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X-RAY STUDIES ON DEHYDRATION AND REHYDRATION OF EXPANSIBLE CLAY MINERALS

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ABSTRACT

Homoionic samples of 3 montmorillonites, 1 beidellite, and 1 vermiculite were heated at 300°C, 500°C, and 700°C. After cooling they were kept at 100% R.H., and the changes in basal spacing were measured and discussed in terms of their mineralogical properties including the DTA curves.

MATERIALS

The following 5 specimens were used.

- M1 Montmorillonite from Tsukinuno, Yamagata Prefecture, Japan.
- M2 Montmorillonite from Shirosaki, Niigata Prefecture, Japan.
- M3 Montmorillonite from Kawasaki, Miyagi Prefecture, Japan.
- B Beidellite from Coalgate, Canterbury, New Zealand.
- V Vermiculite from Odaka, Fukushima Prefecture, Japan.

Chemical analysis was carried out for the Ca-saturated samples by ICP emission and atomic absorption spectrometry, with SiO_2 determination by gravimetric analysis and FeO determination by $KMnO_4$ titration. The result is shown in Table 1. Structural formulae were calculated after making corrections for impurities, quartz, cristobalite, kaolinite, and anatase. The result is tabulated in Table 2.

Thermal analysis was made for 15-20 mg of the Ca-saturated samples with a Rigaku simultaneous DTA-TG apparatus at the heating rate of 10°C/min. The result is shown in Fig.1.

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TABLE 1. Chemical compositions of the specimens employed (weight percent)

	M1	M2	M3	B	V
SiO_2	51.57	56.19	56.10	44.41	32.72
TiO_2	0.12	0.06	0.16	5.95	0.25
Al_2O_3	16.82	13.78	13.57	15.42	14.52
Fe_2O_3	1.66	1.42	1.37	11.29	4.42
FeO	0.31	0.31	0.33	0.22	0.04
MnO	0.01	0.01	0.02	0.07	0.30
MgO	3.11	3.58	3.80	1.41	21.18
CaO	2.68	2.53	2.35	1.86	3.57
Na_2O	0.01	0.02	0.02	0.14	0.01
K_2O	0.01	0.18	0.08	0.34	0.04
P_2O_5	0.01	0.00	0.01	0.21	0.05
$H_2O(+)$	4.67	3.63	3.70	4.75	5.52
$H_2O(-)$	18.94	18.13	18.19	13.67	16.37
Total	99.92	99.84	99.70	99.74	98.99

TABLE 2. Structural formulae of the specimens employed on the basis of $O_{10}(OH)_2$

		M1	M2	M3	B	V
Tetrahedral	Si	3.93	3.99	4.00	3.51	2.72
	Al	0.07	0.01	0.00	0.49	1.28
		4.00	4.00	4.00	4.00	4.00
Octahedral	Ti	--	--	--	--	0.02
	Al	1.51	1.41	1.41	0.98	0.14
	Fe(III)	0.10	0.09	0.09	0.86	0.28
	Fe(II)	0.02	0.02	0.02	0.02	0.00
	Mn	0.00	0.00	0.00	0.01	0.02
	Mg	0.37	0.47	0.50	0.21	2.54
		2.00	1.99	2.02	2.08	3.00
Interlayer	Ca	0.23	0.24	0.22	0.20	0.32
	Na	0.00	0.00	0.00	0.03	0.00
	K	0.00	0.02	0.01	0.04	0.00
	Mg	--	--	--	--	0.09
		0.23	0.26	0.23	0.27	0.41
Charges	Tetrahedral	-0.07	-0.01	0.00	-0.49	-1.28
	Octahedral	-0.39	-0.49	-0.45	+0.02	+0.46
	Interlayer	+0.46	+0.50	+0.45	+0.47	+0.82

EXPERIMENTAL

X-ray diffraction was made with a JEOL computer-aided diffractometer equipped with a monochromator. Experiments on air-dried homoionic samples were made in the atmosphere of 50 % R.H. Ethylene glycol solvation was made by spraying the liquid, and glycerol solvation was made by exposing to the vapour at 110°C

for 4 hours. High-temperature X-ray diffraction was made on a heating stage attached to the same diffractometer. The temperature of the heating stage was calibrated by using the transition points of KNO_3, $KClO_4$, K_2SO_4, and K_2CrO_4. After the high-temperature X-ray experiments, the samples were kept at room temperature and 100% R.H. for 10 days and 30 days, and X-rayed again.

RESULTS AND DISCUSSION

The changes in basal spacing are shown in Fig.2.

Li-saturated montmorillonite does not rehydrate after heating at either 300°C, 500°C, or 700°C. Greene-Kelly (1953) showed that Li-saturated montmorillonite irreversibly collapses by heating even at 200°C, and this is used widely as a test for differentiating beidellite from montmorillonite. The present result is in harmony with the finding of Greene-Kelly.

K-saturated vermiculite shows 10.2 Å basal spacing in the air-dried state, which does not expand by ethylene glycol solvation. This spacing remains unchanged on heating at 300°C,

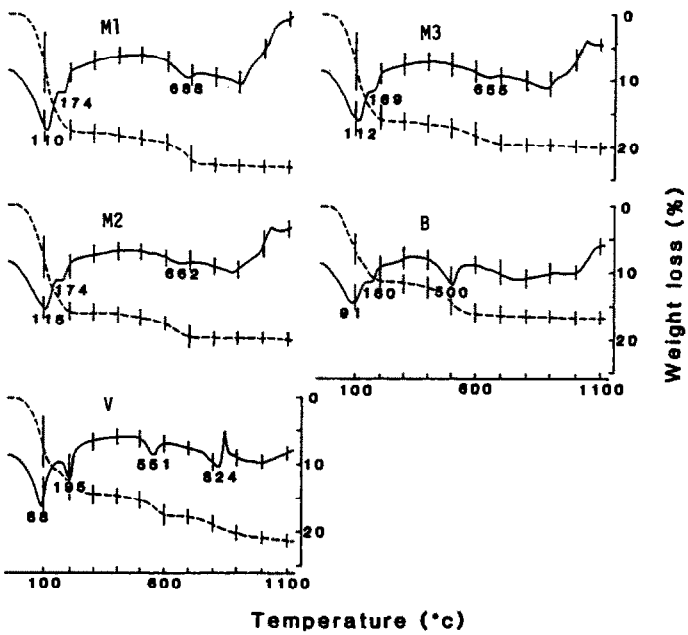
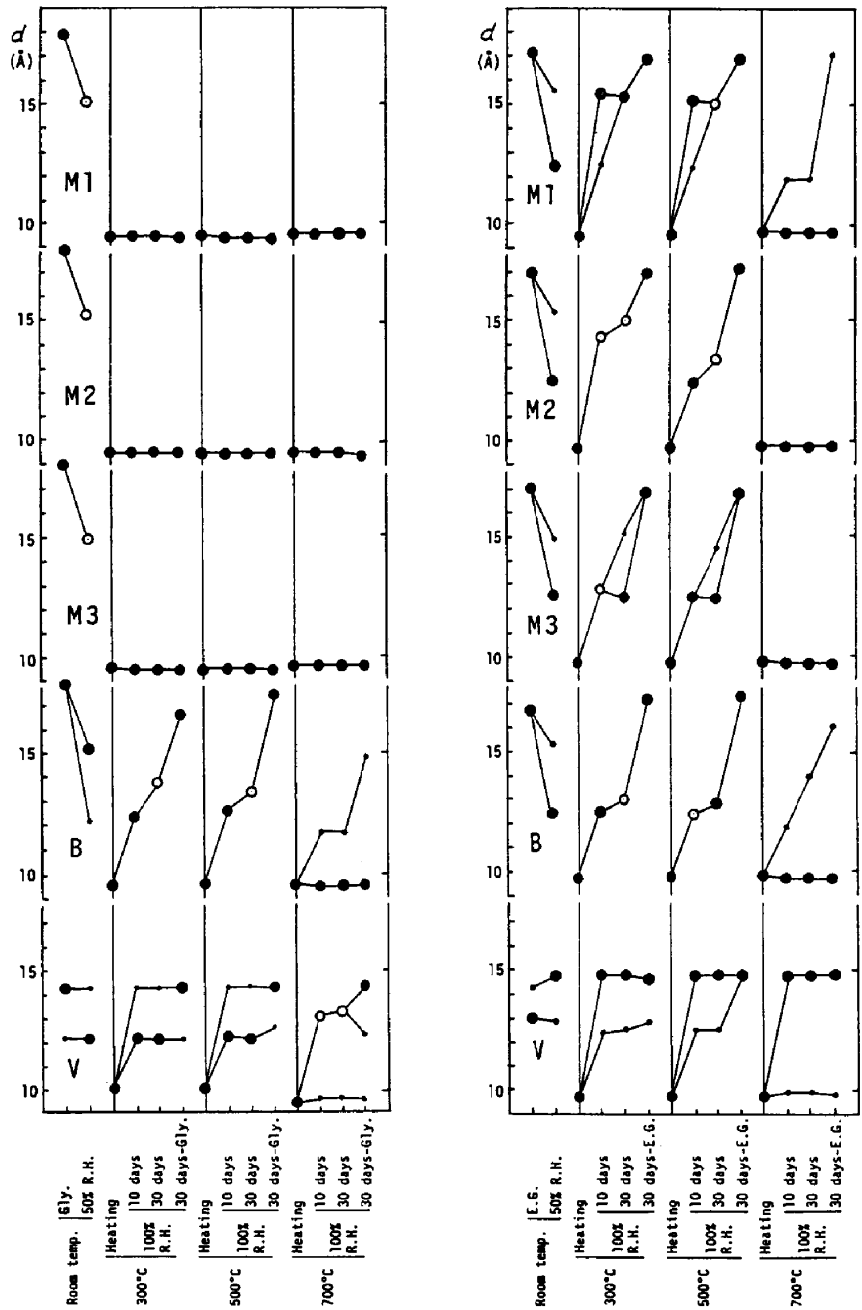
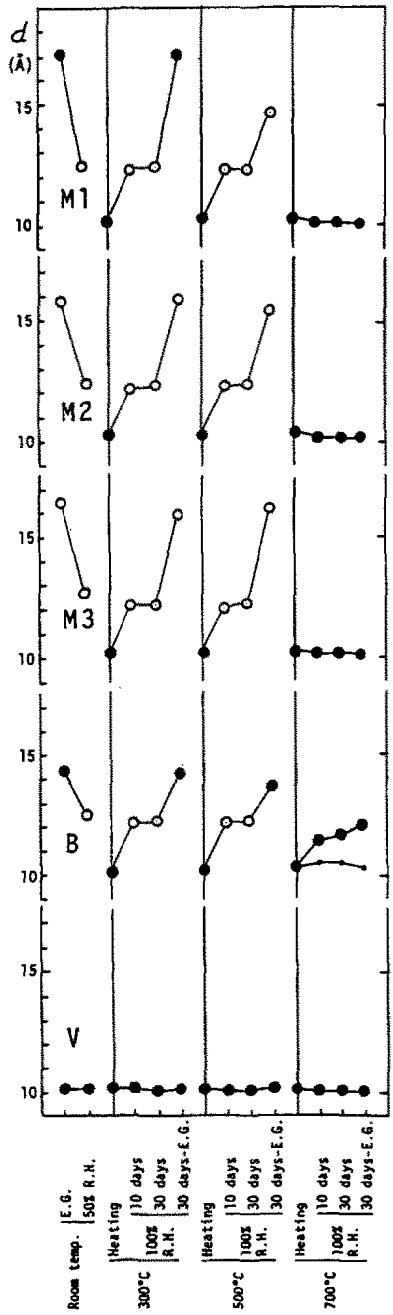


FIG. 1. DTA-TG curves of Ca-saturated samples. Solid line- DTA, broken line- TG.

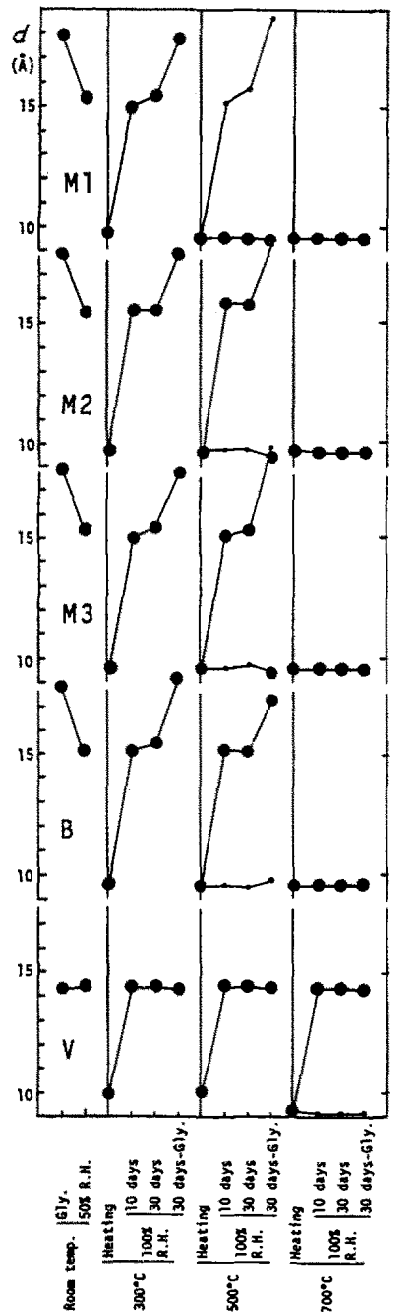


a) Li-saturated form. b) Na-saturated form.

FIG. 2. Changes in basal spacing on dehydration and rehydration. ● - dominant reflection, ○ - dominant reflection accompanied by non-integral higher order, •- subordinate reflection.

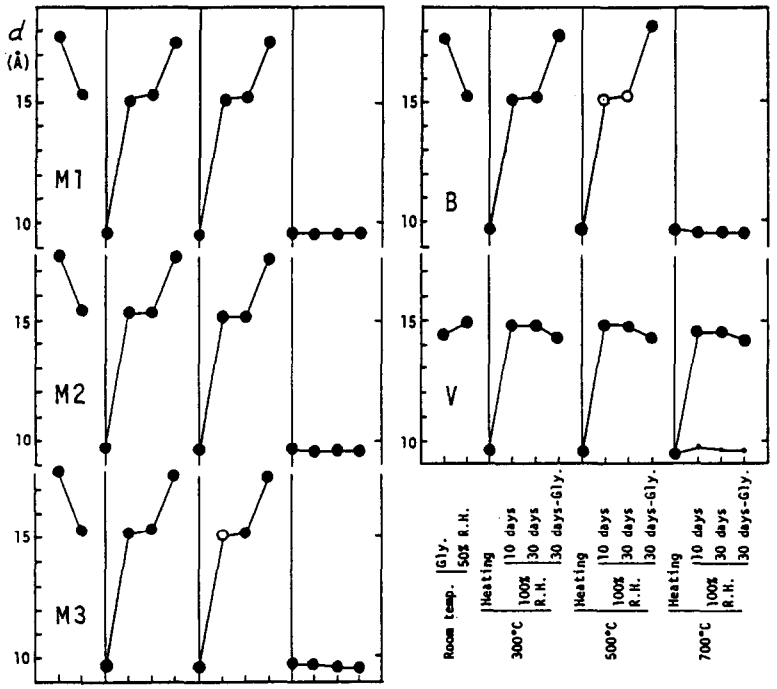


c) K-saturated form.



d) Mg-saturated form.

FIG. 2. (Continued)



e) Ca-saturated form.

FIG. 2. (Continued)

500°C, or 700°C and after keeping at 100% R.H. for 10 days or 30 days.

Montmorillonite saturated with any cation other than Li, beidellite saturated with any cation, and vermiculite saturated with any cation other than K fully rehydrate by keeping at 100% R.H. after keeping at 300°C or 500°C, except for Mg-saturated montmorillonite and beidellite which rehydrate less completely.

Montmorillonite and beidellite do not rehydrate after heating at 700°C except for the Na saturated Tsukinuno montmorillonite and the Li-, Na-, and K-saturated beidellite which rehydrate in part. This is in harmony with the DTA curves which show the dehydroxylation peak below 700°C. Vermiculite saturated with any cation other than K largely rehydrates after heating at 700°C. Vermiculite does not dehydroxylate by 700°C; the endothermic peak at 551°C of the Odaka vermiculite is due to a serpentine impurity.

REFERENCE

Greene-Kelly, R. (1953) Jour. Soil Sci., 4, 233.