

# CLAYS and CLAY MINERALS

at a glance

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## CHLORITE EXAMINATION BY ULTRAMICROTOMY AND HIGH RESOLUTION ELECTRON MICROSCOPY

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Mafic chlorite from Benton, Arkansas was comminuted by rotary blending of an aqueous suspension and the  $-2 \mu\text{m}$  dia. fraction separated by sedimentation. Droplets of a suspension of the  $< 2 \mu\text{m}$  fraction were dried on a layer of Epoxy resin and then additional Epoxy was added and heat-cured at  $48^\circ\text{C}$  to form a resin sandwich. Cross-sections of  $600\text{--}900 \text{ \AA}$  thickness were cut with a Reichert automated ultramicrotome. The sections were collected on standard specimen screens, reinforced by vacuum evaporated C, and examined by transmission electron microscopy. The Phillips EM 200 electron microscope was equipped with a "microgun" source to minimize heating and to improve contrast and high resolution. Images of the (001) chlorite crystallographic planes spaced at  $13.9 \text{ \AA}$  intervals were visible on many of the particle sections. Such imaging depended upon the planes being nearly parallel to the electron beam (within  $0^\circ 10'$ ). Many particles having other orientations therefore did not show the  $13.9 \text{ \AA}$  image. Micrographs made before appreciable irradiation by the electron beam revealed fringes corresponding to the  $7.22 \text{ \AA}$  (002) spacing of chlorite. Loss of the  $7.22 \text{ \AA}$  fringes and reinforcement of those at  $13.9 \text{ \AA}$  resulted from heating of the chlorite in the electron beam. This effect is analogous to the well-known crystallographic effects of heating chlorite at  $550\text{--}760^\circ\text{C}$ .

## TIOGA BENTONITE (MIDDLE DEVONIAN) OF INDIANA

John B. Droste and Charles J. Vitaliano

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The petrography of shale partings in carbonate rocks from eleven cores in the Illinois (Jeffersonville Formation) and Michigan Basins (Detroit River formation) of Indiana indicates the presence of a K-bentonite which is interpreted as the Tioga Bentonite, an important stratigraphic marker in the middle Devonian rocks throughout the central and eastern United States. The clay mineral composition of the Tioga Bentonite of Indiana is interstratified illite and smectite, usually with admixed kaolinite. This

composition stands in striking contrast to the simple illite suite without kaolinite in the normal terrigenous shale partings in the Devonian rocks of Indiana. Euhedral sanidine, high temperature albite, zircon, apatite, and the angularity of quartz grains found associated only with the interstratified clay mineral suite support the volcanic origin of these clay partings.

## MIXED-LAYER KAOLINITE-MONTMORILLONITE: A COMPARISON OF OBSERVED AND CALCULATED DIFFRACTION PATTERNS

B. A. Sakharov and V. A. Drits

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X-ray diffraction patterns for mixed-layer kaolinite-glycerine-saturated montmorillonite were calculated, taking into account the differences of scattering power of the kaolinite and montmorillonite layers. The data were compared with the experimental results for two kaolinite-montmorillonite mixed-layer minerals. The probability parameters and the total number of layers in crystals were established.

## THE EFFECT OF CATION EXCHANGE OF TRIS(ETHYLENEDIAMINE)COBALT FOR SODIUM ON NITROGEN SORPTION BY MONTMORILLONITE

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The cation exchange process between tris(ethylenediamine)cobalt(III) and  $\text{Na}^+$  on montmorillonite was studied by atomic absorption spectrophotometry, X-ray diffraction, differential thermal analysis, and nitrogen sorption at  $78^\circ\text{K}$ . The exchange of  $\text{Co}(\text{en})_3^{+3}$  for  $\text{Na}^+$  was found to be extremely favorable, with a tendency toward segregation of the two kinds of cations in the mixed clays studied. Small amounts of  $\text{Co}(\text{en})_3^{+3}$  were found to lower the nitrogen sorption capacity of  $\text{Na}^+$  montmorillonite while clays with high  $\text{Co}(\text{en})_3^{+3}$  content had greatly enhanced nitrogen sorption. An explanation is offered in terms of a dual role of the  $\text{Co}(\text{en})_3^{+3}$  in determining the kind and amount of nitrogen sorption in the exchanged montmorillonite.

### THE NATURE OF GARNIERITES—I. STRUCTURES, CHEMICAL COMPOSITIONS AND COLOR CHARACTERISTICS

G. W. Brindley and Pham Thi Hang 27

X-ray diffraction patterns of garnierites indicate that most samples resemble serpentine-group minerals, a talc-like mineral, or a mixture of these forms, and give respectively 7 Å and 10 Å basal reflections. From a survey of some 40 garnierites, four predominantly serpentine and seven predominantly talc-like were selected for detailed study. The talc-like garnierites exhibit little variation of the 10 Å basal spacing with low-temperature heating or with immersion in liquids, though some may contain a small proportion of expandable layers. Chemical analyses show considerable deviation of octahedral/tetrahedral cation ratios from the values 3/2 and 3/4 expected for normal serpentine and talc minerals. This deviation may be interpreted in terms of 1:1 and 2:1 layer types, either as separate phases and/or interstratifications, or defect structures of various kinds. The  $H_2O^+$  contents of the talc-like forms of garnierite are considerably greater than that of normal talc and point to a mineral of composition  $3(Mg, Ni)O \cdot 4SiO_2 \cdot 2H_2O$  or  $(Mg, Ni)_3Si_4O_{10}(OH)_2 \cdot H_2O$  a talc monohydrate formula. The green color of garnierites is related to the NiO weight per cent. A color index is derived based on the Munsell color charts.

### THE NATURE OF GARNIERITES—II. ELECTRON-OPTICAL STUDY

Natsu Uyeda, Pham Thi Hang and G. W. Brindley 41

Electron micrographs of 7 Å-type and 10 Å-type garnierites have been recorded at  $5 \cdot 10^4$ – $10^5 \times$  magnifications to show the morphological character of these minerals, and at  $10^6 \times$  magnification to show structural features of the particles. The 7 Å serpentine-like minerals show a great variety of morphological forms including tube- and rod-shaped particles, platy forms and poorly defined, fluffy particles, which are probably aggregates. The 10 Å talc-like minerals show mainly platy forms and fluffy aggregates, and generally few tube or rod-shaped particles. At  $10^6 \times$  magnification, the 7 Å and 10 Å layer spacings are seen directly. In the samples examined, the 7 Å spacings are more clearly and more regularly defined than the 10 Å spacings.

### THE NATURE OF GARNIERITES—III. THERMAL TRANSFORMATIONS

Pham Thi Hang and G. W. Brindley 51

Serpentine- and talc-like garnierites described in Parts I and II were heated at various temperatures up to about 1000°C and after each treatment were cooled and examined by X-ray powder diffraction. At about 550°C, the temperature at which rapid dehydroxylation begins, the serpentine-like garnierites formed a highly disordered phase. When the NiO content was low (approximately < 20 wt %), the disordered phase transformed directly to an olivine phase around 800°C, but when the NiO content was higher, various transitional phases were formed before an olivine phase appeared around 1000°C. With one sample, a sepiolite-like phase was obtained at about 800°C. Several samples showed face-centered cubic modifications between 900°C and 1000°C.

The talc-like garnierites with low NiO content formed an enstatite phase around 800°C directly following the dehydroxylation reaction. With high NiO contents, an olivine phase became increasingly prominent between 850°C and 1000°C. Identification of the mixed crystallizations possibly existing in the initial minerals is scarcely feasible on the basis of the products formed up to 1000°C.

### OPTICAL ABSORPTION SPECTRA OF CLAY MINERALS

Samuel W. Karickhoff and George W. Bailey 59

A preliminary survey of electronic absorption spectra of clay minerals reveals the utility of ultraviolet-visible spectroscopy in the elucidation of structural, physical, and chemical properties of such systems. Spectra, which were obtained from the suspensions, films, and single crystals (where applicable), are interpreted in terms of iron-associated transitions. Microcrystalline clay minerals typically show Fe(III) in octahedral oxo-ligand geometry whereas mica-type minerals may show a range of iron species, including octahedral Fe(III), tetrahedral Fe(III), and octahedral Fe(II). Iron affects the local site geometry and in "high iron" minerals may dictate layer geometry and subsequently the crystalline form.