

CLAYS and CLAY MINERALS

at a glance

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CLAY MINERAL FORMATION IN A DEEPLY WEATHERED BOULDER CONGLOMERATE IN NORTH-EAST SCOTLAND

M. J. Wilson, D. C. Bain and W. J. McHardy 345

The clay minerals formed in a deeply weathered boulder conglomerate of Middle Old Red Sandstone (Devonian) age in north-east Scotland have been studied by a variety of physical and chemical techniques. The granite and granulite boulders in this deposit are weathered most completely. With the exception of microcline, all the feldspars in these rocks—orthoclase feldspar, orthoclase-micropertite, albite and oligoclase—weather to a Chetotype montmorillonite, poor in iron. Electron and optical microscopy indicate that the weathering transformation is a direct one, without the intervention of any intermediate crystalline or well-defined amorphous phase. Structural control of the primary mineral over the formation of the montmorillonite seems to have been a minimal factor and the evidence suggests that the clay mineral crystallized from the soluble or colloidal products arising from the decomposed feldspars. Smaller amounts of kaolinite also formed during weathering but largely from the weathering of muscovite. The environment in which these changes occurred seems to have been alkaline in a relatively closed system. Chemical analyses of related cores and weathered shells of granite and granulite boulders show only a slight decrease of silica and an increase in magnesia. Judging from the extent of alteration to secondary clay minerals, the order of resistance towards weathering of the primary minerals in these rocks is plagioclase = orthoclase < muscovite < biotite < microcline < quartz.

FABRIC OF KAOLINITE AND ILLITE FLOCCULES

Neal R. O'Brien 353

A scanning and high voltage electron microscope study of the fabric of laboratory sedimented moist uncompressed

kaolinite and illite floccules reveals an abundance of face-face flake orientation in the porous clay network. Clays were flocculated in the laboratory in both distilled water and slightly saline (1 g/l. NaCl) water using various clay concentrations. Floccules taken from the moist clay mass were prepared for study by freeze-drying and impregnation with polyethylene glycol.

There is little difference in the fabric of kaolinite flocculated in distilled or slightly saline water. The fabric is dominated by a 3-D network of twisted chains of face-face oriented flakes having the appearance of a stair-stepped cardhouse. Illite floccules in distilled water also consist of abundant face-face oriented overlapping flakes. However, in salt water there is a more even mixture of fabrics—edge to face flocculation of individual platelets and also stepped clusters of face to face oriented flakes, the latter being more abundant.

It is suggested that under the experimental conditions the double layer of each clay particle is compressed resulting in an increase in the importance of van der Waals forces of attraction. As a result flakes approach each other and rotate into a parallel or subparallel position. The resultant dominant fabric is that of a stepped cluster of overlapping flakes.

CLAY MINERAL FORMATION IN AN ALPINE ENVIRONMENT

Robert C. Reynolds, Jr. 361

Vermiculite, mixed-layer vermiculite-phlogopite, and smectite are presently forming from igneous and metamorphic bedrock in the alpine zone of the northern Cascades, Washington. In addition, south-facing exposures of quartz-diorites and metadiorites above snow line are weathering to ferruginous bauxite. Calculations indicate that vermiculite is presently forming from phlogopite schists in this environment at a unit area rate that is approximately six times the average estimated rate of clay erosion for North America. The mineralogical data indicate that chemical weathering in this region is a

quantitatively significant process, and suggest that in the development of current geomorphic concepts researchers may have generally underestimated the importance of chemical weathering in alpine environments.

TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS IN OREGON

G. A. Borchardt, M. E. Harward and E. G. Knox 375

Clay fractions in soils from a transect of the Mazama ash deposit (6600 yr-old) contained more than 80% amorphous material. Instrumental neutron activation analysis was used to compare the trace element composition of the soil clay with the unweathered volcanic glass. The clay fractions had only 10% as much Na as the volcanic glass. Conversely, the rare earth element concentrations were about three times greater and the transition metal concentrations were up to nine times greater in the clay than in the glass. The $< 2\mu$ size fraction therefore contained mostly weathering products rather than fine glass.

The abundances of Cr, Co, Sc and Fe in the clay fraction decreased with depth. The Sc/Fe ratio was approximately 4×10^{-4} for both clay and the unweathered glass. The relationship between elemental concentration in clay and fine sand size separates from the same soil horizons indicated that the clay exists in association with the larger size particles, probably as coatings.

Dilute nitric acid removed about 80% of the rare earth elements La, Nd, Sm, Eu, Tb, Yb and Lu from the clay. Deferration was necessary to remove Ce, a rare earth element that forms insoluble oxides upon oxidation to the Ce⁴⁺ state. The residue of the KOH dissolution treatment contained 2:1 layer silicates that may be derived from primary biotite.

MECHANISMS OF FORMATION OF COLORED CLAY-ORGANIC COMPLEXES. A REVIEW

B. K. G. Theng 383

The interactions of clay minerals with organic compounds which give rise to the formation of colored complexes, are discussed. The color reactions of clays can be ascribed to a charge transfer between the mineral and the adsorbed species. The active sites on the clay are aluminums exposed at crystal edges and/or transition metal cations in the higher valency state at planar surfaces both of which can act as electron acceptors. The pH of the system, the nature of the solvent and that of the exchangeable cation, influence the rate of color development and the final intensity and quality of the color produced. Steric factors also play a part in reactions involving bulky organics. Some practical applications based on color reactions of clays with electron-donating organic substances are described.

ACID CHARACTER OF SAUCONITE: INCREASE IN CATION EXCHANGE CAPACITY ON AGING IN WATER AND THE ROLE OF Zn²⁺ AND Al³⁺ IONS

R. P. Mitra and P. S. Sindhu 391

pH- and conductometric titration curves of acid saucnite, freshly prepared by the action of H-resin on saucnite showed four segments, each, where H⁺, Al³⁺ and Zn²⁺ ions and a weak acid reacted with the added base in the sequence mentioned. The H⁺, Al³⁺ and Zn²⁺ ions, but not the weak acid, could be exchanged for the cations of a neutral salt. The exchangeable Al³⁺ and Zn²⁺ ions were derived from the lateral surfaces by the action of the H-resin. When the acid saucnite was allowed to age in water, the exchangeable H⁺ and Al³⁺ ions were gradually replaced by Zn²⁺ ions giving, finally, a Zn-clay. The pH rose from 4.2 to 6.3 and the total amount of exchangeable cations increased as aging proceeded, when the Zn-clay was formed, the increase in cation exchange capacity was about 70 per cent. Octahedral Al at the edges, carrying positive charges, were discharged by hydrolysis during the aging, causing the net negative charge and, hence, cation exchange capacity, to increase. Aging had little effect on the amount of the weak acid. Zn and Al ions at the edges exercised the weak acid function. Only edge-Zn was active in the fully aged clay.

PREPARATION AND SOLVATION PROPERTIES OF SOME VARIABLE CHARGE MONTMORILLONITES

G. W. Brindley and Gözen Ertem 399

Li-, Na-, K- and Ca-saturated Wyoming montmorillonites have been prepared and used to obtain Li, Na-, LiK- and Li,Ca-montmorillonites with a range of Li contents. These were heated at 220°C for 24 hr, causing the Li⁺ ions to migrate mainly into the layer structure and leaving varying amounts of Li⁺, Na⁺, K⁺ and Ca²⁺ ions in the interlayer positions as determined by exchange with NH₄⁺ ions. The results are only partially consistent with a migration of the Li⁺ ions into vacant octahedral sites up to the limit of the octahedral layer charge. Solvation of the resulting clays with water and various organic liquids showed the following results: With water, acetone and 3-pentanone, expansion of the montmorillonites increased in a step-wise manner with increasing numbers of interlayer cations qualitatively in accord with the field strength of the cations and the dipole moments of the molecules. With ethanol, ethylene glycol and morpholine, swelling with each liquid was practically independent of the number of interlayer cations, within the limits of the prepared materials. It is suggested that for the second group of liquids some mechanism additional to cation-dipole interactions, such as hydrogen bonding to silicate oxygen surfaces, may play an important part.

**AN ANALYSIS OF X-RAY DIFFRACTION LINE
PROFILES OF MICROCRYSTALLINE
MUSCOVITES****H. Kodama, L. Gataineau and J. Mering** 405

Previous studies of the line profiles of the basal reflections of microcrystalline muscovites were refined by an adaptation of the method developed by Maire and Mering. In order to evaluate the variation of interlayer spacings, the method required only relative values of Fourier coefficients, without the correction for instrumental broadening, which was the source of one of the most critical problems previously. Instead of $K\alpha$ radiation, $K\beta$ radiation was used to record line profiles since difficulties associated with the separation of $K\alpha_1$ and $K\alpha_2$

radiations could not be overcome satisfactorily.

The data reconfirmed that the line broadening of (00 l) reflections was due not only to a small particle-size effect, but also to structural disorders involving the variation of the interlayer spacings. For the four specimens investigated here, the mean squares of the variation of interlayer spacings ranged from 0 to 0.0358, the square roots of which were inversely proportional to the total number of interlayer cations. It is considered that the observed distortions were mainly attributed to non-uniform interlayer spaces between silicate layers arising from an irregular distribution of interlayer cations. The data also indicated that the crystallites of all four specimens consisted of a similar number of layers. The method showed promise for the study of the nature and extent of structural disorders in micas or other layer silicate minerals.