

# CLAYS and CLAY MINERALS

at a glance

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## DEFERRATION EFFECT ON STRUCTURAL FERROUS-FERRIC IRON RATIO AND CEC OF VERMICULITES AND SOILS

C. B. Roth, M. L. Jackson and J. K. Syers 253

Deferration by reduction of free  $\text{Fe}_2\text{O}_3$  with  $\text{Na}_2\text{S}_2\text{O}_4$  in the presence of Na citrate and  $\text{NaHCO}_3$  caused a change in valence state of 10-35 per cent of the total structural iron in micaceous vermiculites, soils, nontronite, and muscovite. An increase in  $\text{Fe}^{2+}$  on deferration was accompanied by an equivalent decrease in  $\text{Fe}^{3+}$ . Subsequent treatment with  $\text{H}_2\text{O}_2$  reoxidized the structural  $\text{Fe}^{2+}$  previously formed. Sesquioxide coatings on micaceous vermiculites were examined electron microscopically. These coatings were composed predominantly of  $\text{Fe}_2\text{O}_3$  with approximately 10 per cent by weight of  $\text{Al}_2\text{O}_3$  and small amounts of  $\text{SiO}_2$ , as determined by chemical analysis of the deferration extracts. The cation exchange capacity (CEC) increased 10-60 per cent as a result of deferration of micaceous vermiculites and soils. Treatment of the deferrated sample with  $\text{H}_2\text{O}_2$  restored the  $\text{Fe}^{3+}$  content to approximately the original value but the CEC was not affected. Consequently, the increase in CEC on deferration was attributed to the removal of the positively charged sesquioxide coating. The reversible change in valence of structural iron without an equivalent change in CEC was attributed to deprotonation-protonation of the structure ( $\text{OH}^- \rightleftharpoons \text{O}^{2-}$ ) simultaneous with the oxidation-reduction of iron ( $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ ) in the phyllosilicate layer.

## INTERMOLECULAR INTERACTION IN MONTMORILLONITES: NH-CO SYSTEMS

H. E. Doner and M. M. Mortland 265

The mechanism of interaction between cationic organic molecules satisfying exchange sites in montmorillonite and organic molecules with carbonyl groups was investigated. Dialkyl amides adsorbed on trimethylammonium- and tetramethylammonium-montmorillonite were studied by i.r. spectroscopy. The electronegativity or basicity of the amides, expressed as a summation of the Taft polar

factors ( $\Sigma\sigma^*$ ), was found to be linearly related to the C-O stretching frequency after adsorption on trimethylammonium-montmorillonite. Furthermore, the changes in the C-O and N-H stretching frequencies of the amides and trimethylammonium ion respectively, exhibited a direct linear relationship. Thus, the dialkyl amides were shown to be hydrogen bonded through the oxygen of the carbonyl group to the hydrogen of the trimethylammonium. The (001) spacing of trimethylammonium-montmorillonite was 12.9 Å. Only after the adsorption of amide molecules of the size of N,N-diethylacetamide or larger did this spacing change. Dialkyl amides were adsorbed on tetramethylammonium-montmorillonite, but less energetically than on trimethylammonium-clay. The (001) spacing of tetramethylammonium-montmorillonite was 13.8 Å and remained the same after adsorption of the dialkyl amides. Evidence of hydrogen bonding between the hydrogen of trimethylammonium-ion and some other carbonyl compounds was also noted.

## MULTIPLE-ION DIFFUSION—I. TECHNIQUES FOR MEASURING AND CALCULATING APPARENT SELF-DIFFUSION COEFFICIENTS IN HETEROIONIC SYSTEMS

D. A. Brown, J. E. Dunn and Ben Fuqua 271

This investigation was designed to integrate the quick-freeze technique for ion diffusion with two computer programs to permit the simultaneous measurement and calculation of the diffusivity of a variable number of ions in heteroionic soil systems. Kaolinite clay was prepared so as to have the following percentage saturations of the CEC,  $\text{Sr}^{2+}$  65,  $\text{Mg}^{2+}$  15,  $\text{Rb}^+$  10,  $\text{Na}^+$  5, and  $\text{H}^+$  5. A quadruplicate radioisotope tag consisting of  $^{85}\text{Sr}$ ,  $^{86}\text{Mg}$ ,  $^{86}\text{Rb}$ , and  $^{22}\text{Na}$  was used to measure the diffusivity of each ion. The complex spectra were resolved by use of Schonfeld's revised Alpha-M computer program. A probit-transformation procedure was formulated into a computer program to enable the calculation of each diffusion coefficient. These programs are described and illustrated with the diffusivity of  $^{86}\text{Rb}$  in kaolinite clay.

### STRUCTURAL ORGANIZATION IN AMORPHOUS SILICO-ALUMINAS

**P. Cloos, A. J. Léonard, J. P. Moreau, A. Herbillon and J. J. Fripiat** 279

A structure model for amorphous hydrated or dehydrated silico-aluminas with composition varying between  $0 < \text{Al} : \text{Al} + \text{Si} < 1$  is presented. A central core made from a tetrahedral network in which silicon is partially substituted by aluminium carries a net negative electrical charge. This charge is balanced by more or less polymerized hydroxy-aluminium cations forming a coating around the core. As  $\text{Al} : \text{Al} + \text{Si}$  increases, the number of substitutions in the core increases as well as the complexity of the hydroxy-aluminium cations in the coating. For  $\text{Al} : \text{Al} + \text{Si} \leq 0.8$ , a demixing is observed, leading to the formation of a crystalline pseudoboehmite and bayerite. Upon heating, the coating as well as the demixed phases are transformed into a spinel structure containing tetrahedral aluminium, while the core structure remains unaffected. This model could explain the solubility features, the phosphate reaction, and the catalytic properties of amorphous silico-aluminas.

### LAYERING PHENOMENA IN COLLOIDAL SUSPENSIONS

**S. R. Merchant and E. A. Rosauer** 289

Aged suspensions of microspheres and two kaolinites exhibit several horizontal layers. Particle concentration is greater at the top of a layer; lower layer tops have increasing particle concentrations. Lower layers also settle more rapidly than upper layers; however, an increase in original suspension concentration results in a proportional increase in the particle concentration of comparable layers and causes comparable layers to settle at a slower rate. The average equivalent diameter of particles within and between kaolinite layers is identical. The maximum measured diameters are also identical. Microsphere layers show similar uniformity of average and maximum diameters. Ultimate settling of layers in suspension does not result in observable layers in the sediment. Data are interpreted as indicating that, in a colloidal suspension, particles interact to become observable as definite horizontal layers. A sequence of mechanisms is proposed for layer formation.

### EFFECT OF ACIDITY IN MONTMORILLONITE INTERLAYERS ON THE SORPTION OF ANILINE DERIVATIVES

**S. Yariv, L. Heller and N. Kaufherr** 301

Sorption of aniline and its derivatives by montmorillonite substituted by cations of widely different acidity depends upon the polarizing power of the interlayer cations. I.R. spectra indicate that the anilines are mostly bound to the interlayer cations through water molecules, except in Cs montmorillonite, where bonding to the oxygen surfaces of the alumino-silicate sheets seems to predominate. Anilines

are weak bases, which compete with the oxygen surfaces for protons of acidic interlayer water. Consequently, the tendency of anilines to act as proton donors in the clay interlayers increases with the polarizing power of the exchangeable cation. The concept of "basic" water is introduced to account for some of the features of the spectra of Cs montmorillonite treated with the organic ligands.

### ELECTROCHEMICAL ALTERATION OF CLAY SOILS

**D. H. Gray and J. Schlocker** 309

The composition and physical properties of three clay soils were altered by introducing aluminum under an electrochemical gradient in order to evaluate the role of pH in controlling changes in soil composition and the feasibility of pH buffering during electrochemical treatment. Both X-ray diffraction and selective chemical extraction methods were used to determine the distribution and mode of occurrence of aluminum in the treated samples. Aluminum was detected in the treated samples in both exchangeable form and as a hydroxy-aluminum interlayer. Aluminum oxide minerals such as gibbsite were not detected in any of the treated samples. Mineralization by aluminum ions was speeded and intensified in bentonite soils by buffering the catholyte with carbon dioxide. Plasticity of bentonite soil samples from South Dakota was reduced markedly by electrochemical treatment, whereas the plasticity of an illite soil from Illinois and an illite-montmorillonite soil from Mississippi were relatively unaffected. Nearly all treated samples exhibited some degree of electrochemical induration or mineralization. Induration was most pronounced in bentonite soil samples with high water contents and alkaline pH largely because of hydroxy-aluminum interlayering in the clay. On the other hand interlayering was negligible in illite soil samples with low pH; the main effect of electrochemical treatment in this case was the addition of aluminum in exchange sites.

### THE DETERMINATION OF QUARTZ IN SEDIMENTARY ROCKS USING AN X-RAY DIFFRACTION METHOD

**Roger Till and D. A. Spears** 323

An X-ray diffraction method for determining quartz in sediments is described which is both rapid and precise, with a coefficient of variation of 1.9 per cent. Samples are ignited at 950°C prior to X-ray analysis. This removes the interference of clay peaks, increases the relative intensity of the quartz peaks and reduces the initial matrix variation of samples. The peak area ratio of quartz (4.26 Å) to an added standard boehmite (6.18 Å) is measured. Quartz content is obtained from a working curve constructed using similar rocks of known free silica content, which were analyzed by the method of Trostel and Wynne (1940).