

CLAYS and CLAY MINERALS

at a glance

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EXPERIMENTAL TRANSFORMATION OF A CHLORITE INTO A VERMICULITE

G. J. Ross and H. Kodama

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An orthochlorite (sherdanite) was heated to 610°C to dehydroxylate the hydroxide sheet and to oxidize ferrous iron. The heated sample was shaken for 20 min in a mixed solution of 0.2 N HCl and 0.2 N NaCl to dissolve the dehydroxylated hydroxide sheet. X-ray diffraction, thermal, infrared absorption and chemical analyses showed that the resulting product was similar to Kenya vermiculite. The procedure shows promise for the individual determination of the composition of the hydroxide sheet and of the mica layer in the chlorite structure. The experiments indicate that the hydroxide sheet in orthochlorites must be structurally disturbed before it can be selectively removed. In nature, structural disorganization of the hydroxide sheet of chlorite by dehydroxylation and oxidation of ferrous iron might occur during metamorphic processes, and chlorite to vermiculite transformation could take place during subsequent acid weathering. In pedogenic weathering conditions it is likely that oxidation of ferrous iron plays a major role in initiation of the structural disorder required for the selective removal of the hydroxide sheet in the weathering of chlorite to vermiculite.

the whole system, yet allows for the full development of the clay-cation-water interactions under the experimental conditions. It was found that particle rotation could be accounted for using the measured particle size and normal water viscosity only when the double layer was fully developed, with no free ions or other perturbations. As soon as perturbations were applied, either by adding salts or applying an electric field, the measured particle size and normal viscosity would not account for the data. Either the rotating moiety has to be larger, that is, be a particle plus a water hull, or the viscosity greater, or in some cases both.

PROPERTIES OF REDUCED CHARGE MONTMORILLONITE: TETRA-ALKYLAMMONIUM ION EXCHANGE FORMS

David M. Clementz and M. M. Mortland

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Surface properties of reduced charge montmorillonites (RCM) whose exchange capacities were saturated with tetra-alkylammonium cations, were studied with X-ray diffraction, nitrogen, and water adsorption. Methods were utilized for preparing montmorillonite of varying charge and of swelling reduced-charge clay with ethanol. As charge reduction proceeds, all layers retain some exchangeable cations until about half the original charge is reached at which point collapsed layers begin to appear and increase to about 60 per cent at maximum charge reduction. Charge reduction thus appears to proceed in a non-homogeneous fashion. When saturating exchange sites with tetra-alkylammonium ions in ethanol solvent, intercalation of salt in uncharged layers was noted if the samples were not completely washed. Nitrogen adsorption isotherms at liquid nitrogen temperatures showed considerable interlamellar penetration of tetramethylammonium (TMA⁺) clays, resulting in high calculated surface areas. Much less adsorption on the tetra-*n*-propylammonium (TPA⁺) clays was observed. Surface areas were increased upon reduction of charge up to the point where collapsed layers began to be appreciable, whereupon measured areas decreased. Water adsorption isotherms reflected the hydration properties of the exchangeable cation as well as the surface available for adsorption.

ELECTRO-OPTIC INVESTIGATION OF THE PERMANENT AND INDUCED DIPOLES OF MONTMORILLONITE AS AFFECTED BY ELECTROLYTE CONCENTRATION

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An electrooptic birefringence technique was employed to study the orientation mechanism of montmorillonite in an electric field. The instantaneous reversal of the field polarity produced evidence of a low voltage permanent dipole and a high voltage induced dipole. This technique was used to study the effect of electrolyte concentration on the rotational diffusion coefficient, a measure of the rate at which the particles rotate or relax, within the solution, from a preferred orientation. Thus, a measure of the immediate environment of the particles was obtained that is not an average effect for

MINERALOGY OF PALAGONITIC MATERIAL FROM THE GOLAN HEIGHTS, ISRAEL

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Sideromelane in Pleistocene lapilli-tuff rocks from the Golan Heights had partly altered into palagonite. X-ray and electron diffraction showed that the major part of the clay alteration product is composed of a dioctahedral micaceous mineral with well organized crystallinity along the *a*- and *b*-axes. Very poor basal reflections as well as incomplete expansion upon glycerolation and incomplete collapse upon heating were interpreted as being due to random interstratification with chlorite. Electron microscopy showed the particles to be very similar to montmorillonite tactoids. The thermal behavior as well as surface properties were similar to those of montmorillonite. Differential dissolution analysis and infrared spectroscopy failed to indicate amorphous constituents to any significant extent. Chemically the material was enriched in iron, aluminum and titanium and depleted in alkali and alkaline earth cations.

A minor component of the clay was found to consist of "onion-like" halloysite. It is suggested that palagonite is a natural precursor for montmorillonite in the volcanic glass-montmorillonite alteration series.

ARTIFICIAL ALTERATION OF BIOTITE INTO A 14 Å LAYER SILICATE WITH HYDROXY-ALUMINIUM INTERLAYERS

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Biotite was altered by boiling in 0.2M AlCl₃ solutions, and the products were examined by X-ray powder and single-crystal diffraction, chemical analysis and thermogravimetry. The altered material is a 14 Å clay mineral with hydroxy-Al interlayers. It has a stacking sequence characteristic of vermiculite and its silicate layers are similar chemical composition to trioctahedral vermiculite. The results of extracting the interlayer material with sodium citrate solution, X-ray examinations after heating and thermogravimetry show that the interlayer material is composed of Al associated with OH and H₂O. The chemistry and kinetics of the alteration reaction and the orientational relationship between the altered and original biotites are also discussed.

MINERALOGY AND CATION EXCHANGE PROPERTIES OF LIBBY VERMICULITE SEPARATES AS AFFECTED BY PARTICLE-SIZE REDUCTION

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A vermiculite (Libby, Montana) sample obtained from the Zonolite company contained mostly coarse-grained separates with only 8.7 per cent clay. The 2–50 μm fraction was used for particle-size reduction studies by wet and dry grinding, and size-fractionated into < 2, 2–5, 5–20 and 20–50 μm sizes. About 18 per cent of the sample was attrited to clay after 64 hr of wet grinding, but as much as 59 per cent of the

sample was attrited to clay after only 10 min of dry grinding. There was no evidence of damage to the crystal structure of derived clays or silts except for the 20–50 μm fraction from dry grinding.

The observed CEC values of all the fractions decreased as grinding progressed, except for the 2–5 μm fraction from wet grinding where the CEC increased. The decrease in CEC was attributed to an accumulation of biotite, either as a discrete mineral and/or a mixed-layer assemblage of biotite and vermiculite attrited to the clay fraction. In contrast, the fraction showing an increase in CEC was due to an increased concentration of higher charge-density (CEC) vermiculite. Biotite-free CEC data for vermiculite suggested that, in general, the coarser vermiculite separates had a higher CEC than the finer ones.

The susceptibility of minerals in the Libby vermiculite to cleavage by grinding was: vermiculite > hydrobiotite > biotite.

EXCHANGEABILITY OF POTASSIUM IN HEATED FINE-GRAINED MICACEOUS MINERALS

S. J. Smith and A. D. Scott

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Samples of several naturally fine-grained micaceous minerals were heated at 450°C for 24 hr (after the effects of other temperatures and heating periods were evaluated with the < 2 μm fraction of Grundite) and then characterized in terms of their release of K to NaCl–NaTPB (sodium tetraphenylboron) solutions and other potentially related properties.

This heat treatment produced a substantial increase in the amount of K that each mineral released when first placed in the NaCl–NaTPB solutions (the greatest increase being 22 m-equiv K/100 g in Marblehead illite). Depending upon the mineral heated, the subsequent rate of K release was increased, decreased or unchanged. Also, all the minerals except glauconite exhibited an increase (ranging from 4 to 38 m-equiv K/100 g) in their maximum degree of K release if they were heated. Thus, it was established that the K release behavior of these minerals is not only subject to appreciable alteration by heat treatments but is altered in a manner that varies with the mineral. The nature of these alterations, however, did not clearly identify an involvement of the other mineral properties that were examined. An increase in NH₄- and Cs-exchangeable K occurred when these minerals were heated—presumably as a result of exfoliation. With Morris illite samples, this increase was nearly 28 m-equiv/100 g. Thus, heated samples of these minerals may be useful sinks for the removal of NH₄ and Cs in various wastes.

'VERMICULITE' DETERMINATION ON WHOLE SOILS BY CATION EXCHANGE CAPACITY METHODS

C. B. Coffman and D. S. Fanning

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The proposed method is a modification of one by Alexiades and Jackson (1965). Calcium exchange capacity (CaEC) and

potassium exchange capacity (KEC) are determined, after removal of organic matter and free iron oxides, by saturating the exchange complex with centrifuge washings of pH 7 acetate solutions of Ca or K, respectively. Excess salt in solutions remaining in contact with the soil after saturation is determined by measuring the weight and concentration of the excess solution. The exchangeable cations and excess salt are then replaced by centrifuge washings with 1 N acetate solutions of Mg (for CaEC) or NH_4 (for KEC), after overnight 110°C oven-drying to enhance K fixation for KEC. The replaced cations are determined and CaEC and KEC are calculated. Per cent 'vermiculite' is based on the difference between CaEC and KEC (expressed in m-equiv/100 g) and an assumed 'vermiculite' interlayer exchange capacity of 154 m-equiv/100 g; percentage $V_r = \text{CaEC} - \text{KEC} / 154 \times 100$. The 'vermiculite' interlayer fraction (*VIF*) of the CaEC may also be calculated; $VIF = \text{CaEC} - \text{KEC} / \text{CaEC}$. The measured 'vermiculite' is shown in quotation marks since the method is open to criticism regarding exactly what is being measured, the assumptions made, etc. and to emphasize that the determination procedure is an operational one for the characterization of cation exchange complexes.

Removal of free iron oxides increased both CaEC and KEC values of several soils but percentage V_r was little affected. The amount of K fixation was affected by the drying treatment employed after K saturation (none vs air-drying vs oven-drying). Thoroughly crushing Montana and African vermiculites dramatically increased their CEC and measured 'vermiculite' values, but had little effect with two samples of saponite from chloritic metabasalt.

ON DEHYDRATION OF BOUND WATER OF SEPIOLITE

Hiroshi Nagata, Susumu Shimoda and Toshio Sudo 285

Bound water of sepiolite dehydrates in two steps in the temperature range of 250–650°C, as shown in the TG-curve. These steps are described here as steps II and III. At step II, half of the bound water is removed; other half at step III. From step II to III, discontinuous changes are confirmed in such properties as activation energy of dehydration, *a*-dimension, axial ratio, and intensities and spacings of X-ray powder reflections. A structural state at step II may be recognized as a distinct phase in the dehydration process.

CONTRIBUTIONS OF FOREST OPAL AND ASSOCIATED CRYSTALLINE PHASES TO FINE SILT AND CLAY FRACTIONS OF SOILS

L. P. Wilding and L. R. Drees 295

The scanning electron microscope (SEM) is useful in the identification of biogenic opal. Opaline spheres, cups, and scrolled or convoluted sheets were identified in both soil and vegetative isolates. X-ray diffraction analysis indicates that both alpha quartz and cristobalite were co-associated with the amorphous opaline phase synthesized during life metabolism of deciduous tree leaves. Such crystalline phases were most abundant in the 2–5 μm fraction and many consist of anisotropic rods with parallel extinction of equidimensional bodies with aggregate extinction. Between 2/3 and 3/4 of the total opal isolate from deciduous tree leaves was solubilized when digested for 2.5-min in boiling 0.5 N NaOH. Rate of dissolution was a function of particle-size and tree species. Biogenic opal of forest origin was about 10–15 times more soluble than grass opal, which probably reflects the higher specific surface of the former.