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THE CRYSTAL STRUCTURE OF TOPAZ AND ITS RELATION TO PHYSICAL PROPERTIES

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Abstract

The crystal structure of topaz (*Pbnm*, $a=4.6499$; $b=8.7968$; $c=8.3909$ Å) is described using positional parameters determined by Ladell (1965). It is based on monolayers of oxygen alternating with layers of composition F_2O_1 in the close-packed sequence ABAC. The key structural unit is a crankshaft chain of edge-sharing AlO_4F_2 ortahedra and corner-sharing SiO_4 tetrahedra running parallel to z. This explains the [001] prismatic habit of topaz and the fact that it is optically positive. The perfect {001} cleavage is parallel to the only planes which can be passed through the structure without breaking Si–O bonds. The thermal expansion is greatest perpendicular to the cleavage which is consistent with the fact that {001} represents the plane of the weakest bonds.

The mean Si–O bond length is 1.641 Å, ~0.02 Å longer than that expected for a three-coordinated oxygen. The mean Al–F and Al–O bonds are 1.795 and 1.895 Å, respectively.

In the past five years a concerted effort by the authors and their coworkers to understand the orthosilicates has shown that the steric details of the olivines, the humites, the garnets and zircon can be rationalized in terms of geometrical and electrostatic interactions. Topaz is an important orthosilicate whose structure has not been described since it was determined independently by Pauling (1928) and Alston and West (1928); therefore, we present it here.

In 1965 Dr. J. Ladell of Philips Electronic Instruments, Mount Vernon, New York, chose a topaz fragment "from a large crystal mined in South America" to test the data collection capacity of the new PAILRED automated diffractometer. He used more than 2200 intensities corrected for absorption and secondary extinction in an anisotropic least-squares refinement and obtained an *R* factor of 0.027. He states that "the errors in the locations of the positional coordinates are all less than 5×10^{-4}Å." The topaz positional and thermal parameters are listed in his Table IV. (Ladell, 1965, p. 39). Dr. Ladell did not compute bond lengths or angles or otherwise describe the structure because he was interested primarily in the PAILRED instrumentation, and therefore he kindly granted us permission to use his data in this study.

The cell parameters of this topaz are $a=4.6499(3)$, $b=8.7968(6)$ and $c=8.3909(5)$ Å, $V=343.22$ Å^3; space group *Pbnm* (Ladell, 1965, p. 35). The *b* cell edge indicates that less than 5%(OH) substitutes for F in this specimen (Ribbe and Rosenberg, in preparation). The bond lengths and bond angles are listed in Table 1.

Table 1. Interatomic Distances and Angles for Topaz Calculated from Atomic Coordinates Given by Ladell (1965)

SiO_4 Tetrahedron

Si–O(1)		1.636 Å
O(2)		1.644
O(3)	[2]	1.642
mean		1.641 Å

Interatomic distances		Angles at Si
O(1)–O(2)	2.685 Å	109.9°
O(1)–O(3) [2]	2.675	109.4
O(2)–O(3) [2]	2.697	110.3
O(3)–O(3)	2.650	107.5
mean	2.683 Å	109.5°

AlO_4F_2 Octahedron

Al–F	1.790 Å
F′	1.800
O(1)	1.896
O(2)	1.901
O(3)	1.884
O(3)′	1.897
mean	1.861 Å

Interatomic distances		Angles at Al
F–F′	2.516 Å	89.0°
O(1)	2.573	88.5
O(2)	2.626	90.7
O(3)	2.625	91.2
F′–O(2)	2.592	88.9
O(3)	2.547	87.4
O(3)′	2.645	91.3
O(1)–O(2)	2.525	83.4
O(3)	2.904	100.4
O(3)′	2.730	92.1
O(2)–O(3)′	2.806	95.2
O(3)–O(3)′	2.503	82.9
mean	2.633 Å	89.8°

DESCRIPTION OF THE STRUCTURE

The crystal structure of topaz is based on monolayers of oxygen anions alternating with monolayers of 2(F):1(O) in the close-packed sequence ABAC. One-third of the available octahedral sites are filled with Al and one-twelfth of the tetrahedral sites with Si. The oxygens are coordinated by one Si and two Al atoms, and the fluorine by two Al atoms.

The key structural unit of topaz is shown in Figure 1. Chains of edge-sharing Al-octahedra and corner-sharing Si-tetrahedra are formed between a monolayer of oxygen anions and a monolayer of anions in the ration 2(F):1(O). These chains parallel *z* and are related to similar ones in the next lower layer by the *n*-glide at $\frac{1}{4}$ along *y*, which describes continuous crankshaftlike chains of egde-sharing AlO_4F_2 octahedra parallel to *z*.

Detailed drawings of the octahedron and tetrahedron are given in Figure 2. The F atoms are in *cis* arrangement as in norbergite, but in topaz they are not involved in shared edges. The mean Al–O distance in topaz is 1.895 Å, slightly shorter than that in beryl (1.898 Å) and longer than that in pyrope (1.886 Å). The Al–F bonds are 0.1 Å shorter than the Al–O bonds (Table 2).

Unlike the tetrahedra in the olivines, the humites, the garnets and zircon (which share edges with other polyhedra), the SiO_4 group in topaz

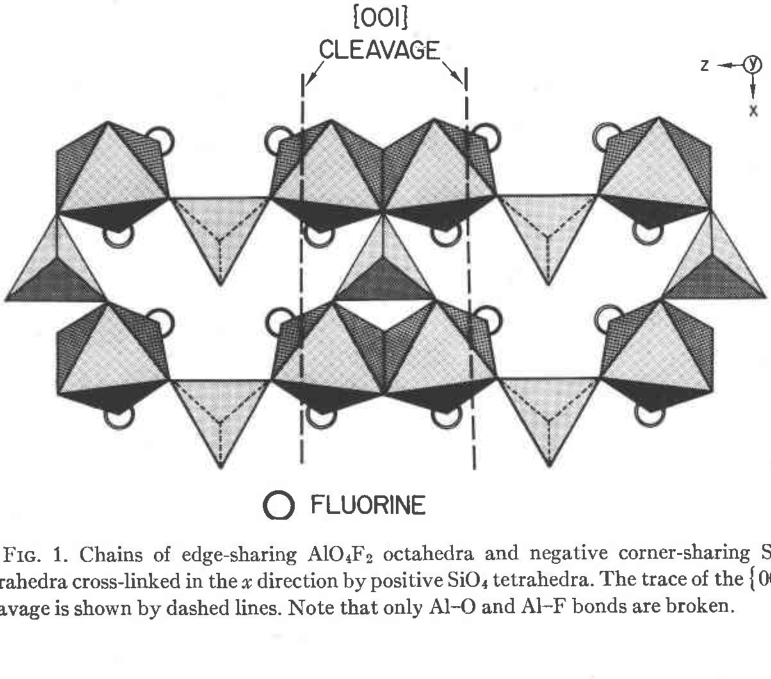

FIG. 1. Chains of edge-sharing AlO_4F_2 octahedra and negative corner-sharing SiO_4 tetrahedra cross-linked in the *x* direction by positive SiO_4 tetrahedra. The trace of the {001} cleavage is shown by dashed lines. Note that only Al–O and Al–F bonds are broken.

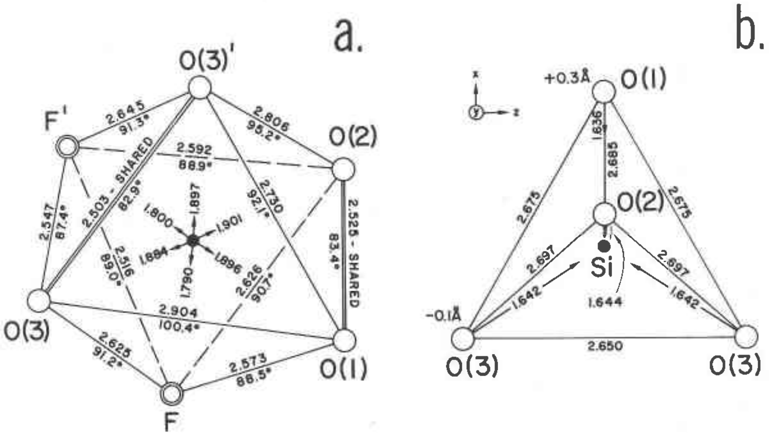

FIG. 2. *a*. The AlO_4F_2 octahedron of topaz. Interatomic distances and O–Al–O angles are labeled. *b*. The SiO_4 tetrahedron. Note that the O(1) atom is 0.3 Å above the level of the oxygen close-packed layer and the O(3) atoms are 0.1 Å below it (see text).

is quite regular; the Si–O bonds are within 0.005 Å of the mean and the O–Si–O angles are within 2° of the ideal tetrahedral angle. The mean Si–O bond length (1.641 Å) is ∼0.02 Å longer than that expected for Si bonded to a three-coordinated oxygen (Brown and Gibbs, 1969). In andalusite and kyanite, which also have three coordinated oxygens and SiO_4 tetrahedra with no shared edges, the mean Si–O bonds are 1.627 and 1.628 Å, respectively. No interpretation is offered for this, although it is consistent with the SiK_β x-ray emission band shift observed by White and Gibbs (1967).

The small distortions of the tetrahedron can be related to the directions of the Al–O bonds to the corners of the SiO_4 group. The net effect is a rotation of the tetrahedron counterclockwise around z, as indicated

TABLE 2. SUMMARY OF MEAN INTERATOMIC DISTANCES FOR TOPAZ

	Mean bond length (Å)		Description
	F	O	
Si	—	1.641	tetrahedral distances
Al	1.795	1.895	octahedral distances
O	—	2.680	tetrahedral edges
O	—	2.514	shared octahedral edges
F	2.516	2.601	unshared octahedral edges
O	2.601	2.694	unshared octahedral edges

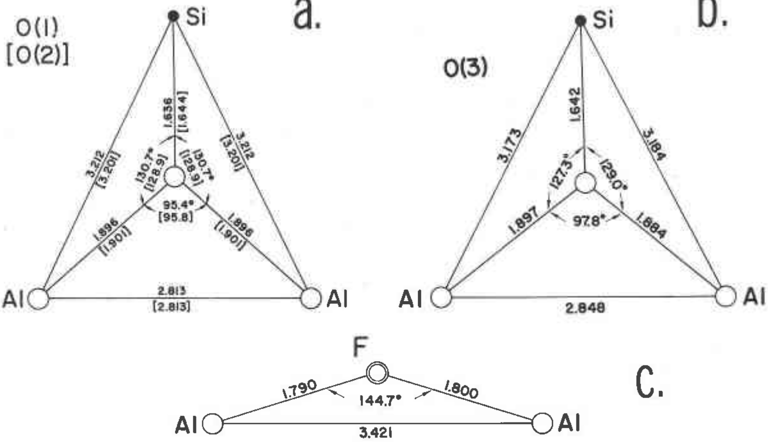

FIG. 3. *a.* Coordination diagram for O(1) and O(2) [in brackets], *b.* for O(3) and *c.* for F. Interatomic distances and angles at the anions are labeled.

by the fact that the O(1) atom is 0.03 Å above and the O(3) atoms are 0.01 Å below the (010) plane of the close-packed array (Fig. 2).

The anion coordination diagrams are shown in Figure 3. In Figures 3a and 3b the Al atoms are situated across shared edges, causing the Al–O–Al angles to be 5–8° wider than the ideal octahedral angle and the Al–O–Si angles to be 1–4° narrower than the 131.8° expected in an ideal close-packed array. The Al–Al distance across the mirror plane (Fig. 3a) is 0.03 Å shorter than that in Figure 3b. This can be related to the placement of the positive SiO_4 tetrahedra that cross-link the chains in the x direction (Fig. 1). The O(3) atoms are bonded to a common Si atom and therefore the O(3)–O(3) distance is short (2.650 Å—Fig. 2b); the effect is to rotate the two edge-sharing octahedra in opposite directions, thereby bringing the Al atoms closer together and giving the chain (Fig. 1) a slightly scalloped appearance. The pair of octahedra that share the O(3)–O(3)′ edge in the oxygen monolayer are not similarly rotated because O(1) and F are not bonded to a common Si atom.

The fluorine ligancy is shown in Figure 3c. In topaz with OH in the F site, the O–H bond is inclined 37° to z in the (010) plane (Isetti and Penco, 1967). This places the proton equidistant from the two Al atoms on the opposite side of the monovalent anion.

RELATION OF PHYSICAL PROPERTIES TO STRUCTURE

The key structural unit in topaz is the crankshaft chain of edge-sharing AlO_4F_2 octahedra parallel to z. It explains the characteristic

[001] prismatic habit of the mineral and its optical properties (Deer *et al.*, 1962):

$$\gamma \| z = 1.616 - 1.638$$

$$\beta \| y = 1.609 - 1.631$$

$$\alpha \| x = 1.606 - 1.629$$

Both α and γ are parallel to the close-packed layers, but γ is parallel to the chain axis. Thus β is normal to both the close-packed layers and the chain. Refractive indices increase with OH substitution for F because of the higher polarizability of OH.

The perfect {001} cleavage which is diagnostic of topaz is parallel to the only planes which can be passed through the structure without breaking Si–O bonds (Fig. 1). Al–O and Al–F bonds are broken in equal numbers.

Kôzu and Ueda (1929) measured the thermal expansion of topaz and found it to be greatest parallel to z, the chain axis. This is consistent with the fact that the {001} cleavage represents the plane of the weakest bonds.

The twinning and intergrowths of topaz have been elegantly described by Gliszczynski (1949) and will not be reiterated here. In conclusion, it should be pointed out that although the morphological drawing, cleavage plane and optical indicatrix orientation are correct in Deer *et al.* (1962, p. 145), the choise of space group setting is in error. The setting should be *Pbnm*, with $a = 4.650$, $b = 8.800$ and $c = 8.394$ Å.

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