

CLAYS and CLAY MINERALS

at a glance

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Neil A. Miner Award

Short Course on Layer Silicates

FLINT CLAY AND A FLINT-CLAY FACIES

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Flint clay is defined as a sedimentary, microcrystalline to crystalline clay (rock) composed dominantly of kaolin, which breaks with a pronounced conchoidal fracture and resists slaking in water. The environment of deposition is commonly lowlying paludal, in basins in either clastic silicate rocks or in karstic carbonates. It is inferred that parent illitic and/or kaolinitic clay colloids were transported into the swamps and there underwent further dialysis, alteration, and eventual crystallization *in situ*, producing a notably homogeneous kaolinite clay possessing interlocking crystalline texture. Flint clay is interpreted as being an intermediate member of a so-called flint-clay facies, which is a claystone sequence ranging from high-alumina minerals formed on the highest part, structurally and/or topographically, of the depositional area, and grading down-structure and/or lower in elevation through flint clay to illite-kaolinite plastic clay and thence to marine illitic shale, all being equivalent stratigraphically.

CATIONIC DIFFUSION IN CLAY MINERALS: II. ORIENTATION EFFECTS

T. M. LAI and M. M. MORTLAND

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The effect of orientation of vermiculite particles on the diffusion of Na ion was measured by a tracer technique. Mathematical relationships of orientation angle, axial ratio of the platelets, and apparent diffusion coefficient were developed and applied to pressed, freeze-dried vermiculite pellets. The experimental results on the diffusion of Na ion in K-vermiculite of clay size gave apparent diffusion coefficients of $2.21 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ when the diffusion flux was parallel with the clay platelets and $0.45 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ when the flux was perpendicular to the clay platelets. For the diffusion of Na into Na-vermiculite, apparent diffusion coefficients were obtained of $1.18 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ when the diffusion flux was parallel with the clay platelets, and $0.18 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$

when the flux was perpendicular to the platelets. For K-vermiculite, the change in apparent diffusion coefficient is a simple one of particle geometry. The Na-vermiculite system exhibited more complicated behavior.

EFFECT OF Al^{3+} AND H^+ UPON THE SIMULTANEOUS DIFFUSION OF ^{85}Sr AND ^{86}Rb IN KAOLINITE CLAY

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The effect of varying concentrations of Al^{3+} and H^+ upon the simultaneous diffusion of ^{85}Sr and ^{86}Rb was measured in salt-free aliquots of clay having different Al:H ratios. Self-diffusion of Sr and Rb was measured at 4, 24, 48, and 75°C. Rb diffusion was not significantly altered as Al^{3+} increased from 12 to 52 per cent. The faster diffusing Rb ion has a greater energy of activation than Sr (4.8-3.6 kcal/mole), however the Arrhenius frequency factor for Rb (a measure of the probability of ion exchange) was much greater for Rb than Sr (28.8 and 0.4×10^{-4} respectively). Altering the Rb and Sr saturation and the complementary ions resulted in changes in the diffusivity, the energy of activation, and the frequency factor for these ions, but not always in the same direction or to the same degree.

SURFACE CONDUCTIVITY AND DIELECTRICAL PROPERTIES OF MONTMORILLONITE GELS

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The theory of the behavior of heterogeneous dielectrics adapted to systems having a surface charge density has been applied to salt free montmorillonite clay gels saturated with Li, Na, K, and Cs. Numerical calculations indicate that the field action must be zero along the small axis of the platelet. Along the long axis, however, the action is complete and the motion of the charge carriers is essentially tangential to the platelet. The values of the surface conductance are of an order of magnitude of 10^{-9} Mho. At temperatures below 273°K, the conduction

appears to be predominantly protonic; the counterions are considered to be disturbing elements in the water layer structures, thus creating a number of lattice defects able to transport the current. Above 273°K, the conduction is essentially due to the adsorbed cations, whose contribution starts during the phase change of the H₂O.

ALUMINUM INTERLAYERS IN LAYER SILICATES: EFFECT OF OH/Al RATIO OF Al SOLUTION, TIME OF REACTION, AND TYPE OF STRUCTURE

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Aluminum interlayers were synthesized under the same experimental conditions in a number of vermiculites and montmorillonites from different sources. Vermiculite fixed Al as well as hydroxy-Al in its interlayers. This produced a stable 14 Å spacing and decreased its cation exchange capacity considerably. Heating at 300°C produced an interstratified mixture, indicating that some interlayers collapsed while others did not. Neither the aging of vermiculite in Al solutions nor their OH/Al ratios changed the stability of the interlayers appreciably. Montmorillonites, on the other hand, did not fix Al ions but did fix appreciable amounts of hydroxy-Al ions. In addition, the stability of the interlayers in montmorillonite increased on aging in hydroxy-Al solutions and exceeded the stability of the interlayers produced in vermiculite. It is postulated that the more expanded interlayer space in montmorillonite provides a favorable locale for the organization of hydroxy-Al ions into gibbsite structure whereas the restricted expansion in vermiculite prevents it.

MEASUREMENT OF EXCHANGEABLE CATIONS IN BENTONITES

M. B. ROLLINS and D. L. POOL

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High-swelling bentonites cannot be analyzed for exchangeable cations with exactly the same techniques used for most soils. In particular, smaller samples of 0.5 g must be used to insure extraction of cations, and a higher centrifugal force must be used to avoid sample losses. The modified method proposed here requires little time, but still compares closely with results obtained by Frink's more extensive method. Results obtained for fourteen western bentonites show good agreement between total exchangeable cations and CEC. Chemical properties for the bentonites were found to change both with geographical location and with location within each deposit.

RETENTION OF CRUDE OIL BASES BY CLAY-CONTAINING SANDSTONE

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Retention of basic components of a crude oil by clay-containing reservoir sandstone was studied by flowing crude oil through cores and monitoring the concentration

of bases in the effluent. Cores that were H saturated, H saturated then aged, and Na saturated, retained 0.82, 0.70, and 0.20 meq base/100 g respectively. Barium exchange capacity values were 0.86, 0.71, and 0.83 meq/100 g. Subsequent floods with water, toluene, and chloroform-acetone removed oil that had increasing concentrations of base and N, indicating that the basic fraction of crude oil was the most difficult fraction to extract from clay mineral surfaces. Retained bases were nitrogenous and the most tenaciously held bases had base/N ratios approaching unity.

WEATHERING AND ORIENTATION IN TRIASSIC CLAY SEDIMENTS OF NEW JERSEY

WILLIAM LODDING and EDWARD STURM

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The composition of clay mineral suites derived from Triassic argillite and shale were compared with those of the consolidated parent sediments. Lockatong argillite, near the weathered zone, is composed mainly of illite, chlorite, and feldspar. In the clay horizon immediately above, illite replaces the feldspar and kaolinite increases upward until, near the top of the weathered zone, it is almost the only clay mineral present. The Brunswick shale contains mainly illite, with some kaolinite, montmorillonite, quartz, and feldspar. In its weathered zone, kaolinite increases gradually upward, montmorillonite decreases, but approximately 30 per cent illite is still found in the top layers. Chlorite in the argillite near the weathered zone is randomly oriented while illite shows strong preferred orientation, probably indicating that chlorite formed in place during weathering. The difference in the diagenetic development of these two Triassic sediments, situated less than 5 miles apart, is striking and must be attributed mainly to the chemical composition and lithology of the parent sediments.

ELECTRON MICROPROBE STUDY OF KAOLIN

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Electron microprobe studies of kaolinite indicate that most of the Fe is evenly distributed throughout the kaolinite and must either be in the structure or occur as very small particles adsorbed on the surface. Most of the Ti is present in anatase impurities, which also contain some Fe and Mg. Fe, Mg, Mn, V, and K are present in biotite. When several types of clay minerals are present it is difficult to obtain quantitative data due to an averaging effect from the very small particles, but useful relative information can be obtained. Although the electron microprobe cannot be used to study compositional variations in individual clay mineral flakes less than a few microns in diameter, considerable information can be obtained about the composition of the non-clay minerals present in clay and shale samples. In order to study compositional variations in the clay minerals and associated minerals, techniques will have to be developed to concentrate and segregate these fine-grained minerals.