

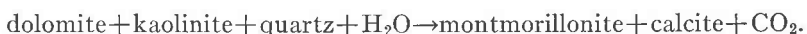
MINERALOGICAL NOTES

THE HYDROTHERMAL SYNTHESIS OF MONTMORILLONITE GROUP
MINERALS FROM KAOLINITE, QUARTZ AND
VARIOUS CARBONATES

A. A. LEVINSON AND R. W. VIAN,¹ *Gulf Research and
Development Company, Pittsburgh, Pennsylvania.*

INTRODUCTION

Montmorillonite group minerals (referred to as montmorillonite(s) in the remainder of this note) have been synthesized for several decades by a number of different methods using mixtures of various glasses, gels, pure oxides, and other chemicals. (For a summary of many of these methods see Deer *et al.*, 1962, pp. 237-238.) In some experiments montmorillonites have been formed by hydrothermal and chemical alteration of natural glasses, rocks, and silicate minerals. Only Coombs (1960) has synthesized a montmorillonite hydrothermally from naturally occurring minerals, specifically calcite, kaolinite, and quartz. His syntheses were achieved after four and eight weeks in the temperature range of 244°-295° C. We have synthesized montmorillonites hydrothermally by using kaolinite, quartz, and any one of several carbonate minerals, particularly dolomite. The dolomite reaction is:



This reaction proceeds easily at 300° C. in two days, and slowly at 175° C. in five days. Water-vapor pressure generated in the bombs ranges from about 130 psi (at 175° C.) to 1245 psi (at 300° C.).

EXPERIMENTAL

Generally, one and one-half grams each of finely-ground kaolinite, dolomite (or other carbonates), and quartz were placed in stainless steel bombs of 150-ml capacity which were then about two-thirds filled with distilled water and sealed. Variations of these conditions (*e.g.*, one-half as much quartz) also were used successfully. The bombs were placed in furnaces and usually held at 300° C. for five days. The products of the reaction and the parent minerals were studied by *x*-ray diffraction methods. Clay minerals formed during the experiments were sedimented onto glass slides and were studied after air-drying, after ethylene glycol treatment, and some after heat treatment in air at 300° C. The results of the experiments are presented in Table 1.

¹ Present Address: Department of Geology and Mineralogy, University of Michigan, Ann Arbor, Michigan.

The montmorillonites were identified by the presence of an *x*-ray diffraction peak at 14–15 Å in the pattern for an air-dried sample; on occasion, a peak at 12.5 Å was recorded rather than one at 14–15 Å. After ethylene glycol treatment, both the 12.5 Å and the 14–15 Å peaks expanded to 17 Å. Selected samples were heat-treated at 300° C. in air for one hour, and the (001) reflection collapsed to 10 Å confirming the iden-

TABLE 1. SUMMARY OF HYDROTHERMAL SYNTHESIS EXPERIMENTS

Run	Temperature	Duration	Reactants	Products
1	300° C.	5 days	Dol., Kaol., Qtz.	Calc., Mont.
2	300° C.	2 days	Dol., Kaol., Qtz.	Calc., Mont.
3	200° C.	5 days	Dol., Kaol., Qtz.	Dol., Kaol., Qtz., Mont., Calc.
4	175° C.	5 days	Dol., Kaol., Qtz.	Dol., Kaol., Qtz., Mont. (Tr.), Calc. (Tr.)
5	300° C.	5 days	Dol., Dickite, Qtz.	Calc., Mont.
6	300° C.	5 days	Siderite, Kaol., Qtz.	Kaol. (Tr.), Qtz. (Tr.), Mont. (Tr.)
7	300° C.	5 days	Siderite, Kaol., Qtz.	Kaol. (Tr.), Qtz. (Tr.), (No Mont.)
8	300° C.	5 days	Magnesite, Kaol., Qtz.	Kaol. (Tr.), Qtz. (Tr.), Mont., (Talc?)
9	300° C.	5 days	Smithsonite, Kaol., Qtz.	Kaol., Qtz., Mont.
10	300° C.	5 days	Calc., Kaol., Qtz.	Calc., Mont., Feldspar
11	260° C.	5 days	Calc., Kaol., Qtz.	Calc., Qtz., Kaol., Mont., (No Feldspar)
12	150° C.	5 days	Calc., Kaol., Qtz.	Calc., Kaol., Qtz. (No reaction)
13	300° C.	5 days	Dol., Kaol.	Calc., Kaol., (No Mont.)
14	300° C.	5 days	Kaol., Qtz.	Kaol., Qtz., (No reaction)

Dol. = dolomite; Kaol. = kaolinite; Qtz. = quartz; Mont. = montmorillonite; Calc. = calcite; Tr. = trace.

tity of montmorillonite. Diffraction evidence for the presence of vermiculite or swelling chlorite is lacking. In general, only a relatively sharp (001) reflection at 14–15 Å was recorded, but infrequently weak (002), (003) and other reflections were also observed.

In the experiments where dolomite, kaolinite, and quartz were used as parent materials, the formation of calcite and montmorillonite, and the disappearance of dolomite, kaolinite, and quartz were confirmed by *x*-ray diffraction analyses. No additional crystalline phases were observed; some brucite was expected on the basis of the studies of Morey (1962).

Without quartz in the system, kaolinite and dolomite did not react at 300° C. in five days. Under these conditions dolomite was destroyed, calcite was formed, and kaolinite appeared unaffected. In the absence of dolomite, kaolinite and quartz appeared unaffected.

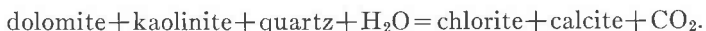
Magnesite, calcite, smithsonite and siderite were each substituted for dolomite and reacted at 300° C. for five days. Without exception the carbonates were destroyed along with much, or all, of the kaolinite and quartz. However, in all these experiments the amounts of montmorillonite formed indicate that the reactions with these carbonates proceed more slowly than with dolomite. Magnesite, calcite and smithsonite produce about equal amounts of montmorillonite at 300° C. in five days. The x-ray diffraction peak height of the (001) montmorillonite reflection produced using dolomite is perhaps 25 times as intense as those produced from any of the other carbonates mentioned above. In the case of siderite, only a very small amount of an expandable 14–15 Å montmorillonitic mineral was produced, but this could not be reproduced in a subsequent experiment.

DISCUSSION

Because of the limited amount of work so far performed, and the absence of any detailed chemical or crystal structure studies, the exact nature of the montmorillonites produced are unknown. The (060) reflection from the montmorillonite produced using dolomite as a starting material occurs at 1.52 Å and, therefore, we suspect that this montmorillonite is trioctahedral. We postulate that the interlayer exchange cations are mostly magnesium in the dolomite and magnesite experiments.

The formation of montmorillonite from kaolinite, dolomite (and other carbonates), and quartz under the relatively mild hydrothermal conditions described above has significant geological and environmental implications. Hydrothermal alteration zones often contain montmorillonite, but the mechanism of formation is either not reported in the literature (Deer *et al.*, 1962, pp. 240–241), or differs from the reaction described in this paper. Hydrothermally formed montmorillonites having important amounts of Mg²⁺ as the interlayer cation can reasonably be expected to be more common than heretofore realized. Foster (1951) has shown that the presence of exchangeable magnesium in montmorillonite clays may be significant.

Chlorite, rather than montmorillonite, has been suggested by Zen (1960), and others, as a product of a metamorphic reaction between a carbonate and some pre-existing aluminum-rich phase. The reaction is (Zen, 1960):



White and Muffler (1965) reported chlorite was formed by the reaction of dolomite and kaolinite in the Salton Sea geothermal area, California. They suggest this reaction is centered at a depth near 1600 feet at which the temperature is less than 200° C. Although they report that montmorillonite occurs in the upper few hundred feet of the cores and cutting from this well, the montmorillonite does not appear to be related to the reaction described in this report.

Of most significance, in our opinion, is the extent to which waters at temperatures of 175° C., or possibly lower, may alter the mineralogical composition of sediments by carbonate-clay-quartz reactions. Published environmental interpretations of sediments based on clays do not seem to take into account the reaction described in this note. Zen (1959) has postulated the formation of chlorite in sediments by means of the same reactions mentioned above for metamorphic rocks; other clay mineral-carbonate assemblages are also discussed.

This preliminary report is specifically designed to call attention to (1) the entire area of carbonate-clay-quartz reactions which may prove important in the understanding of sedimentary rocks, and (2) the ease with which the carbonate ion (under the experimental conditions employed) appears to solubilize quartz. The petrological significance of this type of reaction in hydrothermal alteration and low-grade metamorphism also merits further consideration.

REFERENCES

- COOMBS, D. S. (1960) Lower grade mineral facies in New Zealand. *Report XXI Inter. Geol. Congress, Norway*, pt. 13, 339-351.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1962) *ROCK-FORMING MINERALS*, Vol. 3, *Sheet Silicates*. John Wiley and Sons, Inc., New York.
- FOSTER, M. D. (1951) The importance of exchangeable magnesium and cation-exchange capacity in the study of montmorillonitic clays. *Am. Mineral.* **36**, 717-730.
- MOREY, G. W. (1962) The action of water on calcite, magnesite and dolomite. *Am. Mineral.* **47**, 1456-1460.
- WHITE, D. E. AND L. J. P. MUFFLER (1965) Metamorphism of Upper Cenozoic sediments to greenschist mineral assemblages; Salton Sea geothermal area, California (abs.). *Geol. Soc. Am. Spec. Paper* **82**, 221-222.
- ZEN, E. (1959) Clay mineral-carbonate relations in sedimentary rocks. *Am. Jour. Sci.* **257**, 29-43.
- (1960) Metamorphism of Lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont. *Am. Mineral.* **45**, 129-175.