Studies on the Hydrated Iron Oxides. V : Hydrated Ferric Oxide and Manganese Dioxide Minerals Altered from Siderite and Ferroan Rhodochrosite by Weathering

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Hydrated Ferric Oxide and Manganese Dioxide Minerals Altered from Siderite and Ferroan Rhodochrosite by Weathering*

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(Received September 25, 1959)

Synopsis

Mineralogical study was made of one sample each of weathering products of siderite and ferroan rhodochrosite. The siderite ore from Fukuô Mine, Fukushima Prefecture, had been altered into goethite by weathering, and ferroan rhodochrosite from Yamato Mine of the same prefecture had been altered into an aggregate of goethite, γ-type ramsdellite, pyrolusite and cryptomelane.

I. Introduction

The present author has reported on the results of studies on the mineral composition of hydrated ferric oxides and ferric oxides produced by weathering of pyrite[1], pyrrhotite[2], hematite[3] and magnetite[4]. In this report, the weathering products of siderite and ferroan rhodochrosite will be treated.

Mines producing these minerals are not many in Japan, and ore deposits consisting mainly of such minerals are very rare indeed. So the author had only one sample each of these minerals for study. The hydrated ferric oxide mineral produced by alteration of these two minerals consisted only of goethite, no other limonite minerals being found in the samples.

II. The samples

a) Limonite after siderite: The sample of oxidized siderite was a product from Fukuô Mine, Fukushima Prefecture, which has deposits of limonite genetically correlated with the quaternary volcanism. The siderite ores are irregular aggregates of white fine crystals and contained in the limonite ores, often accompanied by vivianite. The outcrops and the cracks of the siderite ores are highly limonitized, some of the samples being entirely burned into limonite retaining only pseudomorphs of siderite. An example of siderite in the process of limoniti-

(1) M. Nambu, Sci. Rep. RITU, A9 (1957), 215.
(2) M. Nambu, Sci. Rep. RITU, A9 (1957), 527.
(3) M. Nambu, Sci. Rep. RITU, A9 (1957), 534.
(4) M. Nambu, Sci. Rep. RITU, A10 (1958), 453.

zation is shown in Photo. 1.

Photo. 1. Photomicrogram of oxidized siderite from Fukuô
Mine. (Thin section, open nicol, ×50)
A : Siderite B : Goethite C : Cavity

Photo. 2. Photomicrogram of oxidized ferroan rhodochrosite
from Yamato Mine. (Thin section, open nicol,
×50)
A : Ferroan rhodochrosite
B : Goethite, manganese dioxide mixture

b) Limonite after ferroan rhodochrosite: The sample of oxidized ferroan
rhodochrosite was a product from Yamato Mine, Fukushima Prefecture. This
mine consists of manganese deposits formed of more than a dozen parallel veins

occurring in biotite granite. The upper zone of the deposit contains only manganese dioxide minerals, but in the lower zone, the percentage of oxidized ferroan rhodochrosite and manganoan calcite increases gradually and eventually the deposit becomes an aggregate of sheer carbonate minerals containing manganese. Therefore, this deposit is assumed to have been formed by an epithermal fissurefilling ore deposit mainly of manganese bearing carbonate mineral altered into a residual deposit of manganese dioxide ore through weathering. A microphotograph of a sample of ferroan rhodochrosite in the course of oxidation is shown in Photo. 2.

III. Goethite altered from Siderite

The results of chemical analysis of the white siderite forming the central nucleus of the sample and of limonite altered from it are shown in Table 1.

Table 1. Chemical analysis of siderite and goethite.

Mineral Composition	Siderite	Goethite
	wt.%	wt.%
CaO	0.08	tr
MgO	1.10	0.38
MnO	0.63	tr
FeO	56.77	0.67
CO_2	37.95	tr
Fe_2O_3	1.30	83.36
SiO_2	2.32	0.78
Al_2O_3	tr	tr
H_2O+	0.20	12.16
H_2O-	—	2.30
Total	100.35	99.65

Table 2. X–ray powder patterns of siderite and goethite.

Siderite		Goethite	
$d(\text{Å})$	I	$d(\text{Å})$	I
3.59	s	4.22	vs
2.79	vs	3.90	vw(d)
2.56	vw	3.39	w
2.34	m	2.98	vw
2.13	s	2.69	m
1.96	m	2.58	m
1.80	m	2.45	vs
1.73	vs	2.24	w
1.52	w	2.18	m
1.50	m	1.90	vw
1.42	m	1.80	w
1.40	w	1.71	vs
1.38	wv	1.69	vw
1.34	m	1.60	vw
1.28	w	1.55	s
1.23	vw	1.51	w
1.22	w	1.46	m
1.20	m	1.42	w
1.17	w	1.39	vw
1.12	m	1.36	w
1.11	vw	1.31	w
1.09	w	1.26	m
1.08	m	1.14	vw
1.07	m	1.12	vw

Small amounts of Fe_2O_3 and SiO_2 are present in the forms of limonite and quartz respectively. The chemical composition of the limonite sample shows that it is nearly a pure limonite mineral.

The interplanar spacings and the relative intensities of the two samples above as determined by x–ray powder photography were as shown in Table 2. The results show that the samples are of pure siderite and goethite.

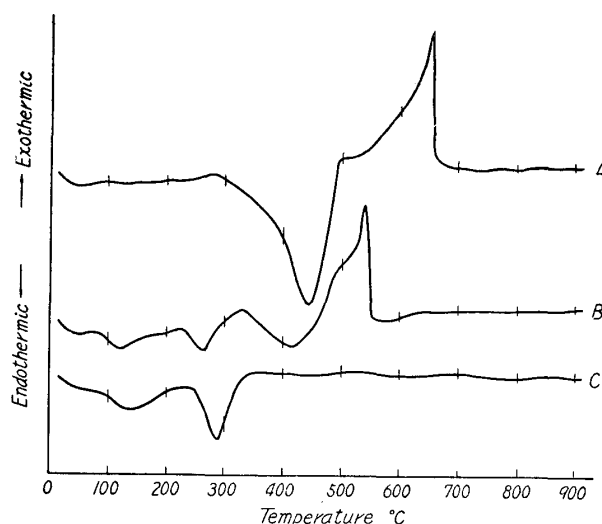The results of differential analysis are shown in Fig. 1. 0.5 gr each of the

Fig. 1. Differential thermal Curves for : A–siderite, B– siderite,
goethite mixture, C– goethite.

samples was used in the analysis and the heating rate was 10°C/min. Siderite (A) showed a conspicuous endothermic peak at 445°C and a steep exothermic peak at 655°C. The former peak is probably due to the dissociation of $FeCO_3$ and the latter to the oxidation of FeO[5]. Goethite (C) showed a faint endothermic peak at 135°C and a more definite peak at 290°C, due to the escape of absorbed water and crystalline water, respectivery. Fig. 1–B shows the differential thermal curve of siderite altered into goethite. The peaks in the curve distinctly show the characteristics of the ore of goethite mixed with siderite.

Goethite after siderite by weathering is believed to be formed by the following chemical reactions :

$$FeCO_3 + CO_2 + H_2O = Fe(HCO_3)_2$$
$$4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2$$
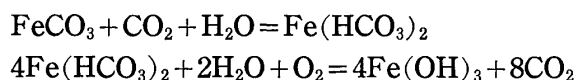
IV. Goethite and manganese dioxide minerals after rhodochrosite

In a sample from Yamato Mine which is in the course of oxidation of ferroan rhodochrosite the cross-section, as shown in Fig. 2, has a nucleus of residual rhodochrosite (A) at the center, surrounded by an intermediate zone (B) of 0.5–1 cm of gray-black hard mineral, which is in turn surrounded by a brown-black

(5) H. E. Kissinger, H. F. McMurdie and B. S. Simpson, J. Amer. Cer. Soc., **39** (1956), 168.

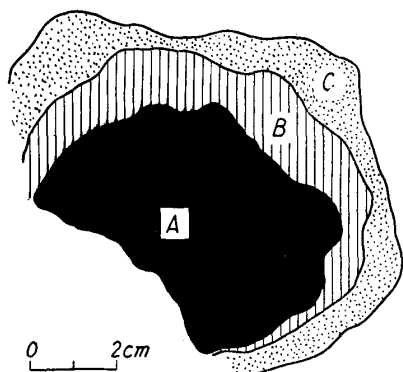somewhat loose zone (C). This fact suggests that the rhodochrosite (A) altered into (B) and then into (C).

Fig. 2. Macroscopic sketch of polished section of oxidized ferroan rhodochrosite.
A : Ferroan rhodochrosite
B : γ-type ramsdellite
C : Pyrolusite, goethite mixture

The results of chemical analysis of the 3 zones above are shown in Table 3 and the results of X-ray powder data in Table 4. The data shows that (A) consists of ferroan rhodochrosite of the chemical composition of ($Mn_{0.57}$, $Fe_{0.39}$, $Ca_{0.03}$, $Mg_{0.02}$) CO_3, and this mineral is richest in iron content of all the rhodochrosites ever known in Japan. The diffraction patterns of (B) show a general similarity to those of ramsdellite, but the patterns are fewer and more widely diffused than the patterns reported by Fleischer and Richmond,[6] the originators of the name ramsdellite. Cole et al.[7] looked upon γ-MnO_2 as ramsdellite of low crystallinity and said that γ-MnO_2 I and γ-MnO_2 II came between the two. In Table 5 are shown the dif-

Table 3. Chemical analysis of three portions in Fig. 2.

Mineral Composition	Ferroan rhodochrosite (A)*	γ-type ramsdellite (B)*	Pyrolusite, goethite mixture (C)*
	wt.%	wt.%	wt.%
MnO_2	—	61.37	53.09
Fe_2O_3	0.36	28.77	30.94
Al_2O_3	tr	0.37	0.37
FeO	22.03	—	—
MnO	30.21	1.73	2.75
CaO	1.49	0.10	0.15
MgO	0.24	tr	tr
BaO	—	0.10	0.16
Na_2O	—	tr	tr
K_2O	—	tr	tr
SiO_2	8.64	1.15	3.95
CO_2	36.62	—	—
H_2O+	0.10	4.08	5.77
H_2O-	0.40	2.29	2.76
Total	100.09	99.96	99.94

* A, B and C illustrated in Fig. 2

fraction patterns of the 3 kinds of γ-MnO_2 described by Cole et al. and that of the ramsdellite-like mineral (B) above in collation. From this table, we may see that the mineral (B) is a compound closely resembling γ-MnO_2, γ-MnO_2 I and γ-MnO_2II. This (B) was found upon chemical analysis to contain 30.94% of Fe_2O_3 and 5.77% of $H_2O(+)$, and was suspected of admixture of limonite. However, since no diffraction pattern of limonite could be detected in its pattern, the

(6)   M. Fleischer and W. F. Richmond, Econ. Geol. 38 (1943), 269.
(7)   W. F. Cole, A. D. Wadsley and W. Walkley, Trans. Elect. Chem. Soc. 92 (1943), 133.

Table 4. X–ray powder patterns of three portions in Fig. 2.

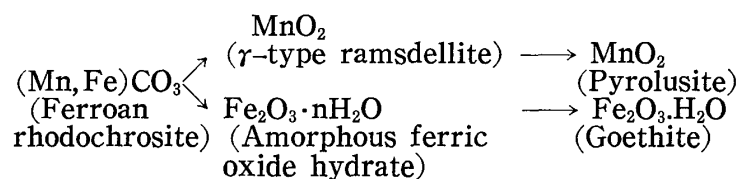| Ferroan rhodochrosite (A)*		γ-type ramsdellite (B)*		Pyrolusite, goethite mixture (C)*			
$d(Å)$	I	$c(Å)$	I	$d(Å)$	I	Remarks**	
3.66	m	4.12	m(d)	4.18	vs		G
3.14	w	2.67	w	3.37	s		G
2.84	vs	2.41	m	3.12	s	P	
2.40	m	2.18	m	2.66	m		G
2.18	s	1.68	s	2.42	s	P	G
1.99	m	1.54	vw(d)	2.21	w	P	G
1.76	s	1.38	w	2.12	w	P	
1.53	w			1.82	w		G
1.43	vw			1.69	m		G
1.37	m			1.66	vw		G
1.22	vw			1.62	s	P	G
1.13	vw			1.55	m	P	
1.10	vw			1.48	vw		G
1.00	w			1.43	vw	P	G
				1.37	m	P	
				1.34	vw		G
				1.30	m	P	
				1.25	w		G
				1.22	vw		G
				1.20	w		G
				1.18	w		G
				1.08	w		G
				1.05	w	P	G
				1.03	w		G
				1.01	w	P	

* A, B and C illustrated in Fig. 2
** P : pyrolusite, G : goethite

Table 5. Comparition of X–ray powder patterns between artificial γ–manganese dioxides and γ–type ramsdellite from Yamato Mine.

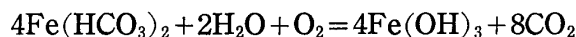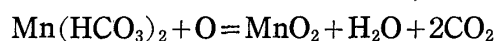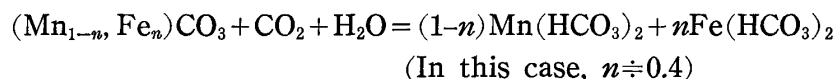| γ-MnO₂		γ-type ramsdellite from Yamato Mine		γ-MnO₂I		γ-MnO₂II	
$d(Å)$	I	$d(Å)$	I	$d(Å)$	I	$d(Å)$	I
						4.38	m
4.02	s(d)	4.12	m(d)	3.94	s	3.82	ms
2.53	vvw	2.67	w	2.57	w	2.68	w
		2.41	m	2.41	m	2.42	ms
				2.33	vw	2.34	w
2.10	ms	2.18	m	2.11	ms	2.12	s
						2.05	w
1.62	vs	1.68	s	1.62	vs	1.63	s
		1.54	vw(d)			1.59	w
1.38	w	1.38	w	1.41	vw	1.43	vw
				1.37	vw	1.35	vw
						1.31	vw
				1.25	vvw		

hydrous iron oxide in it seem to be amorphous. The diffraction patterns of (C) indicate that it consists of a mixture of pyrolusite and goethite.

From the above findings, it may be inferred that ferroan rhodochrosite, by weathering, first alters into γ-type ramsdellite and amorphous ferric oxide hydrate, and thence the former changes into pyrolusite and the latter into goethite by

crystallization, as schematized in the following:

$$
\begin{array}{l}
\text{(Mn, Fe)CO}_3 \nearrow \begin{array}{l} \text{MnO}_2 \\ (\gamma\text{-type ramsdellite}) \longrightarrow \text{MnO}_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad (\text{Pyrolusite}) \end{array} \\
\quad\text{(Ferroan} \searrow \text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O} \qquad\qquad \longrightarrow \text{Fe}_2\text{O}_3.\text{H}_2\text{O} \\
\text{rhodochrosite)} \quad (\text{Amorphous ferric} \qquad (\text{Goethite}) \\
\qquad\qquad\qquad\quad\text{oxide hydrate})
\end{array}
$$

The chemical reactions occurring in the above process may be inferred to be as follows:

$$(\text{Mn}_{1-n}, \text{Fe}_n)\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = (1-n)\text{Mn}(\text{HCO}_3)_2 + n\text{Fe}(\text{HCO}_3)_2$$

$$(\text{In this case, } n \doteqdot 0.4)$$

$$\text{Mn}(\text{HCO}_3)_2 + \text{O} = \text{MnO}_2 + \text{H}_2\text{O} + 2\text{CO}_2$$

$$4\text{Fe}(\text{HCO}_3)_2 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{Fe}(\text{OH})_3 + 8\text{CO}_2$$

The differential thermal curves of the minerals forming the three zones are shown in Fig. 3. Ferroan rhodochrosite shown an endothermic reaction at the
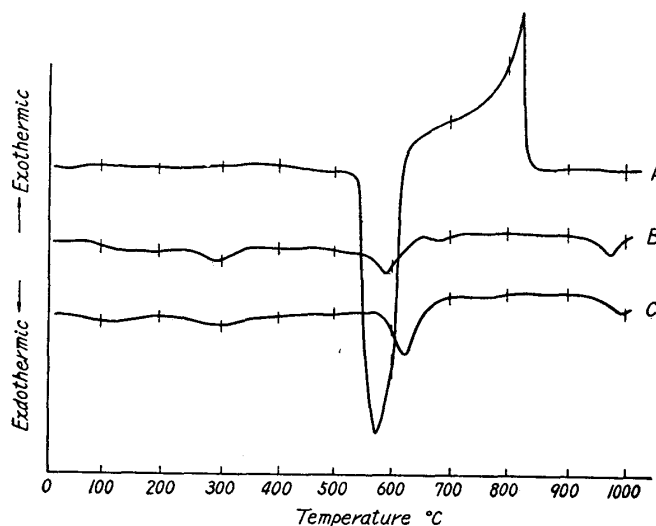

Fig. 3.   Differential thermal curves for : A-ferroan rhodochrosite
B-γ-type ramsdellite, C-pyrolusite, goethite mixture

peak temperature of 575°C and an exothermic reaction at 820°C : the former is due to the dissociation of rhodochrosite and the latter to the transformation of MnO into Mn$_3$O$_4$. The γ-type ramsdellite does not show any very conspicuous exothermic peaks at 590°C and 975°C, due to the double step reduction of 2MnO$_2$→ Mn$_2$O$_3$+O and 3Mn$_2$O$_3$→2Mn$_3$O$_4$+O respectively.

Besides, the gentle endothermic peak below 300°C seems to be due to the dehydration of the amorphous ferric oxide hydrate˞and the exothermic peak to the alteration of amorphous ferric oxide into α-Fe$_2$O$_3$. The exothermic peaks at 625°C and 1,000°C in the curve of (C) are due to the double reduction of MnO$_2$ and the gentle endothermic peak around 300°C to the dehydration of goethite.

These kinds of manganese dioxide ore contain, besides the above γ-type ramsdellite and pyrolusite, also cryptomelane. This last minelal comes forth as

concentric sperical or umbrella-shaped dense minerals. As Allsman[8] has already pointed out, this ore was produced probably by gel-form MnO_2 adsorbing potassium.

Summary

As a part of the serial study of hydrated ferric oxides, natural oxidation products of siderite and ferroan rhodochrosite were studied mineralogically. However, since the occurrence of such oxidized products of the minerals is very scanty in Japan, only one sample each of the oxides could be used as specimens. So, further studies on them with more abundant specimens available are required.

The siderite from Fukuô Mine was altered into geothite by weathering.

The ferroan rhodochrosite from Yamato Mine was altered first into γ-type ramsdellite and amorphous ferric oxide hydrate and thence into pyroluside and goethite respectively.

(8) P. L. Allsman, Min, Eng. 8 (1956), 1110.