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TRANSFORMATIONS OF Al-INTERLAYERED MONTMORILLONITE UPON AGING

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ABSTRACT

Al-interlayered montmorillonite, gibbsite and boehmite have been synthesized at room temperature and 100°C. The Al-interlayered montmorillonite, which shows a basal spacing of 13 Å after heating at 600°C, is the most stable at room temperature for 2 weeks. Over a longer period, gibbsite at room temperature or boehmite at 100°C grows from the Al-interlayered montmorillonite. The hexagonal plates of gibbsite and the laths of boehmite are usually associated with, and grow on, films of the montmorillonite. Gibbsite and boehmite develop well in the *X* and *Y* directions, but have a limited thickness. At room temperature, the SiO_2/Al_2O_3 ratio of the film ranges from 0.9 to 1.25, which is close to that of dioctahedral chlorite and different from that of the film at 100°C (range from 1.8 to 2.7). The gibbsite and boehmite have a SiO_2/Al_2O_3 ratio of 0.19 and 0.56, respectively, which suggests that they grew on the surface of the Al-interlayered montmorillonite films. The pH, CEC, and surface area changed with aging, which suggests that Al-interlayered montmorillonite is sufficiently unstable to peel off the Al-interlayer after longer periods at room temperature and 100°C.

Keywords: Al-interlayered montmorillonite, gibbsite, boehmite, transmission electron microscopy, energy-dispersion analysis.

SOMMAIRE

On a synthétisé montmorillonite interstratifiée avec $Al(OH)_3$, gibbsite, et boehmite à température ambiante et à 100°C. La montmorillonite ainsi alumineuse, qui montre un espacement interfoliaire de 13 Å après chauffage à 600°C, est la plus stable à température de la pièce pour deux semaines. A plus long terme, c'est la gibbsite à température ambiante ou boehmite à 100°C qui croît aux dépens de cette montmorillonite. La gibbsite a une morphologie hexagonale, et la boehmite se présente en lattes. Les deux montrent une association avec les films de montmorillonite alumineuse, et croissent sur la surface de ces films. Gibbsite et boehmite sont bien développées dans les directions *X* et *Y*, mais sont d'épaisseur restreinte. Les films à température ambiante ont un rapport SiO_2/Al_2O_3 entre 0.9 et 1.25, qui est proche de la valeur attendue d'une chlorite dioctaédrique, et qui diffère de celle pour le même maté-

TABLE 1. CHARACTERIZATION OF THE PRODUCTS WITH AGING

		X-RAY DIFFRACTION					TRANSMISSION ELECTRON MICROSCOPY										
							MORPHOLOGY			LATERAL SIZE		THICKNESS					
	days	non treat	glyc	heated 600°C	4.85Å gibbs	6.2 Å boehm	film	hex	lath	hex	lath	film	hex	lath	pH	CEC	surf area
25°C	1	16.37 Å	16.67 Å	13.2 Å	-		abund (0.9-1.25)@	-	-			27-60 Å			6.5	0	286.33
	8	16.99	17.67	9.7-13	-		abund	-	-						6.0	20.44	193.22
	14	17.67	17.67	9.6-13	-		abund	tr	rare						5.9	22.30	192.55
	28	19.21	22.10	9.8-11	tr		abund	tr	rare	0.06 µm					5.2	26.43	294.82
	44	15.78	19.21	10.28	few		comm	few	rare	0.06-0.1					4.6	33.98	384.44
	83	13.81	19.21	10.16	comm		comm (1.08)	comm (0.19)	rare	0.1-0.12		42 Å	38-90 Å		4.3	52.07	506.72
	99	13.81	19.21	9.83	abund		comm	comm	rare						4.1	56.49	515.51
100°C	1	10.40 Å	17.67 Å	14 Å (vw)		-	comm	tr	tr						6.7	21.31	526.35
	8	11.95	18.80	9.41		tr	comm	tr	tr						3.2	51.37	473.71
	14	11.05	18.41	9.21		comm	comm	tr	comm						3.0	48.50	453.71
	28	11.05	19.21	9.61		comm	comm	tr	comm	0.05 µm	0.1-0.16			40 Å	3.4	57.66	521.24
	44	11.33	18.80	9.83		comm	few	rare	comm		0.08-0.2			40 Å	3.3	63.58	573.59
	83	12.11	20.08	9.83		comm	few (1.8-2.7)	rare	abund (0.56)		0.2 µm	32 Å		41 Å	3.0	70.02	639.23
	99	13.00	20.08	10.00		abund	few	rare	abund						3.5	71.33	584.11

Abbreviations: nontreat: nontreatment, glyc glycerol, gibbs gibbsite, boehm boehmite, hex hexagonal, surf surface, tr trace, comm common, abund abundant. Units: CEC in meq/100 g, surface area in m^2/g. @ SiO_2/Al_2O_3 determined by energy-dispersion analysis. (Results are quoted in parentheses).

riau chauffé à 100°C (entre 1.8 et 2.7). La gibbsite et la boehmite montrent un rapport SiO_2/Al_2O_3 de 0.19 et 0.56, respectivement, ce qui fait penser que ces phases croissent sur la surface des films de montmorillonite à interstratifications d'aluminium. Les changements pendant la maturation (pH, capacité d'échange des cations, aire de surface) seraient une indication que telle montmorillonite est suffisamment instable pour que la couche riche en hydroxide d'aluminium soit rejetée avec le temps à température ambiante et à 100°C.

(Traduit par la Rédaction)

Mots-clés: montmorillonite, interstratifications d'aluminium, gibbsite, microscopie électronique par transmission, analyse par dispersion d'énergie.

INTRODUCTION

The fact that aluminum hydroxide can enter in the interlayer of montmorillonite to form Al-interlayered montmorillonite is well known. Investigators have prepared aluminum-interlayered complexes by several methods and have studied their properties extensively, *e.g.*, surface area, cation-exchange capacity and activation energy of chloritization (Shen & Rich 1962, Barnhisel & Rich 1966, Brydon & Kodama 1966, Sawhney 1968, Barnhisel 1969, Lahav *et al.* 1978, Brindley & Kao 1980). But there are very few chemical data on micromorphology of such montmorillonite and associated products. The object of this paper is to illustrate, by transmission electron micrographs (TEM) with energy-dispersion analyses (EDX), the stages of formation of the Al-interlayered montmorillonite, gibbsite and boehmite, which have developed on the surface of films.

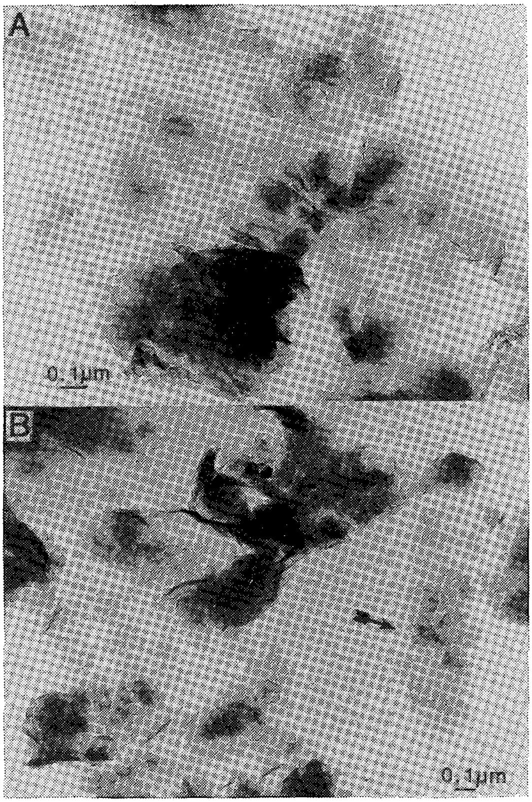

FIG. 1. Electron micrographs of aged products at room temperature. Arrow shows hexagonal gibbsite. A. After aging for 28 days; B. after aging for 44 days.

MATERIALS AND METHODS

Montmorillonite (Wyoming), obtained from Fisher Scientific Company of Canada, was saturated with Na, suspended in water, and stored as 2% stock suspensions. Solutions of 0.54 M NaOH (107.33 mL) and 0.20 M $AlCl_3$ (107.33 mL) were added slowly (drop-wise) to the clay suspension, and stirred constantly and vigorously. The suspensions, with an OH/Al ratio of 2.7, were prepared in this manner, and were kept in teflon containers at room temperature (about 25°C) and at 100°C. The suspensions were occasionally shaken and part of the sample withdrawn after intervals of 1, 8, 14, 28, 44, 84 and 99 days for analysis.

X-ray powder diffraction (XRD)

The clay suspension (about 2 mL) was centrifuged to collect the mineral colloids (about 0.5 g) for 10–20 minutes after washing with water to remove free salt. The samples were dried in air for one day. Humidity around the specimens was not controlled during analysis. XRD analysis was carried out with a Rigaku instrument under ordinary operating conditions. Heat treatment at 600°C and treatment with ethylene glycerol are essential to establish the presence of Al-interlayered montmorillonite.

Differential thermal analysis (DTA)

DTA was carried out with a Rigaku instrument under ordinary operating conditions. The presence of gibbsite and boehmite was confirmed by characteristic endothermic peaks; XRD cannot be used to ascertain the presence of a small amount of aluminum oxides.

Transmission electron microscopy (TEM)

After washing with water to remove free salt, the mineral colloids became good suspensions; artificial modes of aggregation were avoided in preparing the

TEM samples. The clay suspensions spread well over the TEM grids.

Electron-optical studies were done with a Philips EM 400 transmission electron microscope equipped with an EDX 9100/60 analyzer, operating at 100 kV acceleration voltage, spot size 2 μm, condenser aperture 100 μm, objective aperture 30 μm for images, and at 120 kV acceleration voltage, spot size 2000 Å, condenser aperture 50 μm, selected aperture 150 μm, objective aperture 10 μm for electron-microdiffraction patterns. Polystyrene latex particles of 0.109 μm diameter were used to standardize the measurement of thickness by tungsten shadow.

The EDX 9100/60 analyzer contains an anticontamination trap cooled with liquid nitrogen and a beryllium specimen-holder to reduce background noise. The following conditions were used throughout the study: condenser aperture 100 μm; no objective aperture, no diffraction aperture, tilting angle of the specimen holder toward the detector 21°, accelerating voltage 100 kV, spot size 400 Å, emission current 13 A. Under these conditions, Al*Kα* X-ray counts (1.41 to 1.51 kV) and Si*Kα* X-ray counts (1.66 to 1.76 kV) were measured in a 50-second point analysis on each morphologically distinct particle. Background subtraction was made in the semiquantitative analysis mode in the EDX system by using the following 4 points: 1.11, 1.46, 1.72 and 2.36 kV. The Si/Al intensity ratio was determined by comparing the signal with that of pure and standard kaolin KGa-1 (Washington Co., Georgia).

Cation-exchange capacity (CEC) and surface-area analysis

The CEC of the products was determined by the silver thiourea method of Chhabra *et al.* (1975). The surface area of these products was determined by the ethylene glycol monothyl ether method of Carter *et al.* (1965).

RESULTS AND DISCUSSION

XRD

X-ray data for the products collected at room temperature and aged 1 to 99 days are shown in Table 1. After the montmorillonite was aged for 2 weeks, a basal spacing between 16.37 and 17.67 Å was observed. This spacing changes slightly with ethylene glycerol treatment; it changes to 13 Å after heating at 600°C and may then be called Al-interlayered montmorillonite. Furthermore, montmorillonite in the solution aged more than 28 days gives the 4.85 Å basal spacing of gibbsite. Although X-ray diffraction of gibbsite aged for 99 days shows the strong 4.85 Å peak, the basal spacing (13.81 Å) expanded to 19.21 Å with ethylene glycerol treatment, which indicates typical montmorillonite.

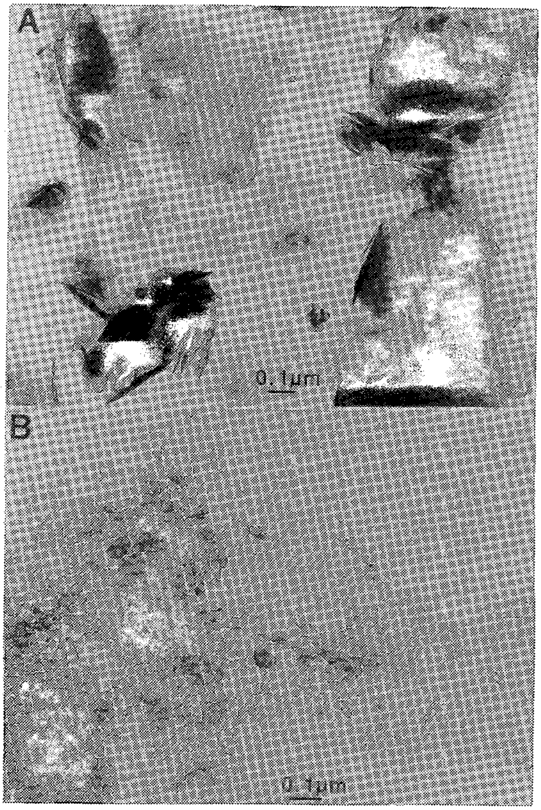

FIG. 2. Electron micrographs of aged products at 100°C. A. After aging for 28 days; B. after aging for 44 days.

After only one day at 100°C, the Al-interlayered montmorillonite was formed; but at longer periods, instead of gibbsite, boehmite of basal spacing 6.2 Å and montmorillonite were observed (Table 1).

The products aged for 99 days at room temperature and 100°C were further confirmed by DTA. The endothermic peaks at 270 and 490°C correspond to gibbsite and boehmite, respectively. Other endothermic peaks at about 100, 660, 940 and 960°C and exothermic peaks at 970 and 990°C correspond to montmorillonite.

Observations by electron microscopy

The montmorillonite starting material shows only film morphology, whereas the product held at room temperature and 100°C shows the following three kinds of morphology: film, hexagonal plate and lath. After aging for 2 weeks at room temperature, films were observed, but they possess a different value of SiO_2/Al_2O_3, which ranges from 0.9 to 1.25. After

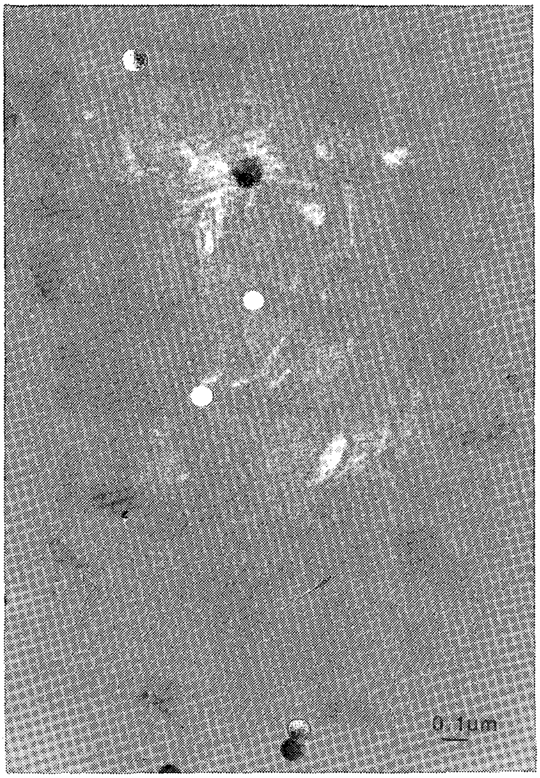

FIG. 3. Electron micrograph of tungsten-shadowed particles after aging 83 days at 100°C, with calibration specimen of Latex (diameter 1090 Å).

aging 28 to 44 days at room temperature, films were still observed (Fig. 1); there are no films that consist of hydrous aluminum oxide only. Hexagonal particles (Fig. 1B) that consist of hydrous aluminum oxide are usually associated with films at room temperature. At 100°C, films were commonly observed after aging for 28 days (Fig. 2A), whereas films are scarce after aging for 44 days, but lath-shaped particles are commonly formed on the films (Fig. 2B). The number of hexagonal particles at room temperature and lath-shaped particles at 100°C increases with aging (Table 1).

The crystal size and thickness are measured by the tungsten-shadow method with polystyrene latex particles (Fig. 3). Relationships between morphology, crystal size, crystal thickness, quantity of crystals, and amount of aging are summarized in Table 1. The lateral size of hexagonal plates and laths increases with aging, and these become relatively homogeneous under the same conditions. The thickness of the films and hexagonal particles is variable, whereas the thickness of the laths has not changed with aging at 100°C.

These values on crystal size and thickness suggest that hexagonal particles of gibbsite developed well in the X and Y directions, but were limited in the Z direction, and therefore appear as hexagonal plates. Lath-shaped particles of boehmite also are of limited thickness. Note that the hexagonal and lath-shaped particles always form on the surface of the films, which suggests that aluminum hydroxide once situated between montmorillonite layers later dissociated and precipitated as $Al(OH)_3$ or $AlO(OH)$ on the surface of montmorillonite layers. The EDX data support these observations.

The electron-microdiffraction patterns for each hexagonal and lath-shaped single crystal (Fig. 4) conform with these observations (Figs. 1, 2, 3). Gibbsite in hexagonal crystals was distinguished by a strong diffraction-maximum at 4.4 Å, along with an isolated major diffraction-maximum at 2.2 Å (Fig. 4A). Boehmite of the lath habit (orthorhombic) was detected by the appearance of the set of three major diffraction-maxima at 1.83 (c), 1.42 (a) and 1.12 Å (b). The vertical direction of the lath-shaped crystals corresponds to the diffraction spot at 1.4 Å (Fig. 4B).

Point analysis by EDX

By using a TEM equipped with an energy-dispersion electron-microprobe analyzer (EDX), genetic relationships between morphology and chemical composition of the samples collected at room temperature, aged 1 and 83 days, and at 100°C, aged 83 days, were investigated (Table 1). These observations reveal that the chemical compositions of the reaction products, which have three kinds of morphology, are all different. The EDX data contribute to the identification of minerals of the same or similar morphology, such as films under different conditions, and also establish the chemical purity of the gibbsite and boehmite.

The chemical composition of the films at room temperature shows that the SiO_2/Al_2O_3 value ranges from 0.9 to 1.25; this finding is in agreement with the values for dioctahedral chlorite, which ranges from 0.6 to 1.2 (Brydon *et al.* 1961, Weaver & Pollard 1973, Sudo & Shimoda 1978). The films aged 83 days at 100°C gave a different SiO_2/Al_2O_3 value, in the range from 1.8 to 2.7, closer to the value of starting montmorillonite, in the range from 2.1 to 2.8, than that of dioctahedral chlorite.

The hexagonal and lath-shaped particles, rich in Al, range from 0.05 to 0.25 and from 0.45 to 0.70 in SiO_2/Al_2O_3 value, respectively. Their averages are 0.19 and 0.56, respectively (Table 1). A small amount of SiO_2 in the hexagonal or lath-shaped particles reflects the chemical composition of the films underneath the particles (see Figs. 1B, 2B) that have not individually formed.

The EDX data also support the X-ray results, which identify the products as Al-interlayered montmorillonite, montmorillonite, gibbsite and boehmite. This effect might suggest that the suspensions with a OH/Al value of 2.7 are immediately contributed to the formation of the dioctahedral chlorite or Al-interlayered montmorillonite, which is unstable enough to peel off after longer period because the aluminum hydroxide minerals are formed on the surface. The CEC data (Table 1) are in agreement with the "pillar" concept. The CEC of the Na-montmorillonite, which is about 80 meq/100 g, decreases to 0–20 meq/100 g as a result of the formation of the Al-interlayered montmorillonite. The surface area for Na-montmorillonite, which is about 650 m^2/g, decreases to 200–300 m^2/g upon deposition of Al-interlayers. The surface area of the aged Al-interlayered montmorillonite with gibbsite or boehmite is over 350 m^2/g during the pH decrease from 6–7 to 3–4 with aging. Aluminum hydroxide cannot fill up the vacant interlayer of montmorillonite under these conditions, but aluminum hydroxide partly enters the interlayer to make the pillar complex or cross-linked montmorillonite (Lahav *et al.* 1978, Pinnavaia 1983) as an Al-chlorite-like mineral.

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REFERENCES

BARNHISEL, R.I. (1969): Changes in specific surface areas of clays treated with hydroxy-aluminum. *Soil Science* **107**, 126-130.

————— & RICH, C.I. (1966): Preferential hydroxy aluminum interlayering in montmorillonite and vermiculite. *Soil Sci. Soc. Amer. Proc.* **30**, 35-39.

BRINDLEY, G.W. & KAO, CHINH-CHUN (1980): Formation, compositions, and properties of hydroxy-Al and hydroxy-Mg-montmorillonite. *Clays Clay Minerals* **28**, 435-443.

BRYDON, J.E., CLARK, J.S. & OSBORNE, V. (1961): Dioctahedral chlorite. *Can. Mineral.* **6**, 595-609.

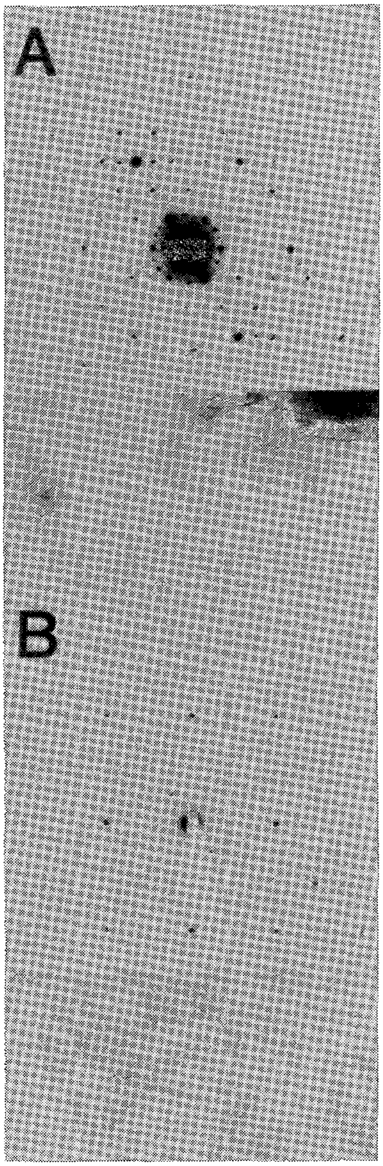

FIG. 4. Electron-microdiffraction patterns. A. Hexagonal crystal of gibbsite after aging 83 days at room temperature; B. lath-shaped crystal of boehmite after aging 28 days at 100°C.

————— & KODAMA, H. (1966): The nature of aluminum hydroxide – montmorillonite complexes. *Amer. Mineral.* **51**, 875-889.

CARTER, D.L., HEILMAN, M.D. & GONZALEZ, C.L. (1965): Ethylene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Sci.* **100**, 356-360.

CHHABRA, R., PLEYSIER, J. & CREMERS, A. (1975): The measurement of the cation exchange capacity and exchangeable cations in soils: a new method. *Proc. Int. Clay Conf.* **1975**, 439-449.

LAHAV, N., SHANI, U. & SHABTAI, J. (1978): Cross-linked smectites. I. Synthesis and properties of hydroxy-aluminum-montmorillonite. *Clays Clay Minerals* **26**, 107-115.

PINNAVAIA, T.J. (1983): Intercalated clay catalysis. *Science* **220**, 365-371.

SAWHNEY, B.L. (1968): Aluminum interlayers in layers silicates effect of OH/Al ratio of Al solution, time of reaction and type of structure. *Clays Clay Minerals* **16**, 157-163.

SHEN, M.J. & RICH, C.I. (1962): Aluminum fixation in montmorillonite. *Soil Sci. Soc. Amer. Proc.* **26**, 33-36.

SUDO, T. & SHIMODA, S. (1978): *Clays and Clay Minerals of Japan. Developments in Sedimentology* **26**. Kodansha-Elsevier, Tokyo-Amsterdam, 259-263.

WEAVER, C.E. & POLLARD, L.O. (1973): *The Chemistry of Clay Minerals.* Elsevier, Amsterdam.

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