

CLAYS and CLAY MINERALS

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HALLOYSITE DEPOSITS IN THE TERRACED HILLS, WASHOE COUNTY, NEVADA

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Large hydrothermal deposits of halloysite clay occur in the Terraced Hills, Washoe County, Nevada and similar bodies probably are present elsewhere in the Basin and Range province. The host rock, an andesitic tuff, is underlain and overlain by volcanic flows; all these rocks are late Miocene to Pliocene in age. The clay bodies are composed mostly of halloysite with some iron oxides, variable amounts of feldspar and quartz, and locally some montmorillonite. Commonly all the pyroclastic unit is altered to halloysite material. In one locality, however, the halloysite body is restricted to the upper part and it is in sharp contact with underlying, partly montmorillonitized tuff. The contact of a clay body with the overlying basalt is distinct. Generally some halloysite is present in the lower part of the basalt and montmorillonite occurs in both materials near their contact. The solutions that altered the tuff were generated during volcanism, rose along high-angle faults, and were restricted to the permeable and otherwise favorable vitric tuff by the capping of relatively impermeable basalt.

THE SELECTIVE ADSORPTION OF SODIUM BY CLAY MINERALS IN LAKES PONTCHARTRAIN AND MAUREPAS, LOUISIANA

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Ion exchange analyses of the clay-sized fraction of sediments in Lakes Pontchartrain and Maurepas suggest the selective adsorption of Na at the expense of Mg. The literature suggests that Mg should be preferentially adsorbed. As the chlorinity of the lake waters increases

from 300 mg/l to 3250 mg/l, the percentage of exchangeable Na increases from 13.6 to 30.6 while the percentage of exchangeable Mg decreases from 65.5-36.8. The observed exchangeable Na percentages are higher than the ones calculated from the sodium-adsorption-ratios. The difference is attributed to an increase in the Na exchange constant of the sediment and therefore an increased selectivity for Na. With an increase in chlorinity, montmorillonite increases from 47 to 61 per cent and the total of the exchangeable cations (Na, Mg, Ca, K) increases from 36 to 82 m-equiv./100 g.

THE I.R. SPECTRA OF INTERLAMELLAR KAOLINITE-AMIDE COMPLEXES—I. THE COMPLEXES OF FORMAMIDE, N-METHYLFORMAMIDE AND DIMETHYLFORMAMIDE

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The i.r. spectra of interlamellar kaolinite complexes with formamide, N-methylformamide and dimethylformamide have been examined. The spectra show that the amides hydrogen-bond, through the C=O group of the amide to the inner surface kaolinite hydroxyls and decrease the intensity of the kaolinite $\nu(\text{OH})$ bands. Hydrogen-bonded kaolinite hydroxyl bands appear at lower frequencies and these have been correlated to the original kaolinite $\nu(\text{OH})$ bands. Other kaolinite bands in the complexes show smaller perturbations of the kaolinite vibrations. Each amide hydrogen-bonds to different groups of hydroxyls. Formamide hydrogen-bonds to the 3690 and 3664 cm^{-1} hydroxyls. N-methylformamide to the 3690 and 3648 cm^{-1} hydroxyls. The interpretation for the dimethylformamide complex is less clear. The $\nu(\text{NH})$ frequencies of formamide and N-methylformamide in the complexes

are intermediate between that in dilute non-polar solution and in the liquid. This could arise from either or both a degree of intermolecular association of the amide when between the kaolinite lamellae, or to weak N-H...O hydrogen bonds to the tetrahedral oxygen sheet of the lamellae.

ADSORPTION OF HYDROXY-AL BY CERTAIN PHYLLOSILICATES AND ITS RELATION TO K/Ca CATION EXCHANGE SELECTIVITY

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The adsorption of hydroxy-Al by the 2-0.2 μ size fractions of muscovite, biotite, K-depleted micas, vermiculite and montmorillonite was studied. The differences in the amounts of hydroxy-Al adsorbed were apparently related to the expansibility and layer charge of minerals, the ionic saturation and degree of K-depletion, the basicity (OH/Al ratio) of the equilibrating hydroxy-Al solution, and the solution-clay ratio. The CEC reduction was not necessarily proportional to the amount of Al adsorbed because CEC reduction may occur through occupation of cation exchange sites by hydroxy-Al, or through hindrance to the entry of the replacing cation to these sites. Aluminum interlayering generally increased the K/Ca cation exchange selectivity (CES) of Na-vermiculite and K-depleted biotite, whereas the K/Ca CES of Na-montmorillonite was little affected. The basicity of the initial hydroxy-Al solution appeared to affect the K/Ca CES of Na-vermiculite and K-depleted biotite by controlling the amount of hydroxy-Al adsorbed. The data indicate that in addition to the "propping effect," hydroxy-Al interlayers may affect the K/Ca CES through the following mechanisms; (1) the "preferential occupation" of Ca adsorbing sites, and/or (2) the "retarding effect" on the entry of the more hydrated Ca ions.

FREEZE-DRIED AND THAWED CLAYS

James Lincoln and Rodney Tettenhorst

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Heating montmorillonites to their dehydroxylation temperatures destroyed their ability to form an aerogel. The breakdown of the aerogel structure coincided with the loss of hydroxyl water from the montmorillonite. Apparently, this loss of water was accompanied by a loss of the layer charge. Particle size and aerogel-forming ability appear to be inversely related properties for at least some montmorillonites. The kaolinite investigated did not form an aerogel in any size fraction. The formation of montmorillonite aerogels from various concentrations of clay was investigated. The texture and physical appearance of these aerogels was examined and presented herein. Thawed clay suspensions exhibited a variety of behaviors. The Volclay bentonite, which apparently formed a true sol was unaffected by freezing. In all other clays at least some of the fine clay particles agglomerated on freezing and large clumps were observed dropping out of the melting ice. After stirring the thawed suspensions less clay was dispersed than in the unfrozen suspension counterparts. Addition of a dispersing agent to these suspensions

caused more clay to remain dispersed following freezing-thawing-stirring.

LOW TEMPERATURE HYDROTHERMAL SYNTHESIS FROM DOLOMITE OR CALCITE, QUARTZ AND KAOLINITE

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Dolomite or calcite, quartz and kaolinite in various proportions were reacted at 250-300°C temperatures and pressures up to 90 bars in a hydrous environment. Reactions which approached completion produced talc, calcite, montmorillonite, anorthite (both metastable hexagonal and stable triclinic polymorphs) and the rare Ca-zeolite, garronite. These reactions are applicable to diagenesis, low-grade metamorphism and hydrothermal alteration.

FLINT CLAY BY HYDROTHERMAL ALTERATION OF SEDIMENTARY ROCK IN MEXICO

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This paper documents the first report of flint clay in Mexico, located at Estola, Guerrero, 199 km south of Mexico City, on Mexico Highway 95. It is the first report (known to the writers) of flint clay formed by hydrothermal alteration. It describes in *in-situ* alteration of a calcareous, silty shale to flint clay (well-ordered kaolinite). The changes during alteration are mineralogical, chemical, and structural. Calcite, comprising about one-third of the shale, quartz and probably some feldspar comprising a scant third, and a mixture of greenish-yellow (limonitic) clay minerals are dissolved or altered ultimately to white kaolinite (monomineralic). Calcium carbonate, free and combined silica, and iron compounds are dissolved, while simultaneously the alumina is relatively enriched. The fissility, inequigranularity, and cementitious fabric of shale are changed to the massively homogeneous, fine-grained, interlocking fabric that is typical of flint clay. The sequence of changes, which overlap, are; (1) dissolution of carbonate minerals, (2) mobility of iron, replacement of quartz and feldspar by kaolinite; and (3) intensive "digestion" of rock substance to homogeneous, essentially monomineralic, kaolinitic flint clay. Alunite, and secondary vein-calcite or gypsum may accompany the flint clay. This occurrence lends support to the concept that flint clay is formed from presumably only sedimentary parent rock.

SEQUENTIAL ACTIVE ALTERATION OF RHYOLITIC VOLCANIC ROCK TO ENDELLITE AND A PRECURSOR PHASE OF IT AT A HOT SPRING IN MICHOCAN, MEXICO

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Sequential alteration of volcanic rock of rhyolitic composition to a precursor of endellite, and thence to tubular

endellite, may be observed at a hot spring about 27 km north of Ciudad Hidalgo, Michoacan, Mexico. Ojo Caliente de Laguna Larga (or Verde) yields H_2S-SO_2 -containing water, temperature about $45^\circ C$, pH 3.5-3.7, from multiple orifices in vesicular and slabby rock with which the water reacts. First-stage alteration of the rock consisted of permeation and dissolution, accompanied by deposition of clay substance in vesicle walls. The clay substance, although "amorphous" to X-rays, yields a weak DTA of endellite, and kaolinite. It is interpreted as a precursor of endellite. Further reaction included continued filling of vesicles and spreading argillation which coalesced between vesicles and other rock pores. Ultimately, the rock was completely "digested" to well-

defined endellite. Strong desilication and depotassication of the rock is indicated by the dissolved substances in the spring water: Si 59.1 (equivalent to $127 SiO_2$) $\mu g/ml$; Al, 1.63; Fe, 0.65; Mg, 0.21; Ca, 178; Na, 0.73; K, 13.7. Despite high K^+ , predominantly high H^+ and Al^{3+} induce formation of endellite. The clay-water system accords well with stability diagrams. Allophane-endellite in Indiana and endellite at Stanford, Kentucky, are formed from cold, strongly acid, meteoric-water solutions high in Si and Al relative to kaolinite dissolved in water. Factors of genesis common to both hot- and cold-water endellite are cited, suggesting that they are permissively critical, but not necessarily restrictive, to the origin of endellite.