

## Crystal structure of pahasapaite, a beryllophosphate mineral with a distorted zeolite rho framework\*

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### ABSTRACT

The beryllophosphate mineral pahasapaite,  $(\text{Ca}_{5.5}\text{Li}_{3.6}\text{K}_{1.2}\text{Na}_{0.2}\square_{13.5})\text{Li}_8\text{Be}_{24}\text{P}_{24}\text{O}_{96}\cdot 38\text{H}_2\text{O}$  is cubic,  $I23$ , with  $a = 13.781(4)$  Å and  $Z = 1$ . Its structure, which has been refined to residuals of 0.047 (unweighted) and 0.035 (weighted) for all 560 reflections, contains ordered  $\text{BeO}_4$  and  $\text{PO}_4$  tetrahedra sharing vertices to form a three-dimensional array of distorted truncated cubo-octahedra ( $\alpha$  cages) linked through octagonal prisms (double 8-rings). Pahasapaite has a distorted zeolite rho-type framework and is therefore structurally related to the faujasite group. Eight  $\text{Li}^+$  and 32  $\text{H}_2\text{O}$  are situated within the cages, and the remaining 6  $\text{H}_2\text{O}$  and the 10.5 ( $\text{Ca}^{2+}, \text{Li}^+, \text{K}^+, \text{Na}^+$ ) are located within and just outside of the double 8-rings, where they obstruct passage between neighboring cages. The double 8-rings consist of two elliptically distorted single 8-rings rotated  $90^\circ$  with respect to one another. Together they define a  $2.2 \times 2.2$  Å aperture (ignoring occluding cations and  $\text{H}_2\text{O}$ ), whereas the cages have a free diameter of about 8 Å. There is a reduction in framework symmetry from the ideal  $Im3m$  in hydrated zeolite rho to  $I43m$  in dehydrated zeolite rho to  $I23$  in pahasapaite. In pahasapaite, this is due to ordering of the framework cations Be and P. Pahasapaite is the first example of a zeolite-like beryllophosphate and may also be considered a relative of the synthetic aluminophosphate molecular sieves.

### INTRODUCTION

In 1971 Flanigen and Grose reported the synthesis of P-substituted analcime, phillipsite, chabazite, and several other zeolite species, with  $\text{P}_2\text{O}_5$  contents as high as 25 wt%. Other workers were unable to introduce more than trace amounts of P into their synthetic zeolites, and it was suggested that some or all of this element was present as phosphate ions intercalated in the zeolite cavities or adsorbed onto crystal surfaces rather than substituted for Al and Si in tetrahedral framework sites (Barrer, 1982). That substitutions of the latter type do occur was demonstrated unequivocally by Artioli et al. (1984), who determined the structure of the P-substituted analcime  $\text{Na}_{13}\text{Al}_{24}\text{Si}_{13}\text{P}_{11}\text{O}_{96}\cdot 16\text{H}_2\text{O}$ . More recently, Flanigen et al. (1986) have reviewed the chemistry of the synthetic aluminophosphate molecular sieves, whose structures are based upon tetrahedral aluminophosphate frameworks, some of which are isotopic with those of various natural zeolites. A variety of other tetrahedrally coordinated cations, including  $\text{Li}^+$  and  $\text{Be}^{2+}$ , may also be substituted for  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  in the frameworks of these compounds.

In addition to these synthetic materials, the minerals kehoeite (McConnell and Foreman, 1974) and viséite (McConnell, 1952) have been alleged to be, respectively,

aluminophosphate and aluminosilicophosphate isotypes of analcime. However, the former is classed as a doubtful species by Fleischer (1987) and the latter is so fine-grained that little can be said with certainty about its structural affinities (Dunn and Appleman, 1977).

We now report the crystal structure of a naturally occurring, zeolite-like phosphate, the mineral pahasapaite, whose tetrahedral framework consists of phosphate ( $\text{PO}_4^{3-}$ ) and beryllate ( $\text{BeO}_4^{2-}$ ) groups ordered in a 1:1 ratio. The chemical, physical, and crystallographic characteristics of this compound have been previously reported by Rouse et al. (1987), who found it to be cubic,  $I23$ ,  $I2_13$ , or  $Im3$ , with  $a = 13.781(4)$  Å and  $Z = 1$ . The chemical formula, as determined from the combined chemical and structural analyses, is  $(\text{Ca}_{5.5}\text{Li}_{3.6}\text{K}_{1.2}\text{Na}_{0.2}\square_{13.5})\text{Li}_8\text{Be}_{24}\text{P}_{24}\text{O}_{96}\cdot 38\text{H}_2\text{O}$ , where “□” represents a vacancy. Its symmetry, unit-cell dimension, and framework composition ( $\text{Be}_{24}\text{P}_{24}\text{O}_{96}$ ) suggest that pahasapaite might be isotopic with analcime ( $\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96}\cdot 16\text{H}_2\text{O}$ ). However, as will be shown presently, the mineral is related not to analcime but to synthetic zeolite rho ( $\text{Na}_9\text{Cs}_3\text{Al}_{12}\text{Si}_{36}\text{O}_{96}\cdot 73\text{H}_2\text{O}$  in its original Cs-Na form), a fact that makes pahasapaite a relative of the faujasite group in a structural, if not chemical, sense. A second framework beryllophosphate occurs in close association with pahasapaite at the type locality, the Tip Top mine, Custer, South Dakota. This is tiptopite,  $\text{K}_2(\text{Li}_{2.9}\text{Na}_{1.7}\text{Ca}_{0.7}$

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TABLE 1. Positional ( $\times 10^4$ ) and thermal ( $\text{\AA}^2 \times 10^3$ ) parameters in pahasapaite

Equipoint	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$	
M(1)	24f	3615(5)	0357(4)	0301(4)	57(4)	42(3)	40(3)	13(3)	-15(3)	-12(3)	46
M(2)	8c	3013(8)	3013(8)	3013(8)	24(4)	24(4)	24(4)	2(5)	2(5)	2(5)	24
P	24f	2771(1)	1240(1)	4224(1)	9(1)	8(1)	10(1)	0(1)	3(1)	0(1)	9
Be	24f	4207(5)	1210(5)	2675(5)	12(3)	6(3)	11(4)	0(3)	7(3)	0(3)	10
O(1)	24f	2246(3)	2178(3)	3914(3)	10(2)	10(2)	16(2)	1(2)	1(2)	-2(2)	12
O(2)	24f	3781(3)	1245(3)	3766(3)	12(2)	20(2)	12(2)	1(2)	2(2)	3(2)	15
O(3)	24f	3791(3)	0329(3)	2041(3)	16(2)	13(2)	16(2)	-1(2)	-4(2)	1(2)	15
O(4)	24f	2160(3)	0383(3)	3889(3)	18(2)	10(2)	16(2)	1(2)	-4(2)	-1(2)	15
H <sub>2</sub> O(1)	8c	3851(3)	3851(3)	3851(3)	39(2)	39(2)	39(2)	-8(2)	-8(2)	-8(2)	39
H <sub>2</sub> O(2)	12d	4768(8)	0	0	15(11)	39(7)	10(5)	23(6)	0	0	21
H <sub>2</sub> O(3)	24f	2171(12)	1095(14)	0714(15)	32(9)	69(12)	51(9)	7(8)	19(8)	6(8)	51
H <sub>2</sub> O(4)	24f	2459(15)	0765(17)	0504(17)	58(13)	93(15)	99(16)	35(12)	46(10)	26(9)	83

Note: Values in parentheses are esd's. Site contents are  $(\text{Ca}_{5.5}\text{Li}_{3.6}\text{K}_{1.2}\text{Na}_{0.2}\square_{1.3})$  for M(1) and 8 Li for M(2); H<sub>2</sub>O(2) to H<sub>2</sub>O(4) are 50% vacant. Anisotropic temperature factors have the form  $\exp -2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + \dots + 2hka^*b^*U_{12})$ .

$\square_{0.7}$ )Be<sub>6</sub>P<sub>6</sub>O<sub>24</sub>(OH)<sub>2</sub>·1.3H<sub>2</sub>O, which Peacor et al. (1987) have shown to be isotypic with basic (hydroxyl) cancrinite.

### STRUCTURE SOLUTION AND REFINEMENT

From a subhedral crystal fragment of approximate dimensions  $0.41 \times 0.64 \times 0.34$  mm, the intensities of 1562 reflections having  $\sin \theta \leq 0.460$  and constituting three asymmetric units were measured with a computer-controlled Supper-Pace diffractometer system, employing Weissenberg equi-inclination geometry and MoK $\alpha$  radiation monochromatized with a graphite flat-crystal monochromator. The intensities were reduced to structure-factor amplitudes by correction for Lorentz-polarization and absorption effects ( $\mu_1 = 8.8 \text{ cm}^{-1}$ ), and symmetry-equivalent reflections were averaged to obtain the final data set of 560 reflections. Of these, 23 had  $|F|_{\text{obs}} < 3\sigma(|F|_{\text{obs}})$  and were considered to be unobserved.

Attempts to determine the structure using the Patterson function and the supposed relationship to analcime were unsuccessful, and recourse was made to direct methods through the MULTAN 78 package (Main, 1978). Intensity statistics produced by MULTAN indicated that the structure was acentric, reducing the choice of space group to *I*23 or *I*2<sub>1</sub>3. Working in *I*23 symmetry, MULTAN revealed the positions of the P atom and its coordinating oxygens, O(1) to O(4), which constitute all of the tetrahedral framework except for the Be atoms. A series of electron-density and difference-electron-density syntheses together with structure-factor calculations revealed the positions of all of the remaining atoms other than H. The structure-factor calculations were carried out with the program SHELX-76 (Sheldrick, 1976) using neutral-atom scattering factors and anomalous-dispersion corrections from the *International Tables for X-Ray Crystallography* (1974) and the reciprocal variances as weights.

Four of the six nonframework sites in Table 1 presented special problems, as their contents are disordered over partially vacant sites. The contents of the M(1) site were constrained to agree with the results of the chemical analysis (Rouse et al., 1987) at  $(\text{Ca}_{5.5}\text{Li}_{3.6}\text{K}_{1.2}\text{Na}_{0.2})$ , i.e., 10.5 atoms disordered over equipoint 24f. H<sub>2</sub>O(2) was initially placed in 6c at  $(\frac{1}{2}, 0, 0)$ , but when difference

syntheses consistently showed a "split atom" on this site, the six H<sub>2</sub>O(2)'s were disordered over 12d at (0.48, 0, 0). Even with this change, H<sub>2</sub>O(2) would not refine satisfactorily and remained nonpositive definite throughout the remainder of the refinement. A second water molecule, initially placed at (0.23, 0.10, 0.06), was also found to be "split" in the difference syntheses and to possess an improbably large isotropic temperature factor,  $U$ , of 0.100(5)  $\text{\AA}^2$ . It was therefore divided into two half-occupied 24-fold positions, H<sub>2</sub>O(3) and H<sub>2</sub>O(4), which represent two closely spaced, alternative positions for the same water molecule. Unlike H<sub>2</sub>O(2), these molecules refined in a satisfactory manner, although their temperature factors remained rather large.

Refinement of the structure with isotropic temperature factors converged to a residual of 0.054. Introduction of anisotropic temperature factors reduced this to the final values of 0.047 (unweighted) and 0.035 (weighted) for all 560 reflections and 0.045 (unweighted) and 0.035 (weighted) for the 537 observed reflections. Table 1 contains the refined positional and thermal parameters; Table 2,<sup>1</sup> the observed and calculated structure factors; Table 3, selected interatomic distances and angles; and Table 4, empirical bond valences calculated from the observed distances and the constants given by Brown (1981).

### STRUCTURE DESCRIPTION

The structure of pahasapaite is based upon a three-dimensional beryllophosphate tetrahedral framework, which may be visualized as an array of truncated cubooctahedra ( $\alpha$  cages) linked together through flat octagonal prisms (double 8-rings). This is shown in its ideal, undistorted form in Figure 1. There are two identical, interpenetrating systems of cages and prisms related to one another by the body-centering translation of the lattice. Access from the cages of one system to those of the other is through shared 6-rings. Both polyhedra (cages and

<sup>1</sup> A copy of Table 2 may be ordered as Document AM-89-417 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 3.** Selected interatomic distances (Å) and angles (°) in pahasapaite

<b>M(1)O<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub> prism</b>			
M(1)–H <sub>2</sub> O(3)			2.306(18)
H <sub>2</sub> O(2)			2.319(12)
O(3)			2.411(6)
O(2)			2.426(7)
H <sub>2</sub> O(4)			2.482(23)
O(4)			2.516(6)
O(2)			2.540(6)
Mean			2.429
<b>M(2)O<sub>3</sub>(H<sub>2</sub>O) tetrahedron</b>			
M(2)–O(1)	1.996(7) × 3	O(1)–M(2)–H <sub>2</sub> O(1)	106.2(5) × 3
H <sub>2</sub> O(1)	1.999(21)	O(1)–M(2)–O(1)	112.5(5) × 3
Mean	1.997	Mean	109.4
O(1)–H <sub>2</sub> O(1)	3.196(7) × 3	O(1)–O(1)	3.319(7) × 3
		Mean	3.258
<b>Phosphate tetrahedron</b>			
P–O(4)	1.522(4)	O(2)–P–O(3)	104.7(2)
O(2)	1.529(4)	O(1)–P–O(4)	107.9(2)
O(1)	1.542(4)	O(1)–P–O(2)	108.0(2)
O(3)	1.545(4)	O(3)–P–O(4)	111.8(2)
Mean	1.534	O(1)–P–O(3)	112.0(2)
		O(2)–P–O(4)	112.4(2)
		Mean	109.5
O(2)–O(3)	2.435(5)	O(2)–O(4)	2.536(6)
O(1)–O(4)	2.478(5)	O(3)–O(4)	2.539(5)
O(1)–O(2)	2.484(5)	O(1)–O(3)	2.559(5)
		Mean	2.505
<b>Beryllate tetrahedron</b>			
Be–O(3)	1.602(8)	O(2)–Be–O(4)	103.5(4)
O(2)	1.614(8)	O(1)–Be–O(2)	105.9(5)
O(1)	1.634(8)	O(1)–Be–O(3)	110.2(5)
O(4)	1.642(8)	O(3)–Be–O(4)	111.5(5)
Mean	1.623	O(1)–Be–O(4)	111.9(5)
		O(2)–Be–O(3)	113.6(5)
		Mean	109.4
O(2)–O(4)	2.556(5)	O(3)–O(4)	2.681(5)
O(1)–O(2)	2.592(5)	O(2)–O(3)	2.691(5)
O(1)–O(3)	2.654(5)	O(1)–O(4)	2.715(5)
		Mean	2.648
<b>T–O–T angles</b>			
P–O(1)–Be	133.9(4)	P–O(3)–Be	131.7(4)
P–O(2)–Be	135.7(4)	P–O(4)–Be	135.6(4)
		Mean	134.2
<b>(H<sub>2</sub>O–H<sub>2</sub>O and H<sub>2</sub>O–O) ≤ 3.2 Å</b>			
H <sub>2</sub> O(4)–H <sub>2</sub> O(4)	2.52(5)	H <sub>2</sub> O(3)–H <sub>2</sub> O(4)	2.97(3)
H <sub>2</sub> O(3)–H <sub>2</sub> O(3)	2.55(3)	H <sub>2</sub> O(4)–O(2)	3.04(2)
H <sub>2</sub> O(4)–O(4)	2.76(2)	H <sub>2</sub> O(3)–O(3)	3.07(2)
H <sub>2</sub> O(2)–O(2)	2.77(1)	H <sub>2</sub> O(3)–H <sub>2</sub> O(4)	3.09(3)
H <sub>2</sub> O(3)–O(4)	2.82(2)	H <sub>2</sub> O(2)–O(2)	3.14(1)
H <sub>2</sub> O(4)–O(3)	2.87(2)	H <sub>2</sub> O(2)–O(3)	3.15(1)
H <sub>2</sub> O(1)–H <sub>2</sub> O(3)	2.93(2)	H <sub>2</sub> O(3)–H <sub>2</sub> O(4)	3.19(3)
H <sub>2</sub> O(1)–H <sub>2</sub> O(4)	2.95(2)	H <sub>2</sub> O(1)–O(1)	3.20(1)
<b>Shortest cation-cation distance</b>			
M(1)–M(1)	1.287(10)	P–Be	2.871(8)
P	3.089(6)	Be	2.912(7)
Be	3.112(9)	Be	2.922(7)
M(2)	4.474(10)	Be	2.930(7)
		Mean	2.909
M(2)–P	2.978(4)		
Be	3.016(9)		
M(2)	7.175(9)		

Note: Values in parentheses are esd's. Very short distances involving M(1), H<sub>2</sub>O(3), and H<sub>2</sub>O(4) are fictitious, as these sites are partially vacant.

**TABLE 4.** Empirical bond valences (v.u.) in pahasapaite

	M(1)	M(2)	P	Be	Σv <sub>a</sub>
O(1)		0.23	1.24	0.50	1.97
		0.23, 0.23			
O(2)	0.09		1.29	0.53	1.91
	0.07				
O(3)	0.10		1.23	0.55	1.88
O(4)	0.08		1.31	0.49	1.88
H <sub>2</sub> O(1)		0.23			0.23
H <sub>2</sub> O(2)	0.12				0.12
H <sub>2</sub> O(3)	0.06				0.06
H <sub>2</sub> O(4)	0.04				0.04
Σv <sub>c</sub>	0.56	0.92	5.07	2.07	

Note: Valences for M(1) were calculated using a weighted average of Ca–O, Li–O, K–O and Na–O. The low sum for M(1) is attributed to the partial occupancy (~44%) of this site.

prisms) are strongly distorted, and the entire tetrahedral framework of pahasapaite is a distorted form of the ideal zeolite rho framework, with symmetry reduced from the ideal *Im3m* to *I23*. We shall return to the relationship between pahasapaite and zeolite rho presently.

The form of the polyhedral distortions in pahasapaite will be seen upon comparison of the ideal (Fig. 1) and actual (Figs. 2, 3) polyhedra. Within the octahedral prisms, the 8-rings are elliptical rather than circular, and paired rings are, in effect, rotated 90° with respect to one another; i.e., the major axes of the two ellipses are perpendicular. The degree of elliptical distortion may be quantified for frameworks of the zeolite rho type using the parameter “Δ,” which was defined by Parise and Prince (1983) as “the separation . . . O(1)–O(2) projected on the (001) plane.” In pahasapaite, Δ is 1.931 Å and is shown in the lower right-hand portion of Figure 3 as the distance between O(1) and O(2), which are the analogues of O(1) and O(2) in the Cs-exchanged zeolite rho structure reported by Parise and Prince (1983). However, this value is not strictly comparable to those of the aluminosilicate rho compounds (cesium rho, ammonium rho, calcium rho, etc.) because Δ is a function of the cell parameter *a*, as well as of the coordinates of O(1) and O(2). Since *a* is a function of the mean tetrahedral bond length in zeolite rho structures (Baur et al., 1988), a “corrected” value of *a* in pahasapaite may be obtained by multiplying it by the ratio of the mean (Si,Al)–O bond length (i.e., 1.638) in the known zeolite rho structures to the mean (P,Be)–O bond length (i.e., 1.579) in pahasapaite, i.e., 13.781 × (1.638/1.579) = 14.30 Å (W.H. Baur, personal communication). This value falls within the 14.225- to 14.880-Å range known for aluminosilicate rho compounds. Multiplying 1.931 Å by 14.30/13.78 gives a “corrected” Δ value of 2.00, which should be directly comparable to those in the aluminosilicate rho structures. Reference to the list of Δ values given by Parise et al. (1984b) shows it to be at the extreme upper limit of the known range for this parameter (0 to 2.0 Å).

The degree of 8-ring distortion may also be expressed by the parameter “EL,” which is defined by Baur et al. (1988) for *I43m* zeolite rho structures as the ratio of the

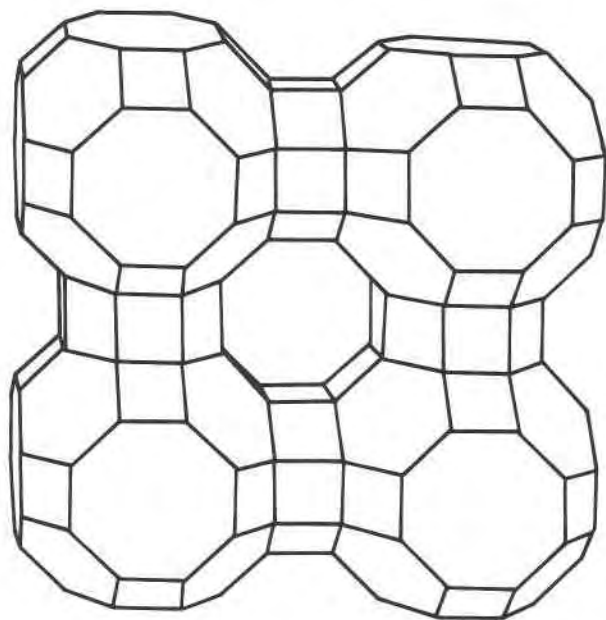


Fig. 1. Polyhedral representation of the undistorted (symmetry  $Im\bar{3}m$ ) tetrahedral framework in zeolite rho. The truncated cubo-octahedra and their linking octagonal prisms form a space-filling array in three dimensions.

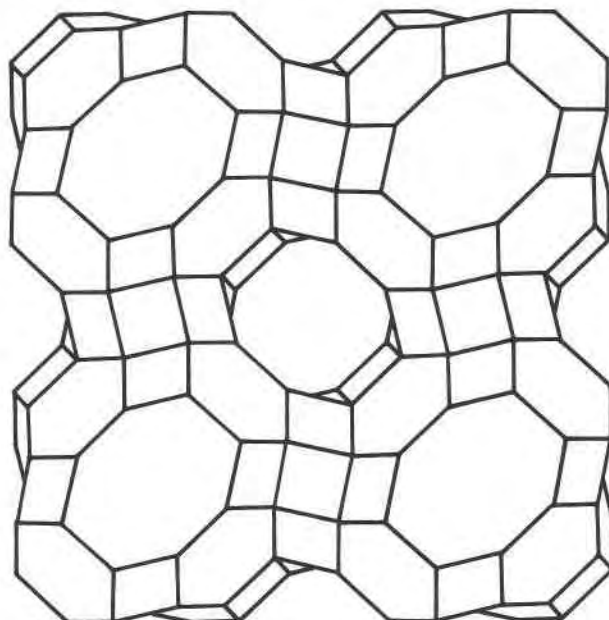


Fig. 2. Polyhedral representation of the distorted (symmetry  $I23$ ) tetrahedral framework in pahasapaite. The diagram corresponds to four unit cells projected onto (001).

$x$  coordinates of O(1) and O(2), i.e., the ratio of the major axis to the minor axis of the ellipse. For pahasapaite,  $EL = \bar{x}[O(1)]/\bar{x}[O(2)] = 0.2212/0.1227 = 1.803$  after transforming and averaging  $x$  and  $y$  coordinates. [This is necessary because O(1) and O(2) have coordinates  $x,y,z$  with  $x \approx y$  in  $I23$  rather than the ideal  $x,x,z$  in  $I43m$ , which is the case for which EL was defined.] The observed value of 1.80 is close to the 1.87 calculated from Baur's equation for EL as a function of  $a$ , using  $a = 14.30 \text{ \AA}$ . Likewise, the aperture size (PS) calculated from his equation for PS as a function of  $a$  is  $2.19 \text{ \AA}$ , which compares well with the observed size (see below) of  $2.2 \text{ \AA}$ . The observed EL and PS values for pahasapaite are, like its  $\Delta$  parameter, near the known limits of 8-ring distortion and small aperture size in zeolite rho structures, the most extreme case in both respects being silver rho, for which  $EL = 1.93$  and  $PS = 2.04 \text{ \AA}$  (Baur et al., 1988). The cell parameter of silver rho,  $14.255 \text{ \AA}$ , is also the smallest known and is the closest to the "corrected"  $a$  of pahasapaite,  $14.30 \text{ \AA}$ .

Each unit cell of pahasapaite contains one complete  $\alpha$  cage, which is joined to identical cages in the six adjacent cells through the double 8-ring prisms. (Each cell also contains portions of eight other cages for a total of two per cell.) The prisms may thus be viewed as apertures through which ionic and molecular species of appropriate size may migrate from one cage to another; i.e., the structure, in effect, contains infinite channels having the sequence -cage-prism-cage-prism-. Moreover, the structure is traversed by three mutually perpendicular sets of these channels, the channels within each set being parallel to

one another and to one of the axes of the cubic unit cell. Each single 8-ring encloses an elliptical  $2.2 \times 6.0 \text{ \AA}$  opening, whereas the  $\alpha$  cage has an average free diameter of  $8 \text{ \AA}$ . The effective shape of the cage-linking apertures is defined by the two 8-rings superimposed (they are rotated  $90^\circ$  with respect to one another), and this is an approximately square orifice of dimensions  $2.2 \times 2.2 \text{ \AA}$ . These dimensions were estimated graphically by drawing circles representing oxygens on the original of Figure 3, assuming a radius of  $1.22 \text{ \AA}$  for oxygen. The latter is the crystal radius of 3-coordinated  $O^{2-}$  given by Shannon (1976), and it would seem to be approximately correct in this case, as the circles on the diagram were tangent to one another (or nearly so).

Having described the channel system in pahasapaite and its potential as a conduit for atomic migration, it must also be said that such migration is limited in the structure as currently constituted. This is because the apertures are obstructed by M(1) cations and  $H_2O(2)$  water molecules, the latter residing inside the double 8-rings at their centers and the former on the cage side of each single 8-ring, just off-center (Fig. 3). However, zeolite rho readily exchanges cations in aqueous solution and also absorbs polar molecules such as ammonia, methanol, ethanol, and dimethyl ether (Anderson and Kevan, 1987; Lutz and Vega, 1986). This is attributed to solvation of the obstructing cations by polar molecules, which may then gain access to the cages. Nonpolar molecules without this solvating ability are excluded from the structure (Anderson and Kevan, 1987). Presumably, the same holds true in pahasapaite.

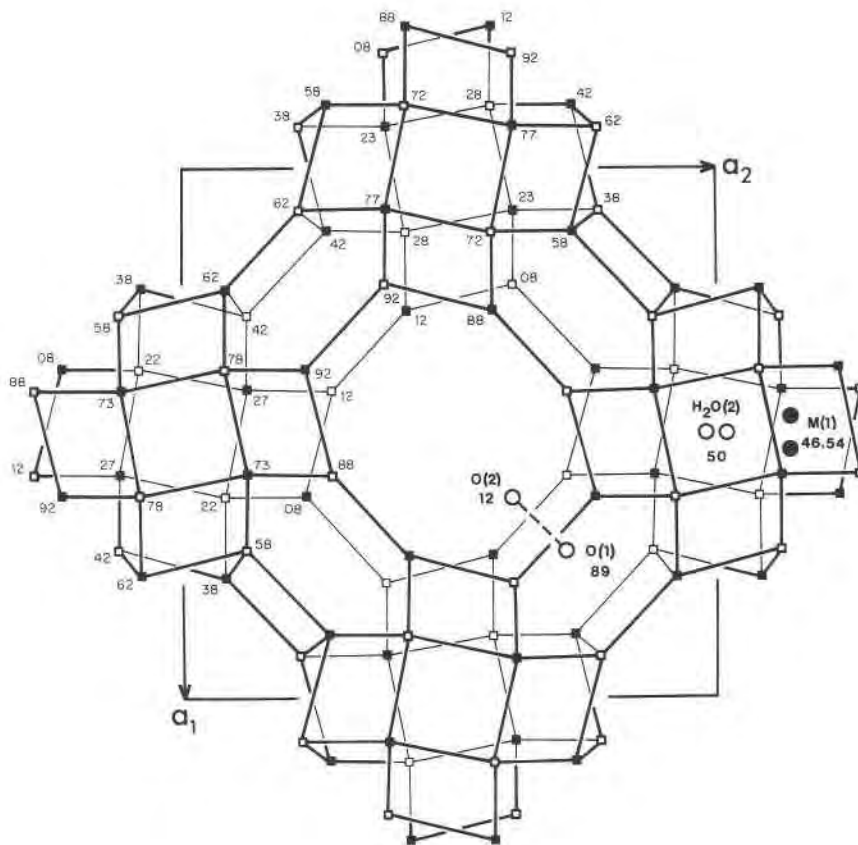


Fig. 3. Tetrahedral node diagram of pahasapaite projected on (001). The black squares represent P and the open squares Be. To improve clarity, the nonframework cations and water molecules have been omitted, except for one M(1) site (black circles) and one H<sub>2</sub>O(2) site (open circles) associated with one of the double 8-rings. This is to illustrate the channel-blocking role of these two species. The "splitting" of M(1) and H<sub>2</sub>O(2) appears as closely spaced pairs of circles. The numbers are z coordinates  $\times$  100.

The nonframework species in pahasapaite are of two types: the cations M(1) and M(2) and the water molecules H<sub>2</sub>O(1) to H<sub>2</sub>O(4). The most notable of these is M(1), which is located just outside of the double 8-rings near their central axes and which contains 10.5 (Ca<sup>2+</sup>, Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>) cations disordered over 24 equivalent positions, the fractional occupancy being necessary to avoid M(1)-M(1) approaches as close as 1.287 Å. The M(1) ions are coordinated by an irregular polyhedron of four framework oxygens and three water molecules, which can be described either as a highly distorted monocapped trigonal prism or monocapped octahedron (Fig. 4). No ionic exchange experiments have been attempted with pahasapaite, but the M(1) ions should be readily exchangeable.

The site M(1) and those of its coordinating water molecules H<sub>2</sub>O(2), H<sub>2</sub>O(3), and H<sub>2</sub>O(4) are approximately half-occupied, with each occurring as a closely associated pair of atoms. If one of the M(1) sites is specified, however, only one specific H<sub>2</sub>O molecule of each of the three pairs leads to reasonable interatomic distances, as listed in Table 3 and illustrated in Figure 4. The alternative choice leads to a symmetry-equivalent polyhedron. More

important, if the M(1) cations at  $(x, y, z)$  and  $(\bar{x}, \bar{y}, \bar{z})$  and related water molecules are specified [rather than M(1) at  $x, y, z$  and  $\bar{x}, \bar{y}, \bar{z}$ ], then the symmetry is lowered to space group *R*3. No evidence was found for such symmetry in the diffraction relations. However, M(1) sites may be

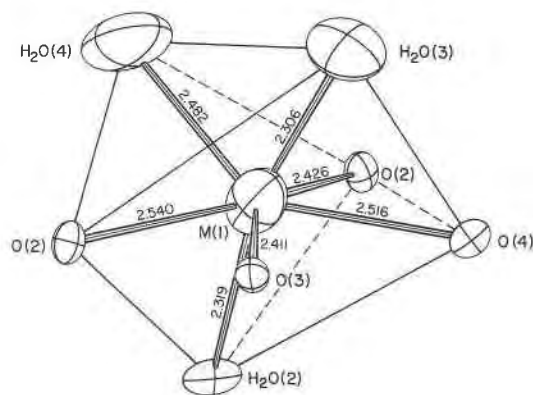


Fig. 4. The coordination polyhedron around M(1) represented as a distorted monocapped trigonal prism, with O(3) being the capping ligand. Drawn with ORTEP-II (Johnson, 1976).

clustered in a correlated way to give rise to domains of symmetry  $R3$ , with such domains related by twinning and giving rise to a crystal with the observed, average symmetry of  $I23$ . Completely random distribution of  $M(1)$ - $H_2O$  clusters is also possible, of course.

The  $M(2)$  sites are located near the centers of the cage 6-rings and are quite different in character from  $M(1)$ , being fully occupied by eight  $Li^+$  ions tetrahedrally coordinated by three framework oxygens and one water molecule. The tetrahedron is almost regular, as the three  $M(2)$ - $O(1)$  distances are equivalent by symmetry and the  $M(2)$ - $H_2O(1)$  distance differs from the others by only 0.003 Å (although its standard error is large). The  $O(1)$ - $M(2)$ - $O(1)$  and  $O(1)$ - $M(2)$ - $H_2O(1)$  angles differ by only 3° from their ideal value (Table 3). Since the  $M(2)$  ion is bonded to three framework oxygens, the  $LiO_3(H_2O)$  tetrahedron shares three of its vertices with  $BeO_4$  and  $PO_4$  tetrahedra, and this, combined with its nearly regular geometry, suggests that the  $LiO_3(H_2O)$  groups could be regarded as an auxiliary part of the beryllophosphate tetrahedral framework. A second important feature of  $M(2)$  is its location near the center of the 6-rings, where it blocks access between the two interpenetrating cage systems.

The water molecule coordinating  $M(2)$  is  $H_2O(1)$ , which is notable in that it is the only one in the structure to be located on a fully occupied site with no disorder. Also notable is  $H_2O(2)$ , which as previously stated, helps to impede ionic and molecular migration through the double 8-rings. The three disordered water molecules  $H_2O(2)$ ,  $H_2O(3)$ , and  $H_2O(4)$  are coordinated only to the  $M(1)$  site, which is partially occupied by a mixture of monovalent and divalent cations ( $Ca^{2+}$ ,  $Li^+$ ,  $K^+$ , and  $Na^+$ ). From this fact one may speculate that the water content of pahasapaite might vary slightly depending upon the number and identity of the ions occupying  $M(1)$ . That is, a water content lower than the current 38  $H_2O$  per cell might be favored by a higher proportion of cations of small size and/or low charge in  $M(1)$  in order to satisfy requirements for lower coordination and charge neutralization.

Nothing can be said with certainty about hydrogen bonding in pahasapaite, as the H atoms could not be located experimentally. However, an inspection of the interatomic distances in Table 3 shows numerous  $H_2O$ -O and  $H_2O$ - $H_2O$  distances between 2.7 and 3.2 Å. [The short  $H_2O(4)$ - $H_2O(4)$  and  $H_2O(3)$ - $H_2O(3)$  distances of 2.5 Å are probably fictitious, as these sites are only partially occupied.] In particular, the  $H_2O(4)$ - $O(4)$ ,  $H_2O(2)$ - $O(2)$ ,  $H_2O(3)$ - $O(4)$ , and  $H_2O(4)$ - $O(3)$  distances between 2.76(2) and 2.87(2) Å are good candidates for hydrogen bonds, as  $O(2)$ ,  $O(3)$ , and  $O(4)$  have slightly low bond-valence sums of 1.91, 1.88, and 1.88 v.u., respectively (Table 4). By contrast,  $O(1)$  has a nearly ideal valence sum of 1.97 v.u., and its closest approach to a water molecule is a long 3.20(1) Å to  $H_2O(1)$ . It will further be noted that  $H_2O(1)$  has the highest valence sum of any water molecule in Table 4 and that it has no approaches to framework oxygens closer than 3.20(1) Å. We therefore suggest that these two atoms,  $O(1)$  and  $H_2O(1)$ , may be the only

oxygens not involved in the presumed hydrogen-bond network in pahasapaite and that the remaining  $H_2O$  molecules form hydrogen bonds to framework oxygens and also to one another. That is, the interiors of the  $\alpha$  cages are almost filled with water molecules alone, whereas all of the nonframework cations are located on the cage walls. It is reasonable to assume that extensive hydrogen bonding occurs among the  $H_2O$  in the cage interiors.

#### RELATIONSHIPS TO OTHER STRUCTURES

The various compounds known collectively as "zeolite rho" crystallize in two space groups,  $Im3m$  and its subgroup  $I\bar{4}3m$ . Parise et al. (1984a) and McCusker and Baerlocher (1984) found that the reduction in symmetry occurs upon dehydration of hydrated forms, but Fischer et al. (1986) noted that some forms of hydrogen rho retain  $Im3m$  symmetry even though they contain no molecular water. [The H is present as bridging hydroxyl groups in the framework according to Wax et al. (1986) and Fischer et al. (1987).] In both space groups the 48 framework Al and Si atoms are disordered over a single 48-fold equipoint. This contrasts with the situation in pahasapaite, where there is no (Be,P) solid solution and the two species are ordered in two 24-fold positions. Consequently, there is a further reduction in symmetry to  $I23$ , which is also a subgroup of  $Im3m$ . This low symmetry allows for extensive distortion of the tetrahedral framework relative to the ideal  $Im3m$  configuration, including an elliptical distortion of the double 8-rings near the extreme upper limit of its known range. In this respect, pahasapaite is comparable only to silver rho and deuterated ammonium rho in Table 2 of Baur et al. (1988).

In Table 5, the nonframework atom sites in pahasapaite are compared with the standard nonframework cation sites in zeolite rho structures (Fischer et al., 1986). Specifically,  $M(1)$  is an "F" site (occupied by  $Na^+$  or  $H_2O$  in cesium rho) and  $M(2)$  is an "A" site (occupied by  $Na^+$  in cesium rho). In addition,  $H_2O(2)$  in pahasapaite occupies the "E" cation site, which in cesium rho is filled by  $Cs^+$  or  $H_2O$ . The "E" and "F" cation sites are those that block the double 8-rings, and  $Cs^+$  is thus the analogue of  $H_2O(2)$  in pahasapaite. Unlike  $H_2O(2)$  in pahasapaite,  $Cs^+$  is located in the ideal ( $1/2, 0, 0$ ) position and is thus not disordered. The  $Cs^+$  site may also be partially occupied by  $D^+$  and  $D_3O^+$  (in deuterated forms) (Parise et al., 1984a, 1984b).

Pahasapaite is one of three minerals known to have structures built up of truncated cubo-octahedra connected by channels, the others being the zeolite paulingite,  $(K, Ca, Na_2)Al_3Si_{11}O_{28} \cdot 12H_2O$  with symmetry  $Im3m$  (Gordon et al., 1966), and the complex, zeolite-like phase ashcroftine, ca.  $K_{10}Na_{10}(Y, Ca)_{24}(OH)_4(CO_3)_{16}Si_{56}O_{140} \cdot 16H_2O$  with average symmetry  $I4/mmm$  (Moore et al., 1987). This polyhedron is also the principal secondary structural unit in the synthetic zeolites Linde A and ZK-5, as well as zeolite rho.

In addition to its relationship to zeolite rho, pahasapaite may be considered a naturally occurring relative of



TABLE 5. Comparison of nonframework atom sites in pahasapaite and zeolite rho

Location	Pahasapaite		Zeolite rho	
	Site	Coordinates	Site	Coordinates
Outside D8R	M(1)	0.04, 0.03, 0.36	F	~(0.05, 0.05, 0.30)
6R center	M(2)	0.30, 0.30, 0.30	A	~(0.28, 0.28, 0.28)
Cage interior	H <sub>2</sub> O(1)	0.39, 0.39, 0.39	—	—
D8R center	H <sub>2</sub> O(2)	0.98, 1/2, 1/2	E	0, 1/2, 1/2
Cage interior	H <sub>2</sub> O(3)	~(0.23, 0.09, 0.06)	—	—
	H <sub>2</sub> O(4)			

Note: Coordinates of pahasapaite atoms have been transformed where necessary to show their correspondence to those given by Fischer et al. (1986) for zeolite rho. The symbols D8R and 6R refer to the double 8-rings (prisms) and to the 6-rings of the  $\alpha$  cages, respectively.

the synthetic aluminophosphate molecular sieves. These include about two hundred compounds and are categorized into more than two dozen structure types (Flanigen et al., 1986). The aluminophosphate frameworks are isotopic with the aluminosilicate frameworks of faujasite, erionite, chabazite, levyne, Linde A, gismondine, and sodalite, and many novel types unknown among the zeolites are also represented. Tetrahedrally coordinated Li, Be, B, Mg, Si, Ti, Mn, Fe, Co, Zn, Ga, Ge, and As may also be substituted into framework cation sites. Pahasapaite might be thought of as a derivative of this group in which substitution of Be<sup>2+</sup> for Al<sup>3+</sup> is complete, producing a beryllophosphate framework. Moreover, the existence of beryllophosphate analogues of basic cancrinite and zeolite rho suggests that a whole family of zeolite-related beryllophosphates, analogous to the aluminophosphate family and having useful properties, may potentially exist. An example is the synthetic, zeolite-like "Beryllophosphate-H" (Na<sub>7</sub>K<sub>7</sub>Be<sub>14</sub>P<sub>14</sub>O<sub>56</sub>·20H<sub>2</sub>O), which has recently been described by Harvey (1988).

Pahasapaite also shows certain chemical and structural similarities to the zeolite-like berylliosilicate mineral hsianghualite (ideally Ca<sub>24</sub>Li<sub>16</sub>Be<sub>24</sub>Si<sub>24</sub>O<sub>96</sub>F<sub>16</sub>), which is cubic, *I*2<sub>3</sub>, with *a* = 12.88 Å (Section of Crystal Structure Analysis, Academia Sinica, 1973). The unit-cell size, space-group symmetry, and framework stoichiometry (T<sub>24</sub>T<sub>24</sub>O<sub>96</sub>) all resemble those of pahasapaite; however, the framework is of the leucite rather than the zeolite rho type, and the large framework cavities are filled with F atoms rather than water molecules. As in pahasapaite, the nonframework cation sites are of two types: two small cation sites, each filled with 8 Li<sup>+</sup>, and two large cation sites, each filled with 12 (Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>). The former closely resemble the small cation site [M(2)] in pahasapaite, as they are situated on one side of the framework 6-rings and are tetrahedrally coordinated by three framework oxygens and one F<sup>-</sup> ion. The latter contain (Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>) like the large cation site [M(1)] of pahasapaite but have distorted cubic rather than monocapped trigonal prismatic coordination. Finally, there is complete ordering of the two species of framework cations in each mineral, leading to a reduction in framework symmetry from the ideal *Ia*3*d* to *I*2<sub>3</sub> in hsianghualite and from the ideal *Im*3*m* to *I*2<sub>3</sub> in pahasapaite.

As previously described, pahasapaite and zeolite rho

are built up by connecting truncated cubo-octahedra through octagonal prisms in three dimensions. An extensive theoretical analysis of the possible frameworks that may be obtained through three-dimensional connection of Archimedean polyhedra was carried out by Moore and Smith (1964) and more recently by Smith and Bennett (1981). The particular framework observed in pahasapaite was described as a theoretical possibility by Moore and Smith well before its discovery by Robson et al. (1973) in the structure of zeolite rho. By connecting truncated octahedra or truncated cubo-octahedra in various ways, one may obtain the frameworks of the feldspathoid mineral sodalite and the zeolite species Linde A, ZK-5, rho, paulingite, and faujasite. The beryllophosphate species pahasapaite thus takes its place in this structural group, as the first zeolite-like (restricting the term "zeolite" to aluminosilicates) natural counterpart of synthetic zeolite rho.

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