

# CLAYS and CLAY MINERALS

of a glance

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Scientific Contributions	1-62
Notes, Letters and News	
Notes	63
Letters	67
News	69

## ANALOGUES OF FLINT CLAYS IN SOVIET LITERATURE

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1

The term "flint clay" used in USA and several other countries, corresponds very closely to the term "toasted bread (sukhar) clay." In both USA and U.S.S.R., the typical occurrences of "toasted clays" are confined to deposits of the lower Carboniferous. In their properties and occurrence the well-studied toasted clays of the Borovichy deposit (Novgorod province) are highly similar to the flint clays of Missouri, differing significantly only in having lower bulk specific gravity and higher porosity than do Missouri flint clays. Varieties with excess free alumina (diaspore, boehmite) are observed both among "toasted" and flint clays. The author suggests the term "toasted complex" (sukharnii kompleks) which corresponds to W. D. Keller's term "flint clay facies." The clays of the "toasted complex" are sediments of ancient swamps and lakes which contained rich vegetation. Their source material was finely dispersed silicate particles transported from dry land. The structure and properties of toasted clays are explained by the precipitation of kaolinite as colloidal clumps in which crystallization occurred with formation of intimate intergrowths and variously oriented segregations.

## PORE SIZE DISTRIBUTIONS IN CLAYS

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7

A knowledge of the distribution of pore sizes in clay and soil bodies is a useful element in the microstructural characterization of such materials. Pore-size distributions and total porosity of a number of reference clays, naturally-occurring subsoils, and commercial clay samples prepared in various ways were determined by mercury porosimetry. The range of equivalent pore diameter explored covered almost five orders of magnitude, from several hundred microns down to approximately 150 Å. The method and its assumptions are critically evalu-

ated, and measurements of the contact angle of mercury on clays yield values of 139° for montmorillonite and 147° for kaolinite and illite clays. The extent of shrinkage on oven-drying prior to mercury intrusion is assessed in each case and found to vary from insignificant to as much as 30 per cent of the pore space, depending on microstructural state and degree of initial saturation. The development of techniques for water removal which do not involve change in pore structure is explored. Some preliminary results for structurally weak saturated clays suggest that critical-region drying and perhaps freeze-drying procedures may be practical.

## THE NATURE OF INTERLAYERING IN MIXED-LAYER ILLITE-MONTMORILLONITES

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25

The nature of interstratification in mixed-layer illite-montmorillonites has been investigated by comparison of diffraction patterns of ethylene glycol and ethylene glycol monoethyl ether treated samples with calculated one-dimensional diffraction profiles. The calculated profiles take into account the effects of particle size distribution, chemical composition, and convolution factors as well as proportions of layers and interstratification type. On the basis of detailed matching of diffraction patterns of monomineralic illite-montmorillonites of known chemical composition, it is concluded that there are three types of interstratification: (1) random, (2) allevardite-like ordering, and (3) superlattice units consisting of three illite and one montmorillonite layers (IMII). By comparison of suites of calculated profiles with the diffraction patterns of many samples of illite-montmorillonites, it is concluded that virtually all illite-montmorillonites with expandabilities from about 40 to 100 per cent are randomly interstratified (allevardite being exceptional); at <40 per cent montmorillonite layers they almost always have ordered interstratification. Allevardite-like ordering predominates in illite-montmorillonites which

have ordered interstratification, with the IMH superlattice varieties confined to samples with about 10 per cent montmorillonite layers.

#### ADSORPTION STUDIES ON KAOLINITES

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37

Adsorption studies have been performed on Georgia kaolins having a broad range of crystallinity and particle size distributions (from  $0.1 \mu$  to  $44 \mu$ ) using  $N_2$  (78°K),  $H_2O$  (273°K), and  $BuNH_2$  (298°K). Using both vapor and liquid phase adsorption techniques, surface affinities of the adsorbates were determined. Modified Frenkel-Halsey-Hill plots were used to compute the preferential adsorptivity of  $H_2O$  vapor over  $N_2$  (hydrophilicity index, H.I.) as a function of crystallinity index, C.I., and particle size. For amine adsorptivity, non-aqueous adsorption isotherms were obtained. Within any geographic deposit, crystallinity exhibits an inconsistent pattern with respect to particle size. A single generality is the tendency for crystallinity to increase toward the fine particle size range,  $D \rightarrow 0.2 \mu$ . Adsorptivities of  $N_2$ ,  $H_2O$ , and  $BuNH_2$  show no dependence upon crystallinity within a given particle size range. However, F.H.H. Compensated slopes, describing the preferential adsorptivity over  $N_2$ , show a definite decrease as crystallinity increases. A striking anomaly occurs in the vicinity of  $0.2 < C.I. < 0.7$  where H.I. increases briefly then returns to the original trend. The rate of decrease of H.I. versus C.I. is consistently steeper with increasing particle size. Adsorption of water vapor most likely occurs as a 1:1 configuration on each silica-alumina edge group, 1:1 on each basal silica, and 1:2 (hindered configuration) on each basal alumina group. The data suggest that amines adsorb preferentially and quantitatively on the edges, i.e. the Lewis and Bronsted acid sites, and follow a Langmuir pattern.

#### POTASSIUM AND CESIUM ION SELECTIVITY IN RELATION TO CLAY MINERAL STRUCTURE

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47

Selectivity of a number of vermiculites, montmorillonites and micas for K and Cs ions was determined by sorption of these ions from equilibrium solutions of diverse concentrations. The selectivity coefficients were related

to the layer charge density and the area of the frayed edges in layer silicates. Montmorillonites had the smallest selectivity for the two ions, while biotite and illite had the greater selectivity. Selectivity of biotite and illite was limited to small concentrations of K, however. At greater concentrations the selectivity of vermiculite for K exceeded the selectivity of the micas. The greater selectivity of vermiculites than montmorillonites for K and Cs ions was attributed to the greater layer charge density is vermiculites. The greater selectivity of micas than montmorillonites and vermiculites was attributed to the frayed edges of micas in addition to their larger layer charge density. As the frayed edges in illite were increased in area by removal of the interlayer K, the selectivity of illite for K also increased; thus confirming the selectivity of frayed edges for the K ions.

#### IRON ALKOXIDE OBTAINED BY REACTING IRON OXIDES WITH GLYCEROL

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53

Goethite, lepidocrocite and hematite were reacted with glycerol and reaction products were studied at various steps of the reaction. After a treatment of 16 hr at 245°C the final form of the reaction product, a deep green soft solid, was obtained whatever the starting material. According to hydrolysis and chemical analysis, the reaction product can be identified as iron alkoxide. Hydrolysis of the solid by boiling water yielded glycerol and a strongly magnetic material characterized by a spinel structure like maghemite and magnetite. The iron alkoxide is seen by electron microscope as large well-formed hexagonal platelets. The similarity between *a* and *b* parameters of this compound and those of brucite suggests that the iron alkoxide structure is based on an iron (II and III) octahedral layer. The glycerol chains should be located between the sheets. Two models were proposed in which iron and oxygen, linked to the chain of glycerol, could be accommodated in octahedral layers giving a basal distance of  $8.1 \text{ \AA}$ . At least two steps are involved in the formation of the iron alkoxide: (1) a rearrangement of the structure of starting material with accommodation of carbon in the structure and (2) a reduction of ferric iron.