Clays and Clay Minerals, 1968, Vol. 16, pp. i–iii. Pergamon Press. Printed in Great Britain

CLAYS and CLAY MINERALS at a glance

Volume 16 **May–June 1968**

SOME RESULTS OF THE STUDY OF CLAY MINERALS IN THE U.S.S.R.

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Clay mineral studies in the U.S.S.R., mainly since 1960, are summarized. Electron diffraction techniques especially have been developed and used extensively. Methods have been developed for simultaneous recording of DTA curves and other properties. Polytypism of phyllosilicates has been studied intensively by Zvyagin and others. Much new information on the structure and morphology of halloysites has been obtained by electron-optical methods. Dehydrated halloysite particles are $2M_1$ polycrystals of prismatic habit consisting of several sectorial zones with a common axis of elongation. Hollow prisms result from liberation of the core zones. Other clay minerals extensively studied include allophane, kaolinites, chlorites ("donbassite" is considered to have precedence over "sudoite" for dioctahedral varieties), alushtite (or tosudite), monothermite, and various zinc-bearing clays. Much attention has been given to physico-chemical and colloid-chemical properties. The natural occurrences and alterations of clays are described in weathering and oxidation zones, in soils, and in Recent and Ancient sediments. Dickite is the most common hydrothermal clay mineral, with donbassite, rectorite, and tosudite also occurring. A table lists 14 hydrothermal deposits and their mineral parageneses. An extensive reference list to Soviet clay literature is appended.

HYDROXY INTERLAYERS IN EXPANSIBLE LAYER SILICATES

C. I. Rich 15

Vermiculites and smectites in soils and sediments are frequently partially interlayered or "chloritized". Dioctahedral expansible layer silicates are those most frequently interlayered, and hydroxy-Al appears to be the principal component of the non-exchangeable interlayer material. The most favorable soil conditions for interlayer formation appear to be: moderate pH (4·6–5·8), frequent wetting and drying cycles, and low organic matter content. In marine sediments, hydroxy-Mg interlayering may be significant. Soil-derived clays containing partially filled hydroxy-Al "brucite" sheets may be filled out with hydroxy-Mg. Under reducing conditions, hydroxy-Fe interlayers may be important. Depending on the OH/Al ratio and Al content of hydroxy-Al interlayers, expansible layer silicates may either promote or retard the formation of gibbsite. Interlayered expansible layer silicates also may be precursors to kaolinite.

CLAY MINERALS AS ELECTRON ACCEPTORS AND/OR ELECTRON DONORS IN ORGANIC REACTIONS

D. H. Solomon 31

Certain clay minerals have the ability to catalyze the polymerization of some unsaturated organic compounds (styrene, hydroxyethyl methacrylate) and yet to inhibit polymer formation from other closely related monomers (e.g. methyl methacrylate). This apparently contradictory behaviour of the clay minerals can be rationalized in terms of electron accepting and electron donating sites in the silicate layers. The electron acceptor sites are aluminum at crystal edges and transition metals in the higher valence state in the silicate layers; the electron donor sites are transition metals in the lower valence state. The catalyzed polymerization involve the conversion of the organic molecule to a reactive intermediate; thus where the clay mineral accepts an electron from the vinyl monomer a radical-cation is formed, where the organic compound gains an electron it forms a radical-anion. The inhibition of polymerization processes involves the conversion of reactive organic intermediates to non-reactive entities. The color reactions on clay minerals are useful in predicting the electron accepting or electron donating behaviour of the clay minerals because they proceed by similar mechanisms to the polymerization reactions. Masking of the crystal edge with a polyphosphate destroys the electron accepting properties of the crystal edge.

DICKITE AND KAOLINITE IN PENNSYLVANIAN LIMESTONES OF SOUTHEASTERN KANSAS

Richard J. Schroeder and John B. Hayes 41

Dickite and kaolinite occur in cavities in phylloid algal limestones, in interstices of biocalcarenites and sandstones, and along joints, fractures, and stylolites in Pennsylvanian rocks exposed throughout 9600 square miles of southeastern Kansas. The stratigraphic interval of approximately 1100 ft extends from the Fort Scott Limestone (Desmoinesian) through the Lecompton Limestone (Virgilian). Dickite is confined to an elliptical area 125 miles long northeast-southwest, extending 60 miles eastward from igneous intrusions in Woodson and Wilson Counties. Dickite is associated preferentially with porous algal mounds. Kaolinite occurs in less porous rocks within the dickite area, and also is abundant well beyond. Heated groundwaters, possibly mixed with magmatic waters, moved readily up-dip and along strike outward from the intrusions through the conduit-like algal mounds; dickite was deposited from such solutions. Where water movement was restricted or where water had traveled tens of miles from the intrusions, water temperature fell below the limit for dickite crystallization, and kaolinite precipitated instead.

RELATIONS OF COMPOSITION TO STRUCTURE OF DIOCTAHEDRAL 2:1 CLAY MINERALS

Charles E. Weaver 51

A ternary plot of the tetrahedral R^{3+} and octahedral R^{3+} populations for the dioctahedral 2:1 clay minerals shows a broad range of compositional variation within each of the major clay minerals. The clay minerals can be subdivided on the basis of total charge, location of the charge, and the relative amounts of Al and Fe^{3+} in the octahedral sheet. The division is natural and is controlled by the misfit between the tetrahedral and octahedral sheets and the need for tetrahedral rotation. The compositions of the tetrahedral and octahedral sheets are interdependent. Whereas muscovite has a lower limit of 1·7 Al octahedral occupancy, illite and montmorillonite have a lower limit of 1·3 Al; still lower Al values result in the formation of a chain structure.

HYDROXYL STRETCHING FREQUENCIES OF SYNTHETIC Ni-, Al-, AND Mg-HYDROXY INTERLAYERS IN EXPANDING CLAYS

J. L. Ahlrichs 63

A prominent high frequency OH stretching vibration is associated with the layers in montmorillonite, with approximate frequencies of 3660 cm^{-1} with nickel interlayers, 3690 cm^{-1} with aluminum interlayers, and 3710 cm^{-1} with magnesium interlayers. Pleochroism studies indicate transition moment of interlayer OH to be at a relatively high angle to the planar surface of the clay crystals. Aluminum interlayers show some evidence of an additional weak absorption in the lower frequency region of 3570–3600 cm^{-1}, which can be shown to not be a water band. Deuteration studies show that flushing with D_2O at room temperature removes water, and heating at 100°C in D_2O vapor exchanges interlayer OH but not the clay crystal OH. Study of the OD stretching of the systems with deuterated interlayers supports observations made in the OH stretching bands.

STRUCTURAL CHARGE SITE INFLUENCE ON THE INTERLAYER HYDRATION OF EXPANDABLE THREE-SHEET CLAY MINERALS

Raymond L. Kerns, Jr. and Charles J. Mankin 73

It has been suggested that the sites of layer charge deficiencies may have an influence upon the amount of hydration that can take place in the interlayers of expandable clay minerals. If the interlayer cation-to-layer bonds are considered ideally electrostatic, the magnitude of the forces resisting expansion may be expressed as a form of Coulomb's law. If this effect is significant, expandable structures in which the charge-deficiency sites are predominantly in the tetrahedral sheet should have less pronounced swelling properties than should structures possessing charge deficiencies located primarily in the octahedral sheet. The relative degrees of interlayer hydration were measured for three samples that differed in location of layer charge sites but had similar interlayer cation compositions. Although no correlation could be made between the degree of interlayer hydration and total surface-charge density, the investigation does not eliminate total surface-charge density as being significant to the swelling properties. The results do indicate a correlation between more intense expandability and predominance of charge deficiencies in the octahedral sheet rather than the tetrahedral sheet.

SURFACE AREA OF MONTMORILLONITE FROM THE DYNAMIC SORPTION OF NITROGEN AND CARBON DIOXIDE

Josephus Thomas, Jr. and Bruce F. Bohor 83

Surface area determinations were made on a montmorillonite with various cations emplaced on the exchangeable sites, utilizing nitrogen and carbon dioxide as adsorbates at 77°K and 195°K, respectively, in a dynamic system. Surface areas from 3-point B.E.T. plots (half-hour adsorption points), with nitrogen as the adsorbate, ranged from 61 m^2/g for Li-montmorillonite to 138 m^2/g for Cs-montmorillonite, thus reflecting a certain degree of nitrogen penetration between layers. The experimental data indicate that the extent of penetration is time-dependent and is also a function of the interlayer forces as governed by the size and charge of the replaceable cation. A further measure of the variation of interlayer forces is provided by the adsorption of carbon dioxide at 195°K. Surface area values ranged from 99 m^2/g for Li-montmorillonite to 315 m^2/g for Cs-montmorillonite. Although the carbon dioxide molecule is larger than the nitrogen molecule, its greater penetration apparently is a result of its being kinetically more energetic (with a larger diffusion coefficient) at its higher adsorption temperature.

INFRARED STUDY OF THE ORIENTATION OF CHLOROBENZENE SORBED ON PYRIDINIUM-MONTMORILLONITE

J. M. Serratosa 93

The pyridinium-montmorillonite complex has the ability to sorb additional aromatic molecules between the layers. The neutral molecules occupy the vacant space produced by the change in orientation of the pyridinium ion from a parallel to a perpendicular position and with the N–H group directed toward the negative unit layer surface. In favorable cases the orientation of the additional neutral molecules can be ascertained by infrared spectroscopy. In complexes of pyridinium-montmorillonite with chlorobenzene it can be shown that the chlorobenzene molecules adopt a vertical orientation but with the halogen bond axes parallel to the layers.

DIFFERENTIATION OF PLEISTOCENE DEPOSITS IN NORTHEASTERN KANSAS BY CLAY MINERALS

Pei-lin Tien 99

Seventy-four samples from eight stratigraphic sections of lower Pleistocene glacial and glaciofluvial deposits in Doniphan County, extreme northeastern Kansas, were analyzed using X-ray diffraction techniques. Clay mineral assemblages of the $<2\,\mu$ fraction of these deposits are nearly identical, consisting of a mixed-layer clay mineral associated with minor amounts of kaolinite and illite. An attempt was made to differentiate units of till and nontill deposits by using the relative intensities of 001 reflections of "mixed-layer mineral", kaolinite, and illite. At least two tills were recognizable. Associated nontill deposits could not be differentiated from one another, although the nontills are easily distinguished from tills.