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Crystal structure and cation distribution of hulsite, a tin-iron borate

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Abstract

Hulsite, $[\mathrm{Sn}^{4+}_{0.20}\mathrm{Fe}^{3+}_{0.27}\mathrm{Fe}^{2+}_{0.36}\mathrm{Mg}^{2+}_{0.16}][\mathrm{Fe}^{3+}_{0.40}\mathrm{Fe}^{2+}_{1.10}\mathrm{Mg}^{2+}_{0.48}]\mathrm{O}_2(\mathrm{BO}_3)$, from Brooks Mountain, Seward Peninsula, Alaska, is monoclinic, $P2/m$, $a = 10.695 \pm 0.004$Å, $b = 3.102 \pm 0.001$Å, $c = 5.431 \pm 0.001$Å, $\beta = 94.21° \pm 0.03°$. The structure contains two infinite octahedral sheets parallel to (100) in accord with the platy habit of the crystals; the brackets in the above formula enclose the cation compositions of the two sheets. One sheet is formed by edge-sharing of two crystallographically distinct octahedral chains; the other is formed by edge-sharing among three such chains. The sheets are held together by corner-linking to boron–oxygen triangles and by an octahedral corner shared by both sheets. Occupancy and cation multiplicity refinements of the five octahedral sites suggest that the two-chain sheet, which is more readily flexible than the three-chain sheet, contains tin and ferric iron in one cation site, ferrous iron and magnesium in the other. Hulsite belongs in the family of 3Å fiber-axis wallpaper structures and is a less-ordered version of the pinakiolite structure. Its structure is distinct from that reported for members of the chemically similar ludwigite-vonsenite series.

Introduction

Hulsite was first described by Knopf and Schaller (1908) from an occurrence at Brooks Mountain, Seward Peninsula, Alaska. The mineral was not satisfactorily characterized for many years because only small amounts of material were available, and separation from associated minerals, particularly magnetite, was difficult. Hulsite was considered, however, to be closely related to members of the ludwigite–vonsenite series, $(\mathrm{Fe}^{2+},\mathrm{Mg})_2(\mathrm{Fe}^{3+},\mathrm{Al})\mathrm{BO}_3\mathrm{O}_2$, which have orthorhombic symmetry. Crystal structures have been described for several ludwigites (Takéuchi, Watanabe, and Ito, 1950; da Silva, Clark, and Christ, 1956) and vonsenites (Bertaut, 1950, calling them boroferrites; Takéuchi, 1956; Federico, 1957, as breislakite). In 1962, Leonard, Hildebrand, and Vlisidis stated that tin, a minor component in ludwigites and vonsenites, is a major component in hulsites. Clark (1965) showed hulsite to be monoclinic and hence crystallographically distinct from the members of the ludwigite–vonsenite series. Diman and Nekrasov (1969) found a maximum of 28 weight percent tin in synthetic hulsites and ludwigite-vonsenites, the amount depending on the partial pressures of oxygen and the temperature during synthesis. Vlisidis and Schaller (1974) gave chemical analyses for natural hulsites, including one for the sample from which one of the crystals for this structural study was selected. They assigned hulsite the chemical formula $(\mathrm{Fe},\mathrm{Mg})^{2+}_2(\mathrm{Fe}^{3+},\mathrm{Sn}^{4+})\mathrm{BO}_3\mathrm{O}_2$.

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TABLE 1. Statistical Averages for Hulsite Data

Normalized Structure Factors E	Averages Experimental	Theoretical Centrosymmetric	Theoretical Acentric
$\|E\|$	0.802	0.798	0.886
$\|E^2-1\|$	1.000	1.000	1.000
$\|E^2\|$	0.953	0.968	0.736
Distribution (%)			
$\|E\| > 3.0$	0.2	0.3	0.0
$\|E\| > 2.0$	4.5	4.6	1.8
$\|E\| > 1.0$	33.3	31.7	36.8

The variation of tin in natural samples ranges from about 6 to 14 weight percent.

In 1969, Konnert, Appleman, and Clark reported orally the results of the crystal-structure analysis of a natural hulsite from one of the samples analyzed by Vlisidis and Schaller (1974); more recently, Kato and Miúra determined and refined the hulsite structure independently.[3] The results agreed within the limits of error and are jointly reported in the present paper. The authors are indicated in the following text as KACF for Konnert, Appleman, Clark, and Finger, and KM for Kato and Miúra.

Experimental data and solution of the structure

The crystals used for both structural studies were from Brooks Mountain, Seward Peninsula, Alaska. The monoclinic symmetry reported by Clark (1965) was confirmed. Statistical averages of the unitary structure factors agree with the theoretical values for a centrosymmetric structure (Table 1). The successful structural analysis establishes *P*2/*m* as the space group of hulsite. The cell constants obtained by least-squares refinement of data collected by KM with Mo*Kα* radiation on a Syntex automated diffractometer equipped with a graphite monochromator are given in Table 2, together with those for pinakiolite and ludwigite. The chemical analysis of the KACF sample (Table 3) was reported by Vlisidis and Schaller (1974). Electron-probe microanalysis by Professor F. Hirowatari of Kyushu University showed Fe, Sn, Mg, and Ca to be uniformly distributed throughout the KM crystal.

Originally, because of the very short *b* axis, KACF collected *h*0*l* projection data on the Weissenberg camera by using a multiple-film technique and Zr-filtered Mo*Kα* radiation. Of the 705 reflections examined, 429 were above the threshold of observation. Lorentz and polarization corrections were made, but the data were not corrected for absorption. All further work with the projection data was done using computer programs from X-RAY 67, *Program System for X-Ray Crystallography,* by J. M. Stewart, University of Maryland, adapted for the IBM360/65 by D. E. Appleman.

In order to solve the structure, it was necessary to assign positions to 11 atoms. KACF found the key to the structure by observing that reflections having both *h* and *l* even consistently have the highest values of the unitary structure factors E: all 48 reflections in which $E \geq 2.0$ have *h* and *l* even; of the 207 reflections in which $E \geq 1.0$, 149 have both *h* and *l* even. This discovery suggested that scattering material is concentrated in the positions that have *x* and *z* coordinates of 0,0; 0,1/2; 1/2,0; 1/2,1/2. The Patterson projection was consistent with this assignment and also indicated the *x* and *z* coordinates of the remaining cation; the rest of the structure was revealed by examination of an electron-density map.

After one cycle of least-squares refinement with the five heavy atom sites assumed to be occupied entirely by iron, the conventional residual *R* factor was 0.20, and the resultant difference Fourier strongly indicated that at least some tin had to be in cation site *M*(1). After two cycles which assumed *M*(1) to be entirely occupied by tin and the other sites by iron, the *R* factor dropped to 0.16. At this point, we de-

TABLE 2. Crystallographic Data for Hulsite, Pinakiolite, and Ludwigite

	Hulsite	Pinakiolite	Ludwigite
	This paper	Moore and Araki (1974)	da Silva, Clark and Christ (1956)
Symmetry	Monoclinic	Monoclinic	Orthorhombic
Space group	*P*2/*m*	*C*2/*m*	*Pbam*
a (Å)	10.695±0.004	21.79±0.01	9.25±0.2%
b (Å)	3.102±0.001	5.997±0.05	12.21±0.2%
c (Å)	5.431±0.001	5.341±0.05	2.998±0.2%
β (°)	94.21±0.03	95.83±0.05	(90)
Cell volume (Å^3)	179.69±0.09	694.3	338.6
Z	2	8	4
Chemical formula	(1)	(2)	(3)
Density (calc.), g/cm^3	4.62	3.79	3.60
Specific gravity (obs)	4.57*	3.88**	

(1) $[(Sn^{4+}_{0.20}Fe^{3+}_{0.27})(Fe^{2+}_{0.36}Mg^{2+}_{0.16})][Fe^{3+}_{0.40}Fe^{2+}_{1.10}Mg^{2+}_{0.48}]O_2(BO_3)$

(2) $[Mg^{2+}_{1.68}Mn^{2+}_{0.09}Mn^{3+}_{1.00}Al^{3+}_{0.05}Fe^{2+}_{0.02}Mn^{4+}_{0.06}]O_2(BO_3)$

(3) $(Mg,Fe^{2+})_2(Fe^{3+},Al)O_2(BO_3)$

* Vlisidis and Schaller (1974) ** Flink (1890)

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[3] Shortly after this paper was submitted for publication, we became aware of another independent determination of the hulsite structure by Yamnova, Simonov, and Belov (1975).

TABLE 3. Chemistry of Hulsite

Vlisidis and Schaller (1974) Sample H-10-C					
Oxide	Wt. percent	Element	Atoms per formula unit	Atoms per formula unit (recalculated to B=1.00)	Positive charge
MgO	10.45	Mg	0.65	0.63	1.26
FeO	42.21	Fe^{2+}	1.47	1.43	2.86
MnO	0.74	Mn^{2+}	0.03	0.03	0.06
B_2O_3	12.98	B	0.93	1.00	3.00
Al_2O_3	1.27	Al	0.06	0.06	0.18
Fe_2O_3	20.02	Fe^{3+}	0.63	0.61	1.83
TiO_2	0.30	Ti^{4+}	0.01	0.01	0.04
SnO_2	12.03	Sn^{4+}	0.20	0.19	0.76
Σ	100.00		3.98	3.96	9.99

cided to obtain three-dimensional data to complete the refinement and perhaps to clarify the site-occupancy problem. Such data were collected with Zr-filtered Mo*Kα* radiation on a Picker automatic diffractometer for a crystal from a sample analyzed by Vlisidis and Schaller (1974). The 1196 data were corrected for Lorentz and polarization factors but not for absorption. Least-squares and site-occupancy refinements, as well as bond distance and angle calculations, were all done using programs written by L. W. Finger.

KM prepared a crystal measuring 0.20 × 0.30 × 0.20 mm for a Syntex automated diffractometer equipped with a graphite monochromator; by using Mo*Kα* radiation, reflections out to $2\theta = 60°$ were measured at a scan rate of 4.0°/min. A computer program written by C. T. Prewitt, SUNY, Stony Brook, was used to reduce the data to a set of 597 independent reflections and to apply polyhedral absorption corrections ($\mu = 100.9$ cm^{-1}). By assuming starting parameters derived from the pinakiolite structure (Takéuchi *et al*, 1950), refinement was carried out using program FLS-4, written by T. Sakurai. All cations were initially assumed to be Fe, and site preferences were determined by changing the cation multiplicities. For the final refinement, seven reflections were excluded; the final R was 0.057. The final positional and thermal parameters obtained by KM are given in Table 4; their calculated and observed structure factors are compared in Table 5. Bond distances and angles are given in Tables 6 and 7.

Structure of hulsite

Moore and Araki (1974) included hulsite in the family of structures they referred to as the "3Å fiber-axis wallpaper structures." Their Figure 1a illustrates an idealized arrangement of octahedral columns and BO_3 triangles mapped on a triangular tessellation for hulsite, warwickite, and wightmanite. Here we would like to consider the three-dimensional nature of the hulsite structure and show how it differs from members of the ludwigite–vonsenite series despite the similarity in chemistry.

The three-dimensional structure of hulsite is built up of octahedral sheets linked by isolated boron–oxygen triangles. The sheets are parallel to (100), corresponding to the platy habit of the crystals. A view of the structure looking along the sheets is shown in Figure 1.

There are two crystallographically distinct octahedral sheets, the $M(1)$–$M(4)$ sheet at $x = 0$, and the $M(2)$–$M(3)$–$M(5)$ sheet at $x = \frac{1}{2}$. Chains of octahedra, formed by the sharing of edges that are perpendicular to (100), run parallel to the fiber ($=c$) axis. These chains in turn share edges to build up infinite octahedral sheets. The $M(1)$ octahedron at $z = 0$ shares an O(4)–O(4)′ edge (2.708Å) with its counterpart one cell translation along b to form the $M(1)$ chains; the $M(4)$ chain at $z = \frac{1}{2}$ forms by $M(4)$ octahedra sharing an O(1) = O(1)′ edge (3.093Å). The $M(1)$–$M(4)$ chains link into a sheet by sharing an O(1)–O(4) edge (2.778Å). At $x = \frac{1}{2}$, $M(3)$ chains at $z = 0$ are formed by sharing O(5)–O(5)′ edges (2.800Å), $M(2)$ chains at $z = \frac{1}{2}$, by sharing another O(5)–O(5) edge (2.789Å); the two chains form a sheet by sharing a third O(5)–O(5) edge equal in dimension to the b axis. This second sheet differs from the first by further sharing edges with a fifth octahedral chain, $M(5)$, formed by sharing O(2)–O(3) edges (3.036Å). The $M(5)$ chains alternate at the edges of the

TABLE 4. Positional and Thermal Parameters for Hulsite

Atom	Position number, Wyckoff notation[1] P2/m	Cation assignment	Coordinates x	y	z	Isotropic temperature factor B(Å^2)
M(1)	1a	$Sn^{4+}_{0.20}, Fe^{3+}_{0.27}$	0	0	0	0.14
M(2)	1g	$Fe^{3+}_{0.20}, Fe^{2+}_{0.30}$	0.5	0	0.5	0.11
M(3)	1d	$Fe^{3+}_{0.20}, Fe^{2+}_{0.30}$	0.5	0	0	0.21
M(4)	1f	$Fe^{2+}_{0.36}, Mg_{0.16}$	0	0.5	0.5	0.11
M(5)	2n	$Fe^{2+}_{0.50}, Mg_{0.48}$	0.2747(2)	0.5	0.2187(4)	0.17
B	2m		0.241(1)	0	0.711(2)	0.18
O(1)	2m		0.112(1)	0	0.697(1)	0.42
O(2)	2m		0.305(1)	0	0.502(1)	0.59
O(3)	2m		0.305(1)	0	0.943(1)	0.30
O(4)	2n		0.091(1)	0.5	0.187(1)	0.37
O(5)	2n		0.469(1)	0.5	0.246(1)	0.32

1. Henry and Lonsdale (1952): space group no. 10, 2nd setting.

TABLE 5. Comparison of Observed and Calculated Structure Factors for Hulsite

k	l	F_{obs}	F_{calc}
$h = 0$			
0	1	37.34	42.31
0	2	81.32	76.84
0	3	-19.34	15.11
0	4	170.88	171.69
0	5	27.43	26.38
0	6	65.32	62.99
0	7	-17.58	18.44
1	-7	51.55	54.31
1	-6	58.35	60.20
1	-5	-11.86	12.80
1	-4	42.23	41.72
1	-2	178.28	182.41
1	-1	48.42	49.96
1	0	89.98	78.61
1	3	111.85	113.02
2	-6	51.42	54.11
2	-3	-9.57	9.56
2	-2	55.97	57.95
2	-1	25.62	26.19
2	0	255.41	248.77
2	4	130.36	129.42
2	5	21.48	22.21
3	-5	-6.22	6.04
3	0	38.93	38.19
3	4	29.41	30.56
3	3	64.71	65.37
3	2	94.70	94.74
3	1	29.94	29.45
3	5	-6.45	6.04
4	0	110.37	120.04
4	1	14.26	14.14
4	2	32.51	33.94
$h = 1$			
0	-7	-10.71	11.12
0	-6	-52.99	51.31
0	-5	-20.99	18.36
0	-4	77.37	72.26
0	-3	29.78	26.50
0	-2	-30.12	26.17
0	0	3.50	3.88
0	1	20.15	20.15
0	2	41.50	38.51
0	3	-77.20	76.40
0	4	-45.55	43.55
0	6	8.51	10.65
0	7	-27.67	29.63
1	-7	-29.78	33.08
1	-6	53.00	54.01
1	-5	-14.99	12.60
1	-4	9.23	9.05
1	-3	-117.00	120.96
1	-2	113.03	115.36
1	-1	39.34	37.33
1	0	45.69	43.19
1	1	-177.54	175.98
1	2	62.62	59.88
1	3	-36.92	37.65
1	4	28.70	34.53
1	6	5.89	6.57
1	7	-30.26	39.25
2	-6	-39.54	42.55
2	-5	-14.52	16.59
2	-4	47.54	52.93
2	-3	16.04	16.86
2	-2	-19.17	19.10
2	-1	-49.61	49.34
2	0	7.67	6.64
2	1	20.12	17.11
2	2	24.01	22.56
2	3	-55.40	53.55
2	4	-32.72	32.29
2	6	6.90	9.47
3	-5	-11.01	11.94
3	-4	6.59	5.02
3	-3	-67.68	71.48
3	-2	56.32	58.16
3	-1	9.27	9.61
3	0	24.57	22.92
3	1	-99.50	89.37
3	2	33.68	32.06
3	3	-22.82	20.17
3	4	23.49	21.04
3	5	-49.66	50.58
4	-2	-10.50	11.98
4	-1	-25.98	27.05
4	1	7.64	5.18
4	2	13.53	10.42
4	3	-34.06	33.91
$h = 2$			
0	-7	44.18	41.82
0	-6	89.53	78.84
0	-4	81.33	71.56
0	-3	85.70	75.72
0	-2	167.24	185.99
0	-1	-6.31	5.59
0	1	50.15	49.43
0	2	137.96	127.61
0	3	9.87	10.80
0	4	82.72	80.64
0	5	7.78	6.55
0	6	70.78	69.82
0	7	27.50	27.79
1	-7	8.39	9.76
1	-6	51.18	49.03
1	-5	96.21	92.44
1	-4	63.21	60.44
1	-3	49.26	51.44
1	-2	53.44	57.94
1	-1	75.10	80.89
1	0	85.92	86.74
1	1	97.58	96.33
1	2	29.13	30.06
1	3	40.48	42.54
1	4	59.74	68.39
1	5	49.47	57.05
1	6	18.98	24.18
1	7	22.32	25.58
2	-6	64.36	68.02
2	-5	-5.85	2.27
2	-4	52.43	56.57
2	-3	48.85	52.09
2	-2	134.91	133.19
2	-1	-6.86	4.93
2	0	74.48	70.01
2	1	32.51	30.67
2	2	117.73	105.06
2	3	11.41	8.24
2	4	62.93	61.13
2	6	51.07	61.79
3	-5	58.73	65.26
3	-4	38.28	43.28
3	-3	24.35	26.02
3	-2	34.33	35.25
3	-1	50.65	47.90
3	0	65.45	60.50
3	1	51.93	46.48
3	2	25.22	20.36
3	3	29.07	24.73
3	4	51.31	51.26
3	5	40.15	42.44
4	-2	69.31	77.56
4	-1	-5168	2.98
4	0	37.61	37.54
4	1	17.99	16.85
4	2	68.72	67.58
$h = 3$			
0	-7	6.06	4.97
0	-6	7.10	5.67
0	-5	-13.06	10.16
0	-3	-22.15	23.83
0	-2	-40.97	44.83
0	0	-28.66	35.89
0	2	-32.93	28.98
0	3	39.99	34.37
0	5	-29.48	25.88
0	6	-22.37	21.73
0	7	12.75	12.53
1	-7	-23.05	24.27
1	-5	-55.83	47.78
1	-4	44.16	40.80
1	-3	-41.34	40.60
1	-2	-8.58	8.88
1	-1	-90.54	89.98
1	0	39.07	36.54
1	1	-59.64	55.13
1	2	27.73	24.05
1	3	-74.69	69.64
1	4	15.09	16.43
1	5	-8.54	9.14
1	6	34.17	38.12
1	7	-34.08	37.18
2	-5	-10.00	10.73
2	-4	-26.71	26.08
2	-3	-20.02	18.73
2	-2	-18.48	15.62
2	0	-27.21	22.59
2	1	-48.34	42.47
2	2	-17.83	14.71
2	3	25.05	24.67
2	5	-23.78	23.97
2	6	-18.41	19.38
3	-5	-34.92	36.30
3	-4	24.88	27.79
3	-3	-22.30	24.28
3	-1	-63.60	58.05
3	0	29.70	28.95
3	1	-27.30	23.44
3	2	18.64	16.26
3	3	-56.24	49.71
3	4	11.68	10.09
3	5	-7.52	9.45
4	-2	-7.71	3.62
4	0	-11.12	10.79
4	1	-26.27	28.01
4	2	-9.28	8.36
$h = 4$			
0	-7	-7.29	7.36
0	-6	73.45	60.64
0	-5	30.81	27.10
0	-4	96.67	96.53
0	-3	-28.82	28.73
0	-2	103.67	116.26
0	-1	49.02	53.11
0	0	183.19	206.50
0	1	7.05	8.13
0	2	106.96	91.60
0	3	24.87	23.99
0	4	176.34	163.20
0	5	36.89	34.60
0	6	37.39	37.75
0	7	-10.16	10.46
1	-7	39.93	38.83
1	-6	34.81	33.28
1	-5	19.21	16.16
1	-4	45.84	42.98
1	-3	70.37	69.85
1	-2	101.12	104.13
1	-1	28.22	30.81
1	0	41.62	42.11
1	1	109.53	107.87
1	2	152.85	152.37
1	3	55.55	55.21
1	4	22.76	22.51
1	5	32.16	33.47
1	6	67.28	73.22
1	7	48.95	53.92
2	-6	50.58	53.22
2	-5	22.41	24.07
2	-4	78.03	78.32
2	-3	-21.14	21.96
2	-2	83.20	80.66
2	-1	40.47	38.73
2	0	149.50	143.98
2	2	68.07	64.41
2	3	18.06	16.80
2	4	121.59	128.29
2	5	25.69	29.05
2	6	29.31	33.65
3	-5	11.80	11.33
3	-4	30.98	32.87
3	-3	45.49	47.15
3	-2	63.85	62.34
3	-1	18.42	17.41
3	0	30.94	27.23
3	1	62.62	56.97
3	2	95.31	88.31
3	3	39.10	36.79
3	4	19.62	19.76
3	5	22.42	24.06
4	-2	45.51	46.19
4	-1	23.90	23.24
4	0	86.12	82.42
4	1	7.04	3.51
4	2	40.33	38.55
$h = 5$			
0	-7	-32.17	27.42
0	-6	-29.41	29.06
0	-5	-16.57	16.41
0	-4	46.97	52.14
0	-3	-7.50	8.49
0	-2	-54.35	55.23
0	-1	-67.24	65.96
0	0	116.97	118.34
0	1	49.00	44.78
0	2	-23.34	18.52
0	3	-54.82	73.65
0	4	8.53	11.10
0	5	13.38	13.40
0	6	16.91	13.38
0	7	-40.39	40.93
1	-7	-29.15	26.77
1	-6	45.28	42.28
1	-5	-56.70	55.43
1	-4	-5.81	2.95
1	-3	-60.06	61.55
1	-2	107.56	114.05
1	-1	-29.64	30.11
1	0	30.27	29.82
1	1	-129.20	131.53
1	2	87.55	84.54
1	3	10.81	11.89
1	4	36.74	39.10
1	5	-92.66	94.85
1	6	13.65	13.18
2	-6	-22.80	25.86
2	-5	-13.67	14.90
2	-4	38.36	39.40
2	-3	-8.09	6.18
2	-2	-39.47	38.13
2	-1	-45.09	43.49
2	0	72.64	71.95
2	1	27.04	28.47
2	2	-14.50	11.28
2	3	-57.54	54.98
2	4	6.09	6.36
2	5	8.60	9.06
2	6	12.47	10.73
3	-5	-38.60	39.96
3	-4	-5.35	3.44
3	-3	-41.27	42.17
3	-2	66.53	63.37
3	-1	-18.30	17.28
3	0	14.71	14.39
3	1	-81.97	76.34
3	2	51.96	48.63
3	3	6.27	2.96
3	4	22.52	23.75
4	-1	-25.13	26.07
4	0	38.03	33.60
4	1	11.22	10.04
$h = 6$			
0	-7	27.25	27.44
0	-6	43.54	43.24
0	-5	-19.82	17.16
0	-4	107.13	110.56
0	-3	68.07	70.28
0	-2	145.03	150.22
0	-1	-33.28	30.28
0	0	87.21	91.62
0	1	50.59	51.62
0	2	192.52	180.33
0	3	-20.76	17.60
0	4	46.50	40.96
0	5	6.82	5.04
0	6	80.86	82.38
1	-7	9.96	7.62
1	-6	61.20	57.22
1	-5	82.62	81.25
1	-4	51.49	51.39
1	-3	-10.80	9.86
1	-2	71.46	78.37
1	-1	127.22	137.04
1	0	102.37	111.43
1	1	8.54	8.63
1	2	44.62	43.13
1	3	47.53	46.19
1	4	72.42	71.13
1	5	37.26	34.09
1	6	18.55	20.02
2	-6	38.11	38.23
2	-5	-12.16	12.03
2	-4	87.22	87.62
2	-3	51.96	52.39
2	-2	107.06	110.80
2	-1	-23.19	22.15
2	0	66.20	67.71
2	1	38.93	37.85
2	2	131.58	134.53
2	3	-11.29	12.80
2	4	33.58	35.29
2	5	6.99	6.07
3	-4	36.36	37.41
3	-2	53.46	50.79
3	-1	80.79	78.00
3	0	68.52	65.47
3	1	9.71	8.12
3	2	31.76	31.24
3	3	32.19	32.70
3	4	49.51	53.62
4	0	40.17	41.54
$h = 7$			
0	-7	18.30	17.77
0	-6	21.72	20.80
0	-5	-17.93	18.63
0	-4	-48.55	46.96
0	-3	11.20	12.26
0	-2	39.70	36.92
0	-1	-16.30	16.71
0	0	-45.09	47.94
0	1	-22.52	23.65
0	2	-12.17	16.26
0	3	-8.69	7.50
0	4	-7.66	5.25
0	5	-28.11	26.36
0	6	-23.30	21.56
1	-6	6.65	2.62
1	-5	-9.56	9.66
1	-4	41.15	45.92
1	-3	-29.91	31.00
1	-1	-74.78	76.20
1	0	47.73	49.82
1	1	-20.54	19.82
1	2	-6.20	1.84
1	3	-81.48	75.73
1	4	28.29	26.97
1	5	-24.46	24.01
2	-6	21.49	17.82
2	-5	-17.57	17.86
2	-4	-39.76	38.31
2	-3	8.18	7.52
2	-2	28.69	29.67
2	-1	-11.84	13.07
2	0	-34.66	33.74
2	1	-20.76	19.00
2	2	-11.32	9.07
2	3	-8.19	6.91
2	5	24.20	24.58
3	-4	32.87	31.02
3	-3	-22.75	24.06
3	-1	-50.45	49.24
3	0	35.14	34.02
3	1	-13.61	14.92
3	2	-6.30	3.25
3	3	-51.32	55.53
3	4	19.78	20.34
$h = 8$			
0	-6	57.82	59.60
0	-5	23.58	25.03
0	-4	69.30	67.53
0	-2	60.50	56.50
0	-1	37.87	37.43
0	0	102.83	110.23
0	1	-13.60	10.87
0	2	62.54	58.86
0	3	43.40	39.06
0	4	89.79	84.92
0	5	6.66	7.16
0	6	44.28	44.47
1	-6	15.23	15.15
1	-5	16.45	17.43
1	-4	47.47	49.53
1	-3	67.35	66.38
1	-2	29.68	29.54
1	-1	34.47	34.69
1	0	44.68	44.57
1	1	53.83	50.58
1	2	59.97	53.61
1	3	51.23	48.38
1	4	20.39	21.65
1	5	35.45	36.07
2	-5	22.39	21.93
2	-4	58.29	57.13
2	-2	47.00	47.97
2	-1	30.25	31.49
2	0	84.03	87.34
2	1	-9.14	10.32
2	2	46.13	47.55
2	3	32.99	33.03
2	4	69.49	74.37
2	5	8.88	5.99
3	-4	38.83	40.11
3	-3	47.64	47.77
3	-2	24.16	23.84
3	-1	20.56	23.84
3	0	33.04	34.36
3	1	34.55	35.83
3	2	41.24	42.06
3	3	31.04	33.77
$h = 9$			
0	-6	-24.72	22.94
0	-4	8.39	6.98
0	-3	-33.37	31.28
0	-2	-28.12	23.57
0	-1	-9.01	8.53
0	0	18.04	16.64
0	2	-16.23	13.57
0	3	-35.83	32.63
0	4	18.92	16.50
0	5	26.77	24.83
1	-6	15.25	14.38
1	-5	-32.42	33.95
1	-4	-4.72	0.81
1	-3	-50.50	48.00
1	-2	52.09	51.97
1	-1	-36.37	34.94
1	0	-9.42	8.25
1	1	-56.27	52.99
1	2	75.48	70.44
1	3	-19.01	16.79
1	5	-47.35	49.04
2	-4	6.53	6.34
2	-3	-26.40	27.67
2	-2	-19.44	20.75
2	-1	-8.32	8.06
2	0	15.76	13.75
2	2	-12.66	11.61
2	3	-27.88	29.15
2	4	15.31	13.30
3	-3	-36.65	35.55
3	-2	33.82	35.62
3	-1	-23.73	25.20
3	0	-6.98	7.79
3	1	-37.42	40.20
3	2	45.73	47.87
$h = 10$			
0	-6	42.43	38.41
0	-5	-10.25	8.78
0	-4	83.44	76.90
0	-3	40.58	38.61
0	-2	74.09	73.82
0	-1	-35.43	38.09
0	0	94.28	102.39
0	1	58.73	62.48
0	2	99.81	97.46
0	3	-29.66	30.11
0	4	52.35	53.19
0	5	21.91	22.36
1	-5	35.47	35.53
1	-4	19.59	18.54
1	-3	13.46	12.28
1	-2	75.89	73.32
1	-1	70.24	66.59
1	0	63.96	60.68
1	2	45.01	41.96
1	3	64.32	62.93
1	4	72.87	74.50
2	-4	66.50	66.31
2	-3	32.72	33.35
2	-2	61.53	62.23
2	-1	-27.27	28.45
2	0	79.72	81.80
2	1	49.99	51.09
2	2	80.17	81.80
2	3	-23.00	23.91
2	4	46.06	46.55
3	-2	56.61	53.75
3	-1	46.62	47.95
3	0	43.82	44.80
$h = 11$			
0	-5	-39.21	36.26
0	-4	-10.76	9.72
0	-3	21.98	19.58
0	-2	33.29	32.45
0	-1	-24.05	24.98
0	0	-29.77	30.60
0	1	-15.11	16.63
0	2	35.41	36.48
0	3	-7.60	5.54
0	4	-27.16	26.88
1	-5	-5.36	3.93
1	-4	44.05	39.24
1	-3	-55.25	52.89
1	-2	-7.07	4.01
1	-1	-15.95	14.95
1	0	74.46	69.99
1	1	-44.22	42.99
1	2	-8.07	7.62
1	3	-49.83	50.35
1	4	35.80	35.93
2	-4	-7.30	9.10
2	-3	17.55	15.15
2	-2	27.66	26.02
2	-1	-22.18	22.32
2	0	-24.54	25.14
2	1	-13.37	14.92
2	2	29.75	29.73
2	3	-6.19	5.69
$h = 12$			
0	-5	23.46	20.63
0	-4	28.87	28.62
0	-2	77.61	77.79
0	-1	32.06	34.45
0	0	49.96	53.24
0	1	-11.07	12.03
0	2	45.70	48.44
0	3	19.46	18.66
0	4	58.97	60.51
1	-4	59.14	54.53
1	-3	53.22	48.73
1	-2	22.32	20.48
1	-1	11.54	11.04
1	0	42.05	41.18
1	-2	20.88	20.48
1	0	40.68	41.18
1	1	52.45	52.84
1	2	32.05	34.60
1	3	10.81	9.62
2	-2	66.25	67.55
2	-1	28.30	29.55
2	2	42.16	43.29
2	2	42.41	43.29
$h = 13$			
0	-3	-16.48	19.10
0	-2	-27.00	26.72
0	1	-13.28	13.78
0	2	-21.72	22.01
0	3	-7.73	9.13
1	-3	-15.71	13.88
1	-2	19.09	17.30
1	-1	-31.00	31.19
1	1	-36.38	35.85
1	2	22.17	21.74
2	-2	-25.05	23.21
2	0	6.90	4.53
2	0	5.94	4.53
2	1	-15.02	13.52
$h = 14$			
0	-3	10.78	12.17
0	-2	42.40	42.57
0	0	48.51	52.29
0	1	27.97	27.69
0	2	54.36	55.42
1	-2	45.59	42.13
1	-1	40.37	38.11
1	0	22.57	19.95
1	1	15.10	14.43
$h = 15$			
0	-1	-33.24	33.99

M(2)–M(3) sheet (Fig. 1), sharing an O(3)–O(5) edge (2.787Å) with M(3) and an O(2)–O(5) edge (2.787Å) with M(2). The M(5) chains help link the two sheets by sharing O(4) corners with the M(1)–M(4) sheet. The BO_3 triangles fit into the remaining space, linking O(1) to the M(1)–M(4) sheet and O(2) plus O(3) to the M(2)–M(3)–M(5) sheet. Note that the M(1)–M(4) sheet is linked only by two corner oxygen atoms to the other structural elements and may thus be expected to provide more flexibility than the other sheet for multiple cation content.

Chemistry of hulsite

The results of the chemical analyses in Table 3 were used in site-occupancy studies. KACF carried out

TABLE 6. Bond Distances (Å) for Hulsite

M(1) octahedron – Sn^{4+},Fe^{3+}

O(1)	2.105(8)	x 2
O(4)	2.059(5)	x 4
ave.	2.074	

Oxygen atom	x	y	z	O-O distance		
O(1)	.112	0	-.303	O(1)-O(4)	2.778(12)	x 4
O(4)	-.091	.5	-.187	O(4)-O(4)'	2.708(11)	x 2
O(4)'	.091	.5	.187	O(1)-O(4)'	3.118(12)	x 4
				ave.	2.900	

M(2) octahedron – Fe^{2+},Fe^{3+}

O(2)	2.086(11)	x 2
O(5)	2.086(3)	x 4
ave.	2.086	

Oxygen atom	x	y	z			
O(2)	.305	0	.502	O(2)-O(5)'	2.788(11)	x 4
O(5)	.531	.5	.754	O(5)-O(5)'	2.789(8)	x 2
O(5)'	.469	.5	.246	O(2)-O(5)	3.104(12)	x 4
				ave.	2.946	

M(3) octahedron – Fe^{2+},Fe^{3+}

O(3)	2.086(4)	x 2
O(5)	2.089(11)	x 4
ave.	2.088	

Oxygen atom	x	y	z			
O(3)	.305	0	.057	O(3)-O(5)	2.787(10)	x 4
O(5)	.469	.5	.246	O(5)-O(5)'	2.800(9)	x 2
O(5)'	.531	.5	.246	O(3)-O(5)'	3.109(13)	x 4
				ave.	2.949	

M(4) octahedron – Fe^{2+},Mg

O(4)	2.020(8)	x 2
O(1)	2.190(6)	x 4
ave.	2.133	

Oxygen atom	x	y	z			
O(4)	.091	.5	.187	O(4)-O(1)	2.778(12)	x 4
O(1)	-.112	0	.303	O(1)-O(1)'	3.093(12)	x 2
O(1)'	.112	0	.697	O(4)-O(1)'	3.168(7)	x 4
				ave.	3.015	

M(5) octahedron – Fe^{2+},Mg

O(4)	1.959(11)	
O(5)	2.072(11)	
O(2)	2.192(4)	x 2
O(3)	2.196(5)	x 2
ave.	2.135	

Oxygen atom	x	y	z	O-O distance		
O(3)	.305	0	-.057	O(3)-O(5)	2.787(10)	x 2
O(2)	.305	0	.502	O(2)-O(5)	2.788(11)	x 2
O(4)	.091	.5	.187	O(2)-O(3)	3.036(8)	x 2
O(5)	.469	.5	.246	O(3)-O(4)	3.138(12)	x 2
				O(2)-O(4)	3.162(11)	x 2
				ave.	2.982	

B triangle

O(1)	1.376(15)
O(2)	1.368(14)
O(3)	1.389(12)
ave.	1.378

Oxygen atom	x	y	z		
O(1)	.112	0	.697	O(1)-O(2)	2.388(14)
O(2)	.305	0	.502	O(1)-O(3)	2.375(13)
O(3)	.305	0	.943	O(2)-O(3)	2.395(8)
				ave.	2.386

Error in parentheses is one standard deviation; for 2.105(8) read 2.105±0.008Å, etc.

least-squares site-occupancy refinements using various cation assignments; KM varied cation multiplicities during the refinements. The results agree and indicate that the tin is in cation site *M*(1), together with iron. Mössbauer results by Alexsandrov, Malysheva, and Rodin (1967) indicate that the tin is in the quadrivalent state; Alexsandrov also concludes that the quadrivalent tin is replacing trivalent iron. Fe^{3+}–O distances average about 2.025Å (in acmite, for example). Sn^{4+}–O distances in comparable structures are not available, but the sum of the ionic radii, 0.71 + 1.40, is 2.11 Å. The average *M*(1)–O bond distance is the shortest average *M*–O of the structure (2.078 Å) and appears to be in accord with the cation assignment and the Mössbauer results. The balance of the iron is distributed over the four cation sites, the refinements suggesting that *M*(2) and *M*(3) contain chiefly iron and that *M*(4) and *M*(5) contain a mixture of magnesium and iron, the latter probably in the ferrous state. The longer average *M*–O bond distances, 2.125 Å in *M*(4) and 2.135 Å in *M*(5), support the assumption of ferrous iron here, a normal average Fe^{2+}–O being about 2.13–2.15 Å. The overall cation assignment does ascribe the greatest variety of cations (Sn^{4+}, Fe^{3+}, Fe^{2+}, and Mg) to the *M*(1)–*M*(4) sheet in accord with the earlier observation that this sheet has a larger number of symmetrically non-equivalent *M* sites than the other sheet.

The microprobe analysis shows the presence of about 1 wt percent calcium oxide distributed uniformly over the sample. The chemical analyses of various hulsite samples by Vlisidis and Schaller (1974) also show up to 1.32 wt percent CaO. Calcium has a much larger ionic radius than tin, iron, or magnesium (1.00 Å for Ca^{2+} compared with 0.69 Å for Sn^{4+}, 0.55 Å for Fe^{3+}, 0.61 Å for Fe^{2+}, and 0.72 Å for Mg^{2+}; Shannon and Prewitt, 1969); therefore it seems unlikely that the hulsite structure can accommodate appreciable amounts of calcium. Thus, the chemical analyses fail to resolve whether the calcium is truly incorporated into the structure or whether it is present as an impurity. Omitting calcium, the idealized chemical formula of these hulsites can be writ-

TABLE 7. Bond Angles for Hulsite

Angles around M(1)

O(1), O(4)	83.7(3)°	x 4
O(4), O(4)'	82.2(2)	x 2
O(1), O(4)'	96.3(3)	x 4

Angles around M(2)

O(2), O(5)	83.9(3)	x 4
O(5), O(5)'	83.9(2)	x 2

Angles around M(3)

O(3), O(5)	83.7(3)	x 4
O(5), O(5)'	84.1(2)	x 2

Angles around M(4)

O(1), O(4)	82.5(3)	x 4
O(1), O(1)'	89.8(2)	x 2

Angles around M(5)

O(4), O(5)	179.1(9)	
O(2), O(3)	87.5(2)	x 2
O(3), O(5)	81.5(2)	x 2
O(2), O(5)	81.6(3)	x 2
O(2), O(3)	163.1(4)	x 2
O(2), O(4)	99.0(3)	x 2
O(3), O(4)	97.9(3)	x 2

Angles around B

O(1), O(2)	119.8(3)
O(1), O(3)	119.4(7)
O(2), O(3)	120.7(8)
Σ	359.9

Error in parentheses is one standard deviation; for 83.4(2), read 83.4±0.2°, etc.

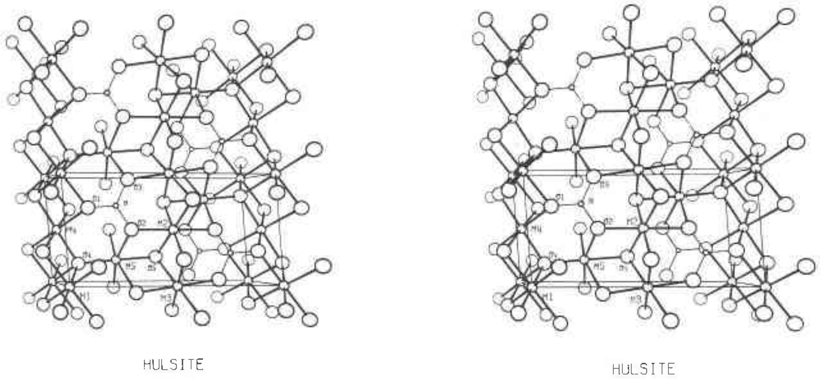

FIG. 1. Stereoscopic-pair view of hulsite looking along b^*. The cell outline is shown with the origin at the lower left, a horizontal. Drawing produced with ORTEP (Johnson, 1965).

ten in a structural way as $[Sn^{4+}_{0.2}Fe^{3+}_{0.3}(Fe^{2+},Mg)_{0.5}]$ $[Fe^{3+}_{0.4}(Fe^{2+},Mg)_{1.6}]O_2(BO_3)$, where the cation compositions of the two sheets are bracketed separately. The range of variation in these elements (and no doubt others of the right size) that can be accommodated without altering the hulsite structural characteristics is not yet established beyond the 28 wt percent upper limit for tin found by Diman and Nekrasov (1969). Apparently this limit corresponds to substituting Sn^{4+} for Fe^{3+} in the first bracket of the formula, so that $M(1)$ would be entirely occupied by tin and the charge would be adjusted by having all ferrous iron, all magnesium, or a mixture of (Fe^{2+},Mg). Thus, compounds having formulas $Sn^{4+}_{0.5}Mg_{2.5}O_2(BO_3)$, $Sn^{4+}_{0.5}Fe^{2+}_{2.5}O_2(BO_3)$, and combinations, as well as $(Sn^{4+},Fe^{3+})_{0.5}(Fe^{3+},Fe^{2+},Mg)_{2.5}O_2(BO_3)$, can be hypothesized.

Comparison of hulsite with pinakiolite and ludwigite

The relationship of hulsite to pinakiolite, $Mg_2Mn^{3+}O_2(BO_3)$, has been discussed by Moore and Araki (1974), who redetermined the structure of pinakiolite and called it an ordered derivative of the hulsite structure. Considering their pinakiolite data in terms of our description of hulsite, we find in pinakiolite Mg(3)–Mn(3) sheets of composition $0.50Mn^{3+}$, $0.42Mg^{2+}$, and $0.08Mn^{4+}$. These sheets correspond to the hulsite $M(1)$–$M(4)$ sheets (first bracket of the hulsite formula). The sheet corresponding to hulsite's $M(2)$–$M(3)$–$M(5)$ sheet (second bracket of the hulsite formula) has become more complex in pinakiolite. It holds Mn(1)–Mn(2)–Mg(1)–Mg(2)–Mg(4), giving it a composition of $0.50Mn^{3+}$, 1.39Mg, $0.01Mn^{4+}$ $(Fe^{3+}?)$, and 0.10 vacancy. The ordering within this sheet is responsible for the C-centered cell and the doubled a and b axes of pinakiolite.

Turning to the ludwigite-vonsenite series, so similar chemically to hulsite but having orthorhombic *Pbam* symmetry, we find a different structure, as previously referenced. This series also has octahedral chains sharing edges parallel to the fiber-axis direction (c), but in this case four crystallographically distinct chains share edges to form a corrugated sheet parallel to (010). The structure is composed of this single sheet, repeated by the a glide plane. The sheets are held together by sharing corners with octahedra of adjacent sheets and, as usual, with corners of the BO_3 triangles.

Further structural and chemical studies of these interesting and curious 3Å fiber-axis wallpaper structures and their accommodating octahedral chains and sheets should reveal many crystal-chemical effects caused by the various cations that the structures can contain.

Acknowledgments

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