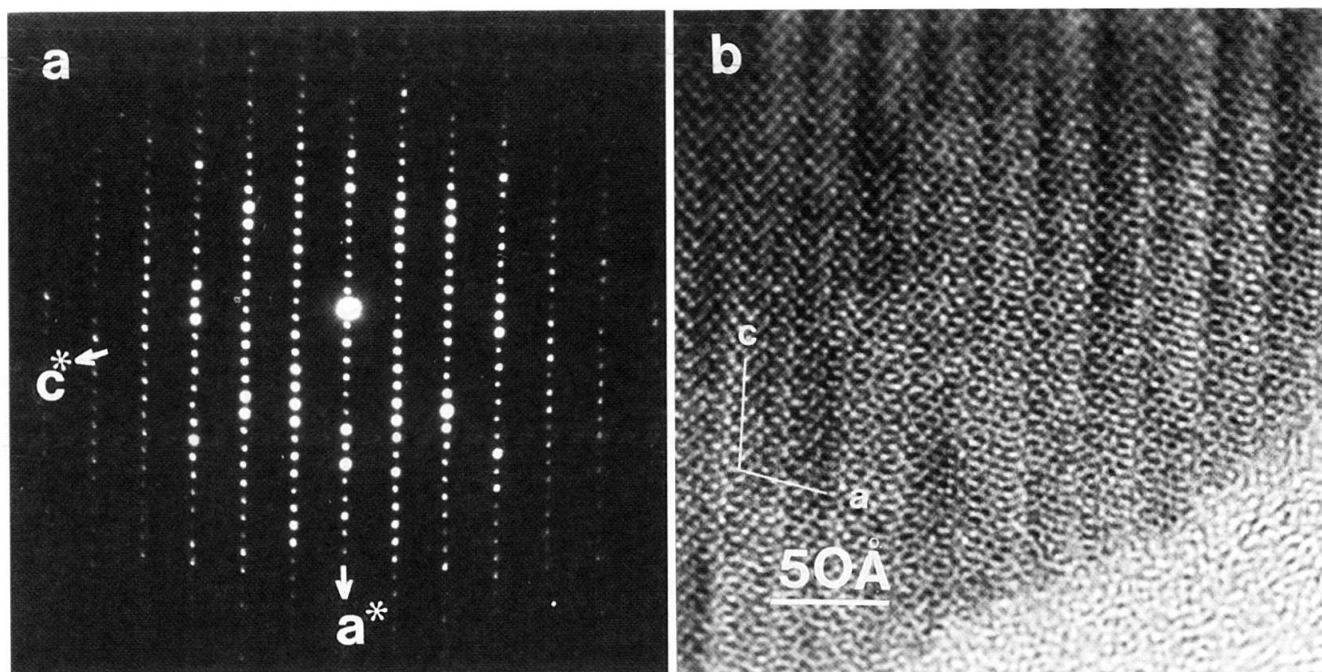


Fig. 6 [010] zone electron diffraction pattern and image for rathite. Note the well ordered nature of the image.

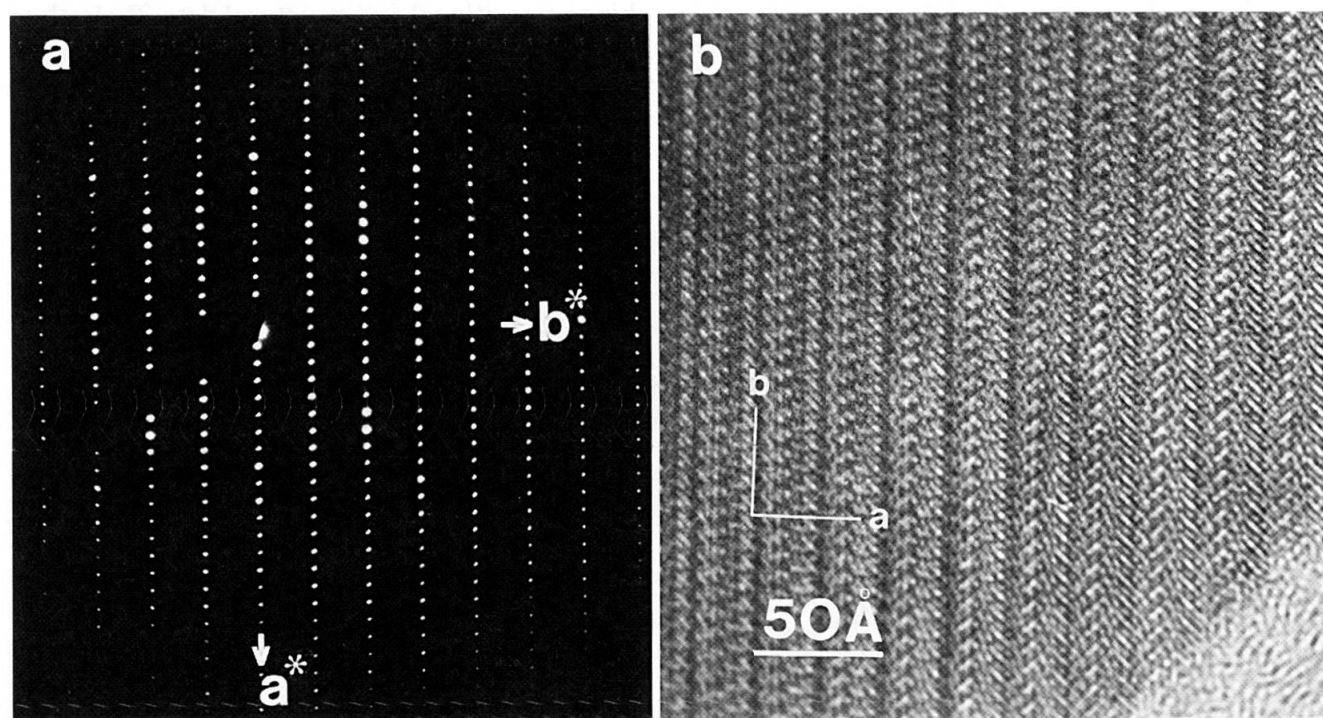


Fig. 7 [001] zone electron diffraction pattern and image for rathite showing the 4,4 herring bone nature of the structure.

tron microprobe analyses gave: Pb 45.48; As, 25.74; S, 24.54; Ag, 3.46; Tl 1.07; Total 100.29 wt% (Graeser unpublished results) and this gives a formula:  $\text{Pb}_{11.48}\text{Ag}_{1.67}\text{Tl}_{0.27}\text{As}_{17.95}\text{S}_{40}$ . The two rathite analyses are fairly close although Ag seems to play the same role as Tl in the second set and the formula calculated from them should be com-

pared to that of dufrénoysite. The compositions are derived from dufrénoysite by the substitution  $(\text{Ag} + \text{Tl}) + \text{As} = 2 \text{Pb}$ . It appears from the structural solution of MARUMO and NOWACKI (1965), that rathite is an ordered intermediate between dufrénoysite and a theoretical end member  $\text{Pb}_8(\text{Ag,Tl})_8\text{As}_{24}\text{S}_{40}$ .



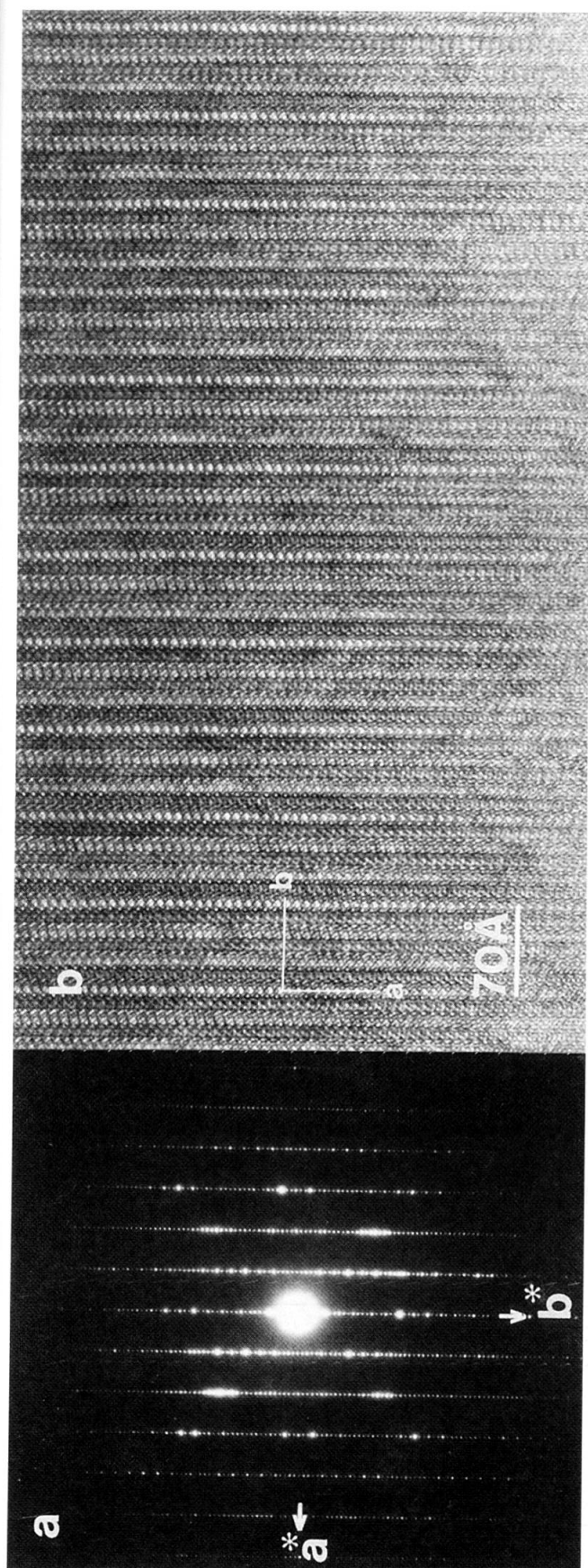


Fig. 8 [001] zone electron diffraction pattern and image for liveingite. Note the well ordered nature of the 70 Å repeat.

The coupled-substitution of  $(\text{Ag} + \text{Tl}) + \text{As} = 2\text{Pb}$  results in a change in cell dimension and in symmetry. Dufrénoysite is monoclinic (pseudo-orthorhombic) with space group  $P2_1$  whereas rathite is triclinic (pseudomonoclinic,  $P2_1/a$ ).

LE BIHAN (1962) reported an pseudo-orthorhombic ( $\beta = 90^\circ$ ) form of rathite which she designated rathite III based on a structure refinement in which  $R \approx 20\%$ . MARUMO and NOWACKI (1965) considered rathite III to be a stacking variant of rathite. Such a polymorph is possible as rathite has the compositional modulation  $\mathbf{q}_p = \frac{1}{2}(\mathbf{a}^* + \mathbf{c}^*)$  for the Pb/As sites in the  $(\text{Pb}, \text{As})\text{S}_{3(+2)}$  strips and it is possible, by simply reordering the Pb/As, to have a pseudo-orthorhombic form with a compositional modulation  $\mathbf{q}_p = \frac{1}{2}\mathbf{c}^*$ .

KUTOGLU (1969) reported the phase diagram for the  $\text{PbS}-\text{As}_2\text{S}_3$  system and rathite and rathite III were the only the sartorite group minerals which could not be produced synthetically. RÖSCH and HELLNER (1959) reported preparing Tl- and Ag-free rathite via hydrothermal methods. However, their report is very brief and it is not clear how their reaction products were identified.

In conclusion, rathite appears to be an extremely rare ordered compositional derivative of dufrénoysite. An exhaustive search of many Lengenbach specimens in the current studies failed to find a specimen of rathite III. This phase maybe an ordering variant of rathite, but the possibility that LE BIHAN (1962) studied a twinned crystal of rathite can not be excluded. The existence of rathite III remains doubtful.

### Liveingite

Liveingite was described from Lengenbach by SOLLY and JACKSON (1901) and as far as can be ascertained it has not been found elsewhere. The rathite II of BERRY (1953) and LE BIHAN (1962) was later shown to be to liveingite (NOWACKI, 1967). The broad topology of the structure was reported by LE BIHAN (1962) and refined in detail by ENGEL and NOWACKI (1970) based on the composition  $\text{Pb}_{18.5}\text{As}_{25}\text{S}_{56}$ . Liveingite is the 4,3,4,4,3,4 homologue with an average  $N = 3.67$  and the first three units are related to the second three by a  $2_1$  screw axis (space group  $P2_1$ ) and the long cell repeat is 70.49 Å. The compositions of the individual homologue units (including the  $\text{PbS}_9$  layers) are very close to  $\text{Pb}_7\text{As}_9\text{S}_{20}$  ( $N = 4$ ) and  $\text{Pb}_5\text{As}_9\text{S}_{16}$  ( $N = 3$ ). The refinement of ENGEL and NOWACKI (1970) showed that the first 4 unit ( $N_4$ ) is slightly different to the second ( $N_4$ ), due to fractional occupancies of one of the As sites and the actual compositions are closer to  $\text{Pb}_{6.75}\text{As}_{9.25}\text{S}_{20}$  and

$\text{Pb}_{6.75}\text{As}_9\text{S}_{20}$ , respectively. However, given the uncertainties associated with the refinement of this large structure, the difference may not be significant. Published chemical analyses for liveingite show little variation in composition or substitution of Ag, Sb or Tl. NOWACKI and BAHEZRE (1963) report minor substitution of Sb for As. Recent discoveries at the new Lengenbach quarry include a Tl-rich liveingite containing about 4 wt% Tl (Graeser, unpublished results). Despite its long polysomatic repeat sequence, which would indicate that some stacking disorder could be expected, extensive HRTEM studies of liveingite and the Tl-rich liveingite failed to reveal any polysomatic disorder. The images are all well ordered and the diffraction spots sharp (Fig. 8).

#### The 115 Å mineral, the 138 Å phase and rathite(IV)

NOWACKI et al. (1963) described a Pb–As–S mineral from Lengenbach with  $a \approx 140$  Å repeat which they denoted rathite IV. This mineral was re-examined by OZAWA and NOWACKI (1974) using single crystal X-ray diffraction photographs and accurate cell parameters where obtained with  $a = 138.3$  Å (see Tab. 1), these authors also noted that the mineral was invariably twinned and occurred in oriented intergrowth with liveingite, with the long axes of the two minerals and the two 7.9 Å axes being parallel. OZAWA and TACHIKAWA (1996) reported results of a TEM study of a Pb–As–S mineral with a 138 Å repeat. They were able to demonstrate that the mineral was not a simple supercell of liveingite but rather a distinct homologue with the structural sequence 4,3,4,3,4,4,3,4,3,4,3,4 (9.8 Å  $\times$  5 + 12.8 Å  $\times$  7 = 138.6 Å) (Fig. 9). They also noted that the mineral occurs with baumhauerite and sartorite rather than with liveingite. It would appear to be identical to rathite IV of OZAWA and NOWACKI (1974). Using the average homologue number of  $N = 3.58$ , and the general formula of MAKOVICKY (1985) ( $\text{Me}^{2+}_{4N-8}\text{Me}^{3+}_8\text{S}_{4N+4}$ ) a calculation of the formula gives  $\text{Pb}_{38}\text{As}_{48}\text{S}_{110}$ . The stoichiometry obtained from the following electron microprobe analysis: Pb 46.82; As, 25.76; S, 24.65; Sb, 0.77; Ag, 2.09; Total 100.09 wt% (Graeser unpublished results) gives a  $\text{Pb}_{32.3}\text{Ag}_{2.8}\text{As}_{49.2}\text{Sb}_{1.0}\text{S}_{110}$ , which is in good accord with the general formula if the coupled substitution of  $2\text{Pb} = \text{Ag} + \text{As}$  and the substitution of Sb for As are taken into account.

The 8.4 Å repeat, indicates that the mineral is compositionally modulated, however details of the nature of the Pb/As ordering in the  $(\text{Pb},\text{As})\text{S}_{3(+2)}$  strips awaits single crystal structure determination.

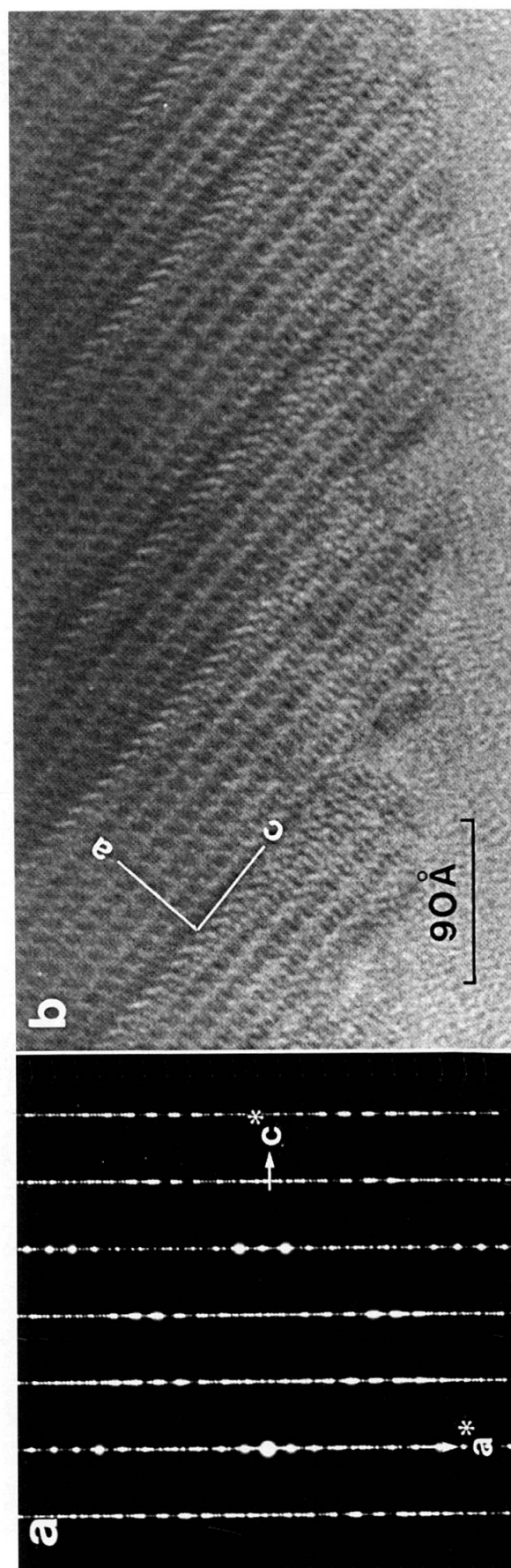


Fig. 9 [010] zone electron diffraction pattern for the 138 Å phase. Note the 4,3,4,3,4,3,4,3,4,3,4 sequence in the image.

OZAWA and TAKÉUCHI (1983) reported a sartorite group mineral with a 115 Å repeat. This mineral was approved by the IMA CNMMN in 1998 but the formal description is yet to be published (GRICE and FERRARIS, 1999). The long cell repeat of 115.75 Å corresponds to the 10 slab sequence is 4,3,4,3,4,4,3,4,3,4, (9.8 Å × 4 + 12.8 Å × 6 = 116 Å) (OZAWA and TACHIKAWA, 1996). The composition reported is  $\text{Pb}_{32}\text{As}_{40}\text{S}_{92}$  is in accord with the general formula for 10 repeat homologue with an average  $N = 3.6$ . The structure is compositionally modulated, as indicated by the 8.368 Å repeat corresponding  $2c_p$ ; however, details of the nature of the Pb/As ordering in the  $(\text{Pb},\text{As})\text{S}_{3(+2)}$  strips and the exact compositions of the  $N = 3$  and  $N = 4$  units are unknown. Given that the mineral is compositionally intermediate between liveingite and baumhauerite, it seems likely that the slabs are similar to those in liveingite ( $N = 4$ ,  $\text{Pb}_7\text{As}_9\text{S}_{20} \times 6$  and  $N = 3$ ,  $\text{Pb}_5\text{As}_9\text{S}_{16} \times 4$ ) and baumhauerite.

#### Baumhauerite and the baumhauerite polytypes

Baumhauerite was described by SOLLY (1903) and is perhaps the most widespread of the sartorite group minerals having been reported from at least five other localities, in addition to Lengenbach (ANTHONY et al., 1990). An antimony analogue of baumhauerite occurs at Madoc, Ontario, Canada (JAMBOR et al., 1982). Baumhauerite-2a was described as a silver-rich mineral with a 2a supercell of baumhauerite (PRING et al., 1990) and a Tl-rich form of baumhauerite-2a was also reported from Quiruvilca, Peru (ROBINSON and HARRIS, 1987; PRING et al., 1990). It was later suggested that baumhauerite-2a was probably a polytype of baumhauerite and a 3a polytype was also reported (PRING and GRAESER, 1994). DUNN (1995) reported baumhauerite from Sterling Hill, New Jersey, which has a 3c supercell ( $3 \times 7.9$  Å). The structure of baumhauerite was determined in detail by ENGEL and NOWACKI (1969) following the earlier approximate determination by

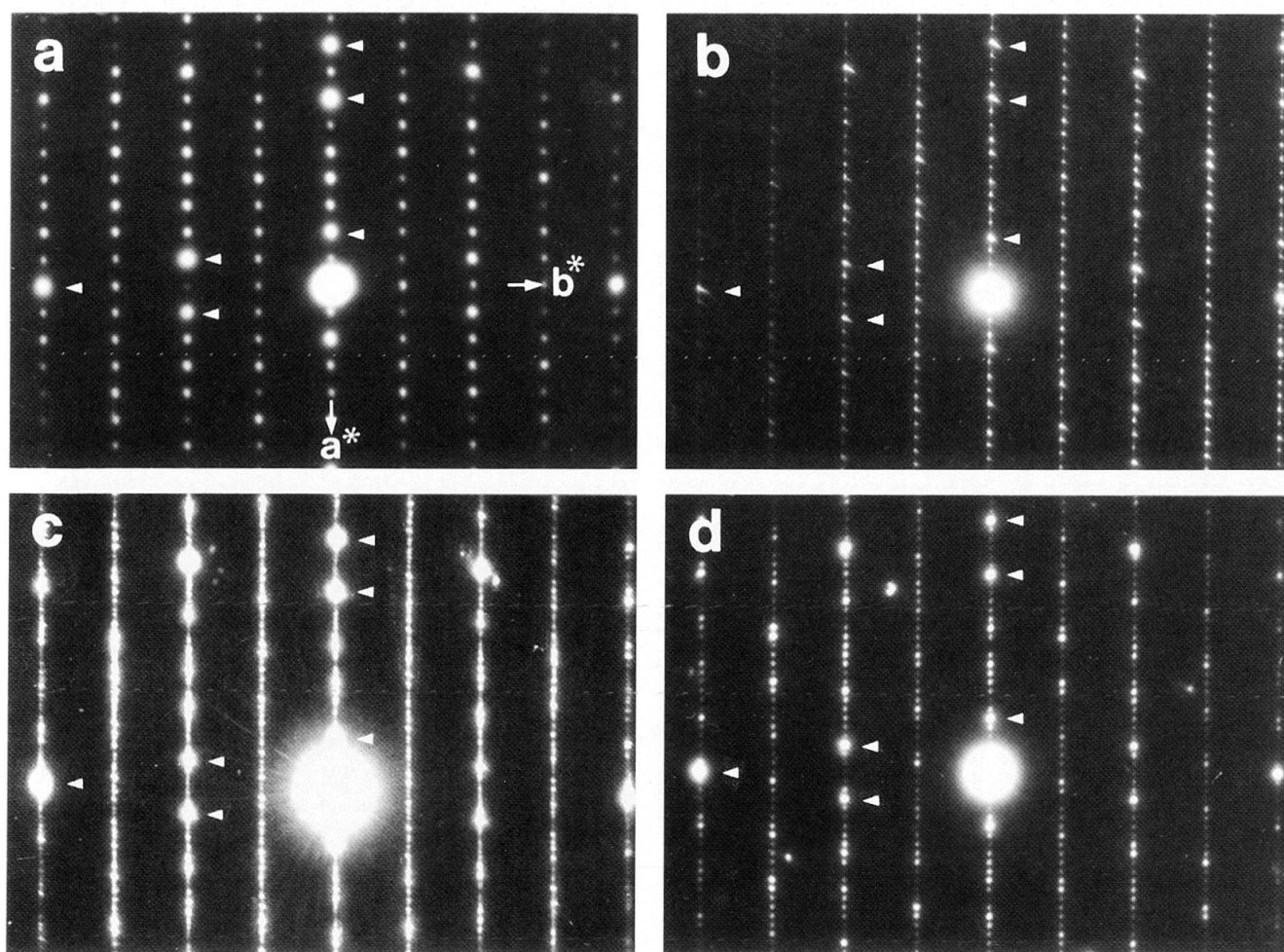


Fig. 10 [001] zone electron diffraction patterns for the baumhauerite polytypes. (a) baumhauerite, (b) baumhauerite-2a, (c) polytypic disorder in baumhauerite and (d) baumhauerite- $\Psi\text{O}3abc$ . Note the common set of subcell reflections, indicated by white arrow heads.



LE BIHAN (1962). In baumhauerite the structural sequence is 4,3. The composition of the  $N = 4$  unit is  $\text{Pb}_7\text{As}_9\text{S}_{20}$ , similar, though not identical to the  $N = 4$  units in liveingite. There is evidence that Ag replaces As on one site in the  $N = 4$  unit. The composition of the  $N = 3$  unit is  $\text{Pb}_5\text{As}_7\text{S}_{16}$  and thus should be compared with the  $N = 3$  unit of sartorite  $\text{Pb}_4\text{As}_8\text{S}_{16}$  (see below). As with the other sartorite minerals discussed above, the baumhauerite structure can be derived by the compositional modulation of simple parent, resulting in a doubling of  $c_p$ . This modulation is also indicated by the distribution of strong subcell reflections in the  $[001]$  zone electron diffraction patterns for

baumhauerite and its 'polytypes' (Fig. 10). Note that the strong subcell reflections are present in all baumhauerite polytypes, including crystal fragments showing strong stacking disorder. High-resolution images corresponding to these diffraction patterns are shown in figure 11.

PRING and GRAESER (1994) showed that polytypism was the result of the periodic inversions of the Pb/As compositional modulation about the  $c$  repeat. Thus, using arrows to denote the relative orientation of the Pb/As in the cells, the sequence in baumhauerite is  $\uparrow\uparrow\uparrow\uparrow\uparrow$  in baumhauerite-2a is  $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$  and in baumhauerite- $\psi\text{O}3abc$ ,  $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow$ . However the ubiquitous presence of Ag or Tl in

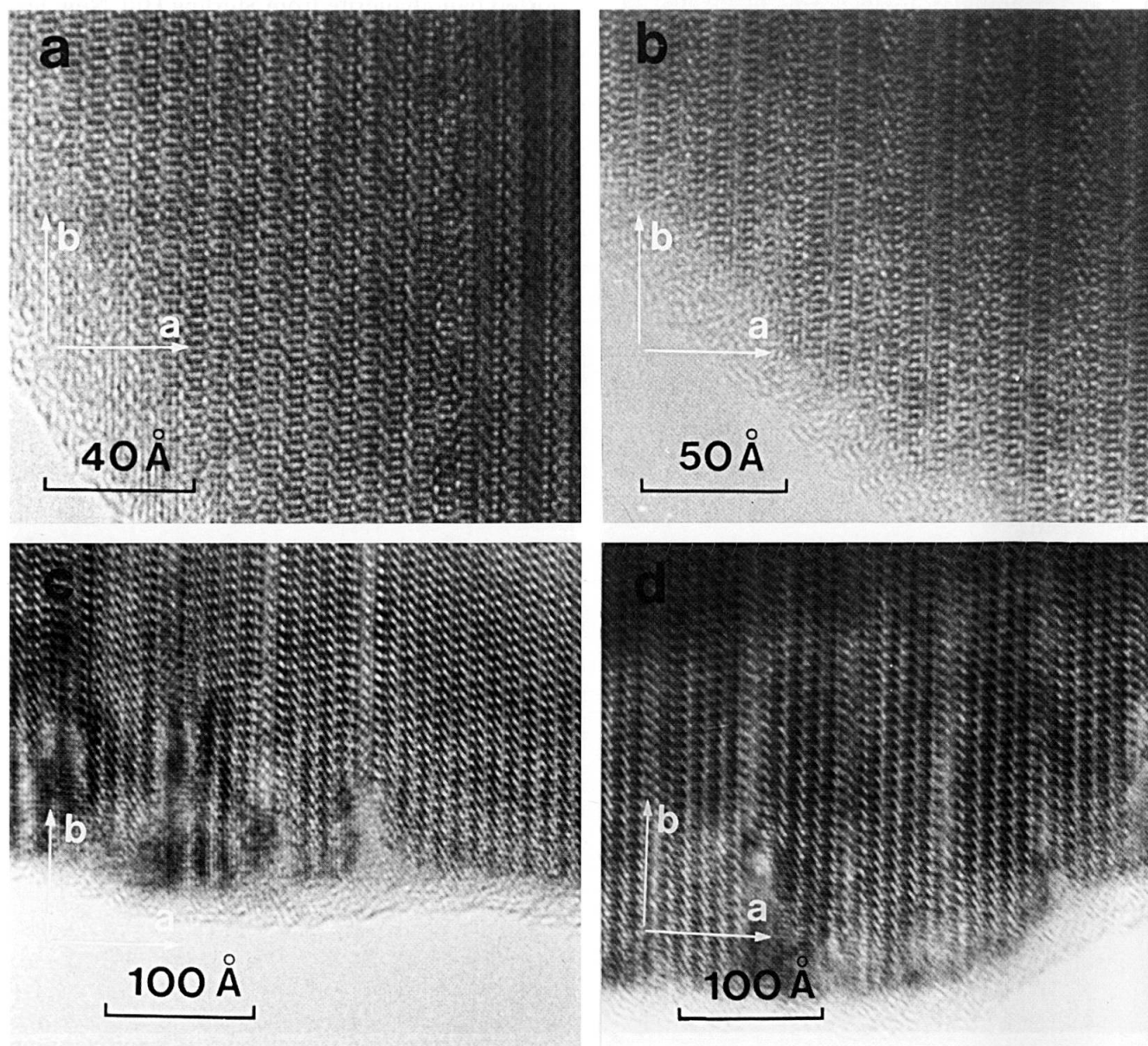


Fig. 11 [001] zone lattice images for the baumhauerite polytypes. (a) baumhauerite, (b) baumhauerite-2a, (c) polytypic disorder in baumhauerite and (d) baumhauerite- $\psi\text{O}3abc$ .

natural baumhauerite-2a indicates that these monovalent ions may play an important role in structural stabilization of the higher polytypes, although the exact structural role is yet to be resolved. PRICE and YEOMANS (1984) noted that, in many polytypic systems, phases are stabilized by impurities, thus obscuring correlations of structure with variables such as temperature and pressure. Longer period polytypes such as  $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow$  and  $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow$ , which have stability fields in PRICE and YEOMANS (1984) theoretical stability diagram have not been observed for baumhauerite.

### Sartorite and complex structural modulations

The sartorite was first described under the name scleroclase by Walterhausen in 1857 (PALACHE et al., 1944). Subsequently Dana proposed the name sartorite, for Sartorius Walterhausen, and this has gained general acceptance amongst English speaking mineralogists (PALACHE et al., 1944). Sartorite has also been reported from the Zuni Mine, Colorado and from the Pitone marble quarry in the Apuane Alps, Italy (ANTHONY et al., 1990). The antimony analogue, twinnite, was originally described by JAMBOR (1967b) from Madoc, Ontario, Canada and twinnite has subsequently been reported from a number of other localities (ANTHONY et al., 1990). Sartorite is the 3,3 homologue, with As fully occupying the cation sites in the  $(\text{Pb,As})\text{S}_{3(+2)}$  strips and the overall stoichiometry is  $\text{PbAs}_2\text{S}_4$ . The simple stoichiometry of sartorite belies the complexity of its crystallography and structure.

X-ray diffraction studies by BANNISTER et al. (1939) showed the mineral to be monoclinic but with a strong orthorhombic subcell,  $a = 19.46$ ,  $b = 7.79$ ,  $c = 4.17$  Å with a  $3a \times b \times 20c$  supercell, i.e.  $a' = 58.38$ ,  $b' = 7.79$ ,  $c' = 83.30$  Å,  $\beta = 90^\circ$ . NOWACKI et al. (1961) confirmed the orthorhombic subcell but found a  $3a \times b \times 11c$  monoclinic supercell and refined the structure of the subcell unit. IITAKA and NOWACKI (1961) further refined the structure, but were unable to resolve the exact nature of the  $\text{As}_2\text{S}_3$  chains running along the  $[001]$  direction. The subcell structure is shown in figure 2.

OZAWA and TAKÉUCHI (1993) examined sartorite by precession X-ray diffraction photographs and selected area electron diffraction. They concluded that two superstructure "forms" could co-exist in the same sartorite crystal: a monoclinic form and an orthorhombic form. Twinning, intergrowth and periodic antiphase boundaries result in the complex array of diffraction patterns observed in some fragments. They concluded that

the superstructures were modulated and suggested that the mineral underwent a displacive phase transition during cooling. In a contemporary study by TEM, PRING et al. (1993) showed that the mineral has a monoclinic (but metrically orthorhombic) subcell, but that the compositional modulation found in the other sartorite group minerals was absent and instead, the structure was displacively modulated. In sartorite the modulation is generally incommensurate and the primary modulation wave vector is  $\sim 6/13$   $(101)^*$ . Some variation in the direction of the primary modulation wave vector was observed. In some crystal fragments the primary modulation wave vector is "locked in" along  $[101]$  giving a commensurate superstructure, with higher harmonics of the wave vectors overlapping and reinforcing each other (Fig. 12a). In other crystal fragments the wave vector was rotated by up to  $3^\circ$  away from  $[101]^*$  towards  $[001]^*$  (Fig. 12b). Crystal fragments containing twinned orientation of the superlattices were also observed. Figure 13 shows an electron diffraction pattern with twinning orientation of the primary modulation wave vector on the  $(001)$  plane: the two directions of the wave vector are labeled. All of the complex supercells reported by earlier workers, were due to twinning and the break down of lateral correlation.

PRING et al. (1993) could not resolve the origin of the structural modulation but concluded that it is probably due to a longitudinal displacements of S and As in the As-S chain which run along  $c$ ; the S atoms which fail to bridge correctly between As atoms and are displaced towards the plane  $(001)$  (see Fig 14). This process leads to the subdivision of the As-S chain into segments of variable length. The Pb atoms in the  $\text{PbS}_9$  planes might also be displaced along  $a$  so as to fill up the gap left by the displacement of the S atoms.

The equivalence of the  $(101)$  and  $(10\bar{1})$  planes in the substructure provides a plausible explanation for the observed twinning. Substitution of Pb for As in the  $(\text{Pb,As})\text{S}_{3+2}$  strips, as observed in baumhauerite could be expected to stabilize the superstructure and 'lock in' the structural modulation to a commensurate value. The presence of a displacive modulation indicates that the mineral undergoes displacive phase transition at higher temperature although no such transitions have yet been reported in the Pb-As-S minerals. When heated in the electron beam in the TEM sartorite decomposes rapidly. KUTOGLU (1969) found that sartorite decomposes to form baumhauerite and liquid at  $305^\circ\text{C}$ .



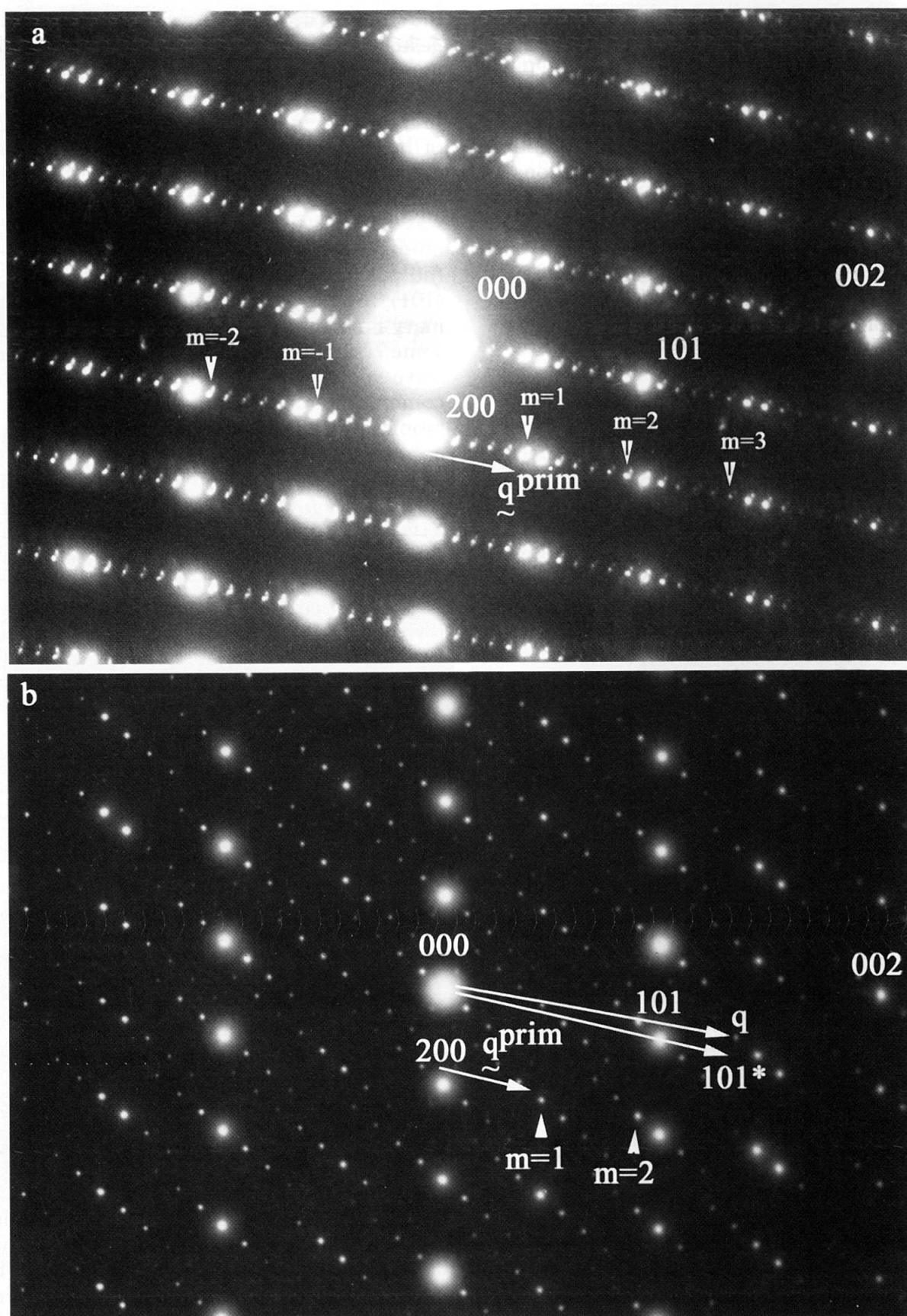


Fig. 12 [010] electron diffraction patterns of sartorite, showing variations in the direction of the displacive modulation. Note that the satellite reflections  $6/13(101)^*$  and  $7/13(101)^*$  are very strong. These satellite reflections represent the primary modulation vector  $\mathbf{G} \pm \mathbf{q}^{\text{prim}}$ , with  $\mathbf{q}^{\text{prim}}$  defined as  $6/13(101)^*$ . The higher order harmonics ( $m = 2, 3, \dots$ ) of  $\mathbf{q}^{\text{prim}}$  are indicated. (a) Commensurate along  $[101]^*$ . (b) Rotated  $3^\circ$  away from  $[101]^*$  towards  $[001]^*$ . The value of  $\mathbf{q}^{\text{prim}}$  is again  $\approx 6/13(101)^*$ .

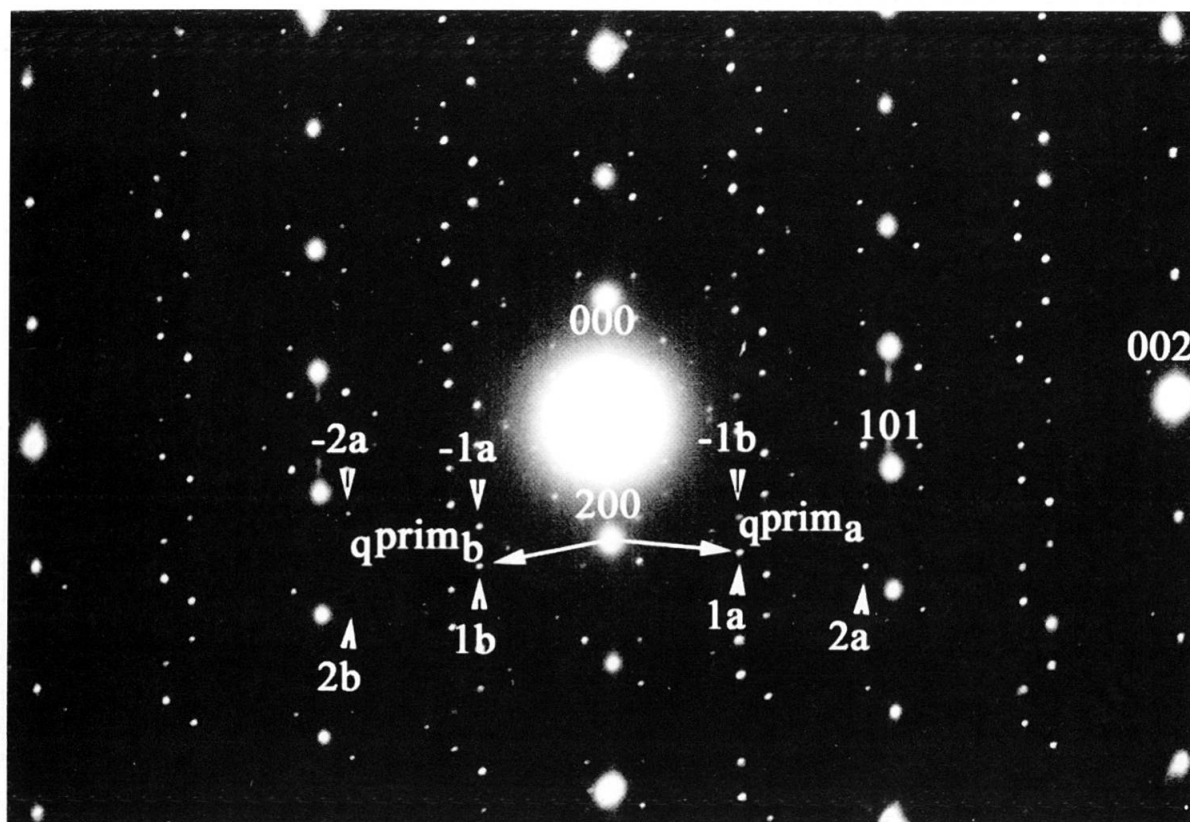


Fig. 13 [010] zone electron diffraction pattern of sartorite showing twinned orientations of the structural modulations. The primary modulation vectors are  $\mathbf{G} \pm \mathbf{q}^{\text{prim}}$ , and  $\mathbf{q}^{\text{prim}}$  are  $6/13(101)^*$  and  $6/13(10-1)^*$ . The higher order harmonics ( $m = 2, 3, \dots$ ) of  $\mathbf{q}^{\text{prim}}$  for each of the twins are indicated.

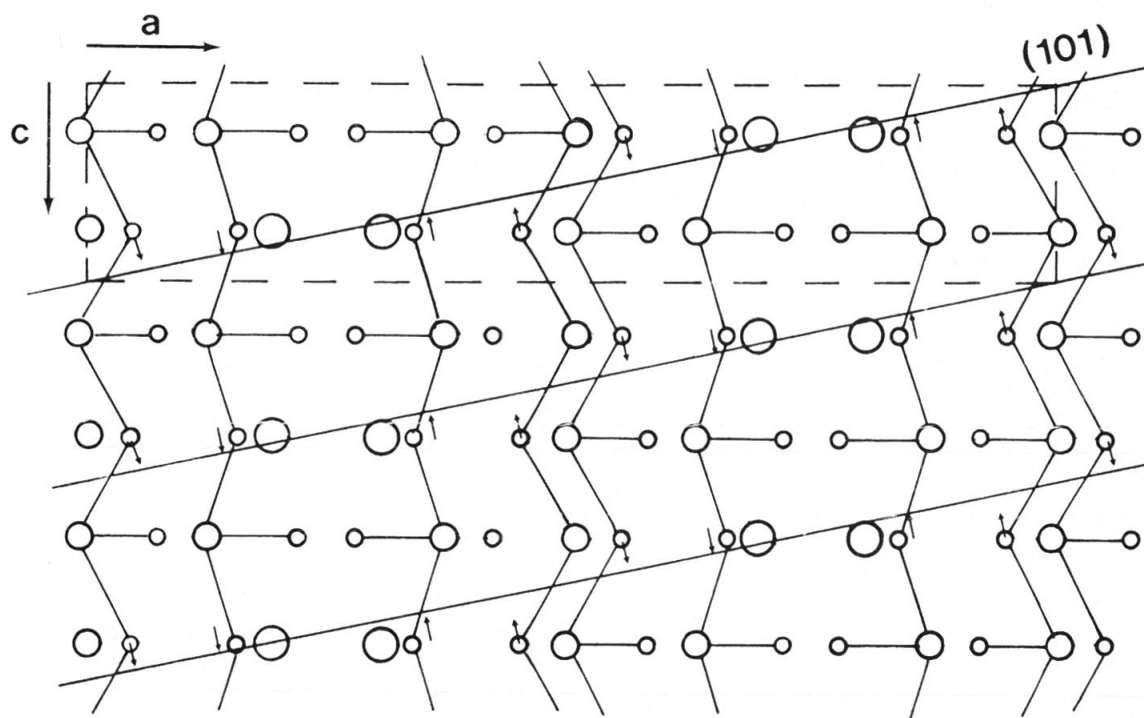


Fig. 14 Schematic structural diagram of the sartorite structure on (010), showing the atomic positions and traces of the {101} planes. The structural modulation is believed to be associated with displacements of atoms in the AsS chains around the {101} planes. The AsS chains running parallel to [001] are divided into segments by displacements of the S atoms toward the (101) planes. Large circles Pb, medium circles As, small circles S.

## Discussion

### POLYSOMATIC DISORDER VERSUS POLYTYPIC DISORDER

Polytypic disorder in baumhauerite together with well ordered baumhauerite polytypes was documented by PRING and GRAESER (1994). The origin of polytypism in baumhauerite is thought to be an inversion of the As/Pb order associated with the compositional modulation along *c*. Most of the other members of the sartorite group also show this form of compositional modulation but polytypes of dufrénoysite and liveingite have not been reported nor found in this study. They, however, do not show the same degree of Ag and Tl substitution as baumhauerite, a possible indication that these elements may play in the stabilization of these polytypes. Rathite however shows significant Tl substitution but no polytypes have been observed for this mineral. The origin of polytypic disorder in baumhauerite may therefore be linked not so much to the high Tl/Ag component but rather to the high As content of the (Pb,As) $S_{3(+2)}$  strips in baumhauerite. These strips contain no Pb in sartorite and the mismatch between the (As) $S_{3(+2)}$  strips and the  $PbS_9$  planes results in complex modulations in the structures. The Pb content of the (Pb,As) $S_{3(+2)}$  strips in baumhauerite is low, particularly in the '3' module, but the Pb stabilizes the As-S-As linkage along *c*. Periodic inversion of the Pb/As order about *c* stabilizes the structure and leads to formation of the polytypes.

Polysomatic disorder was documented in the sartorite group by PRING (1990), however PRING and GRAESER (1994), later showed that some of this disorder was polytypic disorder in baumhauerite. The documentation of "the 115 Å mineral" and the 138 Å phase (OZAWA and TAKÉUCHI, 1983; OZAWA and TACHIKAWA, 1996) has prompted a further re-evaluation of the work of PRING (1990) and some additional data has been obtained in this study. It appears that the original formulation of PRING (1990) that the disordered intergrowth of  $N = 3$  and  $N = 4$  units occurs in the system is correct, although the example given in that paper is in fact stacking disorder in baumhauerite polytypes. Figure 15 shows a disordered region of a crystal found in a crushed grain of the "138 Å phase". The contrast in the images shows bright bands and this appear to be associated with an inversion in the As/Pb order as also observed in the baumhauerite polytypes. Polysomatic disorder is also associated with the stabilization of compositions which have As-rich (Pb,As) $S_{3(+2)}$ . The occurrence of complex structural modula-

tion, polytypism and polysomatic disorder in the sartorite group highlight the inherent mismatch in the two principal structural elements, the  $PbS_9$  planes and the (Pb,As) $S_{3(+2)}$  strips. All three phenomena help to stabilize these minerals.

### PARAGENETIC RELATIONSHIPS

In the sartorite group the transition from dufrénoysite, the most Pb-rich member, to sartorite, the most As-rich member, represents, in structural terms, the progressive introduction of  $N = 3$  modules. The increase in As content is accompanied by progressive inclusion of  $N = 3$  units (liveingite  $N = 3.67$ , "the 115 Å mineral"  $N = 3.6$ , "the 138 Å mineral"  $N = 3.58$ , baumhauerite  $N = 3.5$ ) to sartorite  $N = 3$ . This suggests that the  $N = 4$  unit is stabilized by more Pb-rich compositions, while  $N = 3$  is stabilized by As. At the same time the inherent mismatch between the  $PbS_9$  planes and the (Pb,As) $S_{3(+2)}$  strips in the structural modules is emphasized by the occurrence of complex structural modulations, intergrowths and stacking disorder in the As-rich members of the group. The thermal stability also decreases along the series from the more Pb-rich to the As-rich members.

The occurrence at Lengenbach provides an opportunity to study the paragenetic relationship of the group. There is little doubt that the sartorite group minerals at Lengenbach are the result of reaction and recrystallization during metamorphism. Two main theories for the origin of the deposit have been advocated. GIUSCA (1930) and BADER (1934) proposed that minerals formed in a relatively closed system when a syn-sedimentary stratiform metal deposit recrystallized during Alpine metamorphism. On the other hand, GRAESER (1968, 1977), based on the distribution of the mineral assemblages in the old Lengenbach quarry suggested an open system with the introduction of As, Tl, Ag and Cu into a pre-existing metamorphosed stratiform mineralisation of pyrite, galena and sphalerite. He proposed that the sartorite group minerals were formed during late stage Alpine metamorphism by hydrothermal alteration with the least As-rich minerals forming first and being progressively replaced by the more As-rich minerals as the reaction progressed. The hydrothermal alteration continued until the minerals reached saturation in As or the reaction conditions changed resulting in the crystallization of realgar. Thus one would expect the most As-rich minerals to be formed at the stratigraphic top of the deposit giving way to less As-rich minerals down the stratigraphic sequence. The new quarry at Lengenbach was established in 1987 on the top



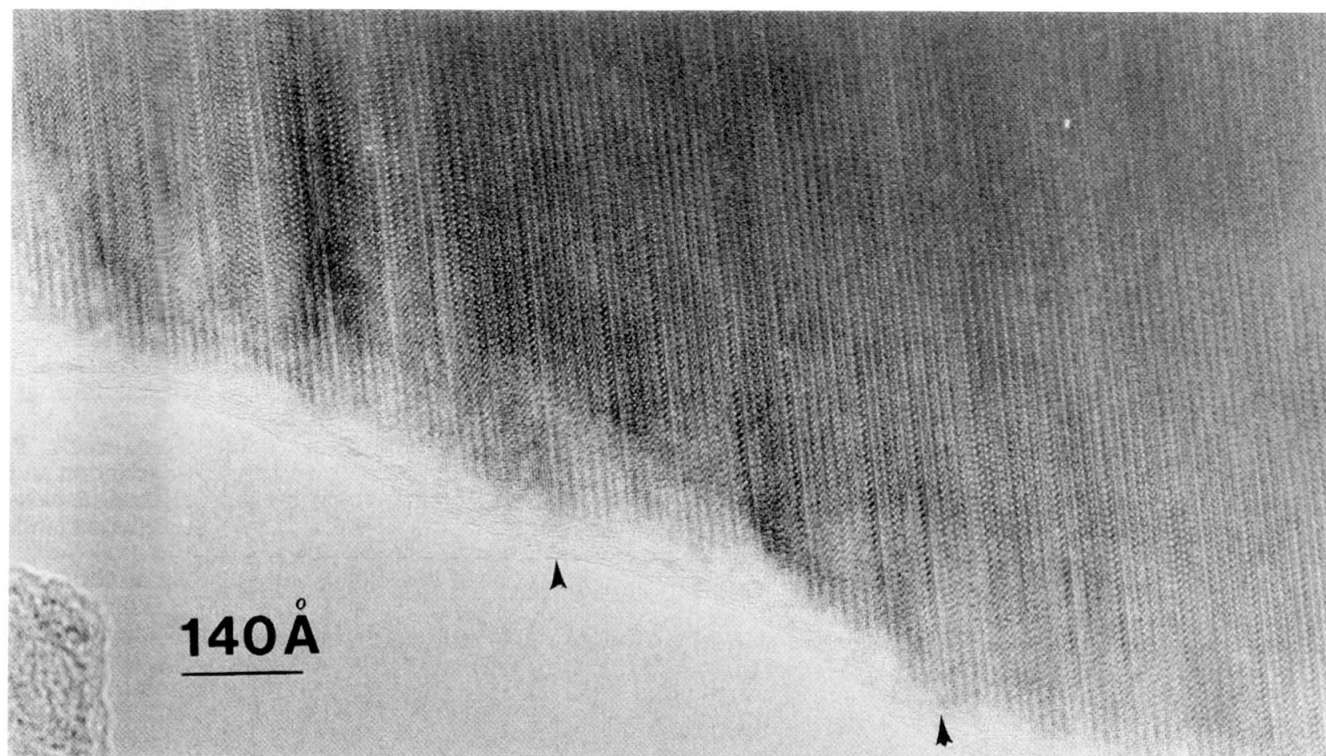


Fig. 15 Electron micrograph showing polysomatic disorder in a sartorite group mineral. The central section of the image (between the black arrows) contains 3 repeats of the 138 Å phase. The modules sequence in the rest of the image is disordered.

most part of the dolomite outcrop and the As-rich members of the sartorite group minerals and realgar were abundant. Based on this model for the deposit PRING (1990) proposed a paragenetic sequence in which dufrénoysite is progressively altered to sartorite via the intermediate minerals via solid state reactions leading to the transformation of  $N = 4$  units to  $N = 3$  units. That is as As-rich hydrothermal alteration proceeded the minerals richer in Pb were transformed to more As-rich minerals by diffusion of As into structures and Pb out in the solid state. The disordered intergrowths reported by PRING (1990) would represent trapped intermediates in the transformation of liveingite to baumhauerite. The occurrence of rathite, an As-rich 4,4 homologue posed problems for this hypothesis. However it is now clear that rathite forms a complex chemical series with dufrénoysite, and the  $N = 4 \Rightarrow 3$  sequence is at least theoretically possible.

Recent detailed geochemical and isotope studies strongly favour the closed system hypothesis (HOFMANN and KNILL, 1996; KNILL, 1996). Evidence of the existence of a former metamorphogenic sulfide melt in Lengenbach was presented by HOFMANN (1994) and suggests, that the present minerals were formed by isochemical metamorphism of a carbonate hosted stratiform

sulfide mineralisation to mid amphibolite facies. These geochemical studies confirm the suggestion of GRAESER (1968) that the As, Tl and Cu found in the Lengenbach minerals were introduced to the deposit by hydrothermal fluids from the crystalline basement now represented in the Monte Leone nappe.

The structural transition in the sartorite group minerals from  $N = 4 \Rightarrow 3$  merely reflects the decrease in thermal stability and an increase in As content and not a paragenetic sequence. The thermal stability of the Pb–As–S minerals was investigated by KUTOGLU (1969). The melting point of the sartorite group decreases from  $> 600$  °C for dufrénoysite to 485 °C for baumhauerite to 305 °C for sartorite. The relatively low thermal stability of the As-rich members of the group reflects that inherent mis-match of the two components of the structural module as noted above. The three long period homologues compositionally between dufrénoysite and baumhauerite: liveingite, “the 115 Å mineral” and the “138 Å phase” represent a progressive increase in the  $N = 3$  units in the structure and As content. The trend to longer period homologues and the stabilization of baumhauerite polytypes suggest that there are only marginal difference in the Gibbs-free energy for various of the As/Pb configurations. This leads

to the possibility that there are additional long period homologues between baumhauerite and sartorite that await discovery.

### Acknowledgements

I wish to thank Dr. W.D. Birch, Museum of Victoria, Melbourne; Dr. B.A. Hoffman and Dr. H. A. Stalder, Natural History Museum, Bern; Dr. G.A. Chinner, University of Cambridge, Dr. P. Henderson, Natural History Museum, London; and Prof. S. Graeser, Natural History Museum, Basel for providing specimens examined in this study. I am grateful to Dr. T. B. Williams, Dr. R.L. Withers and Prof. S. Graeser and other co-workers for their extensive collaborations on various aspects of this project. I would also like to acknowledge the useful discussions with Prof. T. Ozawa, University of Tokyo and the constructive reviews of the manuscript by Drs P. Berlepsch and B. Grob  ty. I am grateful for constructive comments by Dr. Uwe Kolitsch. I would like to thank Dr. D.A. Jefferson of the University Chemical Laboratories, Cambridge for the use of his electron microscopes during this study. Much of this paper was written while I was a visiting fellow commoner at Trinity College, Cambridge and I extend my thanks for the Master and Fellows of that college for their hospitality and financial support. The long term financial support of the Australian Research Council is also gratefully acknowledged.

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Manuscript received July 27, 2000; revision accepted October 23, 2000.