Clays and Clay Minerals, 1968, Vol. 16, pp. 187–189. Pergamon Press. Printed in Great Britain

ELECTRON MICROPROBE STUDY OF KAOLIN

CHARLES E. WEAVER

Geophysical Sciences, Georgia Institute of Technology, Atlanta, Georgia

(*Received* 13 *October* 1967)

Abstract – Electron microprobe studies of kaolinite indicate that most of the Fe is evenly distributed throughout the kaolinite and must either be in the structure or occur as very small particles adsorbed on the surface. In addition to Ti the anatase impurities contain Fe and Mg. Fe, Mg, Mn, V, and K are present in biotite. It is necessary to concentrate the fine-grained mineral impurities in order to study them with the electron microprobe.

INTRODUCTION

THE ELECTRON microprobe X-ray analyzer has been in use since the early 1950's. Since 1960, it has been widely used in the earth sciences. Keil (1967) has published a recent review of the mineralogical applications of the electron microprobe. White *et al.* (1964) have demonstrated that it is possible to obtain quantitative data from microcrystalline powders when individual flakes can be isolated.

The electron microprobe is ideal for the study of sand and silt size materials; however, the size of the electron beam, generally $\frac{1}{2}$–1mμ, limits its use for the study of clay minerals.

Qualitative electron microprobe analyses were made of some kaolinite samples from Georgia to obtain some idea of how the instrument could be used to study the fine grained clay minerals.

Because many minerals are electrically nonconductive, samples have to be coated with a thin film of conductive material. Carbon was used to coat most samples, but aluminum was used on a few samples so that carbon determination could be made.

RESULTS

Several kaolinite samples were dispersed and sedimented on a glass slide. Electron beam scanning pictures of Fe, Ti, Mg, Mn, V, K, C, (Fig. 1) show that they are evenly distributed in the areas photographed. This even distribution indicates these elements are present in the kaolinite structure or are present in other minerals which are fine grained and homogeneously distributed.

The relative intensity and the absolute intensity of the Fe, Ti, and Mg patterns varied from the center to the edge of the slide suggesting that a major portion of these elements is either present in non-kaolinite minerals or is concentrated preferentially in certain kaolinite flakes.

Some of the photographs were enlarged to 6″ × 8″ and printed on transparent film so that overlay comparisons could be made. Little additional information was obtained.

Samples of the same kaolinites were flocculated and sedimented slides prepared. The Fe and Ti were both homogeneously distributed. The Mg had an irregular distribution (Fig. 2) indicating that some of it was present in minerals other than those containing the bulk of the Fe and Ti.

Electron beam scanning pictures of the coarse (predominantly larger than 10 μ) kaolinite book fraction show that most of the Ti is present as large particles 10–25 μ in dia. (Fig. 3). The Fe is homogeneously distributed though occasionally there is a slight concentration in some of the TiO_2 particles. Discrete K concentration can be seen. The Mg is present in minor amounts and is evenly distributed. The K and Mg distribution indicates the K is present in muscovite rather than biotite.

A concentrated suspension of 90 per cent less than 2 μ fraction of kaolinite was centrifuged to produce a clay plug approximately 1·5 in. thick. The clay at the base of the plug had a yellowish color; the center was white; the upper portion gray. Electron beam scanning pictures were made of surfaces at various intervals through the plug. Scanning time was constant for each element so that relative abundance could be estimated. The pictures showing the greatest concentration of each element were assigned a value of 10 and the other pictures proportioned to them.

Clay plug	Element					
	K	Mg	Ti	Fe	Mn	V
Surface	10	5	10	10	—	10
Gray	10	10	8	10	10	—
White	3	4	3	7	2	—
Yellow	9	3	10	8	4	—

— = Not determined.

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press

It is evident from these relative concentration values that the various contaminate elements, except for Fe, are not uniformly distributed.

The whitest clay has a lower concentration of all the elements for which analyses were made. The yellow portion has relatively high concentration of K and Ti. The electron scan pictures of this zone show a uniform distribution for all elements. The gray zone and the surface of the plug have a high concentration of K, Mg, Ti, Fe, Mn and possibly V. The pictures of the surface of the plug (Fig. 4) indicate that the distribution of intensities for K, Mg, Ti, V, and to some extent Fe are similar, indicating that they are probably present in biotite. X-ray analyses confirmed the presence of biotite. Some of the biotite is weathered to vermiculite. The Mn is also presumably in the biotite. Why these relatively coarse biotite flakes should centrifuge out last is not known for certain but it is possible that the suspension was so concentrated that the kaolinite flocculated and settled out more rapidly than the biotite.

A kaolinite sample was treated to float off the Ti and Fe impurities. Chemical analyses indicate that approximately twice as much Ti as Fe was removed by flotation. Electron probe scanning picture of the froth product reflected the relatively high Ti content of the material floated from the kaolinite. The Fe is evenly distributed. Most of the Ti is also evenly distributed but some areas of the slide have Ti concentrations 4–5 μ in dia. These concentrations may not represent discrete Ti-rich grains but may be fine-grained particles adhering to the surface of the calcite grains used as a carrier in the flotation technique. When the calcite was dissolved concentrations of Ti were not observed. X-ray patterns indicate most of the Ti is present in anatase and a lesser amount in rutile.

Concentrations of anatase and rutile were obtained from a 90 per cent less than 2 μ fraction of commercial kaolinite. The method of Raman and Jackson (1965) was used to dissolve the other minerals present. Electron micrographs show the TiO_2 is present as square to subsequent particles generally less than 0·1 μ in dia. The anatase grains are too small to be resolved in electron beam scanning pictures, but the pictures do show that the anatase contains appreciable amounts of Fe and Mg.

This preliminary study indicates that much of the Fe, Ti, Mg, etc., in some Georgia kaolins is present in the minerals anatase, rutile, muscovite, biotite and vermiculite. Some of the Fe, and to a lesser extent Ti, is either present in the kaolinite structure or as fine particles (less than 100Å) adsorbed on the surface of the clay flakes, or in both positions.

A cursory electron microprobe examination of thin sections of other types of clays indicates the probe can be useful for studying the compositional variations of such included grains as dolomite, feldspar, pyrite, phosphate, etc. When several types of clay minerals are present it is difficult to obtain quantitative data due to an averaging effect; however, relative information can usually be obtained, i.e. one clay mineral is richer in iron than another.

Though the electron microprobe cannot be used to study compositional variations in individual clay mineral flakes less than a few μ in dia. considerable information can be obtained about the composition of the non-clay minerals present in clay and shale samples. In order to study compositional variations in the clay minerals and associated minerals, techniques will have to be developed to concentrate and segregate these fine-grained minerals.

Acknowledgments—Thanks are extended to the Thiele Kaolin Company for supporting this study and to J. W. Johnson who made the electron microprobe photographs.

REFERENCES

Keil, Klaus (1967) The electron microprobe X-ray analyzer and its application in mineralogy: *FortsChr. Mineral.* **44**, 4–66.

Raman, K. V. and Jackson, M. L. (1965) Rutile and anatase determination in solis and sediments: *Am. Mineralogist* **50**, 1086–1091.

White, E. W., Denny, P. J. and Irving S. M. (1966) Quantitative microprobe analysis of microcrystalline powders. The Electron Microprobe: *The Electrochem. Soc. Symp., Wash. D. C., 1964*, pp. 791–804. John Wiley, New York.

Résumé—Des études sur le kaolin, effectuées par microsonde électronique, indiquent que la plupart du Fe est réparti de facon uniforme dans tout le kaolin et doit se trouver soit dans la structure, soit en très petites particules adsorbées à la surface. En plus du Ti, les impuretés d'anatase contiennent du Fe et du Mg. Fe, Mg, Mn, V et K sont présents dans le biotite. Il faut concentrer les impuretés minérales fines pour pouvoir les étudier à la microsonde électronique.

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press

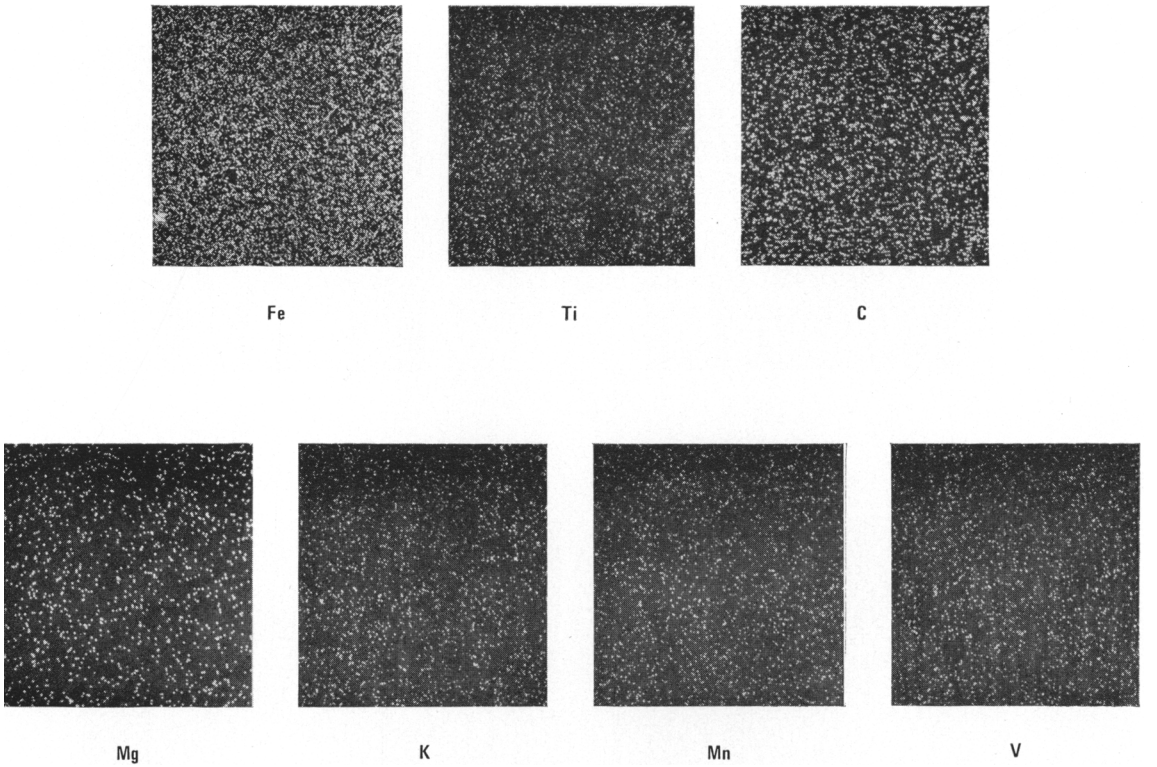
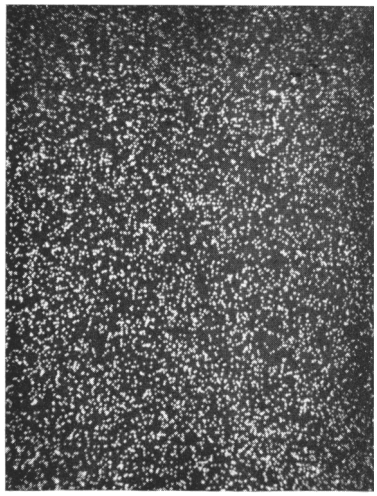
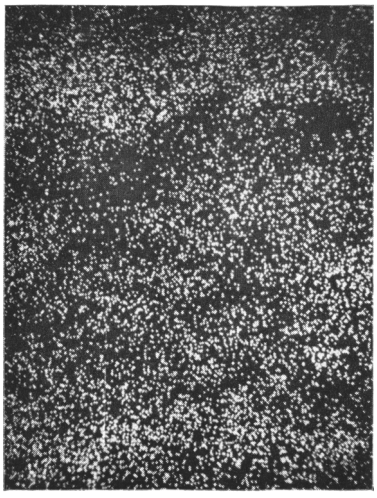


Fig. 1. Electron beam scanning pictures of a sedimented slide of dispersed kaolinite. Width of field is 200 μ.

[*facing page* 188]

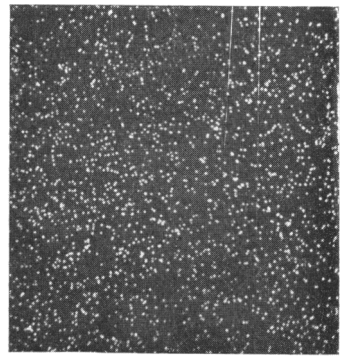


Fe

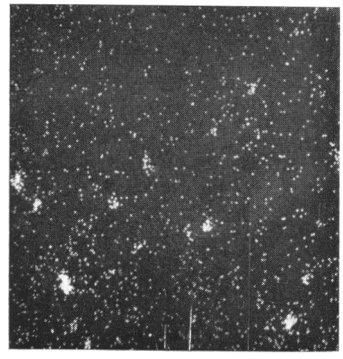


Mg

Fig. 2. Electron beam scanning pictures of flocculated kaolinite. Width of field is $240 \times 180\mu$.



Fe



Ti

Fig. 3. Electron beam scanning pictures of coarse fraction of kaolinite. Width of field is 300μ.

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press

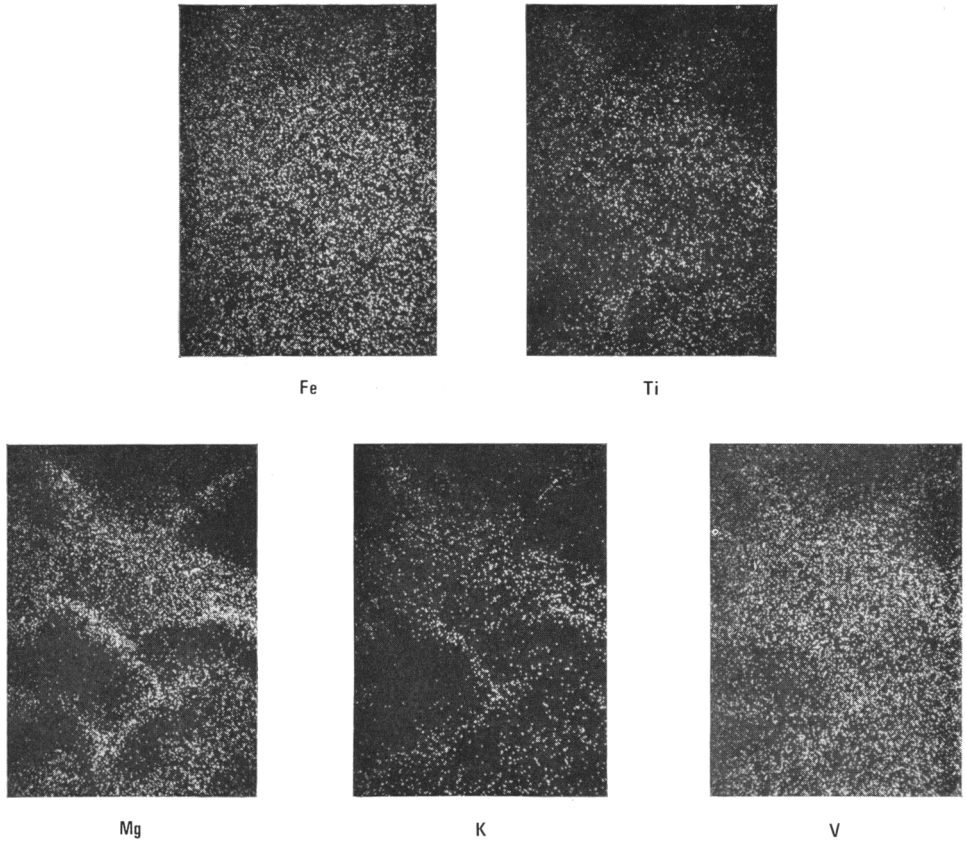


Fig. 4. Electron beam scanning picture of top surface of centrifuged kaolinite plug. Aggregates of fine biotite flakes were concentrated on and near the top surface of the plug. Width of field is $240 \times 180\mu$.

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press

Kurzreferat – Untersuchungen von Kaolinit mit der Elektronenmikrosonde zeigen an, dass der Hauptteil des Fe gleichförmig durch den Kaolinit hindurch verteilt ist und entweder im Gefüge enthalten oder in Form winziger Teilchen an der Oberfläche adsorbiert worden sein muss. Neben Ti enthalten die Verunreinigungen des Anatas Fe und Mg. In Biotit sind Fe, Mg, Mn, V und K gegenwärtig. Die feinkörnigen mineralischen Verunreinigungen müssen konzentriert werden, um der Untersuchung durch die Elektronenmikrosonde zugänglich zu sein.

Резюме—Исследования каолинта электронным микрозондом показывают, что большинство Fe равномерно распределено по всему каолиниту и находится в структуре или-же появляется как очень малые, адсорбированные на поверхности частицы. Кроме Ti анатазовые примеси содержат также Fe, и Mg. В биотите присутствуют Fe, Mg, Mn, V и K. Мелкозернистые минеральные загрязнения приходится концентрировать для того, чтобы подвергнуть их исследванию электронным микрозондом.

https://doi.org/10.1346/CCMN.1968.0160210 Published online by Cambridge University Press