Hydrothermal Synthesis of Braunite in the Systems $MnOOH$-SiO_2, Mn_3O_4-SiO_2, and MnO_2-SiO_2

By

Hidenobu HINO,* Taneo MINATO* and Yoshihiko KUSAKABE*

(Received September 30, 1977)

Abstract

Braunite ($MnMn_6SiO_{12}$) was synthesized at low temperatures with pressures from 1 to 2500 bar in the systems manganite (γ-$MnOOH$)-SiO_2, hausmannite (Mn_3O_4)-SiO_2, and pyrolusite (β-MnO_2)-SiO_2. Braunite-pyrolusite assemblage was produced in the first system and braunite-pyroxmangite ($MnSiO_3$) assemblage in the second system. In the third system, only braunite was formed as solid phase. These reaction equations are as follows.

$$8MnOOH+SiO_2=MnMn_6SiO_{12}+MnO_2+4H_2O$$
$$3Mn_3O_4+3SiO_2=MnMn_6SiO_{12}+2MnSiO_3$$
$$7MnO_2+SiO_2=MnMn_6SiO_{12}+2O_2$$

These reaction temperatures, under 1000 bar H_2O total pressure, are 272°C, 459°C, and 521°C (P_{O_2}=1 bar), respectively. P-T diagrams were constructed to show the stability field of braunite. A good correspondence was found between the braunite assemblage synthesized in our laboratory and those observed in bedded manganese ore deposits.

1. Introduction

Braunite is one of the more common manganese oxide minerals that occur both in thermally and regionally metamorphosed manganese ore deposits. Braunite can be divided into two types from its occurrence. One type is associated with manganese silicate minerals such as rhodonite, pyroxmangite and/or spessartine, and the other with manganese oxide minerals like pyrolusite, bixbyite, and/or manganite. The latter is common in the world, and the former is predominant in Japan.

The formula of braunite is $Mn^{\text{I}}\,Mn^{\text{I}}{}_6SiO_{12}$ and the crystal structure is tetragonal, space group $I4_1/acd$ (De Villiers, 1975,[1] Moor and Araki, 1976[2]). In addition, braunite II with the composition $Mn^{\text{I}}\,Mn^{\text{I}}{}_{14}\,SiO_{24}$ is known to occur in South Africa (De Villiers and Herbstein, 1967).[3] The formula of braunite requires 10% SiO_2, but some of the

* Department of Mineral Science and Technology

analyses of natural braunite show silica percentages different from this figure.

The first synthesis of braunite was made by Byström and Mason (1943).[4] They synthesized both from $MnSO_4+NaSiO_3$ and from $Mn_2O_3+MnSiO_3$ at 900°C in air. Moreover, in a study of the phase equilibria in the system manganese oxide-silica above 990°C in air, Muan (1959)[5] pointed out that braunite was formed as a solid solution of SiO_2 in α-Mn_2O_3 and could contain up to 40% SiO_2. These experiments, however, were made at high temperatures in the air, so that these P-T conditions are different from the natural environment where braunite is formed.

In this study, braunite was synthesized from various manganese oxides and silica gel at low temperatures under pressures below 2.5 kb. Then, the problems mentioned above were discussed. It was consequently proved that braunite was simultaneously formed with other manganese oxide or manganese silicate minerals. Also, it was proved that the species of minerals coexisting with braunite depended on the kind of starting materials and the amount of SiO_2. Hence, the deviation from the ideal SiO_2 content of braunite seems to be caused by the contamination of those associated minerals such as pyroxmangite, rhodonite, quartz, and/or manganese dioxides. The formation of braunite in bedded manganese ore deposits has also been discussed briefly from the phase equilibria investigated in this study.

2. Experimental procedure

Starting materials used for this study are two natural manganese minerals, three synthetic manganese compounds, and silica gel (Table 1). Manganese minerals and compounds were individually mixed in an agate mortor with silica gel having more than its chemical equivalent. These samples with a few drops of water were put in containers of gold tubing (diameter=3 or 5 mm), and they were completely sealed by the welding method. For some runs made at one atmosphere total pressure, a container welded at the bottom and closed by constriction at the top was used. Besides, samples without SiO_2 were also prepared to examine dehydration and deoxidization of the starting materials.

The synthesis was carried out in hydrothermal reactor made of stellite. Pressure gauges, designed to operate between 0–150 bar, 0–300 bar, 0–1000 bar, 0–2000 bar, and 0–3000 bar of total pressure, were used interchangeably. The temperature was regulated within 5°C deviation by using a proportional controller or a PID controller, calibrated periodically by using a millivoltmeter with a Chromel-Alumel.

A very small amount of Na_2CO_3 as a mineralizer, was added to the starting materials in some runs, in which an excess of silica was converted into cristobalite or quartz and the formation temperatures of braunite fell considerably. When Na_2CO_3 was present in excess, a sodium bearing mineral such as manjiroite was formed.

Table 1. Manganese minerals and compounds used for the synthesis of braunite

Starting materials	Remarks
Natural minerals	
Pyrolusite (β-MnO_2)	Coarse grained crystal, Bolani, Orissa, India
Manganite (γ-MnOOH)	Columnar crystal with a small amount of pyrolusite, Ilfeld, Harz, Germany
Synthetic compounds	
amorphous δ-MnO_2	Sub-crystal, reduction of boiling $KMnO_4$ solution with HCl
amorphous γ-MnOOH	Sub-crystal, precipitated from a solution of $MnSO_4$ and NH_4OH under H_2O_2 presence
Hausmannite (Mn_3O_4)	Fine grained crystal, $MnSO_4$ heated in air for 20 hours at 1000°C

The runs to determine the experimental P-T conditions for the formation of braunite lasted for the same period (7 days). The phase identifications were made with the x-ray powder diffraction method using Fe $K\alpha_1$ radiation and scanning electron microscopic observation.

3. Results

Experimental results are given in Table 2–5. The manganese sesquioxide Mn_2O_3 synthesized in this study must be α-Mn_2O_3, because the iron content of each starting material is under 0.1 percent. Since orthorhombic α-Mn_2O_3 transforms into cubic bix-

Table 2. Data on synthesis of braunite in the system synthetic MnOOH-SiO_2.

Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product	Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product
M-61	aM	7	267	1	Bx	M-57	aM S	7	295	500	B P
M-60	aM	7	275	1	Bx	M-51	aM S	7	304	500	B P
M-66	aM	7	262	100	M	M-50	aM S	7	313	500	B P
M-70	aM	7	264	500	M	M-63	aM S	7	285	1200	M
M-71	aM	7	267	500	Bx	M-62	aM S	7	295	1200	B P
M-69	aM	7	275	940	Bx	M-54	aM S	7	285	2000	M
M-67	aM	7	260	1100	M	M-72	aM S	7	290	2000	B P
M-64	aM	7	270	1500	Bx	M-81	aM S+	7	280	1	M
M-68	aM	7	265	2000	M	M-77	aM S+	7	275	60	M
M-55	aM	7	275	2000	Bx	M-78	aM S+	7	285	60	B Cr
M-58	aM S	7	292	60	M	M-76	aM S+	7	282	200	B Cr
M-59	aM S	7	305	100	B P	M-75	aM S+	7	273	500	B Cr
M-65	aM S	7	285	300	M	M-74	aM S+	7	282	500	B Cr
M-53	aM S	7	295	300	B P	M-80	aM S+	7	285	1100	M Cr
M-52	aM S	7	303	300	B P	M-73	aM S+	7	270	2000	M Cr
M-56	aM S	7	285	500	M	M-79	aM S+	7	274	2100	B Cr

aM: synthetic MnOOH, S: silica, B: branuite, P: pyrolusite, Bx: α-Mn_2O_3, M: manganite, Cr: cristobalite, +: addition of Na_2CO_3

Table 3. Data on synthesis of braunite in the system natural $MnOOH$-SiO_2.

Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product	Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product
M-32	M	7	287	1	Bx	M-24	M S	7	301	500	M
M-42	M	7	283	60	M	M-26	M S	7	318	500	B P
M-06	M	2	270	500	M	M-19	M S	7	320	500	B P
M-07	M	2	282	500	M	M-03	M S	7	331	500	B P
M-01	M	2	288	500	Bx	M-12	M S	7	312	640	M
M-43	M	5	280	1950	M	M-09	M S	7	304	670	M
M-45	M	5	290	2050	Bx	M-23	M S	7	306	1300	M
M-44	M	5	295	2050	Bx	M-25	M S	7	313	1300	B P
M-31	M S	7	306	1	B X	M-04	M S	7	296	2330	M
M-15	M S	7	295	80	M	M-10	M S	7	307	2400	B P
M-08	M S	7	305	80	B X M	M-39	M S+	7	292	70	M Q
M-02	M S	7	314	95	B X	M-40	M S+	7	299	100	B P Q
M-16	M S	7	300	200	M	M-41	M S+	7	308	100	B P Q
M-13	M S	7	309	200	B X M	M-28	M S+	7	293	200	M Q
M-21	M S	7	321	200	B X	M-34	M S+	7	300	280	B M Q
M-22	M S	7	330	200	B X	M-33	M S+	7	308	300	B P Q
M-29	M S	7	345	200	B P X	M-05	M S+	7	373	670	B P Mj Q
M-30	M S	7	357	200	B P Q	M-38	M S+	7	300	1000	M Q
M-18	M S	7	309	300	B X M	M-35	M S+	7	295	1100	M Q
M-17	M S	7	320	300	B P X	M-36	M S+	7	440	1100	B Mj Q
M-27	M S	7	330	300	B P	M-37	M S+	7	300	2000	B P Mj Q
M-20	M S	7	315	400	B P X M	M-11	M S+	7	307	2400	B P Q

M: manganite, S: silica, B: braunite, P: pyrolusite, X: Mn_5O_8, Bx: α-Mn_2O_3, Mj: manjiroite, Q: quartz, +: addition of Na_2CO_3

Table 4. Data on synthesis of braunite in the system hausmannite-SiO_2.

Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product	Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product
H-09	H	7	530	500	H	H-47	H S+	7	684	200	B Px H Q
H-24	H	7	582	500	H	H-55	H S+	7	479	350	H Q
H-19	H	7	635	500	Ms H	H-54	H S+	7	530	350	B Px H Q
H-11	H	7	728	500	Ms	H-56	H S+	7	580	350	B Px H Q
H-10	H S	7	526	500	H Cr	H-31	H S+	7	520	500	B Px H Q
H-23	H S	7	582	500	H Cr	H-41	H S+	40	530	500	B Px H Q
H-20	H S	7	635	500	B Px H Tr	H-32	H S+	7	575	500	B Px H Q
H-12	H S	7	726	500	R T	H-38	H S+	7	417	550	H Q
H-36	H S+	7	520	50	H Q	H-37	H S+	7	473	550	B Px H Q
H-40	H S+	7	563	80	H Q	H-58	H S+	7	448	1000	H Q
H-46	H S+	7	626	100	H Q	H-59	H S+	7	469	1000	B Px H Q
H-51	H S+	7	669	100	T H	H-39	H S+	7	421	1700	H Q
H-49	H S+	7	569	200	H Q	H-44	H S+	7	442	1700	H Q
H-57	H S+	7	624	200	B Px H Q	H-35	H S+	7	470	1700	B Px H Q

H: hausmannite, S: silica, B: braunite, Px: pyroxmangite, R: rhodonite, T: tephroite, Ms: manganosite, Cr: cristobalite, Tr: tridymite, Q: quartz, +: addition of Na_2CO_3

Table 5. Data on synthesis of braunite in the system manganese dioxides-SiO_2.

Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product	Run No.	Starting material	Time (days)	Tem. (°C)	Press. (bar)	Product
P-03	P	7	326	500	P	P-04	P S	7	326	500	P
P-14	P	7	419	500	P	P-34	P S	7	455	500	P Cr
P-23	P	7	475	500	P	P-67	P S+	7	450	500	P Q
P-01	P	7	534	500	Bx P	P-02	P S	7	530	500	B P Cr
P-61	Ra	7	303	80	Bx P Cm	P-63	P S+	7	530	500	B P Q
P-05	Ra	7	329	500	Bx P Cm	P-06	Ra S	7	335	500	P Cm
P-07	Ra	7	524	500	Bx P Cm	P-08	Ra S	7	503	500	B P Cm Cr
P-60	Ra	7	277	650	P Cm	P-66	Ra S+	7	524	500	B P Cm Q

P: pyrolusite, Ra: δ:-MnO_2, S: silica, B: braunite, Bx: α-Mn_2O_3, Cm: cryptomelane, Cr: cristobalite, Q: quartz, +: addition of Na_2CO_3

byite by less than one cation % Fe^{3+} impurity (Grant, et al., 1968),[6] the P-T conditions of α-Mn_2O_3 formation in the present system may be similar to that of natural bixbyite.

3-1 Reaction in the system synthetic MnOOH-SiO_2

A study in this system was made in the temperature range 260–313°C with pressures from 1 to 2000 bar. The phase diagram is shown in Fig. 1. Sub-crystalline MnOOH was converted into weakly crystalline manganite in the P-T range below the broken line. The dot-dash line represents the reaction $2MnOOH=Mn_2O_3+H_2O$, showing a good resemblance to the result published earlier by Klingsberg and Roy (1959).[7] Manganite was dehydrated into α-Mn_2O_3 at higher temperatures than this phase boundary under SiO_2 absence, but was prevented from decomposing up to the broken line under SiO_2 presence.

Braunite was simultaneously formed with pyrolusite in the P-T range above the broken line. The reaction equation is as follows:

$$8MnOOH+SiO_2=MnMn_6SiO_{12}+MnO_2+4H_2O \quad (1)$$

This reaction is counterbalanced in the oxidation and reduction of manganese mineral, indicating that braunite is formed by a reduction of manganite and pyrolusite by oxidation. On the other hand, α-Mn_2O_3 formed by dehydration of MnOOH had no stability field under SiO_2 presence. This result is quite consistent with the fact that bixbyite-quartz assemblage is not found in nature.

In the presence of Na_2CO_3 the phase boundary for the reaction (1) shifted from the broken line to the solid line. That is, the reaction temperature fell about 15°C and the metastable field of manganite above the dot-dash line was extremely narrowed. This result indicates that the reaction (1) is irreversible in the present P-T condition. Therefore, it is expected that braunite is formed at a still lower temperature by adding a more suitable mineralizer and by further prolonging a run.

Under Na_2CO_3 presence crystalline manganese dioxide minerals such as pyrolusite and manjiroite could not be identified in products sysnthesized at the P-T condition in the vicinity of the solid line. Nevertheless, amorphous manganese dioxides must have been formed stoichiometorically.

An excess of silica was left amorphous in the products, while it was converted into cristobalite under Na_2CO_3 presence. These amorphous silica and cristobalite which are metastable in the present P-T condition may be finally converted into quartz (Mizutani, 1966).[8]

3-2 Reaction in the system natural manganite-SiO_2

A study in this system was made in the temperature range 270–440°C with pressures from 1 to 2400 bar. The phase diagram is shown in Fig. 2. Compared with the result in the system synthetic MnOOH-SiO_2, a new phase braunite-Mn_5O_8 was obtained at the pressure range 1–450 bar, and the phase boundaries shifted about 10–20°C to higher temperatures. A columnar crystal of Mn_5O_8, 0.2 mm in length, was formed in some runs (Fig. 3).

Manganese oxide with the composition Mn_5O_8 (Osward, Feitkneicht, and Wampetich, 1965)[9] has not been found in nature. This compound is formed in the

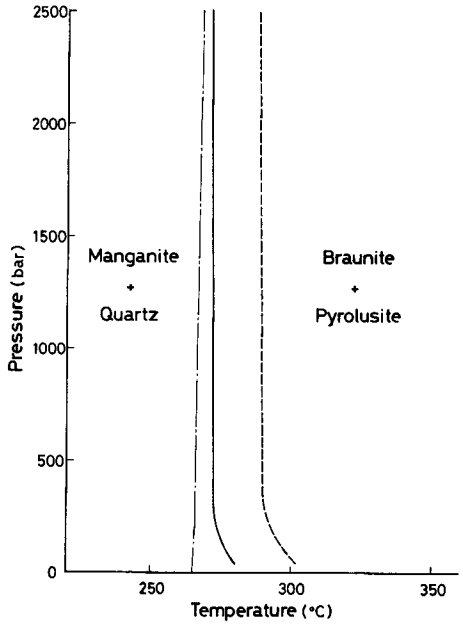

Fig. 1. Pressure-temperature diagram for the reaction in the system synthetic MnOOH-SiO_2. Solid line: the reaction under Na_2CO_3 presence, broken line: the reaction under Na_2CO_3 absence, dot-dash line: the reaction without SiO_2 ($2MnOOH = Mn_2O_3 + H_2O$)

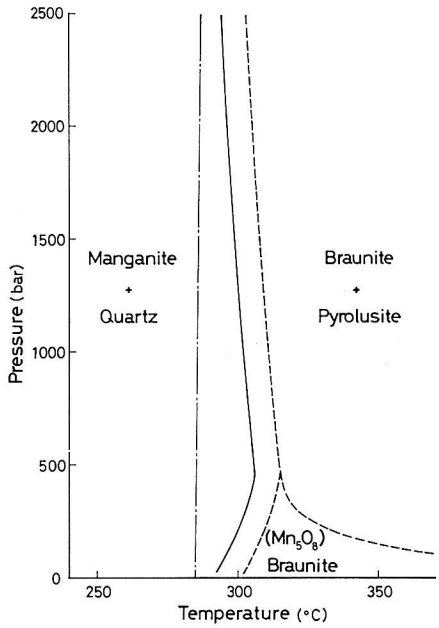

Fig. 2. Pressure-temperature diagram for the reaction in the system natural MnOOH-SiO_2. Solid line: the reaction under Na_2CO_3 presence, broken line: the reaction under Na_2CO_3 absence, dot-dash line: the reaction without SiO_2 ($2MnOOH = Mn_2O_3 + H_2O$)

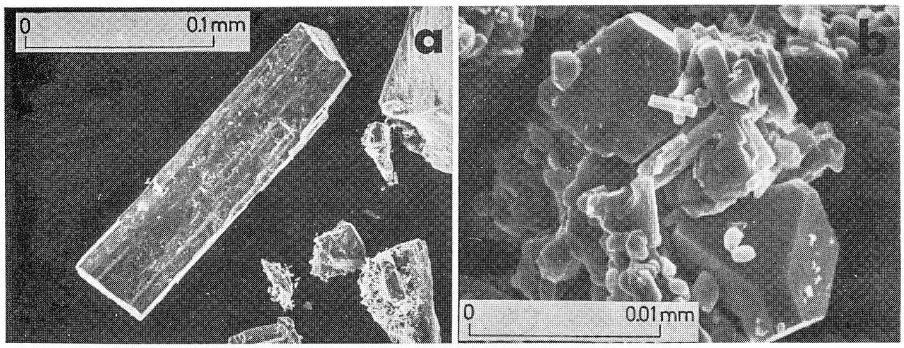

Fig. 3. Crystal of Mn_5O_8 (a) synthesized at 309°C under 200 bar for 7 days and crystal of braunite (b) synthesized at 530°C under 500 bar for 40 days.

course of the oxidation of manganite to pyrolusite, and may be stable in the temperature range of 250–550°C at a low pressure under a suitable oxidizing condition. In this system, the oxidizing condition was produced by the reaction $14MnOOH + 2SiO_2 = 2MnMn_6SiO_{12} + 7H_2O + (O)$. The reaction equations including Mn_5O_8 are as follows:

$$12MnOOH + SiO_2 = MnMn_6SiO_{12} + Mn_5O_8 + 6H_2O \quad (2)$$

$$2Mn_5O_8+SiO_2=MnMn_6SiO_{12}+3MnO_2 \quad (3)$$

Under high pressure in the vicinity of the phase boundary, Mn_5O_8 was formed at the end of a short period of reaction, for instance, in a run which lasted for 2 days at 305°C under 2000 bar, but was converted into braunite and pyrolusite by reaction (3) after 7 days. Further, under Na_2CO_3 presence the phase boundary was reduced about 10°C and the phase braunite-Mn_5O_8 disappeared, being replaced by the phase braunite-pyrolusite. Hence, Mn_5O_8 synthesized in the system natural manganite-SiO_2 is metastable, and therefore braunite-Mn_5O_8 assemblage is not assumed to be found in nature.

As is obvious from the phase diagrams (Fig. 1, Fig. 2), the formation temperature of braunite is higher in the system natural manganite-SiO_2 than in the system synthetic MnOOH-SiO_2. Also the metastable field of braunite-Mn_5O_8 exists in the former system under Na_2CO_3 absence. These differences in the phase diagrams are considered to be caused by the differences in the amount of impurities and crystallinity between natural and synthetic MnOOH. That is to say, increase of impurities in manganite tends to raise the decomposition temperature, and a well crystallized manganite is easily converted into other well crystallized compounds such as Mn_5O_8.

3-3 Reaction in the system hausmannite-SiO_2

A study in this system was made in the temperature range 417–728°C with pressures from 50 to 1700 bar. At higher temperatures (over 600°C), a reducing atmosphere is predominant, which is due to hydrogen gas generated by the interaction of water and reactor. Hence, only divalent manganese minerals such as manganosite, rhodonite or tephroite were formed over 700°C. The formation of braunite in the system hausmannite-SiO_2 is chemically formulated as follows:

$$3Mn_3O_4+3SiO_2=MnMn_6SiO_{12}+2MnSiO_3 \quad (4)$$

This reaction is characterized by the formation of divalent manganese silicate mineral with braunite, and is also counterbalanced in oxidation and reduction of manganese mineral as mentioned in reaction (1). In this study, the silicate mineral coexisting with braunite was pyroxmangite, but under suitable conditions, that is, in the presence of Ca^{2+}, rhodonite is expected to be formed instead of pyroxmangite.

The phase boundary of reaction (4) under Na_2CO_3 presence is shown in Fig. 4. Compared with a run under Na_2CO_3 absence, the reaction temperature at 500 bar remarkably fell about 160°C under Na_2CO_3 presence. Therefore, the reaction (4) is irreversible in the present P-T condition, and is also expected to take place at a still lower temperature.

3-4 Reaction in the system manganese dioxides-SiO_2

Two kinds of manganese dioxides, natural pyrolusite and synthetic δ-MnO_2, were

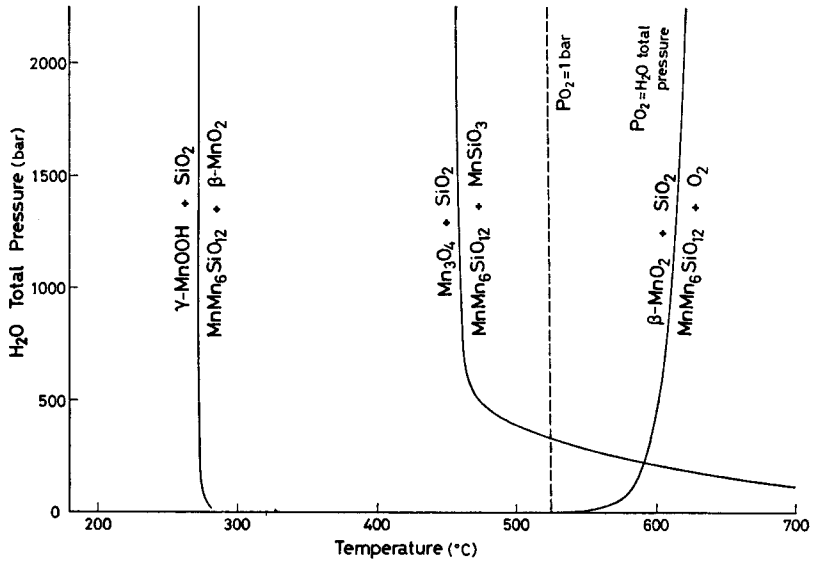

Fig. 4. Pressure-temperature diagram for the reaction in the systems manganite-SiO_2, hausmannite-SiO_2, and pyrolusite-SiO_2.

prepared as starting materials. A study in this system was made in the temperature range 277–534°C under 80, 500, and 650 bar.

Pyrolusite began to be deoxidized into α-Mn_2O_3 at 530°C under 500 bar in the absence of SiO_2. This deoxidization temperature is about 70°C lower than the calculated one, for at that temperature, the atmosphere is still reducing where pyrolusite is deoxidized more actively than hausmannite. The equation for the deoxidization of pyrolusite is as follows:

$$4MnO_2=2Mn_2O_3+O_2 \tag{5}$$

In the presence of SiO_2, pyrolusite began to be converted into braunite at the same P-T condition with reaction (5). This reaction is considered to proceed by following two steps. Pyrolusite is deoxidized into α-Mn_2O_3 by reaction (5) and then α-Mn_2O_3 is converted into braunite by the reaction as follows:

$$4Mn_2O_3+SiO_2=MnMn_6SiO_{12}+MnO_2 \tag{6}$$

The following equation is derived from equation (5) and (6).

$$7MnO_2+SiO_2=MnMn_6SiO_{12}+2O_2 \tag{7}$$

The reaction (7) is characterized by the generation of oxygen gas, indicating the phase equilibria to be a function of oxygen gas partial pressure. As mentioned above, this reaction depends on the deoxidization of pyrolusite, indicated by equation (5), so that the phase boundary of reaction (7) can probably be replaced by that of reaction (5).

Then, the phase boundary of reaction (5) calculated from the value of thermodynamic data is shown in Fig. 4. as that of reaction (7).

The formation temperature of braunite in the system pyrolusite-SiO_2 is above 500°C even if Po_2=1 bar, and is higher than that in another system. The reaction (7) is different from reaction (1), and (4) seems to be reversible, because oxidation of braunite is widely found in supergene manganese oxide deposits.

δ-MnO_2** with the composition MnO_{2-x} ($x<0.5$) was decomposed at 303°C under 80 bar and at 329°C under 500 bar in the absence of SiO_2, being converted into α-Mn_2O_3 and crystalline manganese dioxide minerals such as pyrolusite and cryptomelane. On the other hand, neither manganite nor α-Mn_2O_3, excepting manganese dioxides, could be identified in the products below 300°C (Table 5). Nevertheless, in view of stoichiometory, the decompositions of δ-MnO_2 are chemically formulated as follows:

$$MnO_{2-x}+xH_2O=2xMnOOH+(1-2x)MnO_2 \quad (8)$$

$$MnO_{2-x}=xMn_2O_3+(1-2x)MnO_2 \quad (9)$$

Which one will take place will result from the stability fields of α-Mn_2O_3-manganite. The formation of cryptomelane is caused by the potassium contaminated in δ-MnO_2.

Now, in the presence of SiO_2, manganite or α-Mn_2O_3 formed by decomposition of δ-MnO_2 may be converted into braunite by equation (1) or (6). Then, the reaction equation in the system δ-MnO_2-SiO_2 is derived from equations (1), (6), (8), and (9) as follows:

$$4MnO_{2-x}+xSiO_2=xMnMn_6SiO_{12}+(4-7x)MnO_2 \quad (10)$$

Since the reaction (10) depends on reaction (1), it is assumed that the phase boundary in the system δ-MnO_2-SiO_2 is equal to that of reaction (1). However, in practice, braunite could not be identified in the products synthesized at the P-T condition in the vicinity of that phase boundary.

4. Discussion

The P-T conditions for the formation of braunite in the systems MnOOH-SiO_2, Mn_3O_4-SiO_2, and MnO_2-SiO_2 were experimentally obtained, and the phase diagrams were illustrated, based on these data. On the other hand, the P-T condition for its decomposition by heating could not be determined, because the decomposition temperature exceeds the permitted amount of the apparatus. Then, the decomposition temperature has been estimated as follows on the basis of the previous experimental data. The decomposition temperature depends on two parameters, the amount of SiO_2

** Although δ-MnO_2 essentially contains hydroxyl group and water, its composition is represented by MnO_{2-x} as a matter of convenience in this paper.

and oxygen gas partial pressure, that is, the transformation temperature of Mn_2O_3 to Mn_3O_4 rises largely as the amount of SiO_2 increases (Muan, 1959).[5] Also, highly oxidized manganese compounds are generally deoxidized one after another by raising the temperature. α-Mn_2O_3 is deoxidized into tetragonal hausmannite at 877°C in air (Hahn and Muan, 1960).[10] Consequently, it is assumed that braunite is stable at least up to that temperature without any reducing agent.

Under the presence of a reducing agent, the decomposition of braunite also takes place at low temperatures (Hino and Minato, 1974).[11] For instance, in the presence of glucose a part of braunite is reduced into rhodochrosite at 150°C under 500 bar for 7 days. However, braunite does not change at 400°C in hydrogen flow for 4 hours, though hausmannite is deoxidized into manganosite. Moreover, in the run of reduction by glucose as mentioned above, pyrolusite is completely reduced into hausmannite and rhodochrosite. Therefore, it is understood that braunite is more stable in a reducing atmosphere than other manganese oxide minerals including Mn^{3+} or Mn^{4+}. This inertness may be caused by the fixing of a part of the oxygen in the Si-O bond following the entrance of Si into a crystal lattice.

It is noteworthy that under a condition saturated with SiO_2 braunite is simultaneously formed with manganese dioxides or divalent manganese silicate. An excess of silica does not enter into the braunite structure by the present P-T conditions, but is converted into quartz which is also stable in the stability field of braunite. Moreover, under a condition unsaturated with SiO_2, it is predicted that α-Mn_2O_3 and hausmannite will remain with synthesized braunite, and also that in a certain P-T condition braunite II may be formed. Which species of minerals will coexist with braunite depends on the kind of starting materials, the amount of SiO_2, and also crystallochemically on a small amount of cations such as Na^+, K^+, Ca^{2+}, Al^{3+} and Fe^{3+}. It became clear consequently that braunite genetically coexisted with other manganese minerals and/or quartz.

The x-ray powder diffraction pattern of braunite synthesized in this study is very consistent with natural ones (Table 6). In some natural braunites, d-spacings of 3.33 Å and 2.98 Å with a relative intensity ranging from 5 to 30 are observed (Smithergale, 1929,[12] Harcourt, 1942,[13] Feisher and Richmond, 1943[14], Nambu et al., 1964[15]). In this study, these d-spacings were exclusively observed in products which contained quartz and pyroxmangite. That is to say, 3.33 Å and 2.98 Å correspond to the strongest lines of quartz and pyroxmangite respectively.

Data on braunite obtained from both a chemical analysis and an x-ray diffraction method are rare. Hence, a definite statement cannot be made on the relationship between SiO_2 content and d-spacing. However, 3.33 Å and 2.98 Å braunites contain probably more than 10% silica, because braunite seldom occurs as single crystal, but is closely accompanied with other manganese silicates and quartz. Therefore, it can

Table 6. Observed d-spacing of natural and synthetic braunite. (Fe $K\alpha_1$=1.93597Å with Si standard)

B-1		B-2		P-02		M-03		H-32	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
5.43	3								
		4.73	3					4.74	4
3.49	10	3.49	3	3.49	11	3.49	10	3.49	11
2.716	100	2.716	100	2.713	100	2.715	100	2.713	100
2.513	3			2.499	5	2.516	2		
2.359	10	2.356	8	2.356	13	2.355	10	2.358	11
2.337	3	2.335	3	2.333	6	2.335	3	2.341	4
2.155	8	2.161	5	2.157	8	2.158	8	2.156	7
2.145	8	2.144	8	2.142	12	2.145	10	2.143	10
1.874	2	1.878	2						
1.812	3	1.815	2						
1.739	3	1.738	2						
1.660	21	1.660	16	1.659	21	1.661	21	1.660	24
1.539	3	1.539	3	1.537	6	1.542	5	1.541	5
1.505	1	1.505	2						
		1.468	3						
1.420	9	1.420	8	1.420	8	1.420	10	1.420	9
1.411	6	1.411	5	1.410	6	1.413	5	1.412	6

B-1. From the Ashidani mine, Kyoto pref.
B-2. From the Ananai mine, Kōchi pref.
P-02. Synthesized from pyrolusite at 530°C under 500 bar
M-03. Synthesized from manganite at 331°C under 500 bar
H-32. Synthesized from hausmannite at 575°C under 500 bar

be concluded that the d-spacings of 3.33 Å and 2.98 Å observed in braunite are because of the contamination by quartz and pyroxmangite.

5. Geologic applications

The authors intend to discuss briefly the genesis of braunite in bedded manganese ore deposits on the basis of the present experimental data.

5-1 Braunite-manganese silicates assemblage

Braunite-pyroxmangite or braunite-rhodonite assemblage is often found in Palaeozoic and Mesozoic bedded manganese ore deposits, suffering thermal or regional metamorphism in Japan. Banded braunite-pyroxmangite-quartz ores are found at the Ashidani mine in the Tamba highland, where a small amount of manganosite occurs, indicating that the deposit has suffered thermal metamorphism. Unmetamorphosed deposits in this area are characterized by the presence of a rhodochrosite-haus-

mannite assemblage and occasionally of a chocolate-coloured ore, which is mainly composed of hausmannite (Yoshimura, 1967[16]), Kusakabe, 1968[17]). In the braunite rich ore from the Nodatamagawa mine, well known for its thermally metamorphosed deposits, there are found braunite, hausmannite, rhodonite, tephroite, barite, and occasionally Mn-bearing pyroxene and amphibole (Watanabe et al., 1971)[18]. The presence of tephroite and hausmannite represents an environment unsaturated with SiO_2. Therefore, on the basis of a braunite-pyroxmangite assemblage synthesized in the system hausmannite-SiO_2, it may be concluded that braunite coexisting with divalent manganese silicate minerals in those deposits is not a primary mineral, but a metamorphosed one derived from hausmannite. In addition, the formation temperature of braunite in bedded manganese ore deposits is expected to be lower than the experimental value obtained in this study, considering the reaction of an unconceivably long duration in sediment.

5-2 Braunite-manganese oxides assemblage

Braunite-pyrolusite, braunite-hollandite, braunite-bixbyite, and braunite-manganite assemblages are found in many Precambrian bedded manganese ore deposits suffering regional metamorphism in India. These deposits have been metamorphosed to different grades corresponding to chlorite, biotite, almandine, staurolite-kyanite, and sillimanite zones (Roy, 1968).[19] Braunite-pyrolusite assemblage is found in the chlorite zone such as the Shivrajpur mine area, where pyrolusite-cryptomelane-manganite ore occurs as deep secondary minerals beneath the zone of oxidation (Rasul, 1965).[20] Braunite-hollandite, braunite-bixbyite, and braunite-manganite assemblages are to be found in higher-grade metamorphic zones than chlorite zone, such as the Kajlidongri, Bharweli, Chikla-Sitasaongi and Gowari-Wadhona mine areas. The formation of hollandite depends on the behavior of Ba^{2+} in the process of metamorphism. The presence of bixbyite, which is formed by dehydration of manganite or by deoxidization of pyrolusite, indicates an environment unsaturated with SiO_2. Manganite associated with braunite in a high-grade metamorphic zone is a secondary mineral derived from bixbyite by hydration. The principal minerals coexisting with braunite are manganese dioxides such as pyrolusite and hollandite. The oxidation state of manganese minerals tends to be gradually reduced with progressive metamorphism. For example, hausmannite, vredenburgite, and jacobsite are found in staurolite-kyanite and sillimanite zones. This fact leads to the conclusion that the original minerals of those deposits are highly oxidized manganese minerals. Considering the present experimental data, it is assumed that the original minerals are manganese oxides with the composition MnO_{2-x} like δ-MnO_2. It is interesting to note that manganese nodules found on the ocean floor mainly consist of amorphous manganese oxide with the same composition, and include neither pyrolusite nor cryptomelane.

6. Acknowledgments

The authors are indebted to Mr. K. Kimura, Technical Official of the Department of Mineral Science and Technology, Kyoto University, for his kindly help in our x-ray powder analysis. The expense of this study was partly defrayed by the Scientific Research Grant from the Ministry of Education to which the authors' sincere thanks are also due.

References

1) De Villiers, P. R.: Amer. Mineral., **60**, 1098–1104 (1975).
2) Moore, P. B. and Araki, T.: Amer. Mineral., **61**, 1226–1240 (1976).
3) De Villiers, P. R. and Herbstein, F. H.: Amer. Mineral., **52**, 20–30 (1967).
4) Byström, A. and Mason, B.: Ark. Kemi. Mineral. Geol. 16B, No. **15**, 1–8 (1943).
5) Muan, A.: Amer. Journ. Sci., **257**, 297–315 (1959).
6) Grant, R. W., Geller, S., Cape, J. A. and Espinosa, G. P.: Phys. Rev., **175**, 686 (1968).
7) Klingsberg, C. and Roy, R.: Amer. Mineral., **44**, 819–838 (1959).
8) Mizutani, S.: J. Earth Sci., Nagoya Univ., **14**, 56–88 (1966).
9) Osward, H. R., Feitknecht, W., and Wampetich, M. J.: Nature, **207**, 72–73 (1965).
10) Roy, S.: Econ. Geol., **63**, 760–786 (1968).
11) Hino, H. and Minato, T.: Proceedings of the Ann. Mtgs. of the Society of Mining Geologists of Japan. Oct., 56 (1974)-in Japanese.
12) Smitheringale, W. V.: Econ. Geol., **24**, 481–505 (1929).
13) Harcourt, G. A.: Amer. Mineral., **27**, 62–113 (1942).
14) Fleisher, M. and Richmond, W.: A preliminary report. Econ. Geol., **38**, 280 (1943).
15) Namb, M., Ishii, Y., and Tanida, K.: Bull. Res. Inst. Min. Dress. and Met., Tohoku Univ., **28**, 101–108 (1964)-in Japanese.
16) Yoshimura, T.: Supplement to manganese ore deposits of Japan. Part 1. Manganese mineralization, minerals and ores. (1967)-in Japanese.
17) Kusakabe, Y.: Unpublished D. Eng. thesis. Kyoto Univ. Japan (1968)-in Japanese.
18) Watanabe, T., Yui, S., and Kato, A.: Volcanism and ore genesis. Univ. Tokyo Press. 119–142 (1970).
19) Roy, S.: Econ. Geol., **63**, 760–786 (1968).
20) Rasul, S. H.: Econ. Geol., **60**, 149–162 (1965).