Fresnoite: Unusal Titanium Coordination

Abstract. *The crystal structure of fresnoite,* $Ba_2(TiO)[Si_2O_7]$, *consists of* $[Si_2O_7]^{6-}$ *double groups and titanium-centered square pyramids linked to form flat sheets. Intercalated between these sheets are* Ba^{2+} *ions in highly distorted pentagonal antiprisms. The structure of fresnoite is related to that of melilite,* $(Ca,Na)_2(Mg,Al)[Si_2O_7]$.

Fresnoite, $Ba_2(TiO)[Si_2O_7]$, was one of seven new barium silicate minerals named (*1*) during a geologic study of sanbornite deposits in eastern Fresno County, California. Specimens (*2*) of fresnoite afforded a single, anhedral, wedge-shaped grain having a volume of ~0.007 mm^3.

Two hundred and eighty-six independent intensities, representing the *hk0–hk5* levels, were collected on a manual scintillation counter–diffractometer, Weissenberg-geometry assembly, by use of Zr-filtered Mo radiation. These data, as well as a set of their symmetry equivalents, were corrected for transmission effects and averaged by use of the polyhedral transmission program of Burnham (*3*). The computed linear-absorption coefficient of 119.8 necessitated careful measurement of the grain surfaces for transmission correction.

Table 1. Structural cell data for fresnoite and melilite.

a (Å)	*c* (Å)	Space group	Formula
		Fresnoite (1)	
8.52 ± 0.01	5.210 ± 0.005	*P4bm*	$Ba_2(TiO)[Si_2O_7]$
		Melilite (4)	
7.789 ± 0.005	5.018 ± 0.005	$P\bar{4}2_1m$	$(Ca,Na)_2(Mg,Al)[Si_2O_7]$

Table 2. Atom coordinates for fresnoite.

Element	*x*	*y*	*z*	*B*
Ti	0	0	0.541 ± 0.003	0.11 ± 0.16
Ba	0.3270 ± 0.0002	½ + *x*	0	.74 ± .06
Si	.1277 ± .0009	½ + *x*	.516 ± .005	.23 ± .17
O_1	.289 ± .003	0.576 ± 0.003	.654 ± .006	.54 ± .40
O_2	.122 ± .003	½ + *x*	.211 ± .011	.95 ± .65
O_3	0	½	.628 ± .016	2.00 ± 1.25
O_4	0	0	.222 ± .014	0.50 ± 0.77

The *z*-axis Patterson projection along with the expected tetrahedral geometry of the silicate groups enabled location of all atom positions and furthermore identified the space group as *P4bm*. The oxygen atoms were defined—after location of the other atom species—by identification of the remaining Ba-O vectors. The structure was then established in three dimensions by computation of the approximate *z*-coordinates, followed by full-matrix least-squares refinements of coordinates and isotropic temperature factors. Refinement was allowed to progress until all shifts were within their limits of error, giving *Rhkl* = 0.111 for all reflections. The cell parameters (of Pabst) used by us and final atom coordinates appear in Tables 1 and 2.

The structure, depicted as a polyhedral representation in Fig. 1a, is built of $[Si_2O_7]^{6-}$ double groups linked to Ti-O square pyramids to give flat sheets parallel with {001}. These stacks of sheets are held together by the large Ba^{2+} ions which occur in coordination polyhedra, approximating pentagonal antiprisms, with eight

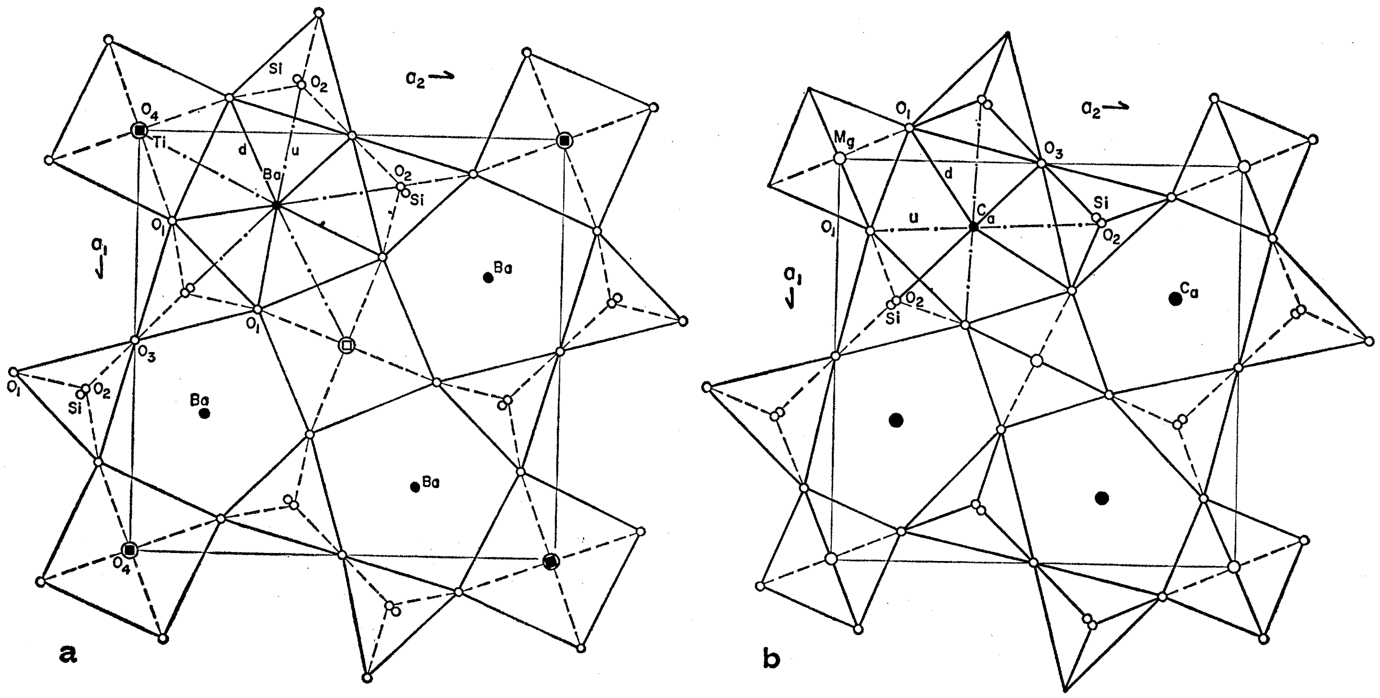

Fig. 1. (a) Crystal structure of fresnoite. Apical oxygen atoms pointing downward are dashed. The Ba–O bonds alternate up (*u*) and down (*d*). (b) Crystal structure of melilite [after Smith (*4*)]. Apical oxygen atoms point upward (solid lines) and downward (dashed lines).

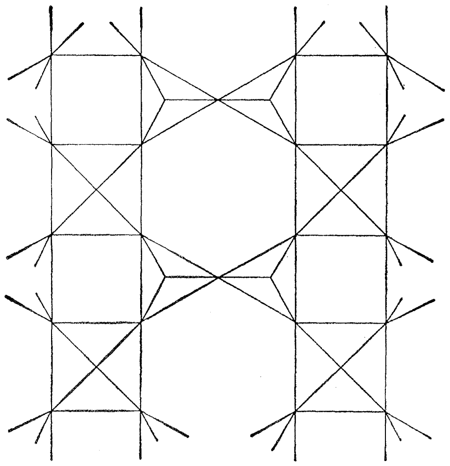

Fig. 2. Postulated crystal structure of lamprophyllite in the yz plane [after Woodrow (*5*)]. Titanium atoms reside in the square pyramids; silicon, in the tetrahedra.

"short" bonds (2.71 to 2.95 Å) and two "long" bonds (3.36 Å). In projection, the structure of fresnoite is strikingly similar to that of melilite, $(Ca,Na)_2(Mg,Al)[Si_2O_7]$ (Fig. 1b; cell parameters in Table 1). The coordinates and cell data come from Smith (*4*). Several differences are interesting: the melilite structure, unlike that of fresnoite, consists of undulating sheets with the symmetry-equivalent $[Si_2O_7]^{6-}$ double groups oriented *upward* and *downward* relative to the c-axis. Further, Ti in fresnoite resides in a square pyramid, whereas Mg in melilite is in tetrahedral coordination. Finally, the Ca^{2+} ions are in distorted square antiprisms of oxygen atoms in melilite. The pronounced sheet-like character of fresnoite, with the loosely held Ba^{2+} ions, affords the good-to-perfect c {001} cleavage relative to the distinct-to-poor c {001} cleavage for melilite.

The most curious feature of fresnoite, however, is the Ti^{4+}-centered oxygen polyhedron. Four oxygen atoms are tetragonally displaced 2.00 ± 0.04 Å from the titanium atom, the fifth (lone) oxygen atom being displaced only 1.66 ± 0.08 Å along c [001], forming a highly compressed square pyramid. The titanium atom is inside the square pyramid, displaced 0.59 Å from the base center. This lone oxygen atom was intentionally placed 2.00 Å from titanium during the refinement of atom coordinates, and it rapidly converged to the short displacement cited above. It is well resolved on the three-dimensional electron-density map.

Let us remark that the compressed square-pyramidal arrangement of oxygen atoms about titanium is not peculiar to fresnoite. The structure of lamprophyllite, $(Ba,Sr,K)Na(Ti,Fe)Ti[Si_2O_7](O,OH,F)_2$, solved for one projection by Woodrow (*5*), led to the sheet structure depicted in Fig. 2. Fortunately his solution was for a z-axis projection, an orientation that enabled us to calculate Ti—O~1.66 Å for the lone pyramidal oxygen atom. Thus the sheets of lamprophyllite are built of the same units as those of fresnoite, although arranged differently.

The Si—O distance for the oxygen atom shared by the tetrahedral pair is 1.65 ± 0.04 Å. The distance for oxygen atoms also associated with the Ti-centered square pyramid is 1.61 ± 0.04 Å, and the "apical" oxygen is displaced 1.59 ± 0.07 Å. Although the standard deviations are high, the overall mean Si—O distance is 1.615 ± 0.050 Å, agreeing with 1.615 Å for the mean suggested (*6*) for Si—O distances in Si_2O_7 groups.

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References and Notes

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Ethylene Formation from Ethyl Moiety of Ethionine

Abstract. *In plants, ethylene is formed in the presence of light and flavin mononucleotide from ethionine and* S-*ethylcysteine. The ethylene is formed from the ethyl moiety of ethionine.*

The formation of ethylene from acetaldehyde by slices (*1*) and particles (*2*) of apple was mediated by flavin mononucleotide (FMN) which caused nonenzymatic formation of ethylene in a model system consisting of acetaldehyde and cysteine (*3*). Yang *et al.* (*4*) reported that ethylene was formed from methionine and its allied compounds in etiolated pea seedlings by FMN and light, and that the two-carbon skeleton of ethylene was derived from carbons 3 and 4 of methionine. We then studied the formation of ethylene from ethionine and *S*-ethylcysteine (*5*) in a model system and found that ethylene was derived from the ethyl carbons of the S-containing amino acids.

The reaction was carried out in a Warburg vessel fitted with a rubber stopper, and ethylene was determined by gas chromatography (Shimadzu model GC-1C) with a hydrogen flame-ionization detector. Ethylene-^{14}C was determined by radio-gas chromatography with a solid-scintillation detector (Shimadzu model LSG-W22) or with a liquid-scintillation counter (Packard model 314 EX) (*6*). The reaction mixture contained in 4 ml: 20 mM potassium phosphate buffer (pH 7.0); 0.5 mM FMN; and 0.1 mM L-ethionine, L-methionine, or *S*-ethyl-L-cysteine. Incubation was carried out at 30°C under illumination by tungsten lamp (from bottom of Warburg vessel, 22×10^3 lu/m^2) and in the dark.

The amount of ethylene formed from ethionine (0.1 mM) and from methionine (0.1 mM) was 10.8 and 6.5 μl (N.T.P.), respectively, in the presence of FMN and light for 30 minutes. However, there was no formation of ethylene from ethionine or from methionine, either in the dark or in the absence of FMN. Light, as well as FMN, was essential for production of ethylene. The rate of ethylene formation from ethionine was greater than that from methionine; this suggested the possibility that the ethyl moiety of ethionine was also transferred to ethylene. Experiments with ethionine-^{14}C (ethyl-1-^{14}C) showed that ethylene was formed from the ethyl carbons of ethionine. Radioactivity of ethylene-^{14}C formed from ethionine-^{14}C (1.7 mg, 12×10^4 count/min) was 3772 count/min in the presence of FMN and light after 30 minutes of incubation. However, in the dark and in the presence of FMN, the radioactivity was reduced to 42 count/min. There was no formation of ethylene-^{14}C in the light and in the absence of FMN.

The results confirm the hypothesis that the *S*-ethyl moiety can also be converted to ethylene with FMN and light. We felt that *S*-ethylcysteine containing the *S*-ethyl moiety in its molecular structure should also produce ethylene; therefore, we experimented further. When *S*-ethylcysteine (0.1 mM) was used instead of ethionine as