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CLAYS and CLAY MINERALS at a glance

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QUANTITATIVE ANALYSIS OF NATURALLY OCCURRING MULTICOMPONENT MINERAL SYSTEMS BY X-RAY DIFFRACTION

Charles A. Moore 325

A theory for the quantitative analysis of multicomponent mineral systems by means of X-ray diffraction is presented. A linear interaction between mineral pairs is postulated. The theory is verified experimentally for bicomponent and tricomponent systems using a variety of sample preparation techniques including random powder mounts, suspensions sedimented onto glass slides, and pressed powder pellets. The minerals studied include quartz, fluorite, kaolinite, glauconite, illite, and montmorillonite. The determination of the linear interaction factors for mineral pairs is treated theoretically and experimentally. Emphasis is placed upon techniques that are applicable to naturally occurring mineral systems. Four approaches are presented for determining linear interaction coefficients for various types of such mineral systems. These approaches are applied to the experimental data and the results are compared. Results accurate within two per cent are commonly obtained. Experimental techniques are discussed and a qualitative and quantitative error analysis is presented. It is shown that the indicated quantities present may not be particularly sensitive to the value of the linear interaction coefficient.

LOW FREQUENCY DIELECTRIC DISPERSION OF CLAY-WATER-ELECTROLYTE SYSTEMS

Kandiah Arulanandan and James K. Mitchell 337

The dielectric properties of saturated kaolinite clay-water-electrolyte systems were determined over the frequency range of $30–10^5$ c./s. Very large dielectric constants are observed at low frequencies. Since the experimental data approach constant values at each end of this frequency spectrum, they can be described by a fairly well defined spectrum of relaxation times. The particle size and orientation, the type and amount of electrolyte, and temperature affect the low frequency dielectric increment and the average relaxation time. Several physical processes, such as relaxation due to dipolar rotational polarization, interfacial polarization, free space charge and bound ion polarization, are examined in an attempt to explain the observed data. It is concluded that there exists at present no theory to explain all the data, but the bound ion polarization mechanism appears to explain some of the results.

ENERGY DISSIPATION OF A KAOLINITE AT DIFFERENT WATER CONTENTS

Arley G. Franklin and Raymond J. Krizek 353

A Georgia kaolinite, at water contents from 55 to 95 per cent, was tested by means of a Weissenberg Rheogoniometer under conditions of pure shear with sinusoidally varying deformation over a frequency range of 3 decades. The results, including time-dependent effects, are expressed in terms of the magnitude of the complex modulus and the phase angle, as developed in the theory of linear viscoelasticity, and stress-strain hysteresis curves. The complex modulus is a two-component quantity, which has a real part associated with the elastic or energy storage characteristics of the material and an imaginary part associated with its viscous or energy dissipation characteristics. Although the complex modulus interpretation is very good for linearly viscoelastic materials, its applicability and usefulness diminishes as the material departs from linear viscoelastic behaviour. On the other hand, the determination of energy dissipation from stress-strain hysteresis curves

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does not depend on any assumption concerning material behavior, because the area enclosed by the curve gives a direct measure of the energy dissipated in a single cycle of deformation. The dissipation characteristics obtained by the two methods are compared and used to illustrate the degree of validity and some limitations of linear viscoelasticity theory.

MINERALOGICAL AND GEOCHEMICAL STUDY OF CLAY MINERAL TRANSFORMATIONS IN THE SEDIMENTARY TRIASSIC JURA BASIN (FRANCE)

Jacques Lucas and Gürol Ataman 365

A detailed study of sediments from the Triassic of the French Jura shows that clay minerals vary continuously with the facies. Near the coasts of the Jura Sea, sediments consisted of sandy, continental detritus and the minerals are poorly crystallized. At the center of the basin, in what was a cation-rich chemical environment, they are well crystallized. A progressive mineralogical variation can be observed from degraded illite to well-crystallized chlorites passing through the intermediate stages of more-or-less regular mixed-layer structures. This variation is due to a true crystalline transformation. Similarly, chemical variation in clay minerals and whole-rock samples are related to the paleogeography of the basin. The distribution of major and trace elements is a function of distance from the Jura Sea coastline and also a function of the mineralogical composition of the fine fraction. The most obvious relationships are: (1) An increase in the concentration of MgO and the percentage of ignition-loss water from the coast towards the deep sea; (2) A decrease in the concentration of SiO_2, Al_2O_3, and TiO_2 as well as that of trace elements such as vanadium, gallium, and cobalt from the coastal regions to the center of the basin; (3) A lack of statistically significant variations in the concentration of Fe_2O_3, Mn_3O_4, B, and Ni throughout the basin. The authors conclude that: (1) Transformations (aggradiations) observed by means of X-ray diffraction methods are in agreement with the chemical analyses; (2) Transformations are contemporaneous with the sedimentation; they are not diagenetic; (3) Clay minerals play an important role in the geochemical balance of sedimentary basins.

X-RAY SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN CLAY MINERALS

Leon J. Johnson 373

An X-ray spectrochemical method is compared with the flame photometer determination of potassium in a series of sixty-five soil clay fractions. Two methods of preparing the clay samples for the X-ray determination were used. In one case a 20 mg sample of clay in suspension was dried onto a plastic disc as a thin film. Potassium was determined by comparing the fluorescence intensity of the unknown with a sample of known composition that was prepared for analysis by the same technique. For the second method a 100 mg sample of dried clay was pressed into a pellet using methyl cellulose as a backing. In this case a National Bureau of Standards sample (NBS-98) was prepared in an identical manner and used as a standard for determining the potassium in the unknown. The results for both techniques were highly significantly correlated with the values as determined by flame photometric analysis. The pellet technique gave a more accurate measure of the potassium content. With the thin films the same sample may be used for X-ray diffraction analysis. In either case the X-ray spectrochemical technique provides a fairly rapid and simple procedure that can be useful for handling large numbers of samples.

ANALYSIS OF IRON IN LAYER SILICATES BY MOSSBAUER SPECTROSCOPY

G. L. Taylor, A. P. Ruotsala, and R. O. Keeling, Jr. 381

Analysis of Mossbauer effect in layer silicates provides a spectroscopic method for determining valences and coordination of iron. In this study Mossbauer spectra were obtained for amesite, cronstedtite, nontronite, glauconite, biotite, lepidomelane, chlorite, minnesotaite, vermiculite, stilpnomelane, and chloritoid. Trivalent iron was detected in tetrahedral coordination. Abundant trivalent iron in octahedral coordination causes quadrupole splitting values of divalent iron in the same mineral to decrease. This phenomenon was noted in cronstedtite and glauconite. In cases where divalent iron predominates in the mineral, the quadrupole splitting is larger. It is generally accepted that ferrous iron is largely in octahedral coordination. This suggests that the octahedral sites may be more distorted when ferric iron is present in the octahedral sheet. In biotite, quadrupole splitting of divalent iron is decreased when trivalent iron is present in tetrahedral sheets. This suggests that there is also more distortion in the octahedral sheet because of iron in tetrahedral positions.

SURFACE ACIDITY OF SMECTITES IN RELATION TO HYDRATION, EXCHANGEABLE CATION, AND STRUCTURE

M. M. Mortland and K. V. Raman 393

Equilibrium studies on clay films exposed to NH_3 and H_2O vapors demonstrate the effect of exchangeable cations on surface acidity and its relationship to hydration. At a relative humidity of 98 per cent the order of acidity on the clay surface as indicated by protonation of NH_3 was $Al > Mg > Ca = Li > Na = K$ for Wyoming bentonite and $Al > Mg > Li > Ca = Na = K$ for nontronite. At a relative humidity of 20 per cent, however, the order was $Al = Mg > Ca > Li > Na > K$ for the bentonite and $Al = Mg > Li > Ca > Na > K$ for nontronite. The largest change in proton donation properties due to hydration effects was in the calcium clays. For Ca-bentonite the Nh_4^+ formation was 16 me/100 g at 98 per cent and 80 me/100 g at 20 per cent relative humidity. In Ca-nontronite, the NH_4^+ formation was 14 and 64 me/100 g for the wet and dry systems respectively. The

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differences in proton donation between the bentonite and nontronite clays are believed to be due to charge site location and its effects on ion hydration. The NH_4^+ formed by the protonation process seemed to exist in different environments in the bentonite and nontronite as indicated in the i.r. absorption spectra.

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