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The structure of junitoite, $CaZn_2Si_2O_7 \cdot H_2O$

R. D. HAMILTON AND J. J. FINNEY

Department of Geology, Colorado School of Mines, Golden, Colorado 80401, USA

ABSTRACT. Junitoite, $CaZn_2Si_2O_7 \cdot H_2O$, is orthorhombic, space group *Ama*2, with $a = 12.510$, $b = 6.318$, $c = 8.561$ Å, Z = 4. The structure, determined on the basis of three-dimensional Mo-$K\alpha$ intensity data for 745 reflections refined to $R = 0.10$. The structure consists of ZnO_4 tetrahedral chains along *b* joined by Si_2O_4 groups along *a* and *c* to form a three-dimensional network. Ca occurs in distorted $CaO_5(H_2O)$ octahedra. The structure shows similarities to hemimorphite and Ca–Zn silicates but represents a unique tetrahedral framework.

KEYWORDS: crystal structure, junitoite.

JUNITOITE was first described by S. A. Williams (1976) in material from the Christmas Mine, Gila County, Arizona. The Christmas Mine is a porphyry copper deposit with its production coming from skarns derived from the intrusion of a complex Laramide-age diorite to granodiorite stock into Palaeozoic carbonates (Perry, 1969). The skarns consist of garnet, wollastonite, and diopside with disseminated sphalerite and chalcopyrite. The junitoite occurs in portions of skarn which have undergone extensive retrograde metamorphism and oxidation. Junitoite is a secondary mineral, associated with kinoite, apophyllite, smectite, calcite, and xonotlite.

The junitoite used in this study was from Christmas Mine material provided by Dr Williams. The sample contained junitoite as thin, colourless, rectangular plates approximately $2 \times 2 \times 0.05$ mm nestled among larger euhedral apophyllite crystals. The apophyllite crystals were encrusting kinoite which was filling fractures in a carbonate breccia.

Space group and cell parameters. Precession photographs were used to verify the data of Williams (1976). He chose the non-standard orientation *Bbm*2 to establish a morphological correspondence between junitoite and hemimorphite. To facilitate calculations we have interchanged the *a* and *b* of Williams (the orientation of *c* is fixed by morphology) yielding the standard *A*-centred orientation, *Ama*2. This orientation will be used throughout this paper.

Examination of precession photographs reveals that, in addition to the extinctions expected for *Ama*2, those *hkl* reflections for *h* odd are very weak, indicating that heavy atoms occupy the 4*a* site, 00*z*, in which atoms are separated by $\frac{1}{2}$ along *a*. There are only five very weak 0*kl* reflections for which *k* is odd, indicating the presence of a pseudo *b*-glide normal to *a*.

The unambiguous assignment of a noncentric space group is possible on the basis of the hemimorphic habit, asymmetric etch pits and pyroelectric effect, all observed by Williams.

Cell parameters, as determined by the least-squares refinement of ten reflections scattered evenly throughout the reciprocal sphere, are: $a = 12.510(7)$, $b = 6.318(3)$, $c = 8.561(6)$ Å, Z = 4 (standard errors are in parentheses). The calculated density of 3.516 gm cm^{-3} matches the value of 3.5 gm cm^{-3} reported by Williams (1976).

Data collection and structure refinement. Diffraction data were collected on a tabular crystal $0.1 \times 0.12 \times 0.05$ mm with the short direction normal to (100). Data were collected using a Syntex $P\bar{1}$ automatic four-circle diffractometer equipped with a graphite monochrometer employing Mo$K\alpha$ radiation. A w-2θ scan was used with a constant scan rate of 2° 2θ per minute. The intensities of 745 reflections with a maximum 2θ of 50° were measured in the positive octant.

Initial values for atomic coordinates were obtained by Patterson and Fourier methods. The Patterson and electron density maps were generated using NRC2 and NRC8 from the NRC crystallographic programs of Ahmed *et al.* (1967).

Refinement of parameters was accomplished using ORFLS (Busing *et al.*, 1962). Refinement was based on weighted intensities. All structure factor calculations were based on neutral atom scattering factors from volume IV of the International Tables for X-ray Crystallography.

Because a majority of the electrons in the unit cell were associated with special positions and the presence of a pseudo *b*-glide the set of all reflections which were not systematically extinct was refined with a weight assigned to each reflection according to the reflection $w = 1/(\sigma^2 F^2)$. σ^2 was calculated according to the method of Cornfield *et al.* (1967)

Table I. Atomic parameters for junitoite
(standard error in parentheses)

Atom	site	X	Y	Z	B(A)^2
Zn(1)	4a	0	0	0.0000	1.23(10)
Zn(2)	4a	0	0	0.4963(14)	0.15(07)
Ca	4b	1/4	0.2462(12)	0.1119(11)	0.40(12)
O(4)	4b	1/4	0.7721(44)	0.3270(28)	0.46(36)
H_2O	4b	1/4	0.2746(64)	0.3785(45)	3.22(87)
Si	8c	0.1316(03)	0.7348(11)	0.2359(12)	0.32(09)
O(1)	8c	0.0437(12)	0.7438(30)	0.3764(19)	0.72(25)
O(2)	8c	0.1213(15)	0.5314(29)	0.1360(31)	1.10(36)
O(3)	8c	0.1263(14)	0.9517(32)	0.1249(31)	1.21(34)

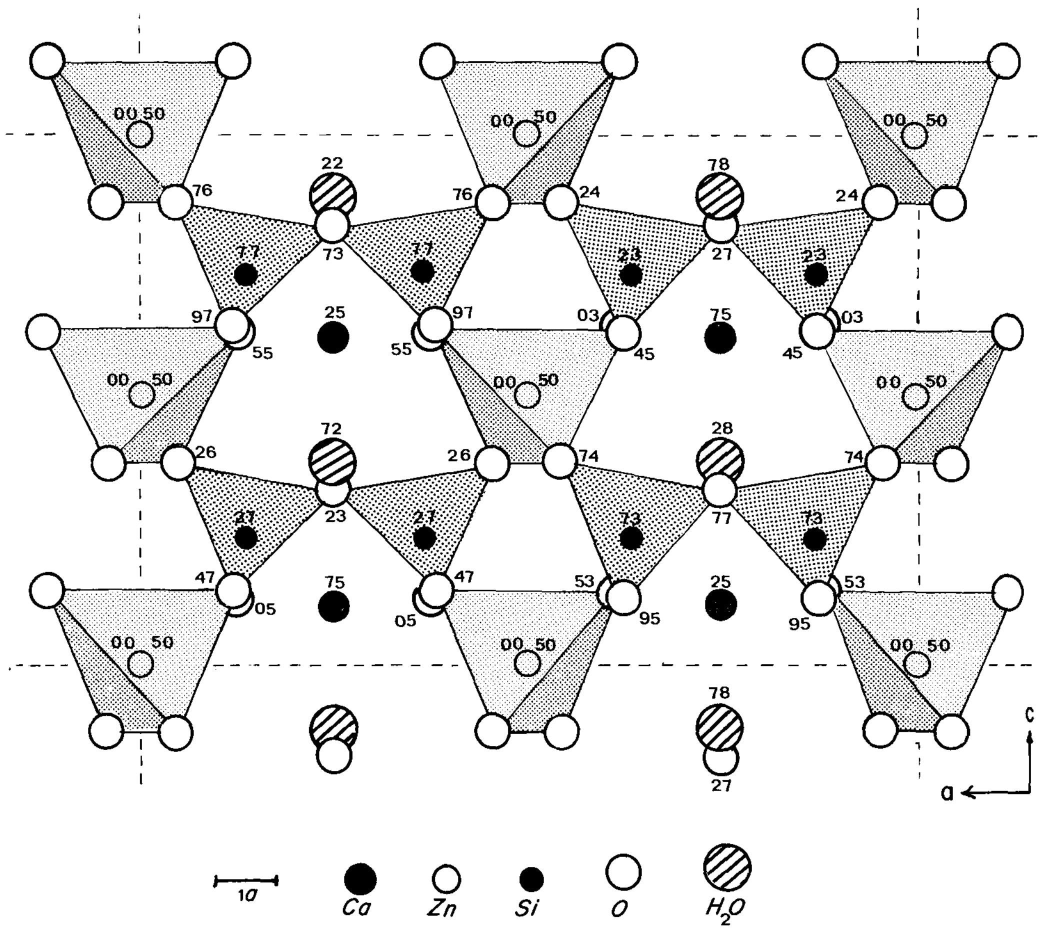

FIG. 1. Junitoite viewed along [010] (y coordinate of atom in hundredths).

to prevent the assignment of unreasonably high weights to the stronger reflections.

The final discrepancy factors for all reflections, using isotropic temperature coefficients were $R = 0.100$ for unweighted data and $R = 0.086$ for weighted data. Attempts at refinement with anisotropic temperature coefficients produced a number of negative coefficients.

The only difference in systematic extinctions between *Ama*2 and *Aba*2 is the $0kl$ reflections. For *Ama*2, $0kl$ reflections are present when $k+l = 2n$, whereas *Aba*2 has reflections present when $k = 2n$, $l = 2n$. Although five very weak reflections can be observed on Weissenberg photographs which indicate the correct space group is *Ama*2, an attempt was made to refine the structure in *Aba*2 because the diffractometer data are compatible with the systematic extinctions for this space group.

It is possible to shift the entire structure intact from *Ama*2 to *Aba*2 by moving the origin so that $(x,y,x)_{Aba2} = (x-\frac{1}{4}, y-\frac{1}{4}, z)_{Ama2}$. Upon shifting the origin the two fourfold zinc positions are transformed into a single eightfold position, and two of the eightfold oxygen sites are recombined into two new eightfold sets. The remaining fourfold special positions transform into equivalent positions in *Aba*2. In space group *Aba*2 the structure refines to $R = 0.097$ and $R = 0.087$. The final atomic position parameters for *Aba*2 differed from the transformed parameters in *Ama*2 by less than the standard error associated with each of the parameters. The final atomic position parameters for space group *Ama*2 are given in Table I.

It is impossible to tell from the final refinement which space group is correct. Although *Aba*2 is preferable based on the degree of freedom it provides the zinc atoms and Pauling's principle of parsimony, *Ama*2 produces less distortion of the coordination polyhedra and provides a structure in which the site symmetry of the cations is more similar to other zinc silicates. The final choice of *Ama*2 is based, however, on the film data.

Description of the structure. Fig. 1 shows a polyhedral drawing of the structure of junitoite viewed along [010]. Fig. 2 is a view along [001] of a portion of the structure bounded approximately by $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Zinc occurs in ZnO_4 tetrahedra which share corners to form continuous ZnO_3 chains along [010]. These chains are linked in the [001] direction by silicon tetrahedra, each of which

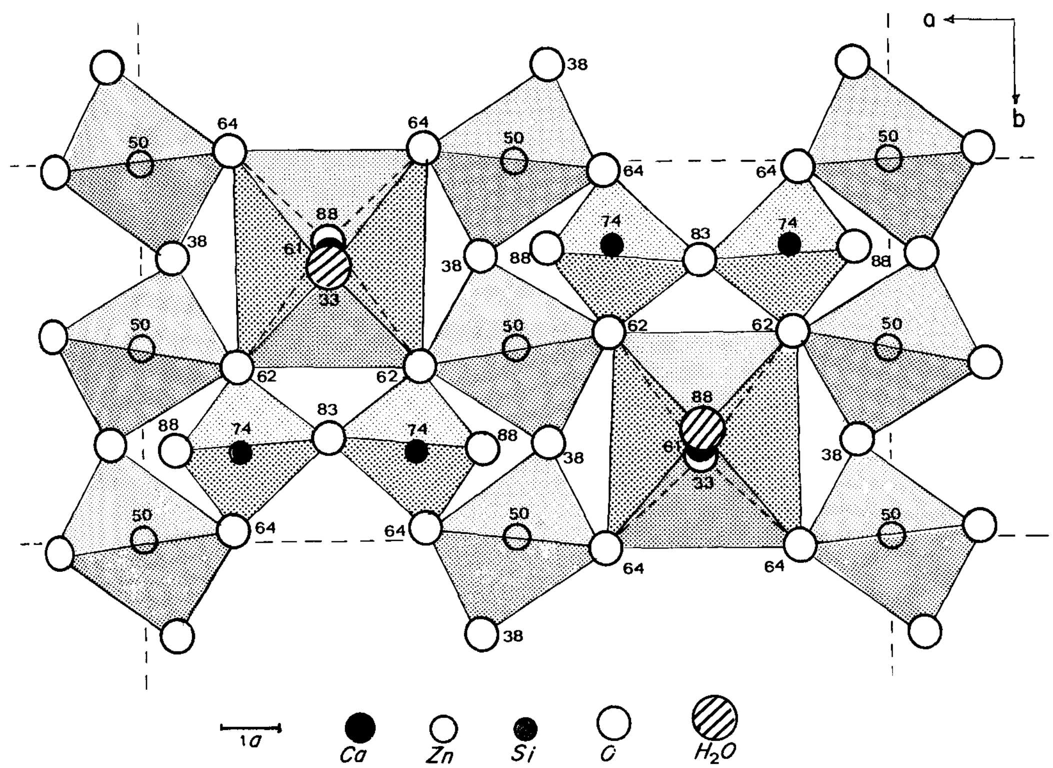

FIG. 2. Junitoite viewed along [001] (*z* coordinate of atom in hundredths).

Table II. Interatomic distances for junitoite (standard error in parentheses, nx refers to n number of equivalent distances)

Zn(1)	- O(1)	2x	1.947(29) Å	Si	- O(1)	1.630(40) Å
	O(3)	2x	1.932(38)		O(2)	1.549(46)
Zn(2)	- O(1)	2x	1.994(35)		O(3)	1.669(46)
	O(2)	2x	1.942(42)		O(4)	1.690(53)
Ca	- O(2)	2x	2.425(40)	Si - O(4) - Si bridging angle		
	O(3)	2x	2.422(40)			122.4°
	O(4)		2.444(47)			
	H_2O		2.291(70)			

is a member of an Si_2O_7 disilicate group, to form zinc silicate sheets parallel to (010). These sheets join through the bridging oxygen of the disilicate groups O(4) along *a* to form a three-dimensional tetrahedral framework.

The two sets of zinc tetrahedra are slightly distorted and not identical, as can be seen from the bond lengths given in Table II. The average tetrahedral angle is close to ideal and the average Zn–O bond length of 1.954 Å is identical to that found in hemimorphite (McDonald and Cruickshank, 1967) and similar to the 1.95 Å average for all zinc silicates.

The Zn(1) and Zn(2) tetrahedra are linked alternately through a shared corner oxygen O(1), forming crenulated ZnO_3 chains. These chains are different from silicate chains in that two oxygens of each tetrahedron O(1) lie in a common basal plane and two lie in common apical plane, O(2) and O(3). Each unit cell contains two sets of these chains along 010 through the origin and related points. The sets have an opposite sense of crenulation as required by the space group symmetry.

The silicon tetrahedra form isolated Si_2O_7 disilicate groups sharing a common oxygen O(4). The disilicate groups are arranged across a mirror plane as they are in hardystonite (Louisnathan, 1969) and hemimorphite (McDonald and Cruickshank, 1967). It may well be that the association of disilicate groups with mirror planes determines the space group, *Ama*2, of junitoite. In *Aba*2 the group falls astride a *b*-glide with a twofold axis through the bridging oxygen, a configuration not found in any other mineral containing Si_2O_7 groups.

The average Si–O bond length, 1.634 Å, is consistent with other silicates and zinc silicates but the range of bond lengths, 1.55 to 1.69 Å, is rather large and the 1.55 Å Si–O bond is unusually short. The Si–O–Si angle through the bridging oxygen is 122.4° which is smaller than the average of 131.5° for all disilicate groups in which the bridging oxygen is in threefold coordination (Baur, 1971).

Calcium occurs in isolated, distorted $CaO_5(H_2O)$ octahedra which lie on a mirror plane. Four oxygens (O(2) × 2, O(3) × 2 lie in a plane approximately parallel to (001) and slightly above the calcium. The Ca–O bond lengths within the plane are 2.42 Å. Below the Ca on the mirror plane at a distance of 2.44 Å is a fifth oxygen, O(4), which is also the bridging oxygen of the disilicate group. Above the Ca at a distance of 2.29 Å is a water molecule. The Ca–O bond lengths fall at the maximum expected value based on ionic radius and observed bond lengths in other structures.

Discussion. Structurally, junitoite is more closely related to hemimorphite $Zn_4SiO_2O_7(OH)_2 \cdot H_2O$ than it is to the calcium zinc silicates hardystonite $Ca_2ZnSi_2O_7$ and clinohedrite $CaZnSiO_4 \cdot H_2O$. Both junitoite and hemimorphite (McDonald and Cruickshank, 1967) contain highly articulated ZnO_3 tetrahedral chains bridged by Si_2O_7 disilicate groups to form a three-dimensional tetrahedral network. In hemimorphite the network is compact except for channels along $\frac{1}{2}$, 0, *X* and 0, $\frac{1}{2}$, *Z* which connect cavities at $z = 0$ and $\frac{1}{2}$ which contain the water molecules (McDonald and Cruickshank, 1967). In junitoite the network forms large isolated cavities elongate along *c*. The cavities contain the Ca in octahedral coordination and the water molecule.

Clinohedrite also contains ZnO_3 tetrahedral chains. These chains are linked by isolated SiO_4 tetrahedrons to form $(ZnSiO_4)$ sheets which are sandwiched between chains of edge sharing CaO_6 octahedra giving a layer-like structure (Venetopoulos and Rentzeperis, 1976). Hardystonite, $Ca_2ZnSi_2O_7$, also has a layer-like structure. The layers are composed of Si_2O_7 disilicate groups joined by isolated ZnO_4 tetrahedra (Louisnathan, 1969).

In junitoite and clinohedrite Ca is in distorted octahedral coordination with oxygen, and the OH and H_2O as available. In hardystonite Ca is an eightfold antiprism.

The zinc silicates as a group have structural features in common and yet each has a unique structural configuration. There are 14 zinc silicate minerals and 11 synthetic zinc silicates with known structures. Of these, 12 are non-centric and 10 of the 12 hemimorphic. In contrast, other zinc compounds and other silicates occur in non-centric space groups only 7% of the time. Clearly structures based on zinc and silicon both in tetrahedral coordinations have some unique features worthy of further investigation.

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