The crystal structure of sinkankasite, a complex heteropolyhedral sheet mineral

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ABSTRACT

The crystal structure of sinkankasite, $Z = 2$, $Mn^{2+}(H_2O)_4[Al(PO_3OH)_2(OH)](H_2O)_2$, triclinic, $a = 9.590(2)$, $b = 9.818(2)$, $c = 6.860(1)$ Å, $\alpha = 108.04(3)$, $\beta = 99.63(3)$, $\gamma = 98.87(3)°$, $V = 590.7(2)$ Å³, space group $P\bar{1}$, has been solved by direct methods and refined to an R index of 7.2% and an R_w index of 7.6% using 2170 unique observed reflections ($|F_o| \geq 5\sigma_F$) collected with MoKα X-ray radiation. The structure contains one distinct Mn^{2+} position, which is octahedrally coordinated by two O atoms and four H_2O groups. There are two distinct Al positions; each is octahedrally coordinated by four O atoms and two OH groups. The two distinct P positions are each tetrahedrally coordinated by three O atoms and one OH group. There are 15 unique H positions, which have been located and refined using soft constraints.

The structure consists of corner-sharing chains of $Al\phi_6$ octahedra, decorated on both sides by $P\phi_4$ tetrahedra. These heteropolyhedral chains are linked through the $Mn\phi_6$ octahedra to form continuous sheets of composition $MnAlP_2O_6(OH)_3 \cdot 4H_2O$. There are two interlayer anion positions, both of which are occupied by H_2O groups. There are eight unique H bonds between the interlayer cations and the sheets on either side, and no other bonding occurs between the sheets. A total of seven unique H bonds occur between anions of the same heteropolyhedral sheet.

INTRODUCTION

Sinkankasite was described as $H_2MnAl(PO_4)_2(OH) \cdot 6H_2O$ by Peacor et al. (1984). It occurs in the Barker pegmatite, South Dakota, as an alteration product of triphylite, where it is associated with other secondary phosphates, including vivianite, hureaulite, carbonate-apatite, strengite, barbosalite, and fluellite. Sinkankasite is multiply twinned by reflection on {100}. However, because sinkankasite is triclinic, there is only random overlap of reflections in reciprocal space (except for those occurring on the twin plane, i.e., {0kl} reflections). Hence single-crystal intensity data can be collected from one component of the twinned crystal if the cell of this component can be oriented. We have determined the crystal structure of sinkankasite in this fashion and report the results here.

EXPERIMENTAL METHODS

A small tabular crystal fragment of sinkankasite from the Barker pegmatite, near Keystone, Pennington County, South Dakota, was mounted on a Nicolet $R3m$ automated four-circle diffractometer. Twenty-one reflections over the range $4° \leq 2\theta \leq 18°$ were centered using graphite-monochromated MoKα X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the 21 automatically aligned reflections by least-squares refinement. Data were collected using the θ-2θ scan method with a 2.3° 2θ scan range and a variable scan rate ranging from 4 to 29.3° 2θ/min. A total of 3650 reflections was measured; the index ranges $0 \leq h \leq 13$, $-13 \leq k \leq 13$, and $-9 \leq l \leq 9$ were covered. Two standard reflections were measured every 50 reflections. There was a gradual decline in their intensities by several percent during data collection; we attribute this decline to crystal deterioration, and the data were scaled based on the standards. We recorded intensity data on a standard ruby crystal immediately after the sinkankasite experiment. There was no significant change in the standard reflections of the ruby crystal during data collection, supporting our assumption that the sinkankasite crystal deteriorated during exposure to the X-ray beam. An empirical absorption correction based on 36 ψ-scans for each of nine reflections over the range $8° \leq 2\theta \leq 54°$ was applied, reducing R (azimuthal) from 10.7 to 4.9%. This agreement index is higher than we normally encounter and is a result of the twinned nature of the crystal (all current absorption-correction routines assume that the data are collected from a single crystal). The data were corrected for absorption, Lorentz, polarization, and background effects; of the 3650 reflections measured, 2170 were classed as observed ($F \geq 5\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from

TABLE 1. Crystallographic data for sinkankasite

a (Å)	9.590(2)	Crystal size (mm)	$0.04 \times 0.24 \times 0.12$	
b (Å)	9.818(2)	Radiation	$MoK\alpha$	
c (Å)	6.860(1)	Total ref.	3650	
α (°)	108.04(3)	$|F| \geq 5\sigma_F$	2170	
β (°)	99.63(3)	Final R	7.2%	
γ (°)	98.87(3)	Final R_w	7.6%	
V (Å³)	590.7(2)			
F_{000}	406	D_{calc}	2.243 g/cm³	
Space group	$P\bar{1}$	μ	1.49 mm⁻¹	

Unit-cell contents $2\{Mn^{2+}(H_2O)_4[Al(PO_3OH)_2(OH)](H_2O)_2\}$
$R = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$
$R_w = [\Sigma w (|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2}$, $w = 1/\sigma_F^2$

Cromer and Mann (1968) and Cromer and Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study. R indices are of the form given in Table 1 and are expressed as percentages.

The possible space groups of sinkankasite are $P1$ and $P\bar{1}$; reflection statistics favor the latter and the successful solution and refinement of the structure verifies that the space group of sinkankasite is $P\bar{1}$. The structure was solved by direct methods, followed by cycles of least-squares refinement and calculation of difference-Fourier maps. Refinement of the positional and isotropic displacement parameters of the complete model (excluding H positions) gave an R index of 13%. Conversion to an anisotropic displacement model, together with refinement of all parameters, gave an R index of 7.5%. At this stage of the refinement, a difference-Fourier map was calculated, and the positions of 15 H atoms were determined. Subsequent cycles of refinement showed that the H positions were characterized by anomalously short O-H bond lengths, a common feature of H positions refined using X-ray data. The soft constraint that O-H distances should be ~0.96 Å was imposed by adding extra weighted observational equations to the least-squares matrix. Only the O-H distance is constrained, and each H position is free to seek its optimum position around the O atom. Refinement of all parameters, including a correction for isotropic extinction, gave a final R index of 7.2% and a R_w index of 7.6%. This relatively high final R index results from the twinned nature of the crystal and its influence on the absorption correction and from the deterioration of the crystal under the X-ray beam. The omission of $0kl$ reflections did not significantly improve the refinement. Final positional and displacement parameters are given in Table 2, observed and calculated structure factors in Table 3, selected interatomic distances and angles in Table 4, and a bond-valence analysis is given in Table 5.[1]

TABLE 2. Atomic coordinates and displacement factors for sinkankasite

	x	y	z	U_{eq} (Å²)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.2887(2)	0.9520(2)	0.6821(2)	145(5)	240(9)	184(7)	39(5)	51(6)	54(5)	65(4)
P1	0.2971(3)	0.6566(2)	0.2606(3)	116(7)	186(12)	161(10)	41(8)	59(9)	41(7)	73(7)
P2	0.2914(3)	0.2566(2)	0.1038(3)	112(7)	187(12)	132(10)	38(8)	19(8)	40(7)	58(7)
Al1	½	½	½	82(12)	149(21)	123(18)	1(14)	30(13)	26(11)	56(11)
Al2	½	½	0	93(12)	190(21)	135(17)	1(14)	50(13)	49(12)	65(11)
O1	0.2899(8)	0.8156(7)	0.3614(8)	178(21)	328(39)	192(27)	72(22)	113(27)	80(23)	79(20)
O2	0.3909(7)	0.6426(6)	0.1003(7)	160(19)	312(36)	227(28)	23(20)	104(26)	97(21)	105(19)
O3	0.3476(7)	0.5873(6)	0.4219(7)	131(18)	225(32)	202(27)	22(19)	63(24)	49(20)	98(18)
O4	0.3857(7)	0.3101(6)	0.3259(8)	149(18)	261(34)	156(25)	41(20)	3(23)	29(21)	72(18)
O5	0.3458(7)	0.3474(6)	-0.0230(8)	163(19)	293(36)	183(26)	48(21)	21(25)	39(22)	102(19)
O6	0.2786(8)	0.0938(6)	0.9937(8)	170(20)	295(37)	172(27)	76(22)	53(26)	66(23)	77(19)
OH1	0.1363(8)	0.5740(8)	0.1438(10)	253(23)	211(37)	303(34)	240(30)	39(29)	-1(27)	125(26)
OH2	0.5789(6)	0.5165(6)	0.2761(7)	110(17)	190(30)	176(24)	1(18)	39(22)	36(19)	74(17)
OH3	0.1351(8)	0.2826(7)	0.1225(9)	205(21)	250(37)	224(29)	128(24)	-5(26)	52(23)	63(21)
OW1	0.2967(9)	0.7677(8)	0.7887(9)	270(26)	505(51)	274(34)	117(26)	155(34)	128(29)	121(24)
OW2	0.5186(9)	0.0040(9)	0.7596(12)	282(26)	255(41)	356(37)	354(35)	58(32)	71(31)	291(30)
OW3	0.2930(9)	0.1405(7)	0.5798(8)	229(23)	397(44)	232(31)	58(23)	23(30)	51(26)	71(21)
OW4	0.0573(6)	0.8887(9)	0.5972(12)	310(27)	291(44)	354(40)	308(35)	81(34)	121(32)	115(30)
OW5	0.0834(8)	0.9186(8)	0.1365(10)	242(23)	256(38)	307(34)	194(29)	53(29)	26(26)	145(25)
OW6	-0.0907(14)	0.5932(12)	0.4146(18)	613(46)	659(78)	542(60)	620(62)	-24(55)	222(56)	212(48)
H1	0.106(13)	0.470(2)	0.073(17)	300*						
H2	0.678(4)	0.547(12)	0.351(17)	300						
H3	0.063(9)	0.193(7)	0.055(17)	300						
H4	0.379(8)	0.737(14)	0.740(18)	300						
H5	0.290(15)	0.667(4)	0.710(16)	300						
H6	0.591(9)	0.071(10)	0.732(18)	300						
H7	0.580(11)	-0.041(12)	0.834(16)	300						
H8	0.397(1)	0.160(12)	0.613(18)	300						
H9	0.288(13)	0.233(7)	0.676(14)	300						
H10	0.015(12)	0.785(3)	0.545(17)	300						
H11	0.000(11)	0.947(11)	0.675(16)	300						
H12	0.139(12)	0.858(11)	0.186(16)	300						
H13	0.081(1)	0.998(9)	0.259(10)	300						
H14	-0.148(12)	0.527(9)	0.465(17)	300						
H15	-0.067(14)	0.510(9)	0.319(14)	300						

Note: displacement factors are multiplied by 10^4.
* Fixed during refinement.

TABLE 4. Selected interatomic distances (Å) and angles (°) in sinkankasite

Mn-O1	2.195(5)	P2-O4	1.521(5)
Mn-OW1	2.158(8)	P2-O5	1.521(7)
Mn-OW4	2.137(8)	P2-OH3	1.578(8)
Mn-O6a	2.188(6)	P2-O6b	1.516(6)
Mn-OW2a	2.120(8)	(P2-O)	1.534
Mn-OW3a	2.170(8)		
(Mn-O)	2.161	Al1-O3c	1.889(7) × 2
		Al1-O4c	1.912(5) × 2
P1-O1	1.517(6)	Al1-OH2c	1.861(6) × 2
P1-O2	1.521(7)	(Al1-O)	1.887
P1-O3	1.520(7)		
P1-OH1	1.573(7)	Al2-O2d	1.904(7) × 2
(P1-O)	1.533	Al2-O5d	1.884(6) × 2
		Al2-OH2d	1.865(5) × 2
		(Al-O)	1.884

Mnφ₆ octahedron

O1-OW1	3.101(10)	O1-Mn-OW1	90.8(2)
O1-OW4	3.014(12)	O1-Mn-OW4	88.2(3)
O1-OW2a	3.051(8)	O1-Mn-OW2a	90.0(3)
O1-OW3a	3.068(9)	O1-Mn-OW3a	89.3(2)
OW1-OW4	3.034(13)	OW1-Mn-OW4	89.9(3)
OW1-O6a	3.118(9)	OW1-Mn-O6a	91.7(2)
OW1-OW2a	2.976(12)	OW1-Mn-OW2a	88.1(3)
OW4-O6a	3.052(8)	OW4-Mn-O6a	89.8(3)
OW4-OW3a	2.129(11)	OW4-Mn-OW3a	93.2(3)
O6a-OW2a	3.104(11)	O6a-Mn-OW2a	92.2(3)
O6a-OW3a	3.035(9)	O6a-Mn-OW3a	88.3(2)
OW2a-OW3a	3.004(12)	OW2a-Mn-OW3a	88.9(3)
(O-O)	3.057	(O-Mn-O)	90.0

P1φ₄ tetrahedron

O1-O2	2.497(9)	O1-P1-O2	110.6(4)
O1-O3	2.527(10)	O1-P1-O3	112.6(3)
O1-OH1	2.453(8)	O1-P1-OH1	105.1(4)
O2-O3	2.513(8)	O2-P1-O3	111.5(4)
O2-OH1	2.523(10)	O2-P1-OH1	109.2(3)
O3-OH1	2.496(9)	O3-P1-OH1	107.6(4)
(O-O)	2.501	(O-P1-O)	109.4

P2φ₄ tetrahedron

O4-O5	2.508(8)	O4-P2-O5	111.1(3)
O4-OH3	2.498(9)	O4-P2-OH3	107.4(3)
O4-O6b	2.510(6)	O4-P2-O6b	111.5(4)
O5-OH3	2.481(10)	O5-P2-OH3	106.4(4)
O5-O6b	2.517(9)	O5-P2-O6b	111.9(3)
OH3-O6b	2.508(10)	OH3-P2-O6b	108.3(4)
(O-O)	2.504	(O-P2-O)	109.4

Al1φ₆ octahedron

O3c-O4c	2.693(9) × 2	O3c-Al1-O4c	90.2(2) × 2
O3c-OH2c	2.681(9) × 2	O3c-Al1-OH2c	91.3(3) × 2
O3c-O4c	2.682(8) × 2	O3c-Al1-O4c	89.8(2) × 2
O3c-OH2c	2.621(8) × 2	O3c-Al1-OH2c	88.7(3) × 2
O4c-OH2c	2.672(9) × 2	O4c-Al1-OH2c	90.1(2) × 2
O4c-OH2c	2.665(6) × 2	O4c-Al1-OH2c	89.9(2) × 2
(O-O)	2.669	(O-Al1-O)	90.0

Al2φ₆ octahedron

O2d-O5d	2.697(8) × 2	O2d-Al2-O5d	90.8(3) × 2
O2d-OH2d	2.669(9) × 2	O2d-Al2-OH2d	90.2(3) × 2
O2d-O5d	2.659(10) × 2	O2d-Al2-O5d	89.2(3) × 2
O2d-OH2d	2.662(7) × 2	O2d-Al2-OH2d	89.8(2) × 2
O5d-OH2d	2.679(7) × 2	O5d-Al2-OH2d	91.2(2) × 2
O5d-OH2d	2.623(9) × 2	O5d-Al2-OH2d	88.8(2) × 2
(O-O)	2.665	(O-Al2-O)	90.0

H bonding

H1-OH1	0.96(3)	H1···OH3	2.02(7)
OH1-OH3	2.818(11)	OH1-H1-OH3	139(9)
H2-OH2	0.96(4)	H2···OW6e	2.14(4)
OH2-OW6e	3.054(14)	OH2-H2-OW6e	161(6)
H3-OH3	0.96(7)	H3···OW5f	1.71(7)
OH3-OW5f	2.599(8)	OH3-H3-OW5f	153(9)
H4-OW1	0.96(11)	H4···O4c	2.46(9)
OW1-O4c	3.409(11)	OW1-H4-O4c	170(10)
H5-OW1	0.96(5)	H5···O3	2.09(12)

TABLE 4.—*Continued*

OW1-O3	2.761(8)	OW1-H5-O3	126(9)
H4-H5	0.95(14)	H4-OW1-H5	60(8)
H6-OW2	0.96(11)	H6···O1c	1.81(11)
OW2-O1c	2.760(11)	OW2-H6-O1c	171(8)
H7-OW2	0.96(12)	H7···O6g	1.89(12)
OW2-O6g	2.837(11)	OW2-H7-O6g	170(10)
H6-H7	1.47(18)	H6-OW2-H7	100(9)
H8-OW3	0.96(2)	H8···O2c	2.61(7)
OW3-O2c	3.379(8)	OW3-H8-O2c	137(9)
H9-OW3	0.46(8)	H9···O5h	1.95(8)
OW3-O5h	2.757(7)	OW3-H9-O5h	140(9)
H8-H9	1.41(14)	H8-OW3-H9	95(9)
H10-OW4	0.96(4)	H10···OW6	1.86(4)
OW4-OW6	2.807(13)	OW4-H10-OW6	170(3)
H11-OW4	0.96(11)	H11···OW5i	1.91(11)
OW4-OW5i	2.866(11)	OW4-H11-OW5i	170(10)
H10-H11	1.61(11)	H10-OW4-H11	114(9)
H12-OW5	0.96(12)	H12···O1	1.90(12)
OW5-O1	2.808(11)	OW5-H12-O1	156(9)
H13-OW5	0.96(8)	H13···OW4i	2.04(12)
OW5-OW4i	2.866(11)	OW5-H13-OW4i	142(10)
H12-H13	1.54(16)	H12-OW5-H13	106(9)
H14-OW6	0.97(12)	H14···O3j	2.43(12)
OW6-O3j	3.359(15)	OW6-H14-O3j	161(9)
H15-OW6	0.96(9)	H15···OH1	2.55(13)
OW6-OH1	3.080(16)	OW6-H15-OH1	115(6)
H14-H15	1.35(18)	H14-OW6-H15	89(9)

Note: a = $x, y + 1, z$; b = $x, y, z - 1$; c = $1 - x, 1 - y, 1 - z$; d = $1 - x, 1 - y, \bar{z}$; e = $x + 1, y, z$; f = $\bar{x}, 1 - y, \bar{z}$; g = $1 - x, \bar{y}, 2 - z$; h = $x, y, z + 1$; i = $\bar{x}, 2 - y, 1 - z$; j = $\bar{x}, 1 - y, 1 - z$.

DESCRIPTION OF THE STRUCTURE

$MnO_2(H_2O)_4$ and $AlO_4(OH)_2$ octahedra

The sinkankasite structure contains one symmetrically unique Mn position that is octahedrally coordinated by two O atoms and four H_2O groups. The H_2O groups are at the equatorial positions of the octahedron, which has a ⟨Mn-O⟩ distance of 2.161 Å and bond lengths ranging from 2.120 to 2.195 Å. Peacor et al. (1984) reported chemical analyses for sinkankasite from the Barker pegmatite. The material they studied contains significant Fe^{2+}; the ratio of Mn^{2+} to Fe^{2+} at this site is about 1.0 to 0.6. The Mn^{2+} and Fe^{2+} species have very similar X-ray scattering factors, and it is not possible to refine their ratios directly using X-ray data. However, the sums of the empirical radii of Shannon (1976) for [6]Mn^{2+}, [6]Fe^{2+}, and [3]O^{2-} are 2.19 and 2.14 Å for the Mn^{2+}-O and Fe^{2+}-O bonds, respectively. The ⟨Mn-O⟩ bond length of 2.161 Å reported here is consistent with the occurrence of both Mn^{2+} and Fe^{2+} at this site.

The structure has two symmetrically distinct Al positions, and both occur on a center of symmetry. Each Al is octahedrally coordinated by four O atoms and two OH groups, and the latter are in a trans arrangement. The ⟨Al1-O⟩ and ⟨Al2-O⟩ distances are 1.887 and 1.884 Å, respectively, fairly close to the sum of the ionic radii for [6]Al, [3]O, and [2]OH (0.535 + 1.353 = 1.888 Å: Shannon,

TABLE 5. Bond-valence analysis (vu) for sinkankasite

	O1	O2	O3	O4	O5	O6	OH1	OH2	OH3	OW1	OW2	OW3	OW4	OW5	OW6	Σ
Mn	0.335					0.341			0.370	0.410	0.358	0.391				2.205
Al1			0.526×2 ↓	0.494×2 ↓				0.567×2 ↓								3.174
Al2		0.505×2 ↓			0.533×2 ↓			0.561×2 ↓								3.198
P1	1.310	1.296	1.300				1.126									5.032
P2				1.296	1.296	1.314			1.111							5.017
H1							0.85		0.15							1.0
H2								0.90							0.10	1.0
H3									0.80				0.20			1.0
H4				0.05						0.95						1.0
H5			0.12							0.88						1.0
H6	0.20										0.80					1.0
H7						0.20					0.80					1.0
H8		0.05										0.95				1.0
H9					0.15							0.85				1.0
H10													0.80		0.20	1.0
H11													0.80	0.20		1.0
H12	0.20													0.80		1.0
H13													0.15	0.85		1.0
H14			0.05												0.95	1.0
H15							0.05								0.95	1.0
Σ	2.045	1.851	1.996	1.840	1.979	1.855	2.026	2.028	2.061	2.200	2.010	2.158	2.141	2.050	2.200	

* Bond-valence parameters from Brown and Altermatt (1985).

1976). Thus, both the site scattering and the observed ⟨Al-O⟩ distances are consistent with complete occupancy of Al1 and Al2 by Al, as indicated by the electron-microprobe analysis of Peacor et al. (1984).

PO₃OH tetrahedra

There are two symmetrically distinct P positions in sinkankasite. Each P is tetrahedrally coordinated by three O atoms and an OH group, thus forming acid phosphate groups. The ⟨P1-O⟩ and ⟨P2-O⟩ distances are 1.533 and 1.534 Å, respectively. The tetrahedra show significant bond-length distortion, with bond lengths ranging from 1.517 to 1.573 Å and 1.516 to 1.578 Å in the P1ϕ_4 (ϕ = unspecified ligand) and P2ϕ_4 tetrahedra, respectively; in each case, the longest bond is to the OH group, as is usually observed for acid phosphate groups because of local bond-valence requirements around the acid ligand (Table 5).

Structure topology

The Alϕ_6 octahedra share one set of trans vertices to form an Alϕ_5 chain extending along the **c** direction. Equatorial vertices of each chain are linked by Pϕ_4 tetrahedra (Fig. 1a) to form a heteropolyhedral chain of stoichiometry Al(PO₃OH)₂(OH). These chains are cross-linked into sheets of the form Mn²⁺(H₂O)₄[Al(PO₃OH)₂(OH)] by linkage of the trans vertices of the Mn²⁺ϕ_6 octahedra with vertices of Pϕ_4 tetrahedra of adjacent chains (Fig. 2). These sheets lie in the (100) plane and are cross-linked into a three-dimensional structure by a network of H bonds (Fig. 3); this arrangement accounts for the perfect {100} cleavage of sinkankasite (Peacor et al., 1984).

H bonding

The H atom positions obtained by constrained least-squares refinement of the positional parameters are rea-

sonable, both in terms of donor and acceptor bond lengths and bond angles (Table 4) and the bond-valence requirements of the donor and acceptor anions (Table 5). There are 15 symmetrically unique H positions in sinkankasite, and H bonding plays two distinct roles in the structure: (1) H bonds bridge between the heteropolyhedral sheets and the interlayer anions, providing the only linkage be-
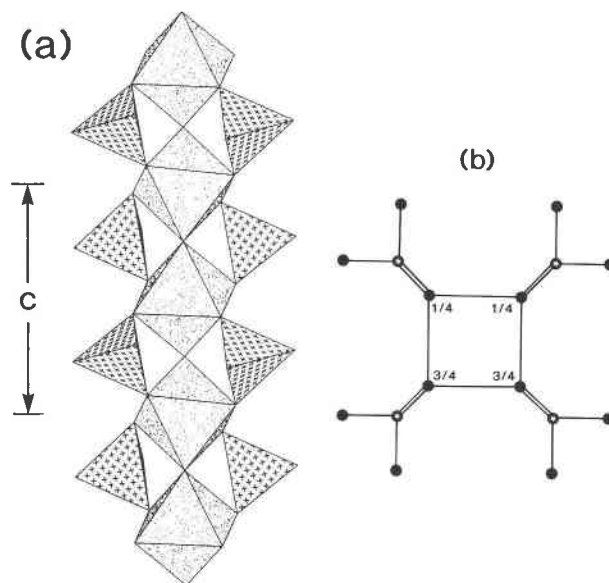

Fig. 1. (a) The Al(PO₃OH)₂(OH) chain in sinkankasite; Alϕ_6 octahedra are shown by irregular dot shading; Pϕ_4 tetrahedra are shaded with crosses; (b) the type VI chain of Moore (1970), showing the octahedral chain viewed down its length, with the relative heights of the tetrahedra shown as fractions of the chain-axis length of ~7 Å.
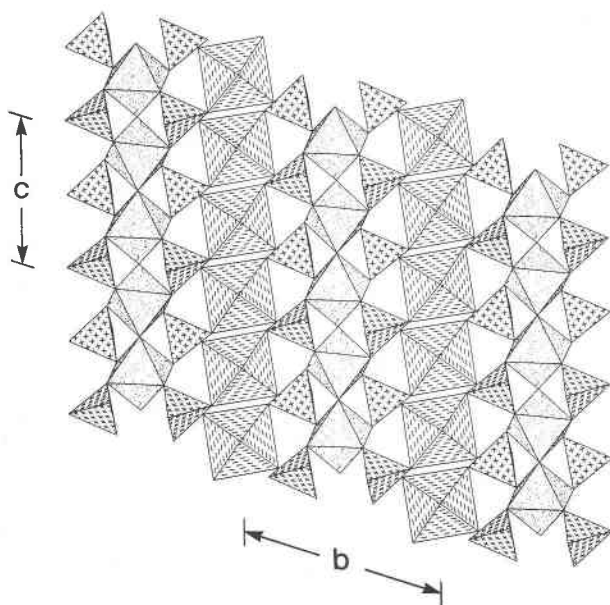
Fig. 2. The $Mn^{2+}(H_2O)_4[Al(PO_3OH)_2(OH)]$ sheet in the structure of sinkankasite; $Mn\phi_6$ octahedra are shaded with dashed lines; other polyhedral shadings are as in Fig. 1.
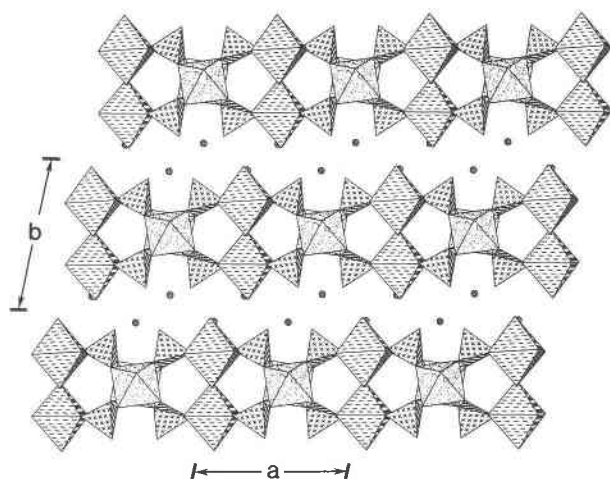

Fig. 3. The structure of sinkankasite projected down [001]; shadings as in Fig. 2; interstitial H_2O groups shown by shaded circles.

tween sheets, and (2) H bonding occurs within the heteropolyhedral sheets.

There are eight H positions that provide linkage between the heteropolyhedral sheets and the interlayer OW5 and OW6 positions (Fig. 4). These H positions participate in the following bonds: OH2-H2···OW6^e, OH3-H3···OW5^f, OW4-H10···OW6, OW4-H11···OW5^i, OW5-H12···O1, OW5-H13···OW4^i, OW6-H14···O3^j, and OW6-H15···OH1. Acceptor distances range from 1.71 Å (strong) to 2.55 Å (weak).

Each of the OW5 and OW6 anions bond to four H atoms. The OW5 anion donates the OW5-H12···O1 and OW5-H13···OW4^i bonds, one of which bonds to the heteropolyhedral sheet on either side, with acceptor distances of 1.90 and 2.04 Å, respectively. The OW5 position also accepts the OH3-H3···OW5^f and OW4-H11···OW5^i bonds, with acceptor distance of 1.71 and 1.91 Å, respectively, and each of these bonds is to the same heteropolyhedral sheet (Fig. 4).

The OW6 anion donates the OW6-H14···O3^j and OW6-H15···OH1 bonds, one of which bridges to the heteropolyhedral sheet on the other side, with acceptor distances of 2.43 and 2.55 Å, respectively, which indicate weak interactions only. The OW6 anion accepts a H bond from each adjacent sheet; the fairly strong OH2-H2···OW6^e and OW4-H10···OW6 bonds have acceptor distances of 2.14 and 1.86 Å, respectively.

Seven H positions participate in H bonds between two anions of the same heteropolyhedral sheet (Fig. 5). These bonds are as follows: OH1-H1···OH3, OW1-H4···O4^c, OW1-H5···O3, OW2-H6···O1^c, OW2-H7···O6^g, OW3-H8···O2^c, and OW3-H9···O5^h, with acceptor distances

ranging from 1.81 to 2.61 Å. These H bonds increase the sheet rigidity and satisfy the bond-valence requirements of the donor and acceptor anions.

General structural relations

The principal structure motif in sinkankasite is the $Al(PO_3OH)_2OH$ chain that we can generalize to the form $M(T\phi_4)_2\phi$, where M is an octahedrally coordinated cation and T is a tetrahedrally coordinated cation. In a paper of fundamental importance, Moore (1970) considered the structural hierarchy of octahedral-tetrahedral chains based on an $M\phi_5$ backbone. He developed a hierarchy of all possible arrangements with a chain of repeat distance of ~7.2 Å and showed that there is a fairly large family of minerals based on these chains.

Sinkankasite has the type VI chain (Fig. 1b) of Moore (1970), designated as the tancoite chain by Hawthorne (1985). This chain is found in a number of structures (Table 6), all of which show the typical ~7.2-Å repeat (6.9–7.3 Å), except for tancoite, which has a doubled repeat distance of 14.07 Å. Sinkankasite shows most affinity with the segelerite-group structures. The latter are treated in some detail by Moore and Araki (1977), who show the relationship of segelerite to jahnsite in terms of cross linkage of dense $X^{2+}M^{3+}(PO_4)_2OH$ slabs by $M^{2+}O_2(H_2O)_4$ octahedra. The solution of the sinkankasite structure raises another aspect of geometrical isomerism (Hawthorne, 1983a) with regard to these structures. Sinkankasite consists of slabs constructed from $M(T\phi_4)_2\phi$ chains that are cross-linked by $MO_2(H_2O)_4$ octahedra, and there is ample opportunity for geometrical isomerism in this general type of arrangement. The possibilities are investigated in Figure 6 for repeat distances of one (~9 Å) or two (~18 Å) chains in the direction of linkage. As is apparent from Figure 1, the $M\phi_5$ chain is modulated such
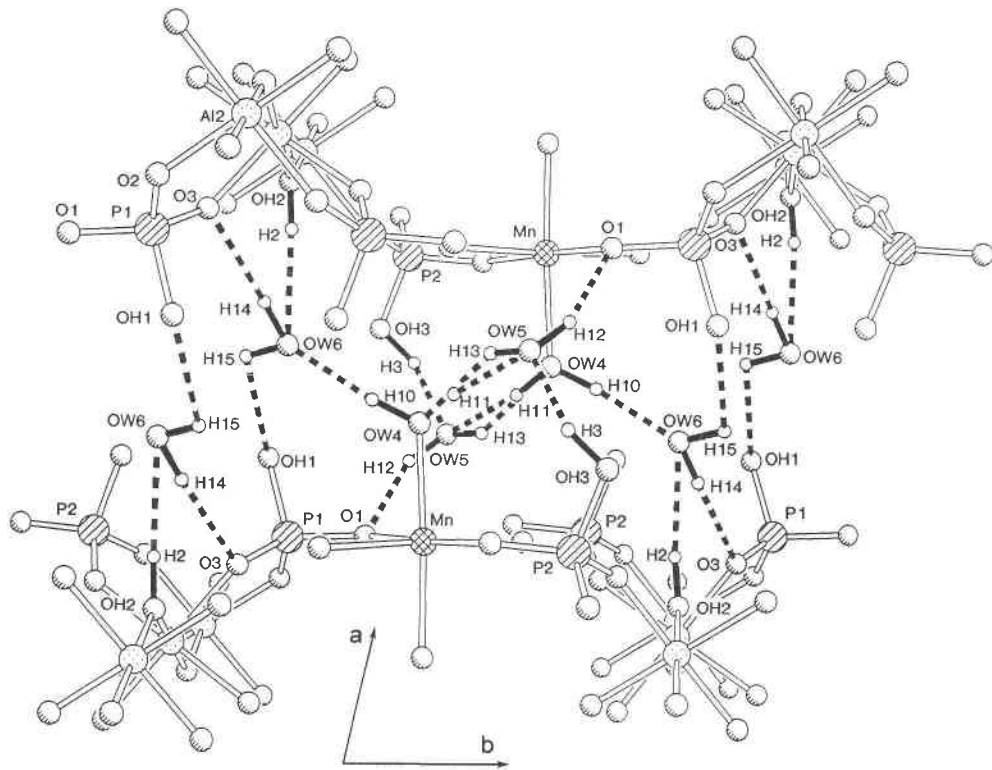
Fig. 4. The structure of sinkankasite projected down [001], showing intersheet H bonds. Al atoms are stippled, Mn atoms are crosshatched, P atoms are parallel ruled, O atoms are shaded in the lower left corner, and H atoms are given as small open circles. Donor H and acceptor H bonds are drawn as heavy solid and broken lines, respectively.
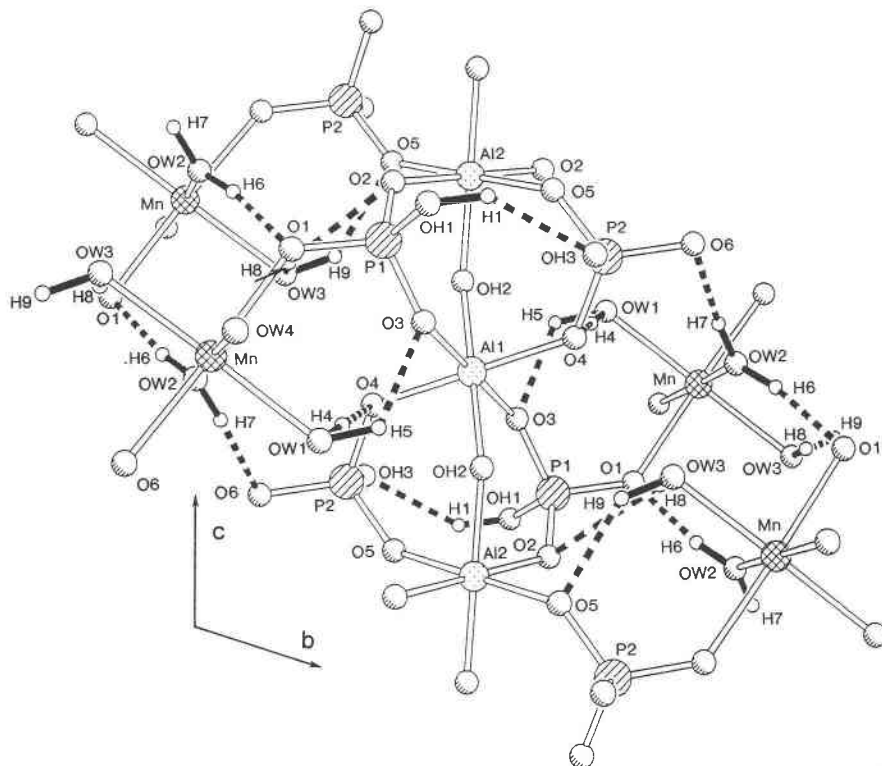

Fig. 5. The structure of sinkankasite projected down [100], showing intrasheet H bonds; legend as in Fig. 4.

TABLE 6. Minerals based on the type VI $M(T\phi_4)_2\phi$ chain of Fig. 1

Mineral	Formula	a (Å)	b (Å)	c (Å)	β (°)	Sp. Gr.	Reference
Tancoite	$Na_2Li[Al(PO_4)_2(OH)]H$	6.948(2)	14.089(4)	14.065(3)		Pbcb	1
Sideronatrite*	$Na_2[Fe^{3+}(SO_4)_2(OH)]\cdot 3H_2O$	7.29(1)	20.56(2)	7.17(2)		Pnn2	2
Jahnsite	$CaMnMg_2[Fe^{3+}(PO_4)_2(OH)]_2\cdot 8H_2O$	14.94(2)	7.14(1)	9.93(1)	110.16(8)	P2/a	3
Whiteite	$CaFe^{2+}Mg_2[Al(PO_4)_2(OH)]_2\cdot 8H_2O$	14.90(4)	6.98(2)	10.13(2)	113.11(9)	P2/a	4
Lun'okite	$Mn_2(Mg,Fe^{2+},Mn)_2[Al(PO_4)_2(OH)]_2\cdot 8H_2O$	14.95	18.71	6.96		Pbca	—
Overite	$Ca_2Mg_2[Al(PO_4)_2(OH)]_2\cdot 8H_2O$	14.72(1)	18.75(2)	7.107(4)		Pbca	5
Segelerite	$Ca_2Mg_2[Fe^{3+}(PO_4)_2(OH)]_2\cdot 8H_2O$	14.826(5)	18.751(4)	7.307(1)		Pbca	5
Wilhemvierlingite	$Ca_2Mn_2[Fe^{3+}(PO_4)_2(OH)]_2\cdot 8H_2O$	14.80(5)	18.50(5)	7.31(2)		Pbca	—
Sinkankasite	$Mn^{2+}(H_2O)_4[Al(PO_3OH)_2(OH)](H_2O)_2$	9.590(2)	9.818(2)	6.860(1)	99.63(3)	P1̄	6
Guildite	$Cu^{2+}[Fe^{3+}(SO_4)_2(OH)]\cdot 4H_2O$	9.786(2)	7.134(1)	7.263(1)	105.38(1)	P2_1/m	7
Yftisite	$Y_4[Ti(SiO_4)_2O](F,OH)_6$	14.949(4)	10.626(2)	7.043(2)		Cmcm	8

Note: references are as follows: 1 = Hawthorne (1983b); 2 = Scordari (1981); 3 = Moore and Araki (1974); 4 = Moore and Ito (1978); 5 = Moore and Araki (1977); 6 = this study; 7 = Wan et al. (1978); 8 = Balko and Bakakin (1975).
* Structure not definitively established.

that tetrahedra can link to vertices of adjacent octahedra. This modulation can occur orthogonal to or in the plane of the sheet formed by the $M(T\phi_4)_2\phi$ chains and their linking $MO_2(H_2O)_4$ octahedra. It is this difference in modulation orientation that combines with the cis and trans possibilities of the linking $MO_2(H_2O)_4$ octahedra to give the possible arrangements of Figure 6. We may divide them into three groups: (1) those arrangements with

the modulation orthogonal to the sheet and only one type of octahedral cross-linkage (Fig. 6a and 6b), where Figure 6a corresponds to the arrangement in sinkankasite, (2) those arrangements with the modulation in the plane of the sheet (Fig. 6c and 6d), corresponding to the arrangements in the hypothetical structure in Figure 4c of Moore and Araki (1977) and segelerite, respectively, and (3) those arrangements with both modulations present (Fig. 6e and
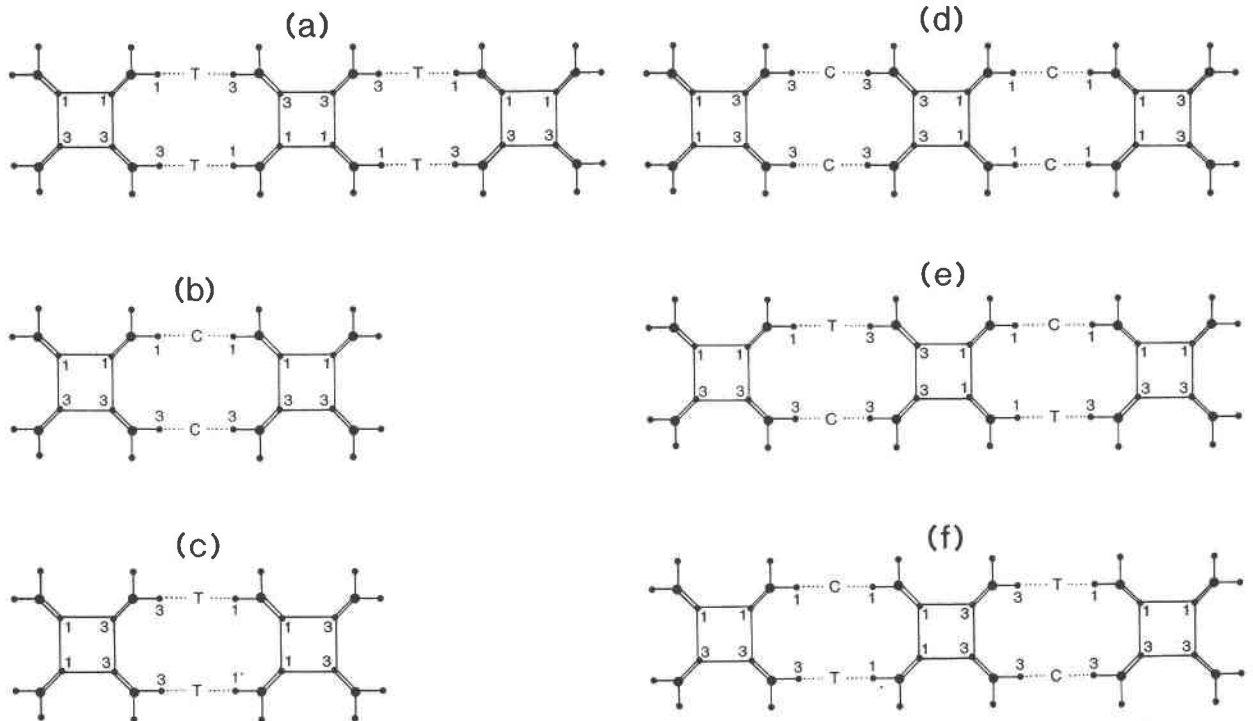

Fig. 6. Possible topologies involving $M(T\phi_4)_2\phi$ chains (viewed end-on and represented as squares) cross-linked by $M\phi_6$ octahedra with the linkages in cis (M_c) or trans (M_t) arrangements, with the modulation direction of the $M(T\phi_4)_2\phi$ chains taken into account; the heights of the tetrahedral linkages are given by symbols 1 (=¼) and 3 (=¾), which are the approximate z coordinates of the T cations for a chain-repeat length of ~7 Å and M cations at $z = 0$ and ½; (a) modulation orthogonal to the sheet and only trans linkages (sinkankasite); (b) modulation orthogonal to the sheet and only cis linkages (not yet known); (c) modulations in the plane of the sheet and only trans linkages (hypothetical structure of Moore and Araki, 1977); (d) modulation in the plane of the sheet and only cis linkages (segelerite, overite); (e), (f) mixed modulations and mixed linkages (not yet known).

6f) (these have not yet been found in crystals). Thus we have a coherent hierarchy of arrangements, two of which have so far been found in structural arrangements of minerals.

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