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The Crystal Structure of Braunite with Reference to Its Solid-Solution Behavior

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Abstract

The crystal structure of braunite ($Mn^{2+}Mn_6^{3+}SiO_{12}$) has been determined by single-crystal X-ray diffractometry. The crystal from Langban, Sweden, has a composition of $Ca_{0.01}Mg_{0.13}Al_{0.02}Fe_{0.17}Mn_{6.72}Si_{0.96}O_{12}$ and is tetragonal, space group $I4_1/acd$, with cell dimensions $a = 9.432(2)$Å, $c = 18.703(7)$Å, $Z = 8$. The structure was refined by least squares using anisotropic thermal parameters to a conventional $R = 0.025$, and consists of units of six cations arranged octahedrally around vacant sites. The Mn^{2+} ion has distorted cubic coordination, the Si^{4+} has tetrahedral coordination, and the three non-equivalent Mn^{3+} ions have distorted octahedral coordinations. The mechanism of silica substitution in the structure is discussed.

Introduction

Braunite ($Mn^{2+}Mn_6^{3+}SiO_{12}$) is one of the more common manganese ore minerals that usually occur in association with bixbyite, hausmannite, and pyrolusite in deposits such as Langban and Jakobsberg in Sweden, as well as in the Postmasburg and Kalahari manganese deposits of South Africa. In the latter deposits it occurs as the principal manganese mineral.

The first structure analysis of braunite was made by Byström and Mason (1943), who determined the basic structure and established its correct formula. The structure analysis was based on space group $I\bar{4}c2$. However, P. R. de Villiers and Herbstein (1967) determined the space group to be $I4_1/acd$, so that the above structure cannot be entirely correct.

The structure of the compound $CaMn_6SiO_{12}$ was determined by Damon, Permingeat, and Protas (1966) on the basis of space group $I4_1/acd$. Unfortunately, this structure was not fully refined, but it conforms closely to that of braunite.

In a study of the phase equilibria in the system manganese oxide–silica in air, Muan (1959) determined the existence of a stable silica-containing phase with the α-Mn_2O_3 structure. The SiO_2 content of this phase can vary from zero to approximately 40 wt percent silica. This compositional field encompasses the α-Mn_2O_3 structure as well as the braunite structure. Since α-Mn_2O_3 is orthorhombic with space group *Pcab* (Geller, 1971) and braunite is tetragonal, this cannot be a true single-phase field.

The present study was initiated to determine the crystal structure of braunite and its relationship to the α-Mn_2O_3 structure. The occurrence of an apparently stable phase field with varying amounts of SiO_2 must also be explained.

Experimental

Difficulty was encountered in obtaining single crystals of suitable quality. Finally, good-quality braunite crystals showing no lineage structure were chosen from the Langban locality in Sweden. The sample was obtained from the U.S. National Museum of Natural History, labelled U.S.N.M. No. 95307. The composition given in Table 1 was determined by microprobe analysis and calculated on the basis of 12 oxygen atoms. Weight percentages of the elements are 0.08 Ca, 0.54 Mg, 0.09 Al, 61.30 Mn, 1.64 Fe, and 4.48 Si.

X-ray measurements were carried out on a ground sphere (see Table 1 for dimensions) mounted on a Philips P.W. 1100 computer-controlled four circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation. The cell dimensions were obtained from least squares analysis of the angular measurements of 25 reflections with 2θ in the region of 40°.

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TABLE 1. Crystal Data of Braunite

Composition : $Ca_{0.01}Mg_{0.13}Al_{0.02}Fe_{0.17}Mn_{6.72}Si_{0.96}O_{12}$	
a (Å)	9.432(2)*
c (Å)	18.703(7)
Space group	$I4_1/acd$
Z	8
ρ_{calc} (g cm^{-3})	4.80
ρ_{obs}	4.77
μ (cm^{-1})	108.2
Crystal diameter (cm)	0.035 ± 0.002
Number of reflections	
Observed	486
Unobserved	108

*Figures in parenthesis represent estimated standard deviations in terms of the last decimal.

The cell data are given in Table 1. The intensities of a unique set of diffractions up to $2\theta = 54.8°$ were collected by the $\omega/2\theta$ scan technique, and the background was measured at the ends of each scan range. The systematically absent reflections are as follows:

hkl reflections : $h + k + l \neq 2n$
$hk0$ reflections : $h \neq 2n$
$0kl$ reflections : $k \neq 2n$
hhl reflections : $2h + l \neq 4n$

This uniquely defines space group $I4_1/acd$ since the *550* reflection, mentioned by Byström and Mason (1943) as being present in braunite, could not be detected.

Corrections for spherical absorption and Lp corrections were applied. The significance level of 5 percent was taken as the criterion for the determination of unobserved reflections ($I \leq 1.65\ \sigma(I)$ where I is the observed intensity.)

The crystallographic programs used were those of the X-ray system of programs (Stewart *et al.*, 1972). The drawings were produced by the program ORTEP (Johnson, 1970).

The structure proposed by Byström and Mason (1943) was verified as correct by Patterson and Fourier methods, and refinement was initiated using space group $I4_1/acd$, and variation of positional and isotropic thermal parameters. The quantity minimized is $R(F) = \Sigma\ \omega(|Fo| - |Fc|)^2$. Scattering factors of neutral atoms were obtained from *International Tables,* vol. III. The conventional R factor decreased to $R = 0.193$, and the temperature factors of all the atoms immediately became negative. The standard deviations of the positional parameters were also excessively high. Examination of the reflection data showed that the low-angle, high-intensity reflections are consistently measured too low.

Refinement then proceeded with a correction for anomalous dispersion, the values being taken from Cromer and Liberman (1970), and with refinement of the extinction parameter g (Larson, 1967). Refinement with isotropic thermal parameters rapidly converged to an R factor $R = 0.041$, with acceptable positional standard deviations and reasonable temperature factors. Refinement of positional and anisotropic thermal parameters, as well as the isotropic extinction parameter, was terminated at $R = 0.025$. The final positional standard deviations have values one-tenth of those determined without isotropic extinction refinement. The value of the extinction parameter is given in Table 2. Because of the similarity of the Mn and Fe scattering factors, and because of the small amounts of Ca, Mg, and Al present, no attempt was made to refine cation occupancies. Final positional parameters with estimated standard deviations are given in Table 2. The anisotropic thermal parameters are given in Table 3, interatomic distances and angles in Table 4, and observed and calculated structure factors are compared in Table 5.

TABLE 2. Positional Coordinates of the Atoms in Braunite

Atom†	Site symmetry		x	y	z
M(1)	222	$Ca_{0.01}Mg_{0.13}Mn_{0.86}$	0	$\frac{1}{4}$	$\frac{1}{8}$
M(2)	$\bar{1}$	$Fe_{0.03}Mn_{0.97}$	0	0	0
M(3)	2	$Fe_{0.03}Mn_{0.97}$	0.03365(8)††	0	$\frac{1}{4}$
M(4)	2	$Fe_{0.03}Mn_{0.97}$	0.23250(5)	0.48250(*)	$\frac{1}{8}$
Si	$\bar{4}$	Si	0	$\frac{1}{4}$	$\frac{3}{8}$
O(1)	1		0.1494(2)	0.3549(2)	0.0544(1)
O(2)	1		0.1451(2)	0.0730(2)	0.0568(1)
O(3)	1		0.4219(3)	0.1340(2)	0.0747(1)

Refinement based on extinction parameter $g = 4.0(1) \times 10^{-3}$

†Origin on center of symmetry

††Figures in parenthesis represent the estimated standard deviations (*esd*) in terms of the lowest number of units cited for the value to their immediate left.

*A parameter so indicated is related by symmetry.

TABLE 3. Thermal Parameters in Å^2 (× 10^4) for the Atoms in Braunite

Atom	U(11)**	U(22)	U(33)	U(12)	U(13)	U(23)
M(1)	124(4)	124(*)	76(5)	-63(4)	0	0
M(2)	55(3)	64(3)	48(4)	-17(3)	- 8(3)	1(2)
M(3)	52(4)	61(3)	57(4)	0	0	10(3)
M(4)	59(3)	59(*)	47(4)	- 6(2)	4(2)	- 4(*)
Si	52(5)	52(*)	52(8)	0	0	0
0(1)	113(10)	82(10)	76(9)	- 8(8)	6(9)	-13(8)
0(2)	90(10)	74(10)	66(9)	- 9(8)	- 7(9)	7(8)
0(3)	104(11)	89(11)	81(9)	6(8)	-11(9)	-14(8)

*A parameter so indicated is related by symmetry

**The anisotropic temperature factor form is

$$T = exp[-2\pi^2(a^{*2}h^2U_{11}+b^{*2}k^2U_{22}+c^{*2}l^2U_{33}+2a^*b^*hkU_{12}+2a^*c^*hlU_{13}+2b^*c^*klU_{23})]$$

Description of the Structure

Structural Arrangement

The underlying features of the braunite structure are two three-dimensional octahedral arrangements of *cations* around vacant sites. These cation arrangements must not be confused with the coordination of oxygen atoms around each of these cations. One arrangement is shown in Figure 1(a). The Si and *M*(1) atoms are situated at the opposite ends of the distorted octahedral cation arrangement defined by the *M*(1), *M*(2), *M*(3), *M*(4), and Si atoms, and referred to as the ($Mn^{2+}Mn^{3+}_4Si$) arrangement. This occurs around the vacant sites defined by the position 0, 1/2, 1/8. The other arrangement, shown in Figure 1(c), consists of an octahedral arrangement of the *M*(2), *M*(3), and *M*(4) atoms. This arrangement, referred to as the (Mn^{3+}_6) arrangement, occurs around the vacant sites defined by 0, 1/4, 1/4 and 1/4, 0, 1/4, and is identical to the cation arrangement in α-Mn_2O_3 (Fig. 1b). Six of the ($Mn^{2+}Mn^{3+}_4Si$) octahedral cation arrangements are grouped around each of the constituent *M*(1) and Si atoms, whereas only four are arranged around the *M*(2), *M*(3), and *M*(4) atoms, the other two arrangements being the (Mn^{3+}_6) ones. The groupings of the ($Mn^{2+}Mn^{3+}_4Si$) and (Mn^{3+}_6) octahedra around the Si and *M*(3) atoms are shown in Figure 2. These arrangements have interesting implications on the substitution of silica in the structure, and will be discussed later.

The arrangement of oxygen atoms around each of the cations is as follows. The *M*(1) atom has distorted cubic coordination. The three non-equivalent *M*(2), *M*(3), and *M*(4) atomic positions each have distorted octahedral coordination, whereas the Si atom is tetrahedrally coordinated with surrounding oxygen atoms.

Coordination Polyhedra

As can be seen from Table 4, the Mn^{2+} cation is situated in a distorted cubic coordination polyhedron, with a large difference between the *M*(1)-O(1) and *M*(1)-O(2) bond lengths. The Mn^{3+} atoms are situated in three non-equivalent distorted octahedra, that around *M*(3) being the most distorted. The distortions were calculated from the formula for the variance of polyhedral angles given by Robinson, Gibbs, and Ribbe (1971) and are shown as σ^2 in Table 4.

The reason for the distortion of the *M*(3) octahedron in braunite lies in the fact that it contributes four bonds to one (Mn^{3+}_6) cation arrangement, and only two bonds to the adjacent (Mn^{3+}_6) octahedron.

TABLE 4. Interatomic Distances in Å and Angles in Degrees—Braunite

	M-0 distance*		0-0 distance		0-M-0 angle
M(1) Polyhedron					
	M(1)-0(1)	2.170[4]**	0(1)-0(2)	2.660^s	68.87
	0(2)	2.508[4]	0(1)-0(2)	2.859^s	75.98
			0(1)-0(1)	2.707^s	77.20
			0(2)-0(2)	2.588^s	62.14
	Average	2.34			
M(2) Octahedron					
	M(2)-0(1)	2.212[2]	0(1)-0(2)	2.859^s	88.70
	0(2)	1.863[2]	0(2)-0(3)	2.602^s	83.97
	0(3)	2.022[2]	0(1)-0(2)	2.924	91.30
			0(2)-0(3)	2.890	96.03
			0(1)-0(3)	3.230	99.35
			0(1)-0(3)	2.744^s	80.65
	Average	2.03	σ^2 = 45.6		
M(3) Octahedron					
	M(3)-0(1)	1.909[2]	0(1)-0(1)	2.782	93.57
	0(2)	1.984[2]	0(1)-0(3)	3.330	105.13
	0(3)	2.277[2]	0(1)-0(2)	2.660^s	86.19
			0(1)-0(3)	3.258	101.89
			0(2)-0(3)	2.695^s	78.16
			0(2)-0(3)	2.602^s	74.94
			0(2)-0(2)	2.902	94.05
	Average	2.06	σ^2 = 137.8		
M(4) Octahedron					
	M(4)-0(1)	1.951[2]	0(1)-0(3)	2.744^s	81.28
	0(2)	1.921[2]	0(1)-0(1)	2.707^s	87.85
	0(3)	2.248[2]	0(1)-0(3)	3.175	98.01
			0(1)-0(2)	2.827	93.78
			0(2)-0(3)	3.214	100.59
			0(2)-0(3)	2.695^s	80.15
			0(2)-0(2)	2.588	84.68
	Average	2.04	σ^2 = 69.1		
Si-0 Tetrahedron					
	Si-0(3)	1.620[4]	0(3)-0(3)	2.649	109.73
			0(3)-0(3)	2.637	108.95
			σ^2 = 0.2		

*Estimated standard deviation for M-0 distances are 0.002Å, for Si-0 distances 0.002Å, and for 0-0 distances 0.003Å. Estimated standard deviations for 0-M-0 and 0-Si-0 angles are 0.1 degrees

**The bond multiplicities are given in square brackets

^{s}The superscript means that this distance represents an edge shared between two polyhedra.

TABLE 5. Observed and Calculated Structure Factors for Braunite

h	k		F_o	F_c	A	B
ℓ = 0						
2	0		127.31	115.75	-120.45	-5.53
4	0		513.71	489.78	679.94	36.95
6	0		74.23	73.95	-74.01	-6.89
8	0		483.95	473.92	548.64	27.51
10	0		78.74	77.73	-77.59	-7.67
12	0		249.71	253.37	259.92	16.89
11	1	L	4.77	0.00	-0.00	-0.00
9	1	L	7.42	0.00	-0.00	-0.00
7	1		10.91	0.00	-0.00	-0.00
5	1	L	4.98	0.00	-0.00	-0.00
3	1	L	2.28	0.00	-0.00	-0.00
1	1		7.83	0.00	0.00	-0.00
2	2		48.81	42.50	42.39	4.83
4	2		11.14	3.48	2.27	2.64
6	2		56.75	55.50	55.53	3.71
8	2		114.43	116.10	-117.05	-3.93
10	2		10.19	3.24	0.91	3.11
12	2		143.35	139.42	-140.23	-9.83
11	3	L	6.32	0.00	0.00	0.00
9	3	L	7.26	0.00	0.00	0.00
7	3	L	4.28	0.00	0.00	0.00
5	3	L	6.48	0.00	0.00	0.00
3	3	L	5.47	0.00	0.00	0.00
4	4		642.76	650.32	954.89	33.78
6	4		37.23	38.80	-38.61	-4.32
8	4		396.11	398.08	435.80	24.36
10	4		45.12	47.38	-47.11	-5.51
11	5	L	4.60	0.00	-0.00	-0.00
9	5	L	6.14	0.00	-0.00	-0.00
7	5	L	4.41	0.00	-0.00	-0.00
5	5	L	6.72	0.00	-0.00	-0.00
6	6		36.02	35.07	-35.04	2.12
8	6		44.14	44.78	-44.79	-1.63
10	6		17.64	16.06	-16.02	1.16
9	7	L	8.96	0.00	0.00	-0.00
7	7	L	8.10	0.00	0.00	0.00
8	8		199.69	204.36	207.58	16.77
ℓ = 1						
11	0	L	5.14	0.00	0.00	0.00
9	0	L	6.45	0.00	0.00	0.00
7	0	L	6.77	0.00	-0.00	-0.00
5	0	L	4.88	0.00	-0.00	-0.00
3	0	L	4.52	0.00	-0.00	-0.00
2	1		33.44	32.29	-32.38	-0.62
4	1		85.26	90.61	-91.35	-7.61
6	1		30.08	28.42	-28.44	-0.60
8	1		233.36	230.95	-238.94	-11.34
10	1		32.56	35.01	34.98	1.90
12	1		112.73	117.48	-117.80	-9.48
11	2		44.43	46.13	46.16	1.44
9	2		13.85	13.30	13.24	-1.22
7	2		8.98	8.42	-8.37	0.87
5	2		65.42	66.90	-67.21	-0.94
3	2	L	0.0	3.37	-3.31	0.61
4	3		188.80	191.83	-199.95	-7.28
6	3		30.10	28.25	-28.26	-0.68
8	3		170.94	170.77	-173.55	-10.42
10	3		43.16	39.52	39.51	1.77
11	4		41.98	41.59	-41.41	-4.17
9	4		49.34	44.96	44.61	5.90
7	4		111.40	112.59	-113.38	-5.96
5	4		226.04	231.64	242.52	7.42
6	5		33.17	33.81	33.82	-1.20
8	5		104.54	102.77	-102.85	-10.38
10	5		21.35	24.64	-24.63	0.71
9	6		78.41	79.10	-79.29	-2.69
7	6		20.86	20.78	20.73	1.50
8	7		94.84	94.86	-94.91	-8.24
10	7	L	8.73	8.58	-8.57	0.37
9	8		138.66	137.17	138.01	8.64
ℓ = 2						
2	0		30.00	27.28	27.33	0.52
4	0		43.19	44.47	44.56	1.91
6	0		114.32	114.08	115.39	3.94
8	0		103.50	101.84	102.36	6.01
10	0		40.11	40.46	39.77	7.60
12	0		121.69	123.60	124.08	8.97
11	1	L	0.51	5.26	4.73	-2.31
9	1		12.44	8.66	-7.27	-4.70
7	1		67.63	69.76	-69.92	-3.64
5	1		127.75	133.53	-136.07	-5.47
3	1		37.59	24.99	24.60	-4.57
1	1		66.88	73.80	-75.04	-5.33
2	2	L	4.52	0.00	0.00	0.00
4	2		37.87	36.58	36.57	2.36
6	2		73.10	75.08	75.37	3.41
8	2		129.91	129.18	130.40	6.46
10	2		94.76	94.73	94.87	7.34
12	2		100.77	101.44	101.47	9.19
11	3		53.57	50.21	49.89	6.16
9	3		19.62	19.89	-19.87	0.97
7	3		28.64	20.89	19.86	6.51
5	3		10.32	7.07	6.51	2.76
3	3		209.21	218.13	232.39	6.25
4	4		9.52	0.00	-0.00	-0.00
6	4		105.23	105.27	106.00	5.62
8	4		65.73	66.62	66.67	4.14
10	4		163.78	163.88	165.71	9.41
11	5		41.75	42.78	42.79	1.55
9	5		95.55	94.19	-94.27	-7.93
7	5		56.84	56.25	56.36	-0.17
5	5		35.01	35.99	-35.30	-7.16
6	6	L	6.54	0.00	0.00	0.00
8	6		100.33	104.02	104.20	9.19
10	6		63.60	64.17	64.16	4.10
9	7		37.69	40.47	-40.43	-2.31
7	7		105.04	104.04	104.27	8.58
8	8	L	0.00	0.00	-0.00	-0.00
ℓ = 3						
11	0	L	4.26	0.00	-0.00	-0.00
9	0	L	3.60	0.00	-0.00	0.00
7	0	L	4.13	0.00	-0.00	-0.00
5	0	L	3.67	0.00	0.00	0.00
3	0	L	6.70	0.00	0.00	0.00
1	0	L	4.83	0.00	0.00	0.00
2	1		139.53	140.26	146.51	4.14
4	1		31.63	31.04	31.06	0.84
6	1		238.48	238.99	251.23	10.09
8	1		12.54	12.75	-12.74	-0.47
10	1		114.41	115.28	115.57	10.61
12	1		46.48	46.23	-46.12	-3.71
11	2	L	0.0	6.88	-6.33	2.71
9	2		49.48	50.39	-50.39	-2.83
7	2		174.80	176.44	180.44	3.86
5	2		97.36	97.89	-98.78	-3.66
3	2		45.59	41.16	-41.07	3.95
4	3		24.16	26.13	26.13	1.09
6	3		205.92	207.08	214.04	10.05
8	3		18.50	16.21	-16.21	-0.03
10	3		171.61	169.40	171.44	10.83
11	4		18.26	16.78	-16.58	-2.64
9	4		14.41	13.60	13.48	1.86
7	4		33.59	32.88	-32.85	-1.82
5	4		27.18	27.65	27.64	1.15
6	5		109.23	108.83	109.35	8.66
8	5	L	3.25	1.62	1.62	0.15
10	5		151.79	150.22	151.49	9.19
9	6		102.04	100.08	-100.33	-6.63
7	6		96.55	98.89	99.05	8.70
8	7		37.10	37.39	37.39	1.39
9	8		31.60	32.82	32.79	1.64
ℓ = 4						
0	0		99.51	94.42	96.86	5.28
2	0		35.01	27.56	27.24	4.49
4	0		51.79	48.18	48.11	4.53
6	0		26.72	29.06	-29.08	-0.64
8	0		21.06	19.36	19.05	3.47
10	0		152.73	149.65	-151.16	-7.57
12	0		22.73	24.28	23.94	4.06
11	1		54.94	54.93	55.00	0.12
9	1	L	8.49	12.65	-12.65	0.02
7	1		93.94	96.26	-96.92	-0.22
5	1		12.05	10.68	10.68	0.04
3	1		77.20	74.87	75.54	0.06
1	1	L	4.12	0.00	-0.00	-0.00
2	2		644.93	640.22	1132.64	39.10
4	2		94.67	92.71	-93.49	-5.45
6	2		557.42	539.36	680.47	31.75
8	2		67.84	67.88	-67.72	-6.88
10	2		316.58	316.99	332.41	21.10
11	3		66.15	66.11	66.24	0.25
9	3		16.84	16.50	16.50	0.02
7	3		73.42	74.58	-74.86	-0.13
5	3		33.47	32.38	-32.41	-0.08
3	3	L	5.33	0.00	-0.00	-0.00
4	4		37.19	36.79	36.64	3.76
6	4		57.59	58.10	-58.24	0.39
8	4	L	4.28	5.60	-5.04	2.45
10	4		109.72	109.38	-109.82	-6.10
9	5		21.08	21.66	21.66	0.10
7	5		39.19	40.68	40.72	0.08
5	5	L	4.81	0.00	0.00	0.00
6	6		400.32	415.24	459.63	25.36
8	6	L	8.11	8.52	-8.13	-2.57
10	6		215.94	220.20	224.32	16.17
9	7		18.16	16.88	-16.88	-0.04
7	7	L	5.45	0.00	-0.00	-0.00
8	8		18.33	14.96	-14.95	0.62
ℓ = 5						
11	0		12.72	0.00	0.00	0.00
9	0	L	3.51	0.00	0.00	0.00
7	0	L	0.00	0.00	-0.00	-0.00
5	0	L	6.13	0.00	-0.00	-0.00
3	0	L	4.00	0.00	0.00	-0.00
1	0	L	6.56	0.00	-0.00	-0.00
2	1		63.17	66.88	-67.30	-4.02
4	1	L	6.25	7.08	7.04	-0.78
6	1		182.55	183.07	-188.04	-9.86
8	1	L	8.40	8.89	-8.88	0.44
10	1		163.80	163.68	-165.53	-10.59
11	2		63.75	64.31	64.36	2.90
9	2		48.44	48.23	-48.22	-2.77
7	2		46.40	48.02	-47.98	3.38
5	2		39.64	41.91	-41.83	-3.52
3	2		254.70	255.54	278.56	4.28
4	3		24.54	21.79	-21.78	-1.05
6	3		133.20	134.82	-136.34	-9.83
8	3	L	7.72	12.06	-12.06	0.05
10	3		146.29	143.39	-144.41	-10.66
11	4		35.30	34.79	-34.71	-2.65
9	4		35.61	35.87	35.84	1.95
7	4		42.51	42.26	-42.27	-1.79
5	4		30.11	31.13	31.13	1.18
6	5		179.71	181.87	-185.61	-8.66
8	5	L	5.61	3.55	3.54	-0.18
10	5		87.82	88.15	-88.02	-8.78
9	6		70.18	71.23	-71.11	-6.39
7	6		173.38	171.67	174.20	8.84
8	7		14.37	13.25	13.20	-1.14
ℓ = 6						
0	0		10.60	0.00	0.00	0.00
2	0		19.47	17.89	-17.89	0.48
4	0		25.87	26.88	26.84	1.88
6	0		77.78	78.70	79.01	3.84
8	0		128.33	128.08	129.24	6.07
10	0		153.93	153.78	155.38	7.80
11	1	L	5.95	3.08	-2.20	2.15
9	1		52.86	54.76	54.64	4.81
7	1		32.34	31.61	-31.46	3.30
5	1		45.36	49.12	48.94	5.31
3	1		170.68	174.08	181.21	4.69
1	1		20.14	5.24	0.79	5.18
2	2	L	5.79	0.00	-0.00	-0.00
4	2		86.31	86.51	87.17	2.44
6	2		63.08	62.76	62.86	3.34
8	2		79.46	77.96	77.99	6.35
10	2		104.29	101.36	101.61	7.23
11	3		55.42	53.00	-52.73	-6.02
9	3		28.60	27.60	27.60	-0.97
7	3		116.62	117.91	-118.80	-6.57
5	3		14.18	8.42	7.98	-2.69
3	3		74.43	66.62	66.70	-5.72
4	4	L	5.14	0.00	0.00	0.00
6	4		75.82	76.06	76.17	5.52
8	4		45.78	46.17	46.04	4.09
10	4		98.20	97.20	97.20	9.09
9	5		65.11	61.20	60.81	7.76
7	5		24.88	22.90	-22.91	0.17
5	5		105.21	110.83	111.55	7.25
6	6	L	8.44	0.00	-0.00	-0.00
8	6		163.91	163.70	165.60	9.32
10	6		47.36	46.21	46.08	3.97
9	7		67.48	69.48	69.58	2.40
7	7		78.63	79.48	-79.29	-8.39
8	8	L	5.13	0.00	0.00	0.00
ℓ = 7						
11	0	L	0.00	0.00	-0.00	-0.00
9	0	L	0.00	0.00	0.00	0.00
7	0	L	6.70	0.00	-0.00	-0.00
5	0	L	5.73	0.00	0.00	0.00
3	0	L	0.00	0.00	0.00	0.00
1	0	L	5.14	0.00	0.00	0.00
2	1		33.93	33.39	-33.44	0.55
4	1		208.99	211.59	221.63	7.74
6	1		8.81	6.98	6.95	0.58
8	1		154.62	156.25	158.15	11.11
10	1		16.81	14.93	-14.83	-1.77
11	2		15.02	11.25	-11.19	1.24
9	2		45.09	47.52	-47.55	-1.38
7	2		41.65	43.85	43.89	0.95
5	2	L	4.71	1.49	1.23	-0.84
3	2		42.81	41.30	41.37	0.64
4	3		163.20	166.43	170.55	7.25
6	3	L	0.00	3.73	3.68	0.60
8	3		134.00	133.18	134.12	10.35
10	3		16.53	16.36	-16.27	-1.70
9	4		114.75	112.84	113.38	6.03
7	4		58.88	60.22	-60.06	-5.87
5	4		72.99	74.24	74.21	7.07
6	5		64.10	65.93	66.09	1.46
8	5		188.90	189.18	192.38	10.52
10	5		45.44	43.75	-43.78	-0.81
9	6		11.58	8.59	8.23	-2.44
7	6	L	8.02	8.72	8.61	1.40
8	7		147.99	147.57	148.80	8.48
ℓ = 8						
0	0		454.44	479.51	655.72	40.02
2	0		59.12	56.24	-56.20	-5.51
4	0		742.36	703.95	1088.67	36.89
6	0		110.51	109.03	-109.79	-6.96
8	0		411.42	407.30	447.62	26.83
10	0		65.23	66.53	-66.24	-7.59
11	1	L	7.42	3.43	3.43	-0.08
9	1		28.00	26.80	26.81	0.16
7	1	L	6.60	5.48	5.48	-0.06
5	1	L	7.71	8.12	-8.12	0.03
3	1		15.92	13.73	-13.73	-0.06
1	1	L	4.34	0.00	-0.00	-0.00
2	2		80.66	78.93	79.36	4.89
4	2		20.10	16.62	16.39	2.74
6	2	L	0.00	3.86	1.27	3.65
8	2		91.91	90.96	-91.32	-3.71
10	2		15.16	18.47	18.19	3.19
11	3		14.76	14.19	14.19	0.16
9	3		18.69	9.09	9.09	-0.04
7	3	L	6.79	4.51	-4.51	0.05
5	3		8.95	7.39	7.39	-0.05
3	3		8.22	0.00	0.00	0.00
4	4		465.73	479.45	571.66	32.63
6	4		24.93	24.55	-24.18	-4.32
8	4		354.60	355.24	378.78	23.80
10	4		37.90	38.12	-37.75	-5.47
9	5		17.64	15.48	-15.48	0.00
7	5		16.94	16.22	-16.22	-0.08
5	5	L	6.17	0.00	-0.00	-0.00
6	6		18.91	21.11	20.98	2.30
8	6		67.80	63.87	-63.97	-1.58
9	7	L	7.62	7.65	7.65	0.03
7	7	L	0.00	0.00	0.00	0.00
8	8		257.38	261.47	268.75	16.66
ℓ = 9						
11	0	L	8.96	0.00	-0.00	0.00
9	0	L	0.00	0.00	-0.00	0.00
7	0	L	7.41	0.00	-0.00	-0.00
5	0	L	2.33	0.00	0.00	-0.00
3	0	L	4.63	0.00	-0.00	-0.00
1	0		7.69	0.01	-0.01	-0.00
2	1		36.57	35.25	-35.30	-0.61
4	1		233.60	240.73	-253.68	-7.65
6	1		14.16	12.41	12.41	-0.47
8	1		118.95	120.17	-120.67	-10.79
10	1		20.29	18.32	18.23	1.91
11	2	L	2.99	1.61	-0.97	1.29
9	2		39.03	36.55	-36.56	-1.30
7	2		25.38	28.18	28.18	0.95
5	2		18.57	20.52	20.51	-0.76
3	2	L	6.83	9.98	9.96	0.61
4	3		81.65	83.47	-83.66	-6.90
6	3		11.43	2.58	-2.51	-0.62
8	3		172.10	170.73	-173.12	-10.10
10	3	L	5.85	9.06	8.91	1.65
9	4		120.75	119.60	120.26	5.97
7	4		104.73	103.12	-103.58	-5.75
5	4		49.91	45.92	45.46	6.91
6	5		60.29	61.34	-61.46	-1.30
8	5		188.55	190.23	-193.36	-10.39
10	5		37.24	37.20	37.21	1.03
9	6	L	7.41	2.33	0.21	-2.32
7	6		35.04	34.80	34.79	1.56
8	7		95.99	96.53	-96.61	-7.92
ℓ = 10						
0	0	L	0.00	0.00	-0.00	-0.00
2	0		26.25	24.15	24.16	0.56
4	0		63.53	61.84	62.02	1.88
6	0		24.46	19.87	19.52	3.75
8	0		55.72	56.33	56.14	5.70
10	0		171.50	171.05	173.18	7.90
11	1	L	9.03	5.73	-5.26	-2.26
9	1		52.66	52.68	-52.56	-4.50
7	1		13.08	13.01	12.59	-3.31
5	1		14.88	14.14	13.27	-4.90
3	1		54.30	58.56	-58.59	-4.41
1	1		110.97	116.93	-118.58	-5.08
2	2	L	6.58	0.01	0.01	0.00
4	2		46.82	47.19	47.22	2.36
6	2		48.58	50.80	50.78	3.32
8	2		84.22	83.13	83.21	6.20
10	2		108.46	107.39	107.70	7.26
9	3		21.85	23.20	-23.20	0.73
7	3		95.94	96.07	96.36	6.46
5	3		16.78	14.42	14.20	2.54
3	3		14.66	15.61	14.52	5.72
4	4	L	5.88	0.00	-0.00	-0.00
6	4		109.64	108.51	109.13	5.56
8	4		76.09	74.11	74.20	4.03
10	4		70.05	70.70	70.28	8.98
9	5		55.58	53.77	-53.32	-7.49
7	5		22.75	19.22	19.22	-0.14
5	5		121.17	122.34	-123.25	-7.00
6	6	L	0.00	0.00	0.00	0.00
8	6		129.03	129.62	130.31	9.05
7	7		61.54	60.37	59.92	8.15
ℓ = 11						
9	0		10.52	0.00	0.00	0.00
7	0	L	7.57	0.00	0.00	0.00
5	0	L	5.78	0.00	0.00	0.00
3	0		9.32	0.00	-0.00	0.00
1	0	L	6.82	0.00	0.00	0.00
2	1		95.69	95.30	96.03	4.03
4	1		28.03	26.74	26.75	0.80
6	1		117.62	116.54	117.17	9.68
8	1		15.21	15.18	-15.18	-0.47
10	1		174.94	174.91	177.00	10.63
9	2		21.04	20.49	-20.31	-2.72
7	2		14.69	10.47	-9.92	3.36
5	2		64.66	63.32	-63.40	-3.57
3	2		115.35	120.72	122.14	4.07
4	3	L	7.56	13.11	1.306	1.06
6	3		170.65	172.13	174.97	9.77
8	3		16.34	17.76	17.76	0.10
10	3		96.55	98.56	98.43	10.35
9	4		42.03	40.96	40.95	1.86
7	4		18.99	18.32	-18.24	-1.76
5	4	L	2.79	2.00	1.71	1.03
6	5		159.26	159.19	161.15	8.70
8	5		13.69	9.15	9.15	0.12
9	6		74.90	75.16	-75.06	-6.52
7	6		135.14	133.96	134.83	8.57
8	7	L	6.91	8.42	8.32	1.32
ℓ = 12						
0	0		38.11	38.86	38.56	5.23
2	0		97.12	94.98	95.62	4.69
4	0		56.94	56.82	56.77	4.60
6	0		113.68	111.82	-112.68	-0.58
8	0		15.24	11.10	10.53	3.50
10	0		99.72	98.05	-98.22	-7.01
9	1		11.92	8.17	8.17	0.16
7	1		49.70	51.41	51.49	0.02
5	1	L	6.19	5.24	-5.27	0.06
3	1		30.66	31.42	-31.44	-0.12
1	1	L	4.39	0.00	0.00	0.00
2	2		587.58	598.98	792.66	37.48
4	2		24.30	23.27	-22.65	-5.39
6	2		474.53	473.04	539.26	30.45
8	2		73.73	74.57	-74.46	-6.86
10	2		267.66	267.07	274.73	20.18
9	3		12.35	11.35	-11.35	-0.12
7	3		46.87	47.62	47.68	0.20
5	3		9.44	10.06	10.06	-0.06
3	3	L	3.81	0.00	-0.00	-0.00
4	4	L	7.96	8.50	7.62	3.77
6	4		15.45	14.81	14.79	0.74
8	4	L	8.24	12.82	12.56	2.58
9	5		13.69	11.11	-11.11	0.06
7	5		18.09	20.55	-20.56	-0.12
5	5	L	7.04	0.00	0.00	0.00
6	6		333.93	338.91	357.76	24.24
8	6		14.07	10.11	9.77	-2.59
7	7	L	4.44	0.00	-0.00	-0.00
ℓ = 13						
9	0	L	4.14	0.00	0.00	0.00
7	0	L	3.91	0.00	0.00	0.00
5	0	L	5.97	0.00	-0.00	-0.00
3	0	L	5.41	0.00	-0.00	-0.00
1	0	L	5.47	0.00	0.00	-0.00
2	1		92.69	94.65	-95.24	-3.90
4	1		31.72	33.76	-33.78	-0.80
6	1		136.93	138.65	-139.90	-9.36
8	1		25.83	25.64	25.64	0.56
10	1		126.76	126.89	-127.38	-10.01
9	2		21.99	21.16	-21.01	-2.55
7	2		118.75	118.42	119.25	3.62
5	2		86.78	87.97	-88.32	-3.45
3	2		30.94	25.66	-25.41	3.70
4	3		21.34	21.98	-21.96	-0.96
6	3		192.49	191.94	-195.66	-9.60
8	3	L	6.32	12.77	12.77	0.22
9	4		20.03	21.21	21.13	1.88
7	4		10.91	1.61	0.42	-1.55
5	4	L	8.44	5.70	5.59	1.10
6	5		93.56	93.94	-94.02	-8.04
8	5		14.86	12.90	-12.89	-0.25
7	6		70.80	73.72	73.44	8.22
ℓ = 14						
0	0	L	3.87	0.01	0.01	0.00
2	0		30.91	32.24	32.26	0.61
4	0		48.68	47.96	47.99	1.86
6	0		39.96	39.01	38.87	3.65
8	0		49.12	48.67	48.40	5.68
9	1		19.18	19.54	19.04	4.40
7	1		39.27	38.94	38.85	3.03
5	1		26.95	20.75	20.18	4.85
3	1		58.07	58.87	-58.88	3.87
1	1		122.35	125.43	126.84	4.93
2	2	L	3.39	0.00	-0.00	-0.00
4	2		20.02	18.25	18.10	2.32
6	2		46.78	46.85	46.80	3.15
8	2		101.76	101.89	102.20	6.27
9	3		13.38	8.79	8.75	-0.85
7	3		21.21	18.83	-17.91	-5.81
5	3		18.78	16.60	-16.42	-2.42
3	3		139.84	143.14	-144.93	-5.57
4	4		10.04	0.00	0.00	0.00
6	4		100.30	101.67	102.06	5.42
8	4		68.31	68.94	68.97	4.02
7	5		34.83	35.77	-35.79	-0.12
5	5		67.46	66.52	66.34	6.72
6	6	L	7.95	0.00	-0.00	-0.00
7	7		66.97	62.78	-62.40	-7.81
ℓ = 15						
9	0	L	7.05	0.00	-0.00	-0.00
7	0	L	8.18	0.00	0.00	0.00
5	0		10.49	0.00	0.00	-0.00
3	0		10.52	0.00	0.00	0.00
1	0		11.59	0.00	0.00	0.00
2	1		49.91	49.67	49.75	0.65
4	1		113.72	113.71	114.38	7.31
6	1	L	0.00	6.51	6.48	0.55
8	1		143.35	144.78	145.80	10.69
9	2	L	7.40	3.37	-3.15	-1.19
7	2		15.17	13.32	-13.30	0.75
5	2		10.17	4.56	-4.49	-0.81
3	2	L	6.69	2.73	-2.68	0.53
4	3		82.21	77.48	77.44	6.87
6	3	L	5.50	2.88	2.83	0.53
8	3		161.04	162.71	164.35	10.16
7	4		116.66	117.45	-118.06	-5.89
5	4		119.09	121.86	122.61	6.89
6	5	L	6.01	1.54	-0.91	1.25
8	5		99.57	100.22	100.17	9.83
7	6		37.91	38.26	38.26	1.38
ℓ = 16						
0	0		632.55	652.69	852.62	38.38
2	0		72.81	71.44	-71.45	-5.63
4	0		443.53	443.04	494.81	34.11
6	0		35.15	37.34	-36.75	-6.76
8	0		348.62	345.59	363.82	25.24
9	1		35.41	31.25	-31.26	0.06
7	1	L	5.68	7.23	-7.23	-0.15
5	1		14.26	10.57	10.57	0.11
3	1	L	6.12	9.29	9.29	-0.06
1	1	L	7.77	0.00	-0.00	-0.00
2	2		32.50	32.61	32.26	4.86
4	2	L	8.56	4.41	-3.33	2.90
6	2		33.31	30.49	30.27	3.79
8	2		73.82	70.78	-70.86	-3.22
7	3		11.30	10.56	10.56	0.14
5	3		14.14	10.81	-10.81	-0.14
3	3	L	6.92	0.01	0.01	0.00
4	4		468.80	475.87	534.24	30.95
6	4		40.24	41.72	-41.52	-4.44
8	4		299.13	299.36	310.28	22.37
7	5		18.41	18.36	18.37	-0.01
5	5	L	4.65	0.00	-0.00	-0.00
6	6		19.23	13.38	-13.17	2.33
ℓ = 17						
7	0	L	5.81	0.00	-0.00	-0.00
5	0	L	8.40	0.00	-0.00	-0.00
3	0		9.59	0.00	-0.00	-0.00
1	0	L	6.31	0.00	-0.00	-0.00
2	1		9.58	12.57	12.56	-0.47
4	1		53.21	49.97	-49.57	-6.87
6	1		25.41	24.69	-24.70	-0.46
8	1		165.05	163.28	-164.87	-10.31
7	2	L	2.94	10.81	10.78	0.87
5	2		23.04	23.89	-23.88	-0.77
3	2		17.97	18.46	18.45	0.60
4	3		136.98	138.87	-140.11	-6.63
6	3	L	5.85	7.74	-7.71	-0.59
8	3		83.51	83.72	-83.47	-9.23
7	4		45.56	43.42	-43.14	-5.21
5	4		135.36	137.46	138.54	6.76
6	5	L	6.17	8.54	8.49	-0.94
ℓ = 18						
0	0	L	0.00	0.00	-0.00	-0.00
2	0	L	7.20	4.09	-4.05	0.59
4	0	L	0.00	1.69	-0.43	1.63
6	0		92.29	91.07	91.34	3.85
8	0		112.90	111.40	111.86	5.50
7	1		15.45	16.27	-16.00	-2.95
5	1		63.67	62.46	-62.42	-4.44
3	1		31.00	30.87	-30.65	-3.82
1	1	L	7.61	10.78	9.92	-4.23
2	2	L	4.05	0.01	0.01	0.00
4	2		40.24	39.90	39.87	2.31
6	2		47.99	47.49	47.43	3.15
7	3		29.86	30.76	30.24	5.70
5	3		17.01	16.95	-16.84	1.97
3	3		46.54	46.98	46.75	5.19
4	4	L	0.00	0.01	-0.01	-0.00
6	4		42.02	43.11	42.84	5.19
5	5		22.72	21.36	-20.50	-6.03
ℓ = 19						
7	0	L	4.61	0.00	-0.00	-0.00
5	0	L	0.00	0.00	-0.00	0.00
3	0	L	7.13	0.00	0.00	0.00
1	0	L	7.54	0.00	0.00	0.00
2	1		36.64	36.59	36.42	3.73
4	1	L	6.17	9.37	-9.35	0.64
6	1		155.99	157.41	158.91	9.34
7	2		61.73	63.16	63.18	3.35
5	2		44.70	41.04	-40.93	-3.36
3	2		60.36	60.04	60.03	3.75
4	3		29.15	24.00	23.99	1.02
6	3		88.45	88.66	88.51	9.02
5	4		34.76	32.23	32.23	1.01
ℓ = 20						
0	0		68.44	68.94	68.91	5.31
2	0		10.73	6.39	-4.40	4.62
4	0	L	8.30	10.13	9.07	4.51
6	0		29.81	29.98	29.99	0.20
5	1	L	5.99	5.40	5.40	0.12
3	1		9.71	3.49	3.49	-0.08
1	1	L	4.72	0.00	-0.00	0.00
2	2		452.44	464.12	514.18	34.48
4	2		67.29	68.62	-68.54	-5.56
6	2		385.35	354.41	373.14	27.96
5	3	L	5.84	1.36	1.35	-0.13
3	3	L	7.77	0.00	-0.00	-0.00
4	4		35.46	37.73	37.55	3.91
ℓ = 21						
5	0	L	2.54	0.00	0.00	-0.00
3	0	L	8.37	0.00	-0.00	-0.00
1	0	L	0.00	0.00	-0.00	-0.00
2	1		46.79	45.76	-45.67	-3.53
4	1	L	7.88	4.20	4.15	-0.62
6	1		118.22	117.64	-118.01	-8.63
5	2		15.53	15.47	-15.17	-3.01
3	2		86.14	86.72	86.94	3.69
4	3		10.26	2.52	-2.40	-0.77
ℓ = 22						
0	0	L	0.00	0.00	0.00	0.00
2	0		10.48	2.80	-2.73	0.62
4	0	L	8.21	11.90	11.78	1.66
5	1		53.25	50.39	50.26	4.27
3	1		69.66	68.20	68.26	3.48
1	1		40.28	39.25	-39.10	3.81
2	2	L	1.77	0.01	-0.01	-0.00
4	2		40.96	39.51	39.47	2.34
3	3		26.94	28.93	28.62	-4.32
ℓ = 23						
3	0		13.48	0.00	0.00	0.00
1	0	L	6.78	0.00	0.00	0.00
2	1		19.70	20.44	-20.44	0.42
3	2	L	3.38	5.71	5.69	0.48
ℓ = 24						
0	0		386.31	390.45	415.25	34.19
1	1	L	1.82	0.00	-0.00	-0.0

This results in a distorted configuration around $M(3)$ since the four contributing bonds must now have angles considerably less than 90 degrees to each other. This is shown very clearly in Figure 1(c), and is analogous to the arrangement around Mn(4) in Mn_2O_3.

It can also be seen that the O–O interatomic distances along shared polyhedral edges are considerably shorter than the unshared ones.

Valence State of the Mn Atoms

It has been stated by many authors (Byström and Mason, 1943; Muan, 1959, among others) that the structural formula of braunite must be $Mn^{2+}(Mn^{2+}Mn^{4+})_6SiO_{12}$ instead of $Mn^{2+}Mn_6^{3+}SiO_{12}$. This conclusion was used to support a proposed mechanism by which silica was incorporated in the structure. Crystallographically it is not possible to have an ordered version of the first formula above since there are three non-equivalent octahedral sites. The distribution of Mn^{2+} and Mn^{4+} over sites $M(2)$, $M(3)$, and $M(4)$ would therefore have to be disordered. To explain the replacement of manganese by silica, it is not necessary to invoke the first model, and the formula $Mn^{2+}Mn_6^{3+}SiO_{12}$ will be used here. Average bond lengths $M(1)$–O, M(2)–O, M(3)–O, and M(4)–O have values of 2.23Å, 2.03Å, 2.06Å, and 2.04Å respectively, which compare very well with the high spin values of Mn^{2+}–O = 2.22Å and Mn^{3+}–O = 2.05Å given by Shannon and Prewitt (1969).

Comparison with $CaMn_6SiO_{12}$

The structure determined by Damon *et al* (1966) for $CaMn_6SiO_{12}$ has the same space group and essentially the same atomic coordinates as braunite. It can therefore be regarded as the Ca end member of a solid solution series between $CaMn_6SiO_{12}$ and $Mn^{2+}Mn_6SiO_{12}$.

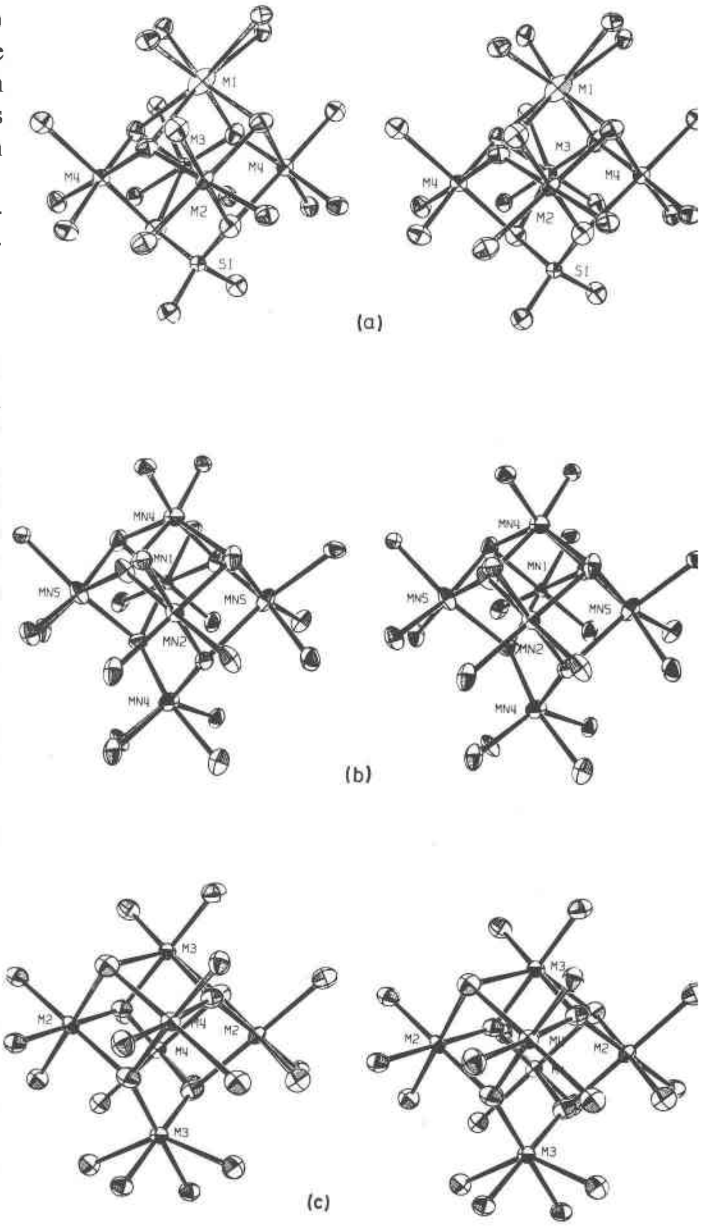

FIG. 1. Atomic arrangements around vacant sites. (a) the $(Mn^{2+}Mn_4^{3+}Si)$ arrangement in braunite; (b) the (Mn_6^{3+}) arrangement in α-Mn_2O_3. (c) the (Mn_6^{3+}) arrangement in braunite.

Comparison of the Braunite and α-Mn_2O_3 Structures

Description

In this discussion, the nomenclature of Geller (1971) will be used for the cell dimensions and atomic positions of Mn_2O_3.

It has long been surmised that the braunite and Mn_2O_3 structures are similar, and the *a* cell dimension of braunite (9.423 Å) is compared with the value of 9.416 Å of Mn_2O_3. The braunite *c* dimension of 18.703 Å is slightly less than twice that of Mn_2O_3 (c = 9.405 Å). From the present investigation of the two structures, it is apparent that the cation positions in braunite correspond closely to those of Mn_2O_3, and that the $M(1)$ atomic positions having cubic coordination correspond to half the Mn(4) octahedral atomic positions in Mn_2O_3 in an ordered fashion. The Si in tetrahedral coordination in braunite corresponds to the other half of the Mn(4) atomic positions in Mn_2O_3. The braunite $M(2)$ atoms correspond to half of the Mn(1), Mn(2), and Mn(3) atomic positions, and the $M(3)$ atoms correspond to the other half of

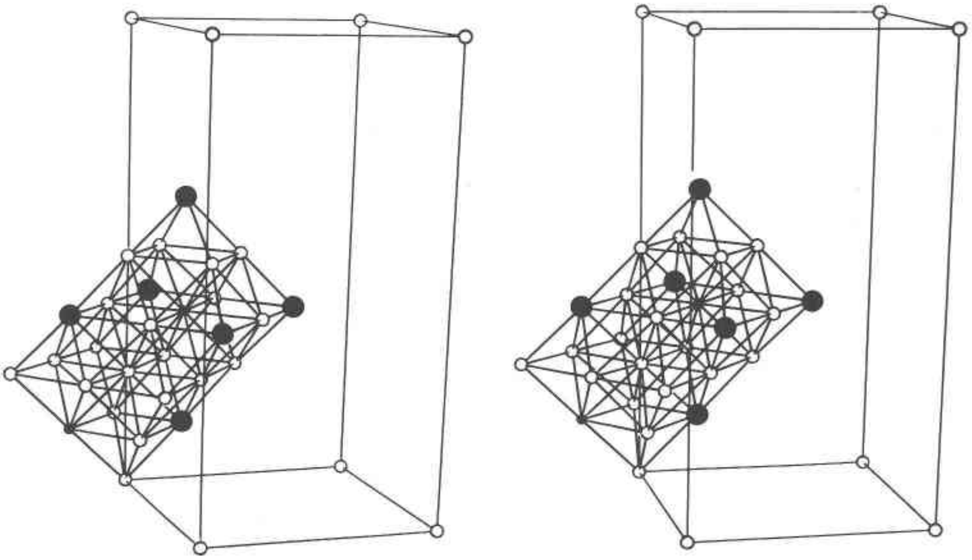

FIG. 2. The arrangements of cations around Si and $M(3)$ in braunite. The largest black circles are Mn^{2+} atoms, the intermediate white ones Mn^{3+}, and the smallest black atoms Si^{4+}

these positions. The braunite $M(4)$ atoms correspond to the Mn(5) atoms in the Mn_2O_3 structure.

The mechanism of the formation of braunite from Mn_2O_3 can now be described as replacement of one half of the octahedral $Mn^{3+}(4)$ in Mn_2O_3 with tetrahedral Si^{4+}, in which the other half of the $Mn^{3+}(4)$ changes to an eight-coordinated Mn^{2+}.

The octahedral cationic arrangement described earlier for the braunite structure is therefore also present in the Mn_2O_3 structure. Figure 1(b) shows the arrangement in the Mn_2O_3 structure, and Figures 1(a) and 1(c) the arrangements in the braunite structure. These show unequivocally that, despite changes in coordination from octahedral to cubic plus tetrahedral, the cation arrangement is still the same, and that small shifts in the oxygen atomic positions are responsible for the change in coordination. It is clear that these structures are very closely related.

Silica Substitution

I propose that silica substitution in the Mn_2O_3 structure occurs by replacement of an Mn^{3+} ion with an Si^{4+} ion. To regain charge balance, the opposite Mn^{3+} in the octahedral cation arrangement reduces to Mn^{2+}. Further substitution of silica will replace two more Mn^{3+} atoms with Mn^{2+} and Si^{4+}. Finally, silica substitution will reach a maximum when all the Mn^{3+} ions are replaced with Mn^{2+} and Si^{4+}. This occurs at a theoretical SiO_2 content of 44.05 wt percent as depicted on the SiO_2–Mn_3O_4 system of Muan (1959). This value is compared with the value of at least 40 wt percent determined experimentally by him.

Any crystal-chemical explanation of silica replacement in the Mn_2O_3 structure must also explain the fact that an apparently stable phase field exists for a wide range of silica contents. It must be mentioned that the phase Mn_2O_3(ss) described by Muan (1959) was identified by powder X-ray methods, and he also mentions the existence of faint additional diffraction lines in some runs, which he ascribed to ordering.

De Villiers and Herbstein (1967) also described a naturally occurring phase, braunite II, which has one half the amount of silica that is present in braunite. This phase has a *c* cell parameter of 37.76 Å, which is twice that of braunite or four times that of Mn_2O_3. It is therefore likely that this phase consists of a braunite cell and two Mn_2O_3 cells in a regular stacking arrangement. This postulate will be tested with a structure analysis of braunite II.

The phase field as described by Muan probably consists of Mn_2O_3 plus similar, but well-defined, phases in which the manganese atoms are replaced by one, two, or three silicon atoms. The intermediate phases will probably be regular stacking arrangements consisting of mixtures of these four basic phases.

There is also the possibility that the experimentally determined phase field consists of a disordered Mn_2O_3 structure with the silicon randomly distributed among the cationic sites in the structure.

This distribution could become ordered after a suitable annealing process.

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