The crystal structure of phosphophyllite

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Abstract

Phosphophyllite from Potosi, Bolivia, Zn₄(Fe,Mn)(PO₄)₂·4H₂O, is monoclinal and crystallizes in space group P2₁/a, with α = 10.97(1), b = 5.40(1), c = 10.55(2) Å, β = 111.1(2)°, and Z = 2. The structure has been solved by Patterson and Fourier methods from 1999 Zr-filtered MoKα data and refined by full-matrix least-squares (including the hydrogen atom) to R = 0.031 (Aₓ = 0.035). The framework consists of [Zn(PO₄)₆] octahedral sheets identical to those in hophase, intergrown with [FeO₆(H₂O)] octahedral sheets similar to those in parahopeline.

Introduction

Phosphophyllite from Hugendob, Bavaria, Zn₄(Fe,Mn)(PO₄)₂·4H₂O, was first described by Lavesmann and Stolte (1920), and 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 hopeline (Stolte, 1924; Wolfe, 1940; Gamidov et al., 1953; Lithaer, 1965; Kowshik et al., 1973), and parahopeline (Kumaraswami and Flinn, 1968; Charn, 1969). Although the topology of hopeline and parahopeline is now known with some degree of precision (Hill and Jones, 1976; Charn, 1969), the phosphophyllite structure has been determined from two-dimensional X-ray data only (Kleber et al., 1961), with the y coordinates estimated on the basis of interatomic distances within the inferred coordination polyhedra. Moreover, the framework determined by Kleber et al. contains a number of unusually short O···O non-bonded distances, and one distance which arises from the sharing of an edge between a ZnO₆ and a PO₄ tetrahedron. Based on an alternative interpretation of the published 000 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 least-squares (Meier and Villiger, 1969) and converged to a structure essentially identical, except in the vicinity of the octahedral sites, to that of hopeline. The present three-dimensional X-ray refinement was initiated in order to determine which of the above models pertains to phosphophyllite.

Experimental

A roughly equal-dimensional cleavage fragment of phosphophyllite from Potosí, Bolivia (crystal volume = 5.8 × 10⁴ cm³) was oriented with the c axis parallel to the a axis of a Picker FACS four-circle diffractometer. Detailed chemical, optical, and X-ray data for material from this locality have been reported by Hill (1976), unit-cell dimensions from that study have been included in the structure. X-ray intensity data for the structure analysis were collected at 25°C using Zr-filtered MoKα radiation (λ = 0.71070 Å) and a 2θ scan rate of 2° per minute. Backgrounds were determined from 10-second stationary counts at both ends of each dispersion-corrected (Alexander and Smith, 1964) scan range (minimum width = 2.4° in 2θ). A total of 6,885 reflections with Δθ ≤ 3° and F ≥ 0 were measured, using these 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 μ value of 70.2 cm⁻¹) effects. Symmetry-equivalent and multiply-measured reflections were averaged (by weight) to yield 2482 unique structure factors, each
with a standard deviation estimated from the equa-
tion \(\sigma = \sqrt{\sigma^2 + (0.037)^2 + (0.02)^2}\), where \(\sigma\) is the cor-
corrected standard deviation and \(\sigma^2\) is derived from counting 
and averaging statistics. Of these data only those
which showed the best correlation 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
solved Fourier syntheses. These atoms were redefined
by least-squares minimization of \(\sum (F_o - |F_c|^2)^2\),
where \(F_o\) and \(F_c\) are the observed and calculated
structure factors, and \(w = 1/\sigma^2\). Refinement with
isotropic temperature factors converged with a con-
ventional \(R\) value of 0.053. Refinement with anis-
tropic temperature factors and the inclusion of an
isotropic extinction parameter (\(P\), as defined and
scaled by Coppens and Hamilton (1970), further re-
duced \(R\) to 0.033.

A Fourier difference synthesis utilizing only those
data with \(|F_o|/\sigma < 0.4\ A^{-1}\) was computed, and peaks
ranging from 0.49 to 0.88 A\(^{-1}\) were found for the
four hydrogen atoms in the asymmetric unit. There
were also a small number of sites peaks with max-
imum density 1.38 A\(^{-1}\) (less than 10% of the mag-
itude of an O atom peak), but these were all located
well within the coordination spheres of Zn, Fe, and P,
and were interpreted as regions of charge deforma-
tion due to chemical bonding. Full matrix refine-
ment, including the H atom positional and isotropic
thermal parameters and using all 1999 reflections,
then proceeded smoothly to convergence (recom-
mended shifts in the final cycle were less than one
tenth of the appropriate \(\sigma\)). The final values of \(R\)
and \(\Delta R = 0.052\) and 0.015 respectively (0.048 and
0.038 for the entire data set of 2482 structure factors).

Scattering factors for Zn, Fe, P, and O (neutral atoms)
were obtained from International Tables for
Crystallography (1974) and were corrected for both
real and imaginary anomalous dispersion com-
ponents. For H, the spherical scattering factor sug-
gested by Stewart et al. (1965) was used. Programs
utilized for solution, refinement and geometry calcu-
lations were local modifications of Dama, Data-
sort, Fourier, Olex2, Olex3, and Ortep2.

Discussion of the structure

Phosphophyllite crystallizes with the topology dis-
played in Figure 1 and the bonding dimensions sum-
marized in Table 4. These results confirm the three-
dimensional framework proposed by Hill (1975) us-
ing the method of distance least-squares (mean values
of 2\(\Delta x, \Delta y, \Delta z\) for the two refinements are 0.06,
0.05, and 0.15 A respectively, although the two-
dimensional structure reported by Kiefer et al.
(1961) remains essentially intact (mean values for 2\(\Delta x\)
and 2\(\Delta z\) are 0.05 and 0.11 A).

In detail, the structure consists of puckered sheets of
corner-sharing tetrahedra of O atoms parallel to
(100), interleaved with sheets of face-sharing vacant
and occupied O octahedra. Zn and P are distributed
equally among the tetrahedral sites to produce a net-
work of three- and four-membered rings identical to
that in heulandite (Hill and Jones, 1970). Not unex-
pectedly, therefore, the deviations from ideal tetrahedron
shape within the layers are very similar in both min-
erals. The longer bonds from Zn and P to the trigonal-
ly coordinated O(3) atom, relative to other bonds
within each tetrahedron, correlate with the larger
sum of covalent bond strengths (Baur, 1970) and
with the amorphous valence angles (Louisian and Gibbons,
1921) associated with O(3) as a result of ring
formation.

The Fe atom occupies one-quarter of the available
sites in the octahedral sheet (the remaining sites are
vacant), giving rise to a fairly regular polyhedron
with mean bond lengths close to the value 2.17 A
expected for Fe\(^{3+}\) in octahedral coordination (Schan-
non and Prewitt, 1969). The O(1) atom of the PO,
group serves as the major link between the tetra-
headral and octahedral sheets. In phosphophyllite this
atom has a less relationship with respect to the other
(water) O atoms of the octahedron, consistent with the
centrosymmetry of the Fe site. In heulandite,
however, the (Zn) octahedron has mirror symme-

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1. The form of the anisotropic thermal ellipsoid is
defined by \(a = \beta = \gamma = 1\). The factors in the
second term are those for the P and Fe(1) atoms,
and the third term is for the Zn(2) atom.

2. To obtain a copy of any of the tables, send a
request to the Ring of the American Crystalline
Society, New York, N.Y., Washington, D.C. 20006. Prices not in stock. 2.00 for
a copy of the microfiche.

3. All programs are included in the World List of Crystallographic
Computer Programs (3rd ed., and supplements).
Table 2. Fractional atomic coordinates and temperature factor coefficients for phosphophyllite

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/a</th>
<th>z/a</th>
<th>x'</th>
<th>y'</th>
<th>z'</th>
<th>T (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.502 (1)</td>
<td>0.0196 (3)</td>
<td>0.490 (3)</td>
<td>0.492 (3)</td>
<td>0.19 (3)</td>
<td>0.49 (3)</td>
<td>0.49 (3)</td>
</tr>
<tr>
<td>P</td>
<td>0.6924 (6)</td>
<td>0.29079 (1)</td>
<td>0.4294 (4)</td>
<td>0.2854 (4)</td>
<td>0.321 (3)</td>
<td>0.47 (4)</td>
<td>0.32 (4)</td>
</tr>
<tr>
<td>O1</td>
<td>0.64 (2)</td>
<td>0.2955 (2)</td>
<td>0.397 (2)</td>
<td>0.286 (2)</td>
<td>0.319 (2)</td>
<td>0.42 (2)</td>
<td>0.31 (2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.102 (2)</td>
<td>0.2979 (2)</td>
<td>0.359 (2)</td>
<td>0.278 (2)</td>
<td>0.305 (2)</td>
<td>0.41 (2)</td>
<td>0.33 (2)</td>
</tr>
<tr>
<td>O3</td>
<td>0.555 (2)</td>
<td>0.2821 (2)</td>
<td>0.330 (2)</td>
<td>0.263 (2)</td>
<td>0.314 (2)</td>
<td>0.39 (2)</td>
<td>0.39 (2)</td>
</tr>
</tbody>
</table>

* The final, H atoms were included in the calculation.

Table 3. Magnitudes of bond angles and interatomic distances in phosphophyllite.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bond angles (°)</th>
<th>Interatomic distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O1</td>
<td>102.56 (3)</td>
<td>2.02 (3)</td>
</tr>
<tr>
<td>Fe-O2</td>
<td>102.56 (3)</td>
<td>2.02 (3)</td>
</tr>
<tr>
<td>Fe-O3</td>
<td>102.56 (3)</td>
<td>2.02 (3)</td>
</tr>
</tbody>
</table>

* The bond angles and distances are given for each bond.

The structure of phosphophyllite is unique within this family of minerals.
chemical group. However, a structural similarity between phosphophyllite and phosphosiderite (magnetite), based on X-ray powder data, has been suggested by Strons (1932) and subsequently confirmed by Moore (1966): the arrangement of PO₄ tetrahedra and Zn atoms is such that subcels within the phosphophyllite structure are closely related to portions of the phosphosiderite framework.

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, 0.96 Å, and are about 0.3 Å shorter than the corresponding average distance measured by neutron diffraction (Baer, 1977). Similar shifts in the apparent X-ray hydrogen position toward the atom to which it is bonded have been documented by a large number of workers (Shrews et al., 1965; Hume, 1968; Hansen et al., 1971; Coppena, 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. displacements (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(2) across one of the vacant octahedra within the octahedral sheet. This configuration appears to be controlled by the linearity of the Fe-O(3)-F linkage (132°) which brings O(3) closer to O(1) than any other oxygen atom. However, the O(1)-H(1) -- O(3) angle also deviates from 109°, reflecting an attempt to relax a compromise with the bonding requirements of O(1). The resultant H(1)-O(1)-H bond angle, 104°, is close to the atom value of 106° documented for crystalline hydrides (Baer, 1971).

In contrast, the hydrogen atoms in the O(2) water molecule are directed toward the octahedral sheet. The H(25) atom participates in a single hydrogen
### HILL STRUCTURE OF PHOSPHOSILICITE

#### Table 4. Phosphosilicite interatomic distances and angles*

<table>
<thead>
<tr>
<th>Interatomic Distance (Å)</th>
<th>Interatomic Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P1_{O1}-O_{2}P_2)</td>
<td>(P1_{O1}-O_{2}P_2)</td>
</tr>
<tr>
<td>(P1_{O1}-O_{2}P_2)</td>
<td>(O_{2}P_2-O_{2}P_2)</td>
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<td>(O_{2}P_2-O_{2}P_2)</td>
<td>(O_{2}P_2-O_{2}P_2)</td>
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<tr>
<td>(O_{2}P_2-O_{2}P_2)</td>
<td>(O_{2}P_2-O_{2}P_2)</td>
</tr>
</tbody>
</table>

* Distances and angles are approximate and subject to error. Radii and temperatures are in terms of the best crystallographic settings.

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bond of normal dimension to O(2), the nearest oxygen to O(3), but the hydrogen bonding scheme for H(2) is more difficult to determine. O(6), O(1) and O(2) are all more or less equivalent from H(2), while O(3), O(1) and O(4) give approximately equal values of O(2) - O(3). Moreover, all these distances are at the upper limit of the range of values observed for hydrogen bonds in other compounds (Baur, 1972). In addition, the balance of electrostatic bond strengths is reflected in the empirical curves of Brown and Shannon (1973), including the contributions of the hydrogen bonds from all atoms except H(2), indicating that O(3), O(4) and O(5) are undercoordinated by a small amount, while O(6) is slightly overcoordinated. Therefore, it can be concluded that the O(2) water molecule is stabilized primarily by the H(2) 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 H(2)-O(2)-H(2) angle is quite close to the expected value of 109°.

Although the symmetry of the \(\text{PO}_{4}/\text{H}_{2}\text{O}\) octahedron in phosphosilicate is significantly different from that of the \(\text{ZnO}_{4}\text{SiO}_{4}\) octahedron in harnelite, the hydrogen bonding scheme proposed for the latter mineral by Whitaker (1975) is essentially analogous to the one determined in the present study. Small differences in atomic coordinates between the two
HILL STRUCTURE OF PHOSPHOMOLYBDITE

structures have, however, stabilized a hydrogen bond between \( H(35) \) and \( O(5) \) in hepatitis, whereas the equivalent atoms in phosphophyllite, \( H(2) \) and \( O(4) \), form no such association.

Acknowledgments

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References


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

Crystal structure of phospophyllite

Table 1. Observed (Po) and calculated (Fe = [AlO] + [Co2+]) structure factors (x10) for phosphophyllite

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End of supplemental material.