UMIAT BENTONITE: AN UNUSUAL MONTMORILLONITE FROM UMIAT, ALASKA

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ABSTRACT

Numerous bentonite clays interbedded with shale and coal are exposed in the interfingering, Cretaceous sediments along the Colville River and its tributaries in northern Alaska. Two bentonite beds of high purity, ten to twelve inches thick are conveniently accessible at Umiat Mountain, four miles northeast of Umiat, Alaska. X-ray diffraction, x-ray fluorescence and other diagnostic techniques revealed the bentonite to be nearly pure montmorillonite with certain beidellitic characteristics. It is proposed that this clay be known as Umiat bentonite.

INTRODUCTION

Numerous extensive bentonite beds have been reported in northern Alaska (Detterman et al., 1963). These bentonites, some of which are interbedded with coal, are well exposed in interfingering Cretaceous sediments along the Colville River and its tributaries. Accurate field descriptions have been given, and stratigraphic relationships seem to be well understood, but as yet a systematic mineralogical characterization has not been reported. The present work was undertaken to provide this information and to uncover possible correlations between clay mineralogy and depositional environment.

Preliminary reconnaissance revealed that two bentonite beds of high purity, ten to twelve inches thick, are conveniently accessible on the south face of Umiat Mountain, about 4 miles northeast of Umiat, Alaska. These two beds and several others of lesser thickness lie in the basal portion of the Seabee formation (Whittington, 1956). The south face of Umiat Mountain consists of black, fissile shale with intercalated bentonites. The sequence is capped by a poorly consolidated subgraywacke. The outcrop is typical of Cretaceous sediments in this area. The rocks are semilithified and are folded into broad open structures. Post depositional lithological changes apparently have been minimal.

Field specimens of the Umiat bentonite are dark green on fresh fractures but cream to buff on weathered surfaces. Biotite flakes are abundant and more or less randomly distributed. The material had an in situ water content of about 20%. The beds fracture conchoidally and appear to be mineralogically homogeneous; no definite stratification within the beds is visible.

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About 100 pounds of bentonite were collected from the two large beds shown in Fig. 1. Portions of this material were studied by x-ray diffraction, electron microscopy and other techniques selected for the purpose of fully characterizing the clay fraction.

**Experimental Methods**

*Preparation of clays.* The calcium clay for x-ray analysis was prepared as follows: Approximately 10 g of material was soaked in 1 liter of deionized water and dispersed with a laboratory stirrer. The suspension was allowed to settle 20 cm for 16 hours in order to obtain the <2µ e.s.d. fraction. The clay fraction was then passed dropwise through a column containing calcium-saturated Amberlite IR-120 exchange resin. Oriented specimens were prepared by repeated centrifugation after the method of Kinter and Diamond (1956). Oriented mounts of lithium-saturated clay were prepared in a manner similar to that described above. The clay was first passed through a mixed bed (Fisher 903525) cation-anion exchange resin that removed soluble salts and converted the clay to the hydrogen form.
Then the suspension was immediately passed dropwise through a lithium-saturated column of Amberlite IR-120 resin.

**X-ray diffraction analysis.** A General Electric XRD-5 diffractometer equipped with a copper-target tube was used for the diffraction studies. The detector system utilized a G.E. No. 6 proportional counter. Peak intensities were obtained by multiplying peak heights, scaled from diffraction charts, by peak widths at half-height. Calcium-saturated oriented aggregates and randomly oriented powder specimens were analyzed in the dry and glycolated conditions over the angular range 2θ = 2 to 100°. A lithium-saturated oriented aggregate was heated for 12 hours at 250° C., and for 12 hours in glycerol at 85° C. (cf. Greene-Kelly, 1955). A diffraction pattern was obtained from this aggregate over the range 2θ = 2 to 35°.

**Electron microscopy.** Electron photomicrographs were obtained with an RCS-3F electron microscope operated at an accelerating voltage of 100 KV. The <2μ e.s.d. raw clay suspension was first passed through a hydrogen-saturated cation exchange resin; a drop of the suspension was then removed and placed on a collodion film supported by a 200 mesh copper grid. The suspension was evaporated to dryness and introduced into the interior of the microscope. During preparation and subsequent handling, the mount was protected against dust contamination.

**Exchange capacity.** The <2μ e.s.d. fraction of raw Umiat bentonite was passed through a hydrogen saturated Rohm and Haas IR-120 cation exchange resin and through a hydroxyl saturated Rohm and Haas IRA-400 anion exchange resin. This treatment removed the dissolved electrolytes present in the raw clay and left the hydrogen saturated Umiat clay suspended in deionized water. A suspension of hydrogen-saturated Wyoming bentonite was prepared in the same manner to serve as a standard for comparison. Nearly complete exchange was accomplished by restricting the total amount of raw clay passed through the resins to 10% of the total capacity of the exchange column before column regeneration. The hydrogen clay suspensions were titrated conductimetrically with 0.1 N NaOH; both suspensions were 0.6% clay by weight. The resulting data were plotted and the two points of inflection were interpreted as representing titratable hydrogen and aluminum. The second inflection point represents the exchange capacity of the clay (Lowe, 1955). From a knowledge of the titer at this point and the weight of clay in the titrated suspension, the exchange capacity was computed. A <2μ e.s.d. sample was also analyzed by the ammonium acetate method (Jackson, 1958).
eluted cations present in the raw clay were determined by the normal spectrophotometric methods.

**Specific surface area.** The specific surface area of the untreated field specimen was determined by nitrogen adsorption; a similar determination was made on untreated Wyoming bentonite for comparison. This method gives an estimate of external surface area only, since nitrogen does not penetrate into the interlamellar space. The total specific surface, assuming all lamellae are expandable, may be computed from the lattice parameters of montmorillonite to be about 800 m²/g. Thus a nitrogen adsorption surface area permits an estimate of the approximate number of lamellae per packet of platelets in the natural state.

**Differential thermal analysis.** The DTA curves for the untreated Umiat and Wyoming bentonites were obtained with an Aminco differential therm analyzer programmed to heat at 8° C. per minute. The reference sample was 40 to 140 mesh Al₂O₃; the analysis was done under air in an Inconel sample block.

Pore size distributions in the naturally occurring clays were obtained using the Aminco-Winslow mercury porosimeter operated to 15,000 psi corresponding to a calculated equivalent capillarv radius of about 0.01 μ.

**X-Ray fluorescence analysis.** Quantitative analyses of Sr, Mn and Ti in the bulk clay and <2μ fraction were performed using x-ray fluorescence methods. For this work, the spectrometer was equipped with a molybdenum tube, a lithium fluoride analyzing crystal, and a helium path. Ten thousand counts were accumulated on each peak and adjacent background; the resulting peak intensity, corrected for background, was compared with similar measurements obtained from the rock standards G-1 and W-1. Corrections were made to compensate for the matrix differences among samples and standards.

Dr. John Hower kindly did a major element analysis of the <2μ fraction by x-ray fluorescence. Details of the procedure are given by Hower et al. (1964).

**Results**

Figure 2 shows the x-ray diffraction pattern of a glycolated, oriented aggregate of the <2μ fraction of the Umiat bentonite, calcium-saturated. The exceeding regularity of the clay-organic complex is indicated by (a) the sharp diffraction maxima, (b) the presence of intense reflections through the 0014, and (c) the rational sequence of the 00l series; the standard deviation of d₀₀₁ is ±0.03 Å, based on reflections from the 005 through the 0014. In this respect Umiat bentonite is equivalent to Wyo-
Fig. 2. X-ray diffraction pattern of <2µ glycolated, calcium-saturated, Umiat bentonite.
The d-spacing of the 060 reflection (d = 1.500 Å) indicates that the Umiat bentonite is dioctahedral. This distinction is of some importance, for data given below indicate that, for some conditions, the dehydration characteristics of the lithium-saturated and heated clay are typical of beidellite and saponite. The dioctahedral character of the Umiat clay precludes classifying the Umiat bentonite as saponite.

Greene-Kelly (1955) has pointed out that some montmorillonoids lose their ability to expand in glycerol after lithium-solvation and heating. He suggests that lithium migrates into vacant octahedral lattice sites and neutralizes the lattice charge producing a nonexpandable pyrophyllite-like material. His work would indicate that normal montmorillonite (i.e., minerals in which the site of the charge is octahedral) undergoes this irreversible collapse, whereas beidellite (of tetrahedral charge) does not. Greene-Kelly’s technique has therefore been regarded as a useful means of distinguishing between montmorillonite and beidellite.

Clay-sized fractions of Umiat and Clayspur bentonite were treated according to the Greene-Kelly procedure and x-ray diffraction patterns shown in Fig. 3 were obtained. The chemical composition of Clayspur bentonite (Kerr et al., 1950) indicates that it is a normal montmorillonite, and accepting the Greene-Kelly criteria, the diffraction pattern of
Fig. 3 is consistent with this view; Clayspur bentonite remained collapsed to a \(d(001)\) of 9.7 Å in the presence of hot glycerol. The Umiat bentonite, on the other hand, expanded to a normal \(d(001)\) of 17.7 Å. On the basis of these data and the Greene-Kelly criteria, one could, therefore, conclude that the clay-sized fraction of the Umiat bentonite consists predominantly of beidellite.

An electron photomicrograph of the Umiat Bentonite is presented in Fig. 4. The mica-like nature of the thin clay particles is clearly evident. Individual lamellae cannot be distinguished but evidence of recently cleaved packets is clearly seen at (a); a good example of the crumpled and folded structures is located at (b). Except for the basal plane no well defined cleavage planes appear; this is characteristic of the 2:1 lattice clay minerals.
The cation exchange capacity of the <2μ fraction of raw Umiat bentonite was found by the ammonium acetate method to be 109 me/100 g dry clay. Of this 0.3 me was lithium, 102 me was sodium, 1.3 me was potassium and 5.6 me was calcium in the natural state. Thus it appears that the exchange complex is predominantly sodium saturated and the ratio of sodium to calcium is about 18 me to one. For comparison, the exchange capacity for Wyoming bentonite was determined by the same method to be 92 me/100 g clay. The titration curves of the two 0.6% hydrogenated clay suspensions are shown in Fig. 5. As has been shown by Low (1955), the first point of inflection corresponds to titratable hydrogen or hydronium ions whereas the second signifies the end point for the titratable aluminum ions present. The cation exchange capacity is, therefore, determined from the abscissa at the second point of inflection. For
Wyoming bentonite it is seen to be about 82 me/100 g clay, in general agreement with previously published values (Low, 1955). The end point for the Umiat bentonite, however, is seen to be about 91 me/100 g clay. The discrepancy between the values determined by the two methods should not be alarming, for this determination is sensitive and known to depend critically upon the methods employed. The significant point is that by either method the cation exchange capacity of Umiat bentonite was found to be about 10 to 15 me/100 g greater than that of Wyoming bentonite.

The specific surface area (external area) by nitrogen adsorption was found to be about 17.5 and 18.0 m²/g (±0.1; average of two determinations) for Umiat bentonite and Wyoming bentonite, respectively. In this respect there is no significant difference between the two clays. Since the total specific surface of 2:1 expanding lattice clays is known from unit cell dimensions to be about 800 m²/gm, both appear to contain on the average about 50 lamellae per packet. This estimate is consistent with the appearance of electron photomicrographs.

Differential thermograms for the two clays are shown in Fig. 6, and pore size distributions obtained by mercury intrusion (0.400 g, dried, field samples) are shown in Fig. 7. The result of the differential thermal
Fig. 7. Pore size distribution of Umiat bentonite compared with that of Wyoming bentonite by mercury intrusion of 0.400 g dried field samples.

Table 1. Results of X-Ray Fluorescence Analysis of Umiat Bentonite

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;2μ fraction</td>
</tr>
<tr>
<td>Titanium</td>
<td>824</td>
</tr>
<tr>
<td>Manganese</td>
<td>96</td>
</tr>
<tr>
<td>Strontium</td>
<td>225</td>
</tr>
</tbody>
</table>

Table 2. Major Element Analysis of Umiat Bentonite (<2μ)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.99*</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>18.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.38</td>
</tr>
<tr>
<td>FeO</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>3.08</td>
</tr>
<tr>
<td>CaO</td>
<td>1.61</td>
</tr>
<tr>
<td>Na₂O</td>
<td>not determined</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Assuming the C.E.C. to be 100 me/100 g, the formula can be shown as \((X_{0.42}) (Al_{1.45} Fe_{0.19^{2+}} Mg_{0.32}) (Si_{0.92} Al_{0.08}) O_{10} (OH)_2\).
analyses shows no differences between the two bentonites, and both curves exhibit only those features normally expected from a 2:1 expanding lattice clay. The porosity data reveal that in the natural state the Umiat bentonite has a somewhat larger number of 5 to 10μ and a smaller number of 20 to 50μ (equivalent cylindrical diameter) pores than does the Wyoming bentonite; otherwise the pore size distributions are also remarkably similar.

The results of the analysis of Umiat bentonite for trace elements by x-ray fluorescence appear in Table 1. The amounts of titanium, strontium and manganese reported in Table 1 are comparable to those reported for the API reference montmorillonite clay minerals (Kerr et al., 1950).

The major element analysis (neglecting H2O) of the calcium-saturated <2μ fraction is shown in Table 2.

DISCUSSION

The nomenclature of the montmorillonite clay minerals is now reasonably well defined. A comprehensive modern survey and bibliography has been published by MacEwan (1961). Definitions and terms used herein are in accord with his usage. The most common variety of montmorillonite has a dioctahedral structure and a lattice charge imbalance derived from the diadochic substitution of divalent cations for octahedral aluminum or ferric ions. Stoichiometrically, however, it is possible to derive a montmorillonite formula in which there are 4 octahedrally coordinated aluminum or ferric ions) per unit cell and some substitution of silicon by tetrahedral aluminum; consequently, the site of lattice charge is tetrahedral. Variations between end member structures of this type comprise the beidellite-nontronite series. Many of the older identifications of beidellite are in doubt (Ross, 1960), but recent work by Greene-Kelly (1955) and Weir (1960) has clearly demonstrated the existence of beidellite as defined above. Beidellite is probably of rare occurrence. The only clearly identified specimens are material from the type locality at Beidell, and the sample from Black Jack Mine, Idaho (Greene-Kelly, 1955).

Umiat bentonite re-expanded after lithium solvation, heating and glyceration; Wyoming bentonite treated in the same manner did not expand. Thus it is evident that this treatment was capable of producing irreversible collapse in montmorillonite (Wyoming bentonite) but not in the Umiat clay. According to Greene-Kelly's criteria, it then appears that the Umiat bentonite may be either (1) beidellite, (2) nontronite, or (3) saponite. The iron content (Table 1) is insufficient for nontronite, and the occurrence of a typical dioctahedral 060 d-spacing clearly precludes identification as saponite. Therefore, according to the Greene-Kelly criteria, Umiat bentonite must be classified as beidellite. The data of
Fig. 5 support this identification. The higher electrical resistance of a suspension of Umiat bentonite compared to a similar suspension of Wyoming bentonite, for all increments of NaOH added indicates a lower exchangeable ion activity for Umiat bentonite. This effect is anticipated in a suspension containing a clay having its electrical charge imbalance in the tetrahedral layer compared to one of octahedral charge, for in the former the exchangeable ions can reside closer to the site of electrical charge and may thus be more tightly held and, consequently, less dissociated.

The results of the Greene-Kelly treatment and the titration curve suggest that the Umiat Bentonite is beidellite. However, the major element analysis provides a formula corresponding to montmorillonite. Moreover, the infrared spectra of the Umiat and Wyoming bentonites are essentially identical, and Russell and Farmer have shown that beidellite and montmorillonite gives distinctive infrared absorption curves. The silica/alumina ratio obtained from a major element analysis is considered to be the best single criterion for distinguishing beidellite from montmorillonite. Unfortunately, if the analysis is done by x-ray fluorescence one cannot correct the results for the possible presence of amorphous silica. An attempt was made to resolve these contradictions, therefore, by a re-examination of the results obtained with the Greene-Kelly technique. The experimental conditions described above were duplicated and identical results were obtained. Then the procedure was altered slightly. The dispersed lithium-clay was flocculated with LiCl, centrifuged and dried. The slight excess of Li present as LiCl was not considered significant. When this material was heated to 250°, it changed from a gray-green to a distinct ferric oxide red. Glycerol solvation produced no expansion of this material.

Six other bentonites from the Umiat area, which we had tentatively identified as beidellite, were also re-examined after drying with excess LiCl. Each showed a marked color change with heating and a complete failure to expand upon glyceration. It appears that, for these clays, the dehydration characteristics are critically dependent on the presence of excess Li ions during heating. Wyoming bentonite showed no such behavior; no expansion with glycerol was noted for samples that were heated after column saturation, or after flocculation with LiCl.

It must be concluded from the chemical analysis and other data, that the Umiat bentonite is probably best classified as a montmorillonite but it differs significantly from Wyoming bentonite. The difference is manifested by a less dissociated ion exchange complex and a sensitivity to the presence of excess lithium ion when subjected to the Greene-Kelly treat-

1 James D. Russell (priv. comm.).
ment. If the latter property is found to be characteristic of other bentonites, then the Greene-Kelly criterion ought to be further investigated and used with caution. The distinct color change upon heating suggests that at high temperatures excess lithium may displace ferrous or ferric ions from the octahedral layer. This behavior is not understood at present, but is being studied further.

**Summary**

Major element, differential thermal, infrared, and x-ray diffraction data indicate that the Umiat bentonite is similar in most respects to Wyoming bentonite, and is, therefore, best classified as a montmorillonite. Titration curves indicate less dissociation of the exchange complex for the Umiat Bentonite, suggesting some structural and/or chemical difference between Umiat and Wyoming bentonite. The Umiat bentonite shows anomalous dehydration characteristics. Columnated lithium-clays subjected to the Greene-Kelly treatment show complete re-expansion with glycerol. If the lithium-clay is heated with excess LiCl, however, the dried material shows a marked color change and a complete loss of expandibility in glycerol.

**Acknowledgments**

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**References**


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