

THE INFLUENCE OF IONIC SUBSTITUTION ON THE HYDROTHERMAL STABILITY OF MONTMORILLONOIDS¹

By

F. A. MUMPTON AND RUSTUM ROY

The Pennsylvania State University, University Park, Pennsylvania

EXTENDED ABSTRACT

Both from the point of view of industrial use and in connection with theories concerning the origin of the montmorillonite minerals it is desirable to study the formation and stability of these minerals under high water pressures and elevated temperatures. Close control of the composition is possible by studying synthesized phases having the desired composition. Using synthetic mixtures one can also study the variation in properties as a function of the ions substituting in the different positions in the montmorillonite lattice.

The experimental techniques used have been described in some detail by Roy and Osborn (1952) and Roy and Roy (1955). Hydrothermal runs were at least two weeks long and all products were characterized by x-ray diffraction patterns and, where significant, by electron microscopy. The "crystallinity" of the synthetic phases was always as good as or better than most natural montmorillonoids. The results are based on data from about 550 runs.

One of the main purposes was to supplement the lower-temperature phase equilibria of the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, studied by Roy and Roy (1952, 1955) and Yoder (1952).

In this system evidence has been found which shows that there are two separate areas of montmorillonoid formation, corresponding to the dioctahedral montmorillonites and the trioctahedral saponites. The montmorillonite group decomposes into pyrophyllite, hydralsite, and silica at about 465° C under 20,000 psi water-vapor pressure, while the saponite group is stable up to about 550° C at the same pressure. At this temperature chlorite, talc, and silica phases appear to replace the expanding saponite structure. For the first time, among the decomposition products of these minerals, well crystallized mixed-layer minerals have been produced synthetically. It is felt that these phases are formed by partial conversion of the expanding structure to nonexpanding layers in situ, and not by direct synthesis from the gels. The fact that these are the only cases in which mixed-layer phases are formed supports the suggestions of Romo and Roy (1955) regarding the possible modes of origin of mixed-layer clays.

The second major purpose of this investigation has been to study the effect of isomorphous substitutions in the tetrahedral, octahedral and interlayer positions of various montmorillonoids on their stability under equilibrium hydrothermal conditions. The substitution of polarizable ions such as Zn^{2+} and Ni^{2+} for Mg^{2+} in the saponite lattice decreases the hydrothermal stability by nearly 200° C, while the introduction of Ga^{3+} for Al^{3+} in the beidellites leads to a similar de-

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TABLE 1.—STABILITY TEMPERATURES OF SYNTHETIC AND NATURAL MONTMORILLONIDS

Mineral name ¹	Cations present	Temp., °C	Decomposition products
Montmorillonite	Mg-Al-Si	465	Chlorite, pyrophyllite, hydral-site
Saponite	Mg-Al-Si	565	Talc, chlorite
Sauconite	Zn-Si	210	Willemite, cristobalite
Sauconite	Zn-Al-Si	340	Willemite, cristobalite
Pimelite	Ni-Al-Si	335	Ni-talc
Hectorite	Li-Mg-Al-Si	430	Talc
Ga-beidellite	Ga-Si	305	beta gallia
Beidellite ²	Al-Si	420	Hydralsite, pyrophyllite
Saponite ³	Mg-Si	275±20	Talc
Stevensite	Mg-Si	250±20	Talc

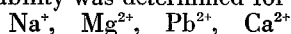
¹ The name is given to represent a family of compositions rather than individual members; typical compositions may be found in the references below.

² Roy and Osborn, 1952

³ Roy and Roy, 1955

crease in the stability by about 150° C. Sauconite, the Zn analogue of saponite (Ross, 1946) has been synthesized from zinc-silica mixtures with or without Al₂O₃. This indicates that any natural sauconite can actually be a member of a solid-solution series. The hydrothermal stabilities of several montmorillonoid minerals, both natural and synthetic, are shown in Table 1.

The nature of the interlayer cation also plays a measurable role in the determination of equilibrium decomposition temperatures. A variation of the order of 20 to 30° C was found in the stability temperature of the same mineral saturated with different cations. These results are presented in Table 2. The following ascending order of stability was determined for four cations:



These results cannot be used for exchange-cation determinations, but they do point up how strongly the so-called exchange cations are held, in that they do not interchange to any great extent with one another in the same bomb, and make a definite difference in the ease of molecular rearrangement. The differences between "exchangeability" of the cations from various sites in the lattice should be regarded as differences of degree rather than of kind.

TABLE 2.—STABILITY TEMPERATURES OF MONTMORILLONIDS SATURATED WITH DIFFERENT EXCHANGE CATIONS

Mineral name	Natural base-exchange cations	Na ⁺	Mg ²⁺	Ca ²⁺	Pb ²⁺
API H-25 montmorillonite	490	455	470	490	480
API H-28 montmorillonite	465	455	455	480	475
Natl. Lead hectorite	430	425	425	455	455
Synthetic saponite	—	560	565	>570	>570

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