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Crystal structure of a Cu-bearing vesuvianite

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ABSTRACT

The crystal structure of a Franklin, New Jersey, blue, Cu-bearing vesuvianite, commonly referred to as cyprine, was determined. The sample of tetragonal space group *P*4/*nnc* had cell parameters of $a = 15.532(3)$ and $c = 11.776(3)$ Å. An *R* value of 4.22% was reached for 1520 unique reflections with $(F_o) > 3\sigma\ (F_o)$.

Although the basic structure is the same as found in previous studies, there are some significant differences. The Franklin vesuvianite shows Jahn-Teller distortion of Cu^{2+} in the B position, the irregular fivefold site on the *c* axis, with elongation along the **c** axis, the B–O(10) direction, and compression in the B–O(6) direction. In addition, both oxygens not bonded to Si, O(10) and O(11), are hydroxyls.

The formula of the Franklin vesuvianite can be written

$$2[(Ca_{18.28}Mn_{0.68})Al_4(Fe_{0.29}Cu_{0.71})(Al_{6.36}Mg_{0.56}Ti_{0.03}Zn_{0.97})(Si_{17.51}Al_{0.49})O_{68}(OH_{8.5}F_{1.5})].$$

INTRODUCTION

The crystal structure of vesuvianite has been studied a number of times since the original structural determination by Warren and Modell (1931). Studies by Coda et al. (1970) of an Italian vesuvianite and by Rucklidge et al. (1975) of three Canadian samples showed nearly identical results.

Rucklidge et al. as a result of their study proposed the formula for one unit cell as

$$2[Ca_{19}Al_4Fe(Al,Mg,Fe)_8Si_{18}O_{70}(OH)_8].$$

Cu-bearing vesuvianites have long been known but have not been previously structurally analyzed. This study was undertaken to determine possible structural differences in vesuvianite containing Cu, an element rarely found in appreciable amounts in silicate minerals.

EXPERIMENTAL DETAILS

The sample chosen for structural analysis was a vivid blue "cyprine" from the collection of the U.S. National Museum. The sample (R3636) was chemically analyzed using an ARL-SEMQ electron microprobe at an operating voltage of 15 kV and a beam current of 0.15 μA. The data were corrected using Bence-Albee factors. The standards used were hornblende(Si, Al, Fe, Mg, K, Ti, Na), wollastonite glass (Ca), apatite (F), managanite (Mn), copper oxide (Cu), and gahnite (Zn) (Jarosewich et al., 1979). Water was calculated from the structural determination.

This fibrous vesuvianite was found to contain 1.91% CuO. The chemical analysis of this sample is shown in Table 1.

The sample was affixed to a fine glass fiber and the unit-cell parameters provided in Table 2 were obtained from the least-squares fit of angular settings of 25 reflections. Violations of the space group *P*4/*nnc* extinction criteria were noted, although the violations were neither numerous nor intense. Although there were 53 random violations out of a possible 467 systematically absent data in the set collected with $N > 2.5\sigma$, there were only 2 at $N > 10\sigma$.

The data were corrected for Lp effects and for absorption (empirical, Ψ-scan); a profile-analysis procedure was used to improve the measurement of weak reflections. Material from the specimen used in the structural analysis was sent to North American Philips Corporation for tests for centrosymmetry. G. M. Loiacono kindly analyzed this vesuvianite for second harmonic generation (SHG). The sample was ground to a powder having a particle size of 20–40 μm and was matched to the proper refractive-index oil ac-

Table 1. Electron microprobe analyses

Oxide	Weight %
CaO	34.79
K_2O	.03
Na_2O	.21
Al_2O_3	18.79
MgO	.77
TiO_2	.05
ZnO	2.65
MnO	1.61
FeO	.72
CuO	1.91
SiO_2	35.71
F	.96
H_2O (calc)	2.60
-O= F	.40
	100.40

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Table 2. Crystal and refinement data

crystal system	tetragonal
group	P4/nnc
a(Å)	15.532(3)
c(Å)	11.776(3)
V(Å^3)	2840.8
Z	2
color	blue
crystal size, mm	0.18 x 0.3 prism
radiation	graphite-monochromated MoKα
diffractometer	Nicolet R3
abs. coeff., cm^{-1}	27.44
scan speed,deg min^{-1}	var. 4-20
2θ scan range, deg	4.0<2θ<55.0
scan technique	omega
data collected	+h, +k, +l
scan width, deg	0.7±Δ ($\alpha_1-\alpha_2$)
weighting factor g*	.00001
meaşured reflectors	1647
unique data with (F_o)>3σ(F_o)	1520
std rflns	3/197
LS parameters	154
data/parameters	9.9
R %(F)	4.22
R_W %(F)	3.51

$^*W^{-1}=G^2(F_o)+gF_o^{\ 2}$

Table 4. Anisotropic temperature factors

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	8(1)	8(1)	9(1)	0	0	0
Si(2)	8(1)	6(1)	7(1)	-0(1)	-0(1)	-0(1)
Si(3)	11(1)	6(1)	8(1)	-0(1)	-0(1)	0(1)
Ca(1)	12(1)	7(1)	7(1)	0	0	0
Ca(2)	7(1)	9(1)	8(1)	0(1)	0(1)	1(1)
Ca(3)	9(1)	10(1)	16(1)	-4(1)	5(1)	-3(1)
Cac	9(1)	9(1)	9(2)	0	0	0
Cub	7(1)	7(1)	19(1)	0	0	0
Al(1)	7(1)	8(1)	7(1)	0(1)	1(1)	-0(1)
Ala	7(1)	6(1)	9(1)	0(1)	-1(1)	-0(1)
O (1)	12(1)	6(1)	10(1)	-1(1)	-0(1)	-1(1)
O (2)	11(1)	11(1)	9(1)	3(1)	-2(1)	-1(1)
O (3)	9(1)	8(1)	8(1)	0(1)	-1(1)	1(1)
O (4)	8(1)	6(1)	10(1)	1(1)	-1(1)	1(1)
O (5)	11(1)	13(1)	10(1)	-1(1)	2(1)	3(1)
O (6)	21(2)	11(2)	14(1)	3(1)	-5(1)	-2(1)
O (7)	8(1)	13(1)	13(1)	0(1)	1(1)	1(1)
O (8)	10(1)	8(1)	11(1)	0(1)	-3(1)	-1(1)
O (9)	13(1)	13(1)	7(2)	0(1)	-0(1)	-2(2)
O (10)	7(2)	7(2)	15(3)	0	0	0
O (11)	7(1)	10(1)	7(1)	-2(1)	-1(1)	-0(1)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h_{11}^{2}a^{*2}U_{11}+k^2b^{*2}U_{22}+\ldots\ 2hka^*b^*U_{12})$

temperature factors (Å^{2}x10^3)

cording to the procedure of Dougherty and Kurtz (1976). The Franklin vesuvianite gave a signal of 4 mV or $I_{2\omega}/I_{2\omega}$ SiO_2 = 0.002 and is therefore acentric, although weakly so.

Owing to the weakly acentric nature of this vesuvianite and the small number of violations to the space group, refinement was carried out in *P4/nnc*.

Initial modeling was done using the atomic coordinates of Rucklidge et al. (1975), although elemental partitioning was somewhat different, reflecting different sample chemistry in the two studies. Ca was assigned to the C site as in the Rucklidge et al. study. Cu, however, was assigned to the B site in this study, whereas Fe was assigned to that site by Rucklidge. This study assigned Al to the general site that can be occupied by Al, Fe, Mg, Mn, Ti, and other elements, whereas Rucklidge et al. chose Al and Fe to represent average scattering factors for this site. Although the SHELXTL program used does not easily allow for refining more than two elements in a single site, the occupancy of an element may be cautiously adjusted to account for a heavier or lighter average atomic weight in the site. Al, as in Rucklidge's study, was the only element in the A position. Least-squares refinement by blocked-cascade methods used anisotropic temperature factors for all non-H atoms; no attempt was made to include H atom contributions. Table 3 gives the atomic coordinates and Table 4 the anisotropic temperature factors for the Franklin vesuvianite. Neutral-atom scattering factors were obtained from the *International Tables for X-ray Crystallography* (1974).

Table 3. Atomic coordinates and factors

Atom	x	y	z	$^*U_{iso}$
Si(1)	-2500	2500	0	8(10)
Si(2)	- 404(1)	1810(1)	3713(1)	7(1)
Si(3)	- 832(1)	-1509(1)	3647(1)	8(1)
Ca(1)	-2500	2500	2500	9(1)
Ca(2)	-1890(1)	441(1)	3793(1)	8(1)
Ca(3)	1012(1)	3197(1)	3889(1)	12(1)
Cac	2500	2500	6452(3)	9(1)
Cub	2500	2500	5588(2)	11(1)
Al(1)	-1127(1)	1214(1)	1266(1)	7(1)
Ala	0	5000	5000	7(1)
O (1)	-2200(2)	1727(2)	858(2)	9(1)
O (2)	-1168(2)	1598(2)	2791(2)	10(1)
O (3)	- 489(2)	2219(2)	755(2)	9(1)
O (4)	- 615(2)	1062(2)	4702(2)	8(1)
O (5)	-1704(2)	146(2)	1785(2)	11(1)
O (6)	1188(2)	2284(2)	5582(2)	15(1)
O (7)	564(2)	1738(2)	3222(3)	11(1)
O (8)	603(2)	4094(2)	5670(2)	10(1)
O (9)	1448(2)	-1448(2)	2500	11(1)
O (10)	2500	2500	3635(5)	28(1)
O (11)	- 39 (2)	619(2)	1363(2)	8(1)

*equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

atom coordinates (x 10^4)

temperature factors (Å^{2}x10^3)

A final *R* value of 4.22% was reached, and the basic structure is the same as that of Rucklidge et al.

DISCUSSION

Table 5 gives bond lengths for the coordination polyhedra of the Franklin vesuvianite. The three Si positions and three Ca positions show no major differences from those of Rucklidge et al., and bond lengths appear consistent and appropriate for the respective elements. The C position on the fourfold axis undoubtedly contains Ca as Rucklidge et al. concluded. The bond lengths for C–O(6) and C–O(9) strongly suggest Ca in this position and are similar to other Ca bond lengths.

In this study, as in Rucklidge et al., Al alone was assigned to the A site. This appears reasonable owing to the shorter mean bond length of 1.892 Å and to a refined unit

Table 5. Interatomic distances in cation coordination polyhedra

Si(1)	O(1)	1.636(3)		
Si(2)	O(2)	1.642(3)		
	O(3)	1.638(3)		
	O(4)	1.678(3)		
	O(7)	1.615(3)		
			1.643	mean
Si(3)	O(5)	1.631(3)		
	O(6)	1.606(3)		
	O(8)	1.624(3)		
	O(9)	1.658(2)		
			1.630	mean
Ca(1)	O(1)	2.323(3)		
	O(2)	2.522(3)	2.423	mean
Ca(2)	O(1)	2.482(3)		
	O(2)	2.424(3)		
	O(3)	2.368(3)		
	O(4)	2.449(3)		
	O(5)	2.425(3)		
	O(5)	2.334(3)		
	O(6)	2.932(3)		
	O(8)	2.317(3)	2.466	mean
Ca(3)	O(3)	2.454(3)		
	O(6)	2.462(3)		
	O(7)	2.497(3)		
	O(7)	2.364(3)		
	O(7)	2.583(3)		
	O(8)	2.596(3)		
	O(10)	2.570(1)		
	OH	2.477(3)		
			2.500	mean
C	O(6)	2.305(3)		
	O(9)	2.619(4)		
			2.462	mean
B	O(6)	2.065(3)		
	O(10	2.300(6)		
			2.112	mean
Al/Fe	O(1)	1.908(3)		
	O(2)	1.894(3)		
	O(3)	1.945(3)		
	O(4)	2.065(3)		
	O(5)	1.982(3)		
	OH	1.929(3)		
			1.954	mean
A	O(4)	1.938(3)		
	O(8)	1.866(3)		
	OH	1.872(3)		
			1.892	mean

occupancy factor with Al scattering factors. The occupancy and temperature factors suggest nothing heavier than Al, although Mg would be indistinguishable from Al, if present in this site.

The general site, with its longer bond length of 1.954 Å, suggests larger cations in this site. The refinement of the occupancy factor gives a value of 1.2, compared to a nominal unit occupancy for this site. This higher occupancy implies a heavier element, along with Al in this site. This element is certainly Zn, as there is nearly one atom of Zn in the formula, and other heavy elements are either in inconsequential amounts or otherwise accounted for. Furthermore, one atom of Zn in this site would increase the average electron density by almost exactly the required amount. No vesuvianite with significant amounts of Zn has been subject to structural analysis. This study clearly shows that the Zn is in the general Al-Fe position, by its influence on occupancy factor, by bond lengths, and by the elimination of all other potential sites.

The remaining cation site, the B site, is a very irregular fivefold site with great differences in B–O bond lengths. This difference between the B–O(6) and B–O(10) distances was either absent or fairly small in previous studies. The Franklin vesuvianite shows a B–O(6) bond length of 2.065(3) Å and a B–O(10) bond length of 2.300(4) Å. This distortion strongly indicates the presence of Cu^{2+} with Jahn-Teller distortion in the B position. The B position contains 0.71 atom of Cu with the remaining 0.29 atom apportioned to Fe^{2+} according to the observations of Manning and Tricker (1975) from Mössbauer studies of vesuvianite. The pronounced elongation along the **c** axis [the B–O(10) direction] and the compression in the B–O(6) direction are typical of a Jahn-Teller distortion for transition-metal ions such as Cu^{2+}, and the configuration of this distortion is also typical of Cu^{2+}.

Vesuvianite has 11 different oxygen positions, with O(10) and O(11) the only oxygens not bonded to Si. Several studies have concluded that O(11) is a hydroxyl and Coda et al. (1970) have suggested that O(10) may in part be a hydroxyl. These hypotheses were tested in this study by bond-strength calculations using the procedure of Donnay and Allmann (1970).

O(1) through O(9) are clearly oxygen atoms, with bond strengths near 2.0, the valence of oxygen. O(10), as previously suggested, is a hydroxyl with a bond strength of 1.1 with B occupied and 0.9 with B unoccupied, and in this vesuvianite O(11) is also always a hydroxyl with a bond strength of 1.3. With the undersaturation of O(7) (1.8) and the oversaturation of O(11) (1.3), a H bond between the two appears likely. The O–O interatomic distance of 2.80 Å makes this almost a certainty. The O(10) to O(10) distance was also examined; the 2.67-Å distance would permit a H bond strong enough to equalize the charges on the two O(10)s.

On the basis of this extra hydroxyl, the formula for this sample is

$$2[(Ca_{18.28}Mn_{0.68})Al_4(Fe_{0.29}Cu_{0.71})(Al_{6.36}Mg_{0.56}Ti_{0.03}Zn_{0.97})\text{-}(Si_{17.51}Al_{0.49})O_{68}(OH_{8.5}F_{1.5})].$$

The formula above corresponds almost exactly to Rucklidge et al.'s (1975) formula for vesuvianite. Ca plus Mn in the Ca and C positions total 19 atoms in theory and 18.96 atoms in the Franklin vesuvianite. If trace amounts of Na_2O present in this site are considered, the actual number is even closer to 19 atoms. The B position contains 1 atom in both theory and in this vesuvianite, and the general Al-Fe position contains 7.92 atoms in this vesuvianite in contrast to 8.0 atoms in the ideal case.

The change of O(10) to OH(10) and the location of Cu in the distorted B site are the most significant features of this vesuvianite.

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