

# NONMONTMORILLONITIC COMPOSITION OF SOME BENTONITE BEDS\*

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## ABSTRACT

Although the wide range of minerals resulting from alteration of tuffaceous rocks under hydrothermal and weathering conditions is well known, the extent of variation in composition of discrete bentonite beds subjected only to normal diagenesis and compaction is perhaps less well known.

Three bentonite samples from the Atoka Formation of Pennsylvanian age are predominantly mixed-layer illite-montmorillonite with subordinate kaolinite. Most bentonites in the Pierre Shale of Late Cretaceous age are entirely montmorillonite, but a few contain some kaolinite; one is predominantly kaolinite; some also contain appreciable interlayer  $\text{Al}(\text{OH})_3$  or  $\text{Mg}(\text{OH})_2$  forming a mixed-layer montmorillonite-chlorite clay; several are composed of considerable clinoptilolite, and one is largely phillipsite. Bentonite beds in the Carmel Formation of Middle and Late Jurassic age differ among themselves in composition; in a few, illite is the dominant clay; in others, mixed-layer chlorite-montmorillonite-illite in different proportions is the dominant clay; kaolinite is common and makes up nearly half of one sample. A rhyolite tuff near Denver, Colorado, has been altered to halloysite. Reasons for variation in the composition of these bentonites are only partly understood.

## INTRODUCTION

The diversity of minerals formed from pyroclastics disseminated in sedimentary rocks under soil-forming or hydrothermal conditions is well known. Some of the minerals, aside from montmorillonite, that are found in bentonitic and altered pyroclastic rocks are kaolinite, halloysite, celadonite, sericite, allophane, and mixed-layer clays from Japan (Sudo, 1951 and 1955, p.187); kaolinite and bauxite minerals from Hawaii (Sherman, 1952); halloysite and nontronite (Hosterman *et al.*, 1960), kaolinite (Fenner, 1916), hectorite and the zeolites clinoptilolite and analcite (Ames *et al.*, 1958) from the United States; and illite and halloysite from Hungary (Mattyasovscky-Zsolnay, 1946).

In contrast, apparently much more uniform products result from the alteration of volcanic detritus in discrete, essentially pure bentonite beds altered *in situ* and subjected only to normal diagenetic processes. Reports in the literature are overwhelmingly of the mineral species montmorillonite or,

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less commonly of other members of the montmorillonite group, especially beidellite (Ross and Shannon, 1926; Denisov and Kovalenko, 1955; Robertson, 1961). The concept of montmorillonite as the dominant component of bentonites is so widespread that bentonite frequently is used as a synonym for montmorillonite. Probably the best-known exceptions to the usual montmorillonitic bentonites are the K-bentonites that are widespread in the eastern United States and Canada and northern Europe in mid-Paleozoic sedimentary rocks and that consist of mixed-layer illite-montmorillonite and rarely chlorite (Weaver, 1953; MacEwan, 1956; Bystrom, 1954; Spjeldnaes and Hagemann, 1955; Yurgenson, 1958). Grim (1953, p.362) mentions illite and kaolinite as minor components of some bentonites; Ponder and Keller (1960) report kaolinite as the dominant alteration product of a partly altered tuff in lake beds of Miocene age in Idaho; and Martin-Vivaldi (1961) reports attapulgite and sepiolite in bentonites in North Africa. The purpose of this paper is to call attention to additional occurrences of nonmontmorillonitic bentonites.

#### ATOKA FORMATION

Clay minerals other than montmorillonite occur in widespread, thin, biotitic, light-colored clay layers in the Atoka Formation of Middle Pennsylvanian age in Oklahoma and Arkansas that have been interpreted as bentonite beds (Frezon and Schultz, 1961). Despite their nonmontmorillonitic composition, these beds have been so interpreted in part because of the contrast in composition between the inferred bentonites and the enclosing shales. The shales contain a mixture of kaolinite, chlorite, illite (as defined by Brown, 1951, p.155), mixed-layer clay, 20–25 per cent quartz, and in some samples, montmorillonite. On the other hand, the bentonites contain mainly mixed-layer illite-montmorillonite, some kaolinite, relatively little quartz, and no chlorite, illite, or montmorillonite (Fig. 1). The mixed-layer clays in the bentonites also give a basal spacing of 29–30 Å; no such feature was observed for the shales. These inferred bentonites are mineralogically similar to the lower Paleozoic K-bentonites, except that the Atoka bentonites also contain 5–10 per cent of moderately well-crystallized kaolinite.

#### PIERRE SHALE

Light-colored bentonite beds, mostly a few inches thick but some several feet thick, are common in the Pierre Shale of Late Cretaceous age in the Great Plains area. The great majority of these bentonites typically consist of montmorillonite. However, some Pierre bentonites contain a little kaolinite, and a sample (Fig. 1) from a bed in the Sharon Springs Member in western Kansas is predominantly kaolinite.

Another much more common variant in some Pierre bentonites is interpreted as a "chloritic" bentonite (Fig. 1). Basal spacings of the material are: (1)

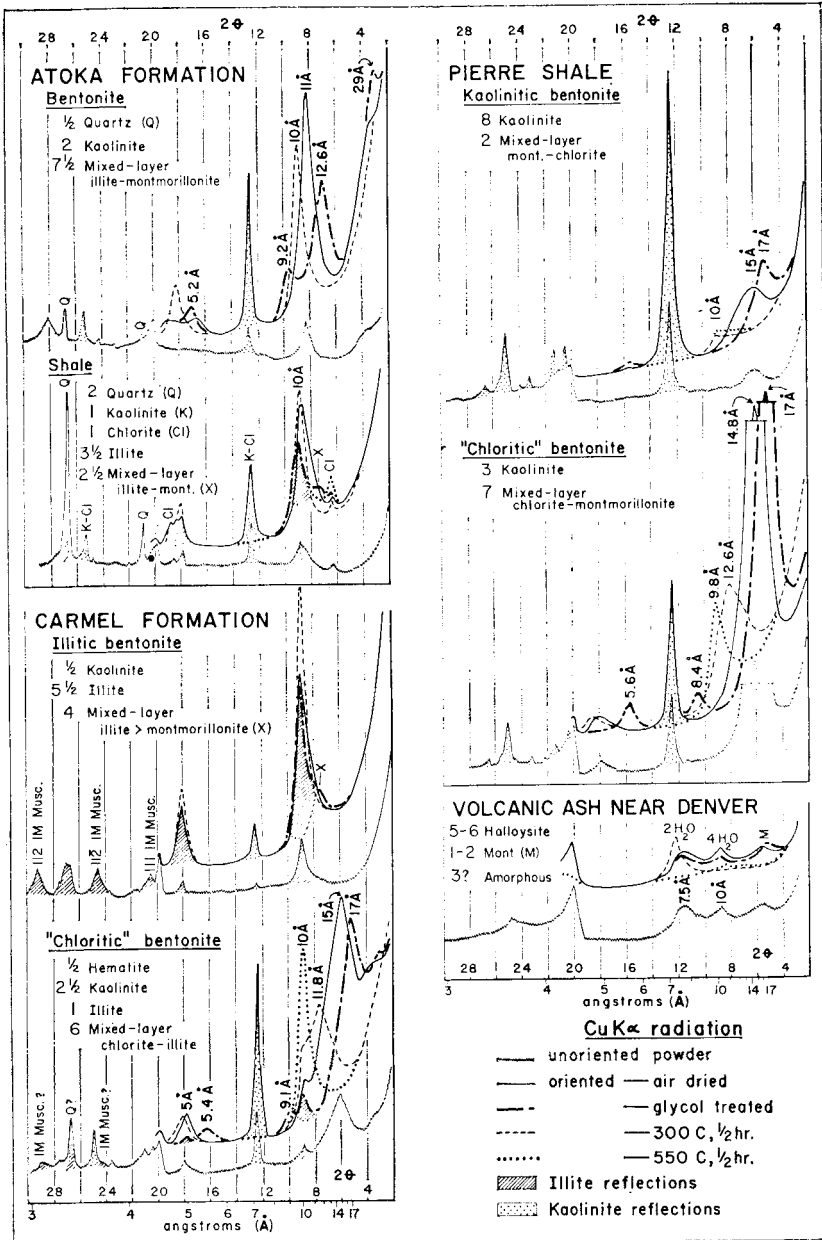


FIGURE 1.—X-ray diffractometer traces of some bentonite samples. Amounts of each mineral are estimated in parts per 10 parts of the total sample.

14.8 Å for air-dried material with little or no second basal reflection; (2) about 17 Å after glycol treatment and 18 Å after glycerol treatment, regardless of whether the material is pretreated with  $Mg^{++}$  or is in its natural state (Fig. 1); (3) 11–13 Å after heating at 300°C for  $\frac{1}{2}$  hr, and generally 9.5–10 Å after heating at 550°C. Between the montmorillonite layers is some material that, unlike the usual exchangeable ion–water complex, is not volatilized at 300°C, and thus the basal spacing does not collapse to the 9.5–10 Å spacing expected for montmorillonite. Nor does the material have the properties typical of either vermiculite or chlorite. Its thermal collapse resembles that of some dioctahedral vermiculites (Hathaway, 1955, fig. 5), but unlike vermiculite it swells with glycol or glycerol. In swelling properties, the material resembles swelling chlorite, but swelling chlorite maintains a basal spacing near 14 Å after heating at 550°C. The material in question generally has an acid pH. It also has a 1.49–1.50 Å 060 spacing indicative of a dioctahedral clay. Structural formulas calculated from chemical analyses of such noncollapsing clays from Pierre bentonites commonly indicate totals for octahedral cations considerably in excess of the ideal 4 per unit cell and also a marked deficiency of calculated interlayer cations. Apparently aluminum cations calculated in the octahedral layer actually occur in interlayer positions. The interlayer  $Al^{3+}$  is commonly associated with  $H^+$  or  $H_3O^+$  which causes the acid pH; the  $Al^{3+}$  tends to hydrate, producing islands of rudimentary interlayer gibbsite that normally are not sufficiently well developed to prevent expansion with glycol or glycerol, or to prevent collapse at 550°C, but are sufficiently stable to prevent collapse at 300°C. The result is a structure resembling the chlorite-like substances produced from montmorillonite experimentally by Caillère and Hénin (1949), Anderson, Jonas, and Odum (1958), Youell (1960), and Slaughter and Milne (1960). Slaughter and Milne (1960) predicted that such chlorite-like material should occur in nature; the Pierre material seems to illustrate such an occurrence.

A few other bentonites from the normal part of the Pierre Shale are similar to the chloritic bentonites in the Sharon Springs Member, except that they have an alkaline pH. They apparently contain exceptionally large amounts of interlayer  $Mg^{++}$  which is hydrated to form a rudimentary brucite-like structure that, like the gibbsite, prevents collapse at 300°C. The brucite-like layers apparently formed in response to the alkaline, reducing conditions prevalent when most of the marine shales of the Pierre were deposited. The gibbsite-like layers, on the other hand, undoubtedly developed at some time when acid conditions prevailed, perhaps during or shortly after deposition. An acid pH at this time is indicated by abundant primary pyrite deposited with some of the Sharon Springs; the acid pH would be caused by the  $H_2S$  that must have been in the water in order to form the pyrite. Another possible period for development of an acid environment is after deposition, when oxidation of pyrite to  $H_2SO_4$  might acidify percolating groundwaters. Other than oxidation of pyrite, however, no obvious effects of post-depositional leaching have been noted in the Pierre samples.

Still another variant in Pierre bentonites, as in many altered volcanic rocks (Deffeyes, 1959), is zeolite. One of Bramlette and Posnjak's (1933) three localities for such zeolitic bentonites was the Sharon Springs Member of the Pierre at Pedro, Wyoming. A few percent of clinoptilolite is present in many shales as well as in bentonite samples from the Pierre, and a bentonite bed north of Chamberlain, South Dakota, is almost entirely made up of this mineral. One bentonite sample from the Gammon Member of the Pierre Shale north of the Black Hills contains considerable phillipsite. Both the clinoptilolitic and phillipsitic bentonites have fairly good shard structures. Elsewhere the same beds are normal montmorillonitic bentonites. Reasons for these differences in alteration are not clear.

### CARMEL FORMATION

Bentonite beds, commonly only a few inches thick, occur in the lower part of the Carmel Formation of Middle and Late Jurassic age in southwestern Utah (Wright and Dickey, in preparation; Schultz and Wright, in preparation). The beds commonly are pale green or purple in contrast with the deep-red enclosing sedimentary rocks. Large euhedral biotite crystals are concentrated at the bottom of the bentonite beds; sanidine is the only feldspar; quartz generally composes only about one percent of the total rock; traces of euhedral apatite, hornblende, and zircon are present. Some of the sanidine and quartz crystals observed in thin sections are euhedral, others are angular and broken. A few areas that have vague shard-like outlines, and possibly a little unaltered glass are present. The biotite in some samples is partly altered to vermiculite, but all other phenocrysts are completely fresh. All the bentonite beds apparently altered from rhyolite tuff.

The clay-mineral composition of the Carmel bentonites is highly variable from one locality to another. Montmorillonite makes up only 10–20 per cent of five of the thirteen bentonite samples studied, and is absent in the other eight. Fairly well crystallized kaolinite makes up 5–50 per cent of all but one bentonite. Mixed-layer clay composes 15–85 per cent of all samples; in these mixed-layer clays, montmorillonite, illite, and chlorite-like layers are the dominant components in different samples. The chloritic component is expandable with glycol (Fig. 1), or glycerol, both before and after  $Mg^{++}$  saturation; it is collapsed to about 10 Å after heating at 550°C, but not at 300°C. Thus, the chlorite-like interlayers are similar to those described for the Pierre bentonites, except that in the Carmel they are interlayered with illite as well as montmorillonite. Illite with no detectable montmorillonite or chloritic interlayers composes 10–55 per cent of all but one of the bentonites. The more illitic samples give good reflections for 1 M muscovite, and even a sample with only 1/10 illite gives some suggestion of this polymorph (note 111 and 112 reflections on Fig. 1). All of the clays in the Carmel bentonites are aluminous, dioctahedral varieties.

The illite in some of the Carmel bentonites would seem to result from a

tendency of potassium-rich rhyolite ash to alter to potassium-rich clay (illite). Other bentonites reportedly altered to illite also are derived from rhyolites (Mattyasovscky-Zsolnay, 1946; Hofmann, 1956). However, in the Carmel Formation, chloritic, montmorillonitic, and kaolinitic as well as illitic bentonites, all apparently altered from identical rhyolite tuffs. One possible reason for the kaolinitic bentonites is suggested by the color of the bentonites, the purple bentonites generally containing more kaolinite than the green bentonites. The bentonites apparently were deposited on a broad tidal flat across which the Carmel sea encroached from the west. Perhaps at some localities more wetting, drying and oxidation which produced the hematite of the purple samples also caused more but still mild leaching of the tuff, thereby favoring development of kaolinite. On the other hand, the variable illite content and types of mixed-layer clay show no perceptible relationship with sample color, geographic location, or environment of deposition. They do show the relationship, however, with the mineralogy of the enclosing sedimentary rocks. These rocks contain not only normal clastic mineral assemblages but also sanidine, biotite, and other primary volcanic crystals like those in the bentonites, as well as clay minerals apparently altered from rhyolitic glass. These clay minerals are similar to the clays in the bentonites; where the clays in the bentonites are illitic, those in the sediments also are illitic, and in many samples the IM muscovite polymorph can be discerned; where the clays are predominantly mixed-layered in the bentonite, similar mixed-layered clays also occur in the adjacent rocks. Therefore, the factor determining the composition of most of the bentonitic material in these Carmel rocks must have been some local feature common to all of the 50–200 ft section of rocks sampled at specific localities, but differing between localities 20–50 miles apart; one possible such factor is the chemical composition of the circulating groundwater in which the volcanic debris altered.

### VOLCANIC ASH NEAR DENVER

A rhyolitic ash bed of Pliocene or early Pleistocene age near Denver, Colorado, has been described by Hunt (1954, p.96) and by Schlocker and Van Horn (1958). Mr. Van Horn supplied the writer with some of their original material. X-ray diffraction data on material from which calcite was removed (Fig. 1) show the crystalline part of the sample to be predominantly halloysite with minor montmorillonite; about  $\frac{1}{4}$ – $\frac{1}{3}$  of the sample appears to be amorphous to X-rays. Identification of the halloysite is confirmed by the potassium acetate procedure of Andrew, Jackson, and Wada (1960) which produced basal spacings of 14.5 Å, 11.6 Å, and 9.9 Å respectively after K-acetate,  $\text{NH}_4\text{NO}_3$ , and water washing plus stabilization at 70 per cent r.h. Although the halloysite presently is partly dehydrated (Fig. 1), it was completely hydrated when removed from the outcrop about 5 years ago (Schlocker and Van Horn, 1958, fig. 1a and b).

An electron micrograph of the halloysitic tuff (Plate 1) shows that the

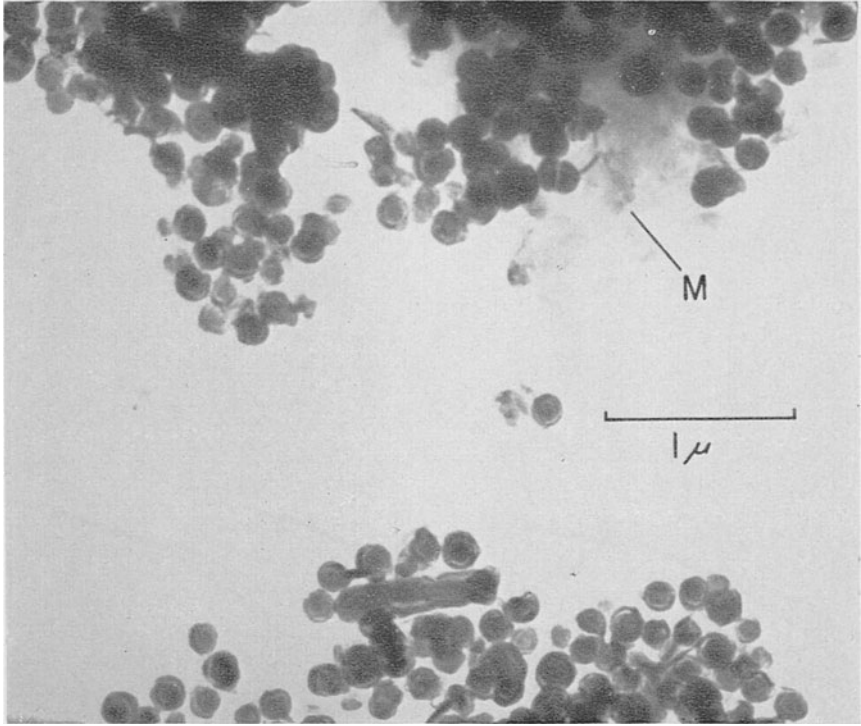


PLATE I. - Electron micrograph of spherical particles in halloysitic tuff near Denver, Colo. M, flakes of montmorillonite.

(Facing p. 174)

sample is composed predominantly of spherical grains about  $\frac{1}{10}$  micron in diameter; a minor part is made up of flakes and a few elongate but apparently nontubular grains. The flakes probably are the 10–20 per cent montmorillonite detected in the X-ray analysis (Fig. 1); the concentric spheres must be halloysite and amorphous material. Similar spherical halloysite particles have been reported in some altered tuffaceous rocks from Japan (Sudo and Takahashi, 1955).

## DISCUSSION

Though not new, the point is worth emphasizing that, just as all montmorillonites are not to be found in bentonites, neither are all bentonites made up solely of montmorillonite. The only unequivocal evidence for calling a rock a bentonite is relict shard or other pyroclastic textures preserved in the clay groundmass, or the presence of primary volcanic minerals like euhedral biotite and sanidine and absence of obviously nonvolcanic components like microcline. Detection of shards is difficult or impossible in many thin sections. Determination of the volcanic character of some of the nonclay minerals commonly can be made, but requires that these minerals be separated from the clays and given special study. The most obvious criteria for deciding which samples merit such special study are the geometry and general appearance of the clay bed in the field. Comparative clay mineral composition of the bed in question and the adjacent rocks may or may not be helpful. If an illite mineral is present, its determination as a 1M muscovite polymorph should mark the sample for further consideration as a possible bentonite. Perhaps one of the least advertised but most easily used criteria, and one very helpful in the examples just mentioned, is the absence or near-absence of quartz; though some bentonites contain appreciable amounts of quartz, many do not; paucity of quartz is a feature that is not common in many clayey sedimentary rocks other than bentonites. The clay mineral composition by itself, though generally suggestive, may also be quite misleading, since many types of clay minerals may occur in bentonites.

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