

STABILITY AND DECOMPOSITION PRODUCTS OF HECTORITE

by

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ABSTRACT

The Hector, California, bentonite has been found unusual in many respects, and its thermal stability under hydrothermal conditions is no exception. It is important that the stability of this bentonite be known, as it is an end member of the saponite series with all cation positions, excluding interlayer, in the structure filled. The information is applicable to studies of wall rock alteration in which saponites occur as alteration products associated with ore deposition.

This saponite has an upper thermal stability limit of 750°C, at 15,000 psi water pressure, at which temperature it decomposes. The only products observed were talc and vapor; above 780°C the decomposition products observed were anthophyllite and vapor. Syntheses on the hectorite composition corroborate these decomposition temperatures and products.

Hydrothermal treatment at temperatures below about 450°C produce no change in the x-ray diffraction pattern of hectorite: on drying, the lattice collapses to a basal spacing (10–12 Å) approaching that of mica, and with ethylene glycol expands to 17 Å. However, after hydrothermal treatment above this temperature and to decomposition at 750°C, the hectorite, after subsequent cooling, collapses on drying at 110°C or less to 9.4 Å, but expands as before to 17 Å with glycol saturation. Without the glycol treatment the resulting material could be mistaken for talc and considered the decomposition product of hectorite at the higher temperatures. This behavior also occurs using the synthetic hectorite but does not occur when using synthetic or natural saponites containing aluminum.

For comparison, the relative stabilities of some dioctahedral and trioctahedral layered minerals are given to show the consistently higher stabilities for the minerals whose octahedral positions are filled.

INTRODUCTION

As reported originally by Foshag and Woodford (1936), hectorite is an end member of the saponite series and contains only a small amount of aluminum. Lithium substitutes for about one-ninth of the magnesium positions in the octahedral layer to provide the excess negative charge which explains the base-exchange capacity, and fluorine substitutes for about one-third of the hydroxyl groups.

The objective of this study was the determination of the decomposition temperature and the decomposition products produced from this end member

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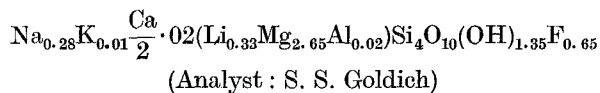
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magnesium montmorillonite under hydrothermal conditions. Research on the synthesis and stability of hectorite was started several years ago in other laboratories¹; results of the preliminary experiments conducted in the Standard laboratory were presented by Sand (1955). A decomposition temperature of about 800°C, under 15,000 psi water pressure, was reported at that time. Mumpton and Roy (1956) have reported a much lower decomposition temperature of 430°C at 15,000 psi.

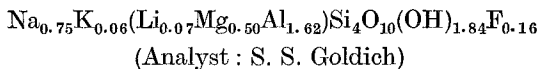
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METHODS OF INVESTIGATION

The pressure reactor vessels used were of the "test tube" type described by Roy, Roy and Osborn (1950). Open gold envelopes were used to contain the samples. Starting materials were hectorite of the composition,



aluminum bentonite from the Hector deposit of the composition,



This formula does not balance electrostatically, but represents the closest approximation that could be made. x-Ray diffraction analysis showed no other phases than 1 percent clinoptilolite present, and the formula was corrected for this. The best explanation for the small amount of excess components appears to be the presence of finely divided unaltered volcanic glass. The chemical analyses for these two bentonites are given by Ames, Sand and Goldich (1958). Synthetic mixtures were prepared by calcination of nitrates and ethyl orthosilicate.

Duration of runs was from 15 min to three weeks under water pressures to 25,000 psi and temperatures ranging from 350 to 850°C.

RESULTS

Hectorite decomposed at 750°C, at 15,000 psi water pressure, to talc and vapor; at 780°C to anthophyllite and vapor. It is not known if all the components are incorporated into the crystalline product or if some is lost to the vapor. Bowen and Tuttle (1949) found that pure anthophyllite in the system $\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ was metastable. Complete decomposition of the hectorite

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required several hours. Syntheses from oxide mixtures of the hectorite composition corroborate these decomposition temperatures and products. Material of the hectorite composition (but with no fluorine) was synthesized within 15 min at temperatures above 700°C and was unchanged after runs at these temperatures of three weeks' duration.

Hydrothermal treatment below 450°C produces no apparent change in the x-ray diffraction pattern of natural hectorite: on mild drying (< 110°C) the lattice collapses to a basal spacing (10–12 Å) approaching that of mica. However, after hydrothermal treatment above this temperature and to decomposition at 750°C, the hectorite, after subsequent cooling, collapses on drying at 110°C or less to 9.4 Å. With ethylene glycol treatment, the lattice expanded as before to 17 Å, which is characteristic of a montmorillonite. The infrared pattern on this phase showed that the hydroxyl content had increased by one and one-half times. This is the amount of hydroxyl increase that would be expected if the fluorine in the hectorite were replaced completely by hydroxyls.

x-Ray diffraction data obtained from film patterns from the collapsed hectorite are given in Table I.

TABLE I.—X-RAY DIFFRACTION POWDER DATA ON HECTORITE, HYDROTHERMALLY TREATED AT 740°C, DRIED AT 110°C

Rel. I	d , Å	Rel. I	d , Å
9	9.4	1	1.408
3	4.84	2	1.391
8	4.68	1	1.360
2	4.12	1	1.334
2	3.82	4	1.315
1	3.70	3	1.288
2	3.40	2	1.261
10	3.16	1	1.182
1	2.95	1	1.168
2	2.72	1	1.152
5	2.59	1	1.134
7	2.51	1	1.114
4	2.399	1	1.063
4	2.252	1	1.048
1	2.192	1	1.020
1	2.132	3	0.990
2	2.083	1	0.977
2	1.979	1	0.951
3	1.988	1	0.916
1	1.856	1	0.911
4	1.722	1	0.893
2	1.626	1	0.888
1	1.584	3	0.878
8	1.442		

This behavior of collapse to the talc spacing also occurs in the synthetic hectorite, produced between 450 and 750°C, but does not occur in synthetic or natural saponites containing aluminum.

As hectorite from Hector, California, is not of consistent composition, grading northwestward from the main deposit into an aluminum bentonite, the hydrothermal stability of the aluminum bentonite also was determined.

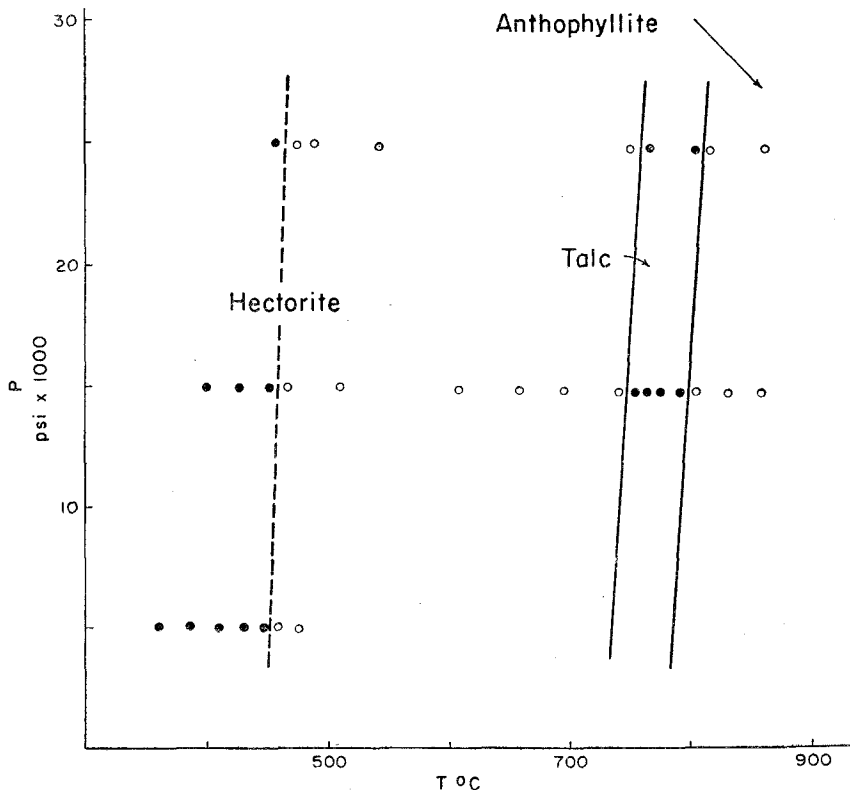


FIGURE 1.— P - T relationships observed for hectorite.

Its composition is given earlier in this paper. The aluminum bentonite decomposed at 440°C to pyrophyllite, quartz, feldspar, and a montmorillonite of different composition.

The P - T relationships observed for hectorite are given in Fig. 1. The dashed "boundary" delineates the field where hydrothermally treated hectorite collapses to the talc spacing on drying. Idealized equations are not given showing reactants and total products, since the distribution of the sodium, lithium and fluorine in the products—solid and fluid—was not determined.

DISCUSSION

Although hectorite was found to be stable to high temperatures, this does not mean that it formed in nature at these temperatures. Hectorite is the product of the alteration of siliceous pyroclastics by calcareous hot springs in a restricted lake environment (Ames, Sand and Goldich, 1956). It is significant that the trioctahedral magnesium montmorillonite forms in the zone of hot springs as an alteration product of an aluminosilicate glass, if magnesium is available (even in low concentration) in the lake waters. This observation had been made by Schroter and Campbell (1940) on another occurrence of saponite formed in a similar environment.

It is well known that the magnesium trioctahedral layered minerals, in which all octahedral positions are filled, are more stable thermally than the aluminum dioctahedral varieties in which only two-thirds of the positions are filled. Table 2 summarizes comparative decomposition temperatures of some layered minerals.

TABLE 2.—COMPARATIVE HYDROTHERMAL DECOMPOSITION TEMPERATURES AT 15,000 PSI

Dioctahedral	<i>T</i> , °C	Trioctahedral
Kaolinite ¹	400 500	Serpentine ²
Pyrophyllite ¹	580 780	Talc ²
Muscovite ⁴	635 1050	Phlogopite ³
Montmorillonite	480 750	Hectorite
	600	Aluminous saponite

¹ Roy and Osborn (1954)

³ Yoder and Eugster (1954)

² Bowen and Tuttle (1949)

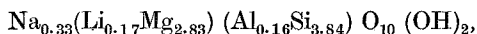
⁴ Yoder and Eugster (1955)

The relative thermal stabilities of the di- and trioctahedral montmorillonites should not be an exception, and the experimental data show that they are not. Most natural saponites, containing aluminum in varying amounts, have a hydrothermal decomposition temperature of between 500 and 600°C. These do not have optimum composition for maximum base-exchange capacity and do not have all cation positions filled. It is logical that with optimum composition, as in hectorite, the highest thermal stability for a montmorillonite should result. This is found experimentally.

In determining decomposition temperatures of members of the montmorillonite group, it must be recognized that a montmorillonite can decompose, in addition to phases such as feldspars and micas, to a montmorillonite of another composition that has a higher stability. This was noted in the decomposition of the aluminum bentonite from Hector. In open systems it is

also difficult to determine the distribution of the alkalis and halogens in the crystalline products and vapor.

The hectorite composition is unique among the montmorillonites in that it can be made to collapse to the talc spacing on drying after hydrothermal treatment. Spangenberg (1938) has reported a similar behavior on drying pimelite, $3(\text{Ni, Mg})\text{O} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O}$, to an interlayer water content of $n = 0.3$. The heat treatment made was not specified, but he states that the resulting x-ray diffraction pattern was equivalent to that of talc. A possible reason for this behavior is no substitution in the tetrahedral layer. It can be hypothesized simply from geometrical considerations that when the source of the excess negative charge is all in the octahedral layer, the field strength of the residual negative charge at an interlayer surface is about one-third of the strength developed when the source of the excess charge is in the tetrahedral layer. This residual charge tends to keep the sheets apart but is countered by the binding force of the interlayer cations. Except for the hectorite composition, and pimelite, the force tending to separate the sheets dominates in the montmorillonites; and on drying, spacings of 12–15 Å usually result. In the micas, however, the binding forces of the cations dominate and a spacing of about 10 Å consistently results. Hectorite, theoretically having the weakest negative charges opposing on the interlayer surfaces, and tending to separate the sheets, collapses to a talc spacing on treatment. This requires that the sodium ion be enclosed completely by the hexagonal pockets of the two opposing silica tetrahedral layers, and that all interlayer water be excluded. When aluminum is introduced into the tetrahedral layer, but with lithium still present in the octahedral layer, the lattice does not collapse to the talc spacing. A synthetic montmorillonite produced from such a composition,



also has a stability of about 750°C but does not show this collapse. The substitution of aluminum in the tetrahedral layer apparently prevents this collapse. This montmorillonite theoretically can not decompose at exactly the same temperature as hectorite, but with an experimental error of $\pm 10^\circ\text{C}$ the difference could not be noted.

A question on nomenclature arises as to whether a designation such as low and high hectorite (or hectorite and parahectorite) should be given; at this time it was believed better to leave the question open for future discussion.

ACKNOWLEDGMENTS

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