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CLAYS and CLAY MINERALS at a glance

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A CHLORITIZED MONTMORILLONITE FROM THE RIO CHIFLON FORMATION (TR) OF ARGENTINA

Gerardo E. Bossi 251

X-ray, chemical, and genetic characteristics of a chloritized montmorillonite mineral species, found in The Rio Chiflon Formation (La Terre, La Rioja, Argentina) are described. The mineral is associated with illite, montmorillonite, and chlorite, plus the non-clay associates analcite and hematite. The Rio Chiflon Formation is of Upper Triassic age, and consists of red sandstones and siltstones representing poorly developed fluviatil cyclothems.

Studies of the Li^+, K^+ and Mg^{2+} varieties of the clay and solvation with glycerol or ethylene glycol have shown that the mineral is a smectite which behaves peculiarly with heating. Between 200° and 600°C the mineral collapses gradually from a basal spacing if 13 Å–10 Å. Regular expansibility with ethylene glycol and glycerol is completely preserved (in the Li^+ and K^+ clays) up to a preheating of 400°C and partially preserved up to 600°C. This behavior has been interpreted as caused by the presence of interlayer contaminants of a hydroxy-cation type. The interlayer cations may be Al, Mg, and Fe (in this order).

The environment of the Rio Chiflon Formation has been evaluated in the light of well-known occurrences of intergradient clays in soils and the presence of analcite and hematite. It is proposed that chloritization has taken place during a soil weathering process, under alkaline conditions with great availability of sodium during alternating dry–humid seasonal climates (oxidation conditions). The stability of the interlayer developed under these circumstances was increased during long burial and diagenesis.

ADSORPTION OF ETHYLENEDIAMINE (EDA) ON MONTMORILLONITE SATURATED WITH DIFFERENT CATIONS—II HYDROGEN- AND ETHYLENEDIAMMONIUM-MONTMORILLONITE: PROTONATION AND HYDROGEN BONDING

P. Cloos and R. D. Laura 259

The form under which ethylenediamine (EDA) is adsorbed from aqueous solution by hydrogen- and ethylenediammonium–montmorillonite was studied as a function of the amount of amine present in the system.

EDA added to the acid clay in quantities lower than or equal to the cation exchange capacity (C.E.C.) was exclusively adsorbed as ethylenediammonium ($EDAH_2^{2+}$) ion. On further addition of diamine the pH of the suspension rose to alkaline values and the monoprotonated species ($EDAH^+$) was the main charge balancing cation.

Evaporating at room temperature "EDA–H–montmorillonite–H_2O" or "EDA–$EDAH_2$–montmorillonite–H_2O" systems containing 300 me EDA/100 g clay did not cause loss of nitrogen, but degassing under high vacuum (10^{-5} mm Hg) did. Nevertheless, excess EDA molecules with respect to the C.E.C. were retained on the clay surface, at the expense of water molecules, through strong asymmetrical hydrogen bonds between their NH_2 groups and the NH_3^+ groups of $EDAH^+$ ions. On heating up to 160°C under vacuum the nitrogen content decreased further, but still remained at a level significantly higher than the C.E.C. value, all NH_3^+ groups remaining involved in strong hydrogen bonding. It is suggested that a "condensation" process takes place, implying evolution of EDA molecules and giving rise to "polymeric" associations between protonated and unprotonated diamine.

Washing the clay suspensions with distilled water did not completely remove excess EDA either, as a con-

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sequence of the equilibrium existing between the ionic species in solution ($EDAH_2^{2+}$ and $EDAH^+$) and on the clay surface. It seems that these species were preferentially adsorbed as "trimeric" associations in which two out of four NH_3^+ groups are hydrogen bonded to NH_2 groups.

After heating at 200°C, nitrogen retained on the clay surface was mainly in the form of NH_4^+ ions. Ammonium formation was enhanced by the presence of excess EDA and was considerably faster than in montmorillonite systems containing EDA coordinated to Cu^{2+} ions.

THE CHLORITE SERIES OF FLAGSTAFF HILL AREA, CALIFORNIA: A PRELIMINARY INVESTIGATION

J. L. Post and C. C Plummer 271

The results of X-ray diffraction, DTA, i.r. spectroscopy, and chemical tests are presented for some chlorites typical of the Flagstaff Hill area. The area is notable for the large variety of chlorite types occurring in considerable quantities. Chlorite, in this area, is found as veins, as pseudomorphs, and as individual crystals. Textures vary from massive, fine-grained aggregates to books which are more than 20 mm in width. Crystals more than 5 mm in size occur in parallel groupings at rock interfaces. Judging from 45 chlorite samples studied, sheridanite is most abundant; clinochlore and ripidolite are common. Penninite and its Cr–chlorite equivalent are less abundant. The parent rock is an irregularly shaped ultramafic body surrounded by low-grade schists and located very close to a granodiorite stock. The original ultramafic rocks have been highly altered by metamorphism and metosomatism into assemblages comprised mainly of serpentine, talc, hornblende, and chlorite with relics of olivine, pyroxene and other less abundant original minerals. Much of the exposed rock is essentially mono-mineralic, mostly consisting of various polytypes of serpentine. Preliminary investigation indicates that the area merits much more study because of the opportunity for readily observing the various chlorite types and determining their genesis, alteration sequences and weathering characteristics. The area, being easily accessible, could also serve as an adequate source for samples to be used as reference standards.

DIRECTIONAL VARIATION OF ELASTIC WAVE VELOCITIES IN ORIENTED CLAY

Arley G. Franklin and Phillip A. Mattson 285

Sonic anisotropy of clay resulting from particle orientation was studied by means of velocity measurements on anisotropically consolidated kaolinite. Samples were prepared from a kaolin–water slurry under consolidation pressures ranging from 80 to 400 psi, with two distinct stress histories. Directional velocity measurements were made over a wide range of water contents as saturated samples were allowed to dry by evaporation to water contents below the shrinkage limit. Directional variation was most pronounced with partial saturation, when directional velocities differed by as much as a factor of two. The degree of sonic anisotropy is seen to correlate with variation in the shrinkage limit, showing a systematic dependence on particle orientation, but no unique relation to consolidation stress exists because of the overriding influence of stress history.

MORPHOLOGICAL EFFECTS ON ILLITE AS A RESULT OF POTASSIUM DEPLETION

Warren D. Huff 295

Several illites and a mixed-layer illite–montmorillonite developed fractures in some particles during progressive removal of interlayer potassium by solutions containing sodium tetraphenylboron. The appearance of the splinters in bundles, some connected to incompletely broken plates, suggests the process is related to the differential release of stresses known to exist as a consequence of octahedral–tetrahedral misfit. The formation of splinters produces additional surface area for ion removal and may influence the rate of vermiculite development.

THE OXIDATION OF OCTAHEDRAL IRON IN BIOTITE

R. J. Gilkes, R. C. Young and J. P. Quirk 303

Oxidation of octahedral ferrous iron in biotite by saturated bromine water results in a loss of both octahedral and interlayer cations. The hydroxyl adjacent to vacant octahedral cation sites adopt an inclined orientation resulting in a more stable environment for interlayer cations. The only structural change accompanying these processes is a decrease in *b*-axis dimension which is linearly related to octahedral ferric iron content. These findings are in agreement with observations made on naturally weathered biotites.

COMPARATIVE CHEMICAL COMPOSITION OF SEDIMENT INTERSTITIAL WATERS

A. S. Parashiva Murthy and R. E. Ferrell, Jr. 317

Interstitial waters squeezed from modern sediments with a 100 psi pressure at laboratory temperature (23°C) are depleted in K and Ca and enriched in Mg when compared to the solutions obtained at *in-situ* temperature (28°C). The changes are especially pronounced when the samples are refrigerated during transport back to the laboratory. The magnitude of the variation in chemical composition was dependent on the element being analyzed as well as the sediment used. The maximum observed depletion in the laboratory was about 12% per degree difference in temperature for potassium. Element ratios in the solutions were affected most seriously. The Mg/Ca and Na/K ratios increased 51 and 60%, respectively.

A water extraction method using sediment to water

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ratios of 1:2, 1:5, and 1:10 was compared with the pressure method. The total composition of the pore fluids obtained by squeezing is greater than expected, corresponding to a sediment to water ratio less than 1:5. The artificially squeezed sediments are yielding pore fluids which are more concentrated than the "in-place" solutions.

The water extraction method yields results which are in agreement with the behavior predicted by the Donnan Principle. It is suggested that the values obtained by successive dilution analyses can be extrapolated to measured moisture contents and used to determine the elemental composition and element ratios in interstitial pore fluids.

CLAY MINERAL SYNTHESIS—III. RAPID HYDROTHERMAL CRYSTALLIZATION OF AN ALUMINIAN SMECTITE

W. T. Granquist, G. W. Hoffman and R. C. Boteler 323

An aluminian smectite with about one Al^{3+}/Si^{4+} replacement per unit cell was batch-synthesized on a large scale (100-gal autoclave) at 300°C and 1240 psig with reaction times of several hours rather than days. This rapid crystallization was related to the use of NH_4^+ was the charge-balancing cation and to partial F/OH substitution. The short synthesis time prompted a study of continuous crystallization. Either of two techniques, flow through a stirred autoclave and through a multi-staged reactor column, produced crystalline product; neither gave the crystallinity of the batch process.

ZEOLITE AS CATALYSTS FOR THE SYNTHESIS OF AMINO ACIDS AND PURINES

J. J. Fripiat, G. Poncelet, A. T. Van Assche and J. Mayaudon 339

This paper attempts to show that the catalytic properties of zeolitic material may play a role in the synthesis of simple biological molecules from gases commonly found in extraterrestrial atmospheres. Linde *X* and *Y* molecular sieves cation-exchanged by Ca^{2+} and Fe^{3+} have been heated in the presence of carbon monoxide and ammonia. Amino-acids and u.v. absorbing substances identified by paper chromatography have been extracted from the solid. HCN, the basic molecule involved in the synthesis of those substances has been detected in the gas phase. It is proposed, on the basis of i.r. results, that the amino-acids are hydrolysis products of an undefined polymer.

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