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#### ELECTRONOSCOPIC STUDIES OF ACID-TREATED KAOLINITE

KENNETH M. TOWE, *Electron Microscope Laboratory,  
University of Illinois.*

#### INTRODUCTION

The purpose of this paper is to present the results of a study of the nature of the detailed morphological changes, if any, that take place when a well-crystallized kaolinite is subjected to treatment with three common acids.

#### EXPERIMENTAL TECHNIQUE

A sample of well-crystallized Georgia kaolinite was selected for investigation. A small amount of the clay was first dispersed ultrasonically in distilled water but was not size fractionated. The three acids used were: HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>. Approximately 10 ml of the kaolinite dispersion was mixed with 20 ml of each of the above acids in its concentrated form. The sulfuric and phosphoric acid-clay mixtures were allowed to stand for 24 hours; the hydrochloric acid for 72 hours. Each of the mixtures was then washed three times in a centrifuge, redispersed and sedimented on each of two glass microscope slides to air-dry. An untreated kaolinite dispersion was similarly prepared. One of the oriented aggregates was used for *x*-ray diffraction analysis and the other for electron microscopy.

The self-shadowed carbon replica technique was employed for the electronoscopic studies. Carbon was evaporated *in vacuo* at an angle of 60° to the oriented aggregate slides. The kaolinite was then dissolved from beneath the carbon using HF. The resulting replicas were washed in distilled water and picked up on copper 200 mesh electron microscope grids. Electron photomicrographs were taken of selected fields.

#### EXPERIMENTAL RESULTS

Examination of the *x*-ray diffractometer traces of each of the samples shows that in no case is there an indication of a reaction product. All of

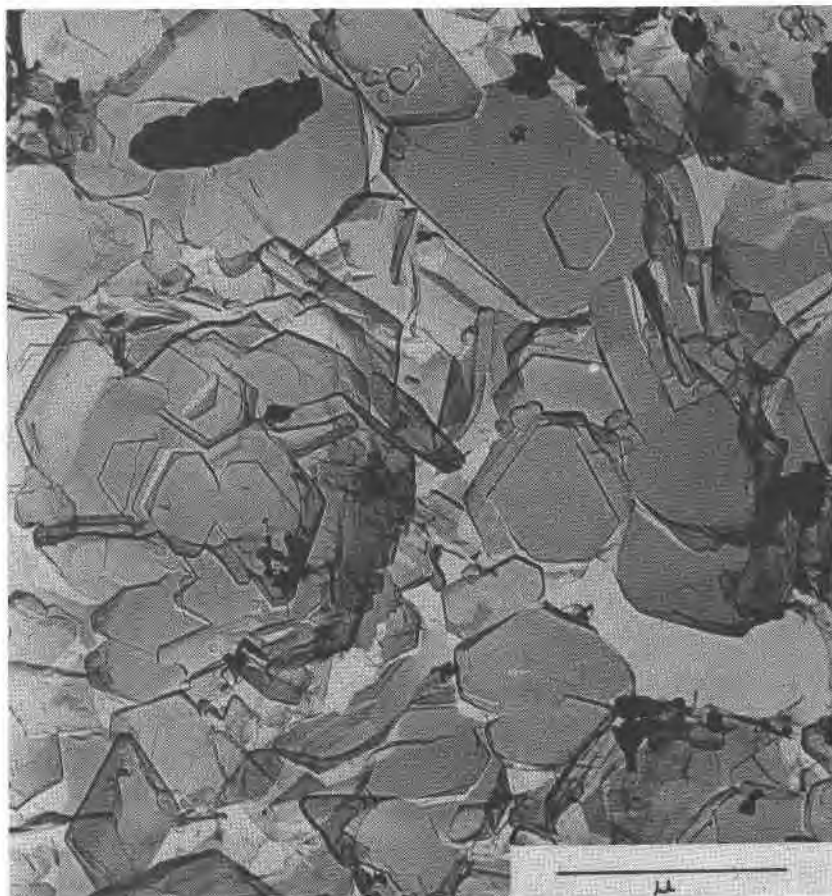


FIG. 1. Kaolinite following treatment with HCl.  $\times 52,000$ .

the patterns are essentially identical except for enhancement of  $hk0$  reflections due to some flocculation in the case of the acid-treated samples. Heat treatment of the slides at  $110^{\circ}$  C. for 24 hours produced no significant changes in the  $x$ -ray patterns.

The electron micrographs, on the other hand, provide more interesting results. As might be expected the kaolinite treated with HCl (Fig. 1) shows no morphological features which cannot also be seen on the untreated clay.

In the case of phosphoric acid, Fig. 2 clearly shows the presence of small amorphous-looking particles occurring together with sharp hexagonal flakes of kaolinite. The average size of these particles is about 300 Å. Figure 3 illustrates the results obtained from sulfuric acid treatment.

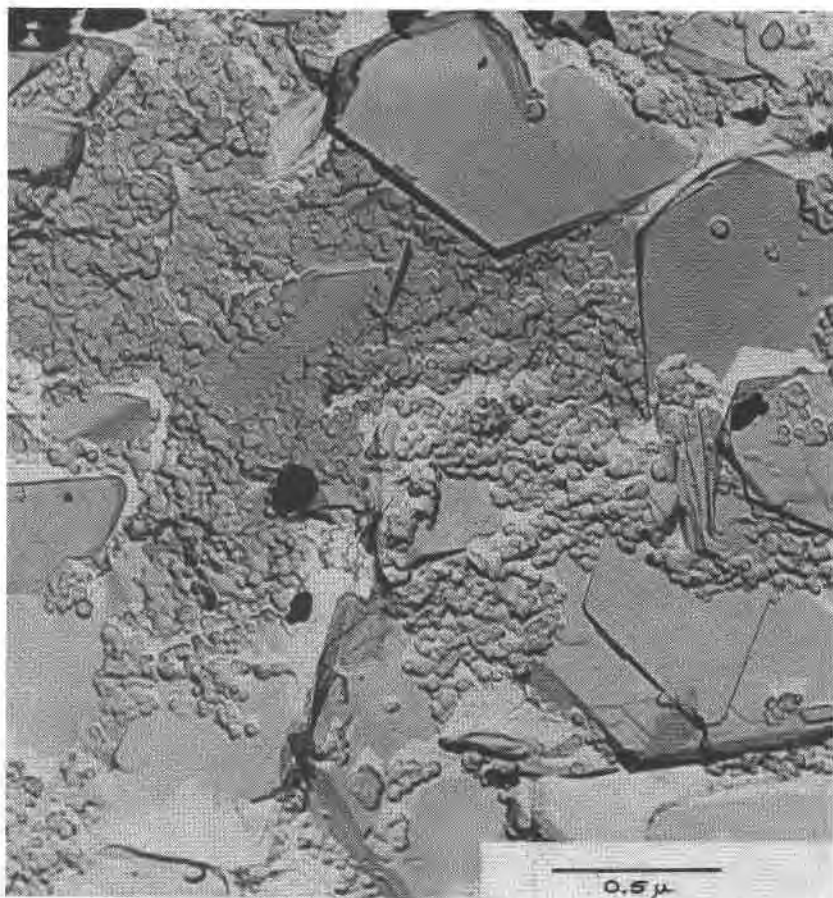


FIG. 2.  $\text{H}_3\text{PO}_4$ -treated kaolinite showing small particles of reaction product.  $\times 76,000$ .

On the basal surfaces of the kaolinite flakes can be seen very small particles making up "chains" that occur in crystallographic orientation. The average size of these particles is about  $100 \text{ \AA}$ . Careful scrutiny of several micrographs indicates that these "chains" are not cleavage edges although they may in some instances coincide with such edges. Their presence on some flakes but not on others suggests that they may be restricted to those kaolinite basal surfaces composed of OH groups.

#### DISCUSSION

The presence of reaction products, undetected by  $x$ -ray diffraction, is shown by electron microscopy in the case of kaolinite treated with phosphoric and sulfuric acids and subsequently washed. At present the precise



FIG. 3.  $\text{H}_2\text{SO}_4$ -treated kaolinite showing reaction product "chains" on basal surfaces.  $\times 76,000$ .

nature of these reaction products is unknown but unpublished  $x$ -ray and transmission electronoscopic work by Murray (1951) have shown that aluminum phosphates and aluminum sulfates form from kaolinites following acid treatments and drying at  $110^\circ\text{C}$ . Using this work as a guide it is not unreasonable to assume that the particles shown in Figs. 2 and 3 are aluminum phosphates and aluminum sulfates respectively. The absence of  $x$ -ray evidence to support this is considered due to the very small particle sizes involved. In addition, poor crystallinity combined with the comparatively small amounts present would also inhibit coherent diffraction effects.

No definite evidence can be found showing changes in the overall

morphology of the kaolinite. The gross hexagonal outline of the flakes is maintained in all cases. The phosphate reaction products tend to group themselves along the edges and in the spaces between flakes. The sulfates, on the other hand, seem to be attached to the basal surfaces of the kaolinite flakes rather than as random aggregates. The difference in solubility between these two reaction products may, in part, account for this effect.

The use of electron microscopy as an analytical tool is emphasized inasmuch as routine *x*-ray analyses failed to detect the changes that had taken place.

#### ACKNOWLEDGEMENTS

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#### SYNTHETIC EMERALD

R. A. LEFEVER, A. B. CHASE, AND L. E. SOBON,  
*General Telephone and Electronics Laboratories, Inc.,  
Palo Alto, California.*

Synthetic emerald has always been of considerable interest as a gem material. Recent work in solid state physics indicates that beryl containing chromium (and other transition metal ions) is also of research interest and may be of value for certain electronic applications (Geusic *et al.*, 1959; Gerritsen, 1962). While emerald has previously been synthesized, by growth from flux systems (Hautefeuille and Perrez, 1888; Dana, 1949; Smith, 1958; and Alexander, 1949) and hydrothermally (Van Praagh, 1947), the procedures employed are inconvenient and/or result in relatively small crystals. Furthermore, successful deposition of single-crystal emerald on seeds using these methods has not been reported. Emerald crystals sufficiently large for gem fabrication have been grown (Smith, 1958), but commercial value of the resulting product has prevented the pertinent data from reaching either the scientific or the patent literature. The purpose of this note is to describe a flux system that shows considerable promise for the synthesis of large emerald crystals.

In the course of exploratory work on the growth of metal oxide and silicate single crystals from molten salts, small emerald crystals were