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Ca-BEARING RECTORITE FROM TOOHO MINE, JAPAN

Key Words—Allevardite, Beidellite, Interstratification, Margarite, Rectorite, X-ray powder diffraction.

Rectorite (allevardite) was recognized by Caillère *et al.* (1950) and Brindley (1956) as a mica-type mineral with sheets of water molecules separating the 2:1 mica-like layers. Brown and Weir (1963) showed that rectorite and allevardite are the same mineral that consists of pairs of mica-like (high charge, non-swelling) and montmorillonite-like (low charge, swelling) layers. Kodama (1966) concluded that rectorite consists of a regular alternation of paragonite-like layers and expandable layers having beidellitic and montmorillonitic compositions. Weaver and Pollard (1975) reported that the mica-like layers generally contain interlayer Na (paragonite), but in some samples K is the predominant cation.

A Ca-bearing rectorite is reported here, which appears to be an interstratified Ca-paragonite/beidellite, from the Tooho mine, Aichi Prefecture, Japan.

MATERIAL AND METHODS

The specimen originated from the Tooho mine ("reseki" deposit), Aichi Prefecture, Japan. This deposit was formed by hydrothermal alteration of andesitic country rock. The dominant clay minerals in this deposit are pyrophyllite, interstratified mica/smectite, and mica, which are concentrated in central, intermediate, and marginal zones, respectively. The rectorite material occurs in a part of the zone of interstratified mica/smectite that has been altered by later hydrothermal activity to a brittle clayey material containing small veinlets of dickite, fluorite, and Li-bearing tosudite (Nishiyama *et al.*, 1975).

The <2-μm fraction of the specimen was used for this study. The impurities in the specimen are 7% quartz, 5% tosudite, 3% topaz, 2% pyrophyllite, 1% dickite, and ~0.2% fluorite. Quantitative estimations of the impurities except fluorite were carried out by X-ray powder diffraction intensity measurement using the method of known additions (Brindley, 1961). The amount of fluorite was estimated from the fluorine analysis of the specimen using a specific ion electrode (Ingram, 1970), after correcting for the fluorine in topaz.

RESULTS AND DISCUSSIONS

X-ray powder diffraction

X-ray powder diffraction (XPD) patterns of an oriented specimen on a glass slide show a regular series of basal reflections (Table 1). The 001 spacing of the mineral is 24.83 Å at 58% relative humidity (RH), and the sequence of the basal reflections (standard deviation, $\sigma = 0.18$) was as good as those of other rectorites (Table 2); therefore this mineral can be described as a 1:1 regular interstratification resembling rectorite.

After the mineral was treated with Mg^{2+} and ethylene glycol (EG), better integral series of the basal reflections having d-spacings of 24.40 and 26.50 Å, respectively, were observed. This means that each expandable layer in the mineral behaved homogeneously. These interlayer characteristics resemble those of rectorite rather than the Funyu material described by Shimoda *et al.* (1974) in which the integral series became less integral after such treatments (Table 2). After KCl treatment, the basal spacing was reduced to 22.23 Å with less regularity ($\sigma = 0.28$) (compare the data for rectorite, Kodama, 1966). With EG treatment of the K^+-saturated specimen, two phases were observed with d-spacings of 26.7 (about 60%) and 23.8 Å (about 40%), which correspond respectively to two and one layers of ethylene glycol in the interlayer position.

Table 3 shows the observed and calculated F values of the XRD basal reflections of the specimen before and after various treatments. Relatively good agreement was obtained. One-dimension Fourier syntheses calculated from the observed F values show the levels of the component layers of the mineral. The levels were measured from the midpoint of the octahedral sheet width on the electron density curves (Nishiyama and Oinuma, 1978) (Table 4). The d-spacing of the mica layer was 9.64 Å for both the untreated and EG-treated specimens and 9.70 Å for the specimen heated at 500°C for 1 hr. These d-spacings are similar to those of rectorite, 9.52, 9.50, and 9.62 Å for the untreated, EG-treated, and 560°C-treated allevardites (rectorite), respectively (Brindley, 1956), rather than to the mica layer of the Funyu sample whose d-spacings were 9.94 and 9.99 Å for untreated and EG-treated materials, respectively.

Chemical composition and structural properties

The chemical composition of the Tooho mineral, corrected for mineral impurities and estimated on an ignited weight basis, is listed in Table 5. From these data the following structural formula can be calculated:

$$(Si_{6.27}Al_{1.73})(Al_{3.87}Fe_{0.13}Mg_{0.04}Li_{0.01})$$
$$(Na_{0.57}Ca_{0.43}K_{0.16})O_{20}(OH)_4.$$

Cations exchanged by 1 N NH_4^+ solution amounted to 0.01% K_2O and 0.83% CaO on an ignited weight basis ($Ca_{0.16}K_{0.002}$ on the basis of one $O_{20}(OH)_4$ structural unit).

Assuming that all interlayer cations in the expandable layer of the mineral are exchangeable and that the cation ratio in the octahedral sheets of the expandable and non-expandable layers remains constant, the structural formula of the mica component of the mineral can be written as

$$(Si_{2.67}Al_{1.33})(Al_{1.94}Fe_{0.06}Mg_{0.02}Li_{0.01})$$
$$(Na_{0.57}Ca_{0.27}K_{0.15})O_{10}(OH)_2$$

and that of the expandable component as

$$(Si_{3.61}Al_{0.39})(Al_{1.94}Fe_{0.06}Mg_{0.02}Li_{0.01})(Ca_{0.16}K_{0.01})O_{10}(OH)_2.$$

These structural formulae show that the mica layer belongs to the margarite (Ca-mica) and the paragonite (Na-mica) series rather than muscovite (K-mica). This conclusion is not contradicted by the XRD data; the thickness of the mica layer and b_0 of the mineral (9.64 and 8.916 Å) match more closely those of paragonite (9.66 and 8.91 Å) or margarite (9.71 and 8.92 Å) than those of muscovite (10.0 and 9.04 Å).

The structural formula of the mineral shows that the expandable component is an Al-rich smectite group. The layer charge of the expandable layer was calculated to be −0.33 per $O_{10}(OH)_2$, and is predominantly due to tetrahedral substitution. Therefore, the term beidellitic layer appears to be appropriate for the expandable component in this mineral. Schultz (1969) reported that after saturation with K^+ and heating at 300°C for 30 min, dioctahedral smectites with a total net

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Table 1. X-ray powder diffraction data for Ca-rectorite before and after various treatments.[1]

	Untreated			Ethylene glycol			KCl			KCl + EG			500°C × 1 hr		
00ℓ	d (Å)	d × ℓ (Å)	I[2]	d (Å)	d × ℓ (Å)	I[2]	d (Å)	d × ℓ (Å)	I[2]	d (Å)	d × ℓ (Å)	I[2]	d (Å)	d × ℓ (Å)	I[2]
1	24.54	25.54	19,957	26.77	26.77	23,248	22.08	22.08	1879	26.29	26.29	3561	20.08	22.08	1272
2	12.27	24.54	6328	13.29	26.58	3546	10.91	21.83	963	13.19	26.38	467	9.88	19.76	1252
										11.94	23.89	280			
3	—		—	8.84	26.52	468	—		—	?			6.558	19.67	114
4	6.281	24.12	44	6.63	26.52	250	5.504	22.01	41	6.707	26.83	44	4.861	19.44	664
5	4.996	24.98	989	5.292	26.46	430	4.483	22.41	30	5.356	26.62	37	3.866	19.33	52
										4.745	23.73	53			
6	—		—	4.428	26.56	173	—		—	—		—	3.209	19.25	1950
7	3.547	24.82	124	3.785	26.49	66	3.186	22.30	276	3.858	27.00	24	—		—
										3.351	23.46	362 (Q)			
8	3.099	24.79	1440	3.308	26.46	1030	—		—	3.351	26.80		—		—
9	2.722	24.49	11	2.945	26.50	298	2.535	22.81	8	2.978	26.80	60	—		—
10	2.488	24.88	13	2.648	26.48	45	—		—	—		—	1.925	19.25	194
11	2.264	24.90	22	—		—	2.006	22.06	28	—		—	—		—
12	2.066	24.79	83	2.206	26.47	13	1.860	22.32	10	1.975	23.70	14	1.602	19.22	22
13	1.917	24.92	190	2.035	26.45	117				—		—	—		—
14	1.787	25.01	5	1.891	26.47	136				1.923	23.93	24	1.376	19.26	17
15	1.665	24.97	3	1.764	26.46	7									
16	1.544	24.70	22	1.661	26.57	4									
17				1.557	26.46	19									
18				—		—									
19				1.392	26.44	2									
20				1.322	26.44	18									
21				—		—									
22				1.200	26.40	11									

[1] Relative humidity 49–58%.
[2] Peak height.



Figure 1. Electron micrograph of the Tooho Ca-rectorite.

layer charge of less than 0.85/unit cell ($0.425/O_{10}(OH)_2$) reexpanded to 17 Å; those with net layer charge of more than 0.85/unit cell did not. After K^+-saturation and EG treatment, the mineral in this study showed two peaks at 26.7 and 23.8 Å, meaning that the beidellitic layer consists of two distinct interlayers which are characterized by less and more layer charges than $0.43/O_{10}(OH)_2$. Simultaneously, the basal reflections became less rational after such treatments, and some complicated interstratified structures may have due to the heterogeneous distribution of layer charges in the beidellitic layers.

The predominant interlayer cation of the beidellitic layer was Ca^{2+}, a fact verified by 001 spacing of the mineral of 24.83 Å at 58% RH and 23.5 Å at 35% RH, similar to the 24.5 Å spacing of Ca-saturated rectorite at 50% RH (Kodama, 1966). Furthermore, Matsuda and Nagasawa (1977) showed that the Ca-saturated expandable layer of a regularly interstratified mica/smectite changes from two interlayers of water molecules to one with decreasing RH from 30% to 10%.

Table 3. Observed and calculated structure factors of the (00ℓ) reflections of the Ca-rectorite before and after various treatments.

	Untreated		500°C × 1 hr		Ethylene glycol	
00ℓ	|F|obs	F cal	|F|obs	F cal	|F|obs	F cal
1	66.8	85.6	14.9	13.7	68.1	89.4
2	74.4	−72.0	29.9	−27.8	54.9	−57.2
3	—	10.9	13.7	13.3	29.9	−24.0
4	12.3	1.3	45.0	−31.3	29.2	22.4
5	73.8	−43.6	16.0	12.5	48.2	−28.7
6	—	10.5	119.3	−95.4	36.8	−26.3
7	37.4	−33.4	—	12.7	26.8	31.3
8	147.6	−107.1	—	−2.1	122.8	−103.9
9	14.8	17.2	—	9.8	75.0	−67.6
10	18.0	13.1	67.4	93.1	32.6	22.9
11	26.0	−31.9	—	8.6	—	21.1
12	56.0	60.5	28.2	29.1	21.7	−26.7
13	92.8	83.2	—	7.2	71.4	50.7
14	15.6	27.2	30.0	−48.1	84.2	94.7
15	13.1	3.7			21.2	32.2
16	41.2	49.2			15.9	−11.8
17					40.4	32.4
18					—	8.0
19					14.7	−30.8
20					47.1	−35.8
21					—	7.5
22					41.5	71.8

Infrared and differential thermal analysis

The OH-stretching absorption band of the Tooho specimen was observed at 3643 cm^{-1} which is the same value as other rectorites. The absorption bands between 825 and 690 cm^{-1} of the Tooho specimen, however, are distinct from rectorites. The absorption bands of quartz at 800, 782, and 695 cm^{-1} and of other mineral impurities obscured the absorption bands of the Ca-rectorite in these regions, but it is likely that the rectorite bands at 808 and 730 cm^{-1} are ambiguous or are shifted

Table 2. Averaged basal spacings (Å) of the Ca-rectorite and other related minerals.

		Untreated	$MgCl_2$	KCl	500°C	EG	$MgCl_2$ + EG	KCl + EG	
A	$\bar{x}$	24.83	24.40	22.23	19.50	26.50	26.81	26.71	23.80
	σ	0.18	0.12	0.28	0.28	0.07	0.14	0.24	—
	n	13	10	8	8	19	13	8	4
B	$\bar{x}$	24.63			19.24[1]	26.48			
	σ	0.12			0.13	0.03			
	n	20			13	16			
C	$\bar{x}$	23.87	24.61	22.3	19.3[2]	26.72[3]			
	(σ)	0.17	0.03	l.r.[4]	l.r.[4]				
	n								
D	$\bar{x}$	24.86	24.92[5]	22.34	19.5[5]	26.74	26.60[5]	26.86	
	σ	0.15		0.25		0.27		0.55	
	n	11		9		13		8	

A = Ca-bearing rectorite; B = allevardite (rectorite) (Brindley, 1956); C = rectorite (Kodama, 1966); D = Funyu sample (Shimoda *et al.*, 1974); $\sigma = [\Sigma(x_i - \bar{x})^2/n]^{\frac{1}{2}}$; n = numbers of measured basal reflections.

[1] 550°C.

[2] 600°C.

[3] Shimoda *et al.* (1974).

[4] Less rational series of diffuse reflections.

[5] Matsuda and Nagasawa (1977).

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Table 4. Lattice spacings of the d(001) and component layers of the Ca-rectorite and related minerals.

Treatment	Ca-rectorite			Allevardite (rectorite)[1]			Funyu sample		
	d(001) (Å)	Component layer		d(001) (Å)	Component layer		d(001) (Å)	Component layer	
		Mica	Exp.[2] (Å)		Mica	Exp.[2] (Å)		Mica	Exp.[2] (Å)
Untreated	24.83	9.64	15.19	24.62	9.52	15.10	24.86	9.94	14.92
EG	26.50	9.64	16.86	26.48	9.50	16.98	26.74	9.99	16.75
500°C	19.50	9.70	9.80	19.24[3]	9.62	9.62			

[1] Brindley (1956).
[2] Expandable layer.
[3] 560°C.

to lower frequencies in this material. The band at 825 cm^{-1}, which is a shoulder of the 808 cm^{-1} band in rectorites, is distinct in this mineral.

Endothermic reactions were noted by differential thermal analysis for the Tooho specimen at 105°, 178°, and 557°C due to dehydration. Smectites having monovalent interlayer cations (Na^+, K^+) show one endothermic peak at low temperature, whereas, those having divalent interlayer cations (Ca^{2+}, Mg^{2+}, and/or Li^+) show two endothermic peaks (Hendricks *et al.*, 1940). Therefore the two peaks at 105° and 178°C of the Tooho specimen are probably due to the dehydration of the smectite (beidellite) layer wherein Ca^{2+} is the interlayer cation.

Electron microscopy

A transmission electron micrograph (Figure 1) shows a very thin flaky habit of the mineral. Folded ribbons which are characteristic of allevardite and also of rectorite (Brown and Weir, 1963) are rare in this sample.

CONCLUSIONS

The mineral from the Tooho "roseki" deposit, Aichi Prefecture, Japan is a regular 1:1 interstratification of mica and expandable layers. The mica layer belongs to a margarite-paragonite series, whereas the expandable layer is similar to beidellite with Ca^{2+} exchange cations. Because the name rectorite has generally been given to regular 1:1 interstratifications of dioctahedral paragonite and smectite, it is convenient to describe the Tooho mineral as a Ca-bearing rectorite. This Ca-bearing rectorite has not previously been reported in natural deposits; however, Eberl (1978) synthesized hydrothermally a Ca-rectorite from a Wyoming bentonite at 400°C.

Table 5. Chemical compositions of the Tooho specimen the Ca-rectorite and related minerals.

	1 (%)	2[1] (%)	3[1] (%)	4[1] (%)	5[1] (%)
SiO_2	47.46	51.98	54.09	54.11	52.22
TiO_2			0.36	0.01	0.16
Al_2O_3	31.52	39.35	38.48	40.38	38.81
Fe_2O_3	1.08	1.44	0.78	0.15	0.86
FeO			0.66		
MgO	0.19	0.25	0.42	0.78	
CaO	2.44	3.46	1.19	0.52	2.49
Li_2O	0.07	0.03			
Na_2O	1.68	2.43	2.69	3.87	2.42
K_2O	0.76	1.08	1.31	0.29	3.02
H_2O+	7.11				
H_2O-	7.20				
F	0.70				
Total	100.21	100.02	99.98	100.23	99.98

1 = Tooho specimen containing impurities. 2 = Ca-bearing rectorite corrected for other mineral impurities. 3 = Allevardite (rectorite) (Hènin *et al.*, 1954 and Brindley, 1956). 4 = Rectorite (Kodama, 1966). 5 = Funyu sample (Shimoda *et al.*, 1974).

[1] On an ignited weight basis.

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