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CLAY MINERALS INTERMEDIATE BETWEEN ILLITE AND MONTMORILLONITE

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During recent investigations of the effects of crystallite size on properties of three-layer clay minerals a series of size fractions of a montmorillonite was obtained. With the natural exchange cations, the 2–4 μ fraction of the clay expanded when solvated with ethylene glycol. After exchanging the natural interlayer cations for either Na^+ or K^+ or Ca^{2+} a portion of the fraction collapsed to a 10 Å d-spacing even when soaked with ethylene glycol. In spite of the fact that these interlayer cations established a strong enough bond between the silicate layers to resist expansion the cations were exchangeable under mild laboratory methods of exchange.

It appears that this material may represent a missing link in the series between montmorillonite and illite. Montmorillonite is normally recognized by interlayer expansion that can be caused by the relatively weak adsorption of water as well as the stronger adsorption of ethylene glycol regardless of the type of ion occupying the interlayer position. These ions are fully exchangeable with ions from salt solutions of moderate concentration. Illite, on the other hand, resists expansion with either water or ethylene glycol, and the interlayer cations are not exchangeable except under long-term treatments with concentrated solutions. A portion of the material described herein (Fraction TA) after exchange with Na^+ or K^+ or Ca^{2+} resembles illite in that it does not expand, but the interlayer ions are exchangeable like those in montmorillonite.

Fraction TA was separated from a Gulf Coast Tertiary bentonitic clay. In addition to the expandable clay, the fraction contains no more than 30% kaolinite; quartz and mica were also present in the silt fraction of natural clay. The mineralogical properties of this sample are not thought to be unique; it is similar to other Gulf Coast Tertiary bentonites described by Roberson (1964).

A high speed centrifuge was used to obtain several size fractions among which was the 2–4 μ fraction which is discussed in this paper. This relatively coarse fraction was divided into three equal portions which were saturated with 2N solutions of KCl, NaCl, and $CaCl_2$, respectively. This exchange reaction, which was repeated to assure as complete exchange as possible, was allowed one hour to reach equilibrium. The clay was then washed free of excess soluble salts by concentrating the clay by centrifugation and diluting with demineralized water. The washing was continued until the supernatant liquid was chloride free by the $AgNO_3$ test. In addition to this test, the supernatant liquid was analyzed by flame photometry to determine if any soluble ions were present.

The cation exchange capacities of the K^+-clay, Na^+-clay, and Ca^{2+}-clay were then obtained by flame photometry after leaching the homoionic clays with a 2N solution of ammonium acetate. The cation exchange capacity data are shown in Table 1.

TABLE 1. CATION EXCHANGE CAPACITIES FOR FRACTION TA.

Cation Composition	Meq/100g.
natural	47
Na^+	51
K^+	41
Ca^{2+}	52

Examination of the *x*-ray diffraction patterns, some of which are shown in Fig. 1, reveals the following:

(1) After glycol solvation, some of the layers diffract at 10 Å in the K^+-clay and Na^+-clay and Ca^{2+}-clay samples, but 10 Å layers are absent or present in very low concentrations in the natural fraction. This shows that some of the expanding silicate layers of the untreated fraction have been rendered non-expanding when exchanged with K^+ or Na^+ or Ca^{2+}.

(2) The intensities of the 17 Å peak in the patterns show that the amount of expanding material has been reduced considerably in the K^+-treated sample, somewhat less in the Na^+-clay, and even less in the Ca^{2+}-clay. Presumably, all the layers that do not diffract at 17 Å after treatment have been converted to non-expanding 10 Å diffracting layers. The intensity of the 17 Å peak may be a more sensitive indication of the amount of conversion than is the height of the 10 Å peak.

(3) When the Na^+-clay is saturated with Ca^{2+} there is a reduction in the 10 Å peak indicating that Ca^{2+} exchanges for some of the Na^+ and re-expands layers.

(4) There is a more intense 10 Å peak for the K^+-treated and Na^+-treated clay at 60% RH than there is after glycolation indicating that fewer of the layers will expand at 60% RH than will expand when solvated with ethylene glycol.

(5) Discrete phases of 10 Å and 17 Å predominate; and there is little indication of random mixed-layering.

(6) Fewer 10 Å layers are formed when finer fractions are saturated with Na^+ or K^+. Ca^{2+} saturation of finer fractions produces no layers that diffract at 10 Å.

Interlayer potassium and ammonium ions are well-known for their ability to bind adjacent silicate layers together strongly enough to prevent expansion. Sodium and calcium ions, on the other hand, have been thought of as being sufficiently different from potassium and ammonium in some way (ionic radius, ion hydration) to prevent them from binding the silicate layers together. The data presented here demonstrate that both sodium and calcium can bind clay layers together, and their ability to do so is related to a particle-size dependent factor. Both sodium and calcium are less effective in producing this bond than is potassium. Any layer that can be collapsed by interlayer sodium ions can also be collapsed by potassium ions, but the reverse is not true.

The question of whether or not all exchangeable ions must come from

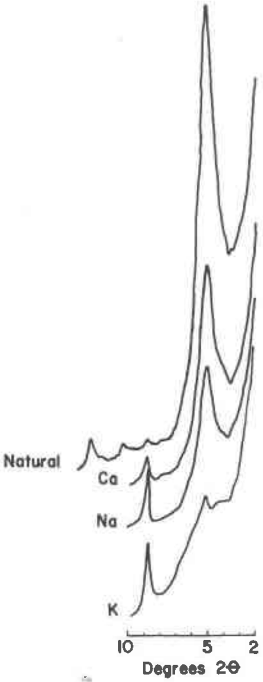

FIG. 1. X-ray diffraction patterns (CuKα radiation) of glycolsolvated Fraction TA in natural state, K^+-treated, Na^+-treated, Ca^{2+}-treated. All samples were air-dried before glycol solvation.

layers that expand can also be faced with these data. A comparison of the CEC values with the diffraction patterns of Fraction TA definitely shows that ions from non-expanding interlayers are being exchanged by normal methods. If there were no unexchangeable cations on any of the treated clays (Table 1), their CEC values should all be the same. Indeed, the Na^+-clay and Ca^{2+}-clay have very nearly equal values. The reduction in CEC from the Na^+ and Ca^{2+} level (51–52 meq/100 g) to 41 meq/100 grams from the K^+-clay, indicates that an estimated less than 20% of the ions on the three-layer clay have been rendered unexchangeable after the kaolinite dilution is taken into consideration. In comparison, it can be judged from the diffraction pattern that more than 80% of the three-layer clay has collapsed to 10 Å. Therefore, more than half of the layers have collapsed but are still exchanging their K^+ ions. Essentially all of the Na^+ and Ca^{2+} interlayer ions on the collapsed clay are exchangeable.

In three-layer clay minerals, the interlayer surface charge varies continuously from a high value for mica downward through illite, then to materials like Fraction TA and finally to montmorillonites. This series also parallels a continuous variation in crystallite size. Mica occurs in large crystals. Illite is smaller, and all montmorillonites consist of extremely small crystals in spite of the fact that there is a considerable variation in size. Samples consisting entirely of montmorillonite can be separated according to size into fractions that have different properties.

Fractionation of certain illitic and mixed-layered montmorillonite-illite shales has been shown to concentrate expanding layers in the fine fraction (Weaver, 1958 and Hower, 1963). The intermediate size fractions would be expected to have combinations of some of the properties of illite and some of montmorillonite.

Weaver (1958) has discussed a three-layer expanding clay mineral that will collapse to 10 Å when K^+-treated and resist expansion. This material is thought to be a weathering product of mica. It is described as illite with only the inter-layer K^+ ions having been replaced and the silicate layer having been unchanged to any marked degree. Restoration of the original illite or mica can be accomplished simply by artificially supplying the necessary K^+ ions. On the other hand, when Fraction TA is treated with K^+ it does not have all the properties ascribed to illite.

A resume of the diagnostic properties for identification of the various members of the three-layer clay series is shown in Fig. 2. The relative particle size range (and hence the surface charge range according to Jonas, 1960) for Fraction TA is shown relative to other clays in the series.

Fraction TA is composed of a range of particle size crystallites in the coarse montmorillonite part of the series. Its size and charge are somewhat smaller than those of illite or the stripped mica as is indicated by

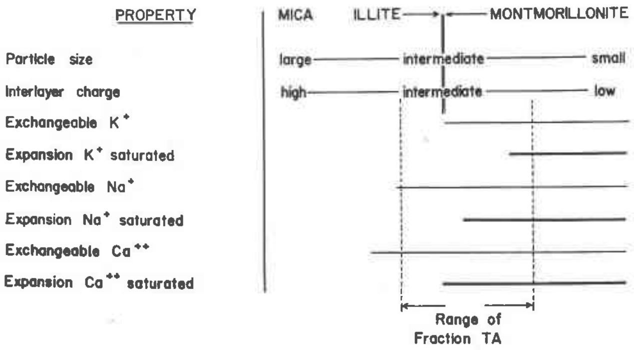

FIG. 2. Cation exchange and expansion properties for the mica-montmorillonite mineral series.

the replaceability of the cations. The crystallite size and charge are greater than those of montmorillonite as is indicated by its resistance to expansion.

It should be restated here that Fraction TA resulted from an effort to isolate a limited range of crystallite sizes. Clays consisting of crystallites whose sizes vary over a much wider range should be expected to have more complex combinations of properties.

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