CLAY MINERALOGY OF SOME PERMIAN BENTONITES FROM THE DELAWARE BASIN AREA, TEXAS¹

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Abstract

Thin, intercalated bentonite beds occur in the Manzanita Limestone Member of the Permian Cherry Canyon formation. These bentonites crop out in the Guadalupe-Delaware Mountains area and have been penetrated by wells in the Delaware basin of Texas and New Mexico. X-ray diffraction analyses indicate that these bentonites, unlike most closely associated bentonites, vary markedly in clay mineral types. The prominent clay minerals noted are: chlorite, illite, randomly mixed-layered illite-montmorillonite, and mixtures of illite and montmorillonite.

INTRODUCTION

Bentonites are generally considered to consist of montmorillonite or randomly mixed-layered illite-montmorillonite. Recently Schultz (1963) has called attention to the diverse clay mineral assemblages of certain bentonites. The purpose of this paper is to note the wide variations in clay-mineral content found in closely associated bentonites in the Cherry Canyon Formation. Five selected samples are used to illustrate the clay types noted.

The bentonite beds studied crop out in the Guadalupe-Delaware Mountains area and have been penetrated by wells in the Delaware basin of Texas and New Mexico (King, 1948) (Fig. 1). The bentonites are associated with limestones of the Manzanita Member of the Cherry Canyon Formation of Permian age as intercalations which vary in thickness from a feather edge to about one foot (Fig. 1).

Bentonite beds are widely distributed in sedimentary rocks (Eaton, 1964; Schultz, 1963; Ross, 1955). Their use as marker beds in stratigraphic correlations has prompted considerable study. Early bentonite investigations were largely descriptive or petrographic in nature (Nelson, 1922; Ross, 1928; Kay, 1931, 1935; Allen, 1932; Rosenkrans, 1934). Ross and Shannon (1926) defined bentonite as "...a rock composed essentially of a crystalline clay-like mineral formed by the devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash...."

Early studies indicated that bentonites consist largely of montmorillonite. This led to the unfortunate situation of using bentonite interchangeably with montmorillonite. Kerr (cited in Ross, 1928, p. 148) determined by x-ray diffraction analysis that the high potassium bentonites differed mineralogically from the montmorillonitic bentonites. Ross (1928) applied the term meta-bentonites to the moderately meta-

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FIG. 1. Map and lithologic log showing approximate sample locations.

morphosed Ordovician high potassium bentonites to distinguish them from the swelling bentonite clays. Kay (1931) used the term metabentonite to designate all the Ordovician bentonites in the eastern United States. In order to clarify the situation, Weaver (1953) designated the high potassium-bearing bentonites "K-bentonites."

With advances in x-ray diffraction techniques and clay crystallography during the last two decades, several clay minerals have been identified in bentonites. Besides montmorillonite; chlorite, illite, kaolinite, and various mixed-layer clays have been found to be principal constituents of certain bentonites. The reader is referred to the excellent summary and examples by Schultz (1963) and to the work of Kerr *et al.* (1950a,b); Weaver (1935, 1956b); Schultz and Wright (1962); Huff (1963); and Lounsbury and Melhorn (1964).

PREVIOUS STUDIES

King (1948) noted that the most striking feature of the Manzanita Limestone Member of the Cherry Canyon Formation is its intercalated beds of altered volcanic ash. These beds appear as apple-green siliceous cherts and shales and as waxy, green, bentonitic clays. The Manzanita Member is 75 to 150 feet thick and the thin altered ash beds occur at various positions (Fig. 1). Five thin-sections of the altered ash were studied by C. S. Ross. He noted (cited by King, 1948, p. 37) that ash structures are generally recognizable under the microscope. However, in some of the softer beds, ash structures are not evident. King (1948) also gave chemical anaylses of two bentonitic clay samples from the Manzanita Member. One showed ash structure under the microscope and contained 9.24% K₂O, the other did not show recognizable ash structures under the microscope and contained 5.02% K₂O. Both the high K₂O content and the marked difference in K₂O content of these samples are noteworthy.

EXPERIMENTAL PROCEDURE

Approximate sample locations are shown on Fig. 1 and are described in the appendix. Sample numbers 1, 2 and 3 are from cores, whereas numbers 4 and 5 are from outcrops. However, no sample-to-sample correlation of a specific bentonite bed is implied.

Color of the samples ranges from pale green to dark grayish green. Lithologically, these samples resemble claystone or shale. Core samples 2 and 3 are translucent along thin fracture edges. The core samples have a waxy appearance and a soapy feel. The outcrop samples are slightly weathered and appear less waxy than do the core samples.

Under the microscope, thin-sections of samples 2 and 3 show welldeveloped outlines of glass shards. The relic shard structure is best developed in sample 3 which shows bubble structures (Fig. 2). The glass shards have been devitrified and altered to clay minerals and secondary quartz. Examination of other Manzanita bentonite samples indicates that glass shards are not always evident, as noted earlier by Ross (King, 1949, p. 37). In some samples glass shards are more apparent in thinsections cut parallel rather than normal to the bedding. Also observed in samples 2 and 3 are angular quartz and feldspar, subrounded biotite, and euhedral pyrite and apatite. The non-volcanic detritus in these bentonite samples is less than 20 per cent. It is inferred from the presence



FIG. 2. Photomicrograph Sample 3 showing relic glass shards and bubble structures. Large black grains are pyrite. Polars not crossed.

of pyrite, which is undoubtedly of authigenic origin, that the ash was altered to bentonite under reducing conditions. Furthermore, since the bentonites are intercalated with marine limestones the environment was alkaline.

X-RAY DIFFRACTION ANALYSIS

Both the bulk powdered sample and the oriented clay-size material were studied. Preparation of the bulk powdered sample consisted of gentle grinding and sieving through 325 mesh. The powdered material was then thoroughly mixed and back-packed into a conventional aluminum Philips mount. The less-than-two micron fraction was prepared by first crushing the sample to pass an 80 mesh sieve. Particle separation was achieved by placing a small beaker containing the sieved sample and water in an ultrasonic cleaner-type disaggregator for five minutes. After removing the soluble salts, the sample material and distilled water were placed in settling cylinders and the less-than-two micron fraction was decanted. Two and one-half milliliters of the claywater suspension was allowed to air dry on glass slides $(26 \times 46 \text{ mm})$ producing oriented clay films. The oriented clay films were x-rayed successively at a relative humidity of about 50 per cent, after vapor glycol treatment (2 hours at 65° C.), and after heat treatments of 300 and 550° C.

A conventional geiger-counter equipped x-ray diffraction unit and recorder were used in this study. Operating conditions were: nickel filtered copper radiation at 40 kilovolts and 17 milliamperes, 1° beam and .006 inch detector slit, scanning speed 1° per minute, chart speed one inch per four minutes.

The x-ray diffraction traces are shown on Figs. 3 and 4. In identifying the clay minerals, procedures followed were those outlined by Weaver (1956a) and supplemented by Brown (1961) and Warshaw and Roy (1961). Mica polymorphs were identified using Yoder and Eugster's (1955) data.

Prominent clay minerals in the bentonite samples are: chlorite (Sample 1); dioctahedral illite, 1M polymorph (Samples 2 and 5); randomly mixed-layered illite-montmorillonite in a ratio between 8:2 and 7:3 (Sample 3); and illite and montmorillonite with minor interlayering (Sample 4).

Moreover, sample 1 is characterized by its unusually high chlorite content. Upon glycolation, the basal chlorite spacing increased about 0.2 Å. From this it is inferred that the chlorite contains about 5 per cent expandable layers. By averaging the higher-order 001 reflections of the air-dried and glycolated clay-size fractions an 001 spacing of 14.24 Å was obtained. This spacing, when compared with Brindley and Gillery's (1956) work, suggests that about one in four of the Si ions are replaced by Al. The "b" cell dimension, computed from the 060 spacing, is 9.21 Å. This spacing is small for chlorites, and from Shirozu's (1958) data it is inferred that the iron content is low. The inferred low iron content is also supported by the relatively strong 002 and 004 reflections compared with the 001, 003 and 005 reflections.

Also present in sample 1 are illite, randomly mixed-layered clay, and minor amounts of quartz, potash feldspar, and a possible trace of pyrite. The interlayered clay consists largely of illite containing an estimated 20 per cent other randomly interlayered clays. The interlayered material is believed to consist of chlorite and montmorillonite. This is suggested by the following: (a) the basal spacing of the air-dried mixed-layered material is 10.6 Å, (b) upon glycolation this spacing increases to about 10.7 Å, (c) after heat treatment at 300° C. or at 550° C. the spacing decreases to about 10.5 Å and at the same time decreases in intensity relative to the 10 Å peak.



FIG. 3. X-ray diffraction traces of bentonite samples 1, 2 and 3.



FIG. 4. X-ray diffraction traces of bentonite samples 4 and 5.

Sample 2 is composed largely of dioctahedral 1M illite. This illite may contain minor expandable material as suggested by the slight asymmetry on the low angle side after glycolation, and the increase in height of the 10 Å peak after heat treatment. Minor chlorite and possibly kaolinite comprise the remainder of the clay mineral fraction. An estimated 25 per cent quartz and a few per cent potash feldspar are also present.

Randomly mixed-layered illite-montmorillonite in a ratio between about 8:2 and 7:3 characterizes sample 3. This ratio is estimated from the 10.6 Å basal spacing of the oriented air-dried sample and the expansion of this spacing to about 11.5 Å upon glycolation. The breadth of this mixed-layered glycolated peak and the lack of higher order reflections suggest that the crystallites are very small or that the percentage of interlayering in the crystallites is not uniform. Also present are chlorite, a relatively large amount of pyrite and small amounts of quartz, and potash and plagioclase feldspars.

Bentonite sample 4 contains considerable illite and montmorillonite. The trace of the air-dried oriented sample exhibits a 10.1 Å basal illite spacing which is slightly asymmetrical on the low angle side. From this it is inferred that the illite contains about 10 per cent expandable material. The basal montmorillonite spacing of the oriented glycolated sample is about 16.9 Å. This spacing suggests that the montmorillonite contains traces of randomly mixed-layered non-expandable material. Also identified in this sample is a moderate amount of quartz and potash feldspar. A minor amount of chlorite is present in the bulk sample but is not detectable in the clay-size fraction.

Sample 5 is a good example of an illitic bentonite. The illite is dioctahedral as indicated by an 060 spacing of 1.501 Å and is of the 1M polymorph type. The similarity of the 10 Å peak in the glycolated and heat treated traces with the air dried oriented trace indicates that the illite contains but negligible amounts of expandable material. Also present in sample 5 are small amounts of quartz, potash feldspar, calcite, and traces of chlorite and montmorillonite.

Conclusions

From the study it is concluded:

- (1) Marked variations in clay mineral types occur in the bentonites of the Manzanita Member of the Cherry Canyon Formation.
- (2) The dominant phyllosilicates are illite, montmorillonite, chloriteand mixed-layered clays.
- (3) Well-developed relic ash structures can be seen under the microscope in about half of the samples.

(4) Quartz percentages of less than 25 per cent characterize these bentonites.

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Appendix

Sample Locations.

Sample 1 Core-Well, Sec. 19, Blk, 54, Twp. 2 Loving Co., Texas.

Sample 2 Core-Well, Sec. 11, Blk. 53, Twp. 2, Loving Co., Texas.

Sample 3 Core-Well, Sec. 3, Blk. 55, Twp. 2, Loving Co., Texas.

Sample 4 Outcrop-U. S. Highway 62 and 180, about 1 mile east of Nickle Creek Bridge, Culberson Co., Texas.

Sample 5 Outcrop—U. S. Highway 62 and 180, about 2 miles west of junction with State Highway 54, Culberson Co., Texas.

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