CONTROLLED SYNTHESIS OF HETEROPOLYTYPIC (MIXED-LAYER) CLAY MINERALS

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ABSTRACT

The conditions for the formation of various heteropolytypic or mixed-layer phases were determined in a hydrothermal study of synthetic mixtures along the join talc—Na-saponite—Na-phlogopite composition. Heteropolytypes of talc and saponite from compositions between talc and a saponite solid solution and of saponite and a 10 Å sodium mica (Na-phlogopite?) from compositions lying between saponite solid solutions and Na-phlogopite have been prepared reproducibly.

At 1 kb in the temperature range 450–575° C, randomly stacked heteropolytypic phases were formed and persisted. At higher pressures the regular heteropolytypes (regularly interstratified or mixed-layer minerals), generally 1:1 phases, were formed. The genesis of heteropolytypes in nature is discussed on the basis of these results.

INTRODUCTION

It is common to find in nature clay minerals made up of an intimate regular or irregular interstratification of two distinct species. The physical properties of such a mineral are, in general, intermediate between those of the two constituent units. An X-ray powder diffraction pattern of the mineral shows the resultant of the interference of X-ray beams diffracted from each of these constituent units. Descriptions of the natural occurrence of this type of mineral, interpretation of X-ray diffraction diagrams, and discussions of genesis recently have received much more attention.

The terms "mixed-layer" mineral or "interstratified" clay have been used for this mixture. Warshaw and Roy (1961), however, in their systematic treatment of the nomenclature problem have attempted to show why another term is preferable. A "mixed-layer" clay is exactly the opposite of what the term says. It is *not* a gross or common mixture of two layer structures: it is a single crystal chemical entity because the "mixing" takes place on an intimate scale of the order of unit-cell dimensions, and parellelism is preserved. The phenomenon of obtaining different phases by stacking *identical* units in different ways is well known as homopolytypism; hence the etymology of heteropolytypism for different stackings of non-identical units. Indeed the "scale of mixing" is such as to put these substances, as it does

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homopolytypes, somewhere between "one phase" and "two phases" (see Romo and Roy, 1955).

Previous attempts to produce artificially these heteropolytypic clay minerals or mixed-layer clays have not been too successful (Romo and Roy, 1955). Synthesis experiments at room temperature employing special chemical treatment (Youell, 1960), or a few runs at elevated temperatures from special compositions (Mumpton, 1956; Mumpton and Roy, 1956; Warshaw, 1960; Koizumi and Roy, 1959), occasionally produced such phases.

Owing to the difficulty of hydrothermally synthesizing these minerals and because of their common occurrence in nature, Romo and Roy (1955) concluded that these mixed-layer phases are thermodynamically metastable and probably formed through a secondary reworking process during weathering. However, the possibility that these phases may form directly from gels and persist stably under some particular pressure, temperature and composition conditions could not be ruled out.

During a study of the cation exchange capacity of synthetic montmorillonoids, Koizumi and Roy (1959) reported that some mixed layers were formed from sodium-rich compositions at 260–450° C and 1 kb. In this study an attempt was made to systematize the preparation of such phases and obtain further data on their stability.

EXPERIMENTAL PROCEDURES

Test-tube type cold-seal hydrothermal vessels were used for the synthesis. The starting materials and a small amount of distilled water were sealed into small gold tubes (2.5 mm or 5 mm in diameter). The quantity of starting materials and water introduced into the gold tube was measured by weighing the tube.

The heating temperature was regulated to $\pm 5°$ C (at the desired temperature). The pressure was adjusted with a high-pressure pump to the desired value after the bomb reached the desired temperature. After the desired period of heating, the bomb was quenched into water and opened. The gold tube was weighed again to determine if leakage occurred.

The products formed were examined for morphology and minor phase content under the microscope and then X-rayed in dry air using a Norelco X-ray diffractometer. Appropriate glycolation and heating studies were made to characterize the existing clay mineral phases. Electron microscope photographs and electron diffraction patterns were used to assist with the mineral identification.

STARTING MATERIALS

Gels prepared by a method (see Roy, 1956) using mixtures of aluminum, magnesium and sodium nitrate solutions and a colloidal silica suspension stabilized by ammonium ions (Ludox AS) were used as starting materials. The compositions prepared lie on the join "talc–sodium phlogopite composi-

tion" in the system Na_2O—MgO—Al_2O_3—SiO_2. Table 1 shows the compositions studied. The compositions of some gels thus prepared were checked by chemical analysis. The differences between the desired and analyzed

TABLE 1.—COMPOSITIONS STUDIED

x^*	SiO_2	Al_2O_3	MgO	Na_2O
0	4.00	0.00	3.00	0.00
	(3.99)	(0.00)	(2.99)	(0.02)†
0.05	3.95	0.03	3.00	0.03
0.10	3.00	0.05	3.00	0.05
0.15	3.85	0.08	3.00	0.08
0.17	3.83	0.09	3.00	0.09
	(3.86)	(0.08)	(2.94)	(0.09)
0.20‡	3.80	0.10	3.00	0.10
0.24	3.76	0.12	3.00	0.12
0.25	3.75	0.13	3.00	0.13
0.33	3.67	0.17	3.00	0.17
	(3.69)	(0.17)	(2.96)	(0.17)
0.40‡	3.60	0.20	3.00	0.20
0.44	3.56	0.22	3.00	0.22
0.51‡	3.49	0.26	3.00	0.26
0.60‡	3.40	0.30	3.00	0.30
0.65	3.35	0.32	3.00	0.32
0.66	3.24	0.33	3.00	0.33
	(3.33)	(0.33)	(3.00)	(0.32)
0.70	3.30	0.35	3.00	0.35
0.75‡	3.25	0.33	3.00	0.33
0.80	3.20	0.40	3.00	0.40
0.85	3.15	0.43	3.00	0.43
0.90	3.10	0.45	3.00	0.45
0.95	3.05	0.48	3.00	0.48
1.00	3.00	0.50	3.00	0.50

 * x in the formula $\frac{1}{2}xNa_2O.3MgO.\frac{1}{2}xAl_2O_3(4-x)SiO_2$.
 † Values in parentheses give molecular ratios obtained from chemical analysis of the prepared gel.
 ‡ Compositions prepared by mixing of two gels of known composition.

composition (listed in Table 1) for all analyzed gels were found to be not greater than ± 0.05 in molecular ratio of oxides. Some intermediate compositions were prepared by mixing two gels in a mechanical vibrator shaker.

RESULTS

Results of a few representative runs are tabulated in Table 2. The data are summarized in Fig. 1 using, for convenience, a binary phase diagram representation. The composition of the entire system can be represented by a

TABLE 2.—RESULTS OF REPRESENTATIVE RUNS

Compo-sition $(x=)$	Run no.	$T°C$	Pkb	Dura-tion days	Phases present	001 spacing of clay min.	
						Non-treated	E.G.
(I) Runs under 1 kb							
0.0	1310	550	1	3	T	9.5 Å	9.5 Å
0.0	1054	700	1	3	T	9.5	9.5
0.0	1097	750	1	4	T + anth.	9.5	9.5
0.05	1284	550	1	3	ML_1	9.9	9.3 + 9.7
0.10	1285	550	1	3	ML_1	10.3	9.4 + 11.3
0.15	1286	550	1	3	ML_1	10.5	9.4 + 13.0
0.17	1001	450	1	3	ML_1	10.8	9.5 + 13.4
0.17	1230	550	1	30	ML_1	10.3	9.5 + 13.5
0.17	1004	550	1	3	ML_1	10.3	9.5 + 13.6
0.17	1011	600	1	3	ML_1	10.1	9.3 + 17.3
0.17	1069	650	1	4	ML_1 + anth.	10.1	9.5 + 17.3
0.17	1082	750	1	4	ML_1 + anth.	9.6	9.7 + 17.3
0.17	1110	800	1	3	mont. + T + anth.	9.6 + 12.6	9.7 + 17.3
0.20	1308	550	1	3	ML_1	11.0	9.4 + 15.2
0.24	1043	450	1	3	mont.	13.0	17.6 + 8.8
0.24	1033	520	1	3	ML_1	11.2	17.3 + 9.0
0.24	1064	550	1	4	ML_1	11.0	17.0 + 9.0
0.24	1070	650	1	4	ML_1 + anth.	10.3	17.3 + 9.5
0.24	1169	700	1	4	mont. + T + anth.	12.6 + 9.3	17.3 + 9.3
0.24	1111	800	1	3	mont. + T + anth.	12.6 + 9.3	17.6 + 9.3
0.25	1287	550	1	3	ML_1	10.8	16.4 + 9.2
0.33	1002	450	1	3	mont.	12.3	17.3
0.33	1009	500	1	3	mont.	13.0	17.3
0.33	1005	550	1	3	ML_1	11.6	17.3 + 9.0
0.33	1015	575	1	3	ML_1	11.6	17.3 + 9.0
0.33	1012	600	1	3	mont. + anth.	11.3	17.0 + 8.8
0.33	1075	650	1	3	T + mont. + anth.	12.6 + 9.7	17.3 + 8.6 + 9.6
0.33	1112	800	1	3	T + mont. + anth.	12.6 + 9.5	17.6 + 9.3 + 8.8
0.40	1205	550	1	5	mont.	12.6	17.6 + 8.8
0.40	1194	575	1	4	mont. + anth.	12.6	17.6 + 8.8
0.44	1065	550	1	4	mont.	12.6	17.6 + 8.8
0.44	1195	575	1	4	mont. + anth.	12.4	17.6 + 8.8
0.44	1203	750	1	4	mont. + anth.	12.6	17.6 + 8.8
0.51	1030	500	1	3	mont.	12.6	17.3 + 8.6
0.51	1059	550	1	3	mont.	12.6	17.3 + 8.6
0.51	1232	550	1	34	mont.	12.6	17.3 + 8.6
0.51	1020	575	1	3	mont. + anth.	12.5	17.3 + 8.6
0.51	1233	700	1	30	mont. + anth.	12.6	17.6 + 8.6
0.51	1129	800	1	3	mont. + anth.	12.5	17.6 + 8.6
0.60	1297	550	1	3	mont.	12.6	17.6 + 8.6
0.60	1311	575	1	3	mont. + anth.	12.6	17.3 + 8.6
0.62	1307	550	1	3	ML_2	12.6	17.0
0.65	1306	550	1	3	ML_2	12.6	15.5
0.67	1003	450	1	3	mont.	12.3	17.6
0.67	1010	525	1	3	mont.	12.6	17.3
0.67	1067	550	1	4	ML_2	12.6	13.9

TABLE 2.—*continued*

Compo-sition $(x=)$	Run no.	$T° C$	Pkb	Dura-tion days	Phases present	001 spacing of clay min.	
						Non-treated	E.G.
0.67	1016	575	1	3	mont. + anth.	12.3	17.0 + 8.6
0.67	1130	800	1	3	mont. + anth.	12.3	17.0 + 8.6
0.70	1305	550	1	3	ML_2	12.6	14.3
0.75	1298	550	1	3	ML_2	12.5	14.0
0.80	1044	450	1	3	ML_2	12.3	13.8
0.80	1229	550	1	30	ML_2	12.6	13.8
0.80	1022	575	1	3	ML_2	12.6	13.8
0.80	1025	600	1	3	ML_2 + anth.	12.8	13.8
0.80	1099	750	1	4	ML_2 + anth.	12.3	13.2
0.80	1131	800	1	3	ML_2 + mica + anth.	12.3 + 10.3	13.2 + 10.3
0.85	1289	550	1	3	ML_2	12.1	13.6
0.90	1299	550	1	3	ML_2	12.1	13.6
0.95	1290	550	1	3	ML_2	11.9	13.4
1.00	1045	450	1	3	ML_2	12.1	13.2
1.00	1291	550	1	3	ML_2	10.8	13.2
1.00	1024	600	1	3	ML_2	10.8	13.4
1.00	1231	600	1	4	ML_2	10.8	13.3
1.00	1081	650	1	3	ML_2 + mica + anth.	12.1 + 10.0	13.0 + 10.0
1.00	1132	800	1	3	ML_2 + mica + anth.	12.1 + 10.2	13.2 + 10.2

(II) *Runs under 3 kb*

Compo-sition $(x=)$	Run no.	$T° C$	Pkb	Dura-tion days	Phases present	Non-treated	E.G.
0.00	1164	700	3	3	T	9.6	9.6
0.17	1133	400	3	10	$ML_1(d)$	10.9	11.6
0.17	1101	500	3	4	$ML_1(o+d)$	24.5 + 10.8	29.4 + 12.1 + 9.0
0.17	1057	550	3	3	$ML_1(o+d)$	17.3 + 10.6	18.7 + 12.3 + 9.1
0.17	1114	600	3	3	$ML_1(o+d)$	16.4 + 10.5	18.4 + 11.6 + 9.1
0.17	1157	700	3	3	$ML_1(d)$ + mont.	12.5 + 10.5	17.0 + 9.2 + 8.4
0.24	1135	400	3	10	mont.	12.1	17.6
0.24	1087	500	3	4	$ML_1(o+d)$	23.2 + 11.2	28.5 + 13.5 + 8.9
0.24	1158	700	3	3	$ML_1(d)$ + anth.	9.5	17.3 + 9.5
0.33	1134	400	3	10	mont.	12.3	17.6
0.33	1102	500	3	4	$ML_1(o+d)$	23.8 + 12.6	27.6 + 17.3 + 14.3 + 8.8
0.33	1058	550	3	3	$ML_1(o+d)$	24.5 + 12.8 + 11.3	27.6 + 17.6 + 13.8 + 8.8
0.33	1185	575	3	4	$ML_1(o+d)$	23.2 + 12.5 + 11.9	27.6 + 17.7 + 8.8
0.33	1116	600	3	3	$ML_1(o+d)$ + anth.	9.8 + 9.0	29.4 + 17.4 + 13.6
0.33	1159	700	3	3	$ML_1(o+d)$ + anth.	22.6 + 12.3 + 11.2 + 9.8	17.0 + 9.5 + 8.6
0.44	1136	400	3	10	mont.	13.0	17.6
0.44	1089	500	3	4	mont.	12.6	17.6 + 8.8

TABLE 2.—*continued*

Composition ($x=$)	Run no.	T° C	*Pkb*	Duration days	Phases present	001 spacing of clay min.	
						Non-treated	E.G.
0.44	1186	575	3	4	$ML_1(o+d)$	$36.8+12.6$	$17.3+8.9$
0.44	1173	600	3	4	mont.+anth.	12.8	$17.0+8.6$
0.51	1103	500	3	4	mont.	12.6	$17.0+8.3$
0.51	1187	575	3	4	mont.	12.8	17.3
0.51	1117	600	3	3	mont.+anth.	12.6	$17.0+8.5$
0.51	1160	700	3	3	mont.+anth.	12.8	$17.3+8.5$
0.67	1188	575	3	4	mont.	12.8	$17.6+8.8$
0.67	1118	600	3	3	mont.+anth.	12.6	17.3
0.80	1139	400	3	10	mont.	12.6	17.3
0.80	1062	500	3	4	$ML_2(d)$	10.5	16.3
0.80	1119	600	3	3	$ML_2(o+d)$	12.5	$30.5+14.7$
0.80	1162	700	3	3	$ML_2(d)+$anth.	12.2	13.4
1.00	1140	400	3	10	$ML_2(d)$	12.6	13.2
1.00	1104	500	3	4	$ML_2(d)$	11.9	13.2
1.00	1120	600	3	3	$ML_2(d)$	12.3	13.4
1.00	1163	700	3	3	$ML_2(d)+$mica+anth.	$12.1+9.9$	$13.2+10.0$

(III) Runs under 0.5 kb

0.00	1209	700	0.5	7	T	9.5	9.5
0.17	1017	450	0.5	7	mont.	12.6	17.0
0.17	1125	500	0.5	14	ML_1	10.3	11.1
0.17	1153	550	0.5	7	ML_1	10.3	10.6
0.17	1178	600	0.5	8	ML_1+anth.	9.8	$17.7+9.6$
0.24	1184	600	0.5	8	T+mont.	$12.6+9.6$	$17.3+9.5$
0.33	1018	450	0.5	7	mont.	12.8	17.3
0.33	1126	500	0.5	14	mont.	12.0	17.3
0.33	1154	550	0.5	7	ML_1	12.3	$17.6+8.8$
0.33	1179	600	0.5	8	mont.+T	$12.5+9.6$	$17.3+9.7+8.6$
0.51	1091	550	0.5	10	mont.	12.8	17.0
0.51	1181	600	0.5	8	mont.+anth.	12.6	$17.7+8.6$
0.51	1213	700	0.5	10	mont.+anth.	12.6	$17.0+8.5$
0.67	1155	550	0.5	7	mont.	12.6	17.0
0.67	1180	600	0.5	8	mont.+anth.	12.5	$17.3+8.6$
0.80	1073	450	0.5	10	ML_2	12.8	13.6
0.80	1092	550	0.5	10	ML_2	12.5	13.8
0.80	1183	600	0.5	8	ML_2+anth.	12.8	14.3
0.80	1221	700	0.5	7	ML_2+anth.	12.6	13.5
1.00	1074	450	0.5	10	ML_2	12.3	13.2
1.00	1093	550	0.5	10	ML_2	12.1	13.1
1.00	1182	600	0.5	8	ML_2+anth.	10.0	13.4
1.00	1214	700	0.5	7	mica+ML_2+anth.	$12.1+10.4$	$13.2+10.3$

Abbreviations used: T = talc; mont. = montmorillonite; anth. = anthophyllite; ML_1 = heteropolytypic phase of talc and montmorillonite layer (disordered stacking); $ML_1(o+d)$ = mixture of ordered and disordered stacking of heteropolytypic phase of talc and montmorillonite; ML_2 = heteropolytypic phase of mica and montmorillonite layer; $ML_2(o+d)$ = same meaning as in case of $ML_1(o+d)$.

formula $\frac{1}{2}x\mathrm{Na_2O}\cdot 3\mathrm{MgO}\cdot\frac{1}{2}x\mathrm{Al_2O_3}\cdot(4-x)\mathrm{SiO_2}n\mathrm{H_2O}$, where the value of x indicates the fractional mol ratios used.

Under a pressure of 1 kb and at 450° C saponite was formed in the composition range of $x = 0.25$–0.75. This phase had a 001 basal spacing of 12.6 Å (in dry air) which expanded to 17.6 Å when glycolated. At higher temperatures the composition range for saponite narrows to $x = 0.40$–0.60 at about 575° C.[1]
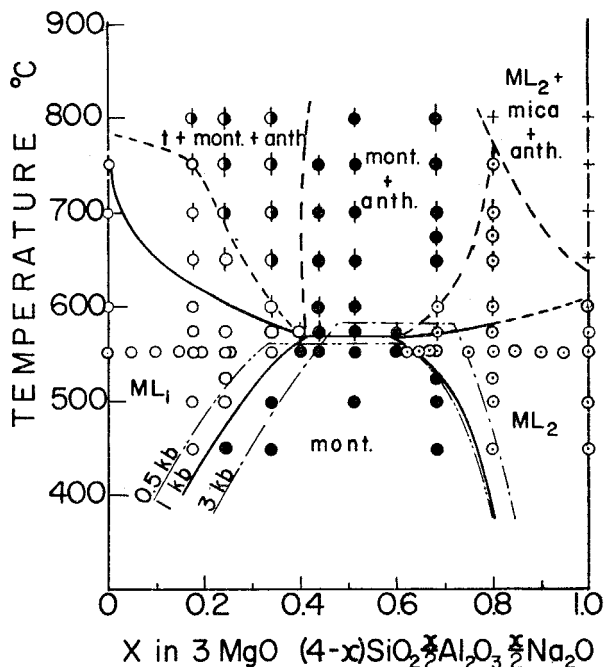

FIGURE 1.—Phase relationships observed in this study. The variation of the extent of the montmorillonoid solid solution field with pressure is shown.

At high temperatures this montmorillonoid phase decomposes to anthophyllite and another phase, which is stable to remarkably high temperatures near 800° C.[2] On both sides of this saponite field (labelled "mont." in Fig. 1), heteropolytypic phases were produced (labelled $\mathrm{ML_1}$ and $\mathrm{ML_2}$).

The variation of X-ray diffraction patterns with the change in composition is represented in Fig. 2. Experiments at 3 kb and 0.5 kb pressures gave results

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[1] Details on the physical properties and the chemical composition will be given separately (J. T. Iiyama and R. Roy, in preparation); the phase is orthorhombic, with $c = 5.29$ Å; $n = 1.62$.

[2] This proves to be a trioctahedral montmorillonoid mineral having the probable general composition of $\mathrm{Na_z(Mg_{3-x}Al_x)(Si_{4-y}Al_y)O_{10}(OH)_2}n\mathrm{H_2O}$ in which $z = y - x$. Details on this phase are given elsewhere (J. T. Iiyama and R. Roy, in press).

essentially the same as those obtained under a pressure of 1 kb except that the montmorillonoid field (the region "mont." of Fig. 1) moves slightly to higher x values at higher pressure and to low x values at lower pressure.
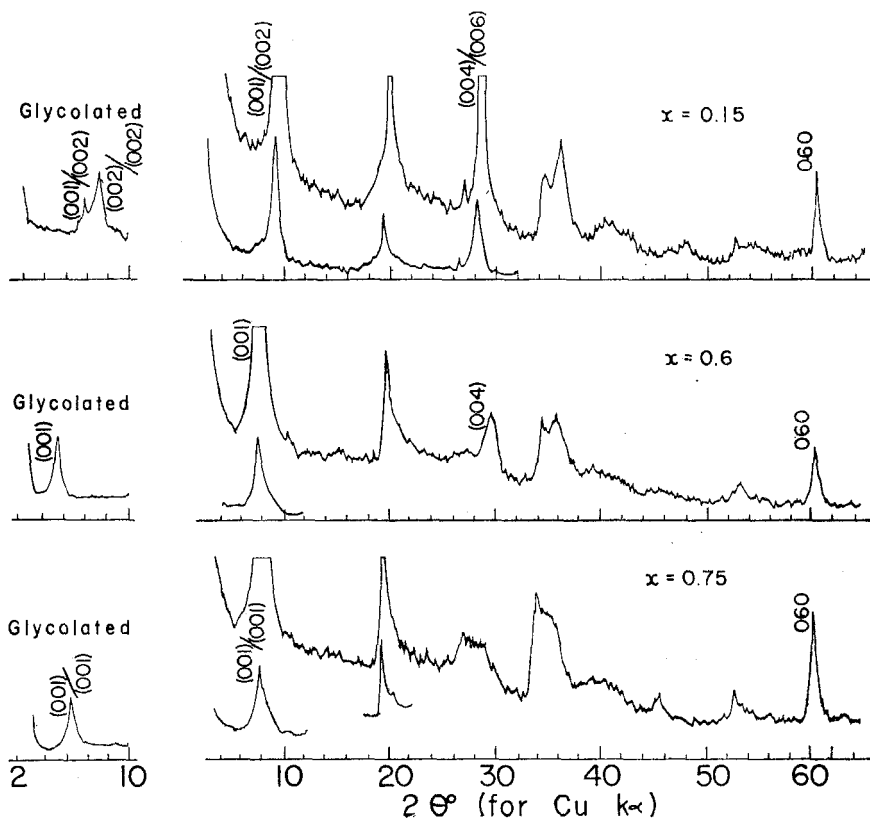

FIGURE 2.—Variation of X-ray diffraction patterns of heteropolytypes obtained, with total composition, non-oriented preparations used. All products were obtained at 550° C 1 kb.

DESCRIPTION OF SYNTHETIC HETEROPOLYTYPES
(MIXED-LAYER MINERALS)

Heteropolytypic Minerals Formed Under a Pressure of 1 kb

Heteropolytypic phases of talc and saponite.—From the compositions $x = 0.05$–0.33 and at the pressure–temperature conditions corresponding to the domain ML_1 of Fig. 1, a series of phases were obtained whose longest interplanar spacing (001/001 of Fig. 2) varied continuously from 9.3 Å to 12.6 Å as the composition was changed from smaller to higher x values

(Fig. 3a). This spacing changes from 9.3 Å to 17.6 Å when the mineral is treated with ethylene glycol, and at the same time a new peak at 9.3 Å–9 Å appeared in the diffraction diagram. This spacing also varied with com-
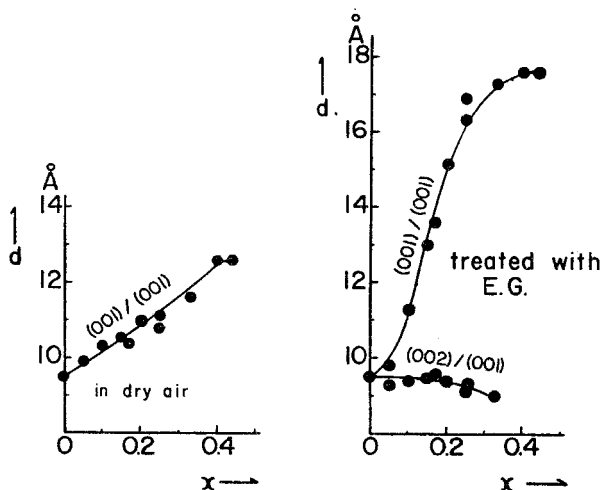
FIGURE 3.—Variation of basal spacings of random heteropolytype of talc and montmorillonoid layers, with total composition. (a) *Left:* Untreated samples X-rayed in dry air. (b) *Right:* Glycolated samples. All samples were obtained at 550° C 1 kb.

position (Fig. 3b). When the mineral is heat-treated, the spacing decreases. It also shows continuous change with the variation in composition (Table 3). As shown in Fig. 2, the series of basal reflections does not correspond to integral orders of the largest spacing. Interpretation of these patterns is based on the well-known relations obtained from the calculations of Brown

TABLE 3.—HEATING EXPERIMENTS ON HETEROPOLYTYPES (MIXED LAYERS)
OF TALC and SAPONITE

x	Run no.	Basal spacing in Å		
		Untreated	110° C	450° C
0.05	1284	9.9	9.8	9.6
0.10	1285	10.3	9.8	9.8
0.15	1286	10.5	10.0	9.9
0.17	1004	10.3	10.3	10.2
0.20	1308	11.3	10.5	10.2
0.24	1064	11.0	10.5	10.0
0.25	1287	10.8	10.4	10.0
0.33	1005	11.6	11.3	10.5

and MacEwan (1950) and Méring (1949) and the examples cited by Weaver (1956), for various series of "mixed layering" of two clays.

From the known compositions it is certain that the phases involved in the heteropolytype are a talc phase (non-expanding) and a saponite (expanding). With this assignment the reflections can be indexed as has been done in Figs. 2 and 3 by using the accepted notation. For example, 002/001, the combined diffraction maximum produced by the interference of the 002 reflection of the saponite layer and 001 of the talc layer. The continuous variation of these peaks with change in composition indicates that the ratio of mixing of constituent layers varies continuously.

At temperatures higher than 575° C in the region ML_1 (Fig. 1), the largest spacings seem to change slightly from the value obtained at lower temperatures (Table 4) for a fixed original composition of the charges. This result may

TABLE 4.—VARIATION IN BASAL SPACING WITH THE TEMPERATURE OF RUN

x	Temp.	Run no.	$d(001)$	$d(001)$E.G.*
0.17	550	1004	10.3 Å	12.6 + 9.1 Å
0.17	575	1014	10.2	13.3 + 9.5
0.17	600	1011	10.1	17.3 + 9.3
0.17	650	1069	10.1	17.3 + 9.3
0.24	550	1064	11.0	13.0 + 9.1
0.24	575	1193	11.0	17.6 + 8.8
0.24	650	1070	10.3	17.3 + 9.5
0.33	550	1005	11.6	17.3 + 9.0
0.33	575	1015	11.3	17.3 + 8.8
0.33	600	1012	11.3	17.0 + 8.8

* Basal spacing 001 of glycolated sample.

indicate an appreciable change in mixing ratio and therefore in the composition of constituent layers. This is quite possible, because the saponites having the composition corresponding to the region "mont." in Fig. 1 are no longer stable at these temperatures and another mineral of the montmorillonite family is formed. This new expanding phase (stable at higher temperatures) must become the expanding layer constituent of the heteropolytypes formed at higher temperatures. This change in composition of the constituent layer will, of course, result in a change in the mixing ratio of the constituents. Because no other phases, even in minor amounts, were formed in the product from these compositions of ML_1 at higher temperatures, it is also possible that the composition of talc was slightly changed. This possibility has been discussed in earlier work (see Stempel and Brindley, 1960; Yoder, 1952).

Heteropolytypes of saponite and mica (sodium phlogopite).—From the compositions $x = 0.6$–1.0 and under the conditions corresponding to the region ML_2 of Fig. 1, phases were obtained whose largest interplanar spacings decrease continuously, as the composition moves toward higher x values, from 12.6 Å to 10.3 Å.[1] An example of the variation in spacing for this series is given in Fig. 4a. After glycol treatment, these spacings expand to 17.6 Å to 13 Å (Fig. 4b). The variation of the spacing of the heated samples with variation in composition is given in Table 5. These characteristic X-ray diffraction patterns can be interpreted as a series of heteropolytypes of expanding saponite and non-expanding 10 Å layer silicate (probably a mica).
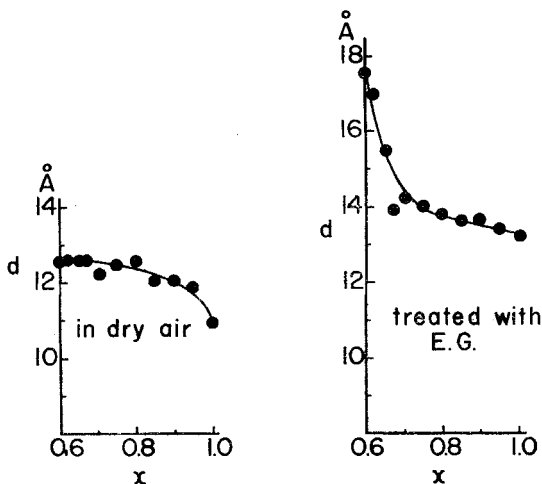
FIGURE 4.—Variation of basal spacings of random heteropolytype of saponite and mica layers, with total composition. (a) *Left:* Untreated samples X-rayed in dry air. (b) *Right:* Glycolated samples. All samples were obtained at 550° C 1 kb.

Though a pure mica phase was not obtained even from the ideal sodium phlogopite composition (a mixed-layer phase was always produced below 575° C and a heteropolytype, mica and anthophyllite at temperatures higher than 575° C), it is highly probable that this mica layer has a composition somewhere around this sodium phlogopite composition.

As the composition of the 10 Å layer does not correspond exactly to the theoretical composition of sodium phlogopite, $NaMg_3AlSi_3O_{10}(OH)_2$, and because only heteropolytypic phases were formed in the domain ML_2, the composition of the saponite layer of this mixed layer cannot lie in the region labelled "mont." of Fig. 1. The situation is explained schematically in Fig. 5.

[1] At higher x compositions, the basal spacing of the saponite layer is very sensitive to atmospheric humidity. In this report X-ray measurements were made in dry air after the specimens had been dried (in air) at 30–60° C. Without these precautions and in typical local August humidities at this laboratory, spacings of 15 to 12 Å were observed instead of 12.6–10.3 Å.

TABLE 5.—HEATING EXPERIMENTS ON HETEROPOLYTYPES (MIXED LAYERS)
OF SAPONITE AND 10 Å LAYER (OBTAINED AT 550° C 1 KB)

x	Run no.	Basal spacings in Å		
		Untreated	110° C	450° C
0.51	1059	12.6 Å	12.5 Å	12.3 Å
0.60	1297	12.6	12.3	12.3
0.67	1067	12.3	10.3	10.8
0.70	1305	12.6	10.3	10.4
0.75	1298	12.5	11.8	10.3
0.80*	1022	12.6	11.5	10.2
0.85	1289	12.1	10.4	10.2
0.90	1299	12.1	10.4	10.4
0.95	1290	11.9	10.2	10.2
1.00	1291	10.8	10.0	10.0

* Product at 575° C.
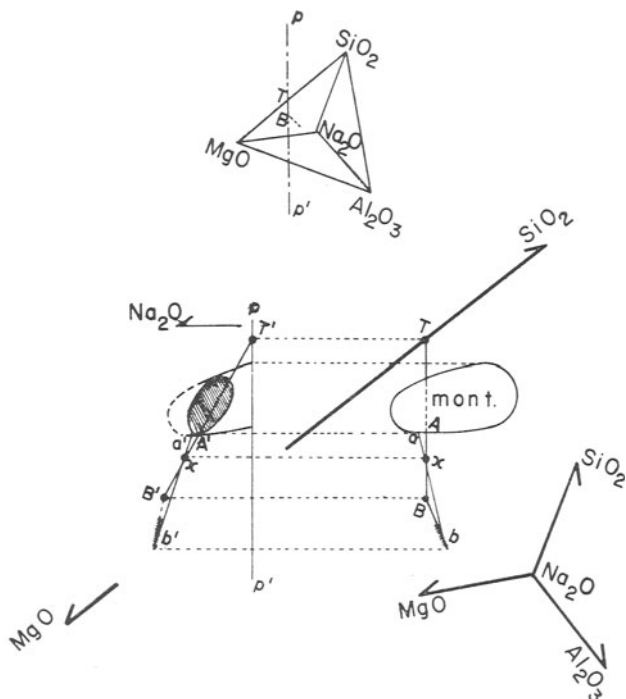
FIGURE 5.—Representation of probable composition of the montmorillonoids and "mica" phases involved in the Na_2O–MgO–Al_2O_3–SiO_2–H_2O system. (See text.)

Instead of obtaining a mixed layer of saponite A and sodium phlogopite of the theoretical composition B, a mixed layer is formed consisting of saponite "a" and mica of composition "b" from composition x. Therefore the exact composition of each constituent layer of this mixed-layer phase cannot be determined.

At 1 kb of water vapor pressure and in the temperature range of 400–575° C, a series of heteropolytypes of talc and saponite was formed on the low x side while saponite and mica layer heteropolytypes were obtained from compositions with high x values.

The proportion of mixing of each constituent layer could be controlled directly by the original composition of the charges (and, of course, secondarily by the temperature). Since the diffraction peaks of these phases have symmetrical profiles, it is possible that these heteropolytype phases have a homogeneous distribution of mixing ratios throughout the sample, as discussed by Brindley and Méring (1951). On the other hand, no regularities in the mode of stacking of constituent layers in the c direction were found: i.e. spacings intermediate between the spacings of the two constituent layers were observed and not the very long spacings between 20 and 50 Å required for regular heteropolytypism.

The Effect of Pressure on the Formation of Heteropolytypes

To study the effect of pressure on the formation of such phases, several runs were repeated under identical conditions except a change in pressure from 1 kb to 0.5 kb or 3 kb.

At a pressure of 0.5 kb, only randomly stacked heteropolytypes were obtained from the composition–temperature conditions indicated (ML_1) in Fig. 1. Although good crystallinity (judged from the diffraction diagram peak intensities) was difficult to obtain at this pressure, even by treatment for 7 days, the shapes of the diffraction peaks were as symmetrical as in the product obtained at 1 kb (Fig. 6c). The heteropolytypes obtained at a pressure of 3 kb differed considerably from those obtained at 1 kb, and are described in the following section.

Formation of Heteropolytypes at 3 kb

Heteropolytypes of saponite and talc layers.—At a pressure of 3 kb, heteropolytypic phases of talc and saponite were formed under about the same composition and temperature conditions (see Fig. 1 for exact conditions) as they were obtained under 1 kb pressure. The X-ray diffraction patterns of heteropolytypic phases obtained at 3 kb are characterized essentially and invariably by the presence of very long, superstructure, basal spacings of 20–24 Å (Fig. 6a). After glycol treatment this spacing increases to 27–29 Å. This long spacing can, of course, be attributed to the fact that the mode of stacking of this product is highly ordered and the spacings of the two constituent layers show additive effects.

With the appropriate proportion of mixing to yield a sequence such as

(talc) (saponite) (talc) (saponite) ... regularly, a spacing of $9.3\,Å + 17.6\,Å = 26.9\,Å$ for the glycolated specimen should be obtained.
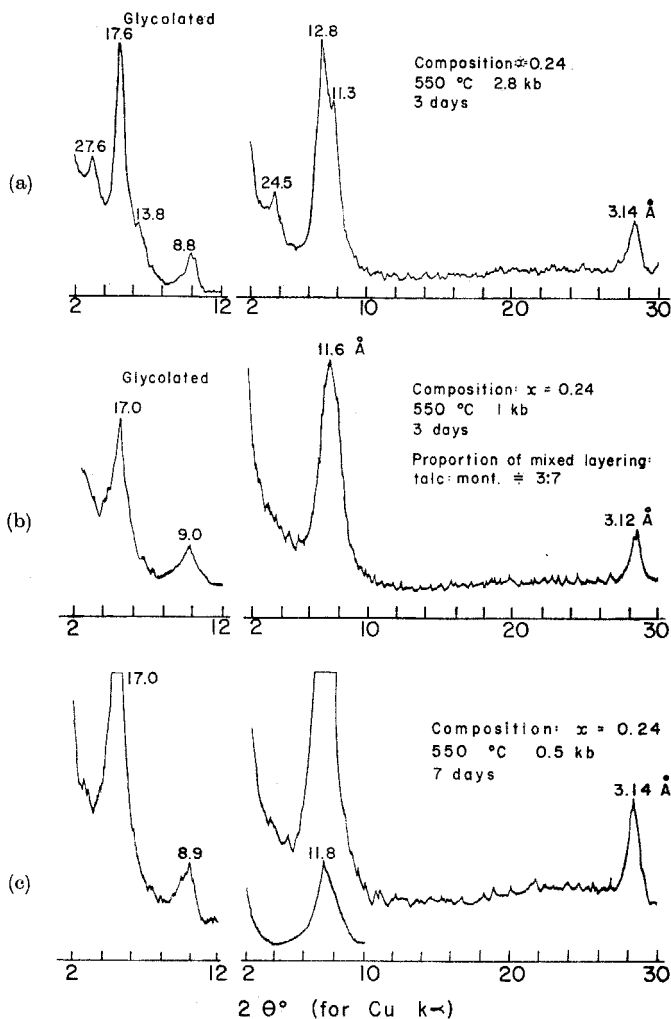

FIGURE 6.—Variation of X-ray diffraction patterns of heteropolytypes with change of pressure. Note consistent formation of ordered or "regular mixed layers" at high pressures. All the samples have the composition $x = 0.24$ and were synthesized at 550° C. Well-oriented preparations were X-rayed.

The values for the products of our series obtained under 3 kb are close to this value but not always identical with it. They also vary with variation in composition and temperature–pressure conditions (see Table 2, II). This fact

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must be attributed to a random stacking of different units which are them-selves regularly stacked. Most of the sample consists of this regular 1:1 heteropolytype of saponite and talc, and this part is mixed in a random manner with ratios of say 4M:5T or 5M:4T. In addition there may be some random heteropolytypes of single units as evidenced by the fact that peaks of 9–10 Å and 12–13 Å are still observed in these products at 3 kb.

The high degree of regularity of stacking in these heteropolytypes is clearly favored by high pressures. However, in no test was obtained a *complete* conversion of random heteropolytypes to a well-ordered phase, which could happen only with an exact 1:1 mixing ratio of the layers.

Heteropolytypes of montmorillonoid and "mica" layers.—Heteropolytypes of a montmorillonite and a 10 Å layer mineral were also formed under 3 kb pressure from the composition and temperature range of ML_2 of Fig. 1. However, the long spacings were only rarely observed, and then had very weak intensity. Almost all the phases observed in the products were random heteropolytypes.

THE PROBLEM OF EQUILIBRIUM STABILITY OF HETEROPOLYTYPES

Almost all the heteropolytypes discussed above (except those formed under 0.5 kb) were obtained by treatment for 3 days. One of the most interesting problems in this area concerns the thermodynamic stability of a hetero-polytypic phase compared with a gross mixture of the same phases. Evidence that such heteropolytypes were generally metastable phases would be pro-vided if one heteropolytype (or mixed-layer) phase separated into two separated phases upon prolonged treatment. Several runs which gave heteropolytypes in 3 days were therefore repeated for a period of 15–34 days (runs 1229, 1230, 1231, 1232, 1233, 1234).

The results were the same as in the 3-day treatments. Indeed, the samples held longer had, in general, sharper diffraction peaks indicating better crystallization. Thus, no experimental evidence was found that indicated that heteropolytypic phases are only metastable; if anything there is an indication, but not proof, that under stated *p-t-x* conditions, they may be stable. The only way to prove the greater stability of the heteropolytypic phase would be to react a gross mixture and obtain a heteropolytypic phase. This possibility was considered extremely unlikely. Attempts were made, however, to produce a mixed layer of talc and saponite starting from a gross mixture of the saponite ($x = 0.51$) and talc synthesized at 550°C 1 kb. A 1:1 (approximate) mixture of talc and saponite was prepared by shaking in a Wigl Bug and placed in a hydrothermal bomb and treated at 550°C for 1 week. Some evidence for a heteropolytype was observed.

A second run did not increase the proportion of heteropolytype in the product. But another run at 3 kb again gave unmistakable evidence for the formation of a heteropolytype from a gross mixture. This may be taken, then, as unequivocal proof that heteropolytypes are more stable than gross

mixtures of the same phase, with the caveat that the formation of the heteropolytype is due to the fact that the actual constituent layers of a gross mixture at equilibrium differ from those used. Hence the formation of the heteropolytype may be only the first step in the reaction to give another gross mixture with different composition of each layer. In any case the results do indicate an unexpectedly "stable" nature for such phases.

All the heteropolytypes formed at low temperatures are decomposed into two or three phases at high temperatures as shown in Fig. 1. Details of these decomposition reactions are treated in a subsequent paper in connection with the discussion of the variation in stability of saponite solid solutions with composition.

DIFFERENTIAL THERMAL ANALYSES

It is obvious that the differential thermal analysis of synthetic saponites and heteropolytypes may provide good standards for these phases, because of their high purity and high crystallinity. For this purpose, however, a large amount of sample is necessary, and saponite $(x = 0.5)$ and heteropolytypes of saponite and talc layer with $x = 0.17$ were prepared in amounts near 0.5 g.

Differential thermal analysis curves for these samples are shown in Fig. 7. All these curves show very sharp thermal reaction peaks, indicating the excellent crystallinity of such phases even though extremely fine grained.

The differences in DTA patterns of ordered and disordered stacking of heteropolytypes is especially noteworthy. Orderly-stacked heteropolytypes grown at 550° C at 3 kb show a strong exothermic peak just after the endothermic reaction due to loss of OH$^-$ from the structure, whereas the randomly stacked heteropolytypes grown at 550° C 1 kb do not have any exothermic reaction.

This difference may be explained partially by the difference in crystallinities of clay mineral phases grown at 1 kb and 3 kb, but it is primarily due to the difference in structures of the decomposition product just after the loss of OH$^-$ from the lattice. Presumably, owing to the high regularity of stacking in the "regularly interstratified" heteropolytypes, they can preserve (metastably) dehydroxylated structures, and these structures are changed to the stable decomposition product via an exothermic reaction. For the random heteropolytypes, the change from hydrous phase to decomposition product seemingly can take place without passing through a metastable phase.

In the heteropolytypes, the existence of a separate endothermic reaction corresponding to decomposition of the talc phase could be expected. But in all the samples examined (the heteropolytypes of talc and saponite layers), there was no trace of this reaction. From this fact one can evaluate the significant thermodynamic differences between heteropolytypes and the corresponding gross mixtures of their constituent layer phases.
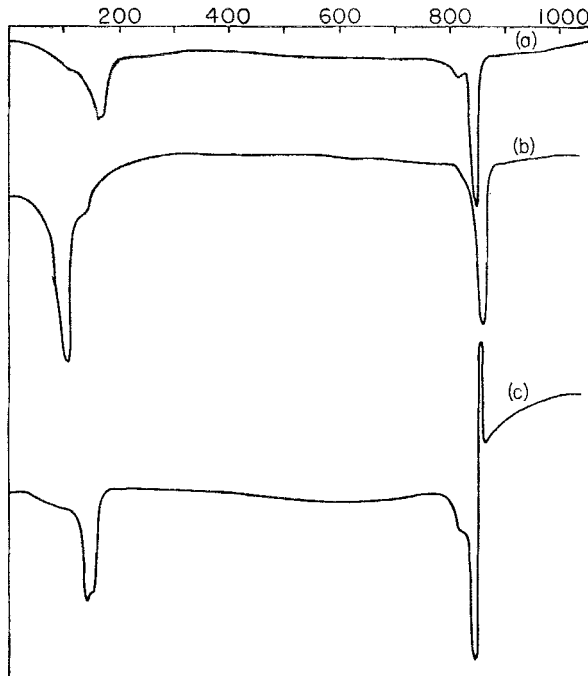
FIGURE 7.—Differential thermal analysis of synthetic saponite, disorderly-stacked heteropolytype, and orderly-stacked heteropolytype ($\sim 8°$ C per min, heating rate). (a) Composition $x = 0.50$; synthesized at 550° C, 1 kb, for 34 days; X-ray and microscopic studies indicate that the product is pure saponite. (b) Composition $x = 0.17$; synthesized at 550° C, 1 kb, for 14 days ; randomly stacked heteropolytype of talc and saponite layers. (c) Composition $x = 0.17$; synthesized at 550° C, 3 kb, for 30 days; well ordered or regularly interstratified heteropolytype of talc and saponite layers.

DISCUSSION AND CONCLUSIONS

A restudy of the hydrothermal reactions of the system along the talc–sodium phlogopite composition join revealed that a field of saponite solid solutions occupies the middle part of this join. This saponite is stable up to about 575° C. On both sides of the saponite field are fields of heteropolytype (or mixed-layer) phases: saponite and talc layers on the low-Na side and of saponite and mica layer on the high-Na side. At 0.5 kb and 1 kb pressure, the synthetic heteropolytype has a random stacking in the c direction and the mixing ratio of the constituent layers is continuously variable according to the composition of the original charges.

At a pressure of 3 kb, highly ordered 1:1 mixed-layer phases can be obtained showing that high pressure favors the formation of more regular ordering of the stacking in heteropolytypic (mixed-layer) phases. Thus the

synthesis of heteropolytypes with controlled mixing ratio and with controlled degree of stacking order has been achieved.

A remarkable degree of persistence under conditions more rigorous than are likely to be encountered in appropriate natural environments was also demonstrated, and the possibility that these phases are *stable* under certain *p-t-x* conditions has been indicated by some experiments.

These observations are in harmony with the natural occurrences of heteropolytype or mixed-layer phases, e.g. as summarized recently by Lucas (1961). Regular stacking in heteropolytypic phases is found mostly in hydrothermal veins, veins in eruptive rocks and from metamorphic rocks, and they are considered as having formed directly as primary phases. On the other hand, randomly ordered heteropolytypic phases, with homogeneous distribution of mixing ratio, are found in sediments of the non-detrital type or from a few hydrothermal clay deposits, while the phases with irregular and heterogeneous distribution came from detrital sediments.

The last probably were formed as the result of the weathering out of certain ions from micas or chlorites; or now, as the result of this work, it is indicated that they could also form directly from gels in sea or lake bottoms, or under the lowest-temperature "hydrothermal" environments.

ACKNOWLEDGMENT

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