BEIDELLITE

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ABSTRACT

The mineral name beidellite has recently fallen into disrepute with mineralogists because many specimens so named before the advent of x-ray diffraction techniques proved on re-investigation to be mixtures. The clay from the Black Jack Mine, Idaho, was early described as a beidellite, and a re-investigation of its properties shows that it is a dioctahedral montmorillonite mineral which contains very little magnesium or iron. The term beidellite is retained for the Black Jack Mine mineral, and recommendations are made to clarify its definition.
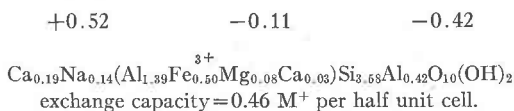
INTRODUCTION

In 1925, Larsen and Wherry gave the name of beidellite to a clay specimen from Beidell, Colorado, which was thought to be a distinct mineral species with definite chemical composition and refractive indices. Many clay rock specimens with similar chemical compositions and refractive indices were later named beidellites, and it seemed probable that beidellites, so defined, occurred more commonly than montmorillonites in many types of clay deposit. When Ross and Hendricks (1945) redefined beidellite as the aluminium-rich end-member of an isomorphous series of dioctahedral montmorillonites, the minerals they listed as beidellites had been identified primarily from their chemical compositions and refractive indices, but x-ray diffraction showed that most of these "beidellites" were mixtures containing other minerals. The composition of the Beidell specimen was among the first to be questioned; Grim and Rowland (1942) interpreted its DTA trace as showing a mixture of minerals. However, it is not certain that all samples of the Beidell specimen were mixtures, and it will be shown later that Nagelschmidt obtained a sample from the original Beidell specimen that probably contained beidellite.

Mineralogists are divided on the use of the term beidellite. Grim (1953 and personal comm.) stated that the term should be abandoned because the type-mineral was discredited, many specimens originally named beidellites are now known to be mixtures of other mineral species, and attempts to re-define the term would lead to still further confusion. MacEwan (1951), Brown (1955), Caillère and Hénin (1957), Mackenzie (1957), and Strunz (1957) all included beidellite in their classifications, whereas Brindley (1955), and Frank-Kamenetsky (1958) omitted it. However, Zvyagin and Frank-Kamenetsky (1959) later stated that beidellite should be used in the sense intended by Ross and Hendricks. Recently Ross (1959) proposed that the use of beidellite be discontinued

because there was no confirmed occurrence of a mineral with a structure and composition similar to that required by Ross and Hendricks' definition. As we think that the Black Jack Mine specimen represents a pure beidellite, in the sense intended by Ross and Hendricks, a difficulty has arisen in naming this mineral. After consultation with several mineralogists, we have decided to retain the name beidellite in the belief that the decision will be acceptable to most clay mineralogists.

PUBLISHED DATA FOR THE CLAY SPECIMENS FROM BEIDELL AND BLACK JACK MINE

Larson and Wherry (1917) first called the clay specimen from Beidell, Colorado, leverrierite but in 1925 renamed it beidellite. They gave optical and dehydration data and a chemical analysis. Nagelschmidt (1938) repeated the optical work, measured the exchange capacity, and calculated the unit formula from the analysis given by Larsen and Wherry,
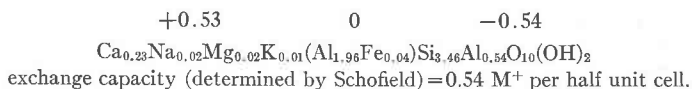
$$+0.52 \qquad\qquad -0.11 \qquad\qquad -0.42$$

$$Ca_{0.19}Na_{0.14}(Al_{1.39}\overset{3+}{Fe}_{0.50}Mg_{0.08}Ca_{0.03})Si_{3.58}Al_{0.42}O_{10}(OH)_2$$

exchange capacity $= 0.46$ M^+ per half unit cell.

Nagelschmidt also showed from x-ray data that the mineral had an expanding lattice, and that, except for a quartz reflection at 3.36 Å, the diffraction pattern from an air-dry specimen could be indexed with reference to an orthorhombic pseudo-hexagonal unit cell: $a = 5.17$ Å, $b = 9.00$ Å, $c = 15.2$ Å. Grim and Rowland (1942) published a DTA trace of the Beidell clay and interpreted it as showing that the specimen was a mixture of halloysite, illite and montmorillonite. X-ray photographs were taken of the specimen, but the patterns were described as poor and indicating only montmorillonite. More recently, Grim has stated (personal comm.) that further samples of the Beidell specimen from the same box in the U. S. National Museum were also confirmed as mixtures and consisted of differing proportions of various mineral species.

Nagelschmidt's x-ray data and the chemical analysis by Larsen and Wherry are evidence that the particular samples investigated were free from illite. The x-ray patterns showed no reflections corresponding to the 10 Å basal spacing of illite, and only a trace of potassium was present. Again, there was no x-ray evidence that halloysite was present, and the unit formula computed by Nagelschmidt had an inter-layer charge of 0.46–0.52 atoms per half unit cell, which is large for a montmorillonite mineral. An admixture of halloysite, with zero charge, would mean that the charge of the montmorillonite mineral present was even larger than the stated value. As the chemical analysis was by Larsen and Wherry and the exchange capacity was measured independently for Nagelschmidt it

is unlikely that either of these samples contained appreciable illite or a large proportion of halloysite. Foster (1954) showed that the beidellite formula, calculated from the analysis by Larsen and Wherry, was very similar to a two to three mixture of kaolinite and montmorillonite. However, if the value for the exchange capacity given by Nagelschmidt was approximately correct, it is extremely unlikely that this Beidell specimen was composed of two-fifths kaolinite, as the remaining montmorillonite would have had the high charge of 0.85 atoms per half unit cell.

The position of the Beidell specimen can be summarised as follows: measurements on the samples used by Larsen and Wherry, and by Nagelschmidt, are consistent with their containing a large proportion of beidellite, but there is too little information about either sample to establish their identity beyond doubt.

The sample of the clay from the Black Jack Mine, Idaho, used by us came from the U. S. National Museum (U.S.N.M. R4762) and almost certainly was part of the specimen described in earlier publications. The Black Jack Mine (BJM) clay was first described as a leverrierite gouge by Shannon (1924), who gave a chemical analysis and optical data. Ross and Shannon (1925) listed it as a beidellite. Nagelschmidt (1938) gave similar data for the Beidell and BJM specimens. The unit formula of the latter, calculated from the analysis by Shannon, was as follows:

$$+0.53 \qquad 0 \qquad -0.54$$
$$Ca_{0.23}Na_{0.02}Mg_{0.02}K_{0.01}(Al_{1.96}Fe_{0.04})Si_{3.46}Al_{0.54}O_{10}(OH)_2$$

exchange capacity (determined by Schofield) $= 0.54$ M^+ per half unit cell.

The x-ray data closely resembled those given for the Beidell specimen and showed an expanding lattice and an orthorhombic pseudo-hexagonal unit cell: $a = 5.14$ Å, $b = 8.93$ Å, $c = 15.1$ Å (additional reflections similar to the *hkl* reflections given in Table 2 were recorded but not indexed). Ross and Hendricks (1945) included the BJM beidellite in their montmorillonite-beidellite series and calculated a unit formula from the analysis by Shannon. Greene-Kelly (1955) gave a partial chemical analysis for the BJM sample used by Nagelschmidt and showed that the lithium-saturated mineral suffered no loss of expanding properties when heated to 200° C. A DTA trace of the BJM-beidellite published by Greene-Kelly (1957) is reproduced in Fig. 1.

Similar data have been published for both the Beidell and BJM specimens, but hitherto no investigator has produced evidence from x-ray diffraction, chemical analysis, and subsidiary techniques, for one subsample of either specimen. Had there been such data for the purer of the Beidell samples, the validity of the species might not now be in doubt,

and to avoid further ambiguity we have re-investigated the BJM specimen fully.

EXPERIMENTAL RESULTS

Quartz was the only crystalline impurity detected in the specimen. The content was small, and most x-ray diffraction patterns showed no quartz reflections.

Powder patterns were obtained from specimens cut from the untreated clay, in which calcium and magnesium were the dominant cations. Additional values of the variable basal spacing were obtained from oriented-

TABLE 1. X-RAY DIFFRACTION DATA; BJM-BEIDELLITE, AVERAGE BASAL SPACINGS IN Å

Specimen Treatment	Inter-Layer Cation		Natural Clay (Ca, Mg)
	Na	Ca	
heated to 280° C.	9.65	9.6	9.55
in air 20° C.	12.45	15.2	15.1
in water	—*	18.6	18.6
in ethylene glycol	16.85	16.85	16.8
in glycerol	17.65	17.6	17.6

* The specimen dispersed to a gel, and no discrete basal reflections were detected.

aggregate specimens saturated with sodium or calcium ions. Table 1 lists the basal spacings measured for the beidellite after various treatments. From three to nine orders of rational sequences of reflections were measured and the values of the basal spacing in Table 1 are means of the product of each spacing and its order (d_{001} was omitted because absorption caused erroneously low values).
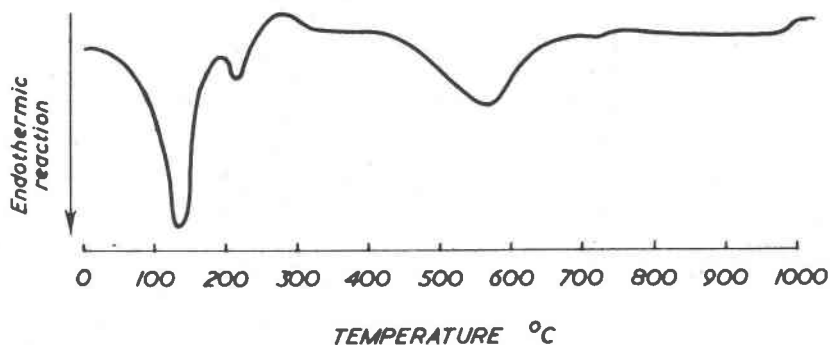

FIG. 1. DTA trace of Ca-BJM beidellite (Greene-Kelly, 1957).

Table 2 shows x-ray data for a Ca-BJM aggregate with inter-layer glycerol. The specimen was set with the sedimentation surface at 40° to the x-ray beam so that $00l$ reflections were recorded on one half of the film and hkl reflections on the other (MacEwan 1951). The spacings usually designated as d001 and d060 in montmorillonite minerals were used to calculate unit cell dimensions for an orthorhombic pseudo-hexagonal unit cell. Calculated values of spacings corresponding to such a cell are given

TABLE 2. X-RAY DIFFRACTION DATA FOR Ca-BJM BEIDELLITE WITH INTER-LAYER GLYCEROL

d(calc.) Å	d(obs.) Å	hkl	d (calc.) Å	d (obs.) Å	hkl
—	17.57	001	2.22 ⎫		041 ⎫
4.48 ⎫		020, 110 ⎫	⎬	2.19	
⎬	4.42		2.17 ⎭		042
4.35 ⎭		021 ⎭	1.695 ⎫		240, 310, 150 ⎫
3.99	3.95	022	⎬	1.693	
3.56	3.54	023	1.687 ⎭		241 ⎭
3.15	3.17	024	1.664	1.663	242
2.77	2.76	025	1.628	1.623	243
2.59 ⎫		200, 130 ⎫	1.581	1.573	244
⎬	2.57		1.526	1.528	245
2.56 ⎭		201 ⎭	—	1.498	060, 330
2.48	2.52	202	1.295	1.293	400, 260
2.37	2.36	203	1.244	1.243	420, 350, 170
2.23 ⎫		204 ⎫	1.121	1.122	440, 080
⎬	2.24		0.979	0.979	460, 530, 190
2.24 ⎭		040, 220 ⎭	0.863	0.864	390, 600

in the first column of Table 2 and appropriate indices in the third; the agreement between observed and calculated spacings is good. The diffraction patterns showed reflections additional to those observed for montmorillonites (MacEwan 1951), but which could be indexed as the $02l$, $20l$, $04l$, and $24l$ series by reference to the unit cell already mentioned. The indexing of these hkl reflections is evidence for a single species, and their occurrence in a montmorillonite mineral suggests that it is more ordered than usual.
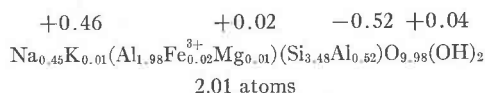
CHEMICAL ANALYSIS

Before they were analysed chemically, samples of the BJM-clay were examined for impurities optically and by x-ray diffraction, saturated with sodium ions, and, when necessary, dispersed and sedimented to remove

quartz. Three complete and three partial analyses were made on ignited
sodium-saturated material using the analytical methods of Shapiro and
Brannock (1956). The results, expressed as the means of the oxides of
each element, were:

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	Total
59.30	36.11	0.50	0.10	0.02	0.11	3.98	100.12

Exchange capacity: 130 m.eq./100 g (ignited weight)
Loss on ignition: 6.3% (ignited weight)

When the analysis is expressed as the unit formula of a 2:1 layer-lattice
mineral, the half unit cell has the following composition:

$$\overset{+0.46}{} \qquad \overset{+0.02}{} \quad \overset{-0.52}{} \overset{+0.04}{}$$
$$Na_{0.45}K_{0.01}(Al_{1.98}Fe^{3+}_{0.02}Mg_{0.01})(Si_{3.48}Al_{0.52})O_{9.98}(OH)_2$$
$$2.01 \text{ atoms}$$

Thermal Data

The principal features of the Ca-BJM DTA trace are well resolved, low
temperature endothermic peaks at 140° and 210° C., the de-hydroxylation
peak at 560° C., and a small exothermic effect at 970° C., at the tempera-
ture of recrystallization of the lattice. There is no high temperature endo-
thermic peak. Equilibrium dehydration measurements showed that, as a
percentage of the ignited specimen weight, 6.3 per cent of water was lost
between 300° and 950° C.

Electron Micrographs

The micrograph in Fig. 2 is of a sample of Na-BJM dispersed on the
electron microscope grid, and indicates the range and distribution of flake
sizes in the specimen. The micrograph in Fig. 3 is of the fraction less than
0.07μ e.s.d. with which dispersion of the sodium-saturated specimen pro-
duced extremely thin flakes. The flakes in both micrographs are pre-
dominantly lath-shaped, varying in length from 30 to 0.1μ, and the de-
tailed outlines of dispersed flakes are very similar irrespective of the size
of the flakes. This again suggests that the specimen is largely composed of
a single mineral species.

Discussion

We have assumed that the chemical analysis of the BJM specimen
could be calculated as the unit formula of a 2:1 layer-lattice mineral. Be-
cause of the special position of beidellite and because Foster (1954) has
adversely criticised the formula of the Beidell specimen, this assumption
will be examined in detail.

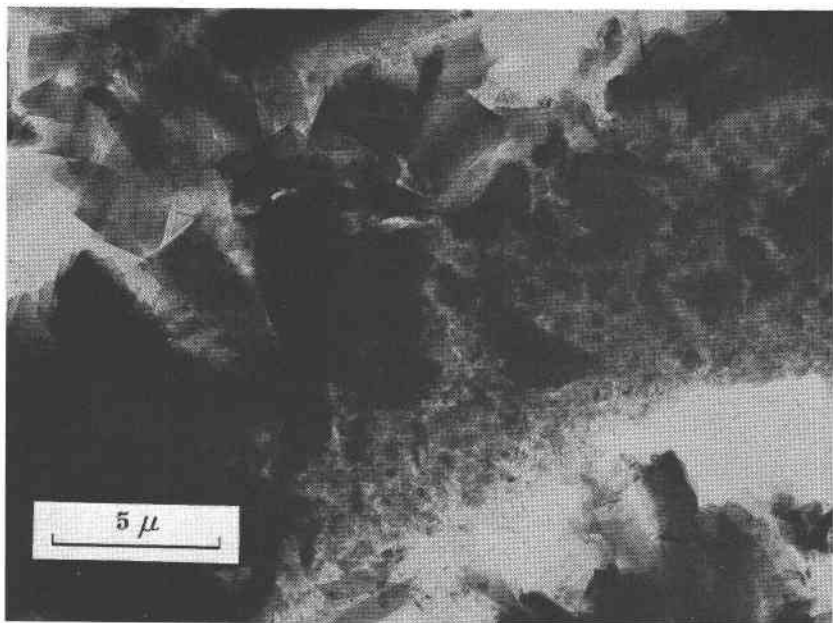In the chemical analysis the sum of the oxides of silicon, aluminium

Fig. 2. Electron micrograph of Na-BJM beidellite. Unshadowed print. A general view of the specimen dispersed in situ on the electron microscope grid, showing the range of flake size.
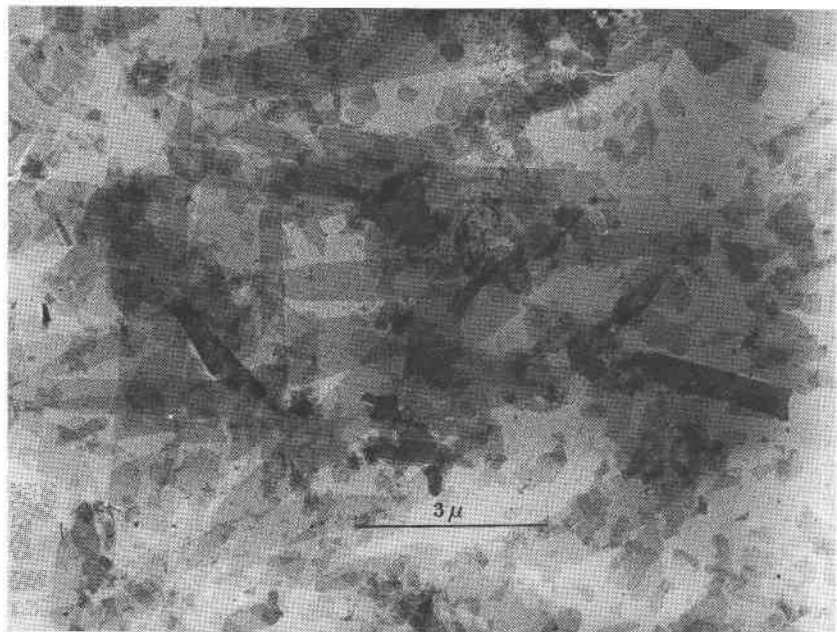

Fig. 3. Electron micrograph of Na-BJM beidellite. Unshadowed print. Part of the $<0.07\mu$ e.s.d. fraction showing the range of size and outline details of the flakes, most of which are a single 2:1 lattice unit in thickness.

and the exchangeable cations comprises 99.4 per cent of the total weight of the ignited material, and the sum of the potassium and magnesium oxides equals only 0.2 per cent. Clearly these figures exclude any significant contamination with illite and montmorillonite. Other contaminants that were mentioned for the Beidell specimen were halloysite and kaolinite, but their presence in the BJM specimen is excluded by the x-ray diffraction data. Again, the uniformity of the particle morphology throughout the whole range of particle size and the small loss on ignition, 6.3 per cent for the temperature range 105–950° C., makes it unlikely that amorphous oxides of silica and alumina are present. Thus all the evidence suggests that the quartz-free BJM specimen is composed of a single mineral species, and that it is a genuine end-member beidellite.

NOMENCLATURE

The mineral name beidellite was defined by Larsen and Wherry (1925), effectively re-defined by Ross and Hendricks (1945), and again slightly modified by MacEwan (1951). Other variants and usages of the term will not be referred to here.

The original definition of beidellite by Larsen and Wherry was: "As no mineralogical name appears to have been assigned to a compact crystalline compound with the 1:3 ratio represented in the Colorado mineral, we now propose to re-name it:— Class: Silicates; Sub-class Hydrous Metasilicates; Division: $R : Si : H_2O = 2 : 3 : x$. Name: Beidellite."
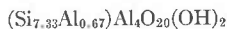
This definition was modified by Ross and Hendricks as follows: "The mineral name beidellite will be used for the member (of the montmorillonite-beidellite series) having a large amount of Al^{3+} in tetrahedral coordination. A suitable formula is:

$$Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$$
$$\downarrow$$
$$Na_{0.33}$$
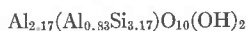
MacEwan (1951) gave the following unit formula for beidellite:

$$(Si_{7.33}Al_{0.67})Al_4O_{20}(OH)_2$$
$$\downarrow$$
$$M^+_{0.67}$$

MacEwan made the end-member beidellite an exactly dioctahedral mineral, a practice later followed by Brown (1955). Foster (1951) supported the correctness of this view when she determined the exchangeable cations of ten of the montmorillonite specimens used by Ross and Hendricks, and showed that, after allowing for exchangeable magnesium, the calculated formulae were much nearer to those of dioctahedral minerals

than had been supposed. We, therefore, prefer to use the dioctahedral formula for beidellite until there is experimental evidence to prove that genuine di-tri-octahedral minerals exist.

Ross and Hendricks defined beidellite as a mineral with a large amount of aluminium in tetrahedral co-ordination. Greene-Kelly (1955) clarified this definition when he proposed that the term beidellite should be used for a mineral with more than fifty per cent of the lattice charge produced by tetrahedral substitution of aluminium for silicon. In recent years some mineralogists have replaced beidellite by the term aluminian montmorillonite for minerals with the approximate tetrahedral composition $Si_{3.80}Al_{0.20}$. Our work on the Black Jack Mine beidellite suggests that the concept of Ross and Hendricks (as modified by MacEwan) of an isomorphous montmorillonite-beidellite series is valid for naturally occurring minerals. If this is so, the term aluminian montmorillonite is unnecessary and its use should be discontinued as the boundary between beidellite and montmorillonite has been adequately defined by Greene-Kelly.

Recommendations on the use of the name beidellite are:

1. Beidellites are montmorillonite minerals, and the term should only be used as a species name for the appropriate member of the montmorillonite group.
2. Naturally-occurring beidellite specimens should ideally contain no non-exchangeable potassium.
3. The term beidellite should be used for the aluminium-rich members of the montmorillonite-beidellite series of minerals, as proposed by Ross and Hendricks (1945), but the composition of the ideal endmember should be restricted to that of an exactly dioctahedral mineral, as proposed by MacEwan (1951) and Brown (1955).
4. The Black Jack Mine beidellite should be regarded as a typical endmember beidellite.
5. Beidellites and montmorillonites should be divided at the composition at which the lattice charges from octahedral and tetrahedral substitution equal one another (Greene-Kelly 1955).
6. Use of the term aluminian montmorillonite should be discontinued.

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Manuscript received March 29, 1961.