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CLAYS and CLAY MINERALS at a glance

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ARGILLIZATION BY DESCENDING ACID AT STEAMBOAT SPRINGS, NEVADA

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Steamboat Springs, Nevada, an area of present-day hot springs, clearly illustrates the genetic dependence of some kaolin deposits on hot-spring activity. Andesite, granodiorite and arkosic sediments are locally altered at the land surface to siliceous residues consisting of primary quartz and anatase, plus opal from primary silicates. These siliceous residues commonly exhibit the textural and structural features of their unaltered equivalents. Beneath the siliceous residues, kaolin and alunite replace primary silicates and fill open spaces, forming a blanketlike deposit. Beneath the kaolin–alunite zone, montmorillonite, commonly accompanied by pyrite, replaces the primary silicates. On the ground surface, the same alteration mineral zones can be traced outward from the siliceous residue; however, hematite rather than pyrite accompanies montmorillonite.

Chemical analysis indicates that sulfuric acid is the active altering agent. The acid forms from hydrogen sulfide that exsolves from deep thermal water, rises above the water table and is oxidized by sulfur-oxidizing bacteria living near the ground surface. This acid dissolves in precipitation or condensed water vapor and percolates downward destroying most of the primary minerals producing a siliceous residue. Coincidence of the water table with the downward transition from siliceous residue to kaolin–alunite signifies decreasing hydrogen metasomatism because of dilution of descending acid by ground water.

In hot-spring areas, beds of siliceous sinter deposited at the surface by hypogene thermal water look, superficially, like areas of surficial acid alteration. Features diagnostic of a surficial alteration are the relict rock structures of a siliceous residue and a kaolin–alunite zone immediately beneath.

INTERLAMELLAR ADSORPTION OF CARBON DIOXIDE BY SMECTITES

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The adsorption of CO_2 at low temperature ($\sim -70°C$) on thin films of homoionic smectites was studied by X-ray diffraction and by i.r. absorption. An increase in the d_{001} spacings of these clay films upon adsorption of CO_2 was observed. In addition, a dichroic effect was readily discernible by comparing the i.r. spectra at two different orientations of the smectite films; i.e. with the film normal and titled 35° with respect to the i.r. beam. The CO_2 stretching vibration at 2350 cm^{-1} was used for the i.r. study. These observations conclusively show that CO_2 intercalates the smectite structure rather than being adsorbed only in pores between clay tactoids—the limiting process proposed by other investigators.

Adsorption isotherm data from earlier surface area studies are reexamined here through application of the Dubinin equation. Again, intercalation is demonstrated by convergence of the plotted experimental data for smectites containing large monovalent interlayer cations toward a pore volume that is near the calculated theoretical value for a monolayer of intercalated CO_2.

Scanning electron photomicrographs of Li– and Cs–smectites provide additional evidence that aggregation differences are not responsible for the large observed difference in BET surface areas obtained for these smectites with CO_2 as the adsorbate. At low magnification, visual differences in macro-aggregates are apparent, but at high magnification no significant differences are observed in the micro-structure of individual aggregates where the major amount of gas adsorption really occurs.

THE INTERACTION OF WATER WITH GOETHITE (α-FeOOH) AND AMORPHOUS HYDRATED FERRIC OXIDE SURFACES

Robert G. Gast, Edward R. Landa and Gordon W. Meyer **31**

The interaction of water with synthetically prepared goethite (α-FeOOH) and amorphous hydrated ferric oxide surfaces was studied using i.r. absorption and water vapor adsorption measurements. I.R. results show that the last traces of physically adsorbed water are removed from the amorphous material by outgassing at 25°C. In contrast, goethite retains approximately a monolayer of physically adsorbed water with similar outgassing. This monolayer of water on goethite, which is presumably hydrogen-bonded at least in part with structural hydroxyls, is readily exchangeable with D_2O.

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Integral entropies of adsorption were evaluated from water vapor adsorption isotherms at 15, 25 and 35°C and compared with values for mobile and immobile layers calculated through application of statistical mechanics (McCafferty and Zettlemoyer, 1970). Entropy values for both the first physically adsorbed monolayer of water on the amorphous material and the second monolayer on goethite were about the same as or greater than those calculated for an immobile layer, indicating strong hydrogen bonding of water by both surfaces. The larger deviation between the entropy values for goethite and those calculated for the immobile layer may be associated with changes in the structure of the first as well as the second physically adsorbed water layers. Surface areas, calculated using the BET method, were 320 and 32 $m^2 g^{-1}$ for the amorphous material and goethite respectively. Since the unit surface activity is probably about the same for the two materials, it follows that as the amorphous material crystallizes to form goethite, there would be a reduction in total surface activity in proportion to the reduction in surface area.

POTASSIUM SELECTIVITY OF CLAYS AS AFFECTED BY THE STATE OF OXIDATION OF THEIR CRYSTAL STRUCTURE IRON

Fawzy M. Kishk and H. M. El-Sheemy 41

The Ca–K exchange isotherms were determined at two temperatures for two highly montmorillonitic iron-rich soil clays in their oxidized and reduced states. The thermodynamic parameters K, ΔG_0, ΔH_0 and ΔS_0 were calculated for the exchange reactions.

It was found that the formation of K–clay from Ca–clay in both the oxidized and reduced state was accompanied by negative free energy, enthalpy and entropy changes. The results indicate that K is more strongly bound than Ca by the clay and the Ca-preference shown by the isotherms may be due to entropy changes in solution.

The oxidation of crystal structure iron resulted in an increase in K selectivity of the clay and a decrease in the free energy, enthalpy and entropy changes of the Ca–K exchange reaction. It was concluded that K is more strongly held by the oxidized clay than the reduced one, which is possibly due to a more nearby dioctahedral character in the oxidized than in the reduced state.

PROPERTIES OF REDUCED CHARGE MONTMORILLONITES: HYDRATED Cu(II) IONS AS A SPECTROSCOPIC PROBE

David M. Clementz, M. M. Mortland and Thomas J. Pinnavaia 49

A series of Cu(II) reduced charge montmorillonites (RCM) of varying charge reduction has been prepared by exchange of the parent Li(I)–Na(I) mineral with $CuCl_2$ in 95 per cent ethanol solution. The Cu(II) exchange capacity, as determined by Na(I) exchange in 1:1 (v/v) ethanol–water, is a linear function of the fraction of Li(I) initially present on the exchange sites, F. Selective Cu(II)-saturation on internal and external sites was achieved at maximum charge reduction ($F = 1{\cdot}0$). Water sorption isotherms and (001) basal spacings are interpreted in terms of an increasing tendency toward interlayer collapse with increasing charge reduction. Because of the higher hydration energy of the Cu(II) ion, however, the fraction of non-expansible interlayers at a given F value is lower than those present in the corresponding Li(I)–Na(I) RCM. Electron spin resonance spectra of oriented samples show that under air-dried conditions (*ca.* 40 per cent r.h.) the predominant Cu(II) species present, whether on internal or external sites, is the planar $Cu(H_2O)_4^{2+}$ ion. The symmetry axis of the ion is oriented perpendicular to the *a–b* plane of the silicate sheets. In the presence of a full partial pressure of water, the Cu(II) ions on the external sites and those which are in expansible interlayers become totally hydrated $Cu(H_2O)_6^{2+}$ and tumble rapidly. The $Cu(H_2O)_4^{2+}$ ions in non-expansible layers retain their restricted orientation on the silicate surface. Some general conclusions have been drawn regarding the nature of charge distribution in the mineral.

INTERLAMELLAR AND MULTILAYER NITROGEN SORPTION BY HOMOIONIC MONTMORILLONITES

M. I. Knudson, Jr. and J. L. McAtee, Jr. 59

Nitrogen sorption by various homoionic montmorillonites was studied at 78°K. The adsorption isotherms in the relative pressure range $P/P_0 = 0{\cdot}05$–$0{\cdot}25$ were found to be either Type I or Type II in the BET classification. The nitrogen sorption process was considered to be predominantly interlamellar when described by a Type I isotherm. With a Type II isotherm, the adsorption was assumed to be predominantly on those surfaces not in the interlamellar regions.

It was concluded that only cations within a certain size range promote significant interlamellar nitrogen penetration in montmorillonites. The role of the smaller cations in nitrogen sorption by montmorillonites seems to be their influence on the external aggregate structures. Very large cations tend to clog up the interlamellar pores as well as some of the external voids.

PROPERTIES OF 'SWELLING' CHLORITE IN SOME MESOZOIC FORMATIONS OF CALIFORNIA

J. L. Post and N. C. Janke 67

Slaty strata and their weathering products comprise a large portion of the geologic formations of the western foothills in the Sierra Nevada, Mid-Northern California. The weathering products of Mesozoic slates in particular, locally known as 'swelling' chlorites, have caused numerous problems in road construction.

A typical stratigraphic section of slates, which includes 'swelling' chlorites, is given for the area of Chili Bar, California, as part of the general geology of the western foothill formations. Remolded slate densities were observed to decrease while measured swelling pressures increased with increasing slate alteration. Swelling pressures in excess of 12·5 psi were observed. Curves are presented in comparison with DTA results showing the effect of alteration on the slate.

The results of X-ray diffraction analyses, in correlation with i.r. data, show a typical slate mineral composition for unaltered material of about one-half chlorite with the

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remainder being about equal portions of muscovite and quartz. The entire chlorite content of the altered slate becomes a regular mixed-layer clay mineral, corrensite, which has been observed to alter to sedimentary vermiculite and Mg–saponite in residual soil. An i.r. absorption peak at 3690 cm^{-1} characterizes the mixed-layer clay mineral. Heat treatment of the mixed-layer clay mineral structure reduces the 14·3 Å basal spacing to 11·8 Å at 540°C, which decreases to 10·6 Å at 850°C, disappearing by 1050°C. Procedures are given for direct quantitative analysis of these three-phase mineral systems using simultaneous linear equations.

Evidence is presented for the alteration minerals formed during weathering of the slate, including Fourier analysis of the mixed-layer clay structure.

SIMILARITIES OF REHYDRATION AND REHYDROXYLATION PROPERTIES OF RECTORITE AND 2*M* CLAY MICAS

Katsutoshi Tomita 79

Various dehydroxylated micas and rectorites were acid-treated. Rectorite-type mixed-layer mineral was formed from $2M_1$ and $2M_2$ and random mixed-layer mineral from 1*M* and 1*Md* mica. Rectorite was formed again from dehydroxylated rectorite. The rehydration and rehydroxylation properties of dehydroxylated rectorite and 2*M* sericites were found to be similar.

INFRARED ABSORPTION AND X-RAY DIFFRACTION STUDY OF BUTYLAMMONIUM COMPLEXES OF PHYLLOSILICATES

J. A. Martin-Rubi, J. A. Rausell-Colom and J. M. Serratosa 87

I.R. absorption and X-ray diffraction data on butylammonium complexes of vermiculites show, when compared with the Wyoming montmorillonite complex, that the tetrahedral location of charge determines the keying of the $-NH_3^+$ groups into the ditrigonal cavities and that these groups have their C_3 axes perpendicular to the layers. The aliphatic chains adopt different conformations depending on the area available per exchange position; they will either, (a) adopt an 'all-trans' conformation with their axes inclined 55° to the silicate planes, when the area available is small, or (b) rotate 120° around the C_1–C_2 bond to adopt a flat disposition relative to the layers, when the area available is larger than the area covered by the organic ion.

A STRUCTURAL INVESTIGATION OF A VERMICULITE–PIPERIDINE COMPLEX

J. E. Iglesias and H. Steinfink 91

A vermiculite–piperidine complex was investigated by a single crystal three-dimensional X-ray diffraction procedure. The complex was prepared by ion exchange of a Na-vermiculite at pH 8. A total of 453 reflections was observed and used in the least squares refinement of the structure. The complex is monoclinic, $C2/m$, $a = 5{\cdot}346(2)$ Å, $b = 9{\cdot}256(3)$ Å, $c = 17{\cdot}57(1)$ Å, $\beta = 96{\cdot}29(9)°$. The final R value was 0·17 using anisotropic temperature factors for the silicate atoms and isotropic temperature factors for the carbon atoms. The occupancy factors of the C atoms were considered as variable parameters. The diffraction data were of poor quality because of stacking faults. The results show that the molecules are randomly distributed over the crystallographic sites in the interlayer space and the peaks appearing in the electron density maps can be interpreted as being due to 2 piperidine molecules and two H_2O molecules. The orientation of the organic molecules is ambiguous. The electron density peaks fit a model in which the molecules are vertical and their planes form a small dihedral angle, and also fit a model in which the plane of the molecules is parallel to (001). It is quite possible that both types of orientations are present.

FACTORS AFFECTING SELECTED AREA ELECTRON DIFFRACTION PATTERNS OF MICAS

Necip Güven 97

Major factors affecting the selected area electron diffraction (SAD) patterns of micas are: lattice properties of the crystal, specimen thickness, orientation of the crystal, properties of the Ewald sphere for electron diffraction, depth of field of the objective lens, and variations in focusing conditions of this lens. Depending on these factors, SAD patterns of $2M_1$ muscovite may display different symmetries. Specimen 'finite' thickness affects the intensity in terms of the 'interference function'. The latter function has been evaluated exactly and the intensity distribution has been calculated along the (*hk*) rows. The observed intensity variations of (*hk*) spots indicate that the focusing conditions of the objective lens are rather critical for the symmetry of SAD patterns.

FURTHER INVESTIGATIONS ON FULVIC ACID–Cu^{2+}–MONTMORILLONITE INTERACTIONS

H. Kodama and M. Schnitzer 107

The major mechanism by which fulvic acid removed Cu^{2+} from Cu^{2+}–montmorillonite was complexation, most likely chelation. This was confirmed by the use of a specific cupric ion electrode which showed that whereas the total Cu^{2+} concentration in the supernatant solutions increased with rise in pH, about 7 per cent of the total Cu^{2+} solubilized by fulvic acid occurred in the 'free' or 'uncomplexed' form at pH 2·5, only 0·6 per cent was similarly distributed at pH 4·5 and 0·0009 per cent at pH 6·5. External surface area measurements by a dynamic BET method showed the following surface areas: 2·5 $m^2\ g^{-1}$ for the fulvic acid, 8·0 $m^2\ g^{-1}$ for the Cu^{2+}–montmorillonite but 16·1 $m^2\ g^{-1}$ for the FA–Cu^{2+}–montmorillonite complex. Electron micrographs of the FA–clay complex confirmed that fulvic acid was adsorbed in interlamellar spaces and on external surfaces of the Cu^{2+}–montmorillonite.

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A COMPARATIVE STUDY OF SIMULATED AND NATURAL WEATHERING OF SOME OKLAHOMA SHALES

J. G. Laguros, Subodh Kumar and M. Annamalai 111

Shales from six locations in Oklahoma were subjected to natural weathering for 2 yr. Simulated weathering of these shales was effected in the laboratory by subjecting them to ultrasonic treatment in a tank type device. Both treatments produced disaggregation. X-ray diffraction patterns for the ultrasonically treated and weathered shales indicated no major changes in the types of clay minerals. However, natural weathering in the field produced degradation of the clay minerals in addition to disaggregation of the shales. Ultrasonic treatment appears to be a good predictive test for determining the durability and weatherability of the shales; however, it can simulate field weathering only so far as the engineering index properties of the shale are concerned. It is not a predictive test where the mineralogical characteristics are of significance.

CRYSTAL IMPERFECTIONS WITH REGARD TO DIRECTION IN KAOLINITE MINERAL

D. G. Williams and C. L. Garey 117

The crystallite sizes in the particles from four fractions of a kaolinite–clay were determined from the broadening of the X-ray diffraction lines. Measurements were made of the <002> and <111> planes whose crystallographic directions correspond to the clay plate thickness and diagonal, respectively. The extent of crystal imperfection was determined by comparing the calculated crystallite size with the mean size based on measurements from electron micrographs. The crystal imperfections were found to be more extensive in the plate diagonal, <111>, than in the plate face, <002>, directions. Electron micrographs of hydrofluoric acid-etched samples revealed plate-edge and plate-face imperfections. The latter show a regularity suggesting a mosaic-like texture in the plate surface. Surface imperfections probably have significant influence on the dispersion and flocculation behavior of kaolinite.

INTERNAL AND EXTERNAL MORPHOLOGY OF TUBULAR AND SPHEROIDAL HALLOYSITE PARTICLES

J. B. Dixon and T. R. McKee 127

Tubular halloysite from Wagon Wheel Gap, Colorado and spheroidal halloysite from Redwood County, Minnesota were examined by transmission electron microscopy. Clay samples were prepared by the following techniques: drop-mounted suspension on carbon support films; thin sections of clay in Araldite epoxy resin; and carbon–platinum–palladium single-stage replicas.

Both types of dehydrated halloysite have interlayer separations between packets of layers. Halloysite tubes are composed of packets as thin as five layers which sometimes reveal a rolled interior configuration in cross sectional view. Thicker tubes are composed of many layers per packet. Some large tubes appear in cross section as folded packets of layers. The interior morphology of spheroidal halloysite particles is more irregular and the layer structure is more discontinuous than in most tubes. The spheroidal halloysite of this study is characterized by external tangential plates with hexagonal shape suggestive of kaolinite.

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