

X-RAY DATA ON A FRACTIONATED REGULARLY
INTERSTRATIFIED CLAY

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ABSTRACT

A 1:1 regularly interstratified clay was examined by X-ray diffraction and shown to be a chlorite:expandable clay mixture. Expandability was not related to particle size. Edge effects of small particles cannot be directly correlated with expansion, charge density or other parameters.

INTRODUCTION

Our intent at the outset of this study was to provide quantitative data pertinent to a suggested relationship of expandability and particle size in clay minerals (Jonas, 1961; Jonas and Roberson, 1960, 1966). We hoped to examine by X-ray diffraction a number of substantially pure essentially regular mixed layer clays and utilize the Fourier transform technique (MacEwan, 1956). Difficulty was encountered in obtaining materials that exhibited a range of particle sizes in the clay region and had the desired X-ray characteristics. Results reported herein were based on data collected from a single specimen that exhibited naturally a spread of particle sizes. The X-ray aspects of this clay and its behavior upon heating indicated that it was similar to a mineral described by Earley, Brindley, McVeagh, and Vanden Heuvel (1956).

GEOLOGIC SETTING

Geologically, the clay is found in cuttings from sands, silts, and silty shales of Cretaceous age in a well near Mambone, Mozambique. It is the predominant clay mineral for almost 3000 feet of section with only minor amounts of illite and kaolinite in association. The rocks are believed to be marine in origin, but the origin of the long-spacing clay is unknown (it could be authigenic). X-ray diffraction and structure analyses were done on samples which contain about 30 percent quartz, 20 percent feldspar, 8 percent calcite (in part from fossils), and rare pyrite.

Earley and Milne (1956) described a long-spacing regularly interstrati-

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fied montmorillonite-chlorite from basalt from an unspecified locality in Mozambique. Basalts have been found in this well, also, but they are several thousand feet deeper in the well. Likewise, they contain traces of a longspacing clay, but neither its exact nature, nor its relationship to the clay described by Earley and Milne have been determined.

EXPERIMENTAL

The clay was separated into various size fractions by sieve, sedimentation, and centrifuge methods. All sizes reported are equivalent spherical diameter. The fractions were $>100\mu$, $50-100\mu$, $3-50\mu$, $2-3\mu$, $1-2\mu$, and $<1\mu$. Care was taken to promote clean separations.

Portions of the four smallest size fractions were sedimented onto glass slides and X rayed after various treatments: (a) room temperature at 65 percent R. H., (b) room temperature in dry air (obtained by passing compressed air through a column of drierite), (c) vapor and liquid glycerol and ethylene glycol, (d) heating for 1 hour at temperatures from 150° to 650°C in 100°C increments, (e) water vapor in a pressure cooker at 105°C for 1 hour. The heated samples were X rayed in a dry atmosphere and the water vapor-treated samples were X rayed in a wet atmosphere. All X-ray data were recorded with a Philips diffractometer and Ni-filtered Cu radiation with a scintillation counter and pulse amplitude discrimination. X-ray data were taken in duplicate.

RESULTS

The quantity of clay varied with size fraction, more was concentrated in the smaller ranges. Quartz and feldspar made up the $>50\mu$ fractions. The amount of these minerals decreased with particle size and only a minor amount of quartz was present in the smallest size fraction. A small quantity of 10 \AA (illite) material and a small quantity of 7 \AA (kaolinite) was detected in all fractions. No attempt was made to insure that equal quantities of clay were present on every slide subjected to X-ray analysis.

X-ray patterns taken under ambient conditions at room temperature and after organic solvation on different size fractions were virtually identical with respect to peak positions and relative intensities. Larger size fractions gave progressively weaker patterns which we attributed to less material diffracting and, perhaps, to poorer orientation of individual particles. A representative diffraction trace of the clay at room temperature is reproduced in Figure 1, and portions of two traces of different size fractions treated with ethylene glycol are shown in Figure 2. The salient features of the pattern shown in Figure 1 are duplicated in Table 1. All of these patterns gave a nearly rational series of orders with a long

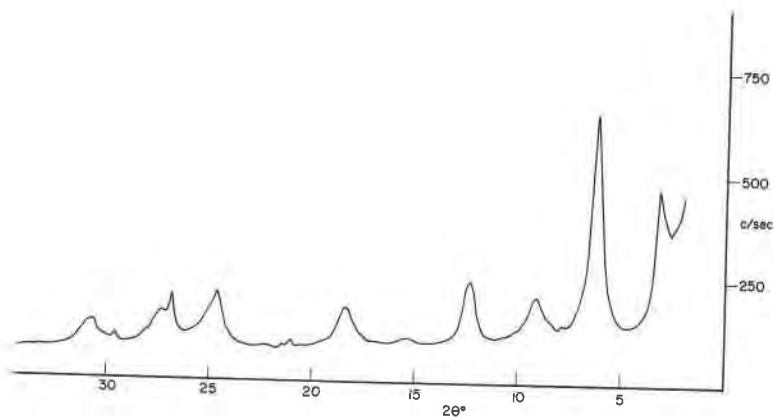


FIG. 1. X-ray pattern of clay fraction air-dried at 65 percent R.H.

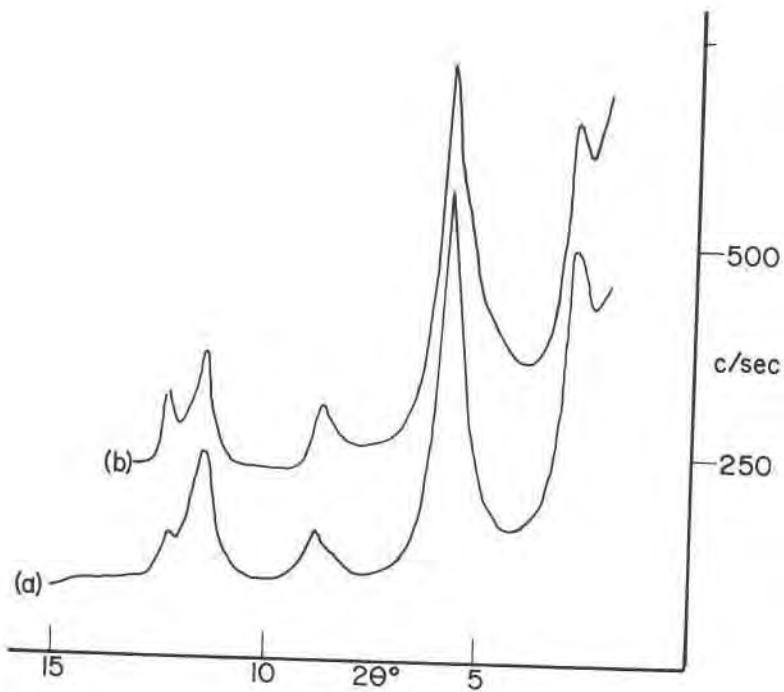


FIG. 2. Portion of X-ray patterns of glycol-solvated (a) minus 1μ and (b) $3-50\mu$ fractions. The intensity scale refers to (a) which is $4\times$ that of (b).

spacing of about 29 Å with water, 31 Å with glycol, and 32 Å with glycerol. Fourier transforms of the X-ray data simply reflected the 1:1 regular nature of the clay and indicated no variation in expandable layers with particle size. Oriented aggregates prepared for X-ray examination were made as thin as possible to avoid deterioration of line profiles. The thickness of these clay aggregates was 0.001 inch as measured by a micrometer. A "transparency factor" that had the form $(1 - e^{-2\mu \text{ tesc } \theta})$ was applied to the I/I_0 values prior to using these values to generate the transforms. A computer program was written in FORTRAN II to calculate the transforms.

TABLE 1. X-RAY DATA OF 1:1 CHLORITE : EXPANDABLE CLAY AT ROOM TEMPERATURE AND 65 PERCENT R. H.

| Order | $d(\text{Å})$ | I/I_0 |
|------------------------------|-------------------|---------|
| 1 | 27.6 ^a | 204 |
| 2 | 14.1 ^a | 344 |
| 3 | 9.72 | 56 |
| 4 | 7.15 | 49 |
| 5 | 5.75 | 3 |
| 6 | 4.82 | 25 |
| 7 | — | — |
| 8 | 3.60 | 24 |
| 9 | 3.27 | 14 |
| 10 | 2.90 | 10 |
| — mean $d = 29 \text{ Å}$ | | |

^a Not included in calculating mean d .

A measurement of the (060) spacing on an irregularly oriented powder indicated that the clay was trioctahedral.

The results of the dehydration studies showed a progressive change from an ordered structure through a disordered stage to another ordered structure with increasing temperature. Upon passing dry air over the sample the low angle peak was replaced by a low intensity broad band that centered at 29 Å and the remaining peaks were broadened and dif-fused. No evidence of the low angle band remained at 350°C. At 550°C a new peak appeared at 22–23 Å and the remaining peaks were noticeably sharpened and stood in approximate integral order. A progressive color change to red was observed on heating that indicated the loss of lattice water as low as 250°C. This behavior is implied by the work of Addison and Sharp (1963) which indicated dehydroxylation is accompanied by the simultaneous oxidation of iron.

DISCUSSION

The solvation and heating experiments indicated that this material was essentially a 1:1 interstratified chlorite:expandable clay. These substances have been discussed by Martin Vivaldi and MacEwan (1960). The exact nature of the expandable layers in this and similar clays is not easily determined. Upon solvation with water or organic molecules these expandable layers behaved the same as do true montmorillonite. Upon heating they eventually collapsed to approximately 9.6–10 Å and formed a regular 22–23 Å interstratification with a 13–14 Å component but, unlike montmorillonite, they collapsed with difficulty.

Our data do not permit a detailed discussion of the nature of the interlayer portion of the expandable layers but suggest an incomplete brucite-type substance. The progressive dehydration and consequent disordering through a random mixed layer stage is cited as evidence. An alternative is that equilibrium may not have been reached at any given temperature below 550°C which would indicate that caution must be used in the interpretation of dehydration data from these substances. The basis for the foregoing statement is the fact that montmorillonite dehydrates quickly and completely at low temperatures or under a stream of dry air.

The results on the fractionated samples indicated no variation in expandability with particle size for this clay. While no generalizations can be made on the basis of the data from one sample, exceptions to the hypothesis that expandability and particle size are inversely related (Jonas and Roberson, 1960) can occur. This result led us to examine the conclusions upon which this hypothesis is based.

Expansion of clay layers is a function of a complex array of factors, one of which is the nature of the substance sorbed. Polar molecules must perform work upon being fixed in the interlayer space. If the work required is greater than the energy released on sorption, no molecules will be sorbed. Separation occurs when the binding energy is less than the work that can be performed by the polar molecules. The work required to separate adjacent sheets equals the area of the sheets times their charge density times the work required to separate unit charge the same distance, which in turn equals the work performed per molecule times the number of molecules sorbed. Particles of unequal size that have the same charge density sorb a constant number of molecules per unit area, *i.e.*, the interlayer molecules have an identical orientation. The foregoing emphasizes that the work-per-unit-area on sorption is independent of particle (area) size. Since an unlimited supply of polar molecules is inherent in these experiments, particles of unequal size will expand or not

depending on whether the energy released on sorption per molecule exceeds the work required per molecule. The areal extent of compositionally identical particles of the same charge density affects expansion only to the extent that atypical edge effects are more predominant for small particles. It is unlikely that these edge effects and consequent expansion can be directly correlated at present with charge density or other factors such as tetrahedral aluminum content.

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