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CLAYS and CLAY MINERALS at a glance

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RELATION BETWEEN SWELLING, WATER PROPERTIES AND *b*-DIMENSION IN MONTMORILLONITE–WATER SYSTEMS

Israela Ravina and Philip F. Low 109

The *b*-dimensions of the unit cells of six different Na-saturated montmorillonites were determined by X-ray diffraction at water contents ranging from 0 to 20 g per g of montmorillonite. In every case, the *b*-dimension increased progressively with water content from its initial value, which was characteristic of each dry montmorillonite, to a final value of 9·0 Å, which was common to all montmorillonites. The latter value was reached when the water contents of the respective montmorillonites were equal to those at maximal swelling. When these water contents were plotted against the corresponding changes in *b*-dimension, a straight line that passed through the origin was obtained.

Different structure-sensitive properties of the water in montmorillonite–water systems (i.e. the partial specific volume, the amount remaining unfrozen at −5°C and the activation energy required for ions to move through it) were available, as functions of the species of exchangeable cation, from previous studies. Relevant *b*-dimensions were determined in the present study. It was found that all of these water properties were correlated with the *b*-dimension of the associated montmorillonite.

Our results indicate that epitaxy exists between the crystal structures of montmorillonite and adsorbed water and that these structures undergo mutual adjustment with each increment of water. The resulting loss of free energy causes water adsorption, i.e. swelling, to occur spontaneously. Swelling stops when no further adjustment takes place. This does not happen until the adsorbed water is several hundred angstroms thick and has achieved a preferred configuration.

DODECYLAMMONIUM–MICA COMPLEXES—II. CHARACTERIZATION OF THE REACTION PRODUCTS

E. E. Mackintosh, D. G. Lewis and D. J. Greenland 125

Interlayer potassium was removed from a wide range of mica mineral by treatment with dilute solutions of *n*-dodecylammonium chloride. On subsequent reaction with the appropriate metal methoxide, the Na^+ or Ca^{2+} form of the altered mica was produced. The properties of the original and sodium saturated samples were compared to assess the changes in water content, charge density and chemical composition (particularly ferrous iron) which resulted from the displacement of potassium.

Calculation of structural formulae was not attempted since it was established that for the altered samples accurate distinction could not be made between adsorbed and structural water. Changes in layer charge are thus expressed on the basis of samples ignited to 1000°C. Charge losses of up to 76 me/100 g were recorded for biotites, smaller charges were noted for phlogopites and no loss was observed for the two muscovites examined.

Oxidation of ferrous iron occurred for all trioctahedral samples, the greatest oxidation occurring in the samples initially high in iron. There was no consistent relationship between the amount of iron oxidized and the loss of layer charge.

All altered samples contained greater amounts of H_2O^+ than the original materials suggesting that protonation of structural oxygens occurred during, or following, removal of potassium.

It is concluded that the alteration of micas by reaction with organic cations is a complex process, differing in detail for different micas, and following a similar path to alteration by reaction with inorganic salts.

ACID–BASE INTERACTIONS AND THE PROPERTIES OF KAOLINITE IN NON-AQUEOUS MEDIA

D. H. Solomon and H. H. Murray 135

In non-aqueous systems, kaolinite can show, in addition to the physical interactions, considerable chemical activity. This study considers the chemical reactions that can occur at the kaolinite surface and explains these reactions in terms of acid–base interactions. In certain applications the chemical activity must be controlled if satisfactory products are to be obtained; for example, when kaolinite is used as a filler in rubber or as a diluent for insecticide powders. The concept of acid–base interactions is used

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to explain rheological and film properties in kaolinite–organic systems. The strength of the surface acid sites of kaolinite varies with the moisture content. At 1% moisture the surface is equivalent to 48% sulphuric acid whereas at 0% it is equivalent to 90% sulphuric acid. Therefore, the moisture level is extremely important and dry kaolinite will promote or catalyze many chemical reactions and where acid–base interactions are involved the presence of even small amounts of water usually retards or inhibits the reaction. Several examples explaining these interactions are given in the paper.

THE OCCURRENCE OF SEPIOLITE AND ATTAPULGITE ON THE SOUTHERN HIGH PLAINS

S. A. McLean, B. L. Allen and J. R. Craig 143

Sepiolite and attapulgite have been found to be common, sometimes the major, clay minerals in calcareous lacustrine deposits on the southern High Plains in West Texas and eastern New Mexico. Deflation debris derived from the basins and calcareous soils developed in the debris and in the lacustrine deposits also often contain either or both minerals. Dolomite is the carbonate commonly associated with sepiolite and calcite has a similar relationship to attapulgite in the lacustrine deposits. Pedogenic formation of sepiolite and attapulgite appears unlikely in the area studied since an association with lacustrine materials was made in a very high percentage of the occurrences.

Sepiolite was found to be highly concentrated in the $< 0{\cdot}2\mu$ fraction. A similar, but less pronounced, distribution was noted for attapulgite. The studies suggest that the minerals have developed authigenically in alkaline lacustrine environments during periods of desiccation. Such an environment, interrupted by more humid periods, would have obtained during dry Pleistocene intervals. Volcanic ash is suggested as the source of the essential silica. The Mg concentration would appear to determine whether sepiolite–dolomite or attapulgite–calcite were formed.

THE TRANSFORMATION OF LEPIDOCROCITE TO GOETHITE

U. Schwertmann and R. M. Taylor 151

The conversion of lepidocrocite (γFeOOH) to its more stable polymorph, goethite (αFeOOH) was followed by observing changes in crystal morphology, oxalate solubility, surface area and X-ray diffraction. In conjunction, kinetics were measured as functions of surface area, temperature, alkalinity and seeding with goethite crystals.

The results suggest that the transformation is not topochemical, but proceeds through the solution phase. The main steps governing the rate of transformation are, (1) the dissolution of lepidocrocite, and (2) the formation of goethite nuclei and subsequent growth. Either of these processes can be rate-determining under appropriate conditions.

THE INFLUENCE OF SILICATE ON THE TRANSFORMATION OF LEPIDOCROCITE TO GOETHITE

U. Schwertmann and R. M. Taylor 159

The mechanism of the transformation of lepidocrocite (γFeOOH) to goethite (αFeOOH) has previously been established and the effect of silicate on the transformation was investigated. Rather than completely inhibiting the reaction, as had been suggested, the presence of Si was found to merely retard the nucleation stage of the transformation. There was found to be no decrease in the dissolution rate of the lepidocrocite due to surface adsorption of Si.

Si has no effect if introduced after the nucleation stage, and under conditions of pH and temperature where the dissolution rate of the lepidocrocite largely determines the rate of transformation, the presence of Si has a reduced effect. The results show that Si is adsorbed and incorporated into the goethite structure, and due to its retarding effect on the nucleation, larger crystals of goethite are formed, many of which are twinned.

It is inferred from the results that the apparent stability of lepidocrocite occurring in soils in association with goethite cannot be attributed solely to the presence of Si in the soil system.

SOME NATURALLY OCCURRING ILLITE–SMECTITE INTERSTRATIFICATIONS

L. Heller-Kallai and Z. H. Kalman 165

Two different types of interstratified illite–smectite are found in a section of Paleozoic sediments in the Negev, Israel. One of these is detectable only by a decrease in peak width and a concomitant increase in symmetry of the 10 Å on glycolation. This material is regarded as illite, randomly interstratified with about 20% expanding layers.

RECOGNITION OF INTERSTRATIFIED CLAYS

J. G. Mills and M. A. Zwarich 169

Difficulties in the interpretation of X-ray diffractograms of soil clays are discussed with reference to clay fractions obtained from glacial till and lacustrine soil parent materials. Diffractograms of the coarse clay fractions are readily interpreted by conventional means but it is difficult to determine if the dominant mineral species of the fine clay fraction is an interstratified mineral or a mixture of discrete montmorillonite and mica. A number of methods of interpretation of diffractograms of interstratified minerals are used with varying results. In the case of clays of small particle size, diffraction peaks crucial to the recognition of interstratification are not resolved due to the peak broadening. This phenonemon causes the diffractogram of a mixture of discrete minerals to resemble that of an interstratified mineral.

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SELECTIVITY EFFECT OF CESIUM ON CLAY SIZE WEATHERED MICA; TRANSMISSION ELECTRON MICROSCOPY STUDIES

M. Gal and C. I. Rich 175

The use of electron diffraction contrast to detect local concentrations of interlayer cations in mica–vermiculites was examined. Cs and Mg, because of their contrasting atomic scattering amplitudes for electrons, were chosen as exchange ions for Ca. Cs was absorbed to the near exclusion of Mg by the clays from the three soils and by weathered clay-size muscovite and phlogopite. The presence of Cs in addition to the other interlayer cations, K and Ca, caused bending and perhaps splitting of the mica–vermiculite layers. Extinction bend contours were common in Cs-treated specimens but not those Ca-treated. After freeze-drying of specimens of Cs–Ca Nason clay, differential destruction by the electron beam of the central core in clay-size vermiculite containing hydrated Ca ions may indicate the edge location of Cs.

INTERLAMELLAR METAL COMPLEXES IN LAYER SILICATES III SILVER(I)–ARENE COMPLEXES IN SMECTITES

D. M. Clementz and M. M. Mortland 181

The complexation of benzene and several methyl substituted benzenes with exchangeable silver(I) on the interlamellar surfaces of Ag(I)–montmorillonite has been studied using spectroscopic methods. There are no physically adsorbed molecules interacting with the internal silicate surfaces and the only chemisorbed species present are those which are coordinated through π electrons to the exchangeable Ag(I) ions. In each case the coordinated species are similar to the previously studied Cu(II)–montmorillonite Type I complexes where aromaticity is retained. Complete replacement of coordinated and other interlamellar water molecules was accomplished with relative ease. Stoichiometric determinations indicate a 2:1 benzene:Ag(I) complex. Similarities between the Cu(II) and Ag(I) complexes are discussed in relation to electronic configurations.

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