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A refinement of the structure of dioptase, $Cu_6[Si_6O_{18}]\cdot 6H_2O$

PAUL H. RIBBE, G. V. GIBBS AND MARTHA M. HAMIL[1]

Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

The crystal structure of dioptase, $Cu_6[Si_6O_{18}]\cdot 6H_2O$ (a = 14.566, c = 7.778 A, $R\bar{3}$), was refined to R = 0.039 using 969 non-zero reflections. The structure consists of puckered trigonal rings of six water molecules with an ice-like configuration sandwiched between similarly puckered trigonal rings of six silicate tetrahedra bonded together laterally and vertically by Cu atoms. The water molecules are hydrogen-bonded to one another and to the bridging oxygens of adjacent $[Si_6O_{18}]$ rings, resulting in O–H distances in the water molecule of 1.1 and 0.9 A. The effective aperture diameter of the [001] channel through the rings is only 2.0 A, preventing zeolitic transfer of the water molecules.

The Si–O bond lengths [Si–O(br) = 1.645, 1.646 A, Si–O(nbr) = 1.617, 1.600 A] can be rationalized in terms of the valence angles within and between the silicate tetrahedra in the $[Si_6O_{18}]$ ring and a Mulliken bond overlap population analysis. The Cu atom is coordinated by four oxygens at 1.95–1.98 A in nearly square-planar array, with two water molecules at 2.65 and 2.50 A forming a tetragonally-distorted octahedron. Bond overlap populations suggest that the nonzeolitic water molecules are not bonded to the copper atom, although the empirical equation of Brown and Wu (1976) gives bond-strength sums around the Cu^{2+} ion of 1.81 for 4-coordination and 1.99 for 6-coordination.

Introduction

The most recent structural investigation of dioptase, $Cu_6[Si_6O_{18}]\cdot 6H_2O$, was undertaken by Heide *et al.* (1955). They found that trigonal $[Si_6O_{18}]$ rings are bonded together both vertically and laterally by Cu^{2+} in approximate square-planar coordination with the nonbridging oxygens in adjacent rings. Their refinement represents a significant improvement on the earlier structure determination by Belov *et al.* (1952). Heide *et al.* found that dehydration of dioptase begins at ~100°C but that water loss is only complete at ~700°C. They reported a concomitant change in color from emerald green to grey black. The dioptase structure was retained after dehydration, at least as nearly as could be determined by powder-diffraction methods. Reabsorption of the water did not occur at 200°C in an autoclave, arguing against the assertion of Belov *et al.* (1952) that the water in dioptase is zeolitic.

The diffuse reflectance spectrum of powdered dioptase has "an intense absorption peak at 13,300 cm^{-1} with a band-width at half-maximum of 6500 cm^{-1}. The characteristic greenish-blue color of dioptase results from transmission near 5000 A" (Newnham and Santoro, 1967, p. K88). Newnham and Santoro also found that dioptase becomes antiferromagnetic near 70 K, the Néel point, and proposed the magnetic structure based on a doubled unit cell with a = 14.61, c = 15.60 A (Fig. 1).

In their refinement of dioptase, Heide *et al.* (1955) located the water molecules and suggested that they are hydrogen-bonded in a puckered 6-membered ring of $\bar{3}$ symmetry. Their data are not sufficiently precise to locate the hydrogen atoms. They also reported Si–O bond lengths to the bridging oxygens of 1.55 and 1.67 A and Si–O bond lengths to the nonbridging oxygens of 1.60 and 1.63 A. These values clearly lack the precision required for a meaningful analysis of bonding, and in order to remedy this situation and to find the hydrogen atoms, we undertook yet another refinement of dioptase (see Hamil and Ribbe, 1971).

Experimental methods

A crystal of dioptase from Renéville, Congo, was analyzed with an electron microprobe, and no sub-

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[1] Present address: Geology Department, Rutgers University, New Brunswick, New Jersey 08903.

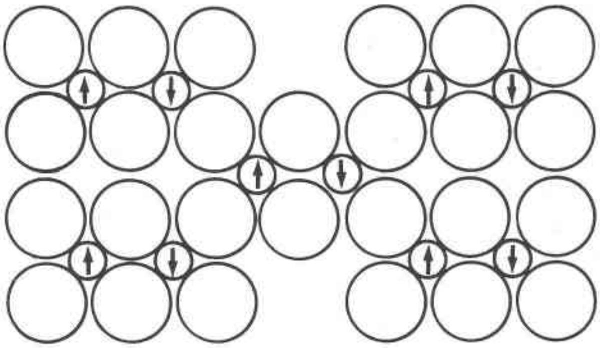

Fig. 1. An idealization of the Cu–O network in dioptase. Arrows in the small circles (Cu) indicate relative spin directions for the proposed magnetic structure. (After Newnham and Santoro, 1967, p. K87).

stituents for either Cu or Si were detected at the 0.02 weight percent level. Lattice parameters were determined on the Picker four-circle goniometer (*a* = 14.566; *c* = 7.778 A). The 969 non-zero structure factors were collected using Zr-filtered Mo radiation, corrected for Lorentz-polarization effects (not absorption), and weighted according to a scheme proposed by Hanson (1965). The structure was refined by conventional least-squares methods in space group $R\bar{3}$. At the last stage of the isotropic refinement, hydrogens were introduced at positions 1.0 A distant from the water oxygen, Ow, in the plane of the three water molecules parallel to (001) and refined. The final least-squares cycle on the anisotropic model yielded an unweighted residual of 0.040 without the hydrogens, 0.039 with the hydrogens. The argument for the validity of the H positions is based on the reasonable water-molecule configuration, as discussed below, and not on refinement statistics.

Atomic coordinates are given in Table 1, anisotropic temperature factors in Table 2, and orientation and magnitude of the principal axes of the thermal ellipsoids in Table 3. Interatomic distances and angles are listed in Table 4. Table 5 contains observed and calculated structure factors.[2]

Table 1. Atomic coordinates and equivalent isotropic temperature factors B of dioptase (standard deviations given in parentheses)

	x	y	z	B(Å^2)
Cu	0.40646(4)	0.40251(4)	0.06303(6)	0.41
Si	0.17563(8)	0.21741(8)	0.04130(13)	0.28
O1	0.07147(21)	0.18088(22)	−0.08273(35)	0.64
O2	0.28070(20)	0.29949(21)	−0.06410(34)	0.48
O3	0.15994(21)	0.26776(21)	0.21385(35)	0.50
Ow	0.14217(29)	0.18201(29)	0.57848(42)	1.5
H1	0.146(5)	0.106(5)	0.559(9)	1.0
H2	0.109(6)	0.162(6)	0.68(1)	1.3

Table 2. Anisotropic temperature factors (× 10^5) of dioptase with standard deviations given in parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	37(3)	59(3)	146(6)	−7(2)	−28(4)	44(4)
Si	51(6)	45(5)	118(14)	30(5)	−3(6)	4(7)
O1	88(15)	129(15)	273(41)	68(13)	7(19)	−10(19)
O2	55(14)	87(15)	144(39)	14(12)	−4(19)	−26(18)
O3	82(14)	134(16)	142(34)	78(13)	−59(18)	−84(20)
Ow	304(22)	281(22)	469(56)	195(19)	53(28)	−9(25)
H1	152*	152*	401*	76*	0	0
H2	208*	208*	548*	104*	0	0

* Isotropic equivalents

Discussion

In dioptase the bridging O1 oxygen is bonded to two silicon atoms in adjacent tetrahedra in the $[Si_6O_{18}]$ ring, whereas the nonbridging O2 and O3 oxygens are each bonded to one silicon and two 4-coordinated copper atoms. The water molecules, Ow, are hydrogen-bonded to one another and to the O1 oxygens. We will discuss the structure in terms of the cooper coordination, the Si–O bond lengths and angles, and the nonzeolitic water molecule.

Table 3. Orientation and magnitude of principal axes of thermal ellipsoids; estimated standard deviations in parentheses

Atom	Axis,r	rms (Å)	Direction angle (°) with respect to a_2	a_1^*	c
Cu	1	0.046(3)	74(11)	99(19)	19(1)
	2	0.050(2)	121(7)	149(7)	89(21)
	3	0.105(1)	36(1)	119(1)	109(1)
Si	1	0.052(4)	27(14)	71(18)	108(13)
	2	0.061(4)	109(22)	19(14)	87(34)
	3	0.065(3)	72(18)	87(34)	19(14)
O1	1	0.073(8)	124(10)	77(16)	37(12)
	2	0.092(7)	93(25)	18(21)	108(19)
	3	0.103(6)	34(10)	78(26)	59(15)
O2	1	0.060(10)	72(8)	134(50)	49(50)
	2	0.068(9)	90(20)	133(50)	137(50)
	3	0.099(6)	18(8)	77(9)	102(10)
O3	1	0.047(11)	78(20)	152(11)	65(22)
	2	0.062(9)	46(10)	100(24)	135(17)
	3	0.114(6)	46(6)	64(5)	55(6)
Ow	1	0.109(7)	122(11)	38(12)	71(6)
	2	0.134(7)	140(11)	127(12)	77(9)
	3	0.163(6)	68(7)	23(6)	98(7)

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[2] To obtain a copy of Table 5, order Document AM-77-045 from the Mineralogical Society of America Business Office, 1909 K St. NW, Washington, D.C. 20006. Please remit $1.00 in advance for a copy of the microfiche.

Table 4. Interatomic distances and angles with standard deviations given in parentheses

Distances (Å)		Angles (°)	
SiO_4 tetrahedron			
Si-O1	1.646(3)	O1-Si-O1'	106.4(2)
Si-O1'	1.645(3)	O1-Si-O2	108.7(1)
Si-O2	1.617(3)	O1-Si-O3	108.7(1)
Si-O3	1.600(3)	O2-Si-O1'	109.1(1)
		O2-Si-O3	112.6(1)
mean	1.627	O3-Si-O1'	111.2(1)
O1-O1'	2.634(4)		
O1-O2	2.651(4)	Si-O1-Si	130.0(2)
O1-O3	2.637(4)		
O2···O1'	2.657(4)		
O2···O3	2.677(4)		
O3···O1'	2.675(4)		
$CuO_4(H_2O)_2$ polyhedron			
Cu-O2	1.952(3)	O2-Cu-O2'	93.3(1)
Cu-O2'	1.959(3)	O2-Cu-O3'	96.8(1)
Cu-O3'	1.983(3)	O2'-Cu-O3"	90.5(1)
Cu-O3"	1.952(3)	O3'-Cu-O3"	82.8(1)
Cu-Ow	2.648(4)	O2-Cu-Ow	92.5(1)
Cu-Ow	2.502(4)	O2-Cu-Ow'	84.4(1)
O2···O2'	2.843(2)	O2'-Cu-Ow	80.4(1)
O2···O3'	2.943(4)	O2'-Cu-Ow'	113.0(1)
O2'···O3"	2.776(4)	O3'-Cu-Ow	79.9(1)
O3'···O3"	2.602(5)	O3'-Cu-Ow'	87.2(1)
		O3"-Cu-Ow	97.0(1)
		O3"-Cu-Ow'	85.6(1)
		Ow-Cu-Ow'	166.2(2)
Others			
Si-Si'	2.981(1)	H1-Ow-H2	95.0(6.4)
Cu-Cu	2.952(1)		
Cu-Cu	3.155(1)	Ow-Ow-Ow	101.2
H1-Ow	1.15(7)		
H2-Ow	0.90(9)		
H1···H2	1.52(10)		
Ow···Ow'	2.705(5)		

The coordination of copper

The Cu^{2+} ion in dioptase is in nearly square-planar coordination with two O2 oxygens at 1.952 and 1.959 A and two O3 oxygens at 1.983 and 1.952 A. Viewed with a stereoscope, the central region of Figure 2 shows that pairs of square-planar $[CuO_4]$ groups share O3–O3 edges opposite a narrowed O3–Cu–O3 angle of 82.8°, forming nearly planar $[Cu_2O_6]$ dimers that are in turn corner-linked to other $[Cu_2O_6]$ groups. These edge- and corner-sharing dimers form a three-dimensional network in dioptase, as schematically shown in Figure 1. Because the O2 and O3 atoms are nonbridging oxygens, it is reasonable to speak of the $[Si_6O_{18}]$ rings as bonded together both laterally and vertically by Cu atoms.

At the opposite vertices of an elongated, tetragonally-distorted octahedron around the Cu^{2+} ion in dioptase are two water molecules, one at 2.502 A and the other at 2.648 A (steric details of the Cu coordination are given in Table 4). This classic Jahn-Teller distortion is also observed in nearly all of the more than fifty Cu^{2+}–(O,OH,H_2O,Cl) coordination polyhedra we have examined in more than 25 mineral species. The Cu–O bond lengths in dioptase are very near the mean for all Cu^{2+}–O distances observed in minerals, and the $Cu\cdots H_2O$ distances are on the average 0.1 A longer than those observed in other minerals except for liroconite, $Cu_2Al(AsO_4)(OH)_4 \cdot 4H_2O$ (Kolesova and Fesenko, 1968), which has $Cu\cdots H_2O$ = 2.55 and 2.75 A. The 4 oxygen–2 water configuration around the copper atom in dioptase is unique among Cu-containing mineral species: in others with water molecules at the vertices of elongated octahedra, hydroxyl groups replace some or all of the oxygens in square-planar coordination.

Extended Hückel molecular orbital (EHMO) calculations of the bond overlap populations between copper and the two water molecules at 2.648 and 2.502 A gave values of −0.02 and 0.00, respectively, affirming the conclusion of Heide *et al.* (1955) that

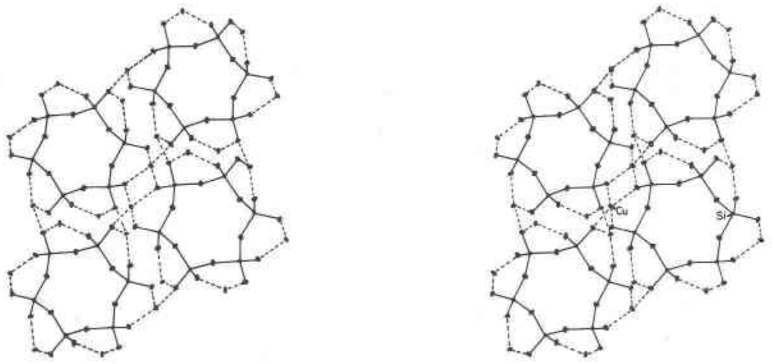

Fig. 2. A stereoscopic drawing of the structure of dioptase viewed down [001], showing the $[Si_6O_{18}]$ rings (solid lines) bonded together by copper atoms (dashed lines represent Cu–O bonds). Water molecules have been omitted (see Fig. 5).

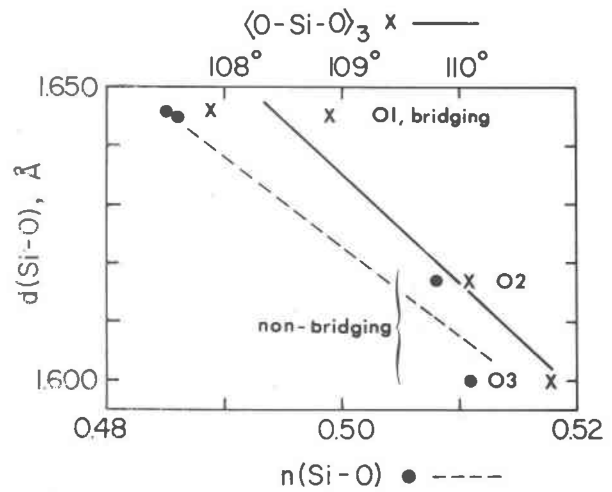

Fig. 3. Plots of the observed Si-O bond lengths, d(Si-O), in dioptase versus n(Si-O) (solid dots, dashed line) and the mean of the three O-Si-O angles, $\langle\text{O-Si-O}\rangle_3$, common to the bond ($X$'s, solid line).

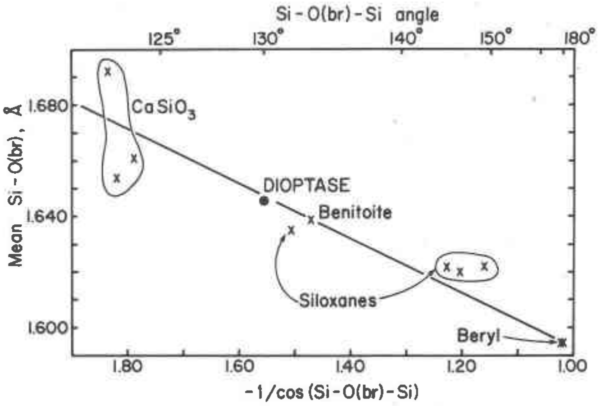

Fig. 4. The mean of the two Si-O(br) bond lengths to a common bridging oxygen in selected single-ring silicate structures versus the Si-O(br)-Si angle and $-1/\cos$[Si-O(br)-Si]. The data points (X's) from the following structures: high-pressure $CaSiO_3$ (Trojer, 1969), siloxanes (Oberhammer, 1972), benitoite (Fisher, 1969), and beryl (Gibbs *et al.*, 1968).

water molecules are not bonded to the copper atoms. On the other hand, the empirical equation of Brown and Wu (1976) gives bond-strength sums around Cu^{2+} of 1.81 and 1.99 for 4- and 6-fold coordination, respectively, suggesting that the water molecules may be bonded to copper.

The Si–O bond lengths and angles

EHMO bond overlap populations, n(Si–O), calculated for the Si–O bonds in the [Si_6O_{18}] ring of dioptase correlate inversely with the observed bond lengths (Fig. 3). Since n(Si–O) values are believed to be a measure of the charge density between nuclei of Si and O, the correlations between d(Si–O) and n(Si–O) are expected. The overlap calculations were performed assuming constant bond lengths and using the observed valence angles. Thus Figure 3 shows that Si–O bond lengths are dependent on the mean of the three O–Si–O angles, $\langle\text{O–Si–O}\rangle_3$, common to the bond. The bridging Si–O(br) bond lengths of 1.645 and 1.646 A are also consistent with the narrow observed Si–O(br)–Si angle of 130° (Brown *et al.*, 1969), and fit perfectly on the regression line in Figure 4 which relates mean Si–O(br) to $-1/\cos$[Si–O(br)–Si] for a number of precisely determined single-ring silicates.

The nonzeolitic water molecule

Six water molecules are sandwiched between pairs of [Si_6O_{18}] rings, as illustrated in Figure 5. They form crown-shaped clusters with $\bar{3}$ symmetry, as in ice, and adjacent molecules are hydrogen-bonded. Figure 6 shows three adjacent molecules and bridging O1 oxygen atoms projected onto the plane of one of the water molecules. The H–Ow–H angle of 95 ±6° and

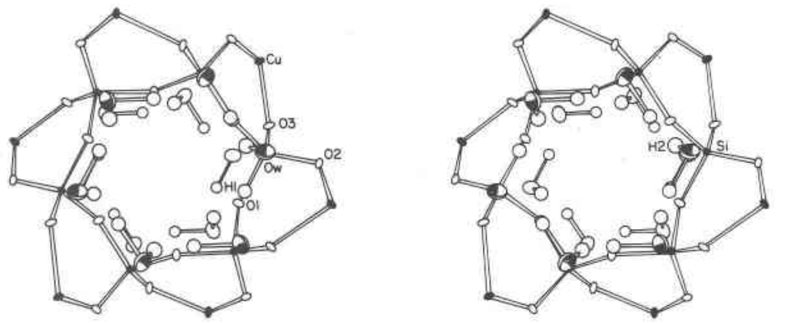

Fig. 5. A stereoscopic drawing of portions of the dioptase structure viewed down [001], showing the orientation of the nonzeolite water molecules in relation to the puckered [Si_6O_{18}] ring.

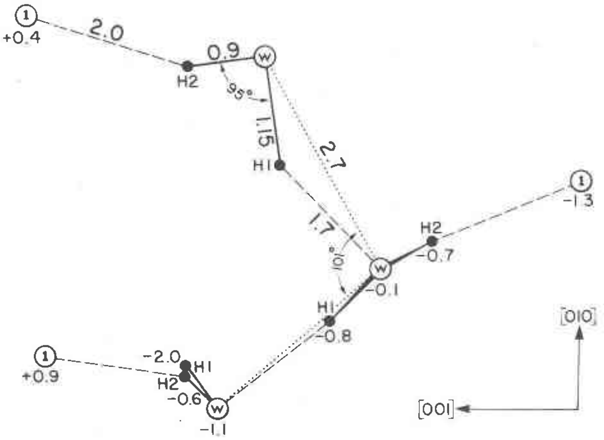

Fig. 6. A projection of three adjacent water molecules (Hl–Ow–H2) and nearest-neighbor O1 atoms onto the plane of the uppermost water molecule. The large numbers indicate interatomic distances (solid lines indicate acceptor bonds, dashed lines donor bonds, and dotted lines Ow· · ·Ow separations). The smaller numbers with signs indicate heights in Angstroms of the atoms above (+) or below (−) the plane of the drawing. [010] in the plane of the drawing whereas [001] is inclined upward at ~30°.

the H–Ow distances of 0.9 and 1.15 A are not statistically different from those observed in water. Each of the hydrogen atoms is distinct, however, in that H1 is bonded to two Ow's at 1.15 and 1.7 A, whereas H2 is bonded to Ow at 0.9 A and to the bridging Ol oxygen at 2.0 A. The Ow· · ·Ow distance of 2.7 A is only 0.06 A shorter than that observed in ice, and the Ow–Ow–Ow angle is 101°, close to the 109.5° angle observed in ice.

Inasmuch as the trigonal [Si_6O_{18}] rings are puckered in dioptase, the (001) channels are much more constricted than those in cordierite, where, for example, the [$Al_2Si_4O_{18}$] rings are fully expanded and have an effective aperture diameter of ~2.8 A (Smith and Schreyer, 1962). The O1· · ·O1 distance through the center of symmetry across the channel in dioptase is 4.77 A, and if one assumes that the diameter of oxygen is 2.7 A, it becomes obvious that the effective aperture diameter is much too small to permit H_2O, which has a kinetic diameter of 2.65 A (Hirschfelder *et al.*, 1954, p. 215), to migrate back into the channels once it has been expelled by heating. Thus the conclusion by Heide *et al.* (1955) that the water in dioptase is nonzeolitic is fully justified, both experimentally and structurally.

Acknowledgments

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References

Belov, N. V., W. P. Butuso and N. I. Golovastiko (1952) Crystal structure of dioptase. *Dokl. Akad. Nauk SSSR, 87,* 953–956.

Brown, G. E., G. V. Gibbs and P. H. Ribbe (1969) The nature and variation in length of the Si–O and Al–O bonds in framework silicates. *Am. Mineral., 54,* 1044–1061.

Brown, I. D. and K. K. Wu (1976) Emprical parameters for calculating cation–oxygen bond valences. *Acta Crystallogr., B32,* 1957–1959.

Fischer, K. (1969) Verfeinerung der Kristallstruktur von Benitoit BaTi[Si_3O_9]. *Z. Kristallogr., 129,* 222–243.

Gibbs, G. V., D. W. Breck and E. P. Meager (1968) Structural refinement of hydrous and anhydrous synthetic beryl, $Al_2(Be_3Si_6)O_{18}$ and emerald, $Al_{1.9}Cr_{0.1}(Be_3Si_6)O_{18}$. *Lithos, 1,* 275–285.

Hamil, M. M. and P. H. Ribbe (1971) The location of the hydrogen atoms in the water molecule of dioptase, $CuSiO_3 \cdot H_2O$. (abstr.) *Geol. Soc. Am. Abstr. Programs, 3,* 315.

Hanson, A. W. (1965) The crystal structure of azulene, S-trinitro-benzene complex. *Acta Crystallogr., 19,* 19–26.

Heide, H. G., K. Boll-Dornberger, E. Thilo and E. M. Thilo (1955) Die Struktur des Dioptas, $Cu_6(Si_6O_{18}) \cdot 6H_2O$. *Acta Crystallogr., 8,* 425–430.

Hirschfelder, J. O., C. F. Curtiss and R. B. Bird (1954) *Molecular Theory of Gases and Liquids.* John Wiley and Sons, New York.

Kolesova, R. V. and E. G. Fesenko (1968) Determination of the crystal structure of liroconite, $Cu_2Al(AsO_4)(OH)_4 \cdot 4H_2O$. *Soviet Phys. Crystallogr., 13,* 324–328.

Newnham, R. E. and R. P. Santoro (1967) Magnetic and optical properties of dioptase. *Physica status solidi, 19,* K87–90.

Oberhammer, H. (1972) The molecular structures of cyclosiloxanes. (abstr.) *Fourth Austin Symposium on Gas Phase Molecular Structure,* 11–12.

Smith, J. V. and W. Schreyer (1962) Location of argon and water in cordierite. *Mineral. Mag., 33,* 226–236.

Trojer, F. J. (1969) The crystal structure of a high-pressure polymorph of $CaSiO_3$. *Z. Kristallogr., 130,* 185–206.

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