THE AMERICAN MINERALOGIST, VOL. 52, JULY–AUGUST, 1967

ORDERING OF TETRAHEDRAL ALUMINUM IN PREHNITE, $Ca_2(Al,Fe^{+3})[Si_3AlO_{10}](OH)_2$[1]

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ABSTRACT

The crystal structure of a prehnite crystal from Tyrol, Austria, ($a=4.646\pm0.002$ Å, $b=5.483\pm0.002$ Å, $c=18.486\pm0.005$ Å, Z=2) has been refined in space group *Pncm*. This refinement verifies the general features of the model proposed in 1959 by Peng, Chou, and Tang and shows further that two aluminum atoms are restricted to one of two tetrahedral positions in the structure. Weak reflections violating both the *n* and *c* glide requirements were observed for the Tyrol material and for prehnites from several other localities. These reflections are interpreted as indicating further fractionation of the two tetrahedral aluminum atoms in the position which has multiplicity four in space group *Pncm*. This fractionation may take place in one of two ways with both ordering schemes leading to a reduction of the space group symmetry. One scheme results in a *P2cm* space group and the other in a *P2/n* space group. Prehnites from several localities appear to be composed of domains of both of these symmetries.

INTRODUCTION

Despite the occurrence of prehnite as a rock-forming mineral, a reasonably complete characterization of its crystal structure was not accomplished until recently by Peng, Chou, and Tang (1959), and Preisinger (1965). Slow progress in the elucidation of prehnite crystal chemistry has been due to a scarcity of suitable single crystals, the relative complexity of its crystal structure, and difficulties in establishing the true space group symmetry.

Among the interesting aspects of prehnite crystal chemistry is the dual role played by aluminum in the crystal structure by taking both octahedral and tetrahedral coordination and the possibility of various ordered distributions for the tetrahedral aluminum. The purpose of the present investigation is to refine the "average structure" of prehnite and to present models for the possible ordered structures.

A single crystal of prehnite from Tyrol, Austria, was used for the refinement of the "average structure" and prehnites from Tyrol, Austria; Ashcroft, British Columbia; Rowan County, North Carolina; Quebec; West Hartford, Connecticut; Farmington, Connecticut; Cornog, Pennsylvania; El Had Kourt, Morocco; Crestmore, California; and Harzburg, Germany, were used for space group studies by precession camera techniques.

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[1] Studies of Silicate Minerals (3). Publication authorized by the Director, U. S. Geological Survey.

UNIT CELL AND SPACE GROUP

There has been much confusion concerning the true space group of prehnite. Gossner and Mussgnug (1931) suggested that the space group is either *P2cm* or *Pncm*. Nuffield (1943) reported that single crystal photographs display systematically missing spectra indicative of space group *Pncm*; however, since this space group is not consistent with the pyroelectric character of prehnite (Traube, 1894) he concludes that his material is twinned with the untwinned crystal having symmetry *P2cm*. Peng, Chou, and Tang (1959) stated that the space group of their material is *Pncm* and used this space group in the solution of the crystal structure. Preisinger (1965) refined the structure of a prehnite from Radautal, Harzburg, in space group *P2cm*.

Our observations on crystals from various localities indicate first, that prehnite has an "average structure" with symmetry very nearly described in space group *Pncm*, second, that weak reflections violating the *n* glide requirements were present on photographs of all crystals examined, and third, that weak reflections violating the *c* glide were found for the majority of crystals examined. In many cases, exposures in excess of 100 hours with MoKα radiation were necessary to reveal the extra reflections. The only systematically missing spectra for all crystals examined were the (00*l*) reflections with $l \neq 2n$. Usual interpretation of these photographs would indicate the space group to be $P222_1$, but this is not correct as will be explained later.

The unit-cell dimensions for the "average cell" of our Tyrol prehnite obtained from X-ray diffractometer measurements and refined by a least-squares technique (Evans, Appleman, and Handwerker, 1963) are $a = 4.646 \pm 0.001$ Å, $b = 5.483 \pm 0.002$ Å, and $c = 18.486 \pm 0.005$ Å. A partial chemical analysis by Mr. Harry Rose, Jr., U. S. Geological Survey, indicates that the formula for the Tyrol material approximates to $Ca_2(Al_{0.94}Fe^{+3}_{0.06})Si_3AlO_{10}(OH)_2$. Electron microprobe scans across several crystals by Mrs. Cynthia Mead, U. S. Geological Survey, detected no chemical inhomogeneities.

INTENSITY DATA

Single-crystal X-ray diffraction data were collected at the University of Minnesota with an equi-inclination single crystal diffractometer equipped with a proportional counter. Ni-filtered Cu radiation was used in the collection of 490 observed reflections which were then corrected for Lorentz and polarization factors. Because of peak splitting, which is described and explained below, some difficulty was encountered in collecting intensities at certain high two theta values.[1]

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[1] Stewart, James M. and Darrel High (1964). Unpublished program system of the University of Maryland, College Park, Md., and the University of Washington, Seattle, Washington.

TABLE 1. ATOM POSITIONAL PARAMETERS AND TEMPERATURE FACTORS

Atom	Coordinate	Peng, Chou, and Tang (1957)	Present study	B (Å^2)
Ca	x	0.0	0.0	0.41
	y	0.5	0.5	
	z	0.103	0.0992±0.0002	
Al	x	0.0	0.0	0.26
	y	0.0	0.0	
	z	0.0	0.0	
Si$_1$	x	0.5	0.5	0.25
	y	0.0	0.0	
	z	0.118	0.1195±0.0003	
(Si, Al)$_2$	x	0.192	0.1895±0.0012	0.20
	y	0.25	0.25	
	z	0.25	0.25	
O(1)	x	0.767	0.7511±0.0021	0.45
	y	0.134	0.1323±0.0018	
	z	0.072	0.0739±0.0006	
O(2)	x	0.384	0.3686±0.0021	0.59
	y	0.192	0.2130±0.0018	
	z	0.172	0.1716±0.0006	
O(3)	x	0.0	0.0	1.55
	y	0.0	0.0	
	z	0.267	0.2687±0.0009	
OH	x	0.188	0.2054±0.0032	.68
	y	0.294	0.3018±0.0027	
	z	0.0	0.0	

REFINEMENT OF THE "AVERAGE STRUCTURE"

Using 400 reflections obeying *Pncm* symmetry and the positional parameters of Peng, Chou, and Tang (1959), four cycles of least-squares refinement were executed utilizing the full matrix of the normal equations. During this calculation in which all observations were assigned unit weights and temperature factors were fixed at $B=1.0$ Å^2 for (Ca), $B=0.5$ Å^2 for (Si,Al), $B=1.0$ Å^2 for (O), and $B=1.0$ Å^2 for (OH), the R value dropped from 22 percent to 14 percent for $|F_o|>0$. Refinement was continued for four additional cycles allowing isotropic temperature factors to vary and the R dropped to 13 percent. The results of this treatment showed that the mean T-O distance for tetrahedron T_1 was 1.62 Å and for T_2 was 1.68 Å. The scattering factor used for both tetrahedral positions was Si^{+2} with the resulting refined temperature factors being 0.24 $Å^2$ for T_1 and 0.43 $Å^2$ for T_2. Both the temperature factors and the mean T-O distances indicated that the tetrahedral aluminum is confined to the T_2 position. After adjusting the scattering factor as ($Si_{.5}^{+2}$ $Al_{.5}^{+2}$) for the T_2 position four additional cycles of least squares were executed giving a final *R* value of 12 percent.

The scattering factors used during the refinement were: Ca^{+2}, Si^{+2}, ($Si_{0.5}^{+2}$ $Al_{0.5}^{+2}$), and O^{-1} (adapted from International Tables for X-Ray Crystallography, Vol. III, 1962, p. 202–205). Programs for the crystallographic calculations, including absorption corrections, were from *"X-Ray 63" Program System for X-Ray Crystallography.*[1]

DISCUSSION OF THE "AVERAGE STRUCTURE"

The positional parameters and temperature factors for the refined Tyrol prehnite and for the prehnite structure of Peng, Chou, and Tang are presented in Table 1. Selected interatomic distances and angles are listed in Tables 2, 3, and 4 and are keyed to Figure 1a for ease in interpretation. A stereo drawing of the structure is presented in Figure 1b. Observed and calculated structure factors are given in Table 5.[1]

Because the general features of the structure have been described by Peng, Chou, and Tang (1959) and Preisinger (1965) only specific points relating to the distribution of tetrahedral aluminum in the structure will be mentioned.

Refinement of the structure in space group *Pncm* enables us to determine the distribution of tetrahedral aluminum between the T_1 and T_2 tetrahedra both sets of which are in special positions with a multiplicity of four. Because the mean T-O distances are 1.622 ± 0.010 for T_1 and 1.674 ± 0.008 for T_2, it is reasonable to assume that the two tetrahedral aluminum atoms are confined to the T_2 position (Smith and Bailey, 1963). Further support for this assignment is given by the temperature factor of oxygen O(3), which links T_2 tetrahedra. Oxygen O(3) has a significantly higher temperature factor ($B = 1.55$ $Å^2$) than the other oxygen atoms in the structure.

Refinement of the *Pncm* data thus leads us to the following conclusions: first, the structure model of Peng, Chou, and Tang is correct in its general features; and second, that tetrahedral aluminum is confined to

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[1] Deposited as Document No. 9459 with the American Documentation Institute, Library of Congress. Copies may be secured by citing the Document number, and remitting $1.25 for photoprints or microfilm, in advance to the Chief, Photoduplication Service, Library of Congress, Washington, D. C.

TABLE 2. INTERATOMIC DISTANCES FOR TETRAHEDRA OF PREHNITE (a) $T-O$ DISTANCES

Tetrahedron	Oxygen atom	Multiplicity	T-O distance (Å)
T_1	O(1)	2	1.612±0.010
	O(2)	2	1.633±0.011
		Average	1.622
T_2	O(2)	2	1.683±0.011
	O(3)	2	1.665±0.005
		Average	1.674

(b) O-O Distances within tetrahedra

Tetrahedron	Oxygen atoms	Multiplicity	O-O distances (Å)
T_1	O(1)-O(1)′	1	2.746±0.014
	O(2)-O(2)′	1	2.635±0.014
	O(1)-O(2)	2	2.675±0.014
	O(1)-O(2)′	2	2.573±0.014
T_2	O(2)-O(2)″	1	2.925±0.015
	O(3)-O(3)′	1	2.827±0.006
	O(2)-O(3)	2	2.741±0.015
	O(2)-O(3)′	2	2.574±0.012

TABLE 3. SELECTED INTERATOMIC DISTANCES IN PREHNITE

Type	From	To	Multiplicity	Distance (Å)
Environment of Ca	Ca	O(3)′	1	2.443±0.018
		O(2)	2	2.684±0.010
		O(1)″	2	2.371±0.010
		OH′	2	2.335±0.010
Al Octahedra	Al	OH′	2	1.910±0.015
		O(1)	4	1.930±0.010
	OH′	O(1)″	4	2.750±0.016
		O(1)′	4	2.681±0.016
	O(1)′	O(1)″	2	2.729±0.014
		O(1)‴	2	2.731±0.015

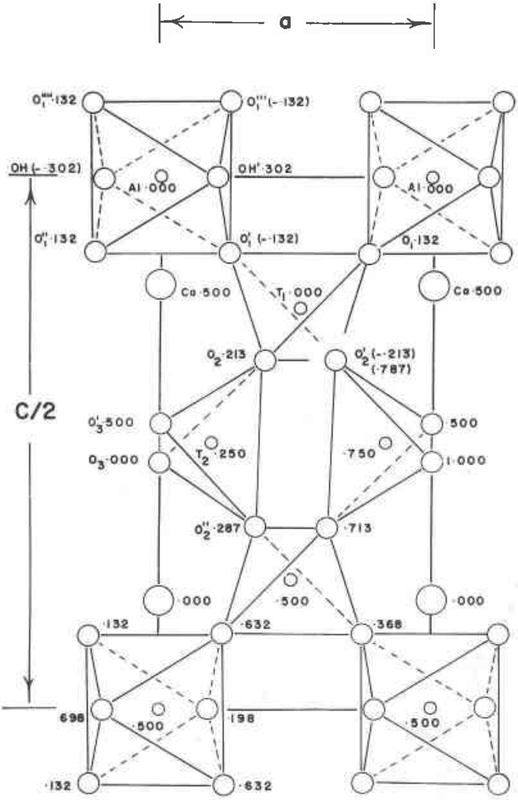

FIG. 1a. Projection along *b* of the crystal structure of prehnite.

the T_2 site. However, the refinement in space group *Pncm* does not tell us whether there is further ordering of the two tetrahedral aluminum atoms in the four-fold T_2 position. This further ordering is indicated by approximately 90 observed reflections violating *Pncm* symmetry.

SIGNIFICANCE OF REFLECTIONS VIOLATING *n* AND *c* GLIDE REQUIREMENTS

There are three symmetrically distinct ways of ordering the two tetrahedral aluminum atoms over the four T_2 positions. All three ways lead to a reduction of the *Pncm* space group symmetry and are illustrated in Figure 2. Ordering scheme A leads to space group *P2cm*. An ordered prehnite with space group *P2cm* has been identified and refined by Preisinger (1965). Ordering scheme B leads to monoclinic symmetry *P2/n*. Ordering scheme C results in space group $P22_12$. Ordering of this type

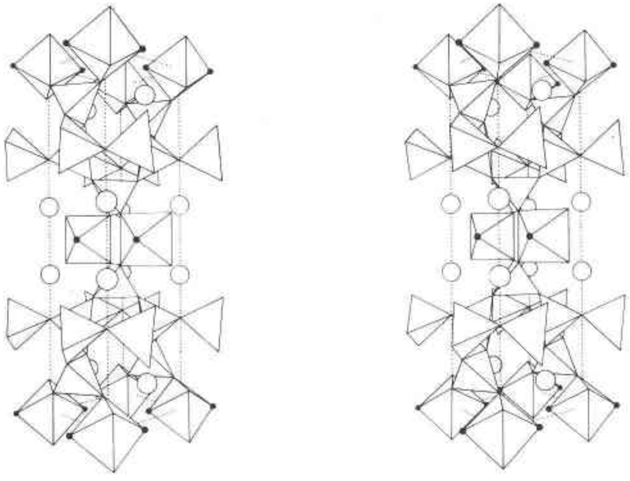

FIG. 1b. Stereographic drawing of the crystal structure of prehnite.

TABLE 4. SELECTED INTERATOMIC ANGLES IN PREHNITE

Type	Atoms	Angle (degrees)
O-*T*-O angles, *T*(1) tetrahedra	O(1)-*T*(1)O(1)′	116.9±0.6
	O(2)-*T*(1)-O(2)′	107.6±0.6
	O(1)-*T*(1)-O(2)	111.1±0.5
	O(1)-*T*(1)-O(2)′	105.0±0.5
O-*T*-O angles, *T*(2) tetrahedra	O(2)-*T*(2)-O(2)″	120.7±0.6
	O(2)-*T*(2)-O(3)′	100.5±0.6
	O(2)-*T*(2)-O(3)′	100.0±0.6
	O(3)′-*T*(2)-O(3)	116.2±0.4
O-Al-O Al octahedra	OH-Al-OH′	180.0±0.0
	OH-Al-O(1)′	91.5±0.4
	OH-Al-O(1)″	88.5±0.4
	O(1)′-Al-O(1)″	90.0±0.4
	O(1)′-Al-O″ ′	90.0±0.4
	O(1)′-Al-O(1)″ ″	180.0±0.4
T-O-*T* and *T*-O-Al Angles	*T*(1)-O(2)-*T*(2)	141.2±0.7
	T(2)-O(3)-*T*(2)′	110.8±0.4
	T(1)-O(1)-Al	129.5±0.6

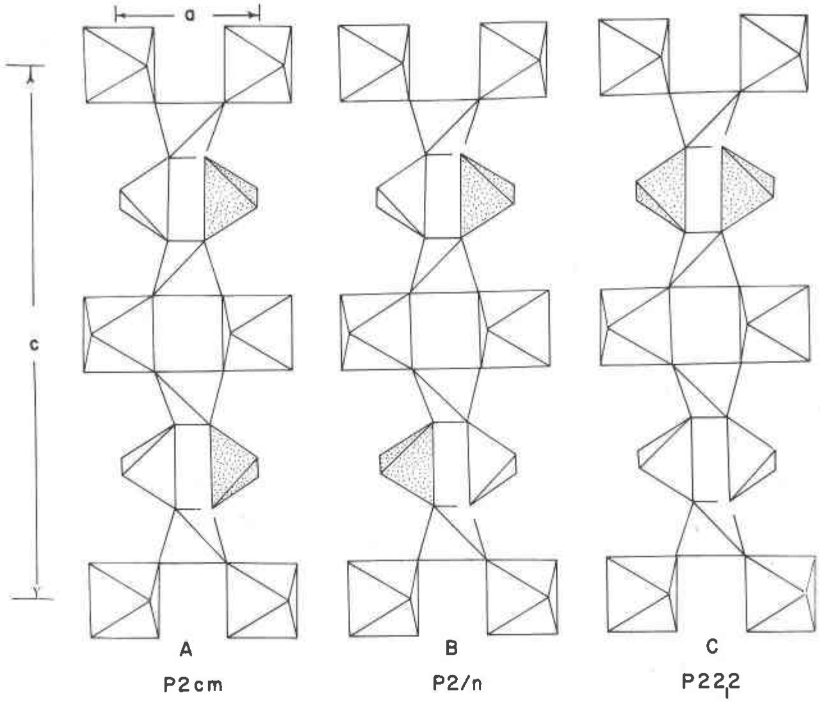

FIG. 2. Three ordering schemes for tetrahedral aluminum in prehnite. Shaded tetrahedra contain aluminum.

does not appear to be feasible since it leads to Al-O-Al linkages which are supposedly unstable in silicates, for example, Lowenstein (1954).

For the *P*2/*n* structure the *a* axis is taken as the two-fold axis. This unconventional setting is used to illustrate the relationship between the *Pncm* "average structure" and the *P*2/*n* ordered structure. The Tyrol prehnite used for the refinement of the structure and the majority of other prehnites studied had apparent symmetry $P222_1$ because the only systematic extinctions were $(00l)$ with $l \neq 2n$. This observation served as a source of confusion for some time since $P222_1$ is not a subgroup of *Pncm* and thus the basic structure could not be refined in this space group. A strong clue to the interpretation of this apparent symmetry was found by the rather peculiar appearance of the 0*kl* precession photographs of several prehnites (Fig. 3). The reflections on these photographs showed a splitting into three maxima. Since photographs with this appearance were found on prehnites from different localities and with the use of different precession cameras it was concluded that the effect was due to the crys-

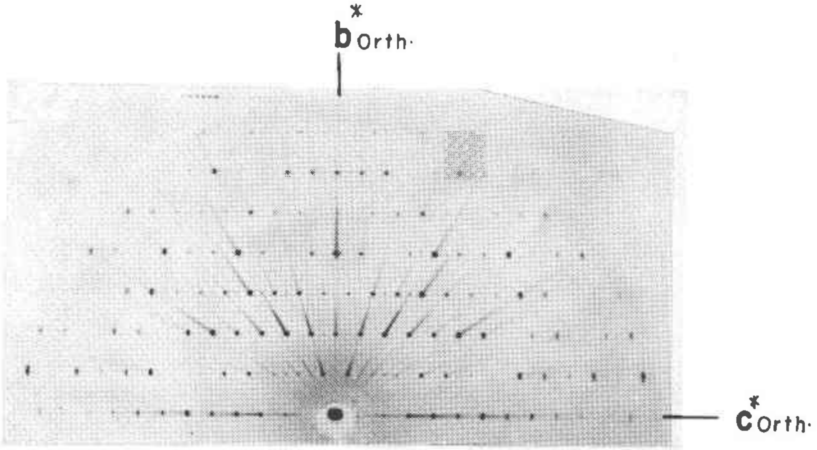

FIG. 3a. 0*kl* precession photograph for a prehnite from Tyrol, Austria. MoKα, 30°μ, 50Kv, 20 Ma, 100 hours. Orthorhombic cell; $a=4.62$ Å, $b=5.47$ Å, $c=18.44$ Å. Monoclinic cell; $a=4.62$ Å, $b=5.47$ Å, $c=18.44$ Å, $\beta=90°45'$, twinned on [010]*.

tals and not the technique. These results were interpreted as being due to two phases in intimate intergrowth in the prehnite crystal, one monoclinic and one orthorhombic. If this were true, reflections violating the *n* glide of the *Pncm* "average structure" could be due to a *P*2*cm* phase and those violating the *c* glide could be due to a twinned *P*2/*n* phase. The

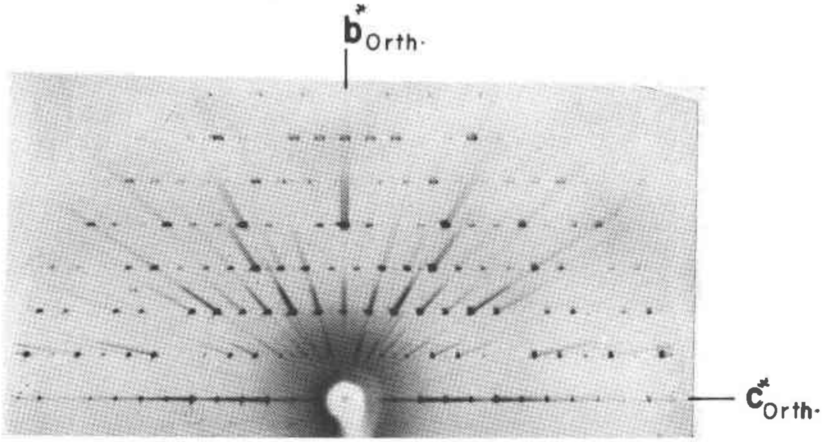

FIG. 3b. 0*kl* precession photograph for a prehnite from Ashcroft, British Columbia. MoKα, 30°μ, 50 Kv, 20 Ma, 78 hours. Orthorhombic cell; $a=4.62$ Å, $b=5.48$ Å, $c=18.44$ Å. Monoclinic cell; $a=4.62$ Å, $b=5.48$ Å, $c=18.44$ Å, $\beta=90°45'$, twinned on [001]*.

only systematic extinction that would remain would be (00*l*) with $l\neq 2n$. The occurrence of intimate intergrowths of twinned monoclinic and orthorhombic domains might well explain some of the peculiar optics reported for prehnite, for example, Deer, Howie, and Zussman (1962) and Dana (1892). In these crystals the *a*-axis of both monoclinic and orthorhombic phases coincide and, therefore, the two-phase nature would be most apparent in the 0*kl* reciprocal lattice nets. Figure 3a illustrates the situation where *b** of the orthorhombic and monoclinic domains coincide. Figure 3b illustrates the situation where *c** of the two phases coincide. In crystals composed of the monoclinic and orthorhombic domains the basic structure would be continuous and only the ordering scheme for tetrahedral aluminum would change. The following interpretations are possible for prehnites with these apparent symmetries:

Pncm	Either a disordered prehnite or photographs not exposed long enough to reveal extra reflections.
P2cm	Crystal composed mainly of ordering scheme A.
P2/n	Crystal composed mainly of ordering scheme B.
$P22_12$	Crystal composed mainly of ordering scheme C. This is considered highly unlikely.
$P222_1$	Crystal composed of domains of both *P2cm* and *P2/n* symmetries.

The relationship between the monoclinic *P2/n* and orthorhombic *P2cm* structures can also be viewed in terms of stacking of the tetrahedral layers. In the *P2cm* structure the stacking would be AA and in the *P2/n* structure the stacking would be AB where B is related to A by 180° rotations.

CONCLUSIONS

Although prehnites have an average structure with symmetry very nearly described in space group *Pncm*, most crystals have an ordered distribution of tetrahedral aluminum leading to crystals with symmetries *P2cm* or *P2/n*. Crystals studied from several localities appear to be composed of both *P2cm* and *P2/n* domains.

Energetically the *P2cm* and *P2/n* polymorphs must be very similar. This is evidenced by the fact that crystals are commonly composed of intimate intergrowths of both polymorphs and different crystals from the same locality show various proportions of the two types. The molar volumes of the two polymorphs would be quite similar. The disordered *Pncm* polymorph, if such exists, would probably be achieved by random rotations of the tetrahedral layers and could be identified on the basis of diffuse or missing reflections violating the glide plane requirements.

ACKNOWLEDGMENTS

We are indebted to Professor E. W. Nuffield, University of Toronto, for supplying a prehnite crystal from Ashcroft, British Columbia, and to Dr. Brian Mason of the U.S. National Museum for supplying prehnites from several localities.

Among the members of the U.S. Geological Survey, we wish to thank Howard T. Evans, Jr., Malcolm Ross, Joan R. Clark, and Daniel E. Appleman for discussions concerning this research and Margaret H. Appleman for the preparation and measurement of several diffractograms and powder films.

Our thanks are extended to Mr. Per Dahlstrom for the preparation of the stereographic drawing.

Part of this research was supported by a grant from the National Science Foundation.

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Manuscript received, July 18, 1966; accepted for publication, September 3, 1966.