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ILLITE FROM FOND DU LAC COUNTY, WISCONSIN

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ABSTRACT

Especially pure, well-crystallized illite from Marblehead, Wisconsin is present in laminated clay pockets in Burnt Bluff Group (Silurian) dolomites. Analysis of this clay shows a lack of quartz and other clay minerals more commonly found associated with illite in other occurrences. Particle size, potassium content, and degree of hydration reinforce the *x*-ray examination in the designation of the Marblehead material as illite.

INTRODUCTION

An especially pure, well-crystallized illite from Fond du Lac County, Wisconsin has been used as a reference clay sample in the Clay Mineralogy Laboratory at the University of Illinois for the past two years. Accumulation of data for this clay material over this period allows a refined characterization of the mineral in regard to structure, composition, and many physical and chemical properties.

Samples of the Marblehead illite from the Burnt Bluff Group (Silurian) were initially obtained by J. G. W. Soderman during the course of field investigations of Silurian bioherms of the eastern and southeastern Wisconsin area (Soderman, 1962). The following description of the illite occurrence is based on Soderman's investigation.

In the quarry of the Western Lime and Cement Company (NE $\frac{1}{4}$, Sec. 7, T 14 N, R 11E) at Marblehead, Wisconsin, the uppermost 77 feet of the Burnt Bluff Group are exposed. The Burnt Bluff Group is capped by *Pentamerus*-rich beds of the Schoolcraft Formation (Manistique Group), while at this location, the base is not exposed. The strata are thin bedded and may exhibit irregular surfaces, especially above stromatoporoidal biostromes.

The illite occurs as large pockets of laminated clay commonly above an irregular surface approximately eighteen feet above the quarry floor. "Small poorly preserved shells (probably ostracods) and minute muscovite flakes extracted from the clay indicate that it is not a product of weathering and secondary concentration but a normal sedimentary deposit" (Soderman, 1962, p. 49). Other clays occurring as thin beds and partings higher in the section also contain illite, however, with variable amounts of quartz and chlorite present as impurities.

SAMPLE ANALYSIS

The illite sample was prepared for analysis by dispersing the clay in distilled water with disaggregation accomplished by gentle stirring. A portion of the dispersed bulk sample was sedimented on a glass slide by air drying. The remainder of the dispersed sample was allowed to settle until the less than two micron fraction could be drawn off. Oriented aggregates of this less than two micron size fraction were made on glass slides by air drying, and on porous plates by the centrifugation method of Kinter and Diamond (1956). Representative portions of the dry bulk sample were ground to less than 200 mesh size and utilized for powder diffraction analysis. A representative part of the less than two micron size fraction was analyzed chemically.

X-ray diffraction analyses were made with a Norelco diffractometer with nickel filtered copper radiation, and appropriate pulse height analyzer settings. The *x*-ray diffraction patterns of the oriented bulk sample, and the less than two micron fraction are shown in Fig. 1. Treatment of the less than two micron fraction oriented slides by heating to 550° C. for one hour, and by exposure to an ethylene glycol atmosphere for seventy-two hours shows no significant change in the location of the basal reflections. The heat treatment produces a slight sharpening of the diffraction reflections, while exposure to glycol induces the development of only a slight asymmetry in the first basal reflection. Upon the basis of these diffraction traces, it is concluded that five per cent or less mixed layering is present in the Marblehead material.

Examination of the less than 200 mesh powder diffraction pattern shows the Marblehead material to be of a $2M_1$ polymorphic type. The position of the (060) reflection (d = 1.5033 Å) discloses the dominant dioctahedral character of the illite. Unit cell dimensions based upon the *x*-ray diffraction data are: a = 5.207 Å, b = 9.020 Å, c = 20.48 Å, $\beta = 94°52'$.

The total exchange capacity of the Marblehead illite has been determined by a number of investigators over the two year period. The use of both calcium and ammonium fixation methods has resulted in an average value of 20.99 meq per 100 grams for this material.

The specific surface area of the Marblehead illite measured by nitrogen adsorption methods is found to be 68.1 square meters per gram (Berger, 1964).

Optical examination of the illite was made by standard oil immersion techniques. The material is found to be non-pleochroic, and biaxial negative ($X \perp 001$) with a 2V of approximately 5°. Birefringence was not measured, but appears by visual estimation to be extremely low. Refractive indices were found to be: $\beta = 1.537 \pm .002$, $\gamma = 1.575 \pm .002$ (α not determined).

These refractive index values are in agreement with other optical data for illites (Grim *et al.*, 1961), and are significantly lower than the generally observed values for fine grained muscovite.

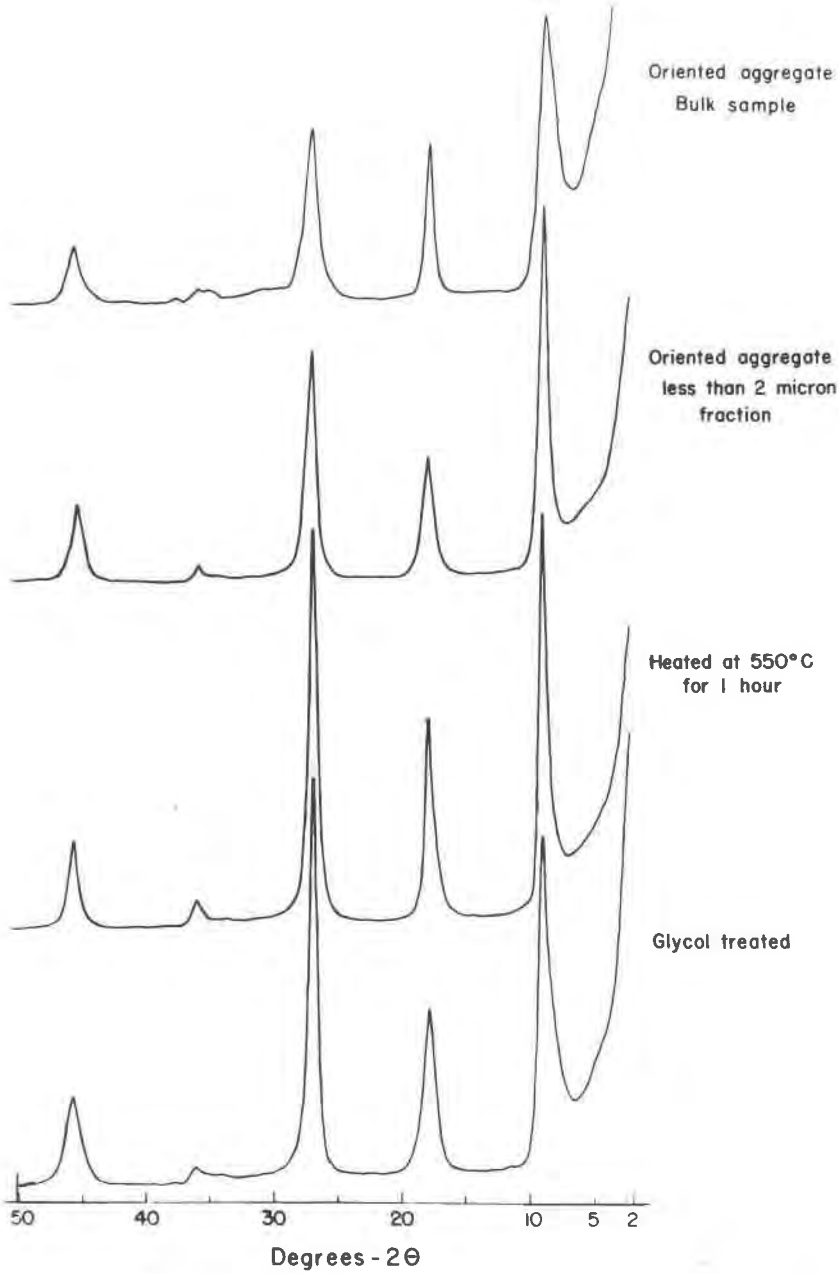

FIG. 1. *X*-ray diffraction patterns of oriented samples.

Chemical and Structural Analysis

Chemical analysis of a representative portion of the less than two micron fraction of the Marblehead material is shown in Table 1. Calculation of the ionic populations according to the methods of Marshall (1949) and Brown and Norrish (1952) are shown in Table 2. The calculations according to Marshall disclose a slight degree of intermediate di-trioctahedral character present due to substitutions for Al in the octahedral positions. This has also been shown for illites of other studies (*i.e.* Mankin and Dodd, 1963).

The Brown and Norrish calculations, in which hydronium ions are postulated as occupants of interlayer sites produced by a deficiency of potassium ions, are somewhat inconsistent with the ideal assumed illite structure, primarily in regard to the interlayer constituents. The octahedral cations total 3.85 in comparison to a theoretical value of 4.00 for dioctahedral structures.

Substitution of Al for silicon in the tetrahedral portions of the layered structure equals 11.6 per cent for the Marshall calculations and 12.9 per cent by calculation according to the Brown and Norrish method. This implies the substitution of one alumnium in eight silicon sites in comparison to the 16.7 per cent aluminum substitution (one-sixth of the tetrahedral sites) commonly accepted (Grim, 1953).

Extremely well-oriented aggregates of the Marblehead material by centrifugation on porous plates produced a regular sequence of basal reflections of 20.10 Å period. One-dimensional Fourier projection of the illite structure computed from the observed intensity data, and based upon the calculated structures derived from the chemical analysis and unit cell contents is shown in Fig. 2. Comparison of the observed and calculated structure amplitudes for models derived from both the Marshall and Brown and Norrish calculations indicate that the Marshall model containing approximately 0.5 H_2O molecules per unit cell in interlayer positions agrees most closely with the complete observed structural plot (R=.105).

In Fig. 2, the areas of the electron density maxima for the octahedral and tetrahedral positions agree with the total atomic numbers of the ions occupying these sites, and indicate confirmation of the semiquantitative nature of the structural analysis.

Discussion

All samples which have been examined of the Marblehead clay material have been found to be exclusively mono-mineralic. Contamination of the illite by quartz, chlorite, or other clay minerals common to numerous other illite occurrences, is in this case, conspicuously absent.

TABLE 1. CHEMICAL ANALYSIS OF REPRESENTATIVE LESS THAN 2 MICRON FRACTION

Constituent	Per Cent
SiO_2	52.87
Al_2O_3	24.90
Fe_2O_3	0.78
FeO	1.19
MgO	3.60
CaO	0.69
Na_2O	0.22
K_2O	7.98
H_2O^-	2.56
H_2O^+	6.73
Ign Loss	6.36
TiO_2	1.02
P_2O_5	—
Total	99.61

Analyst: J. Witters, Illinois State Geological Survey.

TABLE 2. ASSIGNMENT OF ATOMS TO UNIT CELL

		1	2
Non Exchangeable Alkalies	K^+	1.3615	1.3410
	Na^+	.0554	.0554
	Ca^{2+}	.0989	.0974
			H_3O^+ .6657
	Total	1.5158	2.1595
Tetrahedral layers	Si	7.0724	6.9645
	Al	.9276	1.0355
	Total	8.0000	8.0000
Octahedral layer	Al	2.9974	2.8207
	Fe^{3+}	.0789	.0776
	Fe^{2+}	.1334	.1314
	Mg	.7174	.7069
	Ti	.0955	.1013
	Total	4.0266	3.8479
Al sub in tetrahedral layer		11.6%	12.9%

1—calculated according to Marshall, 1949.
2—calculated according to Brown and Norrish, 1952.

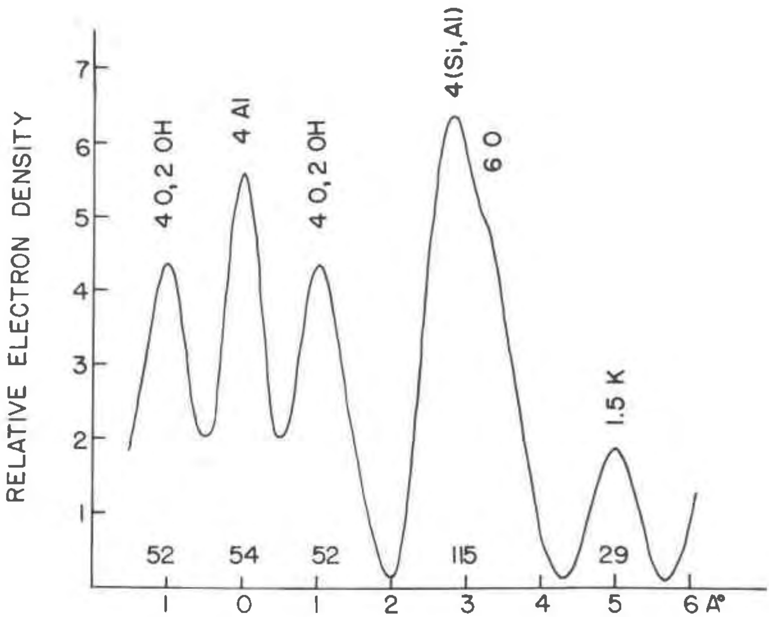

FIG. 2. One-dimensional structural projection of the Marblehead illite.

However, perhaps the most notable feature of this illite is the presence of only a slight amount of any mixed-layer material. Numerous physical and chemical treatments conducted with the Marblehead clay during the past two years have failed to disclose any evidences which could indicate the presence of more than approximately five per cent mixed-layering. This, coupled with the potassium content, degree of hydration, and other basic properties of the clay, in comparison to well-crystallized muscovite, allows designation of the Marblehead material as "illite."

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Professor R. E. Grim has read a preliminary manuscript.

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