

The crystal structure of thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2^1$

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Abstract

Thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2$, is orthorhombic, space group $C222_1$, $a = 6.412(3)$, $b = 13.563(8)$, $c = 8.545(5)\text{\AA}$, with $Z = 4$. The crystal structure has been determined with direct methods and refined to a conventional R-value of 3.2% for all reflections. There are three cation coordination polyhedra, $[\text{MO}_4(\text{OH})_2]^{-8}$, with the cation compositions: $\text{M}(1) = \text{Mg}$; $\text{M}(2) = \text{Ca}_{0.95}\text{Mn}_{0.05}$; $\text{M}(3) = \text{Mg}_{0.59}\text{Fe}_{0.29}\text{Mn}_{0.12}$. The structure is comprised of three basic features: helical chains of $\text{M}(3)$ octahedra parallel to c ; slightly distorted chains composed of alternating $\text{M}(1)$ and $\text{M}(2)$ octahedra parallel to a ; and insular phosphate tetrahedra, which crosslink the $\text{M}(3)$ chains to form a network of channels parallel to a into which the $\text{M}(1)$ - $\text{M}(2)$ chains fit. Thadeuite shows only limited structural similarity to other phosphates of related composition, or to those with which it is associated.

Introduction

Thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2$, was originally described by Isaacs *et al.* (1979) as occurring in phosphate-rich zones in selvages of hydrothermal tin-tungsten veins in the Panasqueira mining district of central Portugal. As originally reported, thadeuite is intergrown with a previously unreported phase, the OH-equivalent of isokite. This material has subsequently been determined to be a new mineral, panasqueiraite, $[\text{CaMgPO}_4(\text{OH},\text{F})]$, described by Isaacs and Peacor (1981). In addition to panasqueiraite, thadeuite is associated with the phosphates fluorapatite, wolfeite and althausite. Thadeuite, wolfeite, panasqueiraite and althausite all have the same general formula type, $\text{M}_2\text{PO}_4(\text{F},\text{OH})$, where the M sites are filled by divalent cations which commonly have octahedral coordination. The structures of each of these minerals associated with thadeuite, discussed in a later section, show only limited similarity to each other. It is unusual for so many compounds to coexist which have the same formula type based on similar cations and yet have diverse structures. We there-

fore initiated an analysis of the thadeuite crystal structure, in order to define its chemical and structural relations to the associated phases.

Experimental procedure

As reported by Isaacs *et al.* (1979), thadeuite is orthorhombic with space group $C222_1$, as determined by a combination of precession and Weissenberg methods. Unit cell parameters, determined by least-squares refinement of 30 reflections obtained by powder diffraction, are $a = 6.412(3)$, $b = 13.563(8)$, $c = 8.545(5)\text{\AA}$, with $Z = 4$. Powder diffraction data are tabulated in Isaacs *et al.* (1979).

Intensity data were obtained using a cleavage fragment measuring approximately $0.30 \times 0.34 \times 0.38$ mm, mounted for rotation about the b -axis of a Weissenberg-geometry diffractometer. $\text{MoK}\alpha$ radiation, monochromated with a flat graphite crystal and detected with a scintillation counter, was used with a Supper-Pace automated diffractometer system, employing a scan across each reflection with background measured on each side. The intensities of 591 reflections were measured, of which only four had intensities below minimum observable values, up to a $\sin\theta$ limit of 0.50 and a k -index limit of 17. All intensities were corrected for Lorentz-Polarization and absorption effects $[\mu(\text{MoK}\alpha) = 38.0 \text{ cm}^{-1}]$. A modified version of the program

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ABSRP written by C. W. Burnham was used for the intensity data corrections. Failure by the tape output unit of the system caused data with $k = 16$ to be eliminated from the output; these data were not remeasured.

Structure refinement

The initial characteristics of the structure were determined by direct methods using the program MULTAN (Main *et al.*, 1971) which readily gave a refinable solution. The $N(z)$ test provided by this program confirmed the non-centrosymmetric nature of the structure. The atomic parameters were refined by least-squares utilizing the program RFINE2 (Finger and Prince, 1975), employing scattering factors of Doyle and Turner (1968) and the weighting scheme of Cruickshank (1965). The results of MULTAN suggested approximate positions for four heavy atoms, presumably cations, and these were all initially set as phosphorus for structure factor calculation purposes since P is of average electron density for the cations in thadeuite. Refinement of only the scale factor and cation positions gave a conventional R-value of 34%. An electron-density function calculated at this stage led to the identification of five additional and apparently anionic sites. Choosing four of the anionic sites, which were arranged tetrahedrally about a cation, to be a $(\text{PO}_4)^{-3}$ unit, the only remaining anion was designated as F for the site (OH,F), and the refinement of all atom positions, 4P, 4O and 1F yielded an R-value of 20%. The refinement converged rapidly with determination of cation occupancies through variation of site occupancies and refinement of coordinates and isotropic temperature factors. Final cycles using anisotropic temperature factors yielded an R-value of 3.2% for all reflections and 2.8% for unrejected reflections, with unobserved reflections and those having individual $R > 0.5$ rejected. The calculated and observed structure factors are listed in Table 1.³ Atomic coordinates and anisotropic temperature factors are listed in Tables 2 and 3, respectively. Selected interatomic distances as calculated using the program ORFFE (Busing *et al.*, 1964) are listed in Table 4. The standard errors given in Table 4 were calculated using standard errors of the unit cell parameters and

Table 2. Atomic coordinates for thadeuite

ATOM	EQUIPOINT		X	Y	Z
	RANK	NOTATION			
P	8	c	.1618(2) ^a	.3382(1)	.0459(1)
M(1)	4	b	0	.1460(1)	1/4
M(2)	4	b	1/2	.0361(1)	1/4
M(3)	8	c	.3541(1)	.3840(1)	.4043(1)
O(1)	8	c	.1199(5)	.2281(2)	.0687(3)
O(2)	8	c	.3328(5)	.3735(3)	.1585(4)
O(3)	8	c	.2733(5)	.1431(2)	.3764(3)
O(4)	8	c	.0347(5)	.3996(2)	.4224(3)
OH	8	c	.1489(4)	.0385(2)	.1322(3)

^aStandard errors in parentheses.

the variance-covariance matrix from the final cycle of refinement.

Description of the structure

Cation ordering

The ordering of cations on the three octahedral sites, M(1), M(2) and M(3), was determined by the following steps. Based on the average chemical analysis for thadeuite (Isaacs *et al.*, 1979), there are approximately 8.8 Mg, 3.8 Ca, 2.2 Fe, and 1.2 Mn atoms per unit cell. Results at early stages of the refinement revealed that coordination polyhedra for

Table 3. Anisotropic temperature factors for thadeuite

ATOM	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	25(2) ^a	11(0)	24(1)	0(1)	3(1)	1(1)
M(1)	11(3)	11(1)	16(2)	0	2(2)	0
M(2)	40(2)	12(1)	40(1)	0	1(1)	0
M(3)	28(2)	16(1)	28(1)	2(1)	1(1)	4(1)
O(1)	74(7)	13(1)	43(4)	2(2)	4(4)	1(2)
O(2)	34(5)	26(2)	41(4)	-4(3)	-8(4)	-6(2)
O(3)	56(6)	22(2)	28(3)	0(2)	-18(4)	-8(2)
O(4)	50(6)	16(1)	38(4)	-3(2)	2(4)	4(2)
OH	63(5)	15(1)	31(2)	5(2)	3(3)	5(1)

^aStandard errors in parentheses; all values are $\times 10^4$

³To obtain a copy of Table 1, order Document AM-82-186 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 4. Interatomic distances for thadeuite

P TETRAHEDRON			M(2) OCTAHEDRON		
P	0(1)	1.531(3) ^a	M(2)	20(3)	2.320(3)
	0(2)	1.536(3)		20(4)	2.377(3)
	0(3)	1.528(3)		20H	2.466(2)
	0(4)	1.535(3)			
0(1)	0(2)	2.520(4)	0(3)	0(3)	3.621(6)
	0(3)	2.495(4)		20(4)	3.725(4)
	0(4)	2.530(4)		20H	2.645(4)
				20H	3.057(4)
0(2)	0(3)	2.516(4)	0(4)	0(4)	3.760(4)
	0(4)	2.482(4)		20H	3.978(4)
0(3)	0(4)	2.470(4)		20H	2.808(4)
M(1) OCTAHEDRON			M(3) OCTAHEDRON		
M(1)	20(1)	2.056(3)	M(3)	0(1)	2.076(3)
	20(3)	2.059(3)		0(2)	2.082(3)
	20H	2.012(3)		0(2)	2.109(3)
0(1)	0(1)	3.458(6)		0(4)	2.064(3)
	20(3)	3.034(4)		OH	2.119(3)
	20(3)	2.811(5)		OH	2.213(3)
	20H	2.634(4)	0(1)	0(2)	3.009(4)
0(3)	20H	2.645(4)		0(2)	3.779(4)
	20H	3.057(4)		0(4)	3.076(4)
				OH	2.634(4)
OH	OH	2.775(5)	0(2)	0(2)	2.653(6)
				OH	3.028(4)
				OH	3.421(4)
			0(2)	0(4)	2.977(4)
				OH	2.866(4)
			0(4)	OH	2.808(4)
				OH	2.834(4)
			OH	OH	2.489(4)

^aStandard errors in parentheses.

M(1) and M(3) are similar with average M–O and M–(OH) distances of 2.04 Å for M(1) and 2.11 Å for M(3), while M(2) was larger, with distances averaging approximately 2.39 Å. It was therefore assumed that all of the Ca (3.8 atoms per cell) would preferentially be ordered on the M(2) site, with the minor deficiency compensated for by 0.2 Mn, since that element generally substitutes for Ca more readily than do Mg or Fe. The occupancies of M(1) and M(3) were determined by allowing the scattering factors for the two sites to vary between those of Mg and Fe, with the remaining Mn accommodated by the scattering factor for Fe, since the scattering factors for Mn and Fe are similar. The results indicated that, within error, only Mg occupies M(1), and that M(3) has occupancy factors 0.59(2) for Mg and 0.41(2) for Fe + Mn. The slightly larger M(3) site is therefore occupied by all of the Fe, that Mn which remains after filling M(2) and the Mg not used in filling M(1), and has the composition

Mg_{4.7}Fe_{2.3}Mn_{1.0}. The assignments result in values of cations per unit cell of 8.7 for Mg, 3.8 for Ca, 2.3 for Fe and 1.2 for Mn, in excellent agreement with the composition as determined by electron microprobe analysis. The values of the M–(O,OH) distances (Table 4) are consistent with this ordering scheme and thus confirm it.

Linkage of the polyhedra

A diagram of the crystal structure of thadeuite is given in Figure 1. There are three large octahedral sites, M(1), M(2), and M(3), on which Mg, Ca, and Mg respectively, are ordered as the principle constituents as described above. Each of the octahedra are defined by two OH ions and four O atoms. The three basic elements of structure which combine to form the full crystal structure of thadeuite are:

- helical chains of M(3) octahedra parallel to *c*;
- slightly distorted chains comprised of alternating M(1) and M(2) octahedra parallel to *a*;
- insular phosphate tetrahedra, which cross-link the M(3) chains to form a network of channels parallel to *a* into which the M(1)–M(2) chains fit.

The observed perfect {010} cleavage leaves both the M(1)–M(2) and the M(3) chains intact.

The M(1)–M(2) chains are formed by sharing of the edge O(3)–OH between the two polyhedral types. Adjacent polyhedra are offset in the *b*-axis direction, as shown in Figure 2. The M(3) chains are formed by edge-sharing between adjacent polyhedra of the same type, with the shared edge alternating between O(2)–O(2) and OH–OH along a given chain. The helical offset between adjacent polyhedra in the *c*-direction is in a clockwise sense if viewed from +*c* (Figure 3). Each phosphate tetrahedron links three separate M(3) chains using three of its vertices, and also is linked to three individual M(1)–M(2) chains, also using three vertices. The (PO₄) group shares its vertices with the other polyhedra in a regular manner:

- O(1) is shared with M(1) and M(3) octahedra;
- O(2) is one end of a shared edge between two M(3) octahedra;
- O(3) is also part of a chain-forming shared edge, here between M(1) and M(2) octahedra;
- O(4) is shared with M(2) and M(3) octahedra.

It can be seen from this that the two chain types, M(1)–M(2) and M(3), are linked together at two points, O(1) and O(4), by sharing vertices with a PO₄ group. In addition, the two types of polyhedral chains are linked together at the OH sites, the only anionic group not bonded to P. Each OH is shared

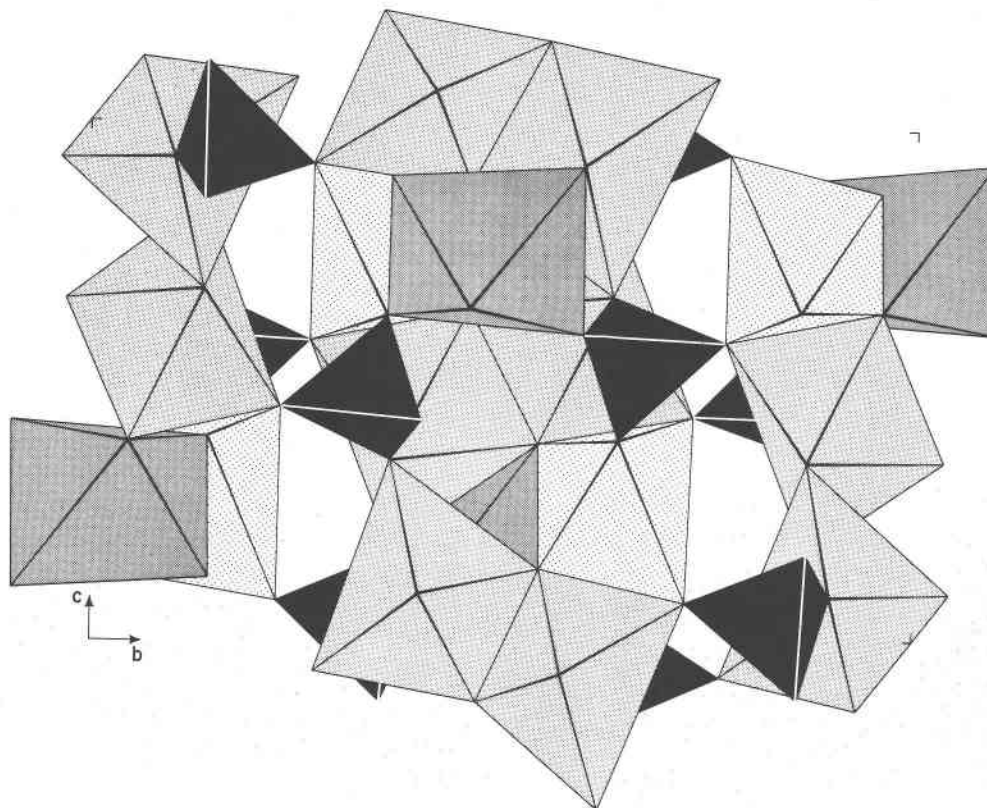


Fig. 1. The crystal structure of thadeuite viewed along a . Black = (PO_4) , stippled = M(1), dark shaded = M(2), light shaded = M(3).

by an M(1), an M(2) and an M(3) octahedron, and from the OH extend three shared edges between polyhedra: an M(1)–M(2) edge, an M(2)–M(3) edge and an M(3)–M(1) edge. In this way, two more complex “hybrid” types of polyhedral chains are formed, M(1)–M(3) and M(2)–M(3). The first type of hybrid is formed by edge sharing along OH–O(1) between M(1) and M(3), yielding a chain of the type [M(1)–M(3)–M(3). . .]. The shared edge is an equatorial edge if viewed from $+a$, and the hybrid chain is parallel to c overall, but zig-zags in the $+a$ direction. The second type of hybrid is formed by edge-sharing along OH–O(4) between M(2) and M(3) producing a chain of the type [M(2)–M(3)–M(3). . .]. This hybrid is also parallel to c , but zig-zags in a more complex fashion.

Related structures

Thadeuite belongs to a group of minerals with the general formula $\text{M}_2(\text{XO}_4)\text{Z}$, with M a divalent cation, X = P or As, and with Z = OH and/or F. The most recent overview of the five major structure

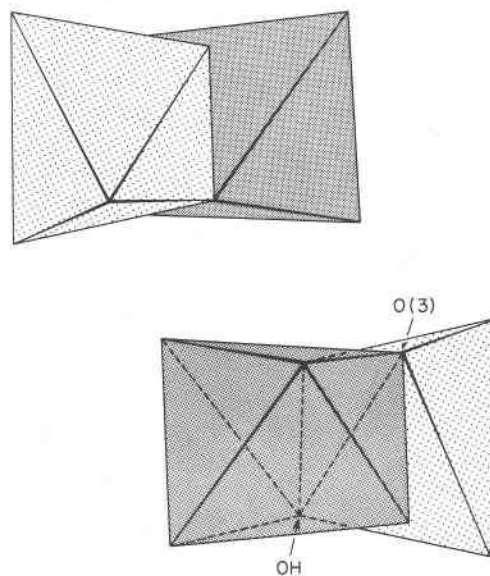


Fig. 2. The M(1)–M(2) chains viewed along a ; one of the M(2) octahedra is transparent to illustrate the shared edge O(3)–OH. Orientation and shading is identical with that in Figure 1.

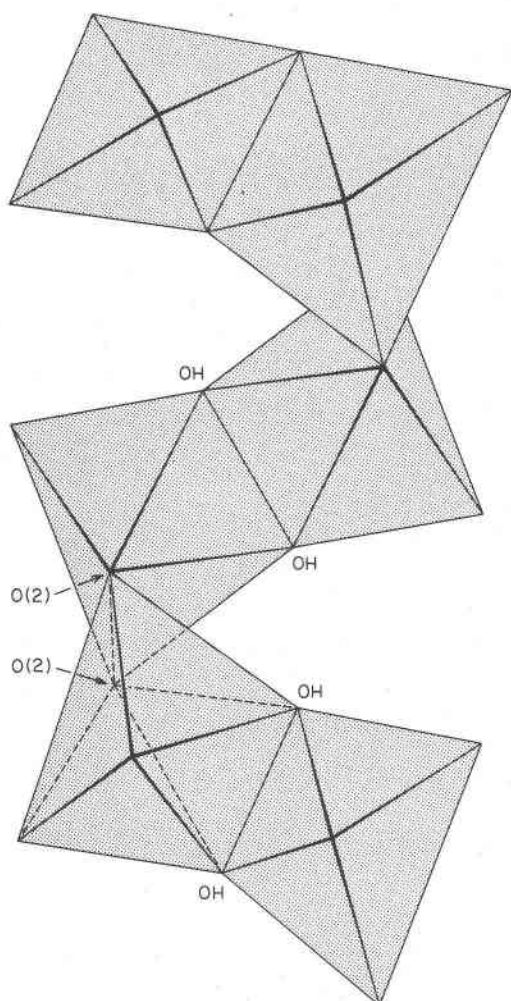


Fig. 3. An $M(3)$ chain viewed along a ; one of the octahedra is transparent to illustrate the alternating shared edges $O(2)-O(2)$ and $OH-OH$. Orientation and shading is identical with that in Figure 1.

types represented by this class of minerals is that of Rømming and Raade (1980). The thadeuite structure bears little resemblance to structures reported for this group, or to those of the three chemically similar phosphates with which thadeuite is associated (panasqueiraite, wolfeite and althausite) even though some species have similar lattice parameters. Panasqueiraite, $CaMgPO_4(OH,F)$, space group $C2/c$, is believed to be isostructural with isokite (Isaacs and Peacor, 1981) which is isostructural with titanite (Povarennykh, 1972). The panasqueiraite structure, by analogy with the titanite structure (Zachariasen, 1930), is dominated by chains of vertex-sharing MgO_6 octahedra parallel to a 6.5\AA translation (a). While the $M(1)-M(2)$ chains

in thadeuite are parallel to a 6.4\AA translation, these two octahedra of quite different size are linked by edge-sharing, not vertex sharing. Wolfeite, $(Fe,Mn)_2PO_4(OH)$, described by Waldrop (1970), has space group $P2_1/a$, with its large cations divided between two types of sites, highly distorted trigonal bipyramids and octahedra. Linkage of polyhedra in wolfeite forms chains parallel to the 12.37\AA (a) and the 13.28\AA (b) translation by alternating between a shared edge and a shared vertex along the chains, a form of polyhedral linkage quite different from that observed in thadeuite. Althausite, $Mg_4(PO_4)_2(OH,O)(F,\square)$, space group $Pnma$, also has highly distorted M^V and M^{VI} sites, the latter forming chains by edge-sharing parallel to the 6.05\AA translation (b) (Rømming and Raade, 1980).

The observed lack of Ca in the wolfeite (<0.1% by weight) and the lack of Fe or Mn in the panasqueiraite (<0.5% by weight) (Isaacs and Peacor, 1981) associated with thadeuite is consistent with the disparate structure types coexisting in the phosphate assemblage. Thadeuite, with one large and two small octahedral sites, can accept Mg and Ca, but wolfeite and althausite, with distorted trigonal bipyramids and octahedra, accept only trace amounts of Ca into their structures. The panasqueiraite in turn hosts Ca in a seven-fold site and Mg in a relatively small octahedrally coordinated site, but contains only trace amounts of Fe^{2+} or Mn^{2+} , which are ions of intermediate size. Thadeuite like panasqueiraite primarily accepts Mg and Ca, ordered on different sites. None of these structures are apparently able to accept large amounts of all of the cations present. It is therefore clear why several minerals with the same general formula type, albeit with dissimilar structures, coexist in the assemblage of Panasqueira phosphates.

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