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THE CRYSTAL STRUCTURE OF GERSTLEYITE $Na_2(Sb,As)_8S_{13}\cdot 2H_2O$: THE FIRST SULFOSALT MINERAL OF SODIUM

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Gerstleyite is monoclinic, a=9.911(8), b=23.05(2), c=7.097(8) Å, β=127.85(7)°, space group Cm, and Z=2. All Sb atoms have essentially 3-fold coordination, forming trigonal SbS_3 pyramids. The SbS_3 pyramids share corners to form a complex chain parallel to [100]. Na-S bonds cross-link the chains into a slab structure parallel to (010). Water molecules coordinate only to Na atoms.

Gerstleyite was first described by Frondel and Morgan,[2)] and was recently reexamined by Mrose and Ingram,[3)] who reported a new chemical formula $Na_2(Sb,As)_8S_{13}\cdot 2H_2O$ (Sb:As=9:1), crystal data and some physico-chemical properties of this mineral. Because of the unique chemical composition: a hydrated sulfide of sodium and antimony, detailed study of the crystal structure was necessary to understand the nature of this rare mineral.

A single crystal fragment of gerstleyite measuring 0.038 x 0.038 x 0.034 mm used for the crystal structure analysis was picked up from the Smithsonian Museum specimens labelled gerstleyite from the type locality, Baker mine, Kern County, Boron, California; specimen numbers NMNH#106916, 124075, 124082, 105939, and 138465.

Crystal data: monoclinic, $Na_2(Sb,As)_8S_{13}\cdot 2H_2O$ (Sb:As=9:1), F.W. 1435.3, space group Cm, a=9.911(8), b=23.05(2), c=7.097(8) Å, β=127.85(7)°, Z=2, D_c=3.723 g·cm^{-3}.

The intensities of independent reflections within $\sin\theta/\lambda < 0.6$ were measured on a Picker FACS-I four-circle automatic diffractometer by 2θ-ω scan method using Zr filtered Mo Kα radiation, and a scan rate was 2.0°min^{-1} in 2θ. A total of 1204 reflections were measured, of which 863 reflections satisfied the condition $|Fo| \geq 3\sigma(|Fo|)$ based on counting statistics and were used for the crystal structure analysis. A three dimensional Patterson synthesis was calculated. Systematic consideration of the Harker sections enabled us to find positions of Sb atoms. Subsequent Fourier and difference syntheses and least-squares refinement revealed the rest of atoms except hydrogen. Arsenic occupancies in antimony sites were determined by the full-matrix least-squares refinement program RFINE-II.[4)] The structure has been refined to R=0.075 ($R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$).

The final positional parameters and temperature factors of nonhydrogen atoms are listed in Table 1, together with the estimated standard deviations of each parameter. Table 2 lists the site occupancies of the arsenic atoms and bond distances of pyramidal Sb-S bonds. All computer programs used in this study unless otherwise noted are from the X-RAY SYSTEM.5) The atomic scattering factors for neutral atoms were those of Cromer and Mann;6) the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.7)

A projection of the structure down the c* axis is presented in Fig. 1. All Sb atoms are essentially three-coordinated by S atoms, forming trigonal SbS$_3$ pyramids. The trigonal pyramids share corners to form complex chains parallel to [100]. Within the chain, the SbS$_3$ pyramids of four Sb(1), two Sb(2), and two Sb(3) share two corners each to form an eight-membered ring. The rings are linked together in a true endless chain by sharing opposite pairs of adjacent pyramids of Sb(1). The SbS$_3$ pyramids of Sb(4) attach to the eight-membered rings by sharing S(5) and S(6) atoms to form three-membered rings. Na atoms link the chains into slabs parallel to (010). The water molecules are coordinated to two Na atoms.

In the structure of gerstleyite, there are clear structural groups of SbS$_3$ pyramids, hence gerstleyite is classified among the sulfosalts rather than the sulfides. The structure falls into the type Va$_2$ (ψ=1.625) of sulfosalt classification

Table 1. Atomic coordinates and isotropic temperature factors.

	x	y	z	B/Å^2
Sb(1)	0.4128(31)	0.4059(2)	0.7933(39)	1.77
Sb(2)	0.0859(31)	0.1685(2)	0.5034(39)	1.51
Sb(3)	0.4846(31)	0.1690(2)	0.5155(39)	1.41
Sb(4)	0.4935(32)	0.2461(2)	0.9829(40)	1.64
S(1)	0	0	0	2.32
S(2)	0.4681(36)	0.4261(7)	0.5159(50)	2.46
S(3)	0.2621(36)	0.1050(6)	0.4541(45)	2.03
S(4)	0.1107(38)	0.4246(7)	0.5248(48)	3.08
S(5)	0.2890(37)	0.1746(7)	0.9451(48)	1.56
S(6)	0.1605(37)	0.3286(8)	0.9551(47)	2.38
S(7)	0.3152(36)	0.2756(6)	0.5757(44)	1.69
Na	0.0103(60)	0.4255(10)	0.0224(75)	4.40
O(1)	0.342(11)	0	0.986(16)	5.09
O(2)	0.159(9)	0.5	0.981(15)	3.39

Table 2. Site occupancies, isotropic temperature factors, and average Sb-S bond lengths.

site	Sb	As	B/Å^2	d_{Sb-S}/Å
Sb(1)	0.83	0.17	1.77	2.42
Sb(2)	0.98	0.02	1.51	2.49
Sb(3)	0.91	0.09	1.41	2.47
Sb(4)	0.88	0.12	1.64	2.46

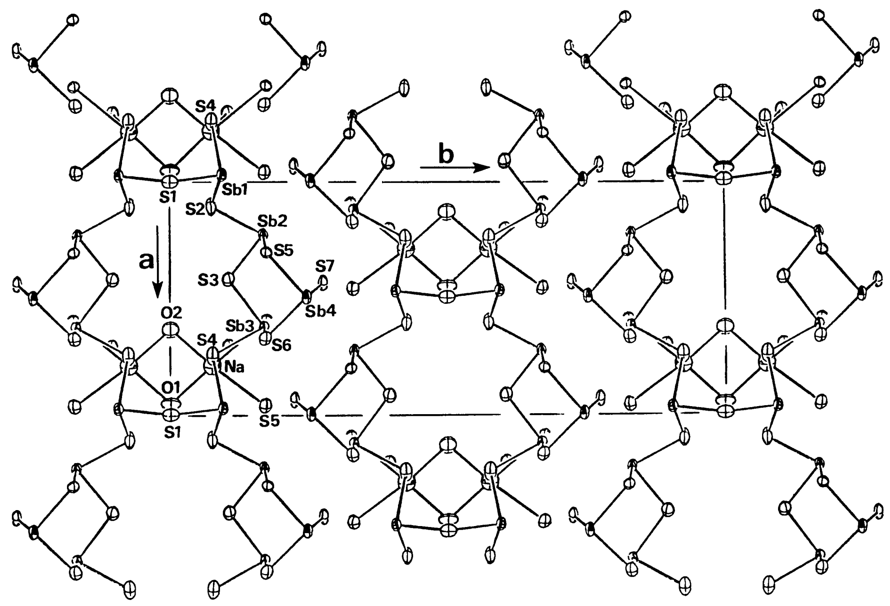

Fig. 1. Projection of the gerstleyite structure viewed along the c* axis.

proposed by Nowacki.[8] This structure is crystal-chemically interesting, because this is the first sulfosalt mineral which contains an alkali metal; moreover, no sulfosalts are known to have water molecules in their structure.

Bond distances are illustrated in Fig. 2. The average Sb-S bond distance is 2.46 Å, which is considerably shorter than average Sb-S bond distance of the bridge bond in sulfosalts (2.54 Å).[9] This difference is ascribed to the substitution of As for Sb. Table 2 shows that the average pyramidal Sb-S bond distance is 2.42 Å for Sb(1), the shortest; then 2.46 Å for Sb(4), 2.47 Å for Sb(3), and 2.49 Å for Sb(2), which is approximately inversely proportional to their arsenic occupancy.

The average Na-S bond distance is 3.06 Å. It is somewhat longer than the usual Na-S bond distances: e.g. average Na-S bond distances are 2.928 Å for α-$NaSbS_2$,[10] 2.909 Å for $NaAsS_2$,[11] and 2.996 Å for Schlippe's salt $Na_3SbS_4 \cdot 9H_2O$.[12]

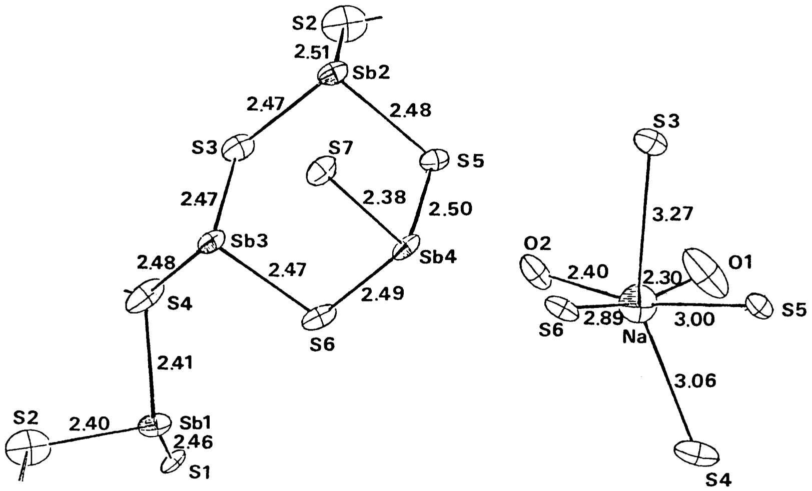

Fig. 2. Coordination about the metal atoms with bond distances in Å.

The Na atoms are also coordinated by two O atoms of water molecules at distances of 2.30 and 2.40 Å (av. 2.35 Å). As a result, the coordination number of the Na atoms is six, yielding a coordination polyhedron of a distorted octahedron. Among sulfides of Na and Sb, the Schlippe's salt is a good example where Na atoms are coordinated by water molecules. The Na-O distances range from 2.359 to 2.423 Å with an average of 2.393 Å,12) which is close to the value for gerstleyite, 2.35 Å. The coordination number six of the Na atom is widely observed in the above compounds: i.e. the Na atoms are coordinated by six S atoms in α-$NaSbS_2$, and $NaAsS_2$; while the Na atoms are bonded to either six O or three O plus three S atoms in the Schlippe's salt.

The Na atom in gerstleyite plays the role of linking the Sb-S chains to form a slab structure parallel to (010). This is comparable to the role of the Ca atom in the structure of sarabauite $CaSb_{10}O_{10}S_6$, where the Ca atoms link the Sb-O chains to form the slab structure parallel to (100).13)

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