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Prehnite: Structural Similarity of the Monoclinic and Orthorhombic Polymorphs and Their Si/Al Ordering

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Two modifications of the naturally occurring mineral prehnite, $Ca_2Al(Si_3AlO_{10})(OH)_2$, are characterized by precise single crystal diffraction methods. The two forms are topologically identical. They differ only in the siting of one Al and one Si atom per unit cell: these switch their places in two of the tetrahedrally coordinated sites. This appears to be the only known case where a silicate occurs with two differently *ordered* tetrahedral distributions of Al and Si atoms. The two forms are not polytypes according to the current definition of polytypes. The two modifications are so similar to each other that they differ only in the eighth coordination sphere.

Buerger's (*1*) classification of the relationships between polymorphs of crystalline solids was very successful in enumerating all the possible cases found so far. However, the polymorphic relationship of the two forms of the mineral prehnite does not fit these categories. In the polymorphs clinoprehnite (monoclinic, space group *P*2/*n*) and orthoprehnite (orthorhombic, space group *P*2*cm*) we find, following Buerger's classification, the bond type to be the same, the first and second coordinations of all atoms to be analogous, and finally no indication that the polymorphs differ in terms of an order/disorder relationship. Instead, to the best of our knowledge, this is the first reported case that two topologically identical modifications of a silicate have two different Si/Al *ordering* schemes and are more similar to each other than two polytypic structures would be.

The crystal structure of prehnite, a layer silicate, $Ca_2Al(Si_3AlO_{10})(OH)_2$, was originally determined (*2*) in the centrosymmetric space group *Pncm*. Later a prehnite from the Radautal, Harzburg, was refined (*3*) in the noncentrosymmetric space group *P*2*cm*. Papike and Zoltai (*4*) studies a single crystal of an iron-containing prehnite, $Ca_2(Al,Fe^{+3})(Si_3AlO_{10})(OH)_2$, from Tirol, Österreich, and refined it in space group *Pncm*. They assumed this to be an average structure and pointed out that one could view the *Pncm* structure of prehnite as an

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intergrowth of both monoclinic prehnites and orthorhombic prehnites. Papike and Zoltai supported this interpretation by precession photographs of prehnite twins showing split reflections suggestive of monoclinic angles of approximately 90.75°. Furthermore, transmission and scanning electron microscopy, optical microscopy, and electron diffraction of prehnite from Glasgow, Scotland (*5*) and from Farmington, Connecticut (*6*) lent further support to this interpretation. However, all untwinned prehnites found in recent work in macroscopic dimensions suitable for single crystal studies have always been orthorhombic (*7*) space group *P*2*cm*; none of them are found to crystallize in space groups *P*2/*n* or *Pncm*. The determination of the putative Si/Al ordering and the unequivocal assignment of the proper space group is only possible by means of a full crystal structure determination, since the systematic absences of X-ray reflections are not sufficiently diagnostic in the case of the three space groups discussed here (*8*).

TABLE I

CRYSTAL DATA, AND MEAN BOND LENGTHS FROM CATIONS TO OXYGEN ATOMS WITHIN COORDINATION POLYHEDRA OF CLINOPREHNITE AND ORTHOPREHNITE FROM STERZING, TIROL, ÖSTERREICH

	Clinoprehnite	Orthoprehnite
Space group	*P*2/*n*11	*P*2*cm*
a (Å)	4.6314(3)	4.6260(2)
b (Å)	5.4839(5)	5.4820(10)
c (Å)	18.4887(16)	18.4826(21)
α (°)	90.611(7)	90
V (Å^3)	469.5(1)	468.7(2)
Z	2	2
D_{calcd} (g · cm^{-3})	2.92	2.92
No. of F_{obsd}	1979	2098
R value	0.021	0.026
4*x* Al(1)–O (Å)	1.716	1.725
4*x* Si(1)–O (Å)	1.631	1.623
4*x* Si(2)–O (Å)	1.625	1.628
6*x* Al(2)–O (Å)	1.923	1.919
7*x* Ca–O (Å)	2.457	2.455

A specimen of prehnite from Sterzing, Tirol, Österreich (Smithsonian Institution No. 3863) was composed mostly of variously intergrown prehnite crystals. It was possible to isolate from this matrix small amounts of single crystal grains of well-crystallized prehnite. The grains were studied by precession, Weissenberg and Laue methods. Some of them appeared to be of orthorhombic metric and showed rather strong reflections violating the *n* glide plane, and a few reflections violating the *c* glide. One grain displayed very clearly monoclinic metric and obeyed the *n* glide extinction better than the orthorhombic crystals, but not perfectly. This indicated that we were dealing with specimens in space groups *P*2*cm* and *P*2/*n*, respectively. Three-dimensional X-ray data for single crystal structure determinations were collected on an Enraf-Nonius CAD4 four-circle diffractometer with Mo-radiation (graphite-monochromator) in Ω step scan mode. They were corrected for Lorentz polarization and absorption effects. The cell constants were refined based on the setting of 25 reflections (see Table I). Electron microprobe analysis showed the chemical composition of the material to correspond well to the formula $Ca_2Al(Si_3AlO_{10})(OH)_2$. The unit cell volumes of both polymorphs are so close to each other that they are likely to have at least very similar, if not identical, chemical compositions. The expected mean Si–O distances for SiO_4-tetrahedra with four and two bridging oxygen atoms are 1.612 and 1.622 Å, respectively (*9*), while the mean Al–O distance is about 1.752 Å in tetrahedral coordination (*9*). Therefore the observed mean bond lengths in the SiO_4 and AlO_4 tetrahedra (Table I) may be interpreted in the following way: site Si(2) is largely, but not exclusively, occupied by silicon, while Al(1) and Si(1) have each a small admixture of Si and Al, respectively (about 10 to 20%). However, it is obvious that Al and Si are predominantly ordered and not occupying randomly positions Al(1) and Si(1), as they would if prehnite were crystallizing in space group *Pncm*, the common supergroup of both *P*2/*n* and *P*2*cm*. In terms of a confirmation by single crystal methods, centrosymmetric orthorhombic prehnite still has to be considered as hypothetical.

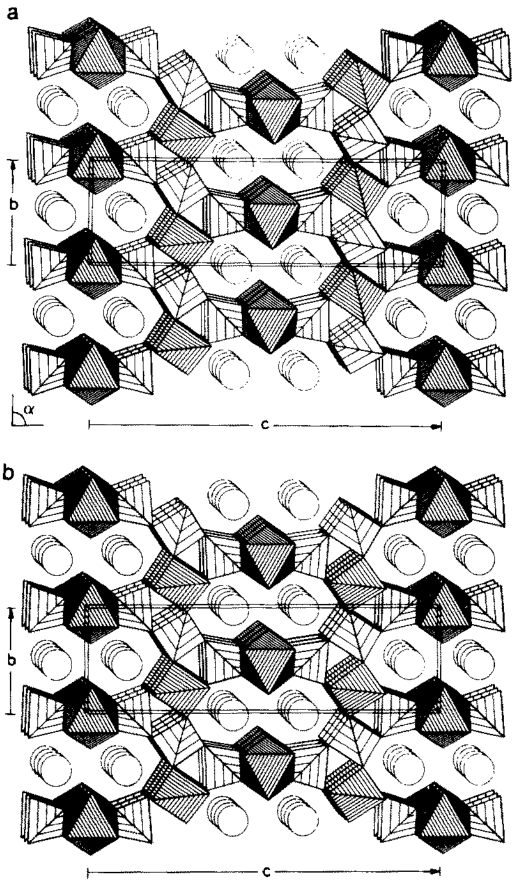

FIG. 1. Polyhedral diagrams of clinoprehnite *a*, almost parallel to the *a* direction (= twofold axis). The tetrahedral Si_3AlO_{10} layer is normal to the plane of the drawing, running top to bottom. The Si- and Al-coordination tetrahedra are located on the twofold axes in 1/4, 1/4, etc. The coordination octahedra around Al(2) are on inversion centers; the chains of inner four-connected tetrahedra with alternating Al and Si occupancy are running top to bottom. Al(2) octahedra and Al(1) tetrahedra are densely shaded, Si(1) and Si(2) tetrahedra are lightly shaded; *b*, polyhedral diagram of orthoprehnite, almost parallel to the *a* direction; twofold axes are as in the monoclinic case; the mirror planes are arranged perpendicularly through the octahedra.

Peng *et al.* (*2*) recognized that the structure of prehnite is unique. The layers have the composition Si_3AlO_{10}, with a T (= Si, Al) to 0 ratio of 4 to 10, as it occurs in many other layer silicates. However, while in the other layer silicates each T coordination tetrahedron has three bridging basal and one terminal apical oxygen atom, in prehnite there are two kinds of tetrahedra: those of the inner chains of alternating Si(1) and Al(1) tetrahedra with four bridging oxygen atoms, and the outer Si(2) tetrahedra with two bridging oxygen atoms connected to the inner chain, and two terminal oxygen atoms which bond to the Al(2) octahedra (Fig. 1). The only difference between the two modifications of prehnite is that the locations of the Al and Si atoms within the inner tetrahedral chain are exchanged for one of the chains in the unit cell (see the right chains within the unit cells shown in Fig. 1). If one starts counting at the Al(1) atom in the lower left corner of Fig. 1a or 1b one has to pass over O–Si(2)–O–Al(2)–O–Si(2)–O–T, before finally at the T atom in the top right corner one encounters an Al(1) atom in clinoprehnite (Fig. 1a), or else an Si(1) atom in orthoprehnite (Fig. 1b). That is why a difference between the two structures is only apparent in the eighth coordination sphere. The two polymorphs are otherwise so similar that the average difference distance of all the Ca, Al, Si, and O atoms from each other in the monoclinic and the orthorhombic cases is less than 0.07 Å, when compared in a common orthorhombic unit cell, obtained by averaging the cell edges of the two polymorphs, while the maximum difference distance is 0.18 Å (for the bridging oxygen atom within the inner chain). To the best of our knowledge this is the only case where a silicate exists in two topologically identical modifications with different Si, Al *ordering* schemes. Cases of structures related to each other, where in one certain cations are ordered, while in the other they are disordered, are common. It is obvious that the energetic difference between clinoprehnite and orthoprehnite must be minute, as is also evidenced by their close association in nature. The two polymorphs are not polytypes according to its accepted definition (*10, 11*). Polytypism is viewed as a special one-dimensional kind of polymorphism, in which layers of constant chemical composition are stacked on top of each other. In prehnite we can rotate a whole layer of the structure consisting of one-half of the unit cell in the *c* direction by 180° about an axis parallel to *c* and generate this way clinoprehnite out of orthoprehnite and vice versa, but the cell translation parallel to the stacking vector (*c* direction) is not altered by this, as it would have to be in the case of polytypism. Thus the two forms of prehnite exhibit a subtle relationship, which makes them even more similar to each other than would be in the case of two modifications related by polytypism. It is not unlikely that similarly small differences in other minerals have been overlooked in the past, because the two polymorphs in question did not involve forms with different metric (monoclinic and orthorhombic in our case).

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