THE CRYSTAL STRUCTURE OF HETEROSITE[1]

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ABSTRACT

The crystal structure of heterosite of composition $(Fe_{0.65}^{3+}Mn_{0.35}^{3+})PO_4$ has been refined. The Fe, Mn atoms occupy the Fe, Mn sites of the primary triphylite structure, the equivalent Li site being vacant. Two opposite (Fe, Mn)—O bonds of the $(Fe, Mn)O_6$ polyhedron are unusually short. Distortions in this polyhedron, resembling those of the $Mn^{3+}O_6$ polyhedron of piemontite, are interpreted as being due to local charge imbalances. These effects occur with either Fe^{3+} or Mn^{3+} occupying this site, and there should therefore be relatively complete solid solution involving these cations.

INTRODUCTION

Members of the solid-solution series triphylite-lithiophilite, $Li(Fe^{2+}, Mn^{2+})PO_4$, undergo alteration, generally first with oxidation of Fe^{2+} to Fe^{3+} and then to Mn^{2+} to Mn^{3+}, with simultaneous leaching of Li to maintain charge balance. The minerals produced in this step-wise fashion are ferrisicklerite-sicklerite, $Li_{1-x}(Fe_x^{3+} Mn_{1-x}^{2+})PO_4$ and heterosite-purpurite, $(Fe^{3+}, Mn^{3+})PO_4$. The structure of triphylite was refined by Finger and Rapp (1970) and that of lithiophilite by Geller and Durand (1960). These phases are isotypic with olivine. Björling and Westgren (1938) determined approximate atom coordinates for heterosite. They showed that, except for loss of Li, this structure is isotypic with that of triphylite, from which it is derived.

Oxidation of Mn^{2+} to Mn^{3+} should give rise to a Jahn-Teller distortion of the octahedron coordinating Mn. Although the site symmetry for this cation (m, with one principal octahedron axis coplanar) is relatively unusual, it is consistent with the usual Jahn-Teller distortion consisting of the relative lengthening of two opposing Mn^{3+}—O bonds. The $Fe^{3+}O_6$ octahedron would not be expected to show Jahn-Teller distortions, and domain structures involving ordering of Fe^{3+} and Mn^{3+} are a possibility. Indeed, Moore (oral comm.) notes that he has observed two phases of slightly differing lattice parameters in a

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sample of heterosite. We therefore have undertaken a refinement of the heterosite structure in order to determine, in part, the nature of the polyhedron geometry produced during the oxidation and leaching process.

<center>EXPERIMENTAL</center>

This study was carried out on a specimen collected by one of us (D.R.P.) from the Fletcher Quarry, North Groton, New Hampshire. The material was chosen because the primary, unaltered triphylite from this locality was known to be relatively rich in Mn. X-ray fluorescence analysis of material from the same sample used in diffraction studies gave a ratio Mn:Fe of 35:65. Physical properties were consistent with complete leaching and oxidation of Mn and Fe to the trivalent state. For example, lattice parameters ($a = 5.83 \pm .01$, $b = 9.79 \pm .01$, $c = 4.769 \pm .005$ Å) were consistent with those of heterosite, as determined by Björling and Westgren for both oxidized and unoxidized material. Structure analysis subsequently confirmed the lack of Li. The formula is therefore $(Fe_{0.65}{}^{3+}Mn_{0.35}{}^{3+})PO_4$. Weissenberg and precession photographs gave results consistent with space group $Pmnb$. The lattice paramaters were determined by least-squares refinement of Debye-Scherrer data which was obtained using MnKα radiation with a 114.6 mm diameter camera. A single overall error function proportional to $\cos^2 \theta$ was refined.

Intensity data were measured using a Supper-Pace automated diffractometer, employing MoKα radiation, pulse-height analysis with a scintillation counter, and a flat-crystal graphite monochromator. The heterosite crystal measured approximately $0.14 \times 0.06 \times 0.06$ mm. All data were corrected for Lorentz-polarization (corrected for a monochromator factor) and absorption factors ($\mu = 51.0$ cm^{-1}). The corrected set of data consisted of 343 symmetry independent structure amplitudes.

Full-matrix least-squares refinement of fractional coordinates as given by Björling and Westgren (1938) resulted in a decrease of the R-factor to only 34 percent. The starting coordinates had been only approximately determined, and there was thus a possibility that at least one of them was so inaccurate as to interfere with convergence to the correct parameters. Since the general shifts in coordinates had been toward those given by Geller and Durand (1960) for lithiophilite, these values were substituted. Refinement of coordinates and isotropic temperature factors resulted in convergence with $R = 5.6$ percent. An electron-density synthesis, ρ (xyz), verified that the site at 000 (the Li site of the parent, primary phase) was indeed vacant, thus confirming that Mn and Fe are both in the trivalent state as required for charge balance. Refinement of the form-factor scale factors was consistent with the relative proportion of Mn and Fe as given by X-ray fluoresence analysis. Refinement of anistropic temperature factors resulted in a final R-factor of 5.0 percent. Structure factors are listed in Table 1[1] and refined structure parameters in Table 2.

DISCUSSION OF THE STRUCTURE

Bond lengths and angles are listed in Tables 3 and 4, with standard errors as calculated with the final least-squares variance-covariance matrix and lattice parameter standard errors. A portion of the structure is shown projected down the c-axis in Figure 1. The basic features of the structure are as given by Bjorling and Westgren. It is derived from the parent phase triphylite, which is isotypic with olivine, through leaching of the Li from the $M(1)$ sites, and oxidation of Mn^{2+} and Fe^{2+} to Mn^{3+} and Fe^{3+} on the $M(2)$ sites. The $M(2)$ octahedra share $O(3)$ vertices to form walls parallel to (010) which are knit together in three dimensions by P tetrahedra through vertex and edge-sharing.

The detailed coordination geometry can readily be explained in terms of charge balance relations. The PO_4 tetrahedron shares one edge with the $(Fe, Mn)O_6$ octahedron, as shown in Figure 1, and this edge length (2.38 Å) is considerably less than the average of six for the tetrahedron (2.51 Å) and twelve for the octahedron (2.78 Å). In triphylite and other olivine-type structures, where three coplanar tetrahedron edges are shared, all three edges are shortened. The P—O distances show the effect of a considerable charge imbalance. $O(1)$ and $O(2)$ have bond strengths of only 1.75, whereas the value for $O(3)$ is 2.25. The P—$O(1)$ and P—$O(2)$ bond lengths of 1.519 and

TABLE 2   FRACTIONAL COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS.
STANDARD ERRORS IN PARENTHESES.

Atom	O(1)	O(2)	O(3)	Fe,Mn	P
x	1/4	1/4	.0461(6)	1/4	1/4
y	.1176(5)	.4417(5)	.1684(3)	.2770(1)	.0935(1)
z	.7131(11)	.1614(11)	.2513(6)	.9449(2)	.3983(4)
β_{11}	.0072(13)	.0068(1)	.0049(8)	.0035(3)	.0038(4)
β_{22}	.0020(5)	.0026(5)	.0019(3)	.0008(1)	.0009(1)
β_{33}	.0072(20)	.0046(1)	.0040(12)	.0047(4)	.0020(6)
β_{12}	0	0	.0010(3)	0	0
β_{13}	0	0	-.0004(8)	0	0
β_{23}	.0015(7)	.0018(8)	-.0003(4)	-.0007(1)	.0001(2)

TABLE 3   CATION-ANION INTERATOMIC DISTANCES FOR
HETEROSITE (THIS STUDY), TRIPHYLITE
(FINGER AND RAPP, 1970), AND PIEMONTITE
(DOLLASE, 1969)

	heterosite	triphylite	piemontite
P-O(1)	1.519 (8) Å	1.535	
O(2)	1.513 (7)	1.536	
2O(3)	1.563 (4)	1.553	
average	1.540	1.544	
(Fe,Mn)-O(1)	1.912 (6)	2.205	M(3)-O(8) 1.861
O(2)	1.914 (6)	2.110	O(4) 1.900
2O(3)	2.030 (4)	2.081	2O(2) 2.031
2O(3)	2.163 (4)	2.251	2O(1) 2.274
average	2.035	2.163	2.062

1.513 Å, respectively, are thus markedly shorter than those for O(3), 1.563 Å. In triphylite, where the corresponding bond strengths are 1.92 and 2.08 respectively, the difference in P—O bond lengths is only 0.018 Å. The difference in geometry of the PO_4 tetrahedra of these two structures is thus clearly due to changes in charge balance resulting from the leaching and oxidation process.

The (Fe, Mn)O_6 polyhedron is a severely distorted octahedron, as

TABLE 4   O-O DISTANCES AND O-CATION-O
INTERATOMIC ANGLES IN HETEROSITE

P tetrahedron

O(1)-O(2)	2.480 (10) Å	109.8 (3)°
2O(1)-O(3)	2.551 (7)	111.7 (2)
2O(2)-O(3)	2.551 (7)	112.1 (2)
O(3)-O(3)	2.377 (8)	99.0 (3)
average	2.510	

Fe,Mn polyhedron

2O(1)-O(3)	2.720 (6)	87.2 (2)
2O(1)-O(3)	2.872 (8)	89.4 (3)
2O(2)-O(3)	2.958 (8)	92.8 (3)
2O(2)-O(3)	2.823 (7)	91.4 (2)
2O(3)-O(3)	2.919 (6)	88.2 (3)
O(3)-O(3)	2.377 (8)	66.7 (3)
O(3)-O(3)	3.455 (9)	116.6 (3)
average	2.868	

reflected in the differences in distances to O(1) and O(2) (1.91 Å), and those to the four O(3) atoms (2.03 and 2.16 Å). Since O(1), Fe, Mn, and O(2) lie approximately on an axis, the polyhedron has the approximate form of an octahedron flattened along a principal axis. As with the PO_4 tetrahedron, the differences in bond lengths are clearly due to the degree of undersaturation of bond strength to O(1) and O(2), relative to the oversaturation to O(3). As shown in Table 3, the relative differences between (Fe, Mn)—O distances in triphylite are dissimilar to those in heterosite. It thus appears that during the oxidation and leaching of triphylite, there is a gradual and continuous change in the average geometry of the (Fe, Mn)O_6 octahedron in re-
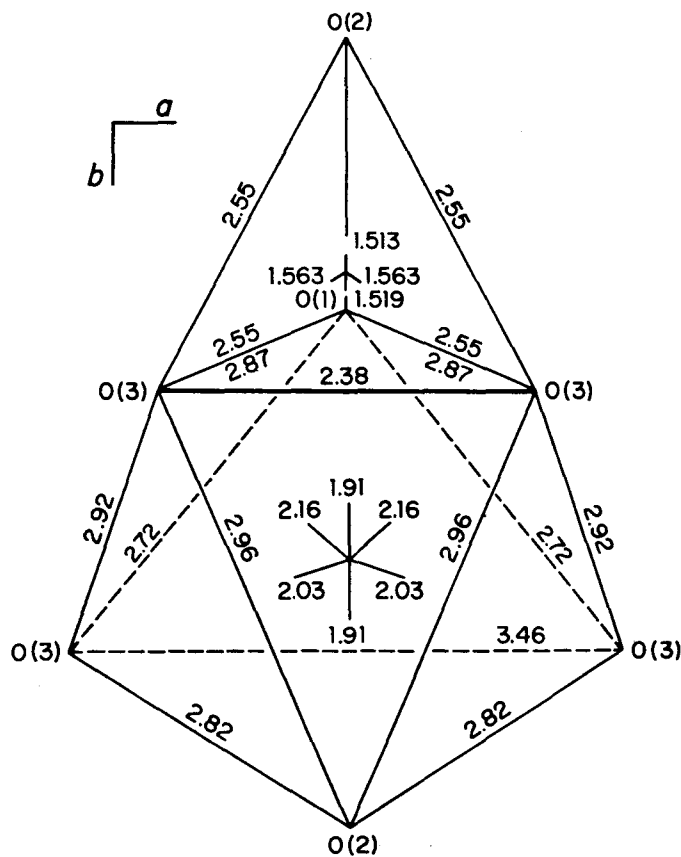

Fig. 1. Edge-sharing PO_4 tetrahedron and (Fe, Mn) O_6 octahedron, with cation-oxygen and oxygen-oxygen interatomic distances (Å). The shared edge is of length 2.38 Å.

sponse to charge redistribution. Hence the degree of polyhedron distortion is, to a first approximation, independent of whether the $M(2)$ site is occupied by Mn^{3+} of Fe^{3+}, except for small differences in ionic radii. A relatively complete solid solution series could therefore exist between Mn^{3+} and Fe^{3+}.

The octahedral coordination polyhedron of Mn^{3+} is usually subject to a Jahn-Teller distortion consisting of a lengthening of two opposing Mn—O bonds, relative to four shorter, coplanar bonds. The opposite bond contractions found in the $(Fe, Mn)O_6$ polyhedron in heterosite is unusual. Strens (1966) has proposed that the opposite bond contraction is more likely to occur when the bond type is highly ionic, while increasing covalency favors elongation. There is an interesting corollary between the coordination of Fe, Mn in heterosite and the $M(3)$ site of piemontite. Burns and Strens (1967) showed that Mn^{3+} substitutes in this site, rather than in $M(1)$ and $M(2)$, as a result of the pronounced distortion in the coordination polyhedron. Dollase (1969) refined the crystal structure of piemontite and confirmed that Mn^{3+} occupies this site (with Al and Fe). He showed that the $M(1)$ and $M(2)$ coordination octahedra are relatively undistorted, and confirmed the distortion for the $M(3)$ site. The site symmetry (m) for $M(3)$ is the same as that of the Fe, Mn site of heterosite, and the polyhedron distortion, as reflected in cation-oxygen distances (Table 3), is surprisingly similar. In addition, Dollase (1968) showed that for the piemontite-type structures, there are significant deviations in charge balance for the anions coordinating $M(3)$. These deviations are similar to those for the oxygen atoms coordinating Fe, Mn of heterosite. The basic cause of the unusual coordinations of the sites occupied by Mn^{3+} in both heterosite and piemontite are therefore similar. Although Mn^{3+} is relatively stabilized with either contraction or elongation of opposing Mn—O bonds, the more common elongation is precluded by charge balance requirements.

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