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Disordered intergrowths in lead-arsenic sulfide minerals and the paragenesis of the sartorite-group minerals

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ABSTRACT

High-resolution transmission electron microscopy has been used to investigate disordered structural intergrowths in lead-arsenic sulfide minerals that occur at Lengenbach, Binntal, Switzerland. Most of the material examined was found to be perfectly ordered; however, some highly disordered specimens were found. The "disordered liveingite," compositionally intermediate between dufrenoysite and liveingite, was found to be a disordered intergrowth of sartorite-like units and dufrenoysite-like units. The sartorite-like units are similar to those found in baumhauerite, whereas the dufrenoysite-like units are similar to those in liveingite. This disordered intergrowth represents a transitional stage in the replacement of dufrenoysite by the more As-rich mineral liveingite. The origins of the lead-arsenic sulfide minerals at the Lengenbach deposit are discussed; two paragenetic sequences are proposed to account for the formation of these minerals.

INTRODUCTION

The development of structural classification systems in which seemingly complicated mineral structures are considered as ordered intergrowths of simple components has done much to emphasize the relationships among minerals. Such structural relationships often reflect similar paragenetic origins for members of a group. In addition to ordered intergrowth structures, disordered intergrowths have been found in a number of mineral systems. The most notable examples are the disordered intergrowths in the biopyribole minerals, which have been studied in considerable detail by Veblen and others (Veblen et al., 1977; Veblen and Buseck, 1979; Mallinson et al., 1980). Other natural disordered intergrowths have been observed in the humites (White and Hyde, 1982a, 1982b) and the manganese oxides of the todorokite group (Turner and Buseck, 1979, 1981). Much recent work has focused on the systematic classification of sulfide mineral systems, particularly those in which the structures can be considered as being composed of ordered intergrowths of distinct structural units (Makovicky, 1981, 1985; Hyde et al., 1979). Although a number of defect structures and disordered intergrowths have been reported from studies of synthetic sulfides (Skowron and Tilley, 1986; Tilley and Wright, 1986; Tilley et al., 1986), to date no examples in natural sulfide minerals have been reported. This is surprising, since many of these minerals are formed in low- to moderate-temperature environments, which favors the formation of ordered and disordered intergrowths.

A systematic study of several sulfide mineral systems was undertaken in an attempt to identify disordered intergrowths. This study focused on the lead-arsenic sulfide minerals (the sartorite group), which are structurally closely related and also occur together at Lengenbach, Binntal, Switzerland. Lattice imaging by high-resolution transmission electron microscopy (HRTEM) was used to identify disordered intergrowths.

THE SARTORITE GROUP

The sartorite group comprises five well-characterized minerals: sartorite, $Pb_4As_8S_{16}$; rathite, $Pb_{12}As_{20}S_{40}$; baumhauerite, $Pb_{12}As_{16}S_{36}$; liveingite, $Pb_{18.5}As_{25}S_{56}$; and dufrenoysite, $Pb_{16}As_{16}S_{40}$; together with a number of other less well-defined minerals (Makovicky, 1985). The sartorite minerals have closely related structures, which are based on the ordered intergrowth of two slightly different structural units. One is the S unit (S representing sartorite), which consists of a strip 3 AsS polyhedra (trigonal pyramids) wide, separated from the next by a chain of PbS tricapped trigonal prisms (Fig. 1a). The sartorite structure consists of two such units in a zig-zag or chemically twinned arrangement (Hyde et al., 1979). The second structural unit is the D unit (D for dufrenoysite), which is 4 AsS polyhedra wide and is again separated from its neighbors by chains of PbS tricapped trigonal prisms (Fig. 1b). [Note that Makovicky (1985) has denoted the S and D units as "3" and "4," respectively]. Two D-type units make up the dufrenoysite and rathite structures; the composition of the D-type units in these minerals differs because of varying degrees of Pb-As substitution, with those in dufrenoysite being the most Pb-rich. When Pb is present in the D- or S-type units, it occupies seven coordinate sites (monocapped trigonal prisms) that are not simply related to the As sites. The D units in dufrenoysite contain 8 As atoms and 4 Pb atoms, whereas in rathite, the D units contain 10 As atoms and 2 Pb atoms. Baumhauerite and liveingite have structures based on the or-

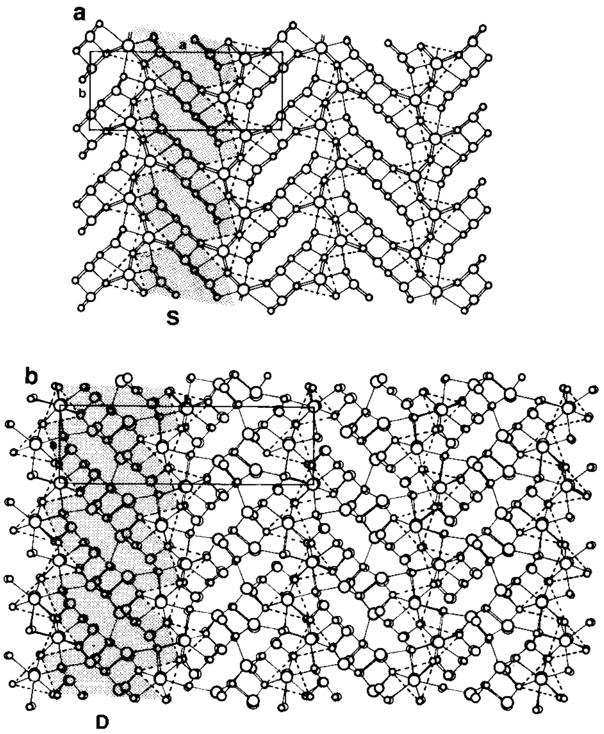

Fig. 1. (**a**) Structural diagram of sartorite showing the atomic arrangement in the S-type unit. (**b**) Structural diagram of dufrenoysite showing the atomic arrangement in the D-type unit. The circles in order of decreasing size: Pb, As, S. The strip of 4 AsS polyhedra in the dufrenoysite structure contains 4 Pb and 8 As sites; in liveingite and baumhauerite the strips contain 3 Pb sites and 10 As sites, and in rathite the composition of the layers is 2 Pb and 10 As sites.

dered intergrowth of S and D units; baumhauerite is SD and liveingite DSDDSD. Again, however, the D and S units have compositions slightly different from those in the other minerals because of Pb-As substitution. The D units contain 3 Pb atoms and 10 As atoms, and the S units 1 Pb and 7 As atoms. In reality there are two types of D units in liveingite: one contains 3 Pb and 10.25 As atoms and the other contains 3 Pb and 10 As atoms. In the following discussions, however, composition 3 Pb, 10 As is used, as the subtle difference in composition does not affect the conclusions regarding the origins of the sartorite minerals. The S units in sartorite contain 8 As atoms and no Pb. (The c cell repeat is doubled to correspond to the other minerals in the group.) Table 1 summarizes the structural data of the sartorite group.

The occurrence of the sartorite group minerals as a suite is restricted to the unusual Lengenbach deposit, in the Binntal, Switzerland, although individual members of the group have been reported from other deposits (e.g., Quiruvilca, Peru, (Robinson and Harris, 1987). At Lengenbach the sartorite minerals occur as well-formed single crystals and homogeneous masses up to several centimeters across in cavities in white dolomite. It has been suggested that these minerals were formed as the result of reactions between As-rich hydrothermal fluids and PbS (galena), causing a progressive replacement of As-poor members by the more As-rich members of the group, the most As-rich minerals being found toward the top of the deposit (Graeser, 1968a, 1977).

ELECTRON MICROSCOPY

Specimens were prepared for examination by crushing in an agate mortar followed by dispersal in acetone and deposition onto Cu support grids, which had been coated with a holey carbon film. It was not possible to prepare ion-thinned samples because of the small size of most specimens and the difficulties in orienting the rough crystal fragments. The minerals were examined in a modified JEOL 200CX electron microscope fitted with a top entry goniometer (C_s = 1.9 mm). The point-to-point resolution and the Scherzer defocus of the instrument in the above configurations was 2.5 Å and −670 Å. A Philips EM430T electron microscope was also used in the preliminary stages of this study.

A large number of specimens were examined; most were found to be perfectly ordered and free from defects. Figure 2 shows an electron diffraction pattern and lattice image for a perfectly ordered liveingite crystal. However, some massive material, which was macroscopically in-

TABLE 1. The sartorite-group minerals

Mineral	Composition	Pb:As	M:S	Structure	Unit cell
Dufrenoysite	$Pb_{16}As_{16}S_{40}$	1.00	1.25	DD	a = 7.90, c = 8.37, b = 25.74 Å, β = 90.35
Liveingite	$Pb_{18.5}As_{25}S_{56}$	0.77	1.287	DSDDSD	c = 7.90, a = 8.37, b = 70.49, β = 90.13
Baumhauerite	$Pb_{12}As_{16}S_{36}$	0.76	1.286	DS	c = 7.90, b = 8.36, a = 22.80 Å, α = 90.05, β = 97.26, γ = 89.92
Rathite I	$(Pb,Tl)_{12}(As,Ag)_{20}S_{40}$	0.75	1.25	DD	b = 7.87, c = 8.47, a = 25.16 Å, β = 100.47
Sartorite	$Pb_4As_8S_{16}$	0.50	1.33	SS	b = 7.89, c = 11 × 4.19, a = 3 × 19.62 Å
Rathite III	$Pb_{12}As_{20}S_{40}$	0.75	1.25	? (DD)	b = 7.91, c = 8.47, a = 24.52 Å, β = 90.00
Rathite IV	n.d.			n.d.	b = 7.92, c = 8.47, a = 138.3 Å
Rathite Ia	$Pb_{14}As_{18}S_{40}$	0.78	1.25	? (DD)	c = 7.91, a = 8.43, b = 25.80 Å, β = 90.00
"Fibrous sulfosalt"	n.d.			? (DD)	c = 7.89, a = 8.47, b = 2 × 25.61 Å

Note: Modified from Makovicky (1985).

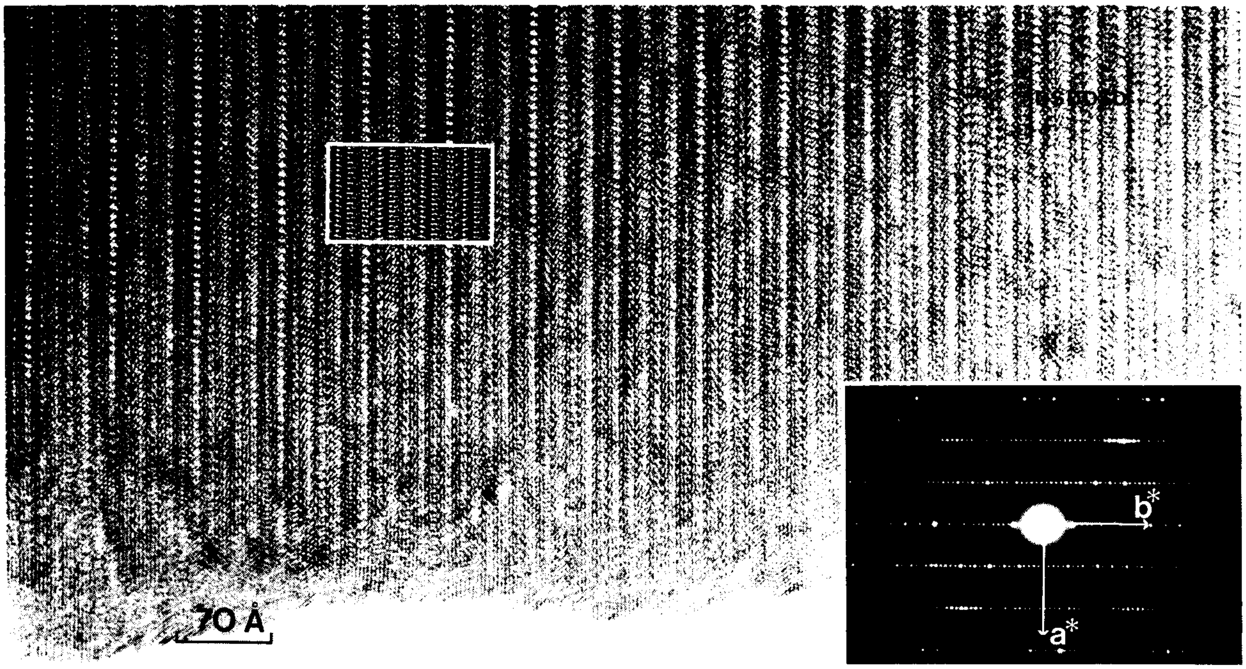

Fig. 2. Lattice image, image simulation, and electron-diffraction pattern of liveingite (specimen BM. 1926 1691) down [001]. Note the sharp spots in the diffraction pattern indicating a perfectly ordered crystal. The image shows the perfectly repeating DSDDSD structural sequence. The image simulation was calculated for a foil 100 Å thick and a defocus of −1570 Å.

distinguishable from liveingite and compositionally between dufrenoysite and liveingite (hereafter termed "disordered liveingite"), was found to be highly disordered and twinned (Fig. 3). The fringe spacings in the image indicate that it consists of an intergrowth of S- and D-type units. The images of the "disordered liveingite" are difficult to interpret because of the similarity of the image motifs of the S and D units and because of the compositional variability of the D and S units. Contrast differences in Figure 3, however, reveal the presence of pairs of SD units similar to those found in baumhauerite and liveingite; these light strips are separated by darker strips of variable width, which are composed of D-type units. The individual S and D units are identified on the micrograph, as is the location of a twin plane. Computer-image simulations calculated using the multislice method (Goodman and Moodie, 1974) confirm that the SD pairs are similar to those in baumhauerite and liveingite (Engel and Nowacki, 1969, 1970) and indicate that the D-type units are similar to those found in liveingite (Engel and Nowacki, 1970). The compositions of the D- and S-type units used in the structural model proposed are (3 Pb, 10 As) and (1 Pb, 7 As) respectively. The image simulations matching the various structural components of the disordered intergrowth are shown in Figure 3. Structural models based on D units with the composition of those in dufrenoysite and rathite were also tested but were found to be unsatisfactory.

The proportions of individual D- and S-type units in the image are in the ratio 5:1, which places the material between dufrenoysite (DD) and liveingite, which has a D:S ratio of 2:1. Electron microprobe analyses revealed the "disordered-liveingite" material to be compositionally homogeneous at the scale of the electron probe beam (5–10 μm) (Table 2). The average composition was determined to be $Pb_{14.1}Ag_{1.1}As_{19.2}Sb_{0.3}S_{40}$, which is consistent with "disordered liveingite" being intermediate to dufrenoysite and liveingite. Ag (and Tl when present) in the sartorite minerals replaces lead in a coupled substitution with As such that $2Pb^{2+} = Ag^{+} + As^{3+}$, with Ag entering the same sites as As rather than Pb. Several weight percent of Ag have been reported in some of the sartorite group minerals, in particular liveingite, baumhauerite, and rathite (Engel and Nowacki, 1969, 1970; Marumo and Nowacki, 1965).

Table 2. Electron-microprobe analysis of "disordered liveingite"

Element	Wt%*	Atomic proportions†
Pb	49.5	14.1
Ag	2.0	1.1
As	24.8	19.2
Sb	0.7	0.3
S	21.8	40
Total	98.8	

Note: Analyses were performed by Dr. W. Birch on the electron microprobe at the Department of Geology, University of Melbourne. The following standards were used: galena (Pb), arsenopyrite (As, S), pure Sb, and pure Ag. The specimen current ranged from 0.015 μA to 0.025 μA with an accelerating voltage of 20 kV.

* Average of six analyses.

† Calculated on the basis of 40 S atoms.

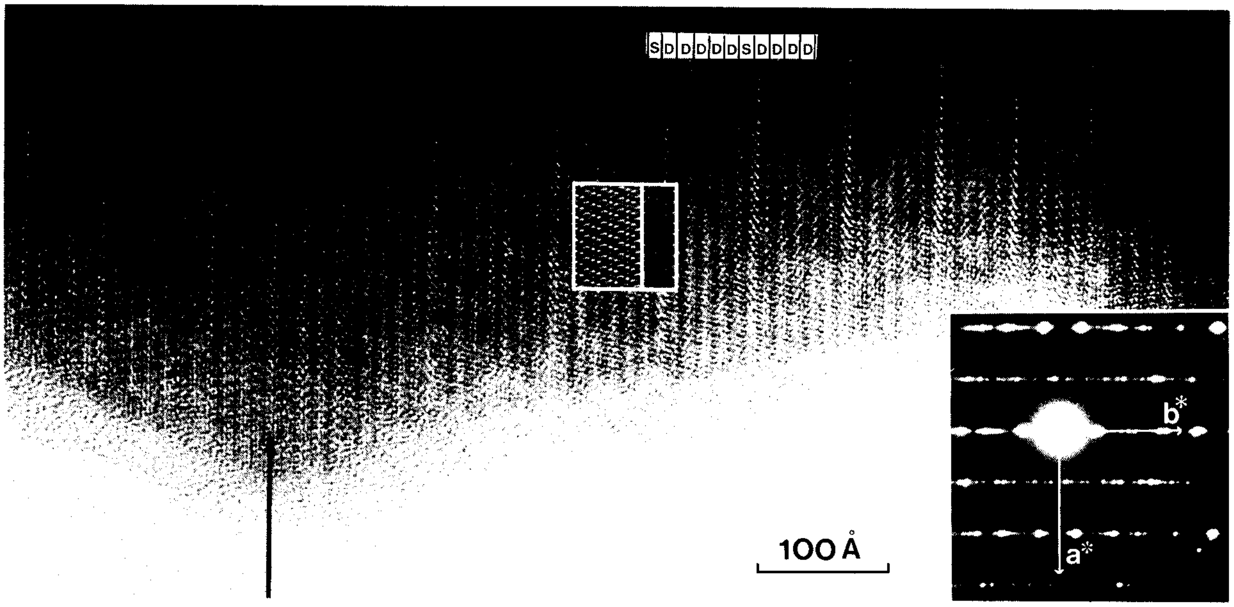

Fig. 3. Electron-diffraction pattern and lattice image down the 7.9 Å axis of the "disordered liveingite" (M35933). The zone corresponds to [001] of liveingite. Note that the reflections in the diffraction pattern are heavily streaked along the *b** direction, which corresponds to the stacking direction of the D and S units. The disordered intergrowth of D- and S-type units is clearly apparent in the lattice image. Note the DS pairs, which are lighter in contrast than the remaining D-type units. The DS pairs are similar to those found in baumhauerite and liveingite, and the other D units are similar in composition to those in liveingite. The arrow toward the edge of the image indicates the location of a twin plane. Computer image simulations of two components of the intergrowth are also shown. The image simulations were calculated for a foil thickness of 75 Å and a defocus of −570 Å.

PARAGENESIS

Graeser (1968a, 1968b, 1969, 1977) proposed that the Lengenbach deposit was originally a syngenetic sulfide-dolomite deposit containing galena and sphalerite, which was invaded by arsenic-rich hydothermal fluids towards the end of the Alpidic metamorphism. These fluids introduced Cu, Ag, and Tl in addition to As into the deposit. Graeser (1968a, 1977) suggested that the lead-arsenic sulfide minerals were formed during metamorphism and hydrothermal alteration with the least As-rich minerals forming first and being progressively replaced by the more As-rich minerals as the reactions progressed. The hydrothermal alteration continued until the minerals reached saturation in As or the reaction conditions changed, resulting in the crystallization of realgar. According to this hypothesis, the first Pb-As mineral to form at Lengenbach was jordanite, which is not simply structurally related to the sartorite group minerals. Jordanite was followed, in sequence, by dufrenoysite, liveingite, baumhauerite, rathite, and sartorite. In terms of the structures of the sartorite group minerals, this sequence can be seen, with the exception of rathite, as a progressive replacement of D-type units by S-type units (an increase in chemical twinning).

The "disordered liveingite" of this study appears to represent a remnant of the transitional state between dufrenoysite and liveingite. A two-stage replacement mechanism is indicated. The first step could involve the replacement of Pb by As in the D-type units. This is required to account for the differences in composition of the D-type units in dufrenoysite (4 Pb, 8 As), liveingite (3 Pb, 10 As), and rathite (2 Pb, 10 As). This process may be followed by the stage in which the S units are formed. This second stage requires either the formation of new S units via the diffusion of Pb, As, and S through the crystal or the transformation of D units into S units via the elimination of an As/Pb site in the D unit and further replacement of Pb by As. Either mechanism suggests that the second stage of replacement requires more energy than the first. The trapping of the "disordered liveingite" structurally intermediate state indicates that these minerals were formed during the retrograde stage of hydrothermal alteration of the deposit.

Two separate paragenetic sequences leading to the formation of the sartorite-group minerals are required to account for the formation of liveingite and rathite. One sequence involves the initial replacement of Pb by As in the D units followed by the formation of S units. The other involves the continued replacement of Pb by As in the D units without formation of S units until the final step, if at all.

The first sequence:

dufrenoysite (DD, DD, DD)
$Pb_{16}As_{16}S_{40}$
→ intermediate (DD, DD, DD)
$Pb_{14}As_{18}S_{40}$
→ liveingite (DS, DD, SD)
$Pb_{18.5}As_{25}S_{56}$
→ baumhauerite (DS, DS, DS)
$Pb_{12}As_{16}S_{36}$
→ sartorite (SS, SS, SS)
$Pb_8As_{16}S_{32}$

The second sequence:

dufrenoysite (DD, DD, DD)
$Pb_{16}As_{16}S_{40}$
→ intermediate (DD, DD, DD)
$Pb_{14}As_{18}S_{40}$
→ rathite (DD, DD, DD)
$Pb_{12}As_{20}S_{40}$
→ sartorite (SS, SS, SS)
$Pb_8As_{16}S_{32}$

The first sequence appears to be dominant at Lengenbach since liveingite, baumhauerite, and sartorite are relatively common in the deposit, whereas rathite is very rare. The evidence of local associations at Lengenbach also suggests that these sequences are correct. Liveingite has not been found with sartorite, nor baumhauerite with dufrenoysite (Graeser, private communication).

Both sequences involve an intermediate "phase," which has a structure based on two D-type units similar in composition to those in liveingite (3 Pb, 10 As) and intermediate to those of dufrenoysite (4 Pb, 8 As) and rathite (2 Pb, 10 As). The identity of the intermediate phase is unclear, and it may not be a stable mineral at Lengenbach. It may, however, be the mineral called rathite I by Le Bihan (1962) and rathite Ia by Nowacki et al. (1964). Le Bihan's rathite I has the formula $Pb_{14}As_{18}S_{40}$, which has an excess of positive charge; however, the mineral also contains traces of Ag and Sb, which may stabilize the mineral. Rathite also has an excess of positive charge ($Pb_{12}As_{20}S_{40}$) but is stabilized by the presence of Tl and Ag. Marumo and Nowacki (1967) considered Le Bihan's rathite I to be identical with dufrenoysite on the basis of their powder patterns; however, this matter is worthy of further consideration.

It is hoped that further work may establish the paragenetic roles of Ag and Tl in these minerals and also clarify the relationships of some of the poorly characterized members of the group, e.g., rathite III and rathite IV. Pring et al. (unpublished manuscript) found that the presence of Ag in baumhauerite is linked to supercell formation in this mineral.

In the wider sense, disordered intergrowths may be quite widespread in sulfide minerals, particularly those that have been subjected to moderate- or lower-temperature metamorphism or hydrothermal alteration during the late stages of their history. The occurrence of this type of nonequilibrium behavior in sulfides provides direct evidence of replacement and other processes in the paragenesis of sulfide deposits. A number of sulfide systems, when considered from a structural point of view, seem particularly likely to exhibit this kind of structural behavior; for example, the lillianite, plagionite, boulangerite, pavonite, and junoite groups. Synthetic studies in several of these systems have revealed disordered intergrowths (Skowron and Tilley, 1986; Tilley and Wright, 1986; Tilley et al., 1986). A closer examination of many sulfide systems appears to be justified.

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