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THE CRYSTAL STRUCTURE OF SHIGAITE, $[AlMn_2^{2+}(OH)_6]_3(SO_4)_2Na(H_2O)_6\{H_2O\}_6$, A HYDROTALCITE-GROUP MINERAL

MARK A. COOPER and FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2

ABSTRACT

The crystal structure of shigaite, $[AlMn_2^{2+}(OH)_6]_3(SO_4)_2Na(H_2O)_6\{H_2O\}_6$, rhombohedral, *a* 9.512(1), *c* 33.074(5) Å, *V* 2591.0(8) Å^3, $Z = 3$, $R\overline{3}$, has been solved by direct methods and refined to an *R* index of 4.2% using 979 observed reflections measured with Mo$K\alpha$ X-radiation. The structural unit of shigaite is a planar sheet of edge-sharing octahedra, $[AlMn_2^{2+}(OH)_6]^{1+}$. These oxycation sheets are intercalated with oxyanion sheets of chemical composition $Na(H_2O)_6\{H_2O\}_6(SO_4)_2$; hydrogen bonding plays a major role in linkage both within the oxyanion sheet and between the structural unit and the oxyanion sheet of interstitial species. This work shows shigaite to contain essential Na and results in a significant revision of the chemical formula. Shigaite is a hydrotalcite-group mineral, the Mn^{2+} analogue of motukoreaite.

Keywords: shigaite, crystal structure, chemical formula, hydrogen bonding, hydrotalcite group.

SOMMAIRE

Nous avons affiné la structure de la shigaïte, $[AlMn_2^{2+}(OH)_6]_3(SO_4)_2Na(H_2O)_6\{H_2O\}_6$, rhomboédrique, *a* 9.512(1), *c* 33.074(5) Å, *V* 2591.0(8) Å^3, $Z = 3$, $R\overline{3}$, par méthodes directes jusqu'à un résidu *R* de 4.2% en utilisant 979 réflexions observées avec un rayonnement Mo$K\alpha$. L'unité structurale est un feuillet d'octaèdres à arêtes partagées, de composition $[AlMn_2^{2+}(OH)_6]^{1+}$. Ces couches oxy-cationiques sont intercalées avec des couches oxy-anioniques de composition $Na(H_2O)_6\{H_2O\}_6(SO_4)_2$; les liaisons hydrogène jouent un role important, aussi bien dans les couches oxy-anioniques qu'entre l'unité structurale et la couche oxy-anionique de l'espèce interstitielle. Nos résultats montrent que la shigaïte contient un atome de sodium, essentiel, ce qui mène à une révision importante de la formule chimique. La shigaïte fait partie du groupe de la hydrotalcite, et est l'analogue à Mn^{2+} de la motukoreaïte.

(Traduit par la Rédaction)

Mots-clés: shigaïte, structure cristalline, formule chimique, liaison hydrogène, groupe de la hydrotalcite.

INTRODUCTION

Shigaite is a sulfate mineral described from Shiga Prefecture, Japan, by Peacor *et al.* (1985). The original formula, $Al_4Mn_7(OH)_{22}(SO_4)_2{\cdot}8H_2O$, the tabular habit and perfect {001} cleavage indicate a sheet structure, and Peacor *et al.* (1985) suggested that shigaite has structural affinities with lawsonbauerite, $(Mn,Mg)_9Zn_4(OH)_{22}(SO_4)_2{\cdot}8H_2O$ (Treiman & Peacor 1982). As part of our interest in $[M\phi_2]$-derivative sheet structures (*M*: octahedrally coordinated divalent or trivalent cation, ϕ: unspecified anion), we have solved and refined the structure of shigaite and present the results here.

EXPERIMENTAL

The material used in this work is from the N'Chwaning mine, Kuruman (Kalahari manganese district), Cape Province, South Africa, and was generously provided by Mr. William M. Pinch. The crystal used in the measurement of the X-ray intensity data, a triangular {001} plate ~0.28 mm on an edge and 0.04 mm thick, was mounted on a Siemens *P*4 automated four-circle diffractometer. Cell dimensions (Table 1) were derived from the setting angles of 37 automatically aligned reflections. Intensities were measured from 4 to 60°2θ ($0 \le h \le 11$, $0 \le k \le 11$, $-46 \le l \le 46$) with scan speeds varying between 1.78 and 29.3°2θ/min; a total of 1988 reflections was measured over one asymmetric unit. Psi-scan data were measured on 12 reflections between 9 and 59°2θ at increments of 5°, and a thin-plate absorption correction reduced *R*(azimuthal) from 3.3 to 2.0% for a glancing angle of 2°. Intensities were corrected for absorption, Lorentz, polarization and background effects, and then reduced to structure factors; 979 reflections were classed as observed ($|F_o| > 5\sigma|F|$).

TABLE 1. MISCELLANEOUS INFORMATION FOR SHIGAITE

a (Å)	9.512(1)	Crystal size (mm)	0.30 x 0.30 x 0.25 x 0.04
c	33.074(5)	Radiation	Mo*K*α/Graphite
V (Å^3)	2591.0(8)	Total No. of *I*	1988
Sp. Gr.	$R\bar{3}$	*No. of *I*	1855
μ (mm^{-1})	2.46	No. of |*F*|	1599
D_c (g.cm^{-3})	2.21	No. of |F_o| > 5σ*F*	979
		R(azimuthal) %	3.3 → 2.0
		R(obs) %	4.2
		wR(obs) %	4.6

Cell content: $3[NaAl_3Mn_6(SO_4)_2(OH)_{18}.12H_2O]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma[F_o^2]]^{½}$, $w = 1/(\sigma F)^2$

* after removal of glancing reflections

STRUCTURE SOLUTION AND REFINEMENT

All calculations were done with the SHELXTL PC (Plus) system of programs; *R* indices are of the form given in Table 1 and are expressed as percentages. The *E* statistics indicate a centrosymmetric structure, and a solution was found in the space group $R\bar{3}$ (Peacor *et al.* 1985). Cation and anion positions compatible with an $[M\phi_2]$ sheet were located and refined, and the relative X-ray scattering powers were used to establish the cation identities. An interstitial (SO_4) group was identified *via* the relative scattering powers at the atom positions, together with the local tetrahedral geometry. Three atom positions were located with scattering powers approximately equal to that of oxygen. One atom is at the origin and is octahedrally coordinated by one of the other atoms with an interatomic distance of 2.47 Å. The central atom was assigned as Na, and the coordinating anion was assigned as an oxygen atom of an H_2O group. The third interstitial atom is not directly bonded to any cation and was assigned as H_2O. Subsequent least-squares refinement confirmed a fully occupied Na site at the origin. Difference-Fourier maps following full-matrix least-squares refinement showed all H atoms in the structure between 0.88 and 0.95 Å from their associated donor oxygen atoms. All H atoms were input into the least-squares refinement with the soft constraint that all O–H distances are approximately equal to 0.98 Å, and all H–H distances in H_2O groups are approximately equal to 1.55 Å. Full-matrix least-squares refinement of all variables with anisotropic displacement parameters for all non-H atoms converged to an *R* index of 4.2%. Final atomic positions and displacement factors are given in Table 2, selected interatomic distances and angles for non-H atoms are given in Table 3, interatomic distances and angles involving H atoms are given in Table 4, and a bond-valence table is given as Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 2. FINAL ATOMIC PARAMETERS FOR SHIGAITE

Site	*x*	*y*	*z*	†U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	−0.0011(1)	0.3336(1)	0.16671(2)	130(3)	66(4)	62(4)	261(3)	8(4)	3(4)	31(3)
Al(1)	0	0	0.16475(8)	75(6)	54(6)	54(6)	118(12)	0	0	27(3)
Al(2)	1/3	2/3	1/6	82(9)	50(10)	50(10)	146(18)	0	0	25(5)
Na	0	0	0	332(17)	336(20)	336(20)	324(33)	0	0	168(10)
S	2/3	1/3	0.03822(7)	182(6)	181(6)	181(6)	184(11)	0	0	91(3)
O(1)	1/3	2/3	0.0063(2)	267(19)	342(22)	342(22)	118(33)	0	0	171(11)
O(2)	0.6144(5)	0.1690(5)	0.0535(1)	296(18)	373(24)	189(19)	322(21)	28(18)	23(20)	138(20)
OH(1)	0.5705(4)	0.1373(4)	0.1374(1)	100(13)	114(17)	72(16)	112(15)	−8(14)	9(14)	46(14)
OH(2)	0.1979(4)	0.0984(4)	0.1346(1)	109(13)	72(16)	101(16)	146(16)	14(14)	21(15)	37(13)
OH(3)	0.2336(4)	0.4698(4)	0.1361(1)	113(14)	125(17)	92(17)	125(16)	−2(15)	2(15)	57(14)
OW(1)	0.1180(5)	0.4236(5)	0.0556(1)	321(19)	280(22)	381(25)	302(21)	77(20)	34(19)	165(21)
OW(2)	0.2036(5)	0.1794(5)	0.0501(1)	315(18)	245(23)	297(22)	384(23)	−13(21)	18(20)	122(18)
H(1)	0.584(6)	0.156(7)	0.1082(3)	*200						
H(2)	0.193(7)	0.109(6)	0.1052(2)	*200						
H(3)	0.197(6)	0.475(6)	0.1087(6)	*200						
H(4)	0.172(6)	0.507(6)	0.035(1)	*700						
H(5)	0.004(2)	0.394(8)	0.054(2)	*700						
H(6)	0.172(6)	0.262(5)	0.055(2)	*700						
H(7)	0.320(2)	0.242(6)	0.045(2)	*700						

† *U* values x 10^4; * fixed in refinement

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) & ANGLES (°) IN SHIGAITE

Mn–OH(1)d	2.171(4)		Al(1)–OH(1)d,f,g	1.915(3)	x3
Mn–OH(1)e	2.177(4)		Al(1)–OH(2),e,h	1.912(3)	x3
Mn–OH(2)e	2.211(3)		<Al(1)–OH>	1.914	
Mn–OH(2)f	2.205(3)				
Mn–OH(3)	2.190(3)		Al(2)–OH(3),f,i,j,k,l	1.912(3)	x6
Mn–OH(3)f	2.199(3)				
<Mn–OH>	2.192		Na–OW(2),a,e,h,m,n	2.470(4)	x6
S–O(1)a	1.472(6)				
S–O(2),b,c	1.473(3)	x3			
<S–O>	1.473				
Mn octahedron					
OH(1)e–OH(2)f	2.610(5)		OH(1)e–Mn–OH(2)f	73.1(1)	
OH(1)e–OH(2)e	3.376(5)		OH(1)e–Mn–OH(2)e	100.6(1)	
OH(1)e–OH(3)	3.367(4)		OH(1)e–Mn–OH(3)	100.9(1)	
OH(1)e–OH(3)f	3.000(4)		OH(1)e–Mn–OH(3)f	86.6(1)	
OH(1)d–OH(2)f	3.346(6)		OH(1)d–Mn–OH(2)f	99.8(1)	
OH(1)d–OH(2)e	2.586(4)		OH(1)d–Mn–OH(2)e	72.3(1)	
OH(1)d–OH(3)	3.000(4)		OH(1)d–Mn–OH(3)	86.9(1)	
OH(1)d–OH(3)f	3.378(5)		OH(1)d–Mn–OH(3)f	101.3(1)	
OH(2)f–OH(2)e	3.081(6)		OH(2)f–Mn–OH(2)e	88.5(1)	
OH(2)e–OH(3)	3.356(5)		OH(2)e–Mn–OH(3)	99.4(1)	
OH(3)–OH(3)f	2.594(6)		OH(3)–Mn–OH(3)f	72.5(1)	
OH(3)f–OH(2)f	3.376(6)		OH(3)f–Mn–OH(2)f	100.1(1)	
<OH–OH>	3.089		<OH–Mn–OH>	90.2	
Al(1) octahedron					
OH(1)–OH(1)	2.797(4)	x3	OH(1)–Al(1)–OH(1)	93.8(2)	x3
OH(1)–OH(2)	2.586(4)	x3	OH(1)–Al(1)–OH(2)	85.0(2)	x3
OH(1)–OH(2)	2.610(5)	x3	OH(1)–Al(1)–OH(2)	86.0(2)	x3
OH(2)–OH(2)	2.823(6)	x3	OH(2)–Al(1)–OH(2)	95.2(2)	x3
<OH–OH>	2.704		<OH–Al(1)–OH>	90.0	
Al(2) octahedron					
OH(3)–OH(3)	2.810(4)	x6	OH(3)–Al(2)–OH(3)	94.6(1)	x6
OH(3)–OH(3)	2.594(6)	x6	OH(3)–Al(2)–OH(3)	85.4(1)	x6
<OH–OH>	2.702		<OH–Al(2)–OH>	90.0	
Na octahedron					
OW(2)–OW(2)	3.173(6)	x6	OW(2)–Na–OW(2)	79.9(1)	x6
OW(2)–OW(2)	3.785(8)	x6	OW(2)–Na–OW(2)	100.1(1)	x6
<OW–OW>	3.479		<OW–Na–OW>	90.0	
S tetrahedron					
O(1)–O(2)	2.415(8)	x3	O(1)–S–O(2)	110.1(2)	x3
O(2)–O(2)	2.396(5)	x3	O(2)–S–O(2)	108.8(2)	x3
<O–O>	2.406		<O–S–O>	109.5	

TABLE 4. DETAILS OF H-BONDING (Å, °) IN SHIGAITE

OH(1)–H(1)	0.98(1)	H(1)–O(2)	1.83(1)
OH(2)–H(2)	0.98(1)	H(2)–OW(2)	1.93(2)
OH(3)–H(3)	0.98(3)	H(3)–OW(1)	1.88(2)
OH(1)–O(2)	2.800(5)	OH(1)–H(1)–O(2)	173(7)
OH(2)–OW(2)	2.891(5)	OH(2)–H(2)–OW(2)	167(5)
OH(3)–OW(1)	2.829(5)	OH(3)–H(3)–OW(1)	163(6)
OW(1)–H(4)	0.98(5)	H(4)–O(1)	1.79(4)
OW(1)–H(5)	0.98(3)	H(5)–O(2)e	1.93(6)
OW(2)–H(6)	0.98(6)	H(6)–OW(1)	1.86(6)
OW(2)–H(7)	0.98(2)	H(7)–O(2)c	1.97(2)
OW(1)–O(1)	2.732(5)	OW(1)–H(4)–O(1)	159(5)
OW(1)–O(2)e	2.840(7)	OW(1)–H(5)–O(2)e	153(6)
OW(2)–OW(1)	2.825(8)	OW(2)–H(6)–OW(1)	170(6)
OW(2)–O(2)c	2.909(6)	OW(2)–H(7)–O(2)c	160(6)
H(4)–H(5)	1.55(5)	H(4)–OW(1)–H(5)	105(5)
H(6)–H(7)	1.55(8)	H(6)–OW(2)–H(7)	105(4)

a: $y, \bar{x}+y, \bar{z}$; b: $\bar{y}+1, x-y, z$; c: $\bar{x}+y+1, \bar{x}+1, z$; d: $\bar{x}+2/3, \bar{y}+1/3, \bar{z}+1/3$; e: $\bar{y}, x-y, z$; f: $y-1/3, \bar{x}+y+1/3, \bar{z}+1/3$; g: $x-y-1/3, x-2/3, \bar{z}+1/3$; h: $\bar{x}+y, \bar{x}, z$; i: $\bar{x}+2/3, \bar{y}+4/3, \bar{z}+1/3$; j: $\bar{y}+1, x-y+1, z$; k: $\bar{x}+y, \bar{x}+1, z$; l: $x-y+2/3, x+1/3, \bar{z}+1/3$; m: $\bar{x}, \bar{y}, \bar{z}$; n: $x-y, x, \bar{z}$

DESCRIPTION OF THE STRUCTURE

Cation coordination

There is one *S* site at the 6*c* position on the 3-fold axis at (⅔, ⅓, *z*). Accordingly, it is coordinated by four oxygen anions in a tetrahedral arrangement, with one anion lying on the 3-fold axis at a distance of 1.472 Å and the other equivalent three anions occupying the 18*f* position at a distance of 1.473 Å. The resulting <*S*–O> distance, 1.473 Å, is typical for tetrahedral (SO_4) groups. There are two distinct *Al* sites, *Al*(1) and *Al*(2),

TABLE 5. BOND-VALENCE TABLE FOR SHIGAITE (*vu*)*

	Mn	Al(1)	Al(2)	Na	S	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	Σ
OH(1)	0.357 0.351	$0.490^{x3}\downarrow$				0.82							2.018
OH(2)	0.321 0.328	$0.494^{x3}\downarrow$					0.86						2.001
OH(3)	0.339 0.331		$0.494^{x6}\downarrow$					0.84					2.004
OW(1)								0.16	0.82	0.85	0.17		2.000
OW(2)				$0.165^{x6}\downarrow$			0.14				0.83	0.86	1.995
O(1)					1.508				$0.18^{x3}\rightarrow$				2.048
O(2)					$1.504^{x3}\downarrow$	0.18				0.15		0.14	1.974
Σ	2.025	2.852	2.964	0.990	6.020	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

* Bond-valence parameters from Brown & Altermatt (1985)

occupying the 6*c* and 3*b* position, respectively. They are both coordinated by six OH anions in octahedral arrangements, and the <*Al*–O> distances of 1.914 and 1.912 Å are typical of Al in this type of coordination. There is one unique *Mn* site that occupies the 18*f* position and is surrounded by six OH groups in an octahedral arrangement. The <*Mn*–OH> distance of 2.192 Å shows the Mn to be divalent. There is one distinct *Na* site; it occupies the 3*a* position at the origin and is surrounded by six H_2O groups at a distance of 2.470 Å, typical for octahedrally coordinated Na.

Structural connectivity

The $Al(1)\phi_6$, $Al(2)\phi_6$ and $Mn\phi_6$ octahedra share edges to form a sheet of the general form $[M\phi_2]$ and of specific form $[\mathrm{AlMn}_2^{2+}(\mathrm{OH})_6]^{1+}$ (Fig. 1). The $Al\phi_6$ octahedra do not share edges, and all anions of the structural unit are coordinated by one Al and two Mn cations (Fig. 1, Table 5). The $Mn\phi_6$ octahedra form a dioctahedral sheet similar to that in gibbsite, and the Al atoms in shigaite occupy the remaining octahedra in the sheet. The resulting sums of the incident bond-valences at the three OH groups of the sheet are close to the ideal value of 2.0 *vu* if hydrogen bonding is taken into account (Table 5). Note that this sheet, $[\mathrm{AlMn}_2^{2+}(\mathrm{OH})_6]^{1+}$ is actually *positively* charged and, therefore, the structural unit is cationic rather than anionic, as is the case in most minerals (Hawthorne 1985).

The arrangement of interlayer species is illustrated in Figure 2. The Na is coordinated by six (H_2O) groups in an octahedral arrangement around the central cation, and four $Na(H_2O)_6$ groups lie at the corners of the unit cell at $z = 0$. The (SO_4) groups are on the 3-fold axes at (⅔, ⅓, $z \approx 0$) and (⅓, ⅔, $z \approx 0$). Each oxygen atom of the (SO_4) group receives 1.5 *vu* from the central S atom, and the remainder of its bond-valence requirements must be satisfied by H-bonding. The (H_2O) group coordinating Na, OW(2), has one H-bond to the O(2) anion of the (SO_4) group, and no H-bonds to the O(1) anion. The other crystallographically distinct (H_2O) group, OW(1), is proximal to two opposing (SO_4) groups and an $Na(H_2O)_6$ group, and is held in place by H-bonding only. The other H-bond from OW(2) links to OW(1), which then H-bonds both to O(1) and O(2) *via* its two H atoms (Fig. 2, Table 5). The interstitial species thus form a sheet of composition $Na(H_2O)_6\{H_2O\}_6(SO_4)_2$ that is linked by a network of H-bonds. Note that the interstitial species have aggregate anionic character, $<Na(H_2O)_6\{H_2O\}_6(SO_4)_2>^{3-}$, a feature that is relatively unusual in oxysalt minerals.

The linkage between the structural unit and the interstitial species is shown in Figure 3. The (OH) groups of the structural unit H-bond to both (H_2O) groups and to the O(2) oxygen atom of the (SO_4) group; details of the individual linkages are given in Tables 4 and 5. The OH(1) group H-bonds to the O(2) oxygen atom of the (SO_4) group, with a bond

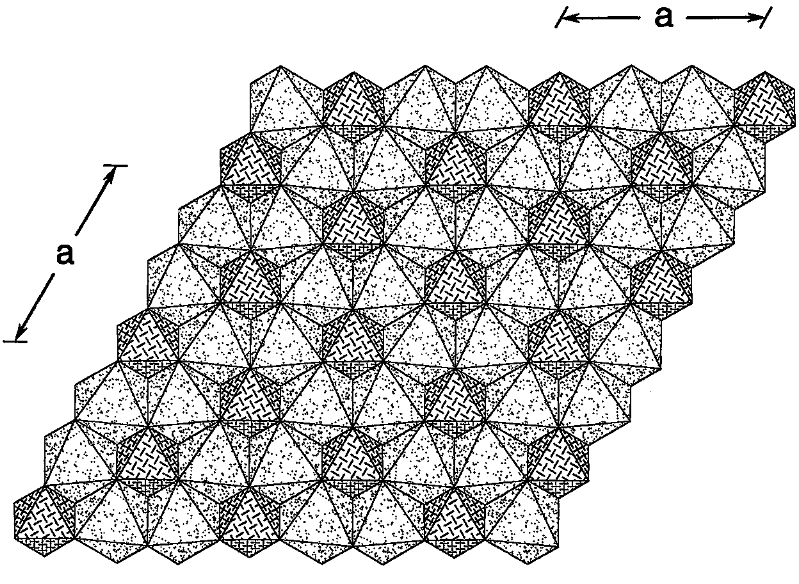

FIG. 1. The structural unit in shigaite projected down [001]; $Mn^{2+}\phi_6$ octahedra are shown by random-dot shading, and $Al\phi_6$ octahedra are shown by dash shading.

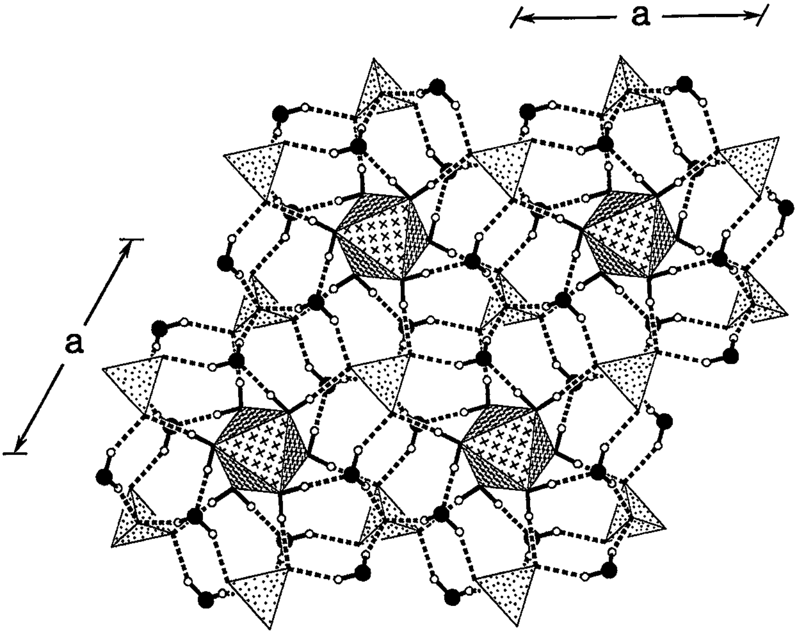

FIG. 2. The interstitial "interlayer" species in shigaite projected down [001]; $Na(H_2O)_6$ octahedra are cross-shaded, SO_4 tetrahedra are random-dot-shaded, oxygen atoms of hydrogen-bonded H_2O groups are shown as black circles, H atoms are shown by small unshaded circles, O–H bonds are shown by thick black lines, and H bonds are shown by broken lines.

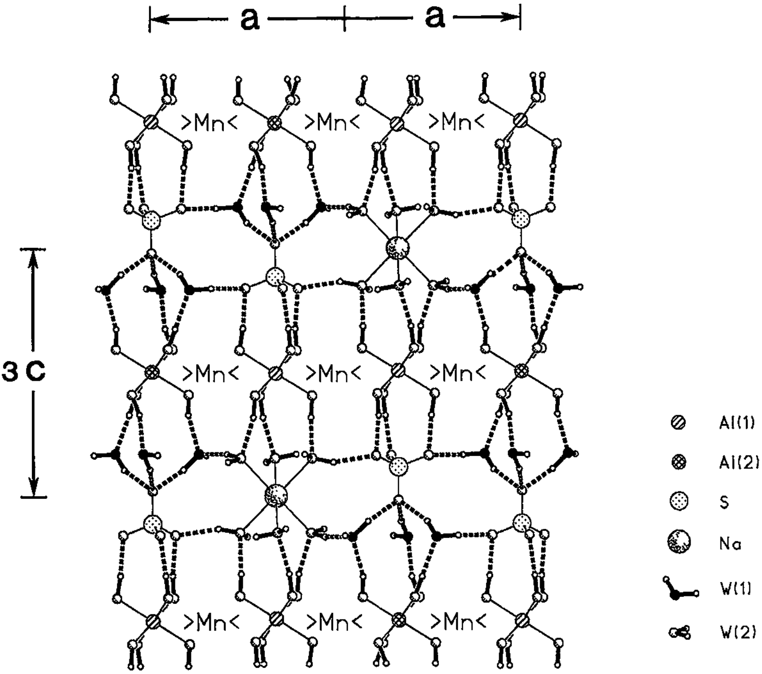

FIG. 3. The crystal structure of shigaite projected down a direction ~5° from [110]; the legend is as indicated in the figure, with the addition that Mn atoms are indicated by the letters Mn and the symbols > and < that indicate that the Mn atoms lie above and below the plane of the diagram.

valence close to the average value (0.15–0.20 *vu*) for oxysalts (Hawthorne 1992). The OH(2) group H-bonds to OW(2), the (H_2O) group that coordinates the interstitial Na atom. The OH(3) group H-bonds to OW(1), the (H_2O) group that is held in the structure by H-bonds only. Note that all O–H...O angles are close to the average value of ~165° observed in inorganic solids.

The sheet-like character of the structural unit is in accord with the tabular habit exhibited by shigaite crystals, and the role of H-bonding in linking the structural units together accounts for the perfect {001} cleavage.

CHEMICAL COMPOSITION

The chemical formula of shigaite was written as $Al_4Mn_7(OH)_{22}(SO_4)_2\cdot 8H_2O$ by Peacor *et al.* (1985). However, the refined structure (Table 2) indicates the formula to be significantly different. The formula of the structural unit is $[AlMn^{2+}_2(OH)_6]$ rather than $Al_4Mn_7(OH)_{22}$. Furthermore, Na is an essential constituent of the interstitial species. How are we sure that the *Na* site in the unit cell is actually occupied by Na? First, the observed scattering power at this site is compatible with complete occupancy by Na. Second, the incident bond-valence at the *Na* site is close to the value of 1.0 *vu* when calculated using the universal bond-valence curve of Brown (1981) for the isoelectronic series Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, P^{5+}, S^{6+}. Similarly, incident bond-valence sums (Table 5) indicate the type of each anion present in the structure. The resulting formula is $[AlMn^{2+}_2(OH)_6]_3(SO_4)_2Na(H_2O)_6\{H_2O\}_6$; in this formula, the structural unit is enclosed in square brackets.

Peacor *et al.* (1985) did not detect Na in their microprobe analysis of shigaite. However, they also analyzed shigaite with a thermoanalyzer attached to a quadrupole mass spectrometer to identify the species evolved during heating. They noted the loss of an unidentified volatile toward the end of the thermoanalyzer run; possibly this was due to the evolution of an Na–(H_2O) complex. However, we cannot explain the absence of Na in their electron-microprobe analysis, as the ideal Na_2O content of our formula, derived from the structure solution, is 2.7 wt%. In order to resolve this point, we have analyzed, by electron microprobe, shigaite from South Africa and both untreated and heated shigaite from Shiga prefecture, Japan. Samples consisted of cleavage fragments glued to a plexiglass disk. Operating conditions were 15 kV and 20 nA, and we used a defocused 30-μm beam. The untreated shigaite instantaneously began to blister under the beam and continued to bubble for several seconds after the beam was blanked. Despite these adverse conditions, a linear plot of accumulated Na counts against time was attained over 4 seconds. The mounting medium was analyzed and found to be devoid of Na. Both the South African and Japanese samples of shigaite gave 1.5 wt% Na; the corresponding value calculated from the formula derived from the crystal structure is 2.0 wt% Na, a reasonable agreement considering the behavior of the sample under the electron beam. We also analyzed the material remaining after thermoanalysis by Peacor *et al.* (1985) and did not detect any Na. Presumably the unidentified volatile identified toward the end of their thermoanalysis run was some type of $Na\phi_n$ complex.

Related structures

Shigaite, $NaAl_3Mn^{2+}_6(SO_4)_2(OH)_{18}\cdot 12H_2O$, is the Mn^{2+} analogue of motukoreaite, $Na_{0.6}(Al_{3.4}Mg_{5.6})(SO_4)_{1.3}(CO_3)_{0.7}(OH)_{18}\cdot i2H_2O$, an important phase in altered submarine basalts (Rodgers *et al.* 1977, Zamarreño *et al.* 1989). The structure of motukoreaite was described by Rius & Plana (1986), but the details of the interlayer region were not clear owing to extensive disorder associated with variable SO_4 and CO_3 contents. However, shigaite forms crystals of much better quality than motukoreaite, and lacks (SO_4), (CO_3) disorder in the interlayer region; hence the hydrogen-bonding details of the anionic sheet are clear in the shigaite structure. All of the minerals in this large family of structures consist of positively charged $[M_n(OH)_{2n}]$ sheets (in which *M* represents divalent and trivalent cations), between which are intercalated both simple and complex anions in order to balance the overall charge of the structure. The $[M_n(OH)_{2n}]$ sheet resembles that in brucite, $Mg(OH)_2$, and the positive charge is produced by substitution of trivalent cations (*e.g.*, Al, Fe^{3+}, Cr^{3+}) for some of the divalent cations (Mg, Mn^{2+}) while maintaining complete occupancy of the octahedrally coordinated sites within the sheet. Shigaite thus belongs to the large family of layered double-hydroxide structures that includes the hydrotalcite and manasseite groups (Frondel 1941, Ingram & Taylor 1967), together with numerous "stuffed" supercell derivatives.

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