The crystal structure of phosphophyllite

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Abstract

Phosphophyllite from Poten, Beltrac, Zn-Pt(PO₄)₄·4H₂O, is monoclinic and crystallizes in space group P2₁/c, with a = 10.37(3), b = 5.88(1), c = 10.55(3) Å, β = 91.14°, and Z = 2. The structure was refined by Patterson and Fourier methods from 1999 Zr-filtered MoKα data and refined by full matrix least squares (including the hydrogen atoms) to R = 0.032 (Rw = 0.033). The framework consists of [ZnO₆] octahedral sheets identical to those in heulandite, intersected with [PO₄]·4H₂O octahedral sheets similar to those in phengite.

Introduction

Phosphophyllite from Hugendorf, Bavaria, was first described by Lehmkuhl and Stotzek (1930), but has been documented in relatively few other localities since then (Hill, 1976). Nevertheless, a large number of studies have suggested close relationships between the crystal structure of phosphophyllite and that of heulandite (Sternberg, 1930; Wolfe, 1940; Gamidov et al., 1968; Likhis, 1965; Kanjuhara et al., 1973), and phosphophyllite (Kannaujia and Finney, 1968; Chan, 1969). Although the topology of heulandite and phosphophyllite is now known with some degree of precision (Hill and Jones, 1976; Chan, 1969), the phosphophyllite structure has been determined from two-dimensional X-ray data only (Kocher et al., 1961), with the 20 coordinates estimated on the basis of interatomic distances within the inferred coordination polyhedra. Moreover, the framework determined by Kocher et al. contains a number of unusual features of O—O non-bonded distances, and one distance which arises from the sharing of an edge between ZnO₆ and a PO₄ tetrahedron. Based on an alternative interpretation of the published (P₂₁) projection, Hill (1975) proposed a new framework with more reasonable O—O distances and no shared edges. The new model was refined by the method of distance least-squares (Meier and Villiger, 1969) and converged to a structure essentially identical, except in the vicinity of the octahedral sites, to that of heulandite. The present three-dimensional X-ray refinement was initiated in order to determine which of the above models pertains to phosphophyllite.

Experimental

A roughly equidimensional cleavage fragment of phosphophyllite from Poten, Bavaria (crystal volume = 2.0 x 10⁻⁶ cm³) was oriented with the c axis parallel to the c axis of a Picker 4-circle diffractometer. Detailed chemical, optical, and X-ray data for material from this locality have been reported by Hill (1976): unit-cell dimensions from this study have been included in the computer X-ray intensity data for the structure analysis were collected at 20°C using Zr-filtered MoKα radiation (λ = 0.7093 Å) and a 2θ scan rate of 2°/min. Backgrounds were determined from 10-second stationary counts at both ends of each dispersion-oriented (Alexander and Smith, 1961) scan range (minimum width = 2.4° in 2θ). A total of 6282 reflections with 2θ > 75° and 2θ > 0 were measured, using three reflections to monitor instrument and crystal stability at frequent intervals: these showed no significant change. Systematic extinctions appropriate to space group P2₁/c were removed, and the resultant data corrected for background, Lorentz, polarization, and absorption (based on actual crystal shape and a u value of 70.22 cm⁻²) effects. Symmetry-equivalent and multiply-measured reflections were averaged (by weight) to yield 2482 unique structure factors, each

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* cif's, given in parentheses, refer to the last decimal place.
with a standard deviation estimated from the equation: 
\[ x = a + 0.032/\gamma \pm 0.032/\gamma \]  
where \( a \) is the corrected new intensity and \( \gamma \) is derived from counting and averaging statistics. Of these data only those 1999 observations with \( \gamma > 2 \) were included in the subsequent least-squares refinement.

**Structure determination and refinement**

The Fe and Zn atoms were located from the Patterson function, and the P and O atoms from partially phased Fourier syntheses. These were refined by least-squares minimization of \( 2\pi[|F_o| - |F_c|]^2, \) where \( F_o \) and \( F_r \) are the observed and calculated structure factors, and \( w = 1/|F|^2 \). Re-refinement with isotropic temperature factors converged to a conventional \( R \) of 0.055. Refinements with anisotropic temperature factors and the inclusion of anisotropic extinction parameters (see 1970), as defined and refined by Coppens and Hamilton (1970), further reduced \( R \) to 0.033.

A Fourier difference synthesis utilizing only those data with \( |F_o| > 0.4 \) A\(^{-1}\) was computed, and peaks ranging from 0.4 to 0.6 A\(^{-1}\) were found for the four hydrogen atoms in the asymmetric unit. There were also a small number of other peaks with maximum density 1.2 A\(^{-1}\), but these were all located well within the coordination sphere of Zn, Fe, and P, and were interpreted as regions of charge deformation due to chemical bonding. Full matrix refinement, including the Fe ion positions and isotropic thermal parameters and using all 1999 reflections, then proceeded smoothly to convergence (recommended shifts in the final cycle were less than one tenth of the appropriate \( e \)). The final values of \( R \) and \( \Delta R = 0.022 \) and 0.035 respectively (0.029 and 0.033 for the atomic data set of 2442 structure factors), with the error in an observation of \( \sigma = 0.022 \). Only 33 reflections were affected more than 3 percent by \( e = 2.3(2) \). Values for \( F_o \) and \( F_r \) of 100 are listed in Table 1. Atomic coordinates and thermal parameters are given in Table 3. The r.m.s. components of thermal displacement and thermal ellipsoid orientations are given in Table 3.

Scattering factors for Zn, Fe, P, and O (neutral atoms) were obtained from International Tables for X-ray Crystallography (1974) and were corrected for both real and imaginary intermittent dispersion components. For 
Fe, the critical scattering factor suggested by Stearns et al. (1965) was used. Programs utilized for solution, refinement and geometry calculations were based on modifications of OXIDATE, DIFUTE, FOURIER, ORFFE, ORFFE3, and ORFFE3.2.

**Discussion of the structure**

Phosphophyllite crystallizes with the tetragonal system in the space group 
\[ D_{4}d \]  
with the tetragonal axis parallel to axes of the unit cell. The unit cell contains two molecules of phosphophyllite per unit cell. The molecules are related by a center of symmetry located at the center of the unit cell. The molecules are arranged in a layer structure, with the layers stacked parallel to the (001) plane. The layers are held together by hydrogen bonds.

The Fe atoms occupy one-quarter of the available sites in the unit cell. The O atoms are arranged in a puckered sheet, with the Fe atoms located at the centers of the puckered sheets. The Zn and P atoms are located at the corners of the puckered sheets, with the Zn atoms forming a square planar coordination geometry.

In conclusion, the structure of phosphophyllite is a unique combination of donor-acceptor interactions and hydrogen bonding, which results in a highly ordered structure with well-defined layers. The structure is stabilized by the strong hydrogen bonding, which results in a compact and well-organized structure.
**Table 2. Fractional atomic coordinates and isotropic temperature factors for phosphophyllite**

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
<th>Xeq</th>
<th>Yeq</th>
<th>Zeq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.0000(1)</td>
<td>0.6667(1)</td>
<td>0.3333(1)</td>
<td>0.0000(1)</td>
<td>0.6667(1)</td>
<td>0.3333(1)</td>
<td>0.0000(1)</td>
</tr>
<tr>
<td>O1</td>
<td>0.3333(1)</td>
<td>0.6667(1)</td>
<td>0.0000(1)</td>
<td>0.0000(1)</td>
<td>0.6667(1)</td>
<td>0.3333(1)</td>
<td>0.0000(1)</td>
</tr>
<tr>
<td>O2</td>
<td>0.6667(1)</td>
<td>0.3333(1)</td>
<td>0.6667(1)</td>
<td>0.0000(1)</td>
<td>0.6667(1)</td>
<td>0.3333(1)</td>
<td>0.0000(1)</td>
</tr>
</tbody>
</table>

The corresponding bridging O atom occupies a site position, thereby giving rise to a primitive/orthorhombic relationship between the unit cells of the two minerals (Wolfe, 1940; Gandinov et al., 1963). Since the tetragonal portions of both frameworks are identical, this relationship allows the structure of hopeline to be obtained in its entirety by polyhedral unfolding of the phosphophyllite unit cell about the (001) plane (Gandinov et al., 1963; Kawamura et al., 1971). In fact, the mode of coordination of the Fe atom in phosphophyllite is the same as that of the orthorhombically-coordinated Zn atom in the closely related mineral parahopeline (Künzler and Finney, 1968; Clae, 1969), although the tetragonal sheet is composed only of four-membered rings and the bridging atom is trigonally coordinated in the latter species. Indeed, the ability of the para-hopeline structure to accommodate a significant amount of Fe (along with Mg and Mn) in the octahedral site (Hill and Mitten, 1974) lends support to the suggestion by Kawamura et al. (1971) that phosphophyllite, hopeline, and parahopeline may be considered to be trimorphs.

Anatase, lamalite, and swinertonite are also members of Wolfe's (1940) family of the type 

$$\text{As}_{2} \text{PO}_{4} \cdot 4 \text{H}_{2} \text{O}.$$ 

The first two species have crystal structures (Ramsay and Zinkeckers, 1969; Abrahams, 1960) unrelated to those of hopeline, para-hopeline, and phosphophyllite, and although its structure is as yet unetermined, wolfeite (Lawrence and White, 1967) also appears to be unique within this
Fig. 1. Unit-cell diagram of the phosphorite crystal structure. Thermal ellipsoids for all atoms except hydrogen are 50% probability surfaces. Hydrogen bonds are indicated by dashed lines. Atoms and the asymmetric unit are labelled with conventional primes.

Hydrogen bonding

The distance and angle parameters describing the two water molecules and their associated hydrogen bonds are given in Table 4. All four O···H distances are within one standard deviation of their average value, 0.86 Å, and are shorter than the corresponding average distance measured by neutron diffraction (Baur, 1972). Similar shifts of the apparent X-ray hydrogen positions toward the atom to which it is bonded have been documented by a large number of workers (Skarman et al., 1968; Havelka, 1968; Hamsen et al., 1973; Cooper, 1974), and are considered to reflect the relatively large distortion of the hydrogen atom electron density during formation of the O···H bond. Under these circumstances, little credence can be attached to the r.m.s. displacement (Table 3) derived from the hydrogen atom thermal parameters, and for this reason no attempt has been made to apply a vibration correction to the O···H distances in Table 4.

Both hydrogen atoms in the O(1) water molecule participate in hydrogen bonds to O(3) atoms one of the vacant octahedrons within the octahedral sheet. This configuration appears to be controlled by the onedimensionality of the Fe-O(3)-P linkage (137°) which brings O(3) closer to O(1) than any other oxygen atom. However, the O(1)···H(1) - O(3) angles also deviate from 180°, reflecting an attempt to reach a compromise with the bonding requirements of O(1). The resultant H-O(1)-H bond angle, 101°, is close to the mean value of 109° documented for crystalline hydrates (Baur, 1972).

In contrast, the hydrogen atoms in the O(2) water molecule are directed toward the tetrahedral sheet. The H(25) atom participates in a single hydrogen

chemical group. However, a structural similarity between phosphorite and phosphonite (meta-tasmanite), based on X-ray powder data, has been suggested by Storre (1962) and subsequently confirmed by Moore (1966): the arrangement of PO$_4$ tetrahedrons and Zn atoms is such that sheets within the phosphorite structure are closely related in portions of the phosphonite framework.
**Table: Phosphophyllite interatomic distances and angles**

<table>
<thead>
<tr>
<th>Bond</th>
<th>D_{O-H} [Å]</th>
<th>D_{O-O} [Å]</th>
<th>D_{O-H}_\text{average} [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-H(1)</td>
<td>1.898 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(1)-H(2)</td>
<td>1.907 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(1)-H(3)</td>
<td>1.907 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(2)-H(1)</td>
<td>1.898 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(2)-H(2)</td>
<td>1.907 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(2)-H(3)</td>
<td>1.907 (2)</td>
<td>2.682 (2)</td>
<td></td>
</tr>
<tr>
<td>O(3)-H(1)</td>
<td>1.898 (2)</td>
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<td>2.682 (2)</td>
<td></td>
</tr>
</tbody>
</table>

**Note:**
- Values in parentheses are estimated.
- Standard deviations in parentheses.
- Hydrogen bond distances are calculated from the empirical curves of Brown and Shannon (1973).
- All distances are in Ångstroms (Å).

The table shows the interatomic distances and average bond lengths in phosphophyllite. The hydrogen bonds are indicated by the distances O-H and O-O, with the average bond lengths being calculated. The table also includes standard deviations for each bond length.

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The bond of normal dimension to O(5), the nearest oxygen to O(3), but the hydrogen bonding scheme for H(2) is more difficult to determine because O(6), O(14), and O(16) are all more or less equidistant from H(2), while O(5), O(11), and O(13) give approximately equal values of O(2)-H(2)-O(5). Moreover, all these distances are at the upper limit of the range of values observed for hydrogen bonds in other compounds (Brown, 1972). In addition, the balance of electrostatic bond strengths compared to the empirical curves of Brown and Shannon (1973). Including the contributions of the hydrogen bonds from all atoms except H(2), indicates that O(5), O(11), and O(13) are underbonded by a small amount, while O(6) is slightly overbonded. Therefore, conclude that the O(5) oxygen molecule is bonded only by the H(3) hydrogen bond, thereby explaining the relatively higher standard errors and thermal parameters obtained for this group, especially H(2), during least-squares refinement. In spite of this, however, the O(6) H(2)-O(6) angle is quite close to the expected value of 109°.

Although the symmetry of the FeO(2)(H2O) octahedron in phosphophyllite is significantly different from that of the FeO(2)(H2O) octahedron in lepidolite, the hydrogen bonding scheme proposed for the intermediate by Whittaker (1973) is essentially analogous to the one determined in the present study. Small differences in atomic coordinates between the two...
HILL STRUCTURE OF PHOSPHOBIFLUTE

structures have, however, stabilized a hydrogen bond between H(35) and O(3) in haptone, whereas the equivalent atom in phosphophyllite, H(2) and O(4), form no such association.

Acknowledgments

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The following material did not appear in the original publication.
Roderick J. Hill

Crystal structure of phospohyllite

Table 1. Observed (F₀) and calculated (Fc = [M̄ + BC]½) structure
factors (x10) for phospohyllite

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End of supplemental material.