

THE CRYSTAL STRUCTURE OF KINOITE

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ABSTRACT

Kinoite, $\text{Cu}_2\text{Ca}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, has space group $P2_1/m$ with cell parameters $a=6.991$, $b=12.884$, $c=5.655 \text{ \AA}$, and $\beta=96^\circ 11'$ with $Z=2$. The structure has been determined using automated diffractometer data. Refinement converged with $R=0.037$ for all observed reflections. The structure consists of ladderlike $(\text{CuO}_2)_n$ chains parallel the c axis, Si_3O_{10} multiple tetrahedra units, and distorted calcium-oxygen octahedra. Alternate pairs of oxygens in the CuO_2 chains are water oxygens that also serve as apices of the calcium octahedra.

INTRODUCTION

Kinoite, described recently, is a copper silicate from the northern Santa Rita Mountains of southern Arizona (Anthony and Laughon, 1970). Cell parameters were reported at that time as $a=6.990(4)$, $b=12.890(3)$, $c=5.654(2) \text{ \AA}$, and $\beta=96^\circ 05(4)'$. (Standard errors, in parentheses, refer to the last digit.) New parameters obtained by least-squares refinement of goniostat angle settings for 14 reflections are in fairly good agreement with those values. Values thus obtained are $a=6.991(2)$, $b=12.884(3)$, $c=5.655(2) \text{ \AA}$, and $\beta=96^\circ 11(2)'$. The previously reported chemical analysis was confirmed by electron microprobe. Systematic omission of $0k0$ reflections with k odd indicates the space group to be $P2_1/m$ or $P2_1$. There are 2 formula units per cell. Measured and calculated densities are 3.16 and 3.19 respectively.

STRUCTURE DETERMINATION

Three-dimensional intensity data were obtained from a sphere of 0.075 mm radius by the use of a Picker FACS-1 automated diffractometer. A total of 2327 intensities were collected using Zr-filtered Mo radiation, representing all unique reflections with $2\theta \leq 70^\circ$. Of these, 370 failed to exceed a value of twice the background count and were rejected as unobserved. Lorentz and polarization corrections were applied in the usual manner, and corrections were made for absorption.

A three-dimensional Patterson synthesis was calculated using all data. Although the solution was not straightforward, copper and calcium atoms eventually were located from an evaluation of the Patterson map.

For the centric case, the Harker section (Fig. 1) showed six clearly defined peaks, five of which were high enough to be Cu-Cu vectors and all of which were high enough to be Ca-Ca vectors. The only peak present on the Harker line had a height one-twelfth that of the origin peak and this height was thought to be inadequate to represent either a copper or a calcium double-weight vector. The lack of a peak at $0, \frac{1}{2}, 0$ added the requirement that the only special positions occupied by heavy atoms be those on the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. The fact that at least two of the six silicons must be in special positions, when considered with regard to an x - z cross-sectional area of approximately 39 \AA^2 , strongly suggested that the structure was acentric.

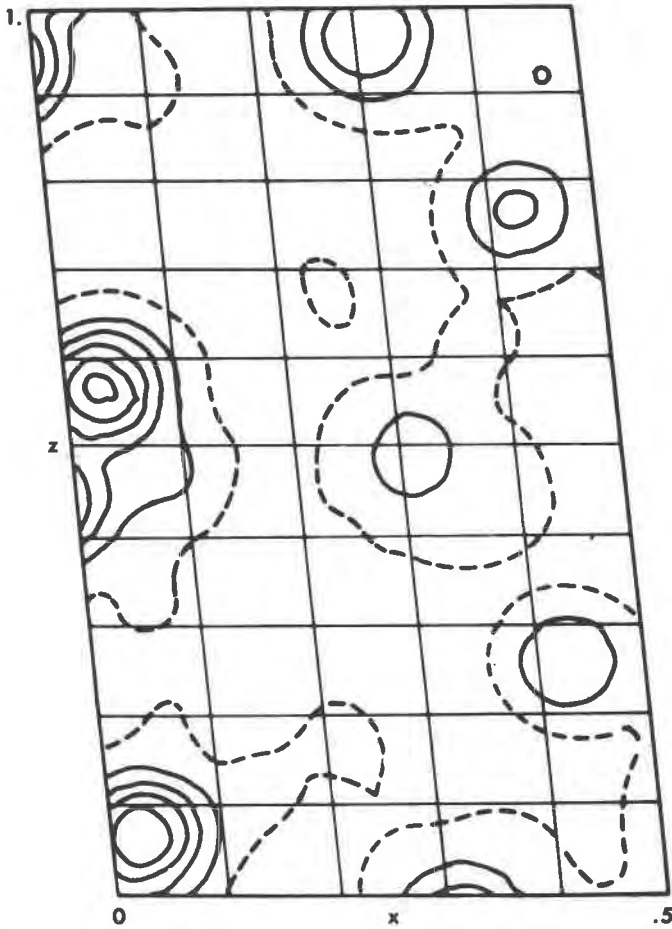


FIG. 1. Patterson Harker section ($y = \frac{1}{2}$). Contour interval is 5 percent of origin peak height. Zero contour is dashed; negative contours not shown.

Peak positions and heights were calculated for all possible permutations of copper and/or calcium positions derived from the Harker section peaks. These positions and heights were then compared with peaks actually observed, but no correspondence was found for the acentric case.

One solution, considered centrosymmetrically, gave a good explanation of the observed Patterson peaks, with a single exception—the Ca-Ca Harker line peak was only 75 percent as high as predicted. This solution was pursued and ultimately found to be correct.

The remainder of the structure was solved by successive cycles of least squares, Fourier, and difference synthesis. It is noteworthy that the Patterson showed no Harker section peak corresponding to the silicon on the mirror plane and no Harker line peak corresponding to the silicon in the general position. For observed reflections, R converged at 0.052 with isotropic B 's.

TABLE 1. ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	B (Å ²)
Cu(1)	0.4819 (1)	1/4	0.2179 (1)	0.51 (1)
Cu(2)	.4884 (1)	1/4	.7139 (1)	.45 (1)
Ca	.8461 (1)	.1061 (1)	.0269 (1)	.54 (1)
Si(1)	.2337 (1)	.0803 (1)	.4518 (2)	.40 (2)
Si(2)	.9432 (2)	1/4	.5477 (3)	.37 (2)
O(1)	.8107 (7)	1/4	.7624 (9)	.69 (6)
O(2)	.0847 (5)	.1485 (3)	.5901 (6)	.94 (5)
O(3)	.4348 (5)	.1475 (3)	.4573 (6)	.64 (4)
O(4)	.8344 (7)	1/4	.2847 (9)	.82 (7)
O(5)	.1539 (5)	.0498 (3)	.1867 (6)	.86 (5)
O(6)	.7201 (5)	.0189 (3)	.3676 (6)	.90 (5)
O(w)	.5073 (5)	.1475 (3)	.9714 (6)	.73 (4)
H(1)	.40	.08	.98	
H(2)	.62	.14	.80	

REFINEMENT

A considerable effort was made to locate the hydrogen positions, but only one position was evaluated with any degree of confidence, at 0.40 x , 0.08 y , 0.98 z .

Final coordinates for all atoms other than hydrogen, given in Table 1, as well as coefficients of the anisotropic temperature factors in Table 2, were calculated ignoring hydrogen. The hydrogen locations given are those from a difference synthesis and must be considered questionable.

The final difference map showed one remaining residual that was approximately 1.3 electrons, but all other residuals were considerably less than 1 electron. Final values of the

TABLE 2. COEFFICIENTS^a OF THE ANISOTROPIC TEMPERATURE FACTORS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.0042 (1)	0.0007 (0)	0.0023 (2)	0.0000	0.0011 (1)	0.0000
Cu(2)	.0033 (1)	.0007 (0)	.0021 (1)	.0000	-.0003 (1)	.0000
Ca	.0032 (1)	.0006 (0)	.0044 (2)	.0003 (0)	-.0006 (1)	-.0003 (1)
Si(1)	.0018 (1)	.0007 (0)	.0033 (2)	.0002 (1)	-.0002 (1)	-.0001 (1)
Si(2)	.0018 (2)	.0006 (1)	.0026 (3)	.0000	.0003 (2)	.0000
O(1)	.0039 (6)	.0017 (2)	.0027 (9)	.0000	.0006 (6)	.0000
O(2)	.0053 (5)	.0014 (1)	.0071 (7)	.0012 (2)	.0014 (5)	-.0003 (3)
O(3)	.0024 (4)	.0013 (1)	.0045 (6)	-.0005 (2)	-.0005 (4)	.0002 (2)
O(4)	.0071 (8)	.0012 (2)	.0030 (9)	.0000	.0002 (7)	.0000
O(5)	.0048 (5)	.0012 (1)	.0055 (7)	.0002 (2)	-.0017 (4)	-.0006 (3)
O(6)	.0057 (5)	.0011 (1)	.0078 (7)	.0010 (2)	.0015 (5)	.0013 (3)
O(w)	.0049 (4)	.0011 (1)	.0044 (7)	-.0001 (2)	.0003 (4)	.0001 (2)

^a Of the expression $T = \exp\{- (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$.

conventional R factor are 0.037 for observed reflections and 0.060 for all reflections, assigning a value of zero to the unobserveds.

Scattering factors used for the final observed and calculated structure factors (Table 3)¹ were those of Hanson and Pohler (1966) and Stewart *et al.* (1960).

DESCRIPTION OF THE STRUCTURE

Although the structure of kinoite exhibits similarities to those of a number of other minerals, it is, nonetheless, unique. The dominant structural feature is a somewhat undulating ladderlike $(\text{CuO}_2)_n$ chain that is essentially parallel to the c axis. In this respect, it resembles the copper silicates shattuckite and plancheite (Evans and Mrose, 1966). Cu is thus in the square planar coordination with oxygen which it seems to prefer (Harker, 1936; Hemholz, 1947; Wells, 1949; Pabst, 1959). The oxygen pair "rungs" of the ladder, alternate units of which are water oxygens, parallel the b axis.

A fifth oxygen is near enough to each of the copper positions that some bonding must exist between them, albeit a weak one. In both instances, the extra oxygens occupy what would be one apex of an octahedron and are at distances (2.24 and 2.45 Å) that are in the expected range of such an apex. No such atoms exist on the opposite side of the coppers; the next nearest approaches are at considerably greater distances and, furthermore, are oxygens whose bonding electrons must be taken by silicons. The resulting coordination polyhedron is a pyramid with the copper occupying a central position in the base.

In addition to the Cu-apical oxygen bond, cross linkage in other directions is provided by Si_3O_{10} multiple tetrahedra units, the ends of which are alternate pairs of oxygens of the CuO_2 ladder (Fig. 2), and distorted calcium-oxygen octahedra, one apex of which is occupied by the water oxygen. As in both ardenite (Donnay and Allmann, 1968) and kornerupine (Moore and Bennett, 1968), the Si_3O_{10} group in kinoite is distributed symmetrically across a mirror plane.

In the classification scheme normally used for silicates, kinoite is clearly a sorosilicate, that group defined by Strunz (1937) as having "terminated groups of SiO_4 tetrahedra." Kinoite belongs to that subgroup of the sorosilicates having SiO_4 in triple tetrahedra units.

Kinoite falls in Type 1 (Isolated Groups of Tetrahedra) of Zoltai's newer (1960) classification. Other silicates of this type are $\text{Na}_4\text{Cd}_2\text{Si}_3\text{O}_{10}$ (Simonev *et al.*, 1968a), $\text{Na}_2\text{Cd}_3\text{Si}_3\text{O}_{10}$ (Simonev *et al.*, 1968b), $\text{K}_3\text{YSi}_3\text{O}_8$

¹ To obtain a copy of Table 3, order NAPS Document 01218 from National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Ave, New York, New York 10001; remitting \$2.00 for microfiche or \$5.00 for photocopies, payable to COMIC-NAPS.

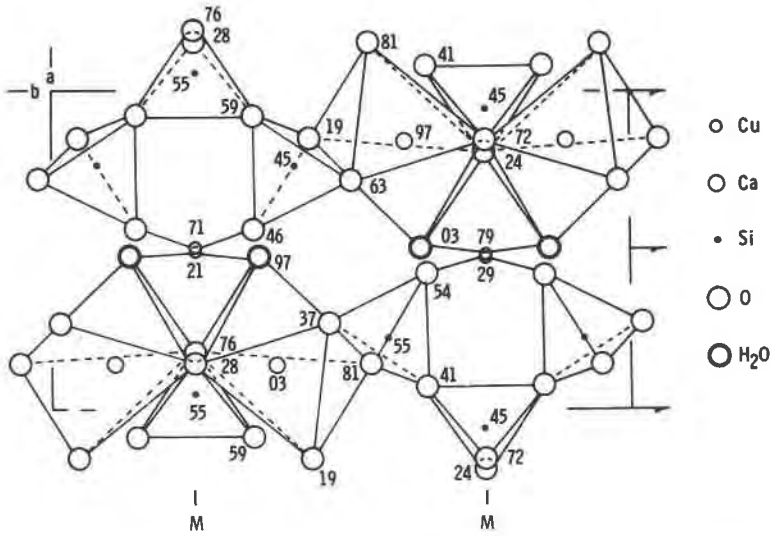


FIG. 2. Projection of the structure of kinoite along c . Heights are indicated as z/c .

(OH)₂ (Maksimov *et al.*, 1968), and perhaps krinovite, NaMg₂CrSi₃O₁₀ (Olsen and Fuchs, 1968).

Bond distances (Table 4) are in good agreement with previously determined structures. The average of all Si-O distances is 1.625 Å, which compares well with the value of 1.623 Å that Smith and Bailey

TABLE 4. SELECTED BOND DISTANCES

Atom pair	Distance (Å)	Atom pair	Distance (Å)
(2) Cu(1)-O(3)	1.944 (3)	Si(1)-O(3)	1.648 (4)
(2) -O(w)	1.942 (4)	-O(5)	1.592 (4)
-O(4)	2.453 (5)	-O(6)	1.646 (4)
(2) Cu(2)-O(3)	1.968 (3)	-O(2)	1.626 (4)
(2) -O(w)	1.959 (4)	Average	1.628
-O(1)	2.240 (5)	Si(2)-O(1)	1.604 (5)
Ca -O(1)	2.378 (3)	-O(4)	1.596 (5)
-O(4)	2.365 (3)	(2) -O(2)	1.642 (4)
-O(5a)	2.344 (4)	Average	1.621
-O(5b)	2.357 (4)	O(w)-H(1)	1.15
-O(6)	2.473 (4)	-H(2)	1.32
-O(w)	2.415 (4)	Average	1.24

Numbers in parentheses indicate number of symmetry-identical bonds.

TABLE 5. SELECTED BOND ANGLES

Atoms	Angle (°)	Atoms	Angle (°)
O(3) -Cu(1)-O(3)	85.6 (2)	O(1) -Si(2) -O(2)	106.1 (2)
-O(w)	94.2 (1)	-O(4)	116.7 (3)
-O(4)	97.8 (1)	O(2) - -O(2)	105.6 (3)
O(w) - -O(w)	85.7 (2)	-O(4)	110.8 (2)
-O(4)	86.7 (1)	O(1) -Ca -O(4)	76.6 (1)
O(3) -Cu(2)-O(3)	84.3 (2)	-O(5a)	110.5 (1)
-O(w)	95.1 (1)	-O(5b)	120.7 (2)
-O(1)	101.5 (1)	-O(6)	145.3 (2)
O(w) - -O(w)	84.7 (2)	-O(w)	73.3 (2)
-O(1)	85.6 (1)	O(4) - -O(5a)	95.5 (2)
Cu(1)-O(3) -Cu(2)	91.4 (2)	-O(5b)	172.4 (1)
-O(w) -	94.1 (2)	-O(6)	80.6 (1)
		-O(w)	79.0 (2)
O(2) -Si(1) -O(3)	107.2 (2)	O(5a)- -O(5b)	83.3 (1)
-O(5)	114.1 (2)	-O(6)	91.8 (1)
-O(6)	102.3 (2)	-O(w)	163.7 (1)
O(3) - -O(5)	111.1 (2)	O(5b)- -O(6)	87.0 (1)
-O(6)	106.6 (2)	-O(w)	100.2 (1)
O(5) - -O(6)	114.7 (2)	O(6) - -O(w)	77.0 (1)
Si(1) -O(2) -Si(2)	140.1 (3)	H(1) -O(w) -H(2)	114°
Si(1) -Si(2) -Si(1)	90.7 (1)		

(1963) predict for (meta-) silicates with no substitution of Al for Si. In the square planar unit, the average Cu-O distance of 1.959 Å is in reasonable agreement with those of 1.91 for Egyptian blue (Pabst, 1959), 1.96 for diopside (Heide and Boll-Dornberger, 1955), and 1.95 for tenorite (Tunnell, 1935). Published values for Ca-O vary widely, and the 2.389 Å distance in kinoite falls nicely within the normal range of such values.

Bond angles (Table 5) also agree well relative to well-refined structures. In particular, the Si-O-Si bridging angle of 140.1° is remarkably close to the value of 140° shown by Liebau (1961) to be the average for well-determined silicate structures.

Temperature factors (Tables 1 and 2) for all atoms are consistent with other silicates; isotropic values for Cu have a range of 0.45 to 0.51; for Ca, 0.54; for Si, 0.38 to 0.41; and for O, 0.64 to 0.95.

The cleavages exhibited by kinoite are explained by an examination of the structure. Both the {010} and {001} cleavages require that four Ca-O bonds be broken per cell, whereas the {100} cleavage calls for no more

than the breaking of four bonds from copper to the fifth (pyramid apex) oxygen and four copper-water bonds, all of which must be quite weak. Breakage in any other direction requires that several bonds of various types be broken.

From a consideration of relative strengths and densities of these bonds, it would be expected that the degree of perfection of the cleavages could be expressed as $\{100\} > \{001\} > \{010\}$. Because of the lack of material, the small size of the crystals, and the habit (tabular in the plane of the b and c axes and elongated slightly on c), this relationship could not be observed. In fact, visual examination indicated that $\{010\}$ was a good-to-excellent cleavage and that $\{100\}$ and $\{001\}$ were distinct and approximately equal in quality, as reported in the original description (Anthony and Laughon, 1970).

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