

The structure of junitoite, $\text{CaZn}_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$

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ABSTRACT. Junitoite, $\text{CaZn}_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$, is orthorhombic, space group *Ama2*, 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 $\text{CaO}_5(\text{H}_2\text{O})$ 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 *Bbm2* 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, *Ama2*. This orientation will be used throughout this paper.

Examination of precession photographs reveals that, in addition to the extinctions expected for

Ama2, those hkl reflections for h odd are very weak, indicating that heavy atoms occupy the $4a$ site, $00z$, in which atoms are separated by $\frac{1}{2}$ along a . There are only five very weak $0kl$ 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 P1 automatic four-circle diffractometer equipped with a graphite monochromator employing Mo- $K\alpha$ radiation. A w - 2θ scan was used with a constant scan rate of $2^\circ 2\theta$ 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 ₂ O	4b	1/4	0.2746(64)	0.3795(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)

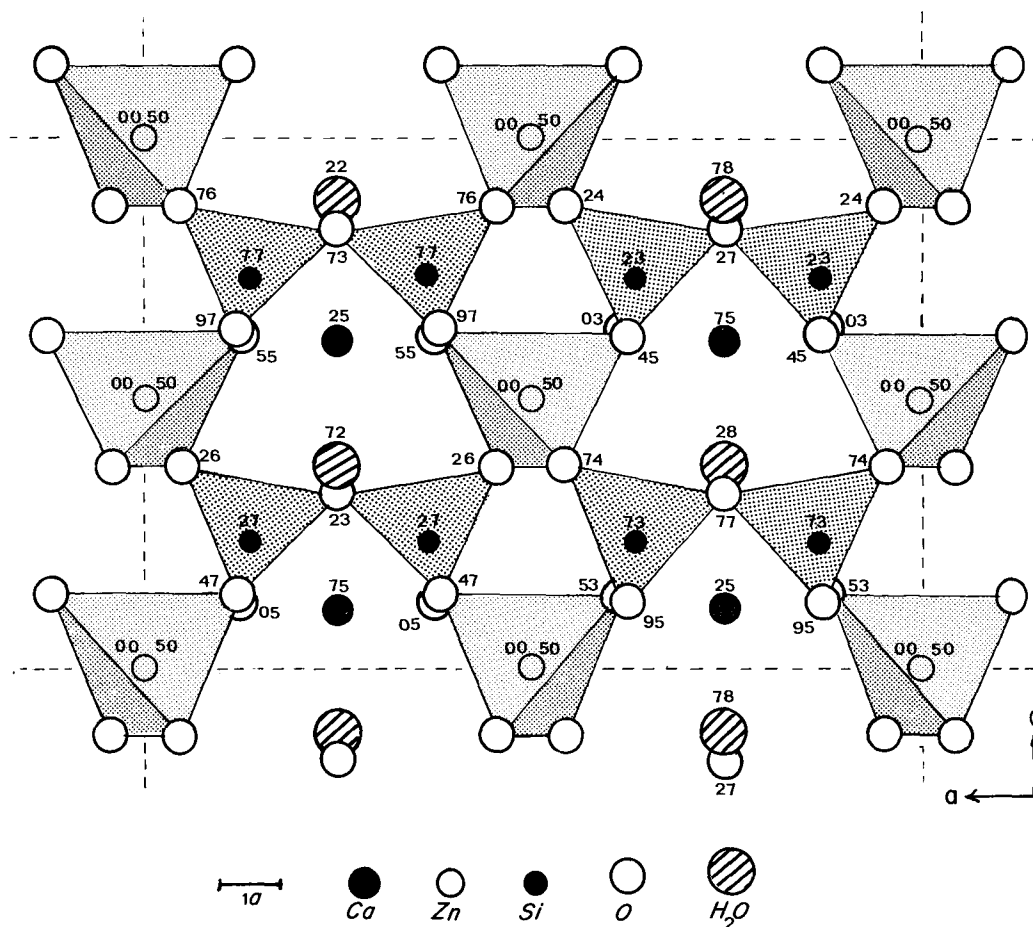


FIG. 1. Junitoite viewed along [010] (y coordinate of atom in hundredths).

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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