

# PROPOSED REFERENCE ILLITE FROM THE OUACHITA MOUNTAINS OF SOUTHEASTERN OKLAHOMA<sup>1</sup>

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## ABSTRACT

An exceptionally pure illitic clay is present in outcrops of the Blaylock Formation (Silurian) in the Ouachita Mountains of southeastern Oklahoma. Unweathered claystone samples from this unit in Beavers Bend State Park have been found to consist of a well-crystallized illite or hydrous mica. Impurities commonly found in illites such as non-clay minerals and non-micaceous clay minerals are conspicuously absent. The sample cannot be classified as a mica because it is hydrated and the particle-size distribution is in the clay size range. A detailed examination of the deposit suggests that it may have value as a reference illitic clay mineral.

## INTRODUCTION

Extensive deposits of reference clays are exceedingly rare in the geologic column. This is particularly true for illites, which commonly are mixed with other clay minerals and quartz. The American Petroleum Institute's Reference Clay volume lists many good reference kaolinites, montmorillonites, and even halloysites, but only two reference illites are included and these are not particularly pure (Kerr *et al.*, 1951). Consequently, the discovery of an occurrence of relatively pure illite in the Ouachita Mountains of southeastern Oklahoma prompted an investigation, sponsored by the Oklahoma Geological Survey, to determine the feasibility of using this material as a reference illite.

Samples were obtained from an outcrop of the Blaylock Formation (Silurian) in Beavers Bend State Park 7.5 miles north-northeast of Broken Bow, Oklahoma. The location of the outcrop is 100 yd east of the entrance to the park on the north side of State Highway 21A in the center of N $\frac{1}{2}$ , NE $\frac{1}{4}$  of section 16, T. 5 S., R. 25 E., McCurtain County, Oklahoma (Fig. 1).

<sup>1</sup> Publication authorized by the Director, Oklahoma Geological Survey.

The outcrop is composed of alternating, discontinuous  $\frac{1}{2}$ - to 1-ft layers of fine sandstone and claystone. The sandstone layers are fine-grained (mean particle size = 0.125 mm) greenish gray, commonly silica-cemented with minor clay bonding, plagioclase feldspar-bearing orthoquartzites. Authigenic chlorite has been reported from some areas of the Blaylock Formation (Hones, 1923, p. 98) but at this locality chlorite is decidedly an unimportant part of the sandstone. At most localities the sandstone is cut by numerous thin quartz veins. The veins average 2–3 mm in width.

The claystone layers are composed of fine-grained, dark olive-gray clay that weathers to light olive-gray and reddish gray. A few small stringers of

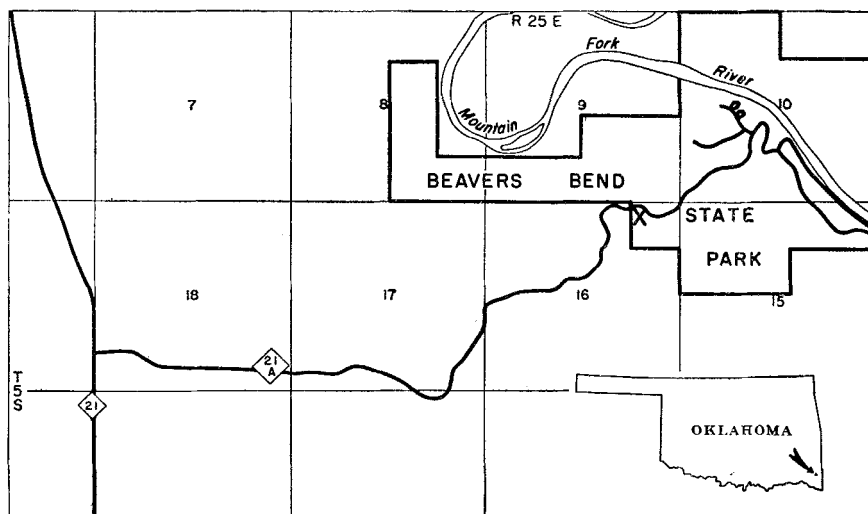


FIGURE 1.—Locality of Beavers Bend illite sample.

fine quartz sand grains are present in some layers. Locally cross-cutting quartz veins (2–3 mm wide) extend from the sandstone layers into and through the claystone layers. The upper and lower surfaces of weathered rhombohedral fracture plates are chatoyant because of the preferred orientation of the *c*-axes of the clay minerals.

### METHODS OF EXAMINATION

Samples were prepared by dispersing the clay in distilled water, using ultrasonic and high speed blender techniques. The dispersed material was sedimented on glass and porcelain slides and air-dried in a laboratory hood for X-ray diffraction study. The  $< 2 \mu$  fractions were obtained by centrifuging dispersed clay samples of bulk material and sedimenting the remaining suspensions upon glass slides. All X-ray diffraction patterns were obtained

with Norelco and Siemens X-ray diffractometers and recorders, using nickel-filtered, copper radiation.

Powder X-ray diffraction patterns of finely ground samples of claystone packed into aluminum sample holders also were run to establish the type of mica polymorphism. In addition, film strips were obtained from powder samples, using a 114.6 mm Debye-Scherrer camera.

A complete wet-chemical analysis of the clay was made from a typical bulk sample.

## RESULTS

Figure 2 shows X-ray diffraction patterns of the bulk material and the  $< 2 \mu$  fraction of a typical sample of clay from the studied locality of the Blaylock Formation. The patterns show a relatively well-crystallized illite

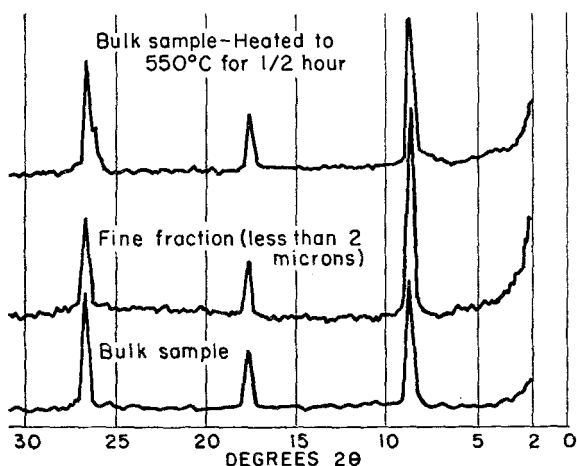


FIGURE 2.—X-ray diffractograms of illite from Beavers Bend State Park. Patterns obtained from sedimented samples run on a Norelco X-ray diffractometer and recorder using Ni-filtered, copper radiation at a setting of 35 kV and 18 mA. Scintillation counter detector with appropriate PHA and scale factor settings.

with no discernible impurities. A few diffractograms from bulk samples show the presence of a small amount of quartz. Figure 2 also contains one diffraction pattern of a sedimented bulk sample that has been heated to  $550^{\circ}\text{C}$  for one-half hour. The presence of a doublet at the  $3.33 \text{ \AA}$  position is caused by a diffraction peak from the porcelain slide.

A packed-powder sample diffractogram (Fig. 3) compared with those of Yoder and Eugster (1955, p. 245) shows this illite to be of the 2M variety and the 060 spacing suggests both di- and trioctahedral character. This suggestion is confirmed by the chemical analysis (Table 1). The analysis can be considered to be that of a good illite, as defined by Brown (1951, p. 155), because it contains less potassium and more water than a well-crystallized mica.

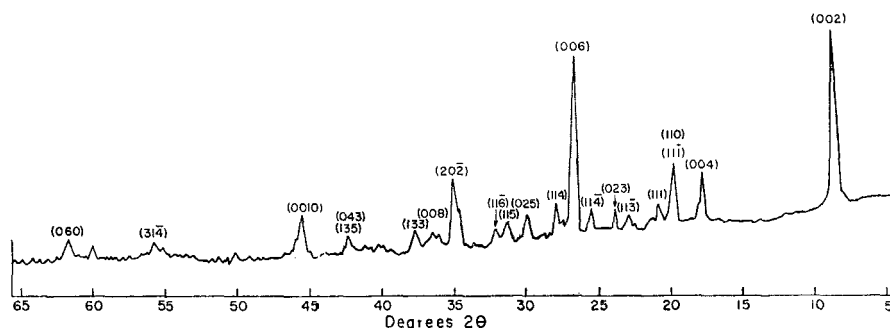


FIGURE 3.—Powder X-ray diffractogram of illite from Beavers Bend State Park. The pattern shows the typical 2M type of mica polymorphism. Diffraction maxima indexed by comparison with data from Yoder and Eugster (1955). Pattern obtained with a Siemens X-ray diffractometer and recorder using Ni-filtered, copper radiation at a setting of 35 kV and 18 mA. Scintillation counter detector with appropriate PHA and scale factor settings.

TABLE 1.—CHEMICAL ANALYSIS OF BEAVERS BEND ILLITE

Constituent	Percent
SiO <sub>2</sub>	49.85
Al <sub>2</sub> O <sub>3</sub>	23.68
Fe <sub>2</sub> O <sub>3</sub>	6.60
FeO	1.87
TiO <sub>2</sub>	1.40
CaO	0.12
MgO	1.86
K <sub>2</sub> O	6.64
Na <sub>2</sub> O	0.34
CO <sub>2</sub>	Nil
SO <sub>3</sub>	—
ZrO <sub>2</sub> + (V <sub>2</sub> O <sub>5</sub> )	0.72
H <sub>2</sub> O +	6.80
Oxide total	99.88

Analysis run on finely ground, thoroughly mixed bulk sample dried at 140° C  
 Analyst: J. A. Schleicher, Oklahoma Geological Survey.

### DISCUSSION

Calculation of the structural formula of this mica by Marshall's (1949) method is given in Table 2. Assignment of ions to the tetrahedral and octahedral positions agrees closely with the typical three-layer sheet silicate. The presence of both ferrous and ferric iron and of magnesium as well as

TABLE 2.—CALCULATION OF STANDARD FORMULA OF BEAVERS BEND ILLITE.  
ASSIGNMENT OF ATOMS TO UNIT CELL FOLLOWING PROCEDURE OF MARSHALL (1949)

Metals as oxides	Results of chemical analysis		Gram-equivalents of cationic constituents		Metal atoms per unit cell	Metal atoms assigned to tetrahedral layer	Metal atoms assigned to octahedral layer	Gram-equivalents of cations assigned to octahedral layer
	As reported	Dry basis	As calculated	On basis of 44 total				
SiO <sub>2</sub>	49.85	53.56	3.565	27.275	6.819	6.819		
Al <sub>2</sub> O <sub>3</sub>	23.68	25.44	1.497	11.453	3.818	1.181	2.637	7.911
Fe <sub>2</sub> O <sub>3</sub>	6.60	7.09	0.266	2.035	0.678		0.678	2.034
FeO	1.87	2.01	0.056	0.428	0.214		0.214	0.428
MgO	1.86	2.00	0.099	0.757	0.379		0.379	0.758
TiO <sub>2</sub>	1.40	1.50	0.075	0.574	0.144		0.144	0.576
ZrO <sub>2</sub> (+V <sub>2</sub> O <sub>5</sub> )	0.72	0.77	0.025	0.191	0.048		0.048	0.192
CaO	0.12	0.13	0.005	0.038	0.019			
K <sub>2</sub> O	6.64	7.13	0.151	1.155	1.155			
Nb <sub>2</sub> O	0.34	0.37	0.012	0.092	0.092			
H <sub>2</sub> O+	6.80							
	99.88	100.00	5.751	43.998	13.366	8.000	4.100	11.899

Calculated negative charge on tetrahedral layer = - 0.101 equivalents.

Calculated negative charge on octahedral layer = - 1.181 equivalents.

Total negative charge per unit cell of 44 atoms = - 1.282 equivalents.

Available base-exchange capacity assumed to arise only from octahedral layer,  $(0.101) \cdot (5.751/44) \cdot (1000) = 13.2$  meq/100 g dry clay.

Experimental determination of base-exchange capacity by titration of H-clay = 12.7 meq/100 g.

TABLE 3.—CALCULATION OF STRUCTURAL FORMULA OF BEAVERS BEND ILLITE.  
ASSIGNMENT OF ATOMS TO UNIT CELL FOLLOWING PROCEDURE OF BROWN AND NORRISH (1952)

Oxides	Atomic proportions (gram atoms)		Atoms per structural unit				Unit cell contents		
	Oxygen	Cations	Si	Tetrahedral	Octahedral	Inter-layer			
SiO <sub>2</sub>	1.6591	0.8296	6.7101	6.7101					
Al <sub>2</sub> O <sub>3</sub>	0.6967	0.4645	3.7570	1.2899	2.4671				
Fe <sub>2</sub> O <sub>3</sub>	0.1239	0.0826	Fe <sub>2+</sub>	8.0000	0.6681				
FeO	0.0260	0.0260	Fe		0.2103				
MgO	0.0461	0.0461	Mg		0.3729				
TiO <sub>2</sub>	0.0350	0.0175	Ti		0.1415				
ZrO <sub>2</sub> (+V <sub>2</sub> O <sub>5</sub> )	0.0117	0.0059	Zr		0.0477				
CaO	0.0021	0.0021	Ca		0.0170	0.0170			
K <sub>2</sub> O	0.0705	0.1410	K		1.1405	1.1405			
N <sub>2</sub> O	0.0055	0.0110	Na		0.0890	0.0890			
H <sub>2</sub> O+	0.3774	0.7548	H	2.1050 = 0.7017 (H <sub>3</sub> O)		0.7017			
	0 = 3.0540		O	4.0000 = 4.0000 (OH)		1.9482			
	99.88%			24.6397 - (H <sub>3</sub> O + OH) = 20		3.9076			

Multiplication factor to convert atomic proportions to atoms per structural unit:

$$O \cdot n = 24 + y = 3.0540n = 24 + y \quad \text{where } y = \text{number of H}_3\text{O ions.}$$

$$H \cdot n = 4 + 3y = \frac{0.7548n = 4 + 3y}{n = 8.0883}$$

Base-exchange capacity:

$$\frac{\text{Equivalents of exchangeable ions}}{n} \times 1000 = \frac{(2) \cdot (0.0170) + 0.0890}{8.0883} \times 1000 = 15.2 \text{ meq/100 g of dry clay.}$$

aluminum in the octahedral layer supports the idea of a mixed di- and trioctahedral configuration.

The base-exchange capacity computed from the Marshall calculation is 13.2 meq/100 g of dry clay. The mean base exchange capacity, determined experimentally by titration in triplicate, is 12.7 meq/100 g. The titration was run by first converting the sample with Rohm and Haas Co. IR-120 cation-exchange resin to a hydrogen clay and then titrating with a 0.1N sodium hydroxide solution. The calculated value of 13.2 meq/100 g and the experimentally determined value of 12.7 meq/100 g of dry clay are in close agreement. These values are lower than the 20–35 meq/100 g of a dry clay normally given for illites (Bradley and Grim, 1961, pp. 231–232). Possible reasons for this difference in base-exchange capacities are (1) larger grain size of the Beavers Bend illite, and (2) the presence of small amounts of montmorillonite in many of the previously described illites.

Investigations by Brown and Norrish (1952) into the reasons for a lower potassium and higher water content of illite as compared with muscovite have led them to the speculation that hydronium ions may substitute at sites normally filled by potassium ions. Accordingly, the chemical analysis obtained for this illite has been recalculated, following the method described by Brown and Norrish (1952, p. 930). The results are given in Table 3. Structural assignments of cations as determined by the Brown and Norrish computation are consistent with the structure assumed for illitic minerals; e.g. 3.91 cations compared with a theoretical value of 4.00 in the octahedral layer, and 1.95 interlayer cations compared with the theoretical value of 2.00. The computed base-exchange capacity resulting from the Brown and Norrish calculation is 15.2 meq/100 g of dry clay as compared with the experimental determination of 12.7 meq/100 g.

The aluminum substitution in the tetrahedral layer resulting from the Marshall calculation is 14.8 percent and from the Brown and Norrish calculation is 16.1 percent. Grim (1953, p. 67) states that illites commonly have about one-sixth (16.7 percent) of the tetrahedral silicon replaced by aluminum.

The preliminary investigation which has been conducted upon this clay suggests that it is a remarkably good reference material, because of the absence of other clay minerals and the presence of an insignificant amount of quartz in some samples and complete absence in others. A thorough study of the Beavers Bend illite and a comparison with other reference illites are being made by the Oklahoma Geological Survey.

#### ACKNOWLEDGMENTS

Among those of the staff of the Oklahoma Geological Survey, the writers wish to thank Mr. John A. Schleicher, geochemist, for making the chemical analysis and Mr. Roy Davis, chief geological draftman, for drafting the illustrations. We also wish to thank Dr. Carl C. Branson, Director, for authorizing publication of this paper.

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