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CLAYS and CLAY MINERALS at a glance

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INTERLAYER BONDING IN KAOLINITE DICKITE AND NACRITE

R. F. Giese, Jr. 145

A simple electrostatic model has been used to demonstrate that the inner surface hydroxyls in kaolinite, dickite and nacrite are responsible for the interlayer bonding in these minerals. The contribution to the interlayer bonding of an individual hydroxyl hydrogen depends on the orientation of the hydroxyl group relative to the 1:1 layer since this orientation determines the H . . . 0 interlayer distance. If this distance is much greater than the sum of the van der Waals radii, 2·60 Å, there is essentially no bond. As the distance becomes less than 2·60 Å, the strength of the interlayer bond increases.

MÖSSBAUER STUDIES OF SMALL PARTICLES OF IRON OXIDES IN SOIL

N. H. Gangas, A. Simopoulos, A. Kostikas, N. J. Yassoglou and S. Filippakis 151

A soil of Attica (Greece) has been studied by Mössbauer spectroscopy and magnetization measurements in order to ascertain the nature and form of iron oxides present in it. The room temperature spectra consist of a paramagnetic doublet and a small magnetic sextet. At liquid nitrogen temperature the magnetic component increases considerably at the cost of the paramagnetic component. This behavior is typical of superparamagnetism exhibited by ultrafine magnetic particles. From the values of hyperfine parameters extracted by computer fits of the spectra, the particles can be identified mainly as α-Fe_2O_3. The theory of superparamagnetism, in conjunction with Mössbauer and magnetization data, is discussed in detail. Application of this theory to the data for the clay fraction of the soil leads to the conclusion that the oxide particles have a size distribution with a mean particle diameter of 131 Å and a width of 14 Å.

DISTRIBUTION OF MAJOR CATIONS IN ESTUARINE SEDIMENTS

A. S. Parashiva Murthy and R. E. Ferrell, Jr. 161

This paper reports the measured distribution of major cations in interstitial, exchangeable and non-exchangeable phases of estuarine sediments. The observed changes in ionic ratios result from the valence and dilution effects in the Donnan equilibrium concept according to which the ion exchanger favors the sorption of divalent ions at the expense of monovalent cations and cations migrate to the outer solution. The above findings have direct application to an interpretation of diagenetic changes in clay minerals.

THE EXPERIMENTAL TRANSFORMATION OF MICA TOWARD SMECTITE. RELATIVE IMPORTANCE OF TOTAL CHARGE AND TETRAHEDRAL SUBSTITUTION

M. Robert 167

This article emphasizes the influence of crystal–chemical composition on the ease of transformation of micas to vermiculite or more smectite-like minerals. The swelling test, with glycerol, of Mg-saturated mineral is used to characterize the degree of transformation.

The main structural factors of this evolution are tetrahedral substitution of Si by Al, and total charge. There is a relation between these two factors, i.e. the lower the tetrahedral substitution, the greater can be the charge without affecting the smectite swelling behavior.

In this respect there is a contrast between tri and dioctahedral micas. In the first, tetrahedral Al is so high ($> 1{\cdot}20$ for Si_4O_{10}) that transformation into smectite must imply modification of the tetrahedral layer. For dioctahedral micaceous phyllites (illites, glauconites) where tetrahedral charge is lower, transformation can be easier. Only a lowering of total charge is needed and reduction-oxidation seems to play a very important role in this process.

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THE LOCATION OF IRON-55, STRONTIUM-85 AND IODIDE-125 SORBED BY KAOLINITE AND DICKITE PARTICLES

A. W. Fordham 175
The autoradiographic method at the electron microscope level has been applied successfully to locate the position or sorbed ions and compounds associated with kaolinite and dickite particles. For suitable isotopes, the limit of resolution was about 0·2 μm and would be conceivably less in the most favorable conditions.

Judged by the location of iodide-125 and strontium-85, the majority of positive sites and also the most reactive negative sites were situated at the edges of the clay particles. These conclusions were supported by normal electron microscope examination of mixtures of clay with charged gold and silver iodide sols.

Iron (III) ions, which have been shown to react with kaolinite by chemisorption mechanisms in 0·15 M systems and by both physical absorption and chemisorption in 0·01 M systems, were, in either case, located at edge-sites on the clay. When intentionally precipitated onto dickite, iron (III) hydroxides were distributed evenly over the clay surfaces. However, precipitation was probably initiated at the particle edges.

Minor exceptions to the above conclusions appeared to be caused by basal surface features such as fracture or stress lines, outgrowths or cavities, and if the clays had not been cleaned, by strongly associated impurities such as iron hydroxides.

AN EXPANSIBLE MINERAL HAVING HIGH REHYDRATION ABILITY

Katsutoshi Tomita and Mitsuhiko Dozono 185
An interstratified mineral (mica–montmorillonite) from a hydrothermally altered andesite in the southern part of Satsuma Peninsula, Japan fully rehydrates after having been heated to 800°C.

ADSORPTION OF PYRIDINE *N*-OXIDE ONTO MONTMORILLONITE

S. Olejnik, A. M. Posner and J. P. Quirk 191
Pyridine *N*-oxide and montmorillonite form interlamellar complexes with basal spacings of 14·7 and 21 Å. The former corresponds to a monolayer with a tilted orientation of the pyridine ring; the latter comprises a double layer of molecules between the clay sheets. Infrared spectra show that pyridine *N*-oxide bonds through the NO group; in the 21 Å complexes it is coordinated to the exchangeable cations through water molecules acting as bridges which themselves are directly coordinated to the cations. In the 14·7 Å complexes a splitting of the ν(NO) band occurs with the more polarizing cations Mg and Ca; the two bands correspond to pyridine *N*-oxide molecules directly coordinated to the cation and to other molecules coordinated through bridging by water molecules. Cs montmorillonite forms complexes with a basal spacing of approximately 14·7 Å which also shows a splitting of the ν(NO) band.

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