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CLAYS and CLAY MINERALS at a glance

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THE I.R. SPECTRUM OF STRUCTURAL HYDROXYLS OF K-DEPLETED BIOTITES

J. Chaussidon 59

The i.r. spectrum of K depleted biotites (structural OH stretching range) has been studied with monocrystals equilibrated at various water contents. Prior to spectroscopic measurements, the samples were submitted to deuteration treatments which displaced the hydration water spectrum to the OD region and made it possible to observe the behavior of the structural hydroxyls without interference from hydration water.

In these conditions it was shown that the high frequency absorption of K depleted biotites (N + l bands) is the sum of two absorptions: the first corresponds to the initial mica spectrum, the second corresponds to the hydrated phase in which component bands (according to Vedder and Wilkins) are shifted by 36 cm^{-1} towards low frequencies.

Simultaneously it was shown that low frequency bands (V bands) decreased in intensity. This unexpected observation has been explained by a partial deuteration of structural OH, which takes place during the preliminary contacts of the samples with D_2O vapour.

GEOCHEMICAL MECHANICS FOR THE DISSOLUTION, TRANSPORT, AND DEPOSITION OF ALUMINUM IN THE ZONE OF WEATHERING

W. H. Huang and W. D. Keller 69

Organic acids in the 0·01M concentration range representing amino-, aliphatic, and aromatic types present in humus dissolve 70–85 ppm Al from Arkansas bauxite at room temperature, whereas 0·03 ppm is dissolved in water. The species of Al in aqueous solution, calculated from stability data, range from Al^{3+} at pH 3 and lower, through $Al_2(OH)_2^{4+}$ at a maximum concentration at pH 4·5, $Al(OH)^{2+}$ at a maximum at pH 4·7, $Al(OH)_2^{+}$ at a maximum at pH 6·0, to $Al(OH)_4^{-}$ at pH 8·5 and higher. In salicylic acid an Al–Sal^{+} complex occurs between pH 1·5 and 8·5, and is at a maximum at pH 4·2. Solubility of Al obviously is pH dependent; also because of the vulnerability of organic acids to oxidation, the solubility and transport of Al is indirectly Eh dependent. Anions that combine with Al include OH to form bauxite, PO_4 to form lateritic phosphate such as the Bone Valley Formation, Fla., and SiO_4 to form allophane or kaolin as noted in the kaolin synthesis by Linares and Huartes. Sponge-like pisolitic or oolitic structures, and mineral veins in bauxites, lateritic phosphates, and some flint clays attest to mobilization of Al in solution. Lignites and humus zones associated with laterites are a logical geologic source of these complexing organic solvents. Although Al is inherently mobile, such commonly available precipitating anions render Al relatively immobile.

CATALYTIC ACTIVITY OF SODIUM KAOLINITES

D. G. Hawthorne and D. H. Solomon 75

Kaolinites, catalytically active for the polymerization of styrene, can be deactivated by treatment with 1N aqueous sodium chloride. Subsequent washing of the sodium kaolinite results in a facile hydrolysis yielding an active hydronium/aluminum kaolinite in which the exchangeable cations act as surface Brønsted acid initiation sites.

THE I.R. SPECTRA OF LYSINE ADSORBED ON SEVERAL CATION-SUBSTITUTED MONTMORILLONITES

Sung Do Jang and Robert A. Condrate, Sr. 79

The i.r. spectra (4000–1200 cm^{-1}) are obtained for several cation-substituted-montmorillonite-lysine complexes that were prepared at their natural pHs. Analyses of the spectra of copper–, cobalt–, nickel– and zinc–montmorillonite films indicate that bidentate chelate complexes which contain protonated ϵ-amino-groups are present in the interlamellar spaces. Investigation of the spectra of the hydrogen–, calcium– and natural–montmorillonite films indicates that the dominant adsorbed species for these complexes is a lysine cation in which both the α- and the ϵ-amino-groups are protonated while the carboxyl group is ionized.

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ELECTRON OPTICAL OBSERVATIONS ON MARBLEHEAD ILLITE

Necip Güven 83

Electron optical observations on Marblehead illite showed the presence of twinned aggregates of lath-shaped crystallites. The selected area diffraction patterns of these aggregates indicate a strict orientational relationship between them.

Original twinned mica flakes display all possible stages of the transformation of these micas into lath-shaped illites, where the *a* and *b* dimensions of layers do not show any noticeable changes, but *c*-dimension becomes shortened in the illites. The transformation seems to involve parting along (110) of the micas, subsequent H_2O and OH inclusion in the structure and other possible chemical changes resulting from the hydration. The morphology and the size of lath-shaped crystallites displaying (001) and (110) forms seem to be responsible for the excess of water and K-deficiency in the Marblehead illite compared to the micas.

Individual illite laths commonly have a length 0·1–4 μ, a width of 0·01–0·1 μ and a thickness varying between 10 and 50 Å.

X-RAY DIFFRACTION AND ELECTRON OPTICAL STUDIES ON SMECTITE AND α-CRISTOBALITE ASSOCIATIONS

Necip Güven and Ralph E. Grim 89

Alteration products of volcanic materials from various localities in Wyoming, USA, Italy, Yugoslavia and Mozambique are mainly smectites and cristobalites with small amounts of kaolinite.

Smectite and cristobalite form separate and intergrown aggregates of microcristallinity. X-ray diffraction studies show that the silica is α-cristobalite with a noticeable stacking disorder. Small aggregates of optically pure α-cristobalite, which were separated by an appropriate mixture of bromoform and carbon tetrachloride, are shown to contain a noticeable amount of smectite on Debye–Scherrer diffraction photographs for the samples from Italy and Wyoming, USA.

Transmission electron micrographs and selected area electron diffraction photographs show, in addition to smectite-α-cristobalite aggregates, the presence of idiomorph single crystals of kaolinite.

SELECTIVE SORPTION AND FIXATION OF CATIONS BY CLAY MINERALS: A REVIEW

B. L. Sawhney 93

Investigations concerning selective sorption and fixation of K and similar cations by clay minerals and soil clays and the mechanisms of these reactions are reviewed. In particular, recent observations on selective sorption of these ions in dilute solutions by weathered micas and vermiculite in relation to the interlayer structures are discussed in detail. Also, implications of the resistance to weathering of small mica particles to cation selectivity by soils are described. Despite the increased understanding of sorption and fixation reactions, the following aspects remain unclear.

First, the mechanism of the collapse of alternate layers in vermiculite on K or Cs sorption has not been unequivocally established. Second, factors that impart stability to the central core of mica particles so that K extraction becomes progressively difficult are now known. Third, inability of Ca or Mg ions to expand interlayers of Cs-saturated vermiculite in contrast to K-saturated vermiculite is not completely understood.

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