

# CLAYS and CLAY MINERALS

at a glance

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## QUANTITATIVE CLAY PETROLOGY: THE TREES BUT NOT THE FOREST?

Kenneth M. Towse

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Gravitational settling and centrifuge techniques have been criticized in the preparation of X-ray specimen mounts for quantitative clay petrology because of the marked mineral segregations that can occur. Although the same factors can operate to produce error in the separation of the traditional less-than-2- $\mu\text{m}$  fraction, this potentially more important source of bias is seldom taken into consideration. A fair representation of the bulk sample deserves at least as much attention as a representative X-ray mount. The most accurate and precise X-ray analyses may be geologically misleading or meaningless otherwise and translate as exercise in precision for its own sake.

## LATH-SHAPED UNITS IN FINE-GRAINED MICAS AND SMECTITES

Necip Güven

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Transmission electron images of fine-grained micas in bentonites exhibit lath-shaped units. These units seem to be associated along the (110) planes—referred to  $2M_1$  mica cell—with perfect registry of their individual lattices. In doing so, they seem to provide lateral growth in the (001) plane. These lath-shaped units are arranged in the [001] direction in modes similar to the stacking of layers in mica polymorphs. Aggregations of lath-shaped units with polycrystalline montmorillonite particles are also observed in several bentonites. From the SAD pattern these laths are inferred to be dioctahedral layer silicates. However, they cannot be exactly identified any further. It is an open question whether these laths have grown from the montmorillonite or are simply entangled with it.

## ORDER AND DISORDER RELATIONS IN THE DISTRIBUTION OF THE SUBSTITUTIONS IN SMECTITES, ILLITES AND VERMICULITES

G. Besson, A. Mifsud, C. Tchoubar and J. Mering

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It is shown that order-disorder relations in the distribution of the isomorphous substitutions are important in the characterization of different 2/1 phyllosilicates and in the determination of their behavior. These order-disorder relations are shown by selected area diffraction patterns obtained from single crystals. The range of layer charges corresponding to smectites (charge per half-cell  $< 0.6$ ) is that for which phyllosilicates are stable with disordered substitutions. Phyllosilicates with charge  $> 0.6$  show anomalous diffusions which indicate that the distributions of exchangeable Ba ions are partially ordered; this result is taken as evidence that the isomorphous substitutions also are partially ordered.

## THE HETEROGENEITY OF THE CHARGE DENSITY IN MONTMORILLONITES

M. S. Stul and W. J. Mortier

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The heterogeneity of the interlayer cation density and the corresponding mean layer charge density due to isomorphous substitution have been determined for six montmorillonite samples. This has been achieved by considering the transition of a monolayer to a double layer complex with alkylammonium ions. The transition is related to the interlayer cation density, together with the variation of the apparent spacings, which in turn is related to the composition of this two-component mixture.

All the samples showed a heterogeneous interlayer cation distribution and a differing mean charge density.

### FABRIC-PROPERTY RELATIONSHIPS IN FINE GRANULAR MATERIALS

Arshud Mahmood and James K. Mitchell

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In this investigation fabric-property relationships were studied in a silty fine sand sized crushed basalt—an artificial 'soil' that has previously been used to simulate lunar soil. The fabric was characterized by measuring preferred orientations of grains, and pore size distribution was determined by mercury intrusion porosimetry. When deposited by pouring, the grains acquired strong preferred orientations in the horizontal direction and formed pores between 1 and 30  $\mu\text{m}$  dia. Densification by static or dynamic compaction resulted in near random grain arrangement and pore sizes between 0.1 and 10  $\mu\text{m}$  dia.

Strength in direct shear and one-dimensional compressibility with the associated lateral stresses were measured. The strength was up to 30 per cent higher when the sample was sheared normal to the preferred orientation of grains than when the shearing was parallel to the orientation direction. This is to be expected, as shearing across the preferentially oriented grains should involve breakage or reorientation of many grains. At a given initial void ratio the compressibility of statically compacted specimens was larger (up to 30 per cent higher axial strain) than that of dynamically compacted specimens at very low stresses. At higher stresses both samples exhibited equal compressibility, suggesting that the grains become more randomly arranged at low void ratios (comparing samples of equal initial void ratios).

### ADSORPTION AND TRANSFORMATION OF HCN ON THE SURFACE OF COPPER AND CALCIUM MONTMORILLONITE

M. Cruz, A. Kaiser, P. G. Rouxhet and J. J. Fripiat 417

Adsorption isotherms of HCN by Cu- and Ca-montmorillonites show that water present in the interlayer space decreases HCN adsorption.

For Ca-montmorillonite, infrared spectra permit distinguishing between HCN interacting with the cations and molecules filling the interlayer space. Both types are removed upon outgassing. The residual water is not displaced by HCN.

On Cu-montmorillonite, species (presumably  $\text{CN}^-$  ions) strongly held by the cations are observed in addition to adsorbed HCN molecules. The residual hydroxyls retained in the interlayer space are removed by the adsorption of HCN. These hydroxyls, either  $\text{OH}^-$  or  $\text{H}_2\text{O}$ , are characterized by two well defined stretching bands.

Infra-red spectra of samples heated below 200°C show that adsorbed HCN is involved in chemical reactions. For both clays, bands appear in the region characteristic of carbonyl and carboxyl groups; the production of ammonium is detected for Cu-montmorillonite. These reactions and the observed spectral features could be accounted for by the formation of formamide.

### AMORPHOUS COATINGS ON PARTICLES OF SENSITIVE CLAY SOILS

E. McKeyes, A. Sethi and R. N. Yong 427

Post-glacial Champlain Sea sediments in Quebec and Ontario are often extremely sensitive. Suggestions of considerable amorphous material in these soils come from X-ray diffraction results, as well as electron micrographs. A method for selective dissolution and analysis of amorphous material is used to study two Champlain Sea deposits. The amorphous material removed amounts to 11–12 per cent of the soils and consists mainly of silica and iron oxide. The treated samples have enhanced X-ray diffraction peaks and much cleaner particles as seen by electron microscopy.

### THE SYNTHESIS OF ZINC SILICATES AT 20°C AND ATMOSPHERIC PRESSURE

K. G. Tiller and J. G. Pickering

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Zinc silicates were synthesized under conditions analogous to surficial weathering environments. The main product, regardless of conditions of precipitation or ageing, was shown by X-ray, i.r., electron microscopic and chemical evidence to be a 2:1 layered zinc silicate equivalent of stevensite. In the presence of aluminium, a 1:1 layered zinc silicate was formed as well, in confirmation of published work. The stability of the zinc silicate, in relation to carbonate, was favoured by the presence of aluminium in the lattice and silicic acid in the equilibrium solution. Zinc layer silicates were formed under conditions that generated orthorhombic zinc hydroxides and/or basic salts in the absence of silicon; the involvement of the brucitic zinc hydroxide ( $\alpha$ -form), as proposed by earlier workers, could not be supported. Crystalline zinc layer silicates were formed by the slow evolution of the initial gels. Such layer silicates, but not willemite or hemimorphite, could have an important role in the control of chemical reactions of zinc in soils.

### SURFACE ACIDITY OF MONTMORILLONITES

M. Frenkel 435

Surface acidity of almost homoionic montmorillonites was measured by titrating selected Hammett indicators adsorbed on the clay with *n*-butylamine.

As expected, the acidity is strongly affected by the exchangeable cations and the degree of hydration of the clay. Greater polarizing ability of the interlayer cations increases both the strength and number of acid sites per  $H_0$  value. The acidity of 'activated' or heated H-montmorillonite does not

exceed that of untreated *H*-montmorillonite. The origin of the negative charge in the montmorillonite appears to affect the acidity of the clay.

It is concluded that the very high acidities reported in the literature ( $H_0 < -5.6$ ) are apparent only and are due to the physisorption of the indicator.

Sample	$\Delta G_f^0$ 'illite formula'	$\Delta G_f^0$ 'muscovite formula'
Fithian illite	-1319.7 kcal/fw	-1334.8 kcal/fw
Grundy illite	-1322.7	-1338.0
Rock Island illite	-1307.3	-1333.2
Marblehead	-1310.8	-1334.2
Gage	(No formula)	-1337.6

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### AQUEOUS DISSOLUTION STUDIES OF ILLITE UNDER AMBIENT CONDITIONS

A. L. Reesman

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Dissolution data on five of the six illites reported by Reesman and Keller (1968) indicate that these illites are more stable than was previously thought. The revised Gibbs free energies of formation ( $\Delta G_f^0$ ) with respect to the 'ideal' illite formula and the muscovite formula are:

Use of muscovite formula as an indirect comparator provides a means of predicting the relative stabilities of these chemically complex materials.

The response of illite-equilibrated solution to a kaolin  $\Delta G_f^0$  was found in all samples in which a 7 Å mineral phase was detected by X-ray diffraction. Stability diagrams based upon the  $\Delta G_f^0$  with respect to ideal muscovite and kaolin formulas show a rather wide range in chemical conditions through which illites and kaolin minerals with differing  $\Delta G_f^0$  would be stable. However, in carbonate rocks and sea water illite is stable relative to kaolin. During the weathering of carbonates the lower pH zones in the clay-rich residuum above the carbonates favor the transformation of illite to kaolin minerals.