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The crystal structure and extent of solid solution of geocronite

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Abstract

Geocronite ($Pb_{28}As_{4+x}Sb_{8-x}S_{46}$, $0 \leq x \leq 8$), an isostructural Sb-bearing analog of jordanite, is monoclinic, space group $P2_1/m$ with $a = 8.963(2)$Å, $b = 31.93(2)$Å, $c = 8.500(2)$Å and $\beta = 118.02(1)°$. The asymmetric unit of geocronite contains three metal layers of four atoms each at approximately $y = 0.05$, $y = 0.15$, and $y = 0.25$. Each of the three layers contains three Pb and one semimetal (As or Sb) site. One of the Pb sites in the first layer is half occupied by semimetals. Of the four As sites in the asymmetric unit of jordanite, only three can expand to accommodate Sb in geocronite. These three expandable sites in the asymmetric unit account for eight Sb atoms in the unit cell. One semimetal site in the asymmetric unit is unable to expand, and this site accounts for four As atoms in the unit cell. The extent of Sb substitution for As in geocronite is thus limited to an As/(As+Sb) value of 0.33.

Introduction

Geocronite is one of 24 sulfosalt phases in the PbS–As_2S_3–Sb_2S_3 system. It is the most PbS-rich of the ternary phases and occurs in many hydrothermal deposits where Pb, As, and Sb mineralization is present.

Geocronite is the Sb-bearing analog of jordanite, $Pb_{28}As_{12}S_{46}$. Reported geocronite formulas vary within the range of $Pb_{26-30}(As, Sb)_{12-14}S_{46-48}$ (Douglass *et al.*, 1954; Roland, 1968; Palache *et al.*, 1944, p. 395–396). Complete Sb substitution for As in geocronite has been reported as the mineral phase schulzite (Palache *et al.*, 1944, p. 396). However, the existence of this mineral has not been confirmed, and synthetic studies (250°–650°C) (Roland, 1968; Salanci and Moh, 1970; Walia and Chang, 1973; Garvin, 1973; Craig *et al.*, 1973; Birnie, 1975) have shown that the stable assemblage for the bulk composition corresponding to pure Sb geocronite is galena (PbS) plus boulangerite ($Pb_5Sb_4S_{11}$). Furthermore, electron microprobe analysis of 120 geocronite samples from 14 localities has shown a range of Sb substitution for As in 116 samples from an As/(As+Sb) value of 1.00 (jordanite) to 0.31 (±0.02) (Birnie, 1975). There is a concentration of analyses at 0.33, and several equilibrium pairs of geocronite (0.33) plus boulangerite (0.00) were observed, indicating that this is the most Sb-rich geocronite that can exist stably within the pressure and temperature range represented by natural samples. Four analyses with As/(As+Sb) values between 0.20 and 0.30 apparently result from Sb contamination when probing a very fine-grained intimately intergrown aggregate of geocronite, boulangerite, and galena. Based on the ideal formula of jordanite, $Pb_{28}As_{12}S_{46}$ (Ito and Nowacki, 1974), geocronite may be assigned a formula of $Pb_{28}As_{4-x}Sb_{8-x}S_{46}$ with $0 \leq x \leq 8$. This compositional range plots in PbS–As_2S_3–Sb_2S_3 composition space along the line with $PbS/(As,Sb)_2S_3 = 4.67$.

Jordanite is monoclinic with space group $P2_1/m$ (Douglass *et al.*, 1954). Reflections with h and l even are strong, indicative of a substructure with $a_{sub} = 1/2\ a$, $b_{sub} = b$, and $c_{sub} = 1/2\ c$. The cell parameters of jordanite are related to those of galena by $a = [1\bar{1}0]_{gn}$, $b = (10/3)\ [111]_{gn}$, and $c = [\bar{1}01]_{gn}$. On these grounds, Wuensch and Nowacki (1966) proposed that the substructure of jordanite is based on a $2 \times 2 \times 10$ array of PbS_6 octahedra stacked along the b axis. The close-packed array of sulfur atoms is interrupted at $y = 0.25$ and $y = 0.75$, where two sulfur layers directly overlie one another, creating metal sites at $y = 0.25$ and $y = 0.75$ having mirror symmetry and trigonal prismatic coordination with sulfur. This substructure model was based on an analysis

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with only h and l even reflections and led to an R of 28.3 percent.

Employing the minimum residual method (Ito, 1973), Ito and Nowacki (1974) solved the full structure of jordanite and refined it to an R of 7.9 percent. The major component of the complement structure, which had been suggested by Wuensch and Nowacki (1966) and was confirmed by Ito and Nowacki (1974), consists of three additional sulfur atoms on or close to the mirror plane in the asymmetric unit.

This study, underway at the time of publication of the Ito and Nowacki (1974) study, was undertaken to solve the crystal structure of geocronite, investigate its possible isostructural relationship with jordanite, and investigate the crystallochemical reasons for the limitation of Sb substitution for As in geocronite at As/(As+Sb) = 0.33.

Specimen description

A sample of geocronite from the Treore Mine, St. Teath, Cornwall, England, was supplied by Dr. Peter Embrey of the British Museum (Natural History) (BM. 1963, 475). A small crystal approximating a tetrahedron 90 μm on an edge was obtained from the sample. An electron microprobe analysis of the sample gave the following chemical composition, in weight percent: Pb = 69.18; As = 4.37; Sb = 9.02; S = 16.55; Cu = 0.29; Fe = 0.10; total = 99.51. The resultant formula, based on the ideal jordanite formula, is $Pb_{28}As_{5.5}Sb_{6.5}S_{46}$. An analysis of 15 random points of the sample showed the As and Sb content to be homogeneous within a range of ± 0.2 atoms.

Space group and unit cell

On the basis of single-crystal diffraction methods, Douglass *et al.* (1954) determined the space group of geocronite to be $P2_1/m$ and suggested on the basis of cell parameters (Table 1) that geocronite and jordanite are isostructural. Jordanite has since been shown to have space group $P2_1/m$ (Wuensch and Nowacki, 1966). The only systematic extinctions in the diffraction patterns of jordanite and geocronite are those of the type $(0k0)$, with k odd. This allows the space group to be $P2_1/m$ or $P2_1$. The $P2_1$ alternative was ruled out for geocronite on the basis of morphology (Douglass *et al.*, 1954) and for jordanite on the basis of morphology and an absence of the piezoelectric effect (Wuensch and Nowacki, 1966; Nowacki *et al.*, 1961).

Precession photos (Mo$K\alpha$ radiation) of the Cornwall geocronite confirmed its space group to be either $P2_1/m$ or $P2_1$; the former was chosen on the basis of considerations just discussed. The crystal showed twinning by reflection across (001). The two twin-related reciprocal lattices showed clearly in b axis precession photographs. The spots of the less predominant twin had intensities of about 1/3 those of its more predominant mate.

TABLE 1: Geocronite and jordanite cell parameters

	a(Å)*	b(Å)*	c(Å)*	β(deg.)*	V(Å^3)*
Geocronite[1]	8.963(2)	31.93(2)	8.500(2)	118.02(1)	2147.5
Geocronite[2]	8.96(3)	31.85(5)	8.48(3)	118.00(17)	2136.7
Geocronite[3]	9.00(2)	31.94(3)	8.52(2)	118.00(17)	2162.5
Geocronite[4]	8.96(3)	31.92(6)	8.48(2)	118.00(17)	2141.4
Jordanite[5]	8.918(1)	31.899(4)	8.462(1)	117.79(1)	2129.5
Galena[6]	8.39	34.24	8.31	120	2087.3

*esd's in parentheses
1. Cornwall, Eng. (this study)
2. Park City, Utah (Douglass et al., 1954)
3. Sala, Sweden (Douglass et al., 1954)
4. Custer Co., Id. (Douglass et al., 1954)
5. Binn Valley, Switz. (Ito and Nowacki, 1974)
6. Based on a galena cell with $a = [1\bar{1}0]_{gn}$, $b = (10/3)\,[111]_{gn}$, and $c = [\bar{1}01]_{gn}$ where $a_{gn} = 5.93$Å.

The crystal was mounted and centered on a Picker four-circle, computer-controlled, diffractometer (FACS-1). The orientations of twelve strong reflections in all octants of reciprocal space were measured in both positive and negative 2θ modes according to the method of Grove and Hazen (1974). Using this orientation data, the cell parameters were refined using the Picker least-squares orientation program (Busing and Levy, 1967). The cell parameters are given in Table 1. There is complete agreement within experimental error of the cell parameters obtained in this study and those of Douglass *et al.* (1954) for c and β. However, one of Douglass *et al.*'s samples shows a slightly longer a axis and another a slightly shorter b axis than obtained in this study. This may be due to differences in the As/(As+Sb) values in the different geocronites.

It should be noted that the geocronite cell is larger than the jordanite cell (Table 1) by 0.5 percent (0.045Å) in a, 0.1 percent (0.3Å) in b, 0.5 percent (0.038Å) in c, and 0.02 percent (0.23°) in β. This is the obvious result of the substitution of the larger atom, Sb, for As.

Data collection

Intensity data were collected on the Picker diffractometer. All reflections within the quadrant of reciprocal space including $\pm h$, $+k$ and $\pm l$ and with 2θ

between 5° and 50° ($0.06 < \sin\theta/\lambda < 0.60$, Nb-filtered Mo$K\alpha$ radiation) were measured. This region included 3960 independent reflections. The peaks were measured using a 2θ scan of 1/2 degree/min. The integrated intensities were corrected for Lorentz and polarization effects, and absorption corrections were computed by numerical integration (Burnham, 1966). The transmission factors varied between 0.09 and 0.21 for geocronite with a linear absorption coefficient of 563 cm^{-1}. A reflection was considered unobserved if its integrated intensity was less than twice the standard deviation of the integrated intensity (Burnham *et al.*, 19771). On this basis, 2287 measured intensities were less than the minimum observable. There were 281 *hk*0 reflections, all of which have intensities contributed to by both twin-related reciprocal lattices. This left a total of 1392 independent observed reflections with intensity contributions from only one twin component. Intensities of 30 reflections were measured in each of the three other symmetry related quadrants of reciprocal space to verify both the diffraction symmetry and the absorption correction.

Structure determination

The atomic positions of jordanite (Ito and Nowacki,1974) were used to initiate the refinement of geocronite. Isotropic temperature factors were assigned a value of 1.50Å²; and the semimetal sites were initially assigned the scattering power of a theoretical atom made up of 46 percent As and 54 percent Sb, corresponding to the proportions of As and Sb in this geocronite crystal.

All structure refinements were carried out using the least-squares refinement program RFINE (L. Finger, 1969, Geophysical Lab, Washington, D.C.). A weighting scheme based on counting statistics was used (Burnham *et al.*, 1971). Atomic scattering factors were taken from Cromer and Waber (1965). Only the 1392 independent reflections were used in the initial refinement. After five cycles of refining the scale factor and atomic coordinates, the refinement converged at R = 12.8 percent.

Two cycles were run in which the isotropic temperature factors were varied. The isotropic temperature factors decreased by about 1.5Å² for the As(4) site and increased by about 1.5Å² for the As(6) site, indicating that Sb probably occupies the former and As the latter site. Site occupancies were changed to reflect this. Neither the Pb(2) nor the As(11) site showed a strong change in B. The Pb(2) site is statistically occupied by two Pb and two semimetal atoms (Ito and Nowacki, 1974), and its semimetal occupancy was assigned one As and one Sb atom. The As(11) site is only half occupied since it is just off the mirror plane, and it was assigned an occupancy of 0.5 As and 1.5 Sb to complete the formula with amounts of As and Sb consistent with the composition of this crystal. Three more refinement cycles were performed, varying the positional parameters and isotropic temperature factors. This refinement converged at R = 12.1 percent.[2] Using all 3679 observed and unobserved reflections, the refinement converged at R = 12.7 percent. There was no significant change in the atomic coordinates or isotropic temperature factors between the refinements using only the independent observed reflections and all independent observed and unobserved reflections. Henceforth, the As(4) and As(11) sites in jordanite (Ito and Nowacki, 1974) will be referred to as the Sb(4) and Sb(11) sites when discussing geocronite.

A three-dimensional Fourier difference synthesis was generated using a Fourier summation computer program (L. Guggenberger, E. I. duPont de Numours and Company, Wilmington, Delaware) and using the 1392 independent observed reflections. The difference map indicated strong apparent anisotropic thermal motion parallel to the b axis for the lead atoms which account for most of the scattering in the crystal. This probably results from errors in the absorption correction. Furthermore, B for some sulfur atoms is unusually low, even negative in some cases, indicating that there is more electron density in these sites than accounted for by the model. It is unlikely that these sites contain metal atoms, so this anomaly must also be attributed to absorption errors. Due to the uncertainty in the absorption correction, it was felt that a more detailed refinement using anisotropic thermal parameters and varying site occupancy was unwarranted.

The final atomic coordinates and isotropic thermal parameters are given in Table 2. The maximum displacement of geocronite atomic coordinates from those of jordanite is ±0.008 for the metal atoms and ±0.02 for the sulfur atoms. The average displacements are ±0.003 and ±0.009 for the metals and sulfurs respectively.

[2] Tabulated observed and calculated structure factors for geocronite may be obtained by ordering Document AM-76-013 from the Business office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

TABLE 2: Geocronite atomic coordinates and isotropic temperature factors

Atom	x*	y*	z*	B*
Pb(1)	0.445(1)	0.0566(3)	0.350(1)	1.3(2)
Pb(2)	0.441(1)	0.0486(4)	0.844(2)	1.4(2)
Pb(3)	0.903(1)	0.0438(3)	0.322(1)	1.3(2)
Sb(4)	0.922(2)	0.0465(5)	0.836(2)	0.8(3)
Pb(5)	0.263(1)	0.1414(3)	0.001(1)	1.5(2)
As(6)	0.271(2)	0.1505(7)	0.511(3)	0.3(3)
Pb(7)	0.788(1)	0.1487(3)	0.018(1)	1.6(2)
Pb(8)	0.790(1)	0.1532(3)	0.516(1)	1.2(2)
Pb(9)	0.120(2)	0.25	0.175(2)	2.2(2)
Pb(10)	0.121(2)	0.25	0.691(2)	1.5(2)
Sb(11)	0.613(3)	0.2214(9)	0.180(3)	0.5(4)
Pb(12)	0.547(2)	0.25	0.638(2)	3.0(3)
S(1)	0.287(7)	0.002(2)	0.000(7)	1.5(1.1)
S(2)	0.307(9)	0.002(3)	0.547(8)	3.0(1.3)
S(3)	0.050(5)	0.085(2)	0.113(5)	0.2(0.7)
S(4)	0.063(7)	0.085(2)	0.686(7)	1.9(1.1)
S(5)	0.656(5)	0.100(2)	0.196(5)	0.0(0.9)
S(6)	0.654(5)	0.090(2)	0.704(6)	0.3(0.8)
S(7)	0.409(6)	0.178(2)	0.370(6)	1.2(0.9)
S(8)	0.405(6)	0.180(2)	0.784(6)	0.7(0.8)
S(9)	0.025(5)	0.183(1)	0.387(5)	-0.4(0.6)
S(10)	0.986(9)	0.202(2)	0.882(9)	2.9(1.2)
S(11)	0.370(6)	0.261(2)	0.051(7)	-1.5(1.2)
S(12)	0.749(9)	0.25	0.021(9)	1.7(1.6)
S(13)	0.746(7)	0.25	0.455(7)	-0.2(0.9)

esd's in parentheses

Discussion of the structure

The general position in space group $P2_1/m$ has multiplicity four, whereas the special positions (inversion centers and mirror planes) have multiplicity two. There are five atoms in the asymmetric unit on mirror plane special positions: Pb(9), Pb(10), Pb(12), S(12), and S(13). Two sites, Sb(11) and S(11), are located just off the mirror plane. Therefore, these must be half-occupied sites, lest two atoms related by the mirror plane be situated unreasonably close together.

The structure of geocronite is based on close packing of sulfur atoms. The close-packed scheme is interrupted at $y = 0.25$ and $y = 0.75$, where mirror symmetry is introduced by two sulfur layers directly overlying one another. The sulfur layers are separated in the structure by approximately 0.1 fractional coordinate along the b axis starting with $b = 0.0$. There are three additional sulfur atoms located on or close to the mirror plane. Metal layers are located between the sulfur layers at $y = 0.05$, $y = 0.15$, $y = 0.25$ (mirror plane) *etc.* The asymmetric unit of geocronite includes the first three sulfur and first three metal layers up to $y = 0.25$.

Each metal layer contains three lead and one semimetal (As or Sb) site. The arrangement of atoms in each layer is shown in Figure 1. The Pb atoms in the $y = 0.05$ layer are coordinated by six sulfur atoms in an octahedral array, typical of close-packed sulfur atoms. The coordination polyhedra about the Pb atoms in the $y = 0.15$ layer increases to seven. In addition to the six sulfur atoms forming an octahedron, a seventh sulfur atom [S(11), S(12), or S(13)],

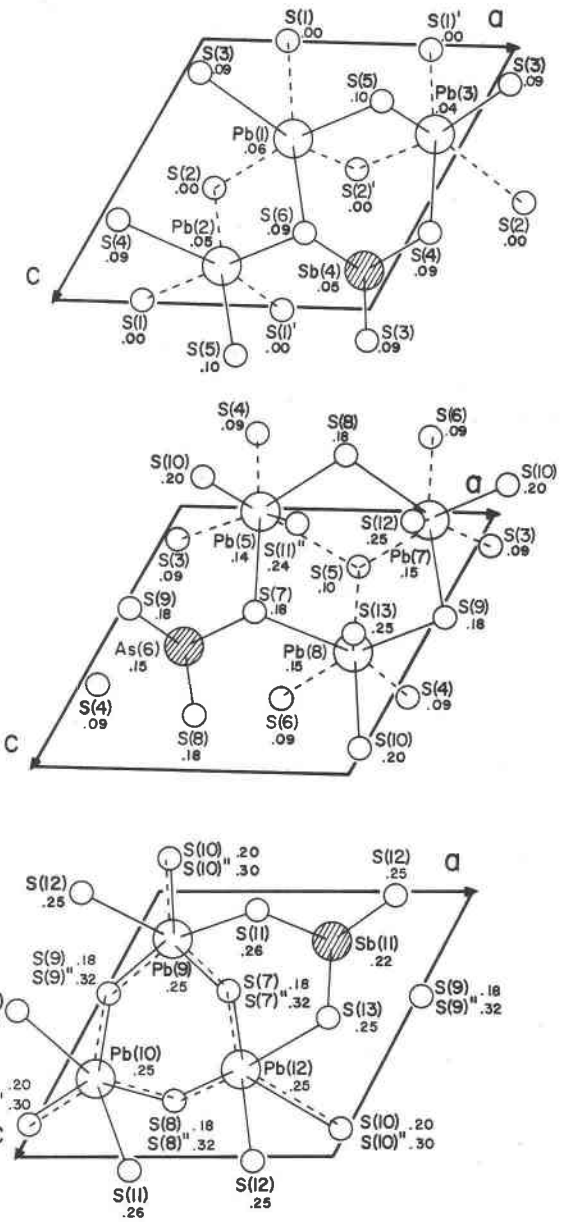

FIG. 1. The crystal structure of geocronite. The three structural layers are projected onto the $y = 0.05$ plane (top), $y = 0.15$ plane (middle), and $y = 0.25$ plane (mirror plane) (bottom). Large open circles represent Pb, large shaded circles represent As or Sb, and small open circles represent S. Single primed and double primed atoms represent those related by the center of symmetry or mirror plane respectively. The b axis fractional coordinates are indicated with each atom.

located on or close to the mirror plane almost directly above the Pb atom, joins the coordination. In the y = 0.25 layer (mirror plane), the Pb atoms are eight-coordinated. The coordination polyhedra are trigonal prisms, the base and top of which are related by the mirror plane. In addition to the six sulfur atoms in the trigonal prism, two other sulfurs [S(11), S(12), or S(13)] join the coordination. These sulfur atoms are at the same level as the Pb atoms and coordinate the Pb atoms through faces of the trigonal prisms.

The semimetals are three-coordinated by sulfurs. The semimetal occupies the apex of a trigonal pyramid, the base of which contains the three sulfur atoms. The semimetals in the Sb(4), As(6), and Sb(11) sites are at a level below the coordinating sulfur atoms. For the semimetals in the Pb(2) site, the three closest sulfur atoms provide the trigonal coordination, and these atoms are at a level below the semimetals. The As–S_3 trigonal pyramids are isolated in the structure. In lead sulfosalts, As is typically trigonally coordinated by sulfur as in gratonite (Ribar and Nowacki, 1969), dufrenoysite (Marumo and Nowacki, 1965), and baumhauerite (Engel and Nowacki, 1969). However, Sb usually prefers 5 or 5+2 coordination in the form of a square-based pyramid of S atoms with Sb near the base. This arrangement is seen in boulangerite (Born and Hellner, 1960), meneghinite (Euler and Hellner, 1960), and stibnite (Bayliss and Nowacki, 1972), but is not seen in geocronite. Geocronite is essentially a lead arsenic sulfosalt with Sb substitution for As in sites that maintain typical As coordination polyhedra.

In geocronite the Pb(2) site is statistically occupied by two Pb atoms, one As atom, and one Sb atom. In jordanite this site is occupied by two Pb and two As atoms. The possibility of variation of the PbS/(As,Sb)$_2$S$_3$ value in geocronite must be considered in light of the Pb(2) site. It accommodates both Pb and a semimetal (As or Sb), and no obvious structural requirements limit the proportion of either. If this site were completely occupied by either Pb or a semimetal, the resulting PbS/(As,Sb)$_2$S$_3$ values of geocronite would be 6.00 and 3.71 respectively. However, no such compositional variation is seen in 120 natural geocronite analyses (Birnie, 1975). The maximum observed variation allows the site to be occupied by 2 ± 1/2 Pb and 2 ± 1/2 (As,Sb). This variation can be accounted for by experimental error. A careful occupancy refinement of this site in jordanite (Ito and Nowacki, 1974) showed that it contained 57.4 ± 1.0 electrons. This corresponds to 1/2 Pb atom [Z(Pb) = 82] and 1/2 As atom [Z(As) = 33].

The fact that occupancy of the Pb(2) site appears limited to 2 Pb and 2 semimetals strongly implies an ordering of the atoms on this site. The ordering could be such that it violates the mirror plane but not the screw axis, thereby reducing the symmetry from $P2_1/m$ to $P2_1$. In the absence of the mirror plane, the Sb(11) and S(11) sites would not have to be half-occupied sites. Ito and Nowacki (1974) divided the Pb(2) site into two distinct atoms, Pb(2) and As(2), and refined the structure of jordanite in space group $P2_1$. They noted no significant change in any atomic parameters. At this stage of the geocronite refinement, the site will be assumed to be disordered, but this point merits more careful examination in the future. Variations in the occupancy of the Pb(2) site may account for the apparent lower PbS/(As,Sb)$_2$S$_3$ values of synthetic jordanite and geocronite (Walia and Chang, 1973; Kutoglu, 1969; Birnie, 1975).

For jordanite, the best model allowed only 1.8 Pb in the Pb(12) site (Ito and Nowacki, 1974). Assuming a balance of valency, the true unit cell content of jordanite is $Pb_{27.6}As_{12}S_{45.6}$ with an ideal formula $Pb_{28}As_{12}S_{46}$. Inasmuch as B for Pb(12) with full occupancy is higher (3.0Å) than the other geocronite metal positions, this site may also be fractionally occupied in geocronite. The calculated density for the ideal formula of geocronite [As/(As+Sb) = 0.46] is 6.56. Palache *et al.* (1944, p. 396) and Douglass *et al.* (1954) report densities of 6.45 and 6.46 (±0.05 respectively for geocronite of approximately the same composition. The calculated density for a geocronite corresponding to the true cell content of jordanite ($Pb_{27.6}As_{5.5}Sb_{6.5}S_{45.6}$) is 6.52. The density for this formula agrees more closely with the measured density of natural geocronite.

The bond distances in geocronite were calculated using the computer program BADTEA (L. Finger, 1968, Geophysical Lab, Washington D.C.) and are listed in Table 3. The major differences in bond distances between those of geocronite and those of jordanite, as reported by Ito and Nowacki (1974), show up in the coordination polyhedra sbout the Sb(4) and Sb(11) sites. In geocronite, the average semimetal–sulfur distances are increased by 0.19 and 0.11Å over those of jordanite for the Sb(4) and Sb(11) sites respectively. The semimetal–sulfur bond distances in the Pb(2) site increase in geocronite by only 0.04Å, whereas bond distances in the As(6) site decrease by 0.01Å. The increased bond distances in the Sb(4) and Sb(11) polyhedra support the assignment of Sb to these sites. The small change in the As(6) bond distances indicates that this site is little

TABLE 3: Geocronite bond distances

Atoms	Distances (Å)*	Atoms	Distances (Å)*
	y = 0.05 layer		
Pb(1)-S(2)'	2.71(7)	Pb(2)-S(2)	2.69(7)
-S(6)	2.90(5)	-S(1)'	2.70(6)
-S(2)	3.07(7)	-S(1)	2.75(5)
-S(5)	3.08(4)	mean 3	(2.71)
-S(1)	3.15(6)	-S(6)	2.99(4)
-S(3)	3.28(4)	-S(5)	3.15(5)
mean 6	(3.03)	-S(4)	3.22(6)
		mean 6	(2.92)
Pb(3)-S(5)	2.65(5)	Sb(4)-S(3)	2.42(4)
-S(1)'	2.85(6)	-S(4)	2.50(6)
-S(3)	2.97(4)	-S(6)	2.54(5)
-S(2)'	2.97(7)	mean 3	(2.49)
-S(4)	3.04(6)	S(3)-S(6)	3.62(6)
-S(2)	3.48(7)	S(3)-S(4)	3.68(6)
mean 6	(2.99)	S(4)-S(6)	3.74(7)
		mean 3	(3.68)
	y = 0.15 layer		
Pb(5)-S(10)	2.93(7)	As(6)-S(9)	2.19(4)
-S(8)	2.96(5)	-S(8)	2.25(5)
-S(7)	3.01(5)	-S(7)	2.27(5)
-S(4)	3.02(6)	mean 3	(2.24)
-S(3)	3.08(4)	S(9)-S(8)	3.49(5)
-S(11)"	3.25(5)	S(9)-S(7)	3.51(6)
-S(5)	3.38(4)	S(8)-S(7)	3.53(6)
mean 7	(3.09)	mean 3	(3.51)
Pb(7)-S(5)	2.79(4)	Pb(8)-S(9)	2.94(4)
-S(3)	2.92(4)	-S(5)	2.95(3)
-S(6)	3.00(5)	-S(4)	3.07(6)
-S(9)	3.04(4)	-S(10)	3.13(1)
-S(10)	3.06(7)	-S(13)	3.14(5)
-S(8)	3.20(5)	-S(6)	3.15(4)
-S(12)	3.25(1)	-S(7)	3.17(7)
mean 7	(3.04)	mean 7	(3.08)
	y = 0.25 layer (mirror plane)		
Pb(9)-S(10)	2.68(7)	Pb(10)-S(11)	2.83(5)
-S(10)"	2.68(7)	-S(10)	2.88(7)
-S(11)	2.92(5)	-S(10)"	2.88(7)
-S(12)	2.94(8)	-S(13)	3.00(6)
-S(9)	3.17(4)	-S(9)	3.16(4)
-S(9)"	3.17(4)	-S(9)"	3.16(4)
-S(7)	3.28(5)	-S(8)	3.20(5)
-S(7)"	3.28(5)	-S(8)"	3.20(5)
mean 8	(3.02)	mean 8	(3.04)
Sb(11)-S(13)	2.26(5)	Pb(12)-S(13)	2.87(5)
-S(11)	2.29(6)	-S(12)	2.89(7)
-S(12)	2.38(7)	-S(7)	3.07(5)
mean 3	(2.31)	-S(7)"	3.07(5)
S(11)-S(13)	3.52(7)	-S(8)	3.11(5)
S(11)-S(12)	3.54(8)	-S(8)"	3.11(5)
S(12)-S(13)	3.70(8)	mean 6	(3.02)
mean 3	(3.59)	-S(10)	3.81(7)
		-S(10)"	3.81(7)
		mean 8	(3.22)

*esd's in parentheses
' indicates atom related by center of symmetry
" indicates atom related by mirror plane

changed from the jordanite structure and is, therefore, occupied by As. The Pb(2) semimetal sites have coordination polyhedra sufficiently large in the jordanite structure (average bond distance = 2.673Å) so that Sb can be housed there with little change.

The As–S_3 and Sb–S_3 bond distances in geocronite are consistent with those reported for other minerals with the same types of coordination polyhedra such as gratonite (Ribar and Nowacki, 1969), dufrenoysite (Marumo and Nowacki, 1967), rathite I (Marumo and Nowacki, 1965), orpiment (Morimoto, 1954), stibnite (Bayliss and Nowacki, 1972), tetrahedrite (Wuensch, 1964), and tennantite (Wuensch *et al.*, 1966).

As was noted earlier, the geocronite solid solution in natural specimens appears to run only to an As/(As+Sb) value of 0.33. Geocronite appears to be unstable at compositions more Sb-rich than As/(As+Sb) = 0.33, at which point the unit cell contains eight Sb and four As atoms. That number of Sb atoms just fills the Pb(2), Sb(4), and Sb(11) sites, leaving the As(6) site with 4 As. The apparent limit of Sb substitution for As in geocronite can thus be explained on the basis of a structure whose geometry will not allow the As(6) polyhedron to expand and accommodate Sb. The As(6) atom (y = 0.15 layer) is coordinated upwards to three sulfurs [S(7), S(8), and and S(9)] that are involved in the trigonal prismatic coordination of lead atoms (y = 0.25 layer). If these three sulfurs were moved up to accommodate Sb in the As(6) site, the trigonal prismatic coordination about the Pb atoms in the layer above would be compressed by twice the amount of the vertical movement of the sulfurs. This is due to the requirements of mirror symmetry perpendicular to b in the trigonal prisms. The trigonal prisms about Pb cannot accommodate this compression. Furthermore the structure cannot merely be expanded along the b axis to accommodate Sb in the As(6) site, for such an expansion would distort the sulfur polyhedra about the other Pb sites.

Nature of other sulfosalt solid solutions

There are numerous partial solid solutions among Pb–As–Sb–S sulfosalts, for example: jordanite–geocronite, dufrenoysite–veenite, boulangerite, and baumhauerite (Walia and Chang, 1973; Birnie, 1975). However, starting with an essentially Pb–As–S structure or Pb–Sb–S structure, neither is able to fully accommodate the other semimetal and complete the solid solution.

This is not the case in the Cu–As–Sb–S or Ag–As–Sb–S sulfosalts. Luzonite (Cu_3AsS_4) and famatinite (Cu_3SbS_4) form a complete solid solution series (Gaines, 1957). Similarly, a complete solid solution exists between tennantite ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_{12}Sb_4S_{13}$) (Wuensch *et al.*, 1966). Pearceite [$(Ag,Cu)_{16}As_2S_{11}$] and antimonpearceite [$(Ag,Cu)_{16}Sb_2S_{11}$] and their polymorphic counterparts, arsenopolybasite and polybasite, also form a complete solid solution series (Hall, 1967).

The reason for the different behavior of the Pb–As–Sb–S sulfosalts as opposed to the Cu–As–Sb–S or Ag–As–Sb–S sulfosalts may be related to the relative bond strengths of the metal–sulfur bonds. Relative bond strengths have been calculated by Povarennykh (1968 and 1971) and are listed in Table 4. These calculations are based on a simple formula that considers the interatomic distances, the coordination number of the metal ion, the valencies of the two ions, the degree of repulsion of electron shells of neighboring atoms, and the number and state of the orbits of valence electrons not involved in the bonding. Table 4 clearly indicates that the Pb–S bonds in coordination polyhedra of the type seen in Pb sulfosalts are weaker than the Cu–S and Ag–S bonds. It is probable that the stronger Cu–S and Ag–S bonds hold their sulfosalt structures together during the progressive substitution of the different semimetals in the solid solution series. However, the Pb–S bonds are sufficiently weak that a structure is easily stretched or collapsed to the point of instability.

Conclusion

Geocronite ($Pb_{28}As_{4+x}Sb_{8-x}S_{46}$, $0 \leq x \leq 8$) is the isostructural Sb-bearing analog of jordanite ($Pb_{28}As_{12}S_{46}$). Three of the four semimetal sites in jordanite can be expanded to accommodate a total of 8 Sb atoms in the structure. However, one site [As(6)] is not able to expand, thereby limiting the extent of solid solution in geocronite to an As/(As+Sb) value of 0.33. This conclusion is consistent with the compositions of natural geocronites.

TABLE 4: Relative bond strengths*

Element & coordination	Relative bond strength
$Pb\text{-}S_8$	0.03
$Pb\text{-}S_6$	0.08
$Cu\text{-}S_4$	0.11
$Ag\text{-}S_3$	0.12
$Cu\text{-}S_2$	0.19
$Ag\text{-}S_2$	0.20
$Si\text{-}O_4$	0.41

*Povarennykh (1968 and 1971)

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