

The crystal structure of braunite II and its relation to bixbyite and braunite

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Abstract

The crystal structure of braunite II, $\text{Ca}(\text{Mn},\text{Fe})_{14}\text{SiO}_{24}$, has been determined on a crystal from the Wessel Mine, near Hotazel, South Africa. It is tetragonal, space group $I4_1/acd$, with cell dimensions $a = 9.431(2)$, $c = 37.774(4)\text{\AA}$. The structure was refined by use of anisotropic thermal parameters and an extinction correction to a conventional $R = 0.058$. The structure consists of an $(\text{A}'\text{ABA})_4$ stacking sequence of three non-equivalent edge- and corner-linked polyhedral sheets. The A- and A'-sheets consist of edge- and corner-linked (Mn,Fe) octahedra, whereas the B-sheets consist of Ca in cubic coordination, Si in tetrahedral coordination, and (Mn,Fe) in octahedral coordination. The A- and A'-sheets are present in bixbyite with stacking sequence $(\text{A}'\text{A})_2$, whereas the stacking sequence of braunite is $(\text{AB})_4$. The A-, A'-, and B-sheets are virtually identical in the three structures. The structure determination confirms the validity of the braunite II structure as proposed previously. Comparative calculated X-ray diffraction data are presented so that distinctions can be made among these three minerals.

Introduction

The crystal structure of bixbyite has been the subject of recent investigations by Norrestam (1967) and Geller (1971). De Villiers (1975) and Moore and Araki (1976) examined the braunite structure and independently pointed out the very close relation between these two structures. Moore and Araki (1976) derive a theory that not only describes the braunite-bixbyite relation but also classifies all fluorite-structure derivatives. They also propose a structure for the compound first described by De Villiers (1946) as ferrian braunite and later designated as braunite II by De Villiers and Herbstein (1967).

This investigation is the continuation of a study of the crystal chemistry of economically important minerals from the Kalahari manganese field, Cape Province, South Africa. It also presents an opportunity to test the validity of the structure of braunite II as proposed by Moore and Araki (1976).

Experimental

A single crystal of braunite II was selected from specimens collected at the Wessels Manganese Mine, near Hotazel, Cape Province, South Africa. A part of

the type material has been deposited at the Royal Ontario Museum, Toronto, Canada, and is registered as M33733 and M34659. Braunite II occurs together with braunite and hausmannite as one of the predominant minerals in iron-rich portions of the mine. The composition given in Table I was determined by electron microprobe analysis using the Bence-Albee correction procedure, and was calculated on the basis of 24 oxygen atoms. Weight percentages of the constituent elements are 52.49 Mn, 10.63 Fe, 2.55 Si, and 3.03 Ca. Synthetic Mn_3O_4 (Mn), magnetite (Fe), and wollastonite (Ca, Si) were used as standards.

X-ray measurements with graphite-monochromated $\text{MoK}\alpha$ -radiation were completed on a roughly spherical crystal (see Table I for dimensions) that had been ground and mounted on a Philips PW1100 computer-controlled four-circle diffractometer. The cell dimensions were obtained from least-squares analysis of angular measurements of 44 reflections collected with a Stoe precision Weissenberg camera, and refined by use of a program by Burnham (1962).

The cell data are given in Table I. The intensities of a unique set of reflections up to $\sin \theta/\lambda = 0.8$ were collected with the $\omega/2\theta$ scan technique, and the back-

TABLE 6: Observed and Calculated structure factors of Diastunite II

	H 10FO	1FCF	H 10FO	1FOC	H 10FO	1FCF	H 10FO	1FCF	H 10FO	1FOC	H 10FO	1FCF	H 10FO	1FOC	H 10FO	1FCF				
H ₀ 6 ₀ 6 ₀			5	965	971		H ₀ 6 ₂ 2			13	463	170	H ₀ 10 ₃		11	301	373			
2 1799 1769	0	1030	950	3	376	342		2	926	668	11	816	676	H ₀ 10 ₉	9	196*	9			
4 1221 12362	9	1820	1896		H ₀ 3 ₂ 1		4	108*	5		3	702	701	7	646	736				
6 1764 771	10	388	373				6	219	2064		7	593	533		5	116*	0			
6 11940 11743	12	3221	3214		4	779	778	8	649	330		5	645	656	H ₀ 6 ₄					
16 1261 1261					6	1126	1098	10	1907	1979	6	184*	0							
12 5924 5849					6	222*	159	12	277*	255	6	891	678		2	1529	1458			
14 16060 15333	13	209*	0	10	313	690	14	3177	3061	10	1297	1604	H ₀ 3 ₃ 3	6	603	614				
H ₀ 1 ₀ 0	11	1670	0	12	232*	27				12	1261	1325	4	43C6	4280	6	24C3	1583		
	9	213*	0	14	974	964	H ₀ 1 ₂ 2				3	663	689	10	1610	1602	12	1262		
15 3010 6	7	229*	0		H ₀ 6 ₁ 1		15	331*	233		8	3003	2972	12	737	673				
32 2536 6							H ₀ 6 ₁ 1			10	541	612	14	1091	1067	H ₀ 7 ₆ 4				
11 375*	0	H ₀ 8 ₀ 0		13	178*	140		13	661	603	13	0*	154	12	1414	1474	*	236*	370	
19 213*	0			11	213*	420		11	635	608	11	209*	109	14	(73	360	11	296*	145	
7 477*	0	6	4020	4594	9	4510	459	7	306	222	9	218*	163				9	552	616	
5 10*	10	3293	1454	7	265*	246		7	134*	1359	7	421	248	H ₀ 4 ₀ 3	15	0*	152			
3 102*	12	326	3302	5	533	485		3	946	911		H ₀ 6 ₂ 2		13	1697	1707	13	193*	123	
1 109*	0						H ₀ 5 ₁ 1			8	520	0	11	1463	1530	11	641	660		
H ₀ 2 ₀ 0	11	154*	0	6	39*	56		H ₀ 2 ₂ 2			12	1925	2C29	7	2261	2262	3	538	515	
2 503 444	9	2C5*	0	6	147*	467		2	189*	0	12	0*	57	5	4616	4696	1	492	0	
6 39C 802	10	199*	146	4	154*	271		H ₀ 3 ₂ 2			H ₀ 5 ₃ 3						H ₀ 5 ₆ 6			
6 1427 1467		H ₀ 10 ₀ 0		12	0*	41		4	171C	1820	11	267*	197	6	229*	182	H ₀ 2 ₄			
6 2693 3023	10	905	853	14	124*	119*		9	571	610	9	92*	60		8	2231	2198	2	682	603
10 4789 3317	12	3300	3317		H ₀ 6 ₂ 1		10	2462	2513	9	10	4133	4120	4	1406	1464	11	665	635	
14 590 440		H ₀ 0 ₁ 1					H ₀ 6 ₂ 1	12	66*	101	H ₀ 10 ₂ 2		12	2275	2211	6	495	491		
H ₀ 3 ₂ 0	15	261*	0	13	299*	110		14	2206	2252	10	177*	0	14	267*	265	H ₀ 1C ₀ 4			
13 430 6	13	280*	0	11	492	548		H ₀ 3 ₂ 2			H ₀ 6 ₃ 3		10	1799	1620	10	133*	2119		
15 273*	9	251*	0	9	670	911		13	336*	249	9	202*	0	11	1131	1119	10	1326	1296	
19 280*	7	362*	0	7	229*	291		11	299*	90	7	294	C	14	681	537	H ₀ C ₀ 2			
3 0*	2	206*	0		H ₀ 7 ₁		9	446	233	15	314*	0	11	433	331	H ₀ 3 ₅ 4				
3 0*	2	206*	0				H ₀ 7 ₁	7	103C	1005	13	296*	0	9	839	646	15	40b	0	
3 0*	0				8	201*	358	5	225*	73	11	0*	0	7	616	696	13	2236	2	
H ₀ 1 ₀ 1					19	232*	219	3	1743	1339	9	202*	0	H ₀ 7 ₃	11	133*	111	0		
H ₀ 1 ₀ 1					12	260*	54		H ₀ 4 ₀ 2		7	294	C	9	242*	308	9	20b	0	
H ₀ 4 ₀ 0					2	1069	1023	H ₀ 0 ₁ 1			5	94*	0	3	1279	2301	7	327	314	
6 17662 16214	4	298	411		11	174*	149		H ₀ 4 ₀ 2		3	126*	0	0	10	981	979	3	369	496
6 5825 6497	5	642	531	11	174*	149		11	1666	1925	12	1779	1720	H ₀ 9 ₃	10	120*	33	198*	0	
H ₀ 5 ₀ 0		H ₀ 2 ₁ 1		12	305	312		10	730	312	6	4743	4722	9	3021	3163	10	1715	1759	
10 449 611	16	3985 4603	12	170*	51	H ₀ 9 ₁	11	174*	149	10	202*	341		12	1746	1720	12	879	845	
12 3985 4603	14	1729	16A2	14	247*	130		10	2604	2409	4	1071	1684	11	1767	1731	4	479	207	
14 550 476	6	542	493	9	247*	130		11	275*	110	6	744	649	11	1767	1731	6	2212	2448	
H ₀ 5 ₀ 0		H ₀ 2 ₁ 1		12	318	324	H ₀ 5 ₂ 2			6	4743	4722	9	3021	3163	6	857	876		
13 2350 0	15	314	35	H ₀ 10 ₀ 1			H ₀ 8 ₂ 3			10	202*	341	14	641	609	10	1715	1759		
14 242*	13	421	333				H ₀ 9 ₃			14	641	609	14	934	1024	12	879	845		
14 242*	11	516	322	11	267*	233		H ₀ 2 ₀ 3			10	120*	33			12	865	594		
14 242*	9	440*	63				H ₀ 1 ₀ 1			12	1371	1361	14	1404	1420	14	1404	1420		
15 970	7	839	552				H ₀ 6 ₂ 4			12	2650	2633	13	321	376					

TABLE 6: Continued

TABLE 6 : Continued

H 10FC		H 10FD		H 10FC		H 16FC		H 10FC		H 10FD		H 10FC		H 10FC		H 10FD		H 10FC									
H 04,10	4 348	406	11 454	291	10 1619	1767	H 0,13	6 1165	1161	4 656	545	H 0,13	6 1165	1161	4 656	545	H 0,13	6 1165	1161	4 656	545						
10 717	705	6 4216	4103	9 386	279	12 1269	1266	H 0,13	6 435	616	11 1296	1277	H 0,14	6 1760	08	10 2011	2095	H 0,14	6 1760	08	10 2011	2095					
12 2400	2634	6 800	842	10 2866	2057	H 0,11	14 876	768	H 0,13	6 3009	2976	7 1902	2019	H 0,14	12 2060	200	10 436	395	H 0,14	12 2060	200	10 436	395				
14 868	839	12 2664	367	H 0,12	10 1956	1990	H 0,13	10 066	691	H 0,13	10 2356	2437	12 1811	1713	H 0,13	12 1811	1713	12 373	152	H 0,13	12 1811	1713	12 373	152			
H 05,10	H 0,2,11	H 0,2,11	H 0,11	H 0,11	13 1294	222	H 0,14	14 427	AC2	H 0,14	10 716	774	H 0,14	10 716	774	H 0,14	14 1176	1159	H 0,14	14 1176	1159	H 0,14	14 1176	1159			
12 504	512	13 700	972	11 1896	1759	H 0,13	9 2650	246	H 0,13	11 1637	1592	H 0,14	13 1637	1592	H 0,14	13 422	369	H 0,14	13 422	369	H 0,14	13 422	369				
11 443	439	11 1453	1469	H 0,12	9 1322	H 0,12	H 0,13	7 426	576	H 0,13	11 052	114	H 0,14	11 052	114	H 0,14	11 465	566	H 0,14	11 465	566	H 0,14	11 465	566			
9 619	602	7 1212	9 1321	1322	H 0,12	H 0,12	H 0,13	5 0	0	H 0,13	13 447	01	H 0,14	11 602	481	H 0,14	11 724	1237	H 0,14	11 724	1237	H 0,14	11 724	1237			
5 648	677	7 1866	270	H 0,12	3 641	554	H 0,12	6 1471	1450	H 0,12	7 707	678	H 0,14	7 707	678	H 0,14	7 2150	2150	H 0,14	7 2150	2150	H 0,14	7 2150	2150			
H 06,10	H 0,233	5 1295	1343	3 5233	5173	H 0,12	2 1730	92	H 0,12	5 1974	210	H 0,14	3 045	039	H 0,14	3 1453	1453	H 0,14	3 1453	1453	H 0,14	3 1453	1453				
6 436	0	H 0,3,1)	H 0,3,1)	H 0,3,1)	6 1857	1637	H 0,12	6 1857	1637	H 0,12	10 1150	1246	H 0,13	2 323	355	H 0,13	6 2639	0	H 0,13	6 2639	0	H 0,13	6 2639	0			
8 2296	2417	4 407	407	8 2602	2570	H 0,12	8 992	1002	H 0,12	12 010	787	H 0,13	4 323	205	H 0,13	6 1991	1605	H 0,13	6 1991	1605	H 0,13	6 1991	1605				
10 2684	36	12 1658	1770	8 458	591	H 0,12	12 1036	936	H 0,12	14 691	734	H 0,13	4 3196	3213	H 0,13	6 1950	1963	H 0,13	6 1950	1963	H 0,13	6 1950	1963				
H 07,10	H 0,10	10 3026	2999	H 0,6,11	12 210	496	H 0,12	10 3026	2999	H 0,12	11 1840	146	H 0,13	6 2719	2756	H 0,13	10 1634	1172	H 0,13	10 1634	1172	H 0,13	10 1634	1172			
13 729	544	14 1222	1076	H 0,6,11	13 596	399	H 0,12	9 936	7436	H 0,12	11 1840	146	H 0,13	10 670	716	H 0,13	12 3676	126	H 0,13	12 3676	126	H 0,13	12 3676	126			
11 00	136	9 755	769	H 0,3,11	11 435	330	H 0,12	11 435	330	H 0,12	12 1109	1076	H 0,13	9 437	436	H 0,13	12 2103	2031	H 0,13	12 2103	2031	H 0,13	12 2103	2031			
7 933	794	13 1790	711	H 0,3,11	9 2076	239	H 0,12	9 2076	239	H 0,12	13 449	591	H 0,13	7 04	0	H 0,13	13 592	662	H 0,13	13 592	662	H 0,13	13 592	662			
H 08,10	H 0,10	11 491	231	9 726	737	H 0,12	11 491	231	H 0,12	10 1211	1174	H 0,13	8 1802	1677	H 0,13	11 902	838	H 0,13	11 902	838	H 0,13	11 902	838				
8 432	0	7 371	366	5 2010	242	H 0,12	11 491	231	H 0,12	12 1109	1076	H 0,13	9 2349	2463	H 0,13	11 1921	1043	H 0,13	11 1921	1043	H 0,13	11 1921	1043				
10 1162	1251	12 504	479	H 0,5,11	13 1790	711	H 0,12	7 462	479	H 0,12	10 1211	1174	H 0,13	10 2907	2857	H 0,13	6 455	0	H 0,13	6 455	0	H 0,13	6 455	0			
12 504	479	H 0,9,10	11 491	H 0,9,11	13 1790	711	H 0,12	9 462	479	H 0,12	12 1109	1076	H 0,13	7 1710	1742	H 0,13	3 3775	3746	H 0,13	10 1616	1750	H 0,13	10 1616	1750			
H 09,10	H 0,9,10	11 491	231	9 726	737	H 0,12	11 491	231	H 0,12	10 1211	1174	H 0,13	8 1802	1677	H 0,13	11 902	838	H 0,13	11 902	838	H 0,13	11 902	838				
11 619	929	10 1547	1542	11 3046	3046	H 0,12	6 622	639	H 0,12	8 1163	1104	H 0,13	9 1643	1643	H 0,13	11 1751	1719	H 0,13	11 1751	1719	H 0,13	11 1751	1719				
9 503	636	12 728	713	14 1070	1009	H 0,12	12 728	713	H 0,12	10 1109	1122	H 0,13	10 1398	1474	H 0,13	10 670	716	H 0,13	10 670	716	H 0,13	10 670	716				
14 10,10	10 2950	0	H 0,6,11	H 0,5,11	2 1200	114	H 0,12	2 1200	114	H 0,12	11 744	674	H 0,13	13 1395	1329	H 0,13	7 075	0	H 0,13	7 075	0	H 0,13	7 075	0			
H 09,11	H 0,9,11	6 3560	3669	5 1755	3455	H 0,12	4 1473	1922	H 0,12	9 0*	0	H 0,13	6 657	796	H 0,13	2 210*	3	H 0,13	3 224*	256	H 0,13	3 224*	256	H 0,13	3 224*	256	
11 619	929	10 1547	1542	11 3046	3046	H 0,12	6 622	639	H 0,12	8 1163	1104	H 0,13	9 1643	1643	H 0,13	4 457	0	H 0,13	4 457	0	H 0,13	4 457	0	H 0,13	4 457	0	
9 503	636	12 728	713	14 1070	1009	H 0,12	12 728	713	H 0,12	10 1109	1122	H 0,13	10 1398	1474	H 0,13	10 670	716	H 0,13	10 670	716	H 0,13	10 670	716				
14 10,10	10 2950	0	H 0,6,11	H 0,5,11	2 1200	114	H 0,12	2 1200	114	H 0,12	11 744	674	H 0,13	13 1395	1329	H 0,13	7 075	0	H 0,13	7 075	0	H 0,13	7 075	0	H 0,13	7 075	0
H 09,11	H 0,9,11	4 769	734	6 1052	965	H 0,12	11 2076	1967	H 0,12	13 226*	430	H 0,13	11 120*	0	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	
13 3210	0	9 1633	1715	7 3757	3809	H 0,12	11 3046	1966	H 0,12	9 161*	0	H 0,13	11 756	756	H 0,13	11 756	756	H 0,13	11 756	756	H 0,13	11 756	756				
9 2130	0	H 0,7,12	H 0,7,12	3 219*	0	H 0,12	12 728	713	H 0,12	10 606	7	H 0,13	9 261*	163	H 0,13	13 95	974	H 0,13	13 95	974	H 0,13	13 95	974	H 0,13	13 95	974	
7 0*	0	H 0,7,12	H 0,7,12	5 375	401	H 0,12	7 0*	109	H 0,12	5 1469	0	H 0,13	7 429	366	H 0,13	11 779	713	H 0,13	11 779	713	H 0,13	11 779	713	H 0,13	11 779	713	
5 2390	0	3 233	0	5 233	0	H 0,12	3 219*	0	H 0,12	1 849	0	H 0,13	7 1719	1794	H 0,13	9 193*	0	H 0,13	9 193*	0	H 0,13	9 193*	0	H 0,13	9 193*	0	
1 233	0	10 2020	2171	12 776	720	H 0,12	10 2020	2171	H 0,12	5 1469	0	H 0,13	5 1191	1134	H 0,13	3 264	0	H 0,13	3 264	0	H 0,13	3 264	0	H 0,13	3 264	0	
H 0,5,11	H 0,5,11	4 769	734	6 1052	965	H 0,12	11 2076	1967	H 0,12	13 226*	430	H 0,13	11 120*	0	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	
2 640	630	H 0,3,12	H 0,3,12	6 1052	965	H 0,12	11 2076	1967	H 0,12	13 226*	430	H 0,13	11 120*	0	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	
1 233	0	6 1052	965	4 4390	4219	H 0,12	11 2076	1967	H 0,12	13 226*	430	H 0,13	11 120*	0	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	H 0,13	11 226*	225	

TABLE 6: Continued

TABLE 6: Continued