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SYNTHESIS AND PROPERTIES OF REGULARLY INTERSTRATIFIED (R=2) MARGARITE (0.67) – BEIDELLITE, A 34 Å PHASE

TOSHIHIKO MATSUDA[1] and MAKOTO KUROSAKI[2]

Department of Earth Sciences, Faculty of Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700, Japan

ABSTRACT

A regularly interstratified (R=2) margarite(0.67) – beidellite was hydrothermally synthesized at 400– 500°C under 1 kbar pressure. The starting material was a mixture of kaolinite, calcium oxide or calcium carbonate, and alumina gel. X-ray powder-diffraction data of a sample saturated with Mg showed that the spacings of basal reflections vary depending on sample preparation. The first-order reflection was observed at 34.6 Å under air-dry condition with 60% relative humidity, 29.1 Å after heating to 600°C, 36.4 and 37.0 Å after solvation with ethylene glycol and glycerol, respectively. The spacing of the 060 reflection was 1.478 Å, indicating its dioctahedral nature. Chemical data gave a structural formula of $Mg_{0.18}\ (Ca_{1.84}Na_{0.22}K_{0.12})\ (Al_{5.97}Fe^{3+}_{0.01}\ Mg_{0.03}Ti_{0.06})\ (Si_{7.35}Al_{4.65})\ O_{30}\ (OH)_6$. A differential thermal analysis showed a few endothermic peaks below 200°C and in the range 500–650°C, and an exothermic peak at 1070°C. XRD and chemical data indicate that the sample is composed of margarite-like and beidellite-like layers in a proportion 0.67:0.33. Infrared absorption of the sample showed major bands at 670–700 cm^{-1} and 900–930 cm^{-1} regions, which are similar to the known values of margarite. These data suggest that the phase exhibits a large extent of substitution of Si by Al.

Keywords: regular interstratified phyllosilicate, R=2 margarite(0.67) – beidellite, synthesis, 34 Å phase.

SOMMAIRE

Nous avons synthétisé un phyllosilicate régulièrement interstratifié (R=2) correspondant à margarite(0.67) – beidellite en milieu hydrothermal dans l'intervalle 400–500°C à une pression de 1 kbar. Le mélange de départ était fait de kaolinite, oxyde ou carbonate de calcium, et un gel d'alumine. Un spectre de diffraction X d'un échantillon saturé en Mg montre que les espacements des réflexions dans le plan du feuillet varient selon le protocole de préparation. La réflexion fondamentale est située à 34.6 Å sous conditions de séchage à l'air avec 60% d'humidité relative, 29.1 Å après chauffage jusqu'à 600°C, 36.4 et 37.0 Å après traitement au glycol d'éthylène et au glycérol, respectivement. L'espacement de la réflexion 060 est 1.478 Å, ce qui témoigne de sa nature dioctaédrique. Les analyses chimiques ont mené à la formule structurale $Mg_{0.18}\ (Ca_{1.84}Na_{0.22}K_{0.12})\ (Al_{5.97}Fe^{3+}_{0.01}Mg_{0.03}Ti_{0.06})\ (Si_{7.35}Al_{4.65})\ O_{30}\ (OH)_6$. Une analyse thermique différentielle montre quelques pics endothermiques en dessous de 200°C et sur l'intervalle 500–650°C, et un pic exothermique à 1070°C. D'après les données en diffraction X et sur la composition chimique, l'échantillon serait fait de couches rappelant la margarite et la beidellite, dans une proportion 0.67:0.33. Le spectre d'absorption infrarouge montre des bandes importantes sur les intervalles 670–700 cm^{-1} et 900–930 cm^{-1}, qui ressemblent ainsi au spectre de la margarite. Ces données montrent qu'il y a un remplacement important du silicium par l'aluminium.

(Traduit par la Rédaction)

Mots-clés: minéral régulièrement interstratifié, R=2 margarite(0.67) – beidellite, synthèse, phase à 34 Å.

INTRODUCTION

Many studies have been done on regularly interstratified dioctahedral minerals having a basal spacing in the range 25 and 30 Å (Bradley 1950, Caillère & Hénin 1950, Brindley 1956, Frank-Kamenetskii *et al.* 1963), but there have been few investigations of minerals with spacings of more than 30 Å. Rectorite with a basal spacing of 25 Å and tosudite with a spacing of 30 Å are generally accepted as regularly interstratifed dioctahedral minerals (Bailey *et al.* 1982). Lazarenko & Korolev (1970) described a 3:1 regular interstratification of a mica and a smectite with a basal spacing of 43.81 Å. Kizaki (1970) described a clay mineral with a basal spacing of 38 Å in rhyolitic tuff, and Sato & Kizaki (1972) suggested that the mineral resulted from

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[1] *E-mail address*: tmatsuda@cc.okayama-u.ac.jp

[2] *Present address*: LABO Japanese Language Institute, 8-4-5 Nishishinjuku, Shinjuku-ku, Tokyo 160, Japan.

a longitudinally disordered structure composed of illite and smectite in a ratio of 7:3. There is no regular interstratified clay mineral with a basal spacing of more than 30 Å that is accepted by AIPEA Nomenclature Committee (Bailey *et al.* 1982).

Regularly interstratified mica–smectite and chlorite–smectite have been synthesized by Ueda & Sudo (1966), Frank-Kamenetskii *et al.* (1972), Matsuda & Henmi (1973, 1974) and Eberl (1978), and the mineralogical properties of a dioctahedral 25 Å phase (1:1 regularly interstratified margarite–beidellite) have been investigated by Matsuda & Henmi (1983). No studies have been done, however, on synthetic, regularly interstratified minerals whose spacing exceeds 30 Å.

Three kinds of regularly interstratified phases with basal spacings of 25, 30 and 33–34 Å have been synthesized from kaolinite by means of hydrothermal treatment and by the addition of various oxides or carbonates (Matsuda & Henmi 1974, 1983). In those studies, a phase with a basal spacing of 33–34 Å was accompanied by a 25 Å phase after hydrothermal treatment of kaolinite plus calcium carbonate. In the present study, we describe for the first time the formation and mineralogical properties of the 34 Å phase, which has been synthesized in an almost pure state.

EXPERIMENTAL PROCEDURES

Mixtures of natural kaolinite, alumina gel, and the reagents CaO, $CaCO_3$, or oxalic acid were used as starting materials. Natural kaolinite from Shokozan, Hiroshima Prefecture, Japan, has a composition close to that of ideal kaolinite (Matsuda & Henmi 1983). The chemical compositions of the starting materials are shown in Table 1 in terms of the atomic ratios of Al, Si and Ca.

Fifty milligrams of starting mixture and 30 μL of distilled water were sealed in a gold or silver capsule. The weight of each sealed capsule was checked before and after the run to detect any leakage. Large-batch (0.5 g) runs were made using larger-diameter silver capsules (5 mm ϕ) in order to prepare enough volume of material for chemical analysis and measurement of important properties.

TABLE 1. ATOMIC RATIOS OF STARTING COMPOSITIONS

No.	Al	Si	Ca	No.	Al	Si	Ca
1	1	0.293	0.251	15	1	0.888	0.229
2	1	0.35	0.331	16	1	0.894	0.183
3	1	0.35	0.662	17	1	1	0.06
4	1	0.5	0.25	18	1	1	0.128
5	1	0.517	0.098	19	1	1	0.155
6	1	0.517	0.511	20	1	1	0.191
7	1	0.517	0.79	21	1	1	0.25
8	1	0.552	0.61	22	1	1	0.257
9	1	0.642	0.245	23	1	1	0.481
10	1	0.667	0.222	24	1	1	0.581
11	1	0.742	0.211	25	1	1	0.691
12	1	0.788	0.036	26	1	2	0.135
13	1	0.844	0.242	27	1	2	0.27
14	1	0.844	0.484				

Composition 4 corresponds to margarite. Composition 10 corresponds to margarite and beidellite in a ratio of 3:1. Composition 11 corresponds to margarite and beidellite in a ratio of 2:1. Composition 16 corresponds to margarite and beidellite in a ratio of 1:1.

Hydrothermal treatments were undertaken with the standard test-tube type of equipment. The samples were heated at 1 kbar and various temperatures for 3 to 67 days. The products were identified by X-ray powder diffraction (XRD) with Cu radiation. The composition was established by wet-chemical method using an ion-exchange resin (Numano 1966).

RESULTS AND DISCUSSION

Formation of a 34 Å phase

Experimental results are shown in Table 2. The 34 Å phase was formed at 400–520°C, together with a 25 Å phase (R=1 regularly interstratified margarite(0.50)–beidellite; Matsuda & Henmi 1983). The 25 Å phase was synthesized over a wide range of temperature (350–520°C), whereas a smectite phase formed at temperatures below 350°C, böhmite formed at 350–450°C from aluminous compositions, and anorthite and margarite formed at temperatures above 450°C.

The conditions of temperature and composition under which the 34 Å phase formed as a single phase are fairly limited. The phase was found between 400 and 500°C, and its composition ranges from margarite to margarite and beidellite in a ratio of 2:1. The 25 Å phase generally formed during short runs, despite the presence of optimal compositions for formation of the 34 Å phase. Figure 1 shows the sheet silicates produced from starting compositions at 450°C in terms of the triangular diagram $CaO–Al_2O_3–SiO_2$.

Concerning the Ca-rich starting material, the choice of $CaCO_3$ gave the 34 Å phase within a shorter time than the use of CaO. Compositions richer in Ca and Al than ideal margarite led to the formation of margarite at 400–500°C, and of the 25 Å phase at lower temperatures. Oxalic acid was not effective in the formation of the 34 Å phase.

XRD pattern of the 34 Å phase

Oriented aggregates of the 34 Å phase were examined by X-ray diffraction (XRD) using Ni-filtered or monochromatized Cu radiation. XRD patterns of oriented aggregates of the phase that were air-dried and glycerolated are shown in Figure 2 (2°–35° 2θ). The phase has 18 basal reflections when air-dried, and over 25 under glycolated and glycerolated conditions. The CV (Bailey *et al.* 1982) value of the air-dried sample is 0.92 for 18 reflections observed and that of the glycerolated sample is 0.67 for 25 reflections except for the first order. Basal spacings were measured for mono-

TABLE 2. RESULTS OF HYDROTHERMAL EXPERIMENTS

Run No.	Comp. No.	Temp. °C	Duration days	Products	Run No.	Comp. No.	Temp. °C	Duration days	Products
1	1	450	21	Mrg	38	11	450	25	34
2	2	450	25	Mrg	39	11	480	5	25
3	3	450	25	Mrg	40	11	480	17	34
4	4*	350	21	25,Bhm	41	11	480	17	34
5	4*	400	14	34	42	11	500	10	34
6	4*	450	3	25,Bhm	43	12	350	55	Smt
7	4*	450	5	25,Bhm	44	12	450	21	25
8	4*	450	7	34,Bhm	45	13	450	25	25,Hyd
9	4*	450	10	34,Bhm	46	14	450	25	34,25
10	4*	450	16	34	47	15	420	38	25,34
11	4*	450	38	34	48	16	450	5	25
12	4*	480	46	34,25	49	17	450	3	Smt,25
13	4*	480	3	25	50	18	450	3	25
14	4*	480	7	34	51	18*	450	3	25
15	4*	480	9	34	52	18*	450	3	25
16	4*	500	2	25	53	19	450	3	25,34
17	4*	500	5	34	54	20	450	3	25,34
18	4*	500	14	34,Bhm	55	21	450	3	25,34
19	4*	550	10	Mrg	56	21	500	3	25
20	5	450	22	25,Bhm, Prl	57	21	450	4	25
21	6	450	22	Mrg	58	21	500	4	25
22	7	450	21	Mrg	59	22	450	5	34,25
23	8	450	29	Mrg	60	22	450	16	25,34
24	9	450	29	25,Bhm	61	23	450	3	An,25,34
25	10	450	7	25,Bhm	62	23*	450	11	25
26	10	450	15	25,Bhm	63	23*	450	11	25
27	10	450	24	34,25,Bhm	64	23	500	4	C2,An
28	10	450	50	25,34,Bhm	65	24	450	3	An,25
29	10	450	67	25,34,Bhm	66	25	450	3	An
30	11	350	39	25,Bhm	67	26**	450	4	(Prl),25
31	11	400	7	25,Bhm	68	27**	450	4	25,(Prl)
32	11	400	39	34,25	69	18	300	7	(Kln)
33	11	420	5	34,25	70	23	600	3	An,C2
34	11	420	38	34	71	23	550	3	25,C2
35	11	450	6	25	72	22	550	3	An,Prl, Hyd,C2
36	11	450	6	25,34,Smt					
37	11	450	10	25,34,Smt	73	22	520	3	C2,25,34

* indicates CaO used as starting material for Ca. ** indicates pyrophyllite used as starting material instead of kaolinite. Symbols: Mrg: margarite, 25: 25 Å phase (margarite–beidellite), 34: 34 Å phase, Bhm: böhmite, Smt: smectite, Prl: pyrophyllite, Hyd: "hydralsite", An: anorthite, C2: $CaAl_2Si_2O_8$ (hexagonal), (Kln): unreacted kaolinite, (Prl): unreacted pyrophyllite.

ionized samples treated with Na, K, Mg, and Ca under air-dried conditions at 60% relative humidity (RH), after treatment with ethylene glycol (EG) and glycerol (Gly), and after heating at 600°C for one hour. Average basal spacings were calculated from basal reflections in the range up to 35° (2θ, Cu*K*α), except for the first order (Table 3). The basal spacings are about 34 and 31.5 Å (at 60% RH) for samples saturated with divalent and monovalent cations, respectively. The former corresponds to two molecular layers of H_2O, and the latter, to one molecular layer. Basal spacings were found to be about 36.5 and 37 Å for glycolated and glycerolated samples, respectively, that are saturated with Na^+, Mg^{2+}, and Ca^{2+}. The spacing is 33 Å for a glycerolated sample saturated with K^+. The expansion characteristics of the sample are similar to those of beidellite (Harward *et al.* 1969, Matsuda 1988). Assuming that the thicknesses of glycolated and glycerolated smectite are 17 Å and 17.6 Å, respectively, the thickness of the non-expandable layer in the sample is about 19.5 Å, which corresponds to two layers of a mica-like component. XRD data show that the phase is a regular (R=2) interstratification of two mica-like layers and one smectite-like (beidellite) layer. A structure analysis of the phase is in preparation. The phase has a 060 spacing of 1.478 Å, and thus is dioctahedral in nature.

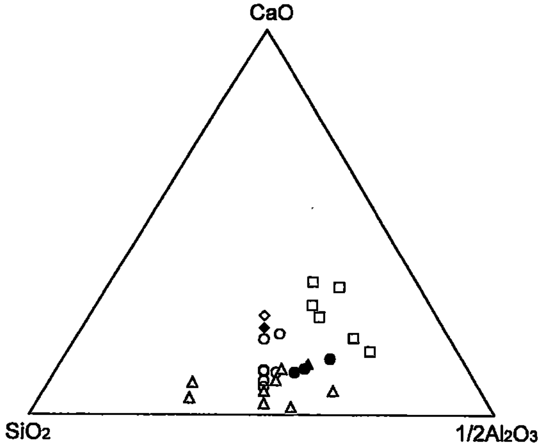

FIG. 1. Product phases at 450°C, plotted in terms of CaO–Al_2O_3–SiO_2. Solid circle: 34 Å phase, open circle: 34 Å phase + margarite–beidellite (25 Å, Matsuda & Henmi 1983), open square: margarite, open triangle: margarite–beidellite (25 Å), solid triangle: margarite–beidellite + böhmite, open rhomb: anorthite, solid rhomb: margarite–beidellite + anorthite.

Chemical composition of the 34 Å phase

The 34 Å single phase containing small amounts of an amorphous or low-crystallinity phase was analyzed

TABLE 3. BASAL (001) AND 060 SPACINGS OF THE 34 Å PHASE

Condition of sample	interlayer cation	spacing
airdried (RH60%)	Ca^{2+}	34.11 Å
	Mg^{2+}	34.60
	Na^+	31.50
	K^+	31.47
after heating at 110°C	Mg^{2+}	30.63
after heating at 600°C	Ca^{2+}	29.1
ethylene glycol	Ca^{2+}	36.39
	Mg^{2+}	36.43
	Na^+	36.46
	K^+	36.21
glycerol	Ca^{2+}	36.73
	Mg^{2+}	36.98
	Na^+	36.69
	K^+	33.03
Greene–Kelly test		37.08
(060)		1.478

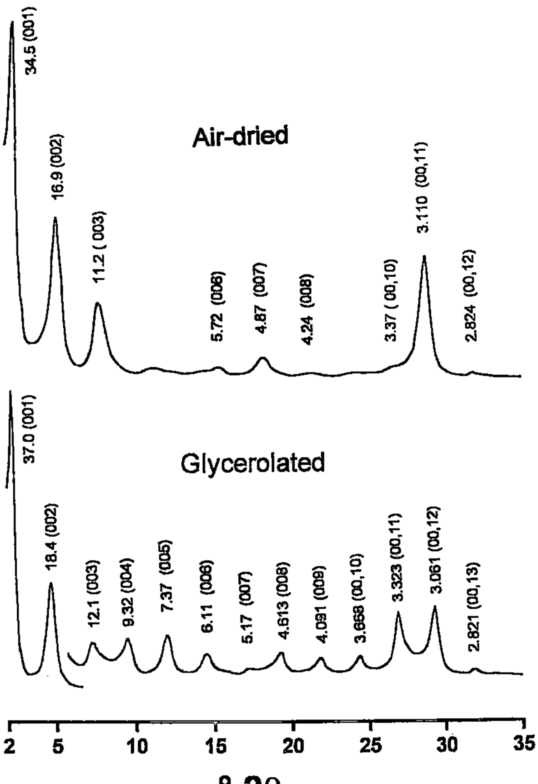

FIG. 2. XRD patterns of the 34 Å phase. Peak positions are in Å; Cu*K* radiation.

chemically. Interlayer cations were saturated with Mg^{2+} before the chemical analyses were performed. Exchangeable cations were extracted with a 0.1 M $CaCl_2$ solution, which was analyzed by atomic absorption spectrophotometry.

The results of chemical analysis and the number of cations based on $O_{30}(OH)_6$ are shown in Table 4. The analysis identifies SiO_2, Al_2O_3, CaO and H_2O as major components, and Na, K and interlayer Mg^{2+} as minor components. The Al content is somewhat low for ideal margarite, but comparable to that in some natural samples (Deer *et al.* 1962). The Al and Ca contents are higher than in the synthetic 25 Å phase (Matsuda & Henmi 1983). Octahedral sites are mostly occupied by Al, and the layer charges mainly originate from Al-for-Si substitution in the sheets of tetrahedra. The calculation of the number of cation assumes that the phase is composed of two layers of margarite and one layer of smectite (beidellite). As seen in Table 4, the chemical compositions of the expandable and non-expandable layers are $Mg_{0.18}Al_2\,(Si_{3.64}Al_{0.36})\,O_{10}\,(OH)_2$ and $(Ca_{1.84}Na_{0.22}K_{0.12})\,(Al_{4.04}Mg_{0.03}Fe_{0.01})\,(Si_{3.69}Al_{4.31})O_{20}\,(OH)_4$, respectively. Interlayer cations within the mica-like layers mostly consist of Ca. The ratio Ca/(Na + K + Ca) is 0.84, which is in agreement with the value for natural margarite (Deer *et al.* 1962, Aoki & Shimada 1965, Guggenheim & Bailey 1975). The proposed formula of the 34 Å phase agrees fairly well with a 2:1 mixture of margarite, $CaAl_2(Si_2Al_2)O_{10}(OH)_2$, as non-expandable layers, and beidellite, $Ex_{0.33}Al_2(Si_{3.67}Al_{0.33})\,O_{10}(OH)_2$, in which Ex represents monovalent exchangeable cations, as expandable layers. The presence of tetrahedrally coordinated Al in this phase is somewhat greater than in an ideal 2:1 mixture of margarite–beidellite.

Thermal analysis

DTA and TG curves were recorded with a Rigaku simultaneous DTA–TG apparatus. About 20 mg of the sample were heated at a rate of 10°C /min. Results for the Ca-saturated sample are shown in Figure 3, together with those for the synthetic 25 Å mineral (Matsuda & Henmi 1983).

The double endothermic peaks that occur below 200°C are attributable to dehydration, *i.e.*, removal of interlayer H_2O, endothermic peaks at 500–650°C are due to dehydroxylation, and a pair of endothermic and exothermic peaks at 1000–1100°C are characteristic of the formation of mullite and wollastonite (Fig. 3). Temperatures associated with the dehydration of the interlayer, the dehydroxylation of structural (OH), and the formation of mullite at the expense of the 34 Å phase, are similar to equivalent discontinuities for the 25 Å mineral.

Two stages of dehydration below 200°C and one main stage of dehydroxylation are shown by TG meas-

TABLE 4. CHEMICAL COMPOSITION AND STRUCTURAL FORMULA OF THE 34 Å PHASE

SiO_2 wt.%	33.95	Tetrahedral		
TiO_2	0.37	Si *apfu*		7.35
Al_2O_3	41.65	Al		4.65
Fe_2O_3	0.08	Charge	(–4.65)	
MgO	0.66	Octahedral		
CaO	7.94	Al		5.97
Na_2O	0.53	Mg		0.03
K_2O	0.44	Fe^{3+}		0.01
P_2O_5	0.04	Ti		0.06
$H_2O(+)$	7.54	Sum		6.07
$H_2O(-)$	6.92	Charge	(+0.24)	
		(Sum)	(–4.41)	
Total	100.12	Interlayer		
		Fixed		
		Ca		1.84
		Na		0.22
CEC (meq/100 g)	28.5	K		0.12
		Sum		2.18
		Charge	(+4.02)	
		Exchangeable		
		Mg		0.18
		Charge		0.36
		(Sum)	(+4.38)	

The proportion of cations in expressed in atoms per formula unit (*apfu*).

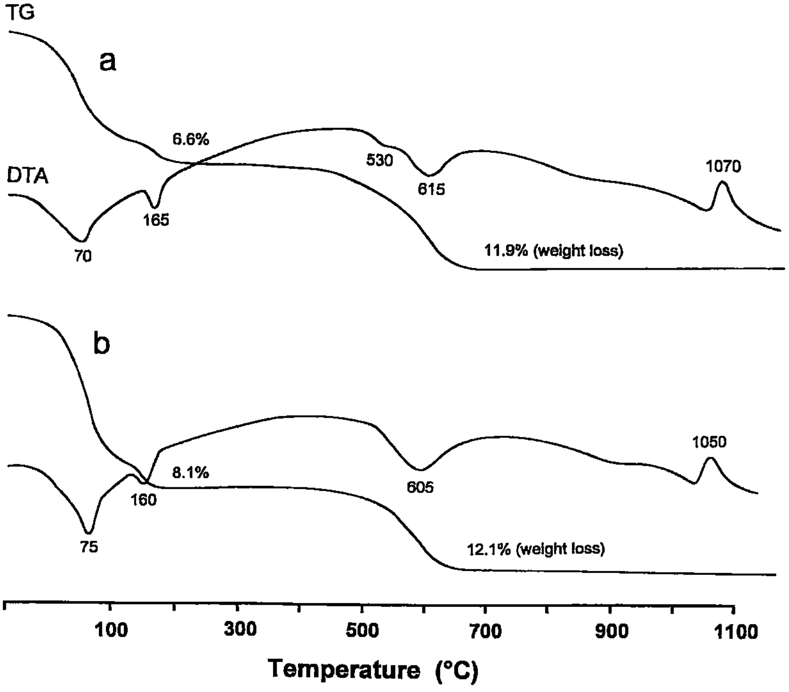

FIG. 3. Differential thermal analysis (DTA) and thermogravimetric (TG) curves for the 34 Å and 25 Å phases; a: 34 Å phase, b: 25 Å phase [synthetic (R=1) margarite(0.5) – beidellite] (Matsuda & Henmi 1983).

urement of the 34 Å phase (Fig. 3). The weight loss from the removal of interlayer H_2O is smaller than that of the 25 Å mineral, although the weight loss due to dehydroxylation is greater than that for the 25 Å mineral. This finding shows that the ratio of non-expandable component layers in the 34 Å phase is much higher than in the 25 Å mineral. The results of thermal experiments are in accord with those of the chemical analysis.

Electron microscopy

Two electron micrographs of the sample were taken with Zeiss EM 902 and JEM–T7 electron microscopes (Fig. 4). The sample consists of particles that range in form from rectangular to ribbon-like, and that are somewhat irregular in shape (Fig. 4a). These images are similar to those of rectorite (Brown & Weir 1963, Matsuda 1984). High-magnification lattice images taken with a JEM–T7 instrument show that the periodic layer-structure, which has about a 30 Å spacing, consist three units of 2:1 layers (Fig. 4b). It may consist of one dehydrated layer of smectite and two layers of margarite, on the basis of its chemical composition.

Infrared spectroscopy

The IR absorption spectra were recorded by a JASCO–A3 grating spectroscope; 200 mg KBr disks containing 1 mg and 0.3 mg of sample were used for the 4000–2800 cm^{-1} and 1200–330 cm^{-1} region, respectively. Spectra in the 4000–2800 cm^{-1} region of OH stretching and in the 1200–330 cm^{-1} region of Si–O, Al–OH and Si–O–Al lattice vibrations are shown in Figure 5. Absorption bands observed at 3650 and 3320 cm^{-1} are due to OH stretching in a dioctahedral 2:1 layer of silicate and in interlayer H_2O (Farmer & Russell 1964). Lattice vibrations of the sample in the 1200–330 cm^{-1} region are similar to those of margarite–beidellite (Matsuda & Henmi 1983) and margarite (Farmer & Russell 1964). The sample absorption at 1030 cm^{-1} is much stronger than that for margarite, but weaker than that for margarite–beidellite (Matsuda 1984, Matsuda & Henmi 1983). This finding suggests that the 34 Å phase has a composition intermediate between margarite and margarite–beidellite. The absorption intensities at 680, 550 and 480 cm^{-1} are also intermediate between those of margarite and margarite–

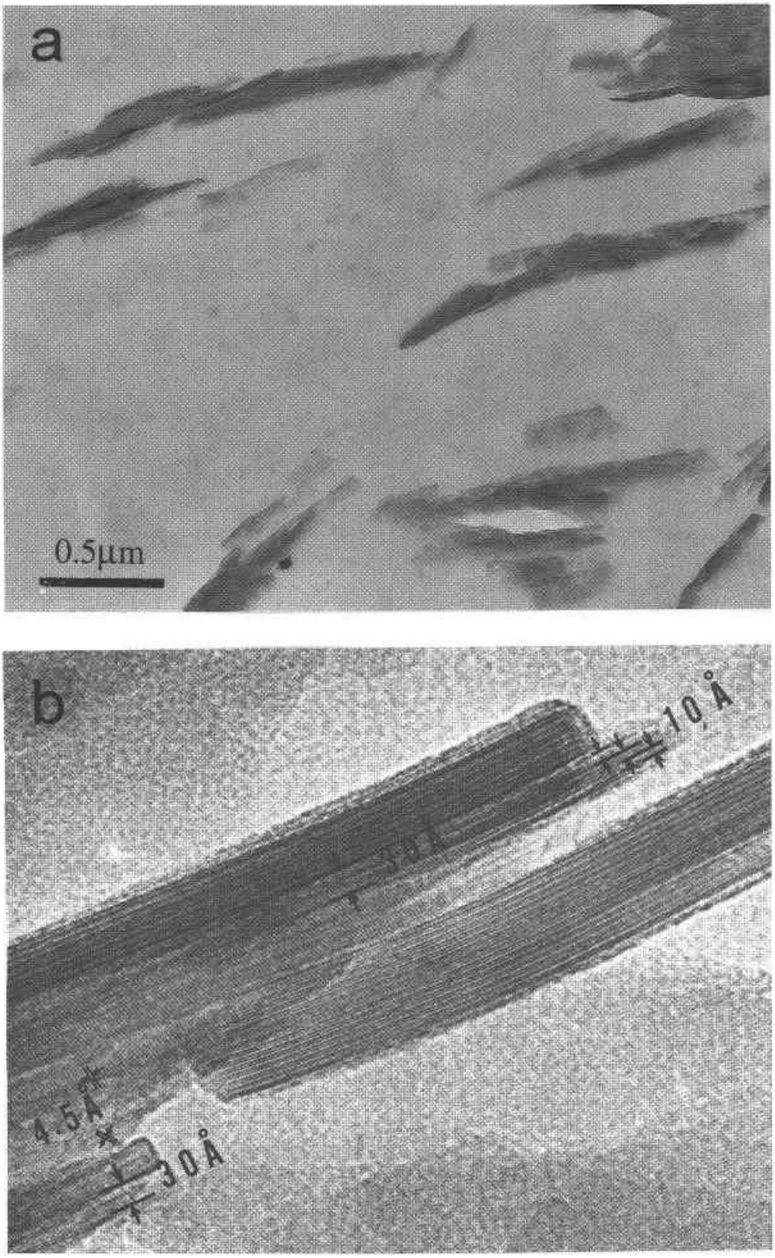

FIG. 4. Electron micrographs of the 34 Å phase; a: typical images of the 34 Å phase, b: high-magnification lattice images of the sample.

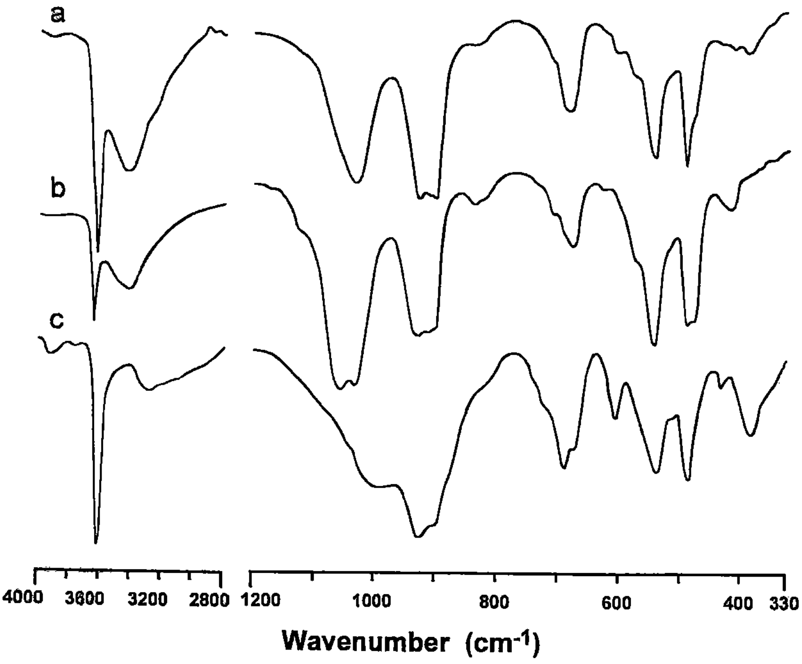

FIG. 5. Infrared absorption spectra of the 34 Å and 25 Å phases and margarite; a: 34 Å phase, b: 25 Å phase (Matsuda & Henmi 1983), c: margarite (Aoki & Shimada 1965, Matsuda 1984).

beidellite. The spectrum of the sample suggests the presence of margarite-like and beidellite-like layers in the proportion 0.67:0.33.

CONCLUSIONS

The chemical and temperature conditions under which regularly interstratified (R=2) margarite(0.67)–beidellite (34 Å phase) can form are limited. This is the first report about the regular interstratification with a basal spacing greater than 30 Å. Optimal starting compositions consist of margarite and margarite–beidellite in a ratio of 2:1. A regularly interstratified (R=1) phase of margarite(0.5)–beidellite (25 Å) commonly occurs in more siliceous compositions. The optimal temperature of formation of the mineral ranges from 400° to 500°C. Margarite and anorthite appear at temperatures higher than 500°C, and (R=1) margarite(0.5)–beidellite(25 Å) and a smectite phase occur at temperatures less than 400°C.

In the IR absorption spectra, the phase gives evidence of two Si:Al ratios in the tetrahedral sites of 2:1 silicate layers, and these correspond to margarite and beidellite.

Electron micrographs also show periodic layered structures of about 30 Å, which indicate that the margarite and dehydrated beidellite layers occur in a 2:1 ratio.

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