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CLAYS and CLAY MINERALS at a glance

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TITANIUM AS FREE OXIDE AND SUBSTITUTED FORMS IN KAOLINITES AND OTHER SOIL MINERALS

D. L. Dolcater, J. K. Syers and M. L. Jackson 71

Titanium in TiO_2 minerals was differentiated from that isomorphously substituted into minerals by the use of dihydrogen hexafluorotitanate (hydrofluotitanic acid, acid, H_2TiF_6), which selectively dissolved minerals containing substituted Ti^{4+}, leaving free crystalline TiO_2 minerals in the residue. Titanium analyses on the original samples and the residues remaining after H_2TiF_6 treatment, by both wet chemical (Tiron) and neutron activation methods, indicated that an average of 86 per cent of the titanium in seven kaolinite samples was present in the residual TiO_2 form (largely anatase), whereas only 28 per cent in two bentonites was present in the TiO_2 form. Residual Ti accounted for 100 per cent of the Ti in synthetic anatase and for 92 per cent of the Ti in coarse clay sized rutile, the latter value suggesting that about 8 per cent amorphous TiO_2 was removed from the nechanically dry ground rutile by the H_2TiF_6 reagent. The Ti present as residual TiO_2 in a variety of other samples ranged from 0 to 100 per cent.

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pH DEPENDENT ION EXCHANGE PROPERTIES OF SOILS AND CLAYS FROM MAZAMA PUMICE

F. W. Chichester, M. E. Harward and C. T. Youngberg 81

Cation exchange capacity (CEC) measurements were made for whole pumice soil samples by several methods, including standard procedures involving cation saturation, excess salt removal, and cation displacement steps, and a $^{45}Ca^{2+}$ radioisotope dilution procedure. Results indicated that the vesicular pores of the pumice soil material affected attainment of ion diffusion equilibria, and, hence, introduced a large source of error in the measurements. On this basis, the validity of ion exchange values obtained for these soils was concluded to be subject to considerable doubt. More important, however, the solute and/or solution exclusion or retention exhibited by pumice particles during the course of CEC procedures was thought to be highly significant with respect to the probable influence exerted on physical, chemical, and biological properties of the soils in the field situation.

Interpretation of pH dependent cation and anion exchange capacity measurements of the $< 2\mu$ clay fraction of the pumice soils was confounded by the occurrence of hydroxy interlayered 2:1 phyllosilicate materials in admixture with the amorphous components. Since the interlayered materials contributed an indeterminate proportion of the total pH dependent charge of the mixture, it was further concluded that the measurement of this property was of little direct value in assessing the relative amounts of amorphous and crystalline components in the clay fractions of the soils investigated. However, the values obtained revealed fundamental aspects of ion exchange behavior which are important to understanding the complex systems involved.

SURFACE AREA OF HOMOIONIC ILLITE AND MONTMORILLONITE CLAY MINERALS AS MEASURED BY THE SORPTION OF NITROGEN AND CARBON DIOXIDE

L. A. G. Aylmore, I. D. Sills and J. P. Quirk 91

The surface areas obtained by application of the B.E.T. theory to adsorption isotherms of nitrogen and carbon dioxide gases at 77°K and 195°K respectively on homoionic samples of illite and montmorillonite clays have been examined. The isotherms were obtained using a standard volumetric adsorption system and the results are compared with those obtained by Thomas and Bohor (1968) using a dynamic sorption system.

Small amounts of residual water have been shown to have a marked influence on the accessibility of the internal surfaces of the montmorillonite clays to nitrogen and carbon dioxide adsorption. In this respect, the standard outgassing procedure under high vacuum seems more efficient than that used in dynamic systems. The present data indicate that provided the sample has been satisfactorily outgassed there is little penetration of nitrogen or carbon dioxide gases into the quasi-crystalline regions of montmorillonite clays. With the exception of the caesium saturated montmorillonites, the surfaces of the clays are more accessible to the smaller nitrogen molecules than to carbon dioxide assuming the values used for molecular area are correct.

ADSORPTION OF SURFACTANTS ON MONTMORILLONITE

Wayne F. Hower 97

Some authors have stated that anionic surfactants are not adsorbed by montmorillonite while others indicate very minor adsorption. Attempts to quantitatively determine the degree of adsorption have shown that certain problems exist which, unless recognized, will completely mask results. Some of these difficulties have been overcome but exact data have not yet been obtained. However, enough information has been gathered to prove that adsorption of anionic surfactants on montmorillonite is real and substantial. Reliable adsorption data for cationic and nonionic surfactants and one having both nonionic and anionic character have been obtained. It is indicated that 550 mg of these surfactants are adsorbed by one gram of montmorillonite. X-ray diffraction data for complexes of all surfactants investigated confirm positive adsorption. However, the thickness of the adsorbed surfactant layers cannot always be quantitatively related to the amount of adsorbed surfactant.

I.R. STUDY OF ALKYL-AMMONIUM VERMICULITE COMPLEXES

J. M. Serratosa, W. D. Johns and A. Shimoyama 107

Two octyl-ammonium vermiculite complexes with different 001 periodicities have been studied by i.r. spectroscopy. In each case i.r. spectroscopy affords information on the orientation of the $-NH_3^+$ groups and the strength of the hydrogen bond between these groups and the silicate oxygen surfaces. Also a perturbation of the vibration of the OH groups of the silicate has been observed that seems to be related to the distance from the center of the layer at which the $-NH_3^+$ groups are situated.

The i.r. results are discussed in relation to the structural models deduced from X-ray analysis.

RECTORITE AND THE RECTORITE-LIKE LAYER STRUCTURES

G. V. Henderson and W. F. Bradley 115

Recurrent reports and analyses of X-ray diffraction data from regularly alternating and nearly regularly alternating structures like rectorite provide opportunity for a descriptive discussion of their nature. MacEwan-transform-based analyses have uniformly shown higher incidence of unlike adjacent layers than would be expected from random distribution.

The continuous Fourier transforms for pairs of 2:1 layer silicate structures evaluated normal to the layers, provide a family of similar curves that are differently stretched out in reciprocal space for different assumed intervals between the two members of a pair.

For each exactly alternating example the relative amplitudes of the ordered reciprocal modes distinguish the instances for which fixed interlayer populations are Na^+ from those for which they are K^+.

For sequences not exactly alternating scattering maxima are displaced from exact incremental positions in conformity with the Hendricks and Teller mixing functions, but relative intensities of adjacent observations still distinguish the alkali identities.

HYDROTHERMAL KAOLINIZATION IN MICHOACAN, MEXICO

Thomas L. Kesler 121

Active kaolinization of middle Tertiary obsidian and rhyolitic breccia in the San Andres range is affected by sulfurous hot waters and hydrous vapors emitted as springs, fumaroles, and geysers. The alteration preserves original rock textures and forms conspicuous aureoles around the hydrothermal vents, which shift about with slumping of the saturated clay. Systematic exploration by 87 test pits with maximum depth of 45 ft permitted inspection of the kaolin in place, and furnished bulk samples for laboratory work. Besides kaolinite, the clay contains unevenly distributed cristobalite and alunite, and traces of mercury. The natural brightness of the pure kaolinite approaches 90 if unstained by weathering, but little of it is pure. The yield of paper-coating fraction is small, and the composition and behavior in slurries are nonuniform. Most of the kaolinized material in the hydrothermal deposits is soft. Some, however, is hard and rock-like. Similar material occurs in clastic sediments of late Tertiary age, suggesting that the hydrothermal activity began at least as early as the Pliocene.