

CLAYS and CLAY MINERALS

at a glance

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CHLORITIZATION OF MONTMORILLONITE BY ITS COPRECIPITATION WITH MAGNESIUM HYDROXIDE.

G. C. Gupta and W. U. Malik

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A magnesium hydroxide-montmorillonite complex prepared at an OH/Mg molar ratio of 2 (16 meq Mg/g clay) and immediately cleaned of any free Mg(OH)₂ behaves like magnesium-chlorite and shows no change during 3 months ageing. Magnesium hydroxide completely precipitates within the interlayer space of montmorillonite. X-ray diffraction analysis, thermal (DTA and TGA) studies, infrared absorption analysis, polarographic reduction behaviour, and cation exchange capacity measurements confirm the transformation of montmorillonite to a chlorite-like structure. Further ageing of the complex results in the release of brucite from the interlayer space and expansion of the complex on glycerol treatment. X-ray analysis of the 6 months aged sample shows the presence of free brucite but not montmorillonite. A small but significant increase in CEC of the complex is observed on ageing. When the Mg(OH)₂-montmorillonite complex is allowed to age in the presence of free Mg(OH)₂ (external to montmorillonite unit layers) in a dry state, a "seeding" effect takes place and the "fixed" Mg(OH)₂ starts coming out from the interlayer space after 10 days.

THERMAL DECOMPOSITION OF ORGANO-AMMONIUM COMPOUNDS EXCHANGED ONTO MONTMORILLONITE AND HECTORITE

Chung Chi Chou and James L. McAtee, Jr.

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A series of organic ammonium ions were exchanged onto clay minerals montmorillonite and hectorite. Thermal effects on these surface modified organic-inorganic complexes were investigated by means of differential thermal analysis and heating-oscillating X-ray diffraction methods. It was found that the organo-clay complexes

were dehydrogenated at temperatures from 180 to 350°C, depending on the organic cation used. Following the dehydrogenation, hydrolysis took place leaving a layer of "carbon" on the clay surface. The "carbon" was then oxidized at a temperature of about 550°C. Investigation of possible correlations between the activation energy of dehydrogenation and basicity, boiling point, ionization potential, molecular structure, and carbon-carbon bond distances of the organic cations showed that the geometric factors outweighed the acid, chemical and electronic factors in determining the effect of montmorillonite and hectorite toward the dehydrogenation of organic ions exchanged on the surfaces of these clay minerals.

ACID DISSOLUTION OF CHLORITES: RELEASE OF MAGNESIUM, IRON AND ALUMINUM AND MODE OF ACID ATTACK

G. J. Ross

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The acid dissolution of 8 chlorites in 2N Si-saturated HCl showed that there was no preferential dissolution of Al in octahedral positions and that the octahedral and tetrahedral sheets in the chlorite structure were equally attacked. An analysis of chemical data suggested a simple two-dimensional diffusion model in which the acid attack on the chlorite particles proceeded from the edges inward leaving a reacted layer which formed a diffusion barrier. Microscopic examination showed, however, that the acid attack was not simply an edge attack but started at any point where cracks, structural defects and weaknesses apparently predisposed sites to acid attack. It was also clear from the formation of etch figures and solution channels that the product layer at least partially dissolved or disintegrated during the progress of acid attack. The residue which remained after acid attack appeared to be an opaline amorphous hydrated silica as indicated by index of refraction measurements. The orderly arrangement of etch figures on flakes of some chlorites reflected

certain crystal symmetry elements. The results indicate that the acid dissolution technique to determine the ratio of Al in octahedral and tetrahedral positions cannot be used as an aid in the calculation of structural formulae for chlorites.

POLYTIPIISM OF TRIOCTAHEDRAL 1:1 LAYER SILICATES

S. W. Bailey

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Polytypism in trioctahedral 1:1 phyllosilicates results from two variable features in the structure. (1) The octahedral cations may occupy the same set of three positions throughout or may alternate regularly between two different sets of positions in successive layers. (2) Hydrogen bonding between adjacent oxygen and hydroxyl surfaces of successive layers can be obtained by three different relative positions of layers: (a) direct superposition of layers, (b) shift of the second layer by $a/3$ along any of the three hexagonal X-axes of the initial layer, with a positive or negative sense of shift determined uniquely by the octahedral cation set occupied in the lower layer, and (c) shift of the second layer by $\pm b/3$ along Y_1 (normal to

X_1) of the initial layer regardless of octahedral cation sets occupied. Assuming ideal hexagonal geometry, no cation ordering, and no intermixing in the same crystal of the three possible types of layer superpositions, then twelve standard polytypes (plus four enantiomorphs) with periodicities between one and six layers may be derived. Relative shifts along the three X-axes lead to the same layer sequences derived for the micas, namely $1M$, $2M_1$, $3T$, $2M_2$, $2Or$, and $6H$. Polytypes $1T$ and $2H_1$ result from direct superposition of layers. Layer shifts of $b/3$ lead to polytypes designated $2T$, $3R$, $2H_2$, and $6R$. The twelve standard 1:1 structures can be divided into four groups ($A = 1M, 2M_1, 3T$; $B = 2M_2, 2Or, 6H$; $C = 1T, 2T, 3R$; $D = 2H_1, 2H_2, 6R$) for identification purposes. The strong X-ray reflections serve to identify each group and the weaker reflections differentiate the three structures within each group. Examples of all four groups and of nine of the twelve individual structures have been identified in natural specimens. Consideration of the relative amounts of attraction and repulsion between the ions in the structure leads to the predicted stability sequence of group $C >$ group $D >$ group $A >$ group B , in moderately good agreement with observed abundances of these structural groups.