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CLAYS and CLAY MINERALS at a glance

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LITHIUM AND POTASSIUM ABSORPTION, DEHYDROXYLATION TEMPERATURE, AND STRUCTURAL WATER CONTENT OF ALUMINOUS SMECTITES

Leonard G. Schultz 115

X-ray analysis of Li^+- and K^+-saturated samples, differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and chemical analysis of 83 samples enable a distinction to be made between Wyoming, Tatatilla, Otay, Chambers, and non-ideal types of montmorillonite, and between ideal and non-ideal types of beidellite. The Greene-Kelly Li^+-test differentiates between the montmorillonites and beidellites. Re-expansion with ethylene glycol after K^+-saturation and heating at 300°C depends upon total net layer charge and not upon location of the charge. Wyoming-type montmorillonites characteristically have low net layer charge and re-expand to 17 Å, whereas most other montmorillonites and beidellites have a higher net layer charge and re-expand to less than 17 Å.

Major differences in dehydroxylation temperatures cannot be related consistently to the amount of Al^{3+}-for-Si^{4+} substitution, nor to the amount of Mg, Fe, type of interlayer cations, or particle size. The major factor controlling temperature of dehydroxylation seems to be the amount of structural (OH). Of 19 samples analyzed by TGA, montmorillonites and the one ideal beidellite that give dehydroxylation endotherms on their DTA curves between 650° and 760°C all contain nearly the ideal amount of 4(OH) per unit cell, but the non-ideal montmorillonites and beidellites that give dehydroxylation peaks between 550° and 600°C do not. Non-ideal beidellites contain more than the ideal amount of structural (OH) and non-ideal montmorillonites seem to contain less, although the low temperature of dehydroxylation of the latter could also be due to other structural defects. Change in X-ray diffraction intensity of the 001 reflection during dehydroxylation suggests that the extra (OH) of beidellite occurs at the apex of SiO_4 or AlO_4 tetrahedrons with the H^+ of the $(OH)^-$ polarized toward vacant cation sites in the octahedral sheet.

ABRASION pH, AN INDEX OF CHEMICAL WEATHERING

Willard H. Grant 151

If a series of rock samples with granitic composition in various stages of chemical weathering is ground in a mortar with distilled water and the pH of the slurry produced is determined, it will be evident that the pH declines as the weathering increases. This relationship can be made useful by plotting abrasion pH against some other index of weathering such as the percentage of clay mineral or the bulk density of the weathered rock. Factors controlling abrasion pH are the cations, such as K, Na, Ca, and Mg, and the amount of clay mineral present.

SOIL MINERALS IN THE Al_2O_3–SiO_2–H_2O SYSTEM AND A THEORY OF THEIR FORMATION

J. A. Kittrick 157

An attempt has been made to assemble the best thermodynamic information currently available for soil minerals in the Al_2O_3–SiO_2–H_2O system at 25°C and 1 atm. Montmorillonite is included by considering its aluminum silicate phase. Diagrams are presented so that the stability of the minerals can be visualized in relation to the ionic environment. Although the Al_2O_3–SiO_2–H_2O system is a very simple one compared to soils and sediments, the stability diagrams depict a mineral stability sequence and mineral pair associations that are in good agreement with natural relations.

According to the stability diagram, mineral pairs that can form an intimate association are gibbsite–kaolinite, kaolinite–montmorillonite, and montmorillonite–amor-

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phous silica. Forbidden pairs are amorphous silica–kaolinite, amorphous silica–gibbsite, and montmorillonite–gibbsite. The formation of intimate mixtures of three or more of these minerals is also forbidden. The stability diagrams predict ion activity relationships that are in reasonable agreement with those obtained from soils and sediments. Amorphous silica probably limits high silica levels, with montmorillonite also forming at high silica levels. Kaolinite forms at intermediate and gibbsite at low silica levels. These minerals in turn probably control the activity of aluminum ions at a level appropriate to the pH. The formation of gibbsite, kaolinite, montmorillonite, and amorphous silica appears to be controlled by a combination of kinetics and equilibria. That is, the kinetic dissolution of unstable silicates appears to control the H_4SiO_4 level. The new mineral(s) most stable at that H_4SiO_4 level appear to precipitate in response to solution equilibria.

KINETICS OF ACID-DISSOLUTION OF PALYGORSKITE (ATTAPULGITE) AND SEPIOLITE

Numan Abdul-Latif and Charles E. Weaver 169

Palygorskite and sepiolite were digested with large excesses of hydrochloric acid at constant temperature for various periods of time. The reaction was found to be of first order with respect to the Mg, Al, and Fe components in the clay and also with respect to hydrochloric acid concentration. The reaction rate constant for Mg is larger than for Fe, which is larger than for Al. Approximately one-third of the octahedral-type cations are extraneous, suggesting that only three of the five octahedral positions are filled. The reaction rate constant of Mg in sepiolite is about 240 times that for palygorskite. This may be an indication that sepiolite is less stable to chemical weathering than palygorskite. The activation energies for Mg, Al, and Fe in palygorskite were found to be the same and equal to about 18·4 kcal/mole. Treatment of partially acid-digested palygorskite with Mg ions under alkaline conditions resulted in an increase in the X-ray intensity of the 10·5 Å spacing, suggesting some of the palygorskite was reconstituted.

NEW DATA FOR TOSUDITE

Susumu Shimoda 179

Tosudite from the Takatama mine is found as an alteration mineral of the wall rocks (tuff and tuffaceous sediments of Tertiary age) of gold–silver–quartz veins. A specimen free from impurities was obtained by the sedimentation method. Chemical compositions: SiO_2 42·14%; Al_2O_3 37·38%; Fe_2O_3 0·30%; MgO 0·08%; CaO 1·65%; Na_2O 0·15%; K_2O 1·40%; H_2O^+ 11·22%; H_2O^- 6·16%; Total 100·48%. A negligible amount of MgO indicates that both octahedral sheets of the chlorite structure are dioctahedral. The structural formula is given as $(K_{0.58}Na_{0.09}Ca_{0.57})(Mg_{0.04}Fe^{3+}_{0.07}Al_{12.05})(Al_{2.28}Si_{13.72})O_{40.00}(OH)_{20.00}(H_2O)_{8.88}$. A reflection at 30 Å with its higher order reflections and another reflection at 1·493 Å are observed. After heating at 300°C, a 27 Å phase has appeared, in which a single plane of water molecules was confirmed as the interlayer water of montmorillonite. The structures in air-dried state and in dehydrated steps were proved by comparing the calculated and observed F-values, and by Fourier synthesis. The DTA and TG curves and the i.r. absorption spectrum are reported in this paper.

REFINEMENT OF THE CRYSTAL STRUCTURE OF NACRITE

Alice M. Blount, I. M. Threadgold and S. W. Bailey 185

The crystal structure of nacrite from Pike's Peak district, Colorado, has been refined by least squares and electron density difference maps utilizing ten levels of data. Complete refinement was inhibited by thick domains involving $a/3$ interlayer shifts in the "wrong direction". The ideal structure is based on a 6R stacking sequence of kaolin layers, in which each successive layer is shifted relative to the layer below by $-\frac{1}{3}$ of the 8·9 Å lateral repeat. This direction is X in nacrite, contrary to the usual convention for layer silicates, because of the positioning of the (010) symmetry planes normal to the 5·1 Å repeat direction. Alternate layers are also rotated by 180°. The pattern of vacant octahedral sites reduces the symmetry to Cc and permits description of the structure as a 2-layer form with an inclined Z axis. Adjacent tetrahedra are twisted by 7·3° in opposite directions so that the basal oxygens approach more closely both the Al cations in the same layer and the surface hydroxyls of the layer below. Interlocking corrugations in the oxygen and hydroxyl surfaces of adjacent layers run alternately parallel to the [110] and [1$\bar{1}$0] zones in successive layers. The upper and lower anion triads in each Al-octahedron are rotated by 5·4 and 7·0° in opposite directions as a result of shared edge shortening. Nacrite has a greater interlayer separation and smaller lateral dimensions than dickite and kaolinite, and the observed β angle deviates by $1\frac{1}{2}$° from the ideal value. These features, as well as its overall lesser stability, are believed due to the less favorable positioning in nacrite of the basal oxygens relative to the directed interlayer hydrogen bonds.

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