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The crystal structure of senandorite (andorite VI): $PbAgSb_3S_6$

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Abstract. The crystal structure of senandorite (andorite VI) was determined taking into account the results of substructure analysis. All Sb atoms form trigonal pyramids, each with three S atoms. All of these pyramids participate in forming two types of polymerized Sb–S units; one, an $Sb_{14}S_{28}$ group extended along the *c* axis; the other, an isolated Sb_2S_4 group. Six non-equivalent Ag atoms each form deformed octahedra with six S atoms. Three of these sites have four short Ag–S bonds tetrahedrally arranged. Sulphur atoms that bridge SbS_3 pyramidal groups do not enter

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the tetrahedral AgS_4 coordination, which is attributed to the steric difficulties encountered.

Introduction

The andorite series represents a structurally related series of sulphosalts minerals which crystallize in the monoclinic or orthorhombic systems having orthogonal or nearly orthogonal lattice constants of $a = 13.0$, $b = 19.2$, $c = (4.3 \times n)$ Å, with $n = 2, 4, 6$, or 24. A species reported to be that of $n = 12$ is actually an intergrowth between those of $n = 4$ and $n = 6$ (Donnay and Donnay, 1954). According to the nomenclature proposed by Moëlo et al. (1984), the species with $n = 2$ (monoclinic) is ramdohrite or fizelyite, that with $n = 4$ (monoclinic, andorite IV of Donnay and Donnay, 1954) is quatrandorite, $n = 6$ (orthorhombic, andorite VI of Donnay and Donnay, 1954; present study) is senandorite, and $n = 24$ (orthorhombic) is nakaseite (Ito and Muraoka, 1960).

After the first report on "ramdohrite" by Ahlfeld (1930), X-ray studies by Nuffield (1945) revealed that the subcells of the andorite series are very similar to each other. The first structural proposal by Hellner (1958) presented the structure in the subcell of senandorite and fizelyite. Kawada and Hellner (1971) determined the average structure in the subcell of senandorite in which Sb and Ag atoms are distributed statistically in one site. It was suggested there that the statistical sites of Sb and Ag in the subcell of $n = 1$ are separated into respective sites in the whole structure. The present study was undertaken to determine the structure in the whole unit cell ($n = 6$) of senandorite.

Experimental

A sample labeled "andorite" from Freiberg (Saxony) was used. It had a metallic luster and dark grey color with no distinct cleavage. Through oscillation photography, a pure six-layered ($n = 6$) specimen was found among numerous polycrystalline fragments.

Crystal data are as follows: $PbAgSb_3S_6$, ideal chemical composition assumed, orthorhombic, space group $Pn2_1a$, $a = 13.005$, $b = 19.155$, $c = 25.622$ Å, $Z = 4$, $D_x = 5.456$ Mg m^{-3}, $\lambda = 0.71035$ Å, $\mu(\text{Mo}K\alpha) = 263.5$ cm^{-1}, crystal shape approximately spherical, $r \simeq 150$ µm.

Intensity data were collected on a Philips four-circle diffractometer. Within the range of $0 < \sin\theta < 0.5$ (Mo$K\alpha$), 2028 independent reflexions were measured. Omitting reflexions with standard deviation $3\,\sigma(F_o) > F_o$, 757 reflexions were used for structure refinement with a weighting scheme of $w = 1/\sigma^2$. Neutral atomic form factors provided by the *International Tables for X-ray Crystallography* (1974) were used.

Structure determination

The structure of the subcell which was determined by Kawada and Hellner (1971) will be called that of the 1C type. The reflexions of *hkl* [$l \equiv 6(\mathrm{mod}\,12)$ for $h \equiv$ odd, $l \equiv 0(\mathrm{mod}\,12)$ for $h \equiv$ even] correspond to that cell and will be called "main reflexions". The present study concerns the cell of the 6C type which is a superstructure with the *c* axis six times the length of that of the 1C-type. Preliminary considerations of the intensity distribution of the satellite reflexions in relation with the main reflexions had to be employed for the determination of the structure of the 6C type because the attempt to extend the atomic positions of the 1C type cell with considerations of the ordering of Sb and Ag atoms and their displacements from the 1C type parameters was not immediately successful.

It was readily seen that the diffraction intensity distribution of senandorite has a remarkable feature; the intensities of the main reflexions are strong and those of the other layers weak. Moreover, the intensity distribution in *hkl* and *hk* $(l+12)$ are very similar to each other.

Furthermore, there are correlative relations between the main reflexions and the remnant which were adopted as starting points for the structure determination. The intensities of:

① *hkl*; $l \equiv (l_{\text{main reflexion}} \pm 1)$

② *hkl*; $l \equiv (l_{\text{main reflexion}} \pm 4)$

are strongly correlated to that of the main reflexion. These relations are implicative of sinusoidal wave-like displacements which in one periodic cycle, in ①, advances six times the length of the 1C type cell in the *c* direction corresponding to the 6C type cell; in ② it advances 1.5 times the length indicating a 3C type subcell. The intensities of *hkl*; $l \equiv (l_{\text{main reflexion}} \pm 3)$ are strong compared to the other satellites, but have no resemblance in intensity distribution with the main reflexions. In course, a 2C type subcell was also adopted for further analysis. Since there is a periodic recurrence in the *l* reflexions, displacement in the *c* direction could be considered to be small for a start.

At the first stage, a trial and error search for the most plausible atomic displacements from average 1C type structure coordinates was done by diversely varying *x* and *y* parameters of sets of atoms whose parameters were believed to be weakly correlated. Refinements (ORFLS, Busing et al., 1962) of the 2C type structure using intensities of only the *hkl*; $l \equiv (l_{\text{main reflexion}} \pm 3)$ reflexions, and the 3C type using the *hkl*; $l \equiv (l_{\text{main reflexion}} \pm 4)$ were carried out. The many possibilities of atomic displacements arising by examining the deformation of atoms in the calculated Fourier maps were exhaustively considered. After confirmation of the 1C type structure by refinement using only the main reflexions, the structures of relatively low *R* factors were chosen as candidates for the most probable 2C and 3C approximation for the 6C type structure regarded as true. Among these possibilities, only one unique solution was obtained satisfying the condition which gives similar hkl; $l \equiv (l_{\text{main reflexion}} \pm 1)$ intensity distributions. During this procedure, a dumbbell-shaped S atom observed in the Fourier map of the 1C type was resolved to round atoms displaced from the (average) 1C type coordinates. The 6C type structure, obtained from the above procedure, has been refined with the parameters including the z coordinate and isotropic temperature factors. Simultaneous refinement of strongly correlated parameters was avoided. Absorption and isotropic extinction were corrected as for a spherical crystal (LINUS, Coppens and Hamilton, 1970) and the final R factor became 4.98% (R_w 5.78%). The atomic parameters are listed in Table 1. Tables of calculated interatomic distances and angles are deposited[1].

Table 1. Atomic coordinates and isotropic temperature factors. All atoms in general positions.

Atom	x	y	z	B
Pb(1)	0.5723(5)	0.7500(4)	0.0343(2)	1.0(1)
Pb(2)	0.5714(5)	0.7358(4)	0.1971(2)	1.2(1)
Pb(3)	0.5760(4)	0.7473(4)	0.3691(2)	0.9(1)
Pb(4)	0.5988(5)	0.7484(5)	0.5466(3)	1.2(1)
Pb(5)	0.5970(5)	0.7490(6)	0.7095(3)	1.5(1)
Pb(6)	0.5883(5)	0.7383(4)	0.8758(3)	1.5(1)
Ag(1)	0.6601(13)	0.3663(8)	0.0424(6)	2.0(3)
Ag(2)	0.6737(14)	0.3509(9)	0.2116(6)	2.9(4)
Ag(3)	0.6699(13)	0.1353(9)	0.3748(9)	3.4(3)
Ag(4)	0.6852(14)	0.3473(9)	0.5470(6)	2.3(3)
Ag(5)	0.6662(13)	0.3519(9)	0.7073(6)	2.3(3)
Ag(6)	0.6707(11)	0.1280(9)	0.8680(7)	2.2(3)
Sb(11)	0.3801(10)	0.4392(6)	0.0454(4)	0.5(2)
Sb(12)	0.3678(11)	0.4407(7)	0.1987(4)	0.8(2)
Sb(13)	0.3799(9)	0.4366(6)	0.3720(5)	1.0(2)
Sb(14)	0.3867(11)	0.4460(6)	0.5497(4)	0.3(2)
Sb(15)	0.3783(10)	0.4414(7)	0.7070(4)	0.5(2)
Sb(16)	0.3791(9)	0.4352(6)	0.8654(4)	0.8(2)
Sb(21)	0.3662(10)	0.0491(7)	0.0320(4)	0.8(2)
Sb(22)	0.3713(11)	0.0506(6)	0.2066(4)	0.5(2)
Sb(23)	0.3725(9)	0.0355(6)	0.3769(5)	1.1(2)
Sb(24)	0.3804(11)	0.0434(6)	0.5375(4)	0.7(2)
Sb(25)	0.3881(11)	0.0409(7)	0.7157(4)	1.1(2)
Sb(26)	0.3785(9)	0.0408(6)	0.8725(6)	1.0(2)
Sb(31)	0.6464(10)	0.1186(7)	0.0378(4)	1.0(2)
Sb(32)	0.6255(10)	0.1353(7)	0.2094(5)	1.2(2)

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[1] Additional material to this paper can be ordered referring to the no. CSD 52512, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 1. (Continued)

Atom	*x*	*y*	*z*	*B*
Sb(33)	0.6309(8)	0.3497(5)	0.3761(5)	0.7(2)
Sb(34)	0.6226(10)	0.1431(6)	0.5418(5)	1.1(2)
Sb(35)	0.6531(8)	0.1199(7)	0.7107(4)	0.4(2)
Sb(36)	0.6528(8)	0.3670(6)	0.8752(6)	0.9(2)
S(11)	0.273(4)	0.330(3)	0.046(2)	1.1(9)
S(12)	0.290(3)	0.325(3)	0.209(2)	0.8(8)
S(13)	0.273(3)	0.334(2)	0.378(2)	0.9(7)
S(14)	0.281(3)	0.337(3)	0.558(2)	0.8(8)
S(15)	0.262(3)	0.341(3)	0.703(2)	1.2(9)
S(16)	0.294(3)	0.327(2)	0.874(2)	0.9(7)
S(21)	0.531(4)	0.589(3)	0.046(2)	1.6(9)
S(22)	0.494(3)	0.596(3)	0.186(2)	0.9(8)
S(23)	0.507(4)	0.600(3)	0.391(2)	1.4(9)
S(24)	0.505(4)	0.595(3)	0.526(2)	1.5(9)
S(25)	0.508(4)	0.596(3)	0.722(2)	1.7(9)
S(26)	0.510(4)	0.591(3)	0.860(1)	0.9(9)
S(31)	0.574(4)	0.234(2)	0.044(2)	1.6(8)
S(32)	0.551(3)	0.255(3)	0.214(2)	1.2(8)
S(33)	0.551(3)	0.234(2)	0.374(2)	0.4(7)
S(34)	0.548(3)	0.263(2)	0.539(2)	1.6(9)
S(35)	0.571(3)	0.231(2)	0.716(2)	0.9(8)
S(36)	0.581(2)	0.247(2)	0.880(1)	0.3(6)
S(41)	0.772(3)	0.495(3)	0.021(2)	0.9(8)
S(42)	0.716(4)	0.482(3)	0.220(2)	1.4(9)
S(43)	0.738(4)	0.498(3)	0.358(2)	1.5(9)
S(44)	0.719(3)	0.478(2)	0.551(1)	0.3(7)
S(45)	0.746(3)	0.489(2)	0.690(2)	0.2(8)
S(46)	0.793(3)	0.509(2)	0.882(2)	1.1(8)
S(51)	0.497(3)	0.900(2)	0.018(2)	0.3(8)
S(52)	0.520(3)	0.893(2)	0.214(2)	0.2(7)
S(53)	0.501(3)	0.896(3)	0.353(2)	0.4(8)
S(54)	0.508(3)	0.902(2)	0.556(2)	0.3(8)
S(55)	0.505(3)	0.887(3)	0.698(2)	0.6(8)
S(56)	0.517(3)	0.905(2)	0.880(2)	0.8(8)
S(61)	0.279(4)	0.163(2)	0.036(2)	0.5(9)
S(62)	0.266(4)	0.156(3)	0.208(2)	1.8(9)
S(63)	0.271(3)	0.148(2)	0.388(2)	0.7(8)
S(64)	0.263(3)	0.150(2)	0.537(2)	0.4(8)
S(65)	0.285(3)	0.153(3)	0.721(2)	1.0(8)
S(66)	0.268(3)	0.152(2)	0.864(1)	0.4(8)

Discussion

All Sb atoms in the senandorite structure have a similar coordination; octahedral with three short and three long bonds with the short ones arranged in a coordination hemisphere forming trigonal pyramids with S atoms where one or two S atoms link neighboring pyramids to each other

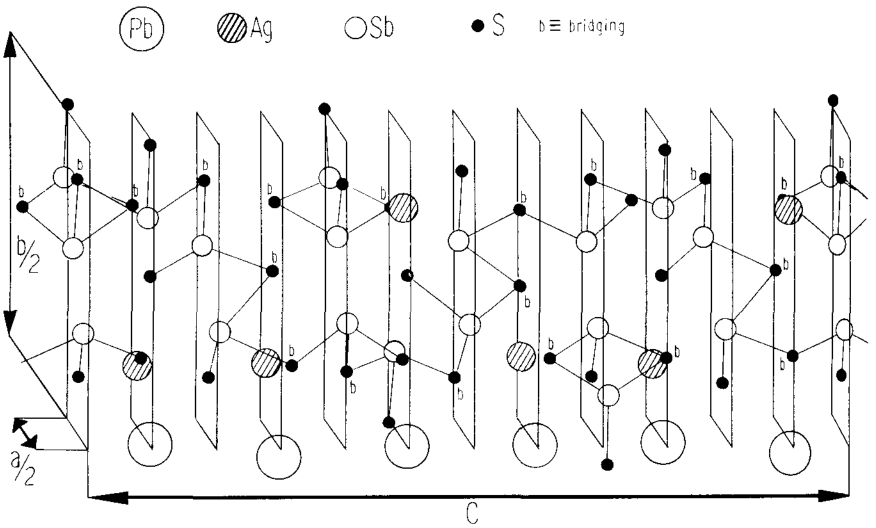

Fig. 1. The structure of one asymmetric unit. $Sb_{14}S_{28}$, Sb_2S_4 groups depicted. Sulphur atoms that "bridge" SbS_3 trigonal pyramids denoted "b".

(Figs. 1, 2). This coordination is characteristic of trivalent group VB (nitrogen group) elements; a lone electron pair is situated in the opposite hemisphere. Though a pentavalent Sb coordination which includes two more S atoms giving a square-pyramidal SbS_5 coordination exists, such as the situation in one of the Sb coordinations in stibnite (Bayliss and Nowacki, 1972), the Sb – S interatomic distances of senandorite does not show any significant trend towards having two intermediately short bonds distinct from the longest one (Fig. 3a). Thus, the Sb – S bonds in senandorite are covalent in nature, and all Sb atoms are trivalent. There are two types of S atoms in the SbS_3 pyramidal group, those that "bridge" SbS_3 pyramids to adjoining ones (bridging, Figure 1) and those which do not (non-bridging). Lengths of the bridging bonds are longer than the non-bridging ones (Fig. 3a), a feature observed in sulphosalts in which Sb atoms are trivalent (Takéuchi and Sadanaga, 1969). In an asymmetric unit of senandorite, four of which form the unit cell, there are two isolated Sb_2S_4 groups, and one chain of $Sb_{14}S_{28}$ which extends in a direction parallel to the *c* axis. The formula for this substance can thus be written $Pb_6Ag_6(Sb_2S_4)_2(Sb_{14}S_{28})$.

Six Ag atoms in an asymmetric unit are coordinated in a distorted AgS_6 octahedron, none of them showing the trigonal pyramidal features of Sb. Three of these sites [Ag(2), Ag(3), Ag(4)] have octahedra flattened along facing vertices with Ag atoms shifted from the center considerably to form what can be considered an AgS_4 tetrahedral coordination (Fig. 2).

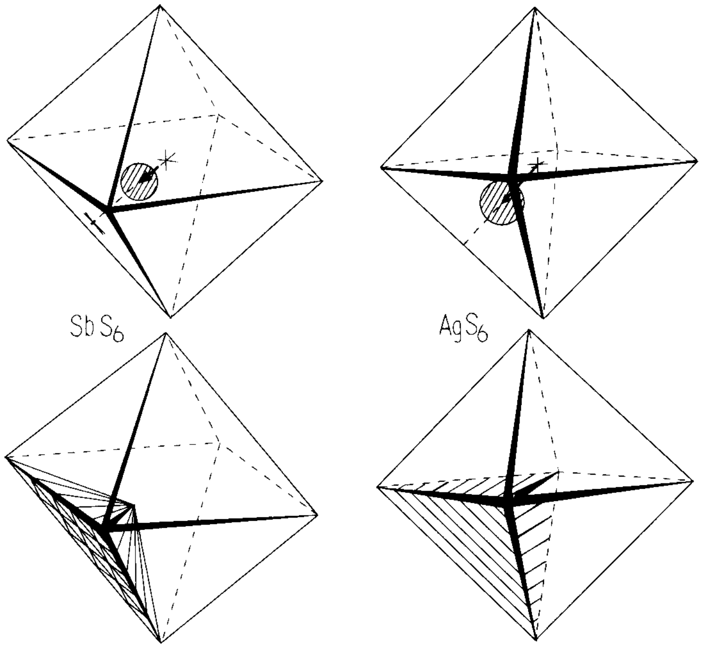

Fig. 2. Schematic drawings of the Sb coordination, showing the tendency towards trigonal pyramidal; the coordination around the Ag atoms with tetrahedral features [Ag(2), Ag(3), Ag(4)].

Although the coordination in Ag complexes is usually the linear X—Ag—X type, it changes quite sensitively with different ligands; with S, Se, P, or As, three- or four-coordination is usually the case (Cotton and Wilkinson, 1966). The largest S—Ag—S angle in each of the three tetrahedra is 142 ~ 151°. This angle is, in a regular octahedron, 180° since these S atoms are on facing vertices. As the sp^3 hybrid character appears, the angle approaches the optimal 109°28′ of a regular tetrahedron. As the bridging S atoms increase in number and participate in the coordination, it becomes no longer possible to consider the Ag coordination to be tetrahedral (Fig. 3b). Bridging S atoms evidently affect the Ag coordination considerably. This may be attributed to a molecular nature of the SbS groups resulting in a structural priority which sterically restricts the bridging S atoms more than the non-bridging S atoms.

Deformation of octahedral PbS_6 coordination occurs when it shares edges with groups having shorter edges (Takéuchi and Sadanaga, 1969), in this case Sb polyhedra. Although all Pb atoms show eight-fold coordination (Fig. 3c), two, Pb(1) and Pb(2), have one elongated bond, indicating a partially sevenfold nature. Among the remaining four, Pb(6), which has the

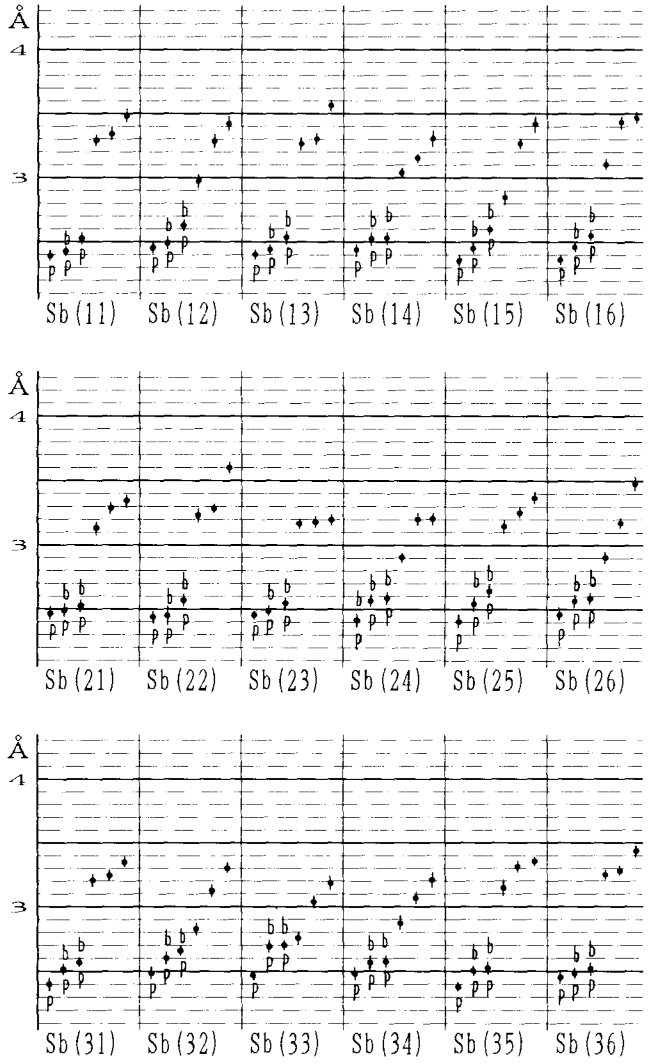

Fig. 3a. Diagrams of bond lengths of the Sb coordination. Bonds to bridging S atoms denoted "b", those in the trigonal pyramidal coordination denoted "p".

least bridging S atoms and is situated near the end of the $Sb_{14}S_{28}$ chain has the least variance of the eight bond lengths. However, the relation between the number of bridging S atoms and the coordination form is weaker than in Ag, probably because Pb can take several types of coordination depending on its environment.

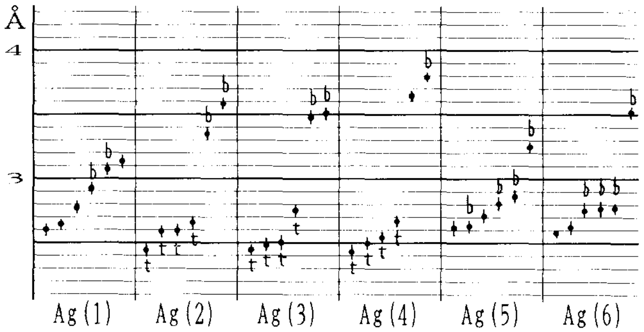

Fig. 3b. Diagram of bond lengths in the Ag coordination. Bonds exhibiting tetrahedral features in Ab(2), Ag(3), Ag(4) denoted "t", those to bridging S atoms "b".

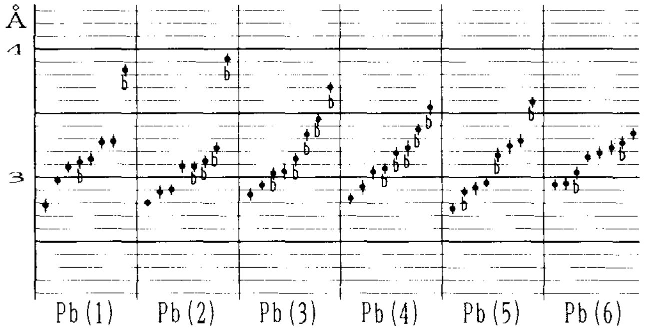

Fig. 3c. Diagram of bond lengths in the Pb coordination. Bonds to bridging atoms denoted "b".

The ability of various sulphosalt structures to accomodate lone electron pairs is one of their conditions of stability (Makovicky and Mumme, 1983). In the present study of senandorite, all of the lone pairs of the SbS groups are more or less directed towards a tubular space extending infinitely along the *c* direction, which coincides with the "lone pair micelles" described for the average 1C type structure of andorite VI by Makovicky and Mumme (1983). It has thus become evident that these micelles play a role in deciding the manner in which the SbS groups and other atoms are packed together in the structure of senandorite.

The relations between the variations of the bonds in the Ag coordination and the number of bridging S atoms give implications that the polymerized SbS groups do have a distinct "molecular" nature, as a unit in the structure. It is obvious in complex salts or molecular crystals that chemical or molecular units take on their unique coordinations. It however seems difficult for ionic crystals, where intramolecular vs. intermolecular distances cannot be easily distinguished, to satisfy the constituents' requirements, which however is accomplished to some extent in senandorite. It is a fair speculation that at high temperatures, minerals of the andorite series all have structures of a 1C or 2C type, whereas through the cooling process, the modulation is frozen in. Since molecular units $Sb_{14}S_{28}$ and Sb_2S_4 can effectively be packed into the structure with complementary relations with the lone pair micelles retained, a coupling with a wave of 1.5C length with a considerable amount of stability is found. The very existence of the molecular groups in senandorite afforded the opportunity to compare otherwise equivalent atoms in various environments with the framework of a single structure.

The above results suggest that there may be ordering into separate sites of atoms in other andorite series minerals which are reported so far as to have mixed sites. Further inquiry of their structures is anticipated.

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References

Ahlfeld, F.: Ramdohrit, ein neues Mineral aus Bolivien. Zentralbl. Mineral. Geol. Paläontol., Abt. A. (1930) 365–367.

Bayliss, P., Nowacki, W.: Refinement of the crystal structure of stibnite, Sb_2S_3. Z. Kristallogr. **135** (1972) 308–315.

Busing, W. R., Martin, K. O., Levy, H. A.: ORFLS, a FORTRAN least-squares program. U.S. Clearinghouse Fed. Sci. Tech. Info. Doc. ORNL-TM-305 (1962).

Coppens, P., Hamilton, W. C.: Anisotropic extinction corrections in the Zachariasen approximation. Acta Crystallogr. **A26** (1970) 71–83.

Cotton, F. A., Wilkinson, G.: *Advanced Inorganic Chemistry*. John Wiley & Sons (1966).

Donnay, J. D. H., Donnay, G.: Syntactic intergrowths in the andorite series. Am. Mineral. **39** (1954) 161–171.

Hellner, E.: A structural scheme for sulfide minerals. J. Geol. **66** (1958) 503–525.

International Tables for X-ray Crystallography. Vol. IV. Birmingham, Kynoch Press (1974).

Ito, T., Muraoka, H.: Nakaseite, an andorite-like new mineral. Z. Kristallogr. **113** (1960) 94–98.

Kawada, I., Hellner, E.: Die Kristallstructur der Pseudozelle (subcell) von Andorit VI (Ramdohrit). Neues Jahrb. Mineral. Monatsh. (1971) 551–560.

Makovicky, E., Mumme, W. G.: The crystal structure of ramdohrite, $Pb_6Sb_{11}Ag_3S_{24}$, and its implications for the andorite group and zinckenite. Neues Jahrb. Mineral. Abh. **147** (1983) 58–79.

Moëlo, Y., Makovicky, E., Karup-Møller, S.: New data on the minerals of the andorite series. Neues Jahrb. Mineral. Monatsh. (1984) 175–182.

Nuffield, E. W.: Studies of mineral sulphosalts: X-Andorite, ramdohrite, fizelyite. Trans. R. Soc. Can. 3rd Ser., Sect. IV **31** (1945) 41–53.

Takéuchi, Y., Sadanaga, R.: Structural principles and classification of sulfosalts. Z. Kristallogr. **130** (1969) 346–368.