Correlation by Spectrographic Analysis of Bentonite in the Gulf Series of Dallas Area, Texas

Eugene Herrin

ABSTRACT

Spectrographic determination of Si:Al and Ca:Mg ratios in bentonite from the Upper Cretaceous Eagle Ford shale of the Dallas area, Texas, indicate that variations in these ratios among different bentonite beds are significantly greater than variations within a single bed. The correlation of one bed over a distance of about 9 miles is supported by both spectrographic and stratigraphic evidence.

Correlation of bentonite in the Dallas area with similar beds near Waco, Texas, 120 miles to the south, now seems possible. If so, the Eagle Ford shale might be divided into time-rock units that would be independent of paleontology.

Bedded bentonite is thought to originate as layers of volcanic ash deposited on the floor of the ocean. It is probably laid down quickly, with little chance for the introduction of detrital impurities (Alexander, 1925, pp. 100-105; Davis, 1941, p. 13; Ross, 1945, p. 65). Bentonite beds which are laterally extensive should serve to define excellent time-rock units, and should in addition reflect the contours of contemporaneous sea bottoms. For this reason it becomes important to correlate bentonite deposits over relatively broad areas.

The bentonite here described is in the Upper Cretaceous Eagle Ford shale of Dallas County, Texas. Sets of seams are difficult to correlate between adjacent croppings because all seams are similar in thickness and lithology. Bentonite also occurs in the Eagle Ford 120 miles to the south near Waco, Texas (Adkins & Lozo 1951, pp. 119-151). If the bentonite in the Dallas and Waco areas could be correlated it would be possible to subdivide the shale into time-rock units that would be independent of paleontologic consideration. It is the purpose of this paper to investigate the possibility of employing spectrographic analysis as an aid in this type of correlation.

A spectrographic study was made to determine whether the Si:Al and Ca:Mg ratios were unique characteristics of individual bentonite seams. First, it was necessary to learn whether these ratios along a single bentonite seam are fairly constant. Second, it was necessary to determine whether the individual bentonite seams have ratios which are signifi-
cantly different from horizon to horizon. Obviously, if the bentonite is to be used for purposes of correlation the variation in \( \text{Si:Al} \) and \( \text{Ca:Mg} \) ratios must be considerably greater from seam to seam than along a single seam.¹

Definition of Bentonite

Bentonite is "... a rock composed essentially of a crystalline claylike mineral formed by the devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash." (Ross, 1945, p. 65). Bentonites are composed mainly of montmorillonite, biedelite, or the two mixed in varying amounts. The formula for montmorillonite is given by Ross (1945, p. 45) as approximately \( 5\text{Al}_2\text{O}_3\cdot2\text{MgO}\cdot24\text{SiO}_2\cdot6\text{H}_2\text{O}(\text{Na}_2\text{O}\cdot\text{CaO}) \) and for biedelite as \( 13\text{Al}_2\text{O}_3\cdot5\text{Al}_2\text{O}_3\cdot38\text{SiO}_2\cdot12\text{H}_2\text{O}\cdot2\text{Na}_2\text{O} \).

The type locality for bentonite is the outcrop area of the Fort Benton formation of Upper Cretaceous Age in southern Wyoming. Analysis of this rock shows it to have a \( \text{Si:Al} \) ratio of 2.06 and a \( \text{Ca:Mg} \) ratio of 0.278 (Davis, 1940, p. 14).

It has been suggested that bentonites are formed from latites and not from highly siliceous volcanic glasses (Ross, 1945, p. 65). The widespread occurrence of bentonites in Texas Cretaceous rocks indicates that volcanoes producing moderately acidic ejectamenta were active in the vicinity of central Texas throughout Cretaceous time. It is important to note that field studies in central Texas have revealed no volcanic rocks, other than tuffs and bentonites, which could be called acidic.

Bentonites in the Dallas Area

Numerous bentonite seams are found in the Eagle Ford shale around Dallas, Texas. This material is usually medium bluish grey to bluish white when fresh and weathers greyish yellow to dark yellowish orange.² The rock is so fine-grained that constituents in the matrix cannot be resolved in thin sections. However, euhedral biotite flakes are common and minute fragments of quartz and feldspar are also present in very small quantities. Thin layers of calcite crystals commonly occur above and below the seams.

¹With hearty thanks to Wilson Bryan and Herbert Robertson, for help in the field; to Dr. Frank C. McDonald and Forrest West, Jr., for advice and assistance in the laboratory; and to Drs. Claude C. Albritton, Arthur Richards, and John W. Harrington for aid, counsel, and guidance in the prosecution of this work.

²Color-names from National Research Council Rock Color Chart.
MAP of the area north of Grand Prairie, Dallas County, Texas, showing localities at which samples of bentonite were collected. (After Taggart, 1953)
Samples of ash from the lower Austin chalk, which overlies the Eagle Ford shale, were tested for solubility in dilute HCl. Although the four-inch bentonite seam tested is bedded with limestone that is 70% soluble in acid, samples from the seam were found to be only 0.05% soluble. These data attest the purity of the bentonite and suggest that there was little or no mixing of ash with bottom sediment during deposition.

X-ray diffraction analysis\(^3\) of bentonite from the Eagle Ford shale (Sample S-1) shows the material to be approximately 90% montmorillonite. Biotite, calcite, and quartz are present in amounts less than 2%.

The Si:Al ratios for the samples examined fall in a range from 6:00 to 15:00. These are relative values and do not represent true chemical ratios, as the accuracy of the spectrographic working curve was not determined. Only the precision of the spectrographic method was investigated, since only relative values are needed in correlation.

Here follows a series of field descriptions and locations of outcrops of bentonite beds sampled and analyzed by the author:

**Locations and Descriptions of Outcrops**

**Outcrop CDN**

- **Location:** 200 yards west of Beltline Road five miles north of Grand Prairie in small stream bank 50 yards south of bridge.
- **Formation:** Eagle Ford shale.
- **Description:** A bentonite bed 8" to 10" thick. Bentonite white weathering dark yellowish orange. Some ground water contamination, i.e., limonite staining evident. The bed is near the surface and traceable over a short distance. Texture extremely fine grained.
- **Samples:** C-1, C-2, C-3, C-4, D-1, D-2, D-3, D-4, N-1, N-2, and N-3. Multiple samples were taken from the same general sampling position in order to test the precision of sampling.

**Outcrop E**

- **Location:** In bank of a small creek 2 miles southeast of Coppell and west of Coppell school, a few hundred yards south of bridge.
- **Formation:** Eagle Ford shale.
- **Description:** A bentonite bed 8" to 10" thick. Pale blue when fresh and weathering to pale yellowish orange with some moderate yellowish brown staining. Extremely fine grained, soapy texture on fresh sample.
- **Samples:** E-1 and E-2. These samples were taken from the same sampling position.

---

\(^3\)Analysis done by Herbert C. Robertson, Jr., with Research, Inc., in Dallas, Texas, May 8, 1953.

\(^4\)For the relative locations of this and the following outcrops, see the location map.
**Outcrop L**

**Location:** On south bank of the West Fork of the Trinity River 150 yards east of Belt Line Road bridge over the river and 50' west of a U.S.G.S. Water Gauging Station.

**Formation:** Eagle Ford Shale.

**Description:** Numerous small bentonite seams are interbedded with the shale and are exposed in the 40' bluff. Only the thicker seams which are present in the lower 12' of the bluff were sampled and described.

Seam (d): 9'9" above river cut shelf. Dark yellowish orange bentonite 2" thick. Not sampled.

Seam (c): 8'3" above shelf. White to pale yellowish orange bentonite weathering to dark yellowish at the top. 3" thick.

Seam (b): 5'4" above shelf. White with pale yellowish orange staining at top. The shale below is case hardened. 4" thick.

Seam (a): 3'5" above shelf. Pale blue bentonite with a definite greasy feel, weathering to dark yellowish orange. 3" thick.

**Samples:**
- L-1, L-2, and L-3: Seam (a).
- L-4, L-5, and L-6: Seam (b).
- L-7, L-8, and L-9: Seam (c).

Samples taken at 4' intervals along each seam.

**Outcrop M**

**Location:** In south bank of drainage ditch parallel to and 70' south of State Highway 114. Outcrop is located 120' east of bridge just south of intersection Esters Road and State Highway 114.

**Formation:** Eagle Ford shale.
Description: Four seams are exposed in a 12' bank.

Seam (d): 7'4" above stream bed. White bentonite weathering pale yellowish orange. Shale below sandy and case hardened. 3" thick.

Seam (c): 4'10" above stream bed. Dark yellowish orange bentonite with concentric rings of darker staining. 1½" thick. Not sampled.

Seam (b): 1'7" above stream bed. Pale yellowish orange bentonite. Calcareous layers were present in shale at top of seam. 2½" thick.

Seam (a): 7" above stream bed. Very pale blue to pale blue weathering dark yellowish orange. Samples obtained were badly weathered. Seam was wet when sampled. 2" thick.

Samples: M-1, M-2, and M-3: Seam (a).
M-3, M-5, and M-6: Seam (b)
M-7, M-8, and M-9: Seam (d)
Samples were taken at 2' intervals along each seam.

FIGURE 2. A 10-inch bentonite bed has been cut by a small reverse fault. The holes in the bed were made during sampling.

Outerop S

Location: Outerop is ¾ mile south and ¼ mile west of intersection of State Highway 114 and Esters Road in the bank of a small stream just south of fence line.

Formation: Eagle Ford shale.

Description: A bentonite bed 9" thick. White to greyish yellow when fresh; weathering dark yellowish orange. The bed is traceable for 100 yards and becomes thinner and predominantly dark yellowish orange to the north. The bed is cut by a reverse fault causing it to be repeated in one part of the outcrop.

Samples: S-1 and S-2: 4' NE of fault.
S-3 and S-4: 7' NE of fault.
S-5 and S-6: 25' NE of fault.
S-7 and S-8: 40' NE of fault.
S-9 and S-10: 70' NE of fault.
(In dark yellowish orange bentonite.)
S-11 and S-12: at fault.

Outerop Q

Location: 200 yards west of the intersection of spur railroad and Belt Line Road in the south bank of railroad cut. Spur railroad is about 4 miles north of Grand Prairie, Texas.
Formation: Eagle Ford shale.
Description: A 3" seam of bentonite located near the top of the railroad cut. It is pale yellowish orange when fresh, but weathers dark yellowish orange. There are two very thin bentonite seams about 4' and 8' below the 3" bed. These were not sampled.
Samples: Q-1 and Q-2: Taken in 3" bed about 60' apart.

Procedure in Spectrographic Analysis

The following instruments are located in the Karcher spectrographic laboratory in the Physics Department of Southern Methodist University.

The spectrograph used was a 2.5 meter stigmatic instrument manufactured by Jarrell-Ash Inc. of Cambridge, Mass., Serial number JA-76-15a. The radius of curvature of the grating was 480 cm. giving a disperser of 7.0 A*/mm.

Samples were excited in a Jarrell-Ash arc stand, No. 66. A water cooled electrode jacket had been added and the stand had been adapted for arcing under controlled atmospheres.

The source unit used was a Baird Associated Inc. multisource, No. AK 1-58, which was equipped with an air-damped high frequency spark. The primary current was 12.5 amperes and the secondary voltage was 25,000 volts, with 40.0 microhenries inductance and 0.010 microfarads capacitance in the spark circuit.

For recording the spectra, we used 35 mm. Eastman-Kodak Spectrum Analysis No. 1 film in 21-inch strips. Film was developed in a vertical tray automatic developing unit built by National Spectrographic Company of Cleveland, Ohio. This developer maintains a constant temperature of 20°C and is designed to assure uniform agitation of the film. The developer used was Eastman-Kodak D-19 with a development time of five minutes.

A Film Projector Comparator Sensitometer, No. 5400, manufactured by Applied Research Laboratories of Glendale, California, was used to determine line densities. The instrument was equipped with a scanning slit having a width of 13 microns, and with a Karcher-Siedel modified scale. This scale is based on a reciprocal density function and is designed to give reliable film calibration for low density values.

*As our font lacks the Swedish open-a, "aas," I have indicated it, not by duplicated aa, but by a post-posed asterisk.
We prepared the electrodes from National Spectrographic carbons 3/16 inch in diameter. The upper electrodes were about 3 inches long and tapered to a sharp point, the length of the tapered section being about 3/8 inch. The lower electrode was about 31/2 inches long with one end hollowed out as an inverted cone; its lowest point 3/32 inch below the rim of the electrode.

The samples were pre-sparked for 20 seconds and then sparked, (i.e., with shutter open) for 30 to 40 seconds depending on variations in the samples. A controlled atmosphere of approximately 80% carbon dioxide and 20% oxygen was provided during sparking in order to reduce the intensity of the cyanogen band spectra in the vicinity of the aluminum line at 3944.0 A. We maintained a 3 mm. spacing between electrodes throughout the sparking period. The film recorded spectra in the 2200 A to 4000 A range.

Film calibration was obtained by use of a Hilger log sector disk. Calibration curves indicated the value of using the Karcher-Siedel scale and also indicated that the emulsion characteristics of the Kodak SA-1 were remarkably constant over a 100-foot spool of film.

Preparation of Standard and Unknown Samples

The working curves were prepared by the use of Bureau of Standards rock samples which had been ground to -300 mesh and heat-dried. Mixing of standard samples in various percentages (20% to 50%) with sodium tetraborate provided necessary dilution as well as a suitable flux.

In order to avoid surface contamination, bentonite samples were taken in the field from a 1-foot core. After the samples had been dried for 12 hours at about 150°C, they were ground to -200 mesh and thoroughly mixed with sodium tetraborate flux in the ratio of 20% bentonite to 80% flux.

After being mixed with flux, about 20 milligrams of the diluted sample was placed in a hollowed electrode. This was enough to fill the electrode completely. By use of an electric baffle oven, the electrodes were slowly heated to 300°C, for it had been found that rapid heating of the samples at low temperatures caused the expulsion of gases which blew the samples from the electrodes. After they had been heated to 300°C, the samples were rapidly heated to 780°C, and then held at that temperature for 3 minutes. This was suffi-
cient to melt the flux and form a small bead in the hollowed electrodes. The samples then were cooled and readied for sparking.

Working curves showing the relation between the intensity ratios and concentration ratios for the Si 2881.6 : Al 3944.0 and the Ca 3158.9 : Mg 2802.7 line pairs had been approved. These curves expressed only the relative variation of Si:Al and Ca:Mg ratios. As the curves were not checked with standard bentonite samples, any systematic error included in the values determined could not be detected.

Explanation of Statistical Table

S is standard deviation and is defined by the following relation: 

\[ S = \pm \sqrt{\frac{\sum d^2}{n}} \]

where \( d \) = deviation of individual values from mean (\( \bar{x} \)), and \( n \) = number of values.

Standard deviation expresses the reliability of a single observation.

The arithmetic mean (\( \bar{x} \)) is given by 

\[ \bar{x} = \frac{\sum x}{n} \]

where \( x \) = individual values.

In order that the reliability of single observations may be compared for sets of data having sufficient mean values, the standard deviation is expressed as a percentage. This value, called the relative deviation (\( C \)), is defined by: 

\[ C = \frac{S}{\bar{x}} \]

and is given as a percent ratio.

In Series L, M, and N, the mean value presented is based on data from three samples. The reliability of such an arithmetic mean is given by: 

\[ C_x = \frac{C}{\sqrt{n}} \]

where \( C \) = relative deviation for method used, and \( n \) = number of samples.

Tests of typical bentonite samples from outcrop CDN show the precision for Si:Al ratios to be approximately ±10% relative deviation and for Ca:Mg to be about ±23%. Sampling Tests, in which several samples taken from the same position at outcrop CDN, indicated that the sampling error exceeded ±20% relative deviation for both Si:Al and Ca:Mg ratios.\(^5\) These results show the spectrographic precision to be greater than sampling precision indicating that further refinement of the spectrographic technique is not necessary.

Stratigraphic Correlation of Bentonite

After sampling and spectrographic analysis had been

\(^5\)These data are not included in the following table. The precision limits were obtained by sparking the same sample twenty times and computing Ca:Mg and Si:Al ratios for each sparking.
## Statistical Table

<table>
<thead>
<tr>
<th>Precision Test</th>
<th>Sample</th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T-8</strong></td>
<td></td>
<td>( \bar{x} = 0.65 )</td>
<td>( \bar{x} = 6.9 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( s = 0.141 )</td>
<td>( s = 0.45 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( n = 11 )</td>
<td>( n = 12 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 22%</td>
<td>c = 6.5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S-(1-12)</strong></td>
<td></td>
<td>( \bar{x} = 0.89 )</td>
<td>( \bar{x} = 11.9 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( s = 0.24 )</td>
<td>( s = 3.00 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( n = 12 )</td>
<td>( n = 12 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 27.0%</td>
<td>c = 20.1%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>N-(1,2,3)</strong></td>
<td></td>
<td>( \bar{x} = 0.94 )</td>
<td>( \bar{x} = 8.13 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( s = 0.30 )</td>
<td>( s = 1.73 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( n = 9 )</td>
<td>( n = 9 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 32%</td>
<td>c = 21.3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T-(1-8)</strong></td>
<td></td>
<td>( \bar{x} = 7.17 )</td>
<td>( \bar{x} = 7.17 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( s = 0.94 )</td>
<td>( s = 0.904 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( n = 8 )</td>
<td>( n = 8 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 12.6%</td>
<td>c = 12.6%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>L-(1,2,3)</strong></td>
<td></td>
<td>( \bar{x} = 4.31 )</td>
<td>( \bar{x} = 4.31 )</td>
</tr>
<tr>
<td><strong>L-(4,5,6)</strong></td>
<td></td>
<td>( \bar{x} = 7.76 )</td>
<td>( \bar{x} = 7.76 )</td>
</tr>
<tr>
<td><strong>L-(7,8,9)</strong></td>
<td></td>
<td>( \bar{x} = 4.89 )</td>
<td>( \bar{x} = 4.89 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M-(1,2,3)</strong></td>
<td></td>
<td>( \bar{x} = 0.40 )</td>
<td>( \bar{x} = 5.12 )</td>
</tr>
<tr>
<td><strong>M-(4,5,6)</strong></td>
<td></td>
<td>( \bar{x} = 0.32 )</td>
<td>( \bar{x} = 6.51 )</td>
</tr>
<tr>
<td><strong>M-(7,8,9)</strong></td>
<td></td>
<td>( \bar{x} = 0.63 )</td>
<td>( \bar{x} = 8.00 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series Samples</th>
<th></th>
<th>Ca:Mg</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>E-(1,2,3)</strong></td>
<td></td>
<td>( \bar{x} = 0.68 )</td>
<td>( \bar{x} = 8.07 )</td>
</tr>
</tbody>
</table>
completed, an attempt was made to correlate the bentonite seams on field evidence alone. Stratigraphic control is difficult to establish in the Eagle Ford shale, because of a scarcity of outcrops. For this reason, it was necessary to assume a uniform dip of 60 feet per mile to the east for the Eagle Ford. The various composite sections (Chart I) are based on plane-table surveys as to elevation and horizontal position. The horizontal relations between the three composite sections were taken from correlated aerial photographs of the area; however, a rather inaccurate topographic map was used to obtain elevations.

The results of the projection of these beds into one strike-section is shown graphically in Chart I. Obviously, even allowing for 25% error in stratigraphic location of the beds, it is improbable that correlation can be correctly made between any beds except N and E. The correlation of N and E is supported by similarity in thickness as well as by stratigraphic location.

**Conclusions**

The relative deviations of samples taken from individual bentonite beds are shown to be only slightly greater than sampling deviation (See Statistical Table). It may be assumed that other bentonite beds in the area have similar characteristics; that is, the variations of Si:Al and Ca:Mg

---

6This dip is based on subsurface information obtained from deep water-wells in the vicinity of Dallas.
ratios along any one of them is approximate to the value of sampling deviation.

Chart I shows that mean values computed for individual bentonite beds differ significantly among themselves. Only in the case of bed N and E are the mean Si:Al ratios similar and it is important to note thickness and stratigraphic position. Beds S, N, and E are all similar in thickness, but bed S differs from the other two in vertical position in the section. Spectrographic data support the stratigraphic positioning of these beds.

The results of this investigation indicate that spectrographic analysis of bentonite beds provides data which, in addition to the usual field measurements, aid substantially in their correlation. By the methods described in this paper it might be possible to correlate bentonites in the Eagle Ford shale between Dallas and Waco and thus establish time-rock divisions within this formation.

REFERENCES


Ross, Clarence R. & Hendricks, Sterling B., (1945) Minerals of the Montmorillonite Group, USGS. Prof. Paper 205-B.

Taggart, J. N. (1953) Problems in Correlation of Terraces along the Trinity River in Dallas County, Texas, Master's Thesis in Geology, Southern Methodist University, Dallas, Texas (Unpubl.).

SELECTED SPECTROGRAPHIC BIBLIOGRAPHY


Harvey, Charles E. (1950) Spectrochemical Procedures, Published by Applied Research Lab., Glendale, California.


