

FACTORS EFFECTING MAXIMUM HYDROTHERMAL STABILITY IN MONTMORILLONITES

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ABSTRACT

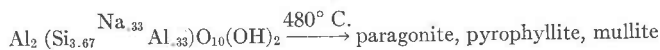
The relative importance of the factors effecting maximum thermal stability in montmorillonites in hydrothermal systems was investigated. The influencing factors considered were 1) interlayer cations, 2) composition, and 3) types of lattice substitutions.

Initial studies were concerned with the aluminum and magnesium montmorillonites because they are most commonly found in hydrothermal alteration zones associated with ore deposition.

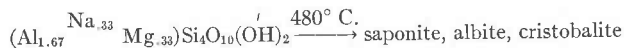
The absence of an interlayer alkali cation (Na) causes low decomposition temperatures of about 300° C. for magnesium montmorillonites and 400° C. for aluminum montmorillonites as compared to 750° C. and 480° C., respectively, when the alkali is present. With optimum substitution, saponites have considerably higher maximum stabilities than the aluminum montmorillonites. Lattice substitutions (in all cases to give excess charge corresponding to maximum base exchange capacity) in montmorillonites effecting maximum hydrothermal stability are as follows:

A. for aluminum montmorillonites

1. substitution of Al for Si in tetrahedral coordination

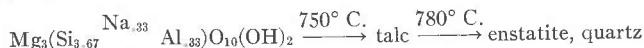


2. substitution of Mg for Al in octahedral coordination

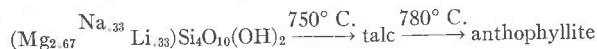


B. for magnesium montmorillonites

1. substitution of Al for Si in tetrahedral coordination



2. substitution of Li for Mg in octahedral coordination



Equivalent stabilities within experimental error result if optimum substitution is in the octahedral or the tetrahedral layer. A marked decrease in stability results when substitution in the lattice deviates from the optimum amounts, although still retaining electrostatic balance by changing the amounts of other cations; for example, in the saponites: Al_{.33} (750° C.), Al_{.22} (680° C.), Al_{.11} (275° C.), and Al_{.00} (255° C.).

INTRODUCTION

The hydrothermal stabilities of several critical aluminum and magnesium montmorillonite compositions were determined in an attempt

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to establish the relationships between composition and thermal stability for this largest family of montmorillonites. Much of the stability data reported, especially on the magnesium montmorillonites, have been on compositions without the most common exchange ion, sodium. The stability data herein reported are on compositions including sodium as the exchange cation, in addition to a few compositions without sodium to demonstrate the effect on stability when exchangeable sodium is absent.

Early syntheses of montmorillonites are summarized by Ross and Hendricks (1945). These contributions were not concerned with stabilities. Aluminum montmorillonites were synthesized by Roy and Osborn (1954) who reported a maximum hydrothermal stability of 420° C. for a pure aluminum montmorillonite with H⁺ as the base exchange cation. Roy and Roy (1955) synthesized magnesium-aluminum-silica montmorillonites of widely variable compositions which were stable to a maximum of 480° C. These authors considered Mg, or a hydrated complex, as the exchangeable base in the above compositions. A pure magnesium saponite was found by them to have a stability of 275 ± 20° C.

Sand (1955) reported the hydrothermal decomposition temperature of hectorite as about 800° C. at 1000 atmospheres water pressure. Mumpton and Roy (1956) studied the influence of ionic substitution on the hydrothermal stabilities of montmorillonoids. Decomposition temperatures of 430° C. and 565° C. respectively were reported for hectorite and an aluminous saponite. Two areas of montmorillonoid formation were indicated. The natural dioctahedral montmorillonites were reported by them to be stable generally to about 465° C. and the trioctahedral saponites to about 550° C. at 20,000 psi water vapor pressure.

Recent work on the hydrothermal stability of synthetic and natural hectorite by Sand and Ames (1957) has indicated that trioctahedral hectorite is stable to 750° C. at 1000 atmospheres.

METHODS OF INVESTIGATION

Hydrothermal equipment used was essentially of the kind described by Roy, Roy, and Osborn (1950). "Test tube" type reactor vessels were employed in conjunction with a water pressure system with a limit of 2000 atmospheres.

Synthetic mixtures of calcined silicic acid and nitrates, oxides plus a sodium salt, and calcined nitrates plus ethyl orthosilicate were used as starting materials. These mixtures were contained in gold envelopes.

X-ray diffraction and infrared absorption techniques were employed for identification of the resulting phases. All samples were either vapor

or "wet" solvated with ethylene glycol to identify the montmorillonites by the characteristic 17 Å basal spacing, using the technique of Brunton (1955).

RESULTS

Approximately 150 stability and synthesis runs were made on the compositions shown in Table 1.

TABLE 1. CRITICAL RUNS

Composition	T	P(atm.)	Time	Phases
TRIOCTAHEDRAL MONTMORILLONITES				
<i>Tetrahedral substitution</i>				
Na _{.33} Mg _{3.00} Si _{4.00}	230	1000	5 days	mont.
Na _{.33} Mg _{3.00} Si _{4.00}	260	1000	5 days	talc
Na _{.33} Mg _{3.00} (Al _{.11} Si _{3.89})	260	1000	2 days	mont.
Na _{.33} Mg _{3.00} (Al _{.11} Si _{3.89})	285	1000	3 days	talc and mont.
Na _{.33} Mg _{3.00} (Al _{.16} Si _{3.84})	540	1000	3 days	mont.
Na _{.33} Mg _{3.00} (Al _{.16} Si _{3.84})	560	1000	3 days	talc and mont.
Na _{.33} Mg _{3.00} (Al _{.22} Si _{3.78})	665	1000	3 days	mont.
Na _{.33} Mg _{3.00} (Al _{.22} Si _{3.78})	690	1000	3 days	talc and mont.
Na _{.33} Mg _{3.00} (Al _{.33} Si _{3.67})	740	1000	2 days	mont.
Na _{.33} Mg _{3.00} (Al _{.33} Si _{3.67})	780	1000	2 days	talc and enstatite
<i>Octahedral substitution</i>				
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	450	1000	3 days	mont. (>mica spacing on drying)
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	740	1000	1 day	mont. (talc spacing on drying)
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	750	1000	5 days	mont. and talc
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	760	1000	8 days	talc
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	780	1000	5 days	talc and anthoph.
Na _{.33} (Mg _{2.67} Li _{.33})Si _{4.00}	800	1000	7 days	anthoph.
Nat. hectorite	425	1000	7 days	mont. (>mica spacing on drying)
Nat. hectorite	560	1000	8 days	mont. (talc spacing on drying)
Nat. hectorite	750	1000	5 days	mont. and talc
Nat. hectorite	765	1000	4 days	talc
Nat. hectorite	820	1000	8 days	anthoph.
<i>Both octahedral and tetrahedral substitution</i>				
Nat. saponite (Milford, Utah)	530	1000	2 days	mont.
(Ca/2) _{.21} (Mg _{2.85} Al _{.04}) (Al _{.30} Si _{3.70})	550	1000	2 days	talc

TABLE 1. (continued)

Composition	T	P(atm.)	Time	Phases
$\text{Na}_{.33}(\text{Mg}_{2.83}\text{Li}_{1.17})(\text{Al}_{1.16}\text{Li}_{3.84})$	740	1000	5 days	mont.
$\text{Na}_{.33}(\text{Mg}_{2.83}\text{Li}_{1.17})(\text{Al}_{1.16}\text{Li}_{3.84})$	760	1000	5 days	talc and anthoph.
<i>No alkali exchangeable ion</i>				
$\text{Mg}_{3.00}(\text{Al}_{1.16}\text{Si}_{3.84})$	300	1000	7 days	mont.
$\text{Mg}_{3.00}(\text{Al}_{1.16}\text{Si}_{3.84})$	325	1000	7 days	talc
$(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$	250	1000	3 days	mont.
$(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$	300	1000	3 days	talc
DIOCTAHEDRAL MONTMORILLONITES				
<i>Tetrahedral substitution</i>				
$\text{Na}_{.33}(\text{Al}_2(\text{Al}_{.33}\text{Si}_{3.67}))$	470	1000	5 days	mont.
$\text{Na}_{.33}(\text{Al}_2(\text{Al}_{.33}\text{Si}_{3.67}))$	490	1000	5 days	paragonite+pyrophyllite+mullite
<i>Octahedral substitution</i>				
$\text{Na}_{.33}(\text{Al}_{1.67}\text{Mg}_{.33})\text{Si}_{4.00}$	470	1000	5 days	mont.
$\text{Na}_{.22}(\text{Al}_{1.67}\text{Mg}_{.33})\text{Si}_{4.00}$	490	1000	5 days	ab+saponite+cristobalite

Table 1 gives the critical runs and resulting decomposition temperatures, within $\pm 10^\circ \text{C.}$, and products.

Table 2 is a summary of the maximum hydrothermal stabilities of the various compositions.

Table 3 lists the relative intensities and "*d*" spacings for the synthetic saponite, $\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$, dried at 110°C. and also vapor solvated with ethylene glycol. Note the second order basal spacing on the dried sample.

DISCUSSION

The assumption is made here that the ions actually went into the structural positions indicated in these montmorillonite compositions given in Table 1. Runs made on compositions that gave defects or "holes" in the structure, or when sodium was omitted as a base exchange ion (leaving H^+), yielded montmorillonites of much lower maximum stability. As the cation exchange capacity cannot be explained reasonably unless the ions in the resulting montmorillonites are in the structural positions indicated, and the high hydrothermal stabilities resulted when the compositions had optimum substitution for maximum base exchange capacity, this assumption is believed to be valid.

There appears to be little or no overlapping of the trioctahedral and dioctahedral montmorillonite fields except at low temperatures. These low temperature hybrids usually form defect structures that are less

TABLE 2. A SUMMARY OF STABILITY DATA FOR THE VARIOUS MAGNESIUM
 MONTMORILLONITE COMPOSITIONS AT 1000 ATMOSPHERES
 OF WATER PRESSURE

Starting Composition	Maximum Stability
<i>Tetrahedral substitutions</i>	
$\text{Na}_{.33}\text{Mg}_{3.00}\text{Si}_{4.00}$	255° C.
$\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.11}\text{Si}_{3.89})$	275° C.
$\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.16}\text{Si}_{3.84})$	550° C.
$\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.22}\text{Si}_{3.78})$	680° C.
$\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.33}\text{Si}_{3.67})$	750° C.
<i>Octahedral substitutions</i>	
$\text{Na}_{.33}\text{Mg}_{3.00}\text{Si}_{4.00}$	255° C.
$\text{Na}_{.33}(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$	750° C.
$\text{Na}_{.33}(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$ [natural hectorite]	750° C.
<i>Na vs. H as base exchange cation</i>	
$\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.16}\text{Si}_{3.84})$	550° C.
$\text{Mg}_{3.00}(\text{Al}_{.16}\text{Si}_{3.84})$	310° C.
$\text{Na}_{.33}(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$	750° C.
$(\text{Mg}_{2.67}\text{Li}_{.33})\text{Si}_{4.00}$	275° C.
<i>Both octahedral and tetrahedral substitution</i>	
$\text{Ca}/2_{.21}(\text{Mg}_{2.85}\text{Al}_{.04})(\text{Al}_{.30}\text{Si}_{3.70})$ natural saponite	540° C.
$\text{Na}_{.33}(\text{Mg}_{2.83}\text{Li}_{.17})(\text{Al}_{.16}\text{Si}_{3.84})$	750° C.

stable than the 480° C. maximum of the dioctahedral montmorillonite of optimum composition.

Sand, Roy, and Osborn (1957) reported the maximum stability of dioctahedral montmorillonites in the system $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ to be 480° C. at 1000 atmospheres of water vapor pressure. The maximum hydrothermal stability occurs on the composition $\text{Na}_{.33}\text{Al}_{2.00}(\text{Al}_{.33}\text{Si}_{3.67})$ according to Sand and Crowley (1956). An equivalent stability within experimental error results when optimum substitution is in the octahedral layer: $\text{Na}_{.33}(\text{Mg}_{.33}\text{Al}_{1.67})\text{Si}_{4.00}$. These compositions represent optimum substitutions for maximum base exchange capacity in dioctahedral montmorillonites. As the composition of the starting material deviates from this composition, the hydrothermal stability becomes lower than 480° C. The dioctahedral (aluminum) montmorillonites are, in effect, defect structures with two-thirds of their octahedral positions filled. This condition weakens the structure so that a maximum hydrothermal stability of 480° C. is reached with optimum substitution of aluminum for silicon in the tetrahedral position or magnesium for aluminum in the octahedral layer.

With the same optimum substitutions in the trioctahedral (magne-

TABLE 3. X-RAY DIFFRACTION POWDER DATA FOR THE SYNTHETIC SAPONITE $\text{Na}_{.33}\text{Mg}_{3.00}(\text{Al}_{.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$. INTENSITIES WERE VISUALLY ESTIMATED

Dried at 110° C.		Vapor solvated with ethylene glycol	
I/I ₀	d, Å	I/I ₀	d, Å
10	12.3	10	17.0
2	6.15	5	8.5
4	4.58	4	5.69
5	3.10	5	4.58
4	2.63	8	3.37
3	2.53	3	2.81
1	2.34	4	2.58
1	2.295	1	2.36
1	2.067	1	2.30
2	1.734	1	2.106
7	1.529	1	2.085
3	1.323	1	1.868
1	1.274	3	1.738
1	1.054	7	1.535
1	.999	3	1.326
2	.886	1	1.277
		1	1.233
		1	1.055
		2	1.002
		3	.887

sium) montmorillonites, a maximum hydrothermal stability of 750° C. is attained. The magnesium trioctahedral montmorillonites, with optimum substitution, exceed the hydrothermal stability of aluminum dioctahedral montmorillonites by 270° C. The optimum exchange capacity of the trioctahedral montmorillonites also can be achieved in three ways: 1) by substitution of lithium in the octahedral position for magnesium, 2) substitution of aluminum in the tetrahedral position for silicon or 3) a combination of octahedral and tetrahedral substitution. (Ross and Hendricks, 1945). Either manner of attaining maximum cation exchange capacity results in a maximum hydrothermal stability of 750° C. at 1000 atmospheres pressure. These montmorillonites cannot have identical decomposition temperatures, but appear equivalent within the experimental error of $\pm 10^\circ$ C.

The results also clearly indicate that magnesium, acting as the base exchange cation with or without H^+ , forms either a hydrogen-based montmorillonite or a defect structure. Either of the above conditions results in a much lower hydrothermal stability than if the proper amount of base exchange cation is added to the starting composition. The low hydrothermal stabilities reported by Roy and Roy (1955) for montmoril-

lonites synthesized in the system magnesia-alumina-silica-water were due to either the formation of defect structures or H^+ based montmorillonites. The maximum stability of $430^\circ C.$ for natural hectorite reported by Mumpton and Roy (1956) might have been due to misidentification of the "talc" decomposition phase (Sand and Ames, 1957).

These results emphasize the existence of the two distinct structural series, the dioctahedral (aluminum) montmorillonite and the trioctahedral (magnesium) montmorillonites, with some overlapping of these two series at lower temperatures by formation of defect structures. These latter montmorillonites have lower hydrothermal stabilities than the optimum compositions and separate into the di- and trioctahedral montmorillonite at higher temperatures before the dioctahedral montmorillonite decomposes, with the trioctahedral montmorillonite persisting to higher temperatures. This was demonstrated on an aluminum montmorillonite containing some magnesium from Hector, California (Sand and Ames, 1957) and on a defect saponite from an occurrence near Milford, Utah. Determination of the stabilities of these defect montmorillonites formed by hydrothermal alteration can fix the upper temperature limit of the altering solutions.

SUMMARY AND CONCLUSIONS

The controlling factors which result in a montmorillonite composition having the highest hydrothermal stability are as follows:

1. All possible cation positions in the lattice occupied; e.g., a trioctahedral montmorillonite such as hectorite.
2. Optimum substitution in either tetrahedral or octahedral coordination to provide excess negative charge for maximum base-exchange capacity.
3. The presence of exchangeable ions, other than H^+ , to satisfy the interlayer charge.

All three conditions must obtain; when they do, a maximum hydrothermal stability of $750^\circ C.$ results for saponite as compared to $480^\circ C.$ for aluminum montmorillonite. Deviations from these optimum conditions have a more pronounced affect on the stability of the saponites than on the aluminum montmorillonites.

As the montmorillonite lattice can accommodate many variations in both kinds and amounts of ion substitution, including in a negative sense the defect structures, as well as variations in layer stacking, hydrothermal treatment effects a reorganization of some of the montmorillonites into a montmorillonite composition of higher stability plus other decomposition products such as mica and a silica polymorph. Even in hectorite, which satisfies all three conditions for high hydrothermal

stability but which was formed in a hot spring environment, a structural change is caused by the high P-T treatment. Although still remaining an expanding montmorillonite, it approaches talc closely in structure when dried. Electron micrographs of the hydrothermally treated hectorite show it to be recrystallized into thicker stacks of very well defined pseudo-hexagonal crystals as compared to the very thin laths of the as-formed hectorite.

Studies of this type on a wide range of compositions of natural montmorillonites, formed in a variety of environmental conditions, would be informative, as most of these are formed during the operation of kinetic processes which cannot be duplicated in the laboratory under the equilibrium conditions currently employed and necessitated by present equipment limitations.

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