

CLAYS and CLAY MINERALS

at a glance

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MIXED-LAYER KAOLINITE-MONTMORILLONITE FROM THE YUCATAN PENINSULA, MEXICO

L. G. Schultz, A. O. Shepard, P. D. Blackmon and H. C. Starkey 137

Clay beds 1-2m thick and interbedded with marine limestones probably of early Eocene age are composed of nearly pure mixed-layer kaolinite-montmorillonite. Particle size studies, electron micrographs, X-ray diffraction studies, chemical analyses, cation exchange experiments, DTA, and TGA indicate that clays from three different localities contain roughly equal proportions of randomly interlayered kaolinite and montmorillonite layers. The montmorillonite structural formulas average $K_{0.2}Na_{0.2}Ca_{0.2}Mg_{0.2}(Al_{2.5}Fe_{1.0}Mg_{0.5})(Al_{0.75}Si_{7.25})O_{20+}(OH)_4$, with a deficiency of structural (OH) in either the montmorillonite or kaolinite layers. Nonexchangeable K^+ indicates that a few layers are mica-like. Crystals are mostly round plates $1/10$ to $1/20 \mu$ across. The feature most diagnostic of the mixed-layer character is an X-ray reflection near 8 \AA after heating at 300°C . The clays are inferred to have developed by weathering of volcanic ash and subsequent erosion and deposition in protected nearshore basins.

MECHANISMS CONTROLLING THE PERMEABILITY OF CLAYS

Gholamreza Mesri and Roy E. Olson 151
Coefficients of permeability, calculated using Terzaghi's theory of one-dimensional consolidation, are reported for smectite, illite, and kaolinite, in water, methyl and ethyl alcohol, benzene and carbontetrachloride. When the pore fluid was water the clays were homoionized to either the sodium or calcium form and the pore water electrolyte concentration was varied. The coefficients of permeability are evaluated in terms of both mechanical and physico-chemical variables. It appears that the coefficients of permeability are mainly influenced by mechanical effects, particularly the distribution of void sizes and the tortuosity of the channels. The coefficient of permeability is maximized if the flow channels consist of many small channels and a relatively few large ones,

through which the main flow occurs. Physico-chemical variables exert great influence on the coefficient of permeability through their influence on dispersion or aggregation of the clay particles.

STRUCTURAL FACTORS CONTROLLING STACKING SEQUENCES IN DIOCTAHEDRAL MICAS

Necip Güven 159
Deviations in the symmetry of mica single layers from the ideal arrangement with all atoms in hexagonal arrays are caused by the structural factors such as compositional variation (substitutions), order-disorder, and distortions. The derivative crystal structure theory as applied to mica polymorphism, implies that the ideal symmetry of the mica single layer ($C2/m$) can be altered to one of its standard subgroups by these structural factors. The "derivative structure" of the single layer may allow a unique interlayer and a specific intralayer configuration and result in a regular stacking sequence.

RELATION OF POTASSIUM EXCHANGE AND FIXATION TO DEGREE OF WEATHERING AND ORGANIC MATTER CONTENT IN MICACEOUS CLAYS OF PODZOL SOILS

G. J. Ross 167
The rates of K exchange of untreated and peroxide-treated micaceous clays from five Podzol soils of increasing degrees of weathering were determined using sodium tetraphenyl boron. In addition, the amounts of K fixed against NH_4 were measured. The Ae horizon clays of these soils contained mainly interstratified mica-vermiculite-montmorillonite whereas the C horizon clays contained mica of a more discrete nature.
As was expected, there was an inverse relationship between rates of K exchange and degrees of weathering of the Ae horizon clays. However, in the samples from each of these soils except in those of the most weathered one, the K exchange rate of the interstratified mica from the Ae horizon was higher than that of the less weathered,

more discrete mica from the corresponding C horizon. The abundance of hydrated edges and layers exposing K exchange sites in the Ae micas probably contributed to their higher rates of K exchange. Amounts of K fixed in the Ae horizon clays were not related to degrees of weathering.

Removal of organic matter from the Ae horizon clays by peroxide considerably increased both the rates of K exchanged and the amounts of K fixed. These increases were attributed to the elimination of a blocking effect of adsorbed organic matter on K exchange and fixation.

CATION MIGRATION INTO EMPTY OCTAHEDRAL SITES AND SURFACE PROPERTIES OF CLAYS

R. Calvet and R. Prost

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The migration of small cations into the empty octahedral sites of dioctahedral clays allows one to study the local appearance in the lattice of trioctahedral structure and the consequences of the exchange capacity decrease on the solvation properties. The results concern essentially the montmorillonite saturated by lithium. Computations based on a point charge model shows the necessity for the OH groups to undergo a reorientation when the lithium ions are within the octahedral sites. This change of orientation was studied by i.r. spectroscopy which allows one to estimate the amounts of lithium present in the lattice. By analogy with i.r. results obtained for the Li, Mg, Ca and K montmorillonites, one can say that the non-exchangeable lithium which is not within the octahedral sites must be in the bottom of the hexagonal cavities. Moreover, it is shown that the solvation properties of the clay depend on the number of exchangeable cations and on the nature of the solvent. The clay does not swell with water when the amount of exchangeable cation is lower than 50 per cent of the exchange capacity. This limit is 30 per cent with glycerol, and 20 per cent with ethylene glycol.

ANTIGORITE—ITS OCCURRENCE AS A CLAY MINERAL

G. W. Brindley and Persio de Souza Santos

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A white clay from the Jatoba talc mine, Castro, Parana, Brazil, is shown by chemical analysis, X-ray and electron diffraction, and by thermal analysis to be essentially pure

antigorite in the strict sense of the term. Single crystal electron diffraction patterns give various values for the long *a* parameter, with 43.5 Å perhaps the most commonly occurring, *b* = 9.25 Å, *d*(001) = 7.25 Å. X-ray powder diffraction gives *d*(001) = 7.26 Å and *b* = 9.23 Å. Electron micrographs show irregular platy and lath-like crystals of about 0.5–2 μ size with large development of (001) planes and with *b* in the direction of elongation. Other crystals are observed with very unusual forms, some having holes through them. They show mainly *0kl* diffraction patterns and lie with the basal (001) planes normal to the stage of the instrument. The chemical analysis agrees closely with the ideal serpentine composition and the differential thermal analysis curve is consistent with antigorite.

THE EFFECT OF EXCHANGEABLE CATIONS ON THE SORPTION OF CHLOROPHYLLIN BY MONTMORILLONITE

N. Kaufherr, S. Yariv and L. Heller

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The sorption of commercial K–Cu chlorophyllin by a sample of montmorillonite saturated with different exchange ions was studied. The organic anions are sorbed on external surfaces while K displaces most of the exchangeable cations of the clay. These also affect the amount of material peptized and the relative orientation and aggregation of the particles.

SURFACE CHEMISTRY OF THERMALLY DECOMPOSED ORGANO-MONTMORILLONITE COMPLEXES

W. H. Slabaugh

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The hydrophilic–hydrophobic properties of four thermally decomposed organoclays, the octadecylammonium–, the dimethylaryloctadecylammonium–, and the dimethyldioctadecylammonium–bentonites and the dimethyldioctadecylammonium–hectorite, were examined through adsorption isotherms with nitrogen, water vapor, and hexane. Along with DTA and TGA results, these clay complexes appear to undergo transitions from low to higher degrees of hydrophilicity as more and more of the hydrocarbon chains are dehydrogenated at successive temperatures up to 400°C.