Ca-RECTORITE FROM SANO MINE, NAGANO PREFECTURE, JAPAN

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Abstract—Rectorites containing various amounts of Ca were found at the Sano Mine, Nagano Prefecture, Japan. The Ca content in nonexchangeable form varied from 1.0 to 3.9% CaO. With more than 3.4%, they may be called Ca-rectorite. Chemical data of the most Ca-rich sample showed that Ca was the dominant interlayer cation, and gave a structural formula of $(Mg_{0.16})_{EX}(Ca_{0.59}Na_{0.27}K_{0.17})_{FIX}[Al_{3.94}Mg_{0.08}Fe_{0.07}Ti_{0.01}](Si_{5.85}Al_{2.15})O_{20}(OH)_4$. This sample is apparently the most Ca-rich rectorite reported to date. The Greene–Kelly test and an intercalation examination by octadecylammonium indicated that the expandable component layers were beidellitic. Assuming the tetrahedral composition of the expandable component layers are similar to the average tetrahedral composition of beidellite of $(Si_{3.6}Al_{0.4})$, the tetrahedral composition of the mica-like component layers was calculated to be $(Si_{2.25}Al_{1.75})$. This was closer to a brittle mica (margarite) than to a true mica. Examination of chemical data for several Ca-rectorite samples from different localities, including those from the Sano Mine, showed a trend of increasing Ca content as Al increased and Si decreased. Ca-rectorite exhibited characteristic infrared absorption bands at 480, 670–700 and 900–930 cm^{-1}, which became more intense as Ca content increased. These bands also corresponded to major absorption bands of margarite.

Key Words—2:1 Layer Silicate, Margarite, Rectorite, Regular Interstratification, Smectite/Brittle Mica.

INTRODUCTION

Rectorite is a 1:1 regularly interstratified mineral of a dioctahedral mica and dioctahedral smectite. The mineral may be classified further into Na-, K- and Ca-rectorites, depending on the dominant interlayer cation in the mica component (Bailey et al. 1982). Although the mica component is usually a true mica-type, this presumption is not always correct with Ca-rectorites, since the Ca cation is divalent. Where Ca-rectorite consists of smectite and a true mica, half of the non-expandable interlayer sites are occupied by Ca ions and the remaining sites are vacant. The amount of Ca required for this is approximately 3.2% as CaO. In theory, the amount may be doubled by increasing the layer charge of true mica (from 1⁻ to that of brittle mica (2⁻). Thus, for rectorites in which the Ca-content exceeds 3.2% CaO, the layer charge of the mica component in the Ca-rectorite will approach that of brittle mica.

Ca-bearing rectorite-type minerals were reported from hydrothermal pyrophyllite–kaolinite deposits in Japan (Brindley and Sandalaki 1963; Matsuda et al. 1981; Nishiyama and Shimoda 1981; Matsuda 1984). For these Ca-rectorites, the nonexchangeable Ca content (as CaO) ranged from 1.21 to 3.46 wt%, which was accompanied by various contents of nonexchangeable Na and K. Recently, Matsuda (1991) examined Ca-rectorites from a pyrophyllite deposit in the Sano Mine, Nagano Prefecture, Japan, and found Ca-rectorites containing CaO with more than 3.8%.

Ca-bearing rectorite-type minerals were hydrothermally synthesized by Frank–Kamenetskij et al. (1973), Matsuda and Henmi (1974) and Eberl (1978). Rectorites close to the Ca end member were synthesized and studied by Matsuda and Henmi (1983).

The purpose of this paper is 1) to describe 2 Ca-rectorites from the Sano Mine and 2) to compare these Ca-rectorites with other rectorites and a synthetic Ca-end member rectorite.

SAMPLES AND METHODS

Ca-rectorites from a pyrophyllite deposit in the Sano Mine, Kakuma, Nagano Prefecture, Japan (Matsuda 1991), were studied. The Sano Mine is situated near the Kakuma hot spring area in the northeast part of Nagano Prefecture. The deposit was formed by hydrothermal alteration of porphyrite in the late Tertiary Period (Inoue 1963). The dominant clay minerals are pyrophyllite, illite and minor clay minerals of kaolinite, beidellite, rectorite-type interstratified minerals, tosudite and chlorite. Ca-rectorites occur as pseudomorphs after plagioclase in an alteration zone around the deposit. Na- and K-rectorites occur in a vein cutting a pyrophyllite ore body and alteration zone.

Two rectorites with high Ca content were studied. For comparison, a synthetic regularly interstratified margarite–beidellite (Matsuda and Henmi 1983) and other rectorites from Mitsuishi, Okayama Prefecture (Matsuda et al. 1981), and from Fort Sandeman, Pakistan (Kodama 1966), were examined also.

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Table 1. X-ray data for the glycerolated samples saturated with Mg.

00l	Sample 1820			Sample 529		
	d(Å)	I	d(Å)xl	d(Å)	I	d(Å)xl
1	28.09	847	28.09†	28.39	1108	28.39†
2	14.01	174	28.02†	12.123	213	28.24†
3	9.267	84	27.80	9.276	87	27.83
4	6.923	40	27.69	6.921	42	27.68
5	5.495	7	27.47	5.518	14	27.59
6	4.588	31	27.53	4.587	42	27.52
7	3.933	23	27.53	3.927	22	27.49
8	3.442	33	27.54	3.443	35	27.54
9	3.065	42	27.58	3.058	48	27.52
10	2.723	4	27.23	2.742	4	27.42
11	2.503	7	27.53	2.502	6	27.52
12	—	—	—	—	—	—
13	—	—	—	—	—	—
14	1.963	6	27.48	1.962	9	27.42
15	1.832	5	27.48	1.831	5	27.45
16	—	—	—	—	—	—
17	1.615	3	27.46	1.619	3	27.52
18	1.527	3	27.49	1.518	3	27.32
19	1.443	2	27.42	1.441	3	27.38
20	1.372	3	27.40	1.380	4	27.60
av			27.51			27.52
CV			0.463			0.483

† Excluded from CV calculations.

Samples 529 and 1820 contained mineral impurities of quartz, kaolinite, illite, beidellite, chlorite and diaspore, which could not be entirely removed even by a hydraulic elutriation method. Impurity contents after the treatment were estimated by X-ray diffraction (XRD) analysis using the standard addition method. Estimated impurities were quartz (2.3 ± 1.5%), kaolinite (4.5 ± 2.5%) and illite (2.5 ± 2%) for sample 1820 and quartz (2 ± 1.5%), kaolinite (6 ± 3%), illite (2 ± 1.5%) and beidellite (2 ± 1.5%) for sample 529.

XRD analysis was conducted on oriented aggregates under conditions of 50% relative humidity (RH), solvation with ethylene glycol (EG) and glycerol (Gly) treatment and after the Greene–Kelly test (Greene–Kelly 1953) and heating at 600 °C. The $d(001)$ spacing was obtained by averaging the observed values of higher-order basal reflections recorded in the range between 2 and 30 °2θ, CuKα. All reflections except for the first order were considered. To check the regularity of interstratification, another set of XRD data for glycerolated samples saturated with Mg was prepared using monochromated Co radiation in a wide range from 2 to 80 °2θ, from which coefficients of variation (CV) were calculated to determine the rationality of basal reflections observed. The CV is defined by $100s/\bar{d}(001)$, where s is the standard deviation and $\bar{d}(001)$ is the average $d(001)$ value. The 060 spacings were measured on randomly oriented samples.

Chemical analysis was performed by traditional wet methods using Mg-saturated samples. The data were corrected for impurities as determined by XRD. Cation exchange capacity (CEC) was determined by measuring Mg extracted with 0.1 M SrCl$_2$ from the Mg-saturated samples. The amount of Mg in the supernatant was determined by an atomic absorption spectrophotometer. Ultrathin section samples for electron microscopic observations were prepared using a diamond knife on a Reichert Ultracut E ultromicrotome after untreated samples were embedded in Epon 812. Some of the grids on which ultrathin sections had been mounted were immersed and treated with a dilute octadecylammonium chloride solution at about 65 °C for 24 h. Then the treated grids were washed with water–alcohol and dried (Lagaly and Weiss 1969; Vali et al. 1992). Ultrathin-section samples before and after the treatment were examined by electron microscopy. Electron micrographs were taken with a Zeiss EM 902. Infrared absorption spectra in the 4000–250 cm^{-1} region were recorded by the KBr method, using a Perkin Elmer 16FPC Fourier transform infrared (FT-IR) spectrophotometer.

RESULTS AND DISCUSSION

XRD Data

After solvation with EG and Gly, more than 15 basal reflections were observed. Observed spacings and intensities of 00l reflections for glycerolated samples are shown in Table 1. Calculated CV values were 0.46 for sample 1820 and 0.48 for sample 529, which is less than the 0.75 judged as an upper value for regular interstratification (Bailey et al. 1982). The CV values of these samples were somewhat larger than those for rectorites from Allevard, France, 0.25 (Brindley 1956); from Sandeman, Pakistan, 0.11 (Kodama 1966); and Ca-bearing rectorites from Mitsuishi, 0.15 (Matsuda et al. 1981) and Tooho, 0.20 (Nishiyama and Shimoda 1981); but smaller than the CV value of 0.67 for a synthetic margarite–beidellite (Matsuda and Henmi 1983). These observations indicate that structural irregularity may increase with Ca content.

In Table 2, basal spacings after the EG and Gly treatments, the Greene–Kelly test and 600 °C heating are shown for comparison. The d-spacing changes were similar to those of other rectorites and synthetic Ca-rectorite. The 060 spacing of sample 529 is at 1.484 Å and indicates that it is dioctahedral.

Chemical Data

Chemical analyses, after corrections for impurities, and resulting structural formulae are given in Table 3. Note that Ca is the major nonexchangeable interlayer cation, with lesser amounts of Na and K. The tetrahedral Si/Al ratios in the formulae for the 2 samples were about 2.7, which is much smaller than 4–5.5 for common Na- and K- or Na-K rectorites (Kodama et al. 1969). This suggests that the nonexpandable com-

Table 2. Basal spacings (Å); $d(001)$ and 060 spacing of Sano sample with RH 50 ± 2%.

Condition of sample	Sample 529	†	‡	§	¶
Air-dry, Na-saturated	21.96	22.22	22.0	22.00	22.03
Air-dry, Mg-saturated	24.80	24.61	24.9	24.64	25.05#
Ethylene glycol + K-saturated	26.8; 24.0	—	26.4	26.8; 24.6	26.57
Glycerol + Mg-saturated	27.52	27.33	27.4	27.41	27.52
After Greene–Kelly's test	27.05	27.33	—	—	—
After heating at 600 °C	19.3	19.3	19.6	19.2	19.3
060 spacing	1.484	1.484	—	1.485	1.479

† Kodama (1966).
‡ Brown and Weir (1963).
§ Matsuda et al. (1981).
¶ Synthetic margarite/beidellite (Matsuda and Henmi 1983).
# Ca^{2+}.

ponent layers of the 2 samples have higher Al-for-Si substitution in the tetrahedral sheets compared with Ca-poor rectorites.

Since there is no way to separate the chemistries of the nonexpandable and expandable component 2:1 layers of the mineral, the structural formula of each type of layer was assumed. The Greene–Kelly test indicated that the expandable layers of the mineral were beidellitic. Thus, the idealized structural formula $Ex_{0.4}Al_2(Si_{3.6}Al_{0.4})O_{10}(OH)_2$ was assumed for the beidellitic

component layer (Post and Nobel 1993). The formula is similar to beidellite samples from the Black Jack Mine (Weir and Greene-Kelly 1962) and the Sano Mine (Matsuda 1988). The structural formulae are given as:

$$(Ca_{0.59}Na_{0.27}K_{0.15})(Al_{1.94}Mg_{0.08}Fe^{III}_{0.07}Ti_{0.01})$$
$$(Si_{2.25}Al_{1.75})O_{10}(OH)_2$$

for sample 1820 and:

$$(Ca_{0.57}Na_{0.21}K_{0.16})(Al_{1.92}Mg_{0.15}Fe^{III}_{0.06}Ti_{0.01})$$
$$(Si_{2.24}Al_{1.76})O_{10}(OH)_2$$
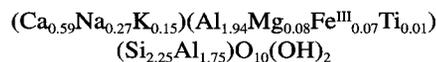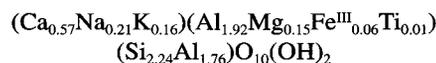
for sample 529.

Table 3. Chemical analyses and cation composition based on $O_{20}(OH)_4$ of Sano samples.

	1820	529
SiO_2	41.25	41.52
TiO_2	0.07	0.11
Al_2O_3	36.48	36.70
Fe_2O_3	0.67	0.53
MgO	1.27	1.63
CaO	3.97	3.80
Na_2O	0.99	0.77
K_2O	0.83	0.90
P_2O_5	0.01	0.01
$H_2O(+)$	7.19	7.30
$H_2O(-)$	6.99	6.29
Total	99.72	99.58
Tetrahedral		
Si	5.85	5.84
Al	2.15	2.16
Octahedral		
Al	3.94	3.92
Fe	0.07	0.06
Mg	0.08	0.15
Ti	0.01	0.01
Interlayer; nonexchangeable		
Na	0.27	0.21
K	0.15	0.16
Ca	0.59	0.57
Exchangeable		
Mg	0.16	0.19
Charge	+44.00	+44.01
CEC (meq/100 g)	44.0	53.2
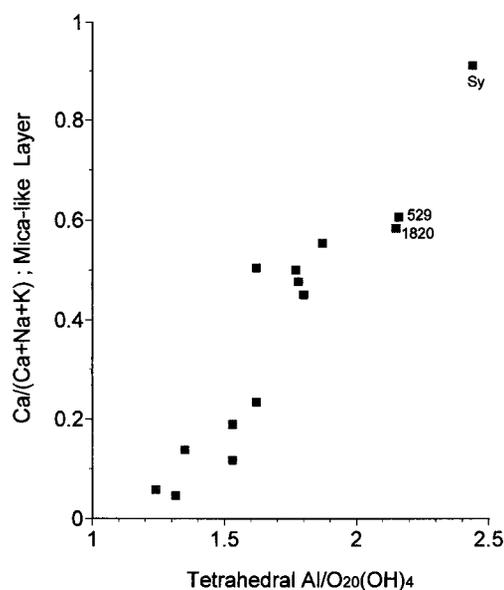
Figure 1. Relationship between tetrahedral $Al/O_{20}(OH)_4$ and interlayer cation ratio $Ca/(Ca+Na+K)$ in the nonexpandable layers of Ca-bearing rectorite-type minerals from the pyrophyllite deposits, Japan. Key: 1820, 529 = samples in the present study; Sy = synthetic margarite–beidellite (Matsuda and Henmi 1983). Data other than 529, 1820 and Sy are from Kodama et al. (1969), Matsuda (1984, 1991), Matsuda et al. (1981) and Nishiyama and Shimoda (1981).

Table 4. Assigned cation compositions to smectite-like and mica-like components for Sano samples.

	Sample 1820		1		2	
	sm	ma	sm	ma	sm	ma
Tetrahedral						
Si	3.6	2.25	3.6	2.39	3.6	2.11
Al	0.4	1.75	0.4	1.61	0.4	1.89
Octahedral						
Al	2	1.94	2	1.88	2	1.96
Fe		0.07		0.07		0.07
Mg		0.08		0.08		0.09
Ti		0.01		0.01		0.01
Interlayer						
Fixed						
Na		0.27		0.27		0.28
K		0.15		0.17		0.14
Ca		0.59		0.60		0.62
Exchangeable						
Mg	0.16		0.16		0.16	
Charge	+21.92	+22.08	+21.98	+22.08	+21.98	+22.08
	Sample 529		**1**		**2**	
	sm	ma	sm	ma	sm	ma
Tetrahedral						
Si	3.6	2.24	3.6	2.44	3.6	2.12
Al	0.4	1.76	0.4	1.56	0.4	1.88
Octahedral						
Al	2	1.92	2	1.86	2	1.92
Fe		0.06		0.06		0.06
Mg		0.15		0.14		0.16
Ti		0.01		0.01		0.01
Interlayer						
Fixed						
Na		0.21		0.21		0.23
K		0.16		0.19		0.17
Ca		0.57		0.57		0.62
Exchangeable						
Mg	0.19		0.19		0.19	
Charge	+21.98	+22.02	+21.98	+22.02	+21.98	+22.02

Key: sm = smectite-like layer; ma = mica-like layer; 1 = the most siliceous case; 2 = the most aluminous case.

Most of the interlayer sites are occupied by Ca, and the Al content of the tetrahedral sites is higher than a true mica. Therefore, the compositions of the 2:1 layers of these samples are much closer to margarite (Deer et al. 1962), a brittle mica, than true mica. Figure 1 shows the relationship between Ca/(Ca+Na+K) of the interlayer sites in the mica-like component and overall tetrahedral Al of rectorite-type minerals based on published analyses. Most Na- and K-rectorites have lower tetrahedral Al occupation. The figure shows a clear trend that tetrahedral Al increases as Ca content increases.

To determine the effect of impurities on the determined structural formula, we calculated the formula with upper and lower limits of contamination. Structural formulae given above are based on the average values of impurities. Sample 1820, for example, showed quartz ranging from 3.8 to 0.8%, kaolinite from 7 to 2% and illite from 3.5 to 0.5%. Table 4 gives the most siliceous and aluminous cases in consideration of these impurities. With the most aluminous case, compositions of the tetrahedral sheets are similar to margarite (Guggenheim and Bailey 1975). For the most siliceous composition, compositions of the tetrahedral sheets fall on the boundary between true mica and margarite. In either case, Ca/(Ca+Na+K) ratios of interlayer cations in nonexpandable layers exceed 57%.

Nonexchangeable cation proportions are shown in a Na-K-Ca triangular diagram (Figure 2) for the 2 samples studied here and for published compositions. The diagram illustrates that samples 529 and 1820 from the Sano Mine are the most Ca-rich rectorite published (Brindley and Sandalaki 1963; Matsuda et al. 1981; Nishiyama and Shimoda 1981). The diagram also shows that all rectorites with but 1 exception contain more than 1 nonexchangeable interlayer cation.
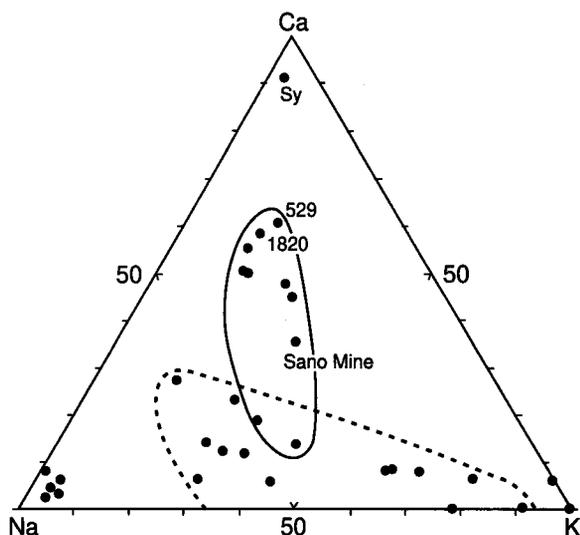
Figure 2. Ca-Na-K plots of interlayer cations in mica-like layers of rectorite-type minerals. The area enclosed by a solid line represents the Sano mine; the area enclosed by dotted line represents pyrophyllite deposit. Symbols are same as for Figure 1. Data other than in Figure 1 are Bradley (1950), Brindley (1956), Brown and Weir (1963), Cole (1966), Henin et al. (1954), Heystek (1957), Kodama (1966), Pevear et al. (1980) and Rateyev et al. (1969).

Differential Thermal Analysis (DTA)

The DTA curve of sample 529 is shown in Figure 3. Two endothermic peaks at 60 and 125 °C were due to the removal of hygroscopic and cation-hydrated water, respectively. An endothermic peak at 553 °C (accompanied at 486 °C) was caused by dehydroxylation, and an exothermic peak at 995 °C was related to the crystallization of mullite. The dehydroxylation temperature was close to that observed on Black Jack Mine beidellite (Greene-Kelly 1957) and Sano Mine (Matsuda 1988).

Electron Micrograph

Ca-rectorites from the Sano Mine consist of particles with primarily ribbon or lath shapes, although these shapes are not well defined or uniform (Figure 4a). Lattice images of sample 529 show layer struc-
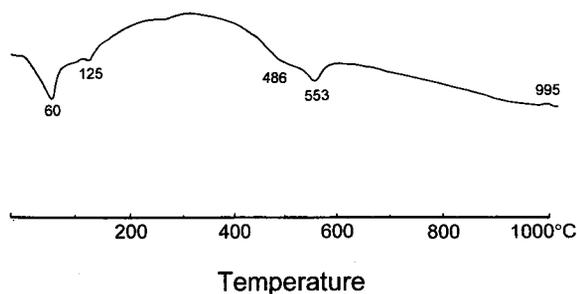
Figure 3. DTA curve of sample 529.
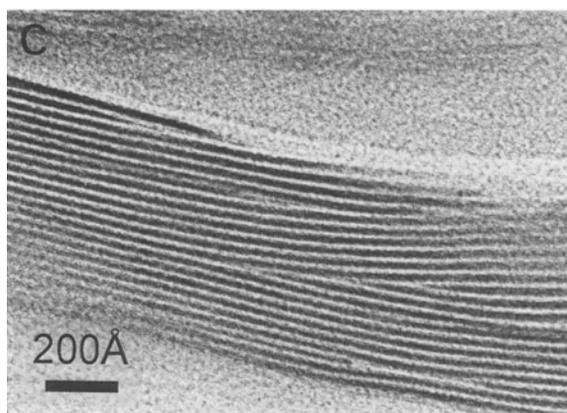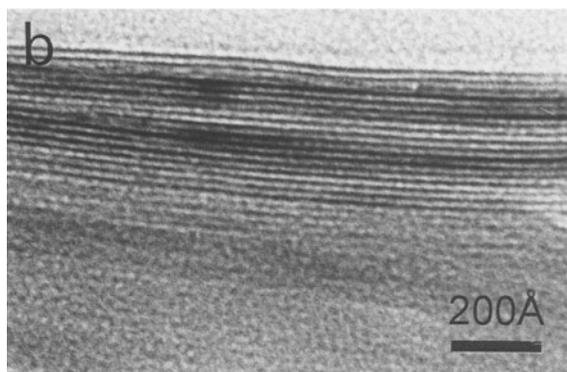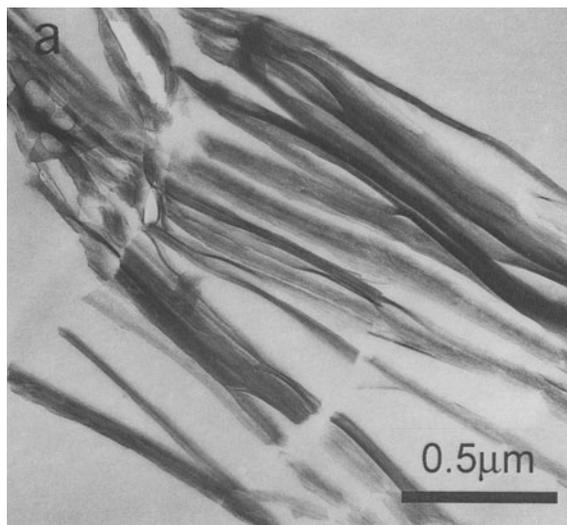
Figure 4. Transmission electron micrographs of samples. a) Sample 529. b) Lattice images showing 19.2-Å spacing for untreated sample 529. c) Lattice images showing 31.0-Å spacing for sample 1820 after treatment with octadecylammonium ions.

tures with 19.2-Å spacing, which corresponds to the sum of the dehydrated smectite and mica spacings (Figure 4b). Lattice images of sample 1820 treated with octadecylammonium show periodic layer struc-
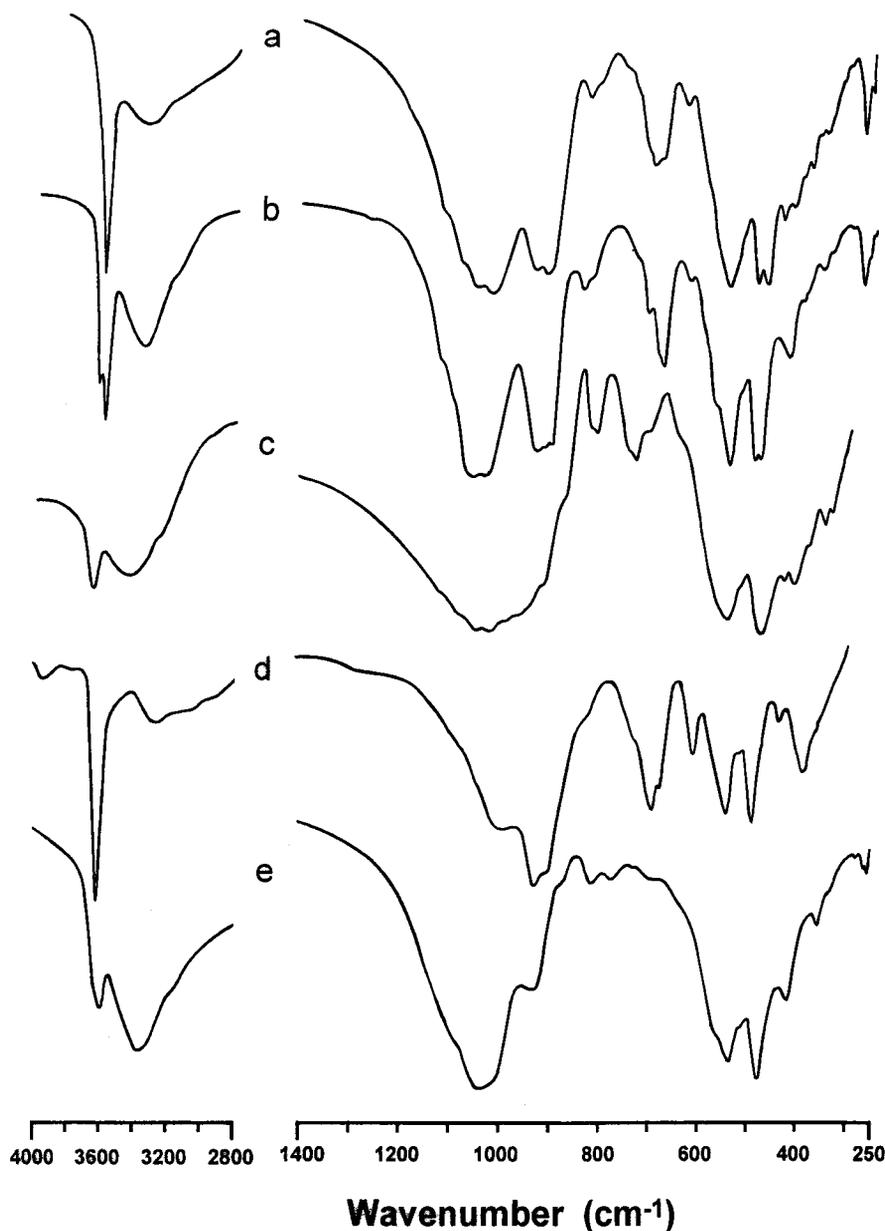
Figure 5.   IR absorption spectra. a) sample 1820. b) synthetic margarite–beidellite (Matsuda and Henmi 1983). c) rectorite, Bulchistan Pakistan (Kodama 1966, 1985). d) margarite, Shin-Kiura Mine, Japan (Aoki and Shimada 1965; Matsuda 1984). e) beidellite, Sano Mine, Japan (Matsuda 1988).

tures of 31.0-Å, indicating that the expandable component layers are beidellitic (Figure 4c; Lagaly and Weiss 1969; Lagaly 1979). These results are consistent with the regularly interstratified structure as determined by XRD.

Infrared Absorption Spectra

Infrared (IR) absorption spectra of sample 1820, synthetic regularly interstratified margarite–beidellite (Matsuda and Henmi 1983), rectorite (Kodama 1966, 1985), margarite (Aoki and Shimada 1965; Matsuda 1984) and beidellite (Matsuda 1988) are shown in Figure 5. The synthetic Ca-rectorite and sample 1820 showed characteristic absorption bands in the regions of 900–930, 670–700 and 470–490 cm^{-1}. A separate peak occurs at 470–490 cm^{-1}. This peak only occurred in samples that contain a considerable amount of Ca. Na-rectorite shows no absorption bands in the region of 900–930 cm^{-1} but does show absorption near 750 cm^{-1} instead of 670–700 cm^{-1} (Farmer and Russell
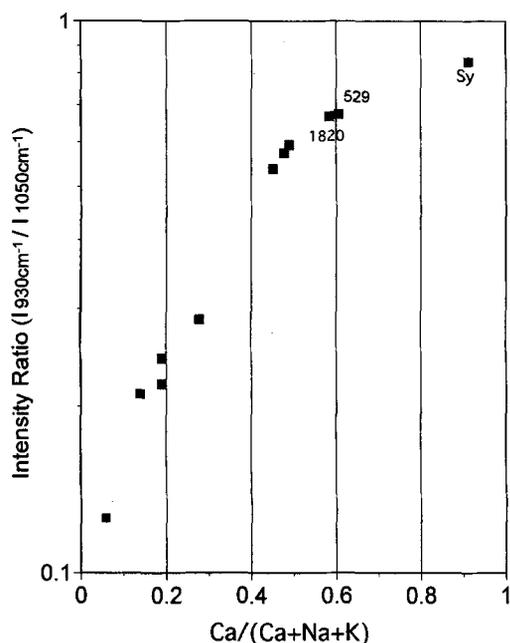
Figure 6. Relationship between Ca/(Ca+Na+K) of nonexpandable layers and relative intensity ratio $I_{930cm^{-1}}/I_{1050cm^{-1}}$. Symbols are the same as for Figure 1.
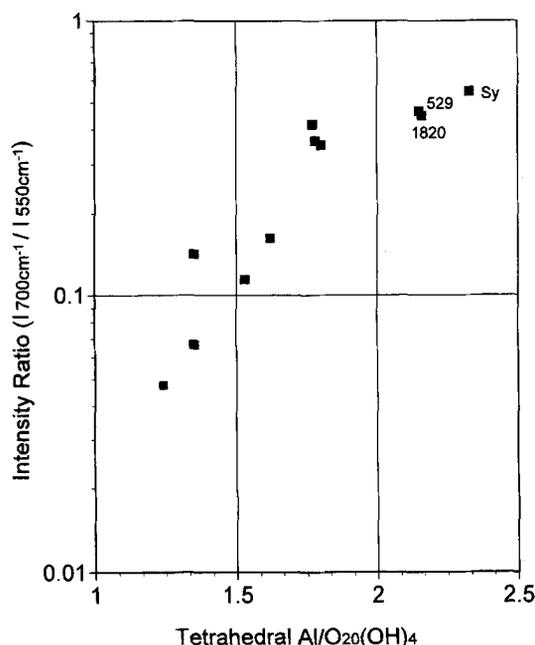
Figure 7. Relationship between tetrahedral $Al/O_{20}(OH)_4$ and relative intensity ratio $I_{700cm^{-1}}/I_{550cm^{-1}}$. Symbols are the same as for Figure 1.

1964; Kodama 1985). The absorption bands in the region of 900–930 and 670–700 cm^{-1} are believed to be caused by Al-for-Si substitution in the tetrahedral site as in the margarite structure (Farmer and Russell 1964). Absorption bands in the region of 900–930 and 670–700 cm^{-1} were relatively small for sample 1820 in comparison with the synthetic Ca-rectorite with 2: 1 layers similar to margarite (Figure 5). Peak intensities of absorption bands in the regions of 900–930 and 670–700 cm^{-1} increased as the Ca content in the mica-like layers increased (Matsuda 1991). The relationship between relative intensity of absorption bands at 900–930 cm^{-1} and Ca content of mica-like layers of rectorite is shown in Figure 6. Similarly the relationship between relative intensity of absorption bands at 670–700 cm^{-1} and tetrahedral Al is given in Figure 7. Positive correlations between absorption band intensities and chemical compositions (Al content of tetrahedral sheets and Ca content) are observed. The Al substitution for Si in the tetrahedral sites increases as the amount of interlayer Ca of the nonexpandable component layers increases.

CONCLUSIONS

The 2 most Ca-rich rectorites from the Sano Mine were presented, and compared with Ca-, Na- and K-rectorites from other localities. CV values of glycerolated samples saturated with Mg indicated that the component layer sequence in the samples shows a good regular alternation.

The chemical data showed that nonexchangeable Ca exceeds 50% of the total interlayer population. The Greene–Kelly test, the dehydroxylation temperature as shown by the DTA curve and an intercalation treatment with octadecylammonium indicated that the expandable component layers were beidellitic. Assuming that the composition of the expandable layer is similar to that of beidellite, the composition of the nonexpandable mica-like component layers was determined to be close to margarite. The Al-for-Si substitution in tetrahedral sites increased as the content of Ca increased. The largest Al substitution obtained for the samples from the Sano mine was $Si_{2.25}Al_{1.75}$ as compared with Si_2Al_2 for the ideal margarite tetrahedral sheets.

Characteristic absorptions associated with the tetrahedral Al-for-Si substitution occurs in the regions of 900–930 and 670–700 cm^{-1}. Based on chemical analyses and IR spectra, the nonexpandable layers of the mineral have a margarite composition rather than a paragonite composition typical of Na rectorite, or a muscovite composition for K-rectorites.

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