THE NATURE OF TiO$_2$ IN KAOLINITE

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Abstract—SEM, TEM, and electron probe studies indicate that the anatase in Georgia kaolins, and probably anatase in general, consists of subspherical particles (TiO$_2$ pellets) 0.05–0.1 μm dia. Some pure anatase aggregates may be pseudomorphic after ilmenite and have a tabular shape, but much of the anatase is formed from Ti that occurs as scattered ions in the octahedral sheets of biotite. When removed from the biotite this material forms TiO$_2$ pellets. These pellets can occur as: single pellets; irregular aggregates; layered aggregates; spherical aggregates; mixed aggregates (with kaolinite); coated aggregates (with kaolinite). Physical energy can be used to break TiO$_2$–kaolinite aggregates, separate single TiO$_2$ pellets from kaolinite plates and remove kaolinite coatings from TiO$_2$ aggregates.

Al and Si are present in all TiO$_2$ aggregates and the Si–Al ratio is lower in the aggregates than in the kaolinite. An amorphous Si–Al compound may be present and act as a cement.

The anatase apparently is formed from Ti that is released from the parent mineral as Ti (OH)$_4$. The Ti (OH)$_4$ precipitates to form an amorphous hydrous oxide gel which dehydrates to form a granular aggregate of small anatase crystals.

INTRODUCTION

Titanium oxide nearly always is reported in chemical analyses of kaolinite. Values commonly range from 0.2 to 2.5% TiO$_2$. The amount of Ti present is determined largely by the composition of the parent material (Weaver and Pollard, 1973). Hydrothermal kaolinite and kaolinite formed by the weathering of feldspar and muscovite in granitic and pegmatitic rocks generally have a low Ti content. Of the common source minerals, Ti is most abundant in the dark minerals, including ilmenite, garnet, biotite, augite, etc.; kaolin deposits derived from biotite-rich granites, granite gneiss and schists, such as those in Georgia, have a relatively high Ti content.

Most of the TiO$_2$ is present as anatase though minor amounts of rutile are present in some deposits. The rutile mostly is inherited and the anatase formed authigenically from the chemical weathering of the other Ti containing minerals. Dolcater *et al.* (1970), using a solution technique, found that 15% of the Ti in Georgia kaolins apparently was in the kaolinite structure.

Electron probe studies (Weaver, 1968) indicate the anatase contains minor amounts of Fe and Mg. Sayin and Jackson (1976), using a selective dissolution technique, found 0.5–3.1% Fe present in the anatase from Georgia kaolinites. These impurities are presumably responsible for the gray color of the anatase. This gray color decreases the whiteness of the kaolinite and considerable effort is expended to remove it. The Fe apparently accounts for the weak magnetic properties of the anatase that allow some of it to be removed by a strong magnet.

In order to obtain some information about the morphology, size, location and aggregation characteristics of anatase in Georgia kaolinite deposits, samples were subjected to a variety of treatments and examined with the scanning electron microscope (SEM), energy dispersive X-ray analyser (EDX), transmission electron microscope (TEM) and electron probe.

Tabular anatase crystals are occasionally seen in Georgia kaolinite; however, most of the anatase occurs as rounded subspherical grains. Figure 1 shows the wide range in size, less than 0.02–1.0 μm, of tabular TiO$_2$ crystals. Many tabular grains are hollow, which suggests that they formed around an ilmenite core.

PELLETS AND AGGREGATES

Electron probe studies indicate that Ti occurs both as finely disseminated material and as discrete grains ranging from 1 to 30 μm dia. The distribution of these two types is best observed in clay plugs that are formed by centrifuging thick slurries of kaolinite. A clay plug was impregnated with plastic, sawed down the middle and examined with the electron probe. The lower portion contains concentrations of Ti particles that are rectangular in shape (15–28 μm long and 2–7 μm high) suggesting the particles are disk or plate shaped (Fig. 2). The background Ti is relatively low, confirming other experiments which show that the coarse fraction of kaolinite is low in Ti when the large TiO$_2$ aggregates are removed. The amount of background Ti increases upward and the Ti aggregates become smaller and less well defined. The upper portion of the clay plug contains only finely dispersed Ti, a distribution expected in a gravity separation.

A scotch tape peel was made of the exterior surface of the clay plug (before plastic impregnation) and examined with the electron probe. Although data

from the surface and the interior of the plug are not quantitatively comparable, the pictures of the surface of the plug indicate that large Ti particles are more abundant than in the center of the plug. At the base of the plug Ti particles range from 10 to 25 μm in size (distribution is uneven). Higher in the plug the Ti particles are relatively uniform in size (5–7 μm), but systematically decrease in abundance giving way to background.

The fine kaolinite fraction (less than 1 μm) was examined in order to get a better look at the finely disseminated TiO$_2$ particles. SEM and electron probe pictures of the fine fraction show the Ti is evenly distributed and occurs as discrete Ti pellets 0.05–1.0 μm in size.

The fine fraction of a kaolinite sample was given a sonic treatment and then centrifuged. The bottom of the centrifuged kaolinite plug was quite black. The SEM picture (Fig. 3) shows that the black areas consist of a dense cluster of 0.1 μm Ti pellets. Transmission electron microscope (TEM) pictures (Fig. 4) of a replica of the bottom of the clay plug show a few square (cubic) particles but most are rounded. The particles range from 0.05 to 0.20 μm with 0.10 μm being a good average value. Though considerable kaolinite is present, the Ti pellets tend to cluster together to form Ti aggregates consisting of 2–10 or more pellets. The picture suggest that the Ti pellets, under these conditions (calgon, sonic treatment, centrifuge), have more of an affinity for each other than for kaolinite.

A duplicate was impregnated with plastic and fractured approximately perpendicular (actually curved parallel to plug surface) to the length of the plug. Figure 5 shows the Ti is concentrated on the bottom and is relatively scarce in the body of the plug.

These pictures indicate that it is possible to separate and fractionate the individual Ti pellets in the fine fraction of kaolinite. The application of energy apparently separates these pellets from the kaolinite and decreases the viscosity enough to allow them to settle through the kaolinite.

In order to observe the coarse TiO$_2$ particles a sample of crude kaolinite was dispersed with calgon, given a 15 min intense sonic treatment and the coarse fraction collected by gravity settling. The majority of the TiO$_2$ aggregates range from 5 to 10 μm but some are up to 80 μm dia. Most aggregates consist of TiO$_2$ pellets (Fig. 6) but some contain appreciable proportions of kaolinite flakes (Fig. 7). Figure 8 shows a peculiar aggregate which consists of a 15 μm aggregate of spherical and disk-shaped particles which in turn are composed of closely packed TiO$_2$ pellets. There is definite layering in some of these particles, but others appear to be spherical with no evidence of layering. There is some suggestion that the particles are cemented. The finest fraction of the gravity settled sample contains some 2–7 μm, relatively pure TiO$_2$ aggregates that, in general, resemble those in the coarser fraction (both pure and impure).

The TiO$_2$ aggregates in magnetic concentrates of gently dispersed samples of crude kaolinite are 5–10 μm dia. The aggregates appear to consist of small, 0.10–0.20 μm, kaolinite flakes with a few TiO$_2$ pellets. The energy dispersive X-ray (EDX) patterns indicate the concentration of TiO$_2$ is stronger than suggested by the pictures. The distribution of the thin kaolinite flakes suggest that they are a coating on TiO$_2$ particles rather than a random mixture of the two (Fig. 9 and 10).

When the crude clay is mixed with more intensity (blender) the TiO$_2$ aggregates in the magnetic concentrate are relatively pure and have little or no coating of kaolinite (Fig. 11). Apparently the application of energy causes the kaolinite flakes to be released. The background Ti appears to be higher than in the non-blended samples suggesting that some of the high kaolinite-low TiO$_2$ aggregates have been broken.

Figure 12 is an example of a TiO$_2$ aggregate that was not removed by the magnet. EDX patterns confirm that the particle is rich in Ti, but the SEM pictures suggest the particle is composed of kaolinite plates. The Ti EDX map (Fig. 12) outlines the plate pattern in detail suggesting some of the plates may have a high Ti content; however the spectra indicate Si and Al are present.

Many of the TiO$_2$ aggregates that were not attracted by the magnet have a relatively high kaolinite content much of which appears to act as a coating. The kaolinite coating appears to be thicker and better developed than that on the kaolinite coated Ti particles that were removed by the magnet. As these samples were prepared by relatively intense mixing in a blender, the kaolinite must be strongly bonded to the anatase.

Less TiO$_2$ was removed by magnet from the fine grained east Georgia clay than from the coarser central Georgia clay. Many of the large TiO$_2$ particles from the east Georgia samples are coated and intimately mixed with small, thin subhexagonal flakes (similar to Fig. 9). These flakes appear to be kaolinite though EDX spectra indicate that very little Si and Al is present. Either these flakes are TiO$_2$ or they occur as a relatively thin coating on the TiO$_2$ aggregates.

Most of the TiO$_2$-rich particles, which are concentrated by gravity settling, contain more kaolinite than those removed by the magnet.

PROCESSED CLAY

During commercial processing the kaolinite is dispersed and the coarse fraction removed by centrifugating. Most of the TiO$_2$ removed from the commercial clay by magnetic means consists of aggregates of TiO$_2$ pellets that are considerably more pure than those removed from the crude clay. Of particular interest is the presence of plates of TiO$_2$ pellets (Fig. 13). Plates are both parallel and at 90° to each other. The pellet plates are 0.10–0.30 μm thick. This is the
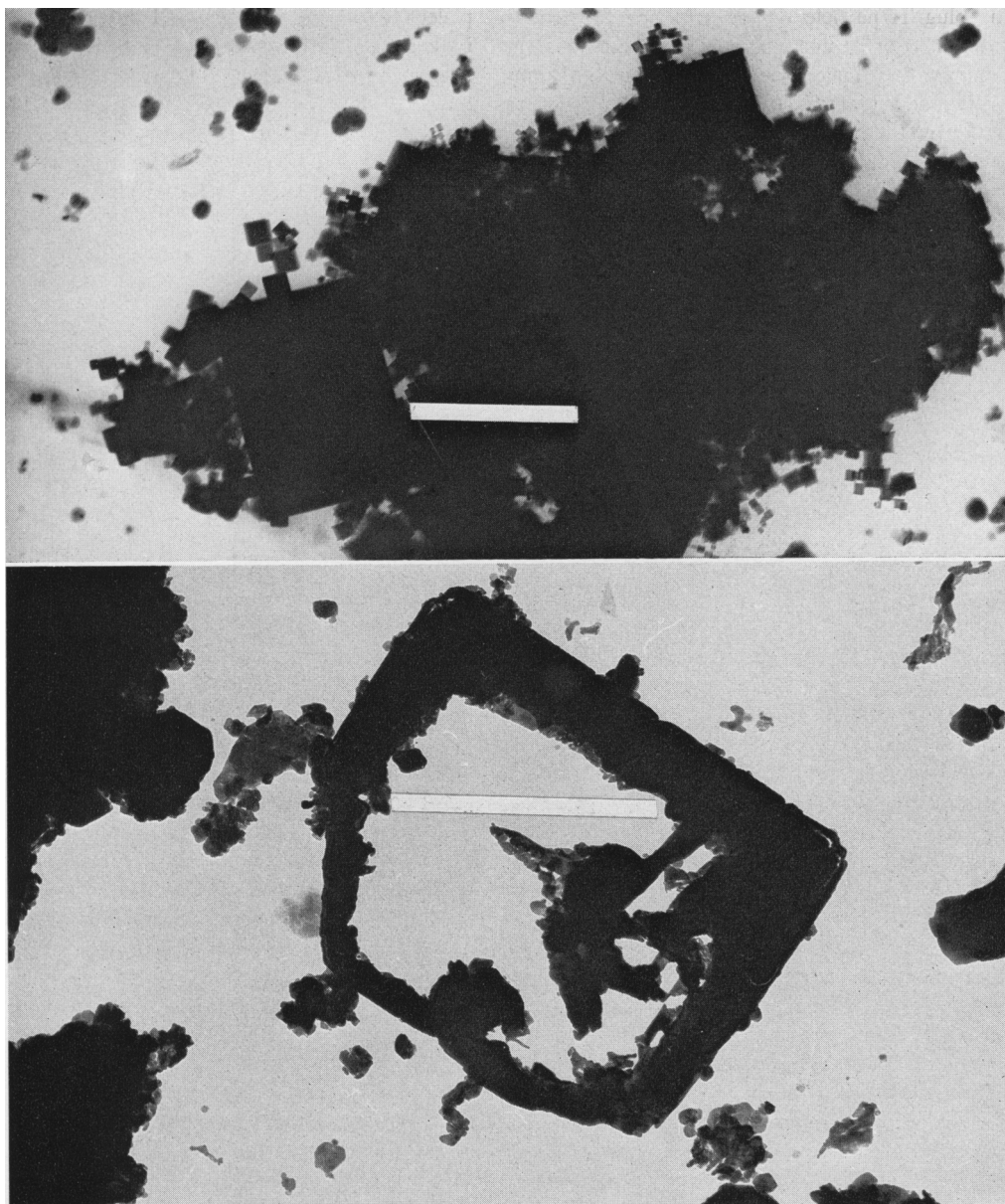
Fig. 1. Upper, tabular anatase in dissolved kaolinite residue. Lower, hollow tabular anatase in dissolved kaolinite residue.
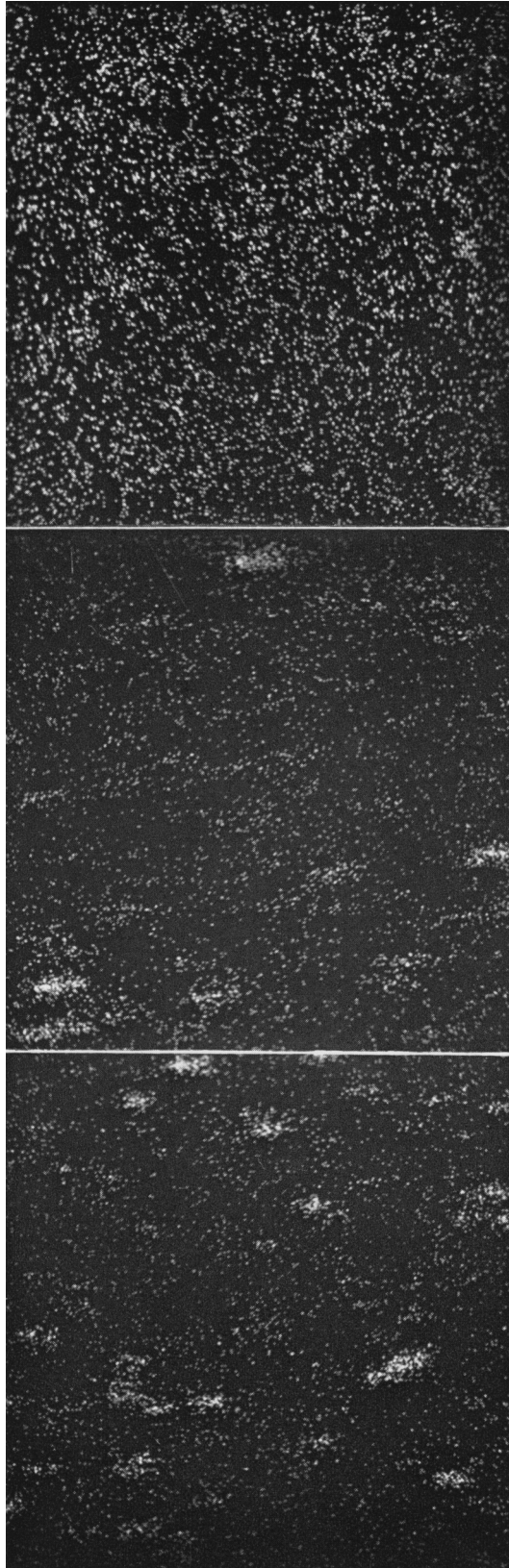
Fig. 2. Electron probe pictures showing vertical distribution of Ti in a clay plug formed by centri-fuging. Clay was commercially processed and pH adjusted to 3.5. Pictures are 200 μm in width.
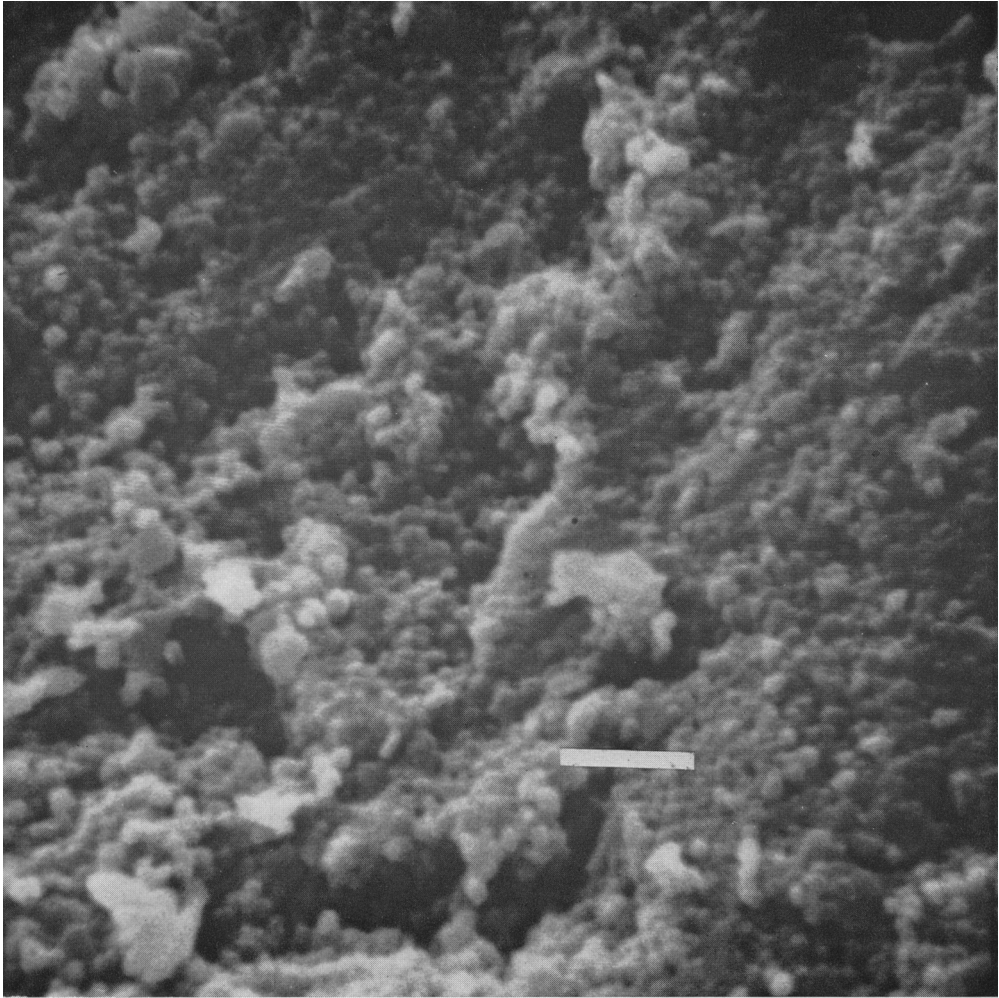
Fig. 3. Layer of TiO_2 pellets on bottom of centrifuged fine kaolinite fraction.
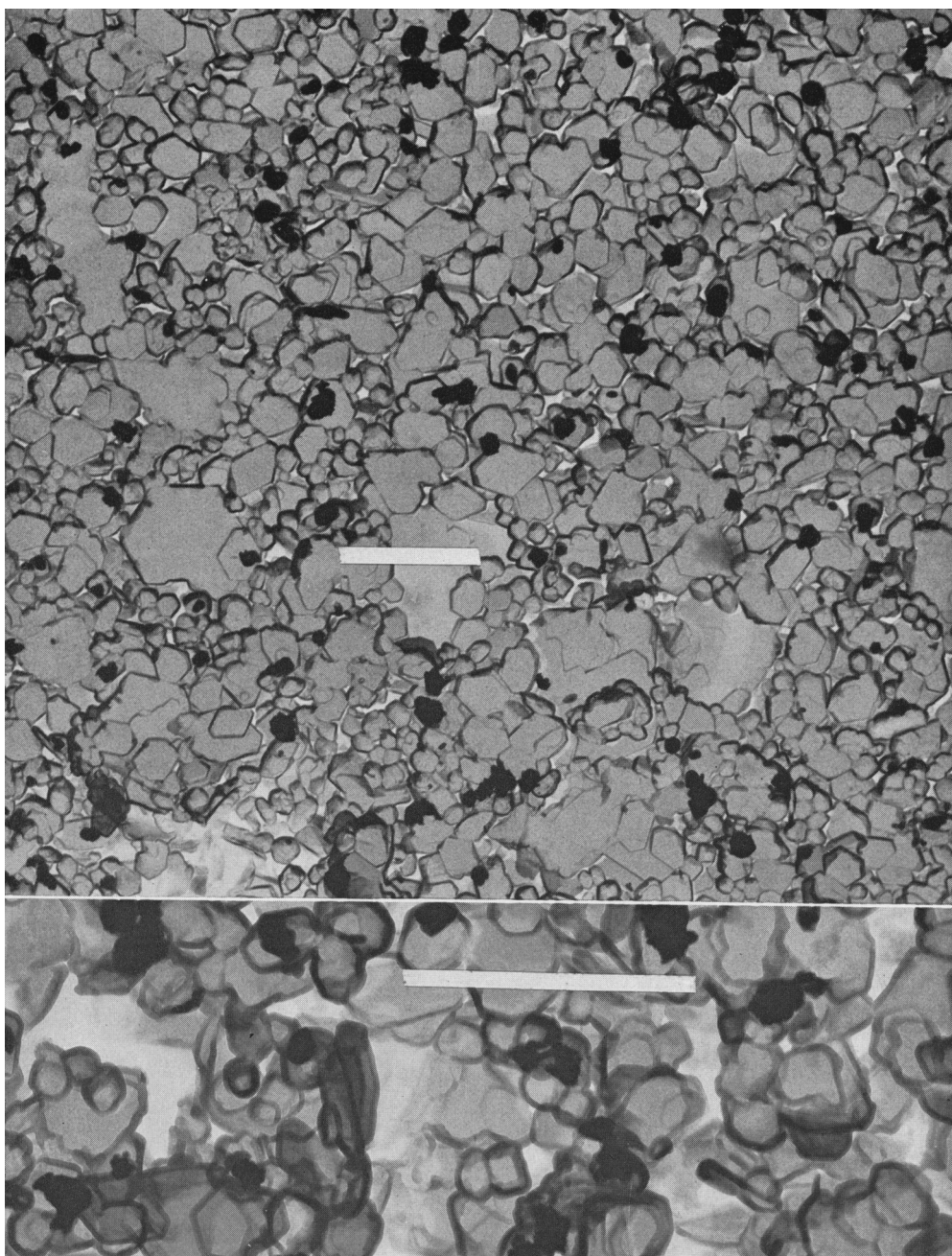
Fig. 4. TEM picture of replica of bottom of centrifuged clay plug. Only fine fraction was centrifuged. Isolated and small aggregates of TiO_2 pellets are abundant.
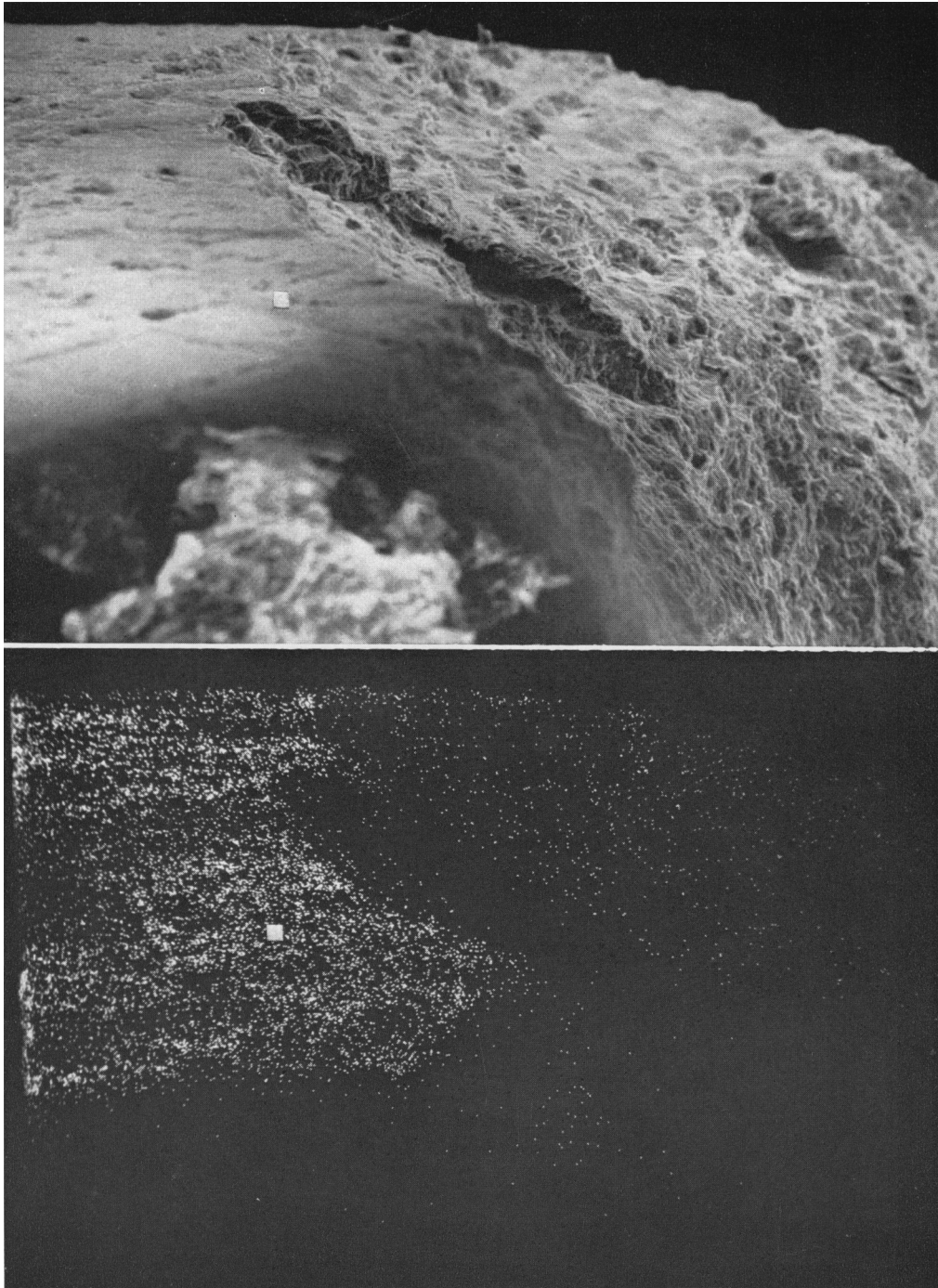
Fig. 5. Ti distribution (EDX) on bottom and fractured side of clay plug.
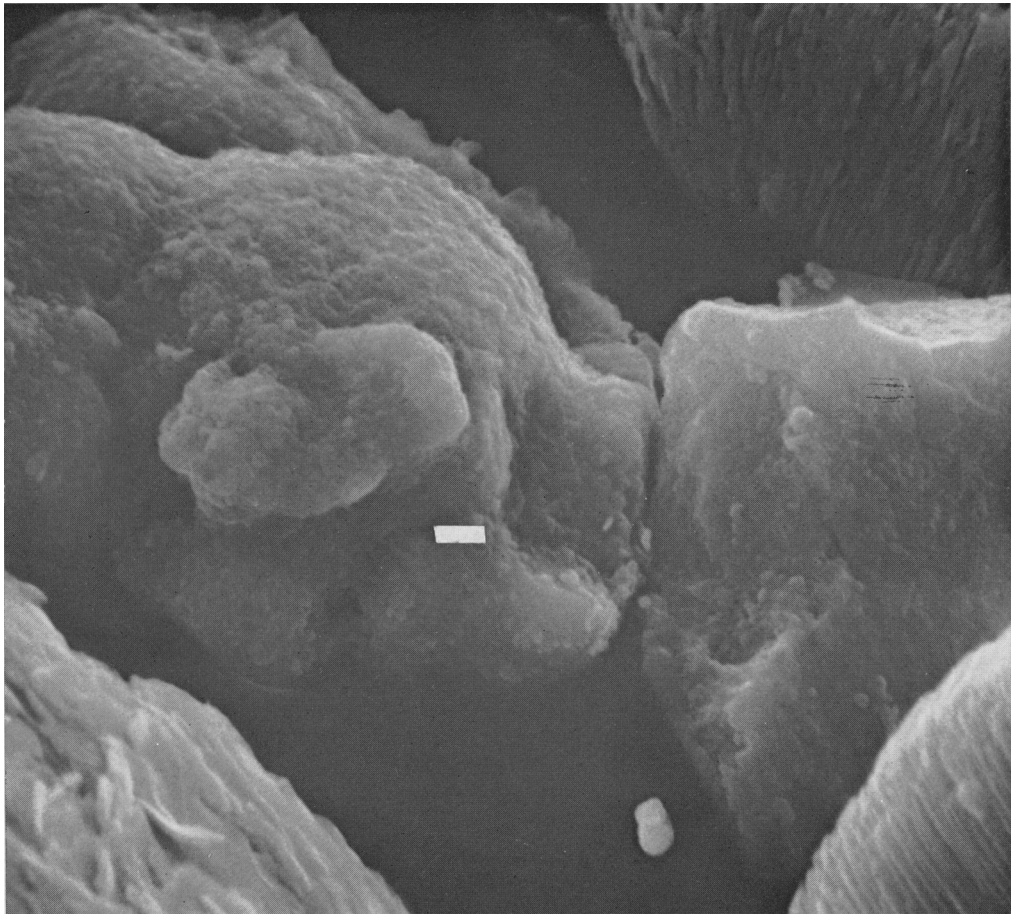
Fig. 6. Two aggregates of pure densely packed TiO$_2$ pellets at base of dispersed, sonic treated gravity settled sample of crude
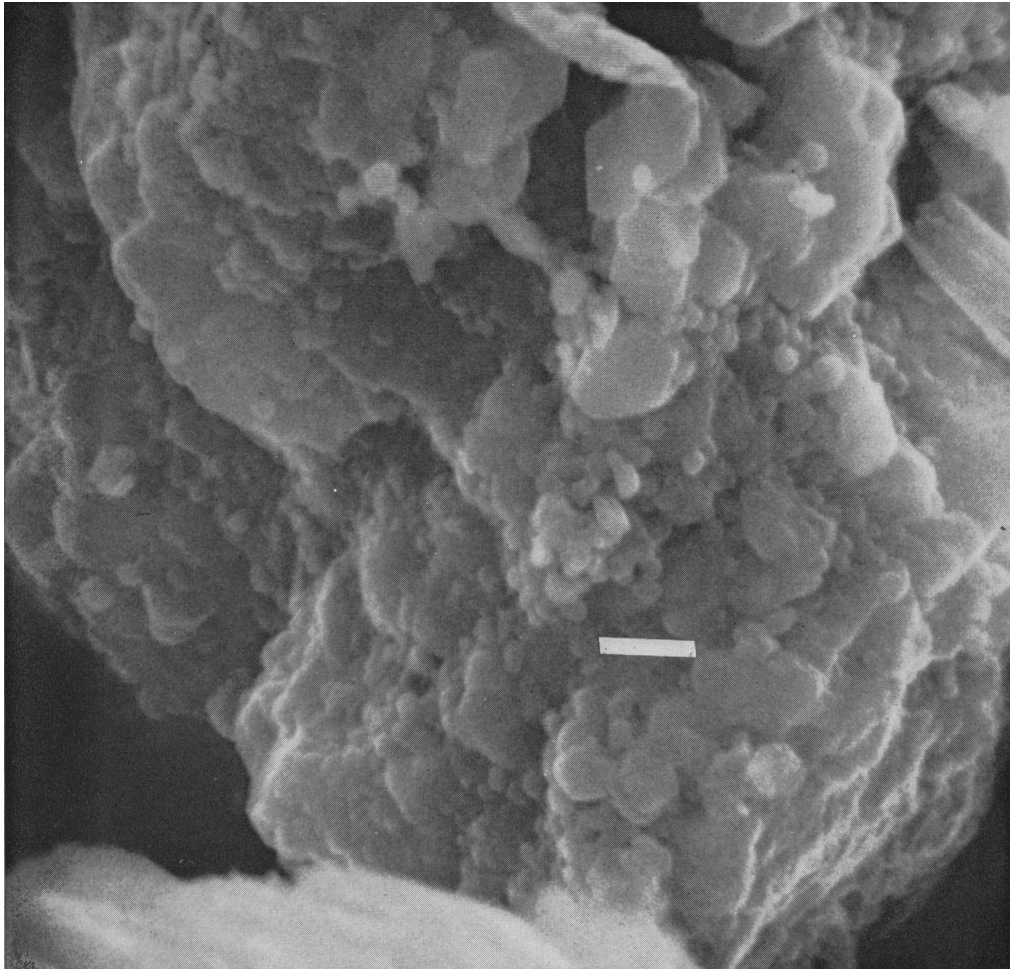
Fig. 7. Aggregate from same sample as in Fig. 6, consisting of a mixture of TiO_2 pellets and small kaolinite flakes.
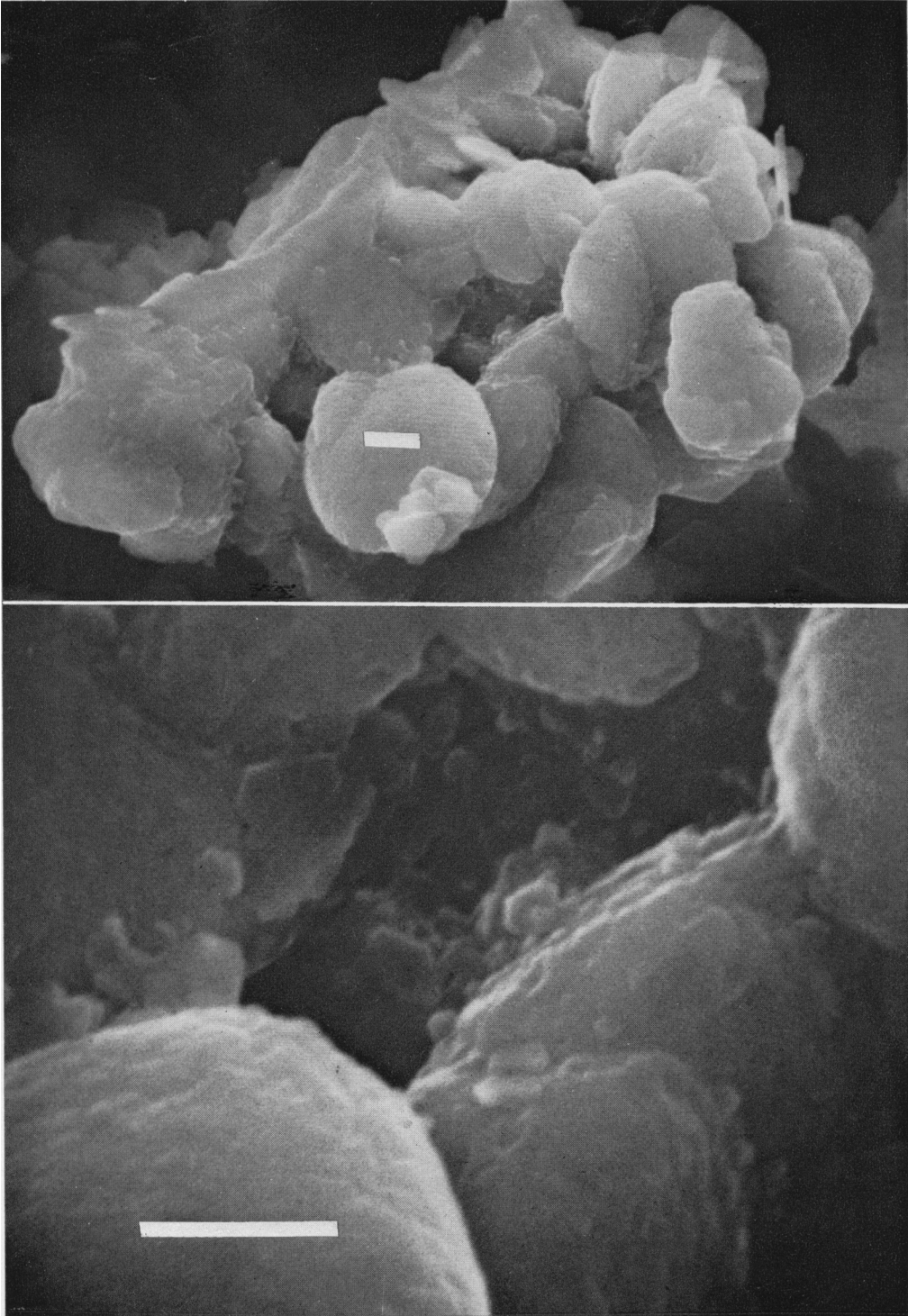
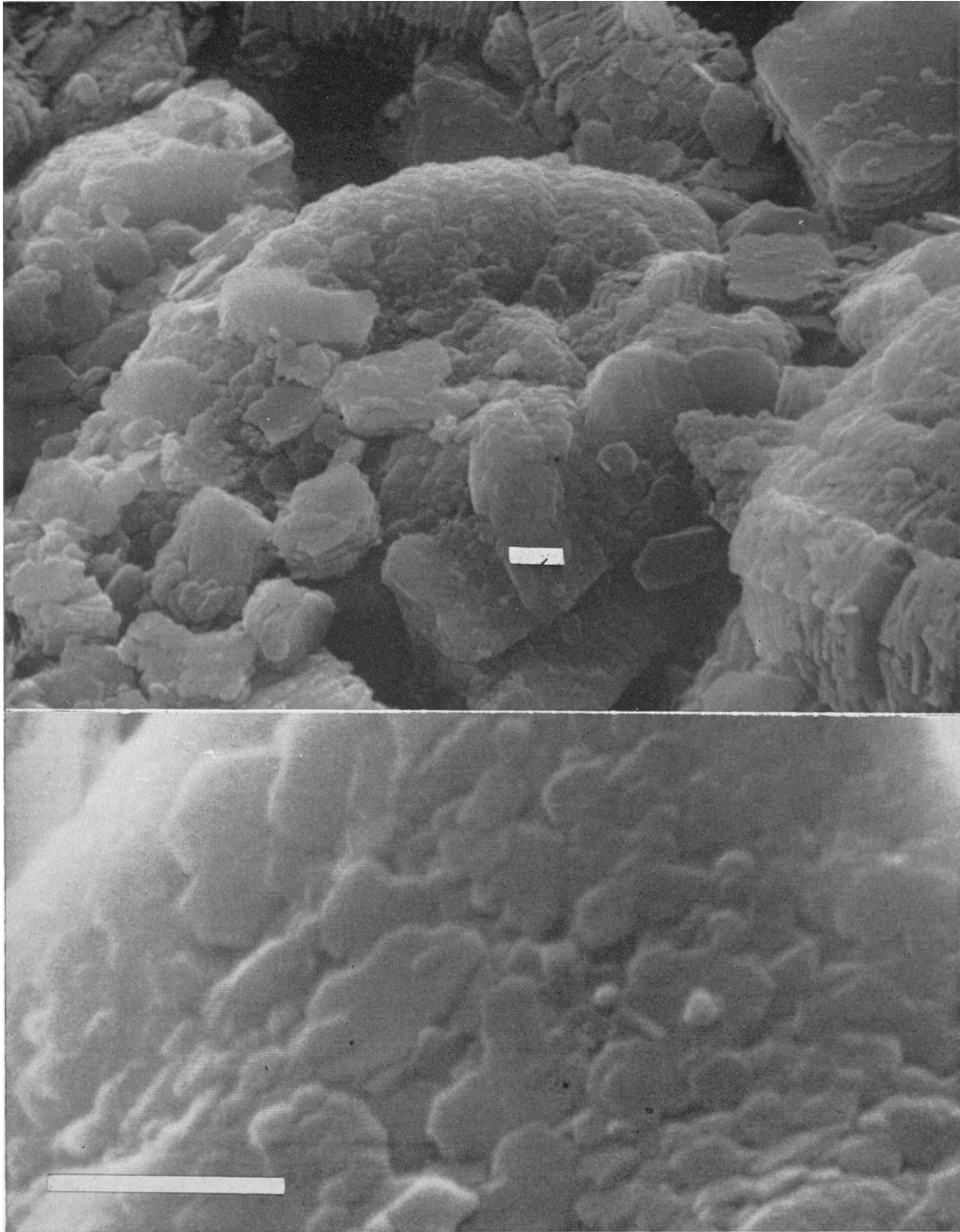Fig. 8. Cluster of spherical and disk-shaped aggregates of TiO_2 pellets.

Fig. 9. Kaolinite coated disked shaped TiO_2 aggregate in magnetic concentrate from crude sample. Dispersing agent used but only minor energy was applied. EDX picture confirms grain is composed largely of Ti. High magnification picture shows kaolinite coating surface.

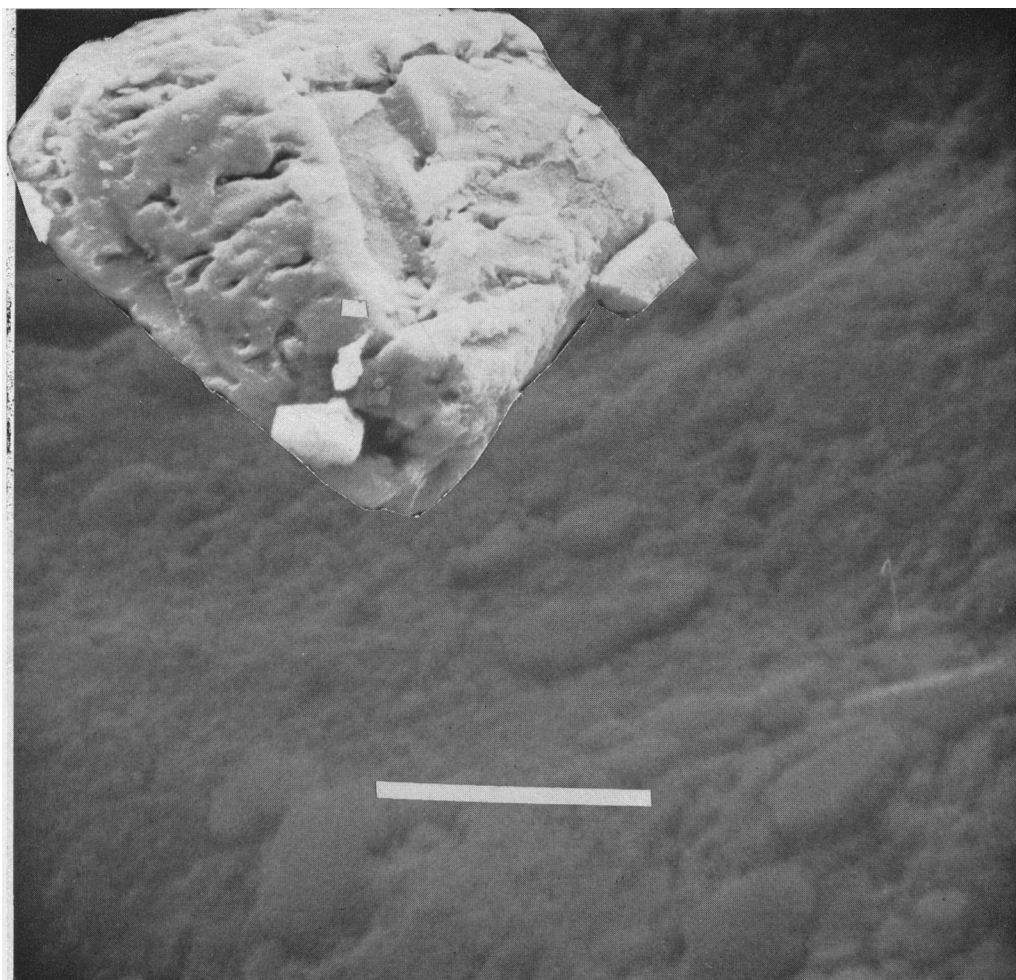Fig. 10. EDX picture of low magnification SEM picture in Fig. 9.

Fig. 11. Pure TiO$_2$ aggregate from magnetic fraction of crude. A few small kaolinite flakes can be seen. Both dispersing agent and energy applied.
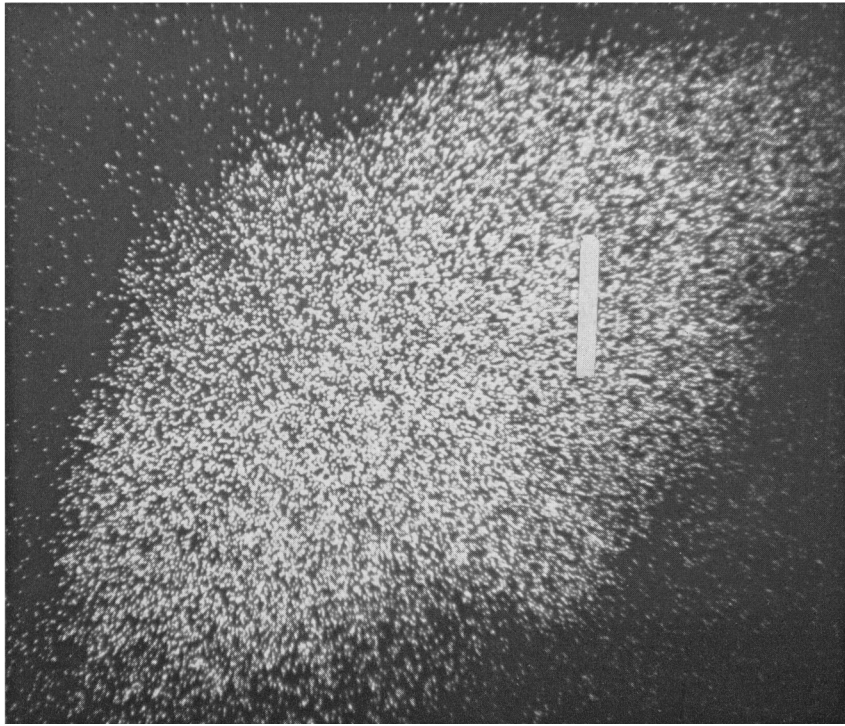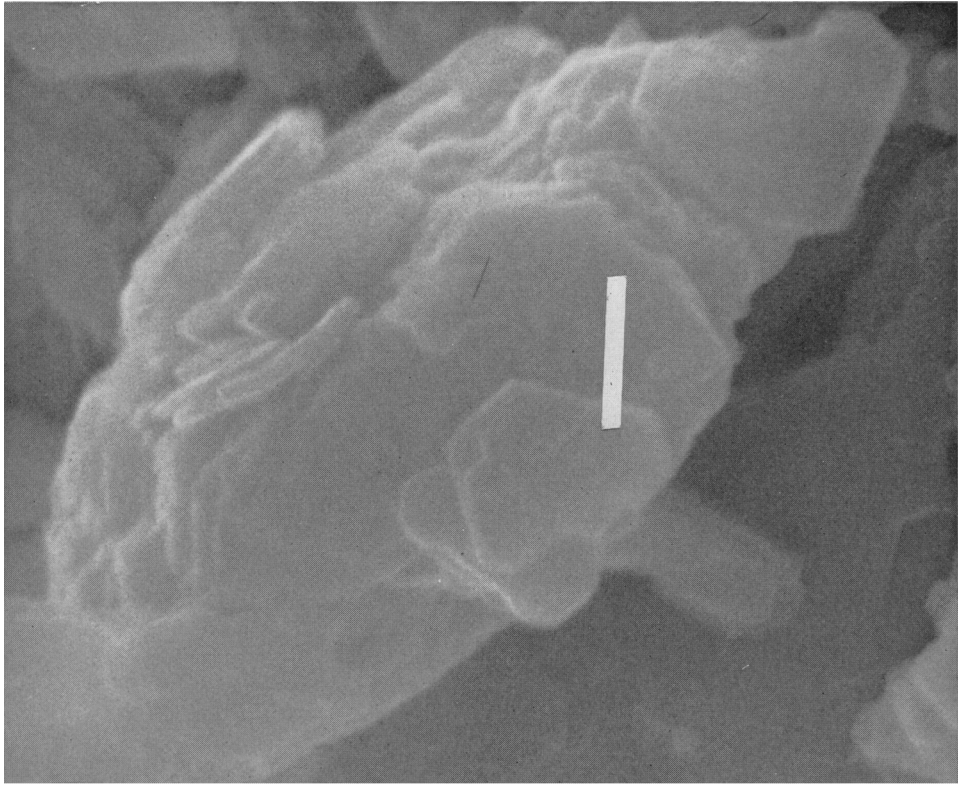
Fig 12. Kaolinite coated TiO₂ particle from non-magnetic fraction of crude, EDX map is for Ti. Both dispersing agent and energy applied.
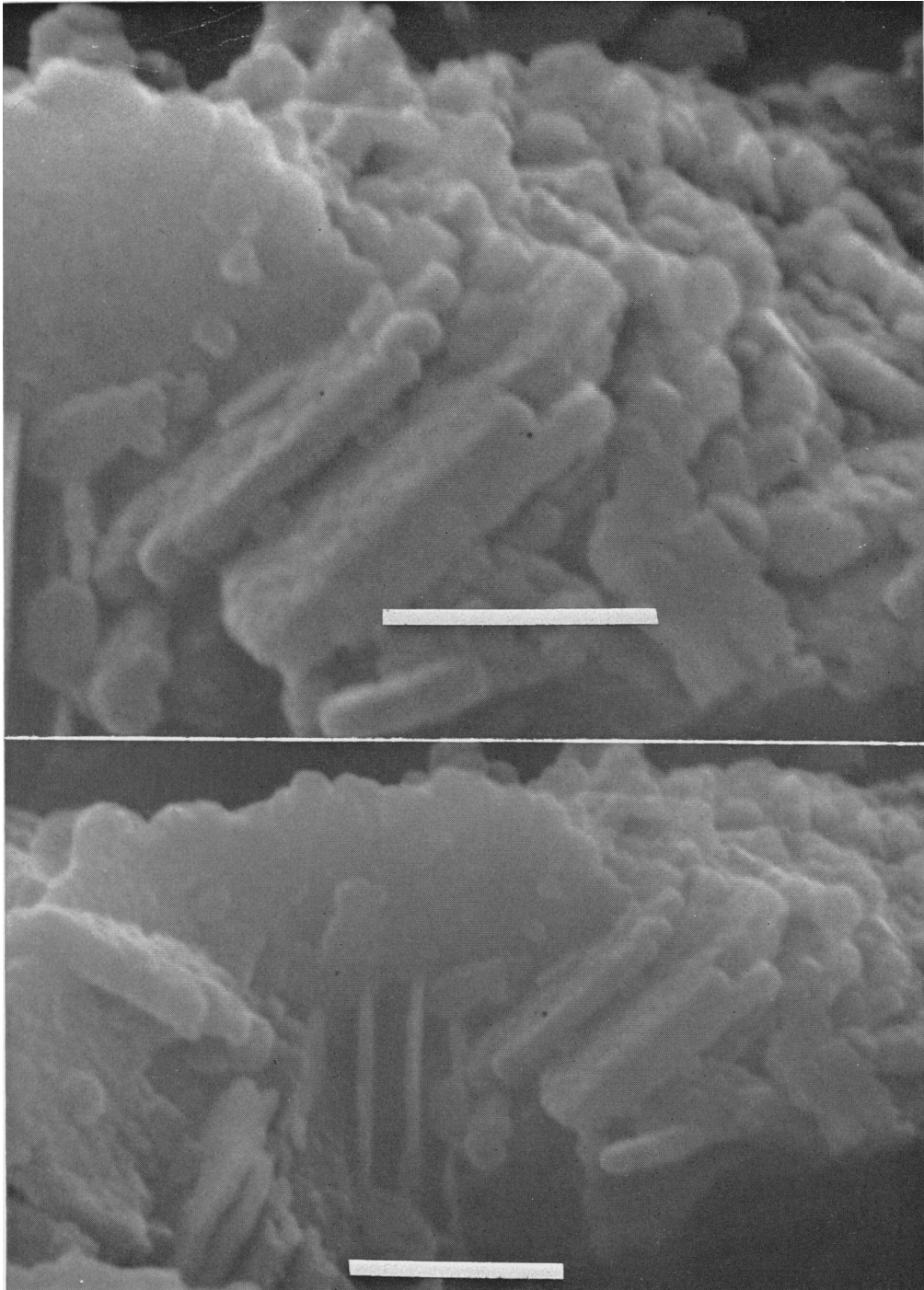
Fig. 13. Plates of TiO_2 pellets in commercially processed kaolin. These plates are similar in thickness to kaolinite plates.
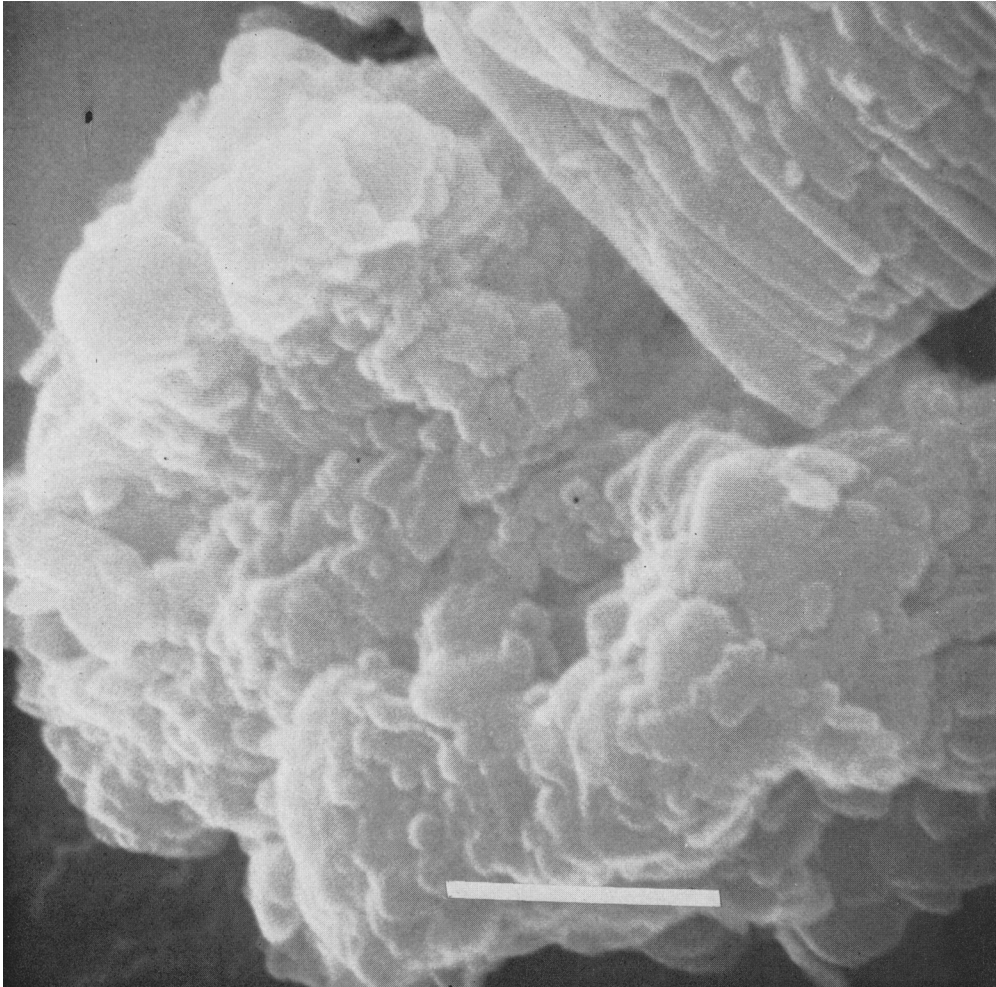
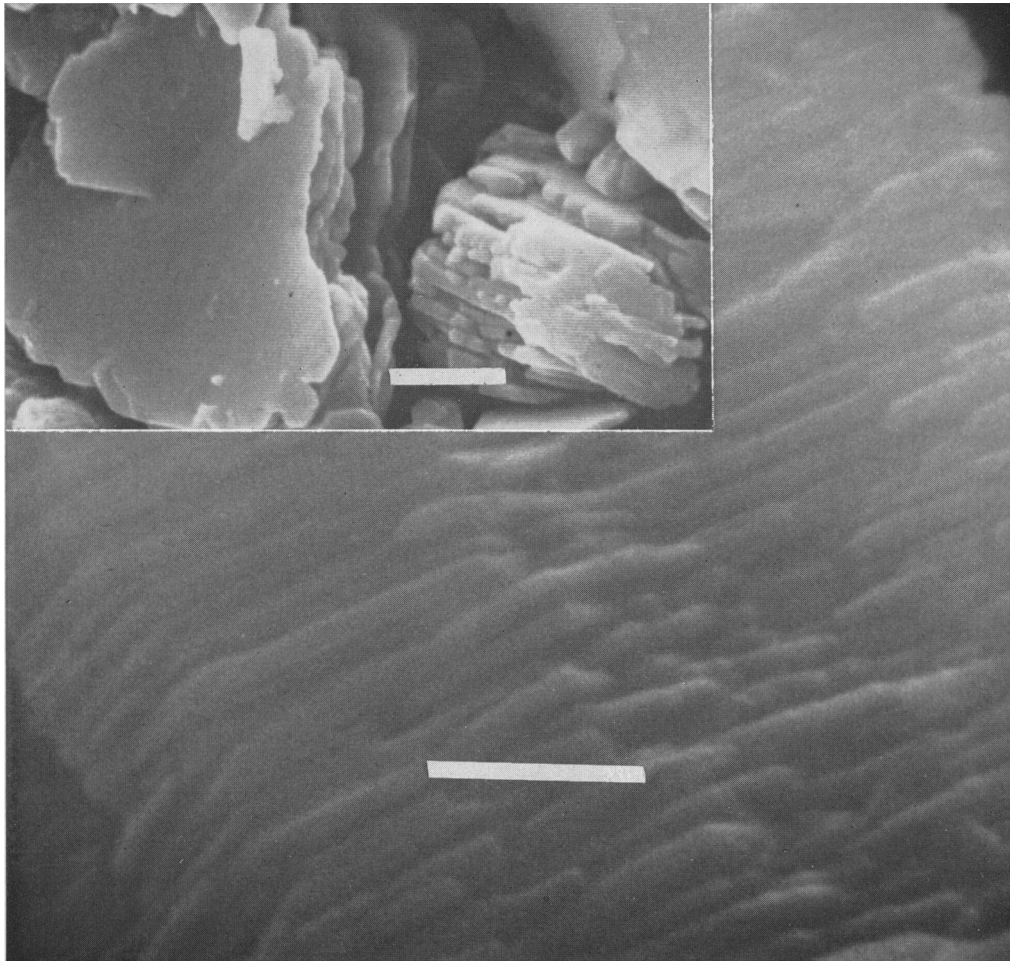Fig. 14. TiO₂ aggregate with layers of Ti pellets and possibly kaolinite flakes.

Fig. 15. Three kaolinite stacks that appear to contain layers or partial layers of TiO_2 pellets.

same thickness as most kaolinite plates. It is quite possible that these TiO$_2$ plates occur interlayered with kaolinite plates. The smooth edges of the TiO$_2$ plates indicate they would be difficult to identify. Such obvious TiO$_2$ plates were not seen in the magnetic fraction of the crude clay. The morphology suggests these plates were made or rearranged during processing.

A commercial sample was blended and passed through the magnet. TiO$_2$ aggregates containing TiO$_2$ plates were still present. The plates are parallel to each other and similar in general shape to kaolinite plates. The TiO$_2$ plates, whenever they formed, appear to be quite stable.

Figure 14 shows a relatively pure TiO$_2$ aggregate and a kaolinite book. The former consists of ~ 0.1 μm TiO$_2$ pellets that are organized in a plate-like fashion. Some of the edges of these plates have hexagonal shapes suggesting there may be some interlayered kaolinite plates. The kaolinite book has plates the same thickness as the TiO$_2$ pellets. TiO$_2$ pellets occur on the edges of some of these plates suggesting that they could be plates of TiO$_2$. Serrated and rounded edges, resembling those of the TiO$_2$ plates (Fig. 13), are commonly observed on plates in kaolinite books (Fig. 15). At least visually it appears that kaolinite and anatase plates could be interlayered. Resolution of the EDX analyser is not good enough to confirm this.

RELATION OF Ti TO Si–Al

EDX spectra were made of a number of particles that had a wide variation in TiO$_2$ content. Figure 16 is a plot of the peak intensity ratio of Al–Ti vs Si–Al. There are two trends. For particles with an
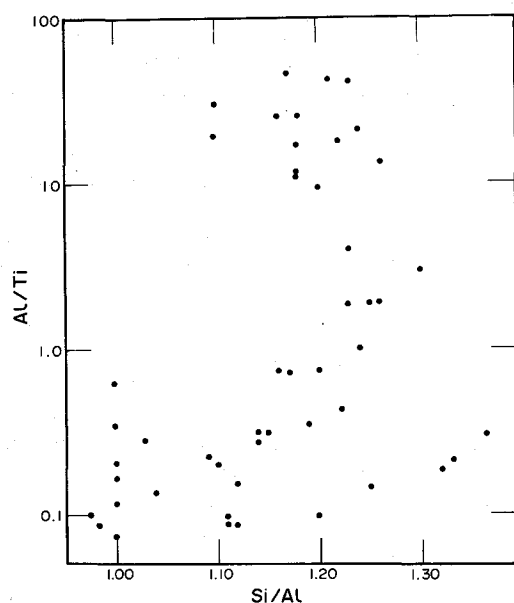

Fig. 16. Graph showing how Al–Ti varies as a function of the Si–Al ratio. Data obtained from EDX spectra.

Al–Ti peak intensity ratio larger than one, the Si–Al peak intensity ratio decreases as the Al–Ti ratio increases. This trend is partially, but not entirely, forced by the Al. As Al increases relative to Si it also increases relative to Ti. As the Si–Al range is so small relative to the Al–Ti range the forced correlation should be small.

When the Al–Ti ratio is less than one, the trend reverses. As the Si–Al ratio decreases the Al–Ti ratio decreases; or, as Al increases relative to Si it decreases relative to Ti. This suggests the "extra" Al is not associated with the TiO$_2$ but with the Si. If the variation in the apparent Si–Al ratio is due to differential adsorption of X-rays by the Ti one would expect the relation between the three components to be constant rather than to reverse.

On a more empirical basis, when the Ti peak is less than one inch high the Si–Al peak ratio averages 1.20; when it is more than five inches high the average is 1.03. There is relatively little overlap.

Commercial anatase was mixed with crude kaolinite and 28 spectra made. The Si–Al ratio was relatively constant (average 1.18) and independent of the Al–Ti ratio. It does not appear that the differential adsorption of X-rays by Si and Al in the presence of Ti is a major factor.

Jepson and Rowse (1975) made a detailed electron microscope microprobe analysis of individual kaolinite particles from an English kaolin and a Goergia kaolin and established that the Al:Si atom ratio varied from kaolinite particle to kaolinite particle. Thus, it is possible that the variable Si–Al ratio noted in the present study is real.

The Al may substitute for Ti in the anatase but the fact that both Si and Al are present in all Ti aggregates and at high Ti values Al increases relative to Si and decreases relative to Ti suggests this is not the explanation. Other possibilities are that the kaolinite associated with the TiO$_2$ aggregates has a relatively high content of tetrahedral Al and a relatively high negative layer charge which causes it to be preferentially attracted to the TiO$_2$ or some of the Al may be present as an Al hydroxide or in amorphous Si–Al compounds cementing the TiO$_2$ pellets. Sagin and Jackson (1976) found that Ti-rich (74–91% TiO$_2$) magnetic concentrates contain appreciable Si and Al but found no kaolinite (X-ray). They concluded the concentrate contained 6–16% amorphous relics of muscovite-derived vermiculite and/or kaolinite.

Minor Fe is present in most of the TiO$_2$ particles and it is generally more abundant in the particles removed by the magnet than in those that are not removed. The Ti/Fe ratio varies widely.

CONCLUSIONS AND SUMMARY

Some pure anatase aggregates may be pseudomorphic after ilmenite and have a tabular shape, but much of the anatase is formed from Ti that occurs as scattered ions in the octahedral sheets of biotite

and other dark minerals. When removed from the biotite this material forms TiO_2 pellets. In kaolin deposits these pellets are bonded to each other and to kaolinite plates. The bonding may be electrostatic and/or chemical (cementing agent).

Commercial anatase is made by dissolving ilmenite and precipitating pure TiO_2. The TiO_2 consists of small pellet-shaped particles similar to those associated with kaolin, but slightly larger (0.1–0.3 μm).

The anatase in Georgia kaolins and probably anatase in general, consists of basic subspherical particles (Ti pellets) 0.05–0.1 μm dia. These pellets can occur as: single pellets, irregular aggregates, layered aggregates, spherical aggregates, mixed aggregates (with kaolinite) and coated aggregates (with kaolinite). There is some evidence that plates of TiO_2 pellets occur interlayered with kaolinite plates but the pictures were not conclusive. The pellets and aggregates can be mobilized in slurries by chemical and physical treatment. The application of energy is essential. High shear breaks large TiO_2–kaolinite aggregates, separates single TiO_2 pellets from kaolinite plates and removes some of the kaolinite coating from TiO_2 aggregates. It also decreases viscosity, allowing for easier separation.

The Si–Al ratio of the TiO_2 aggregates is lower than that of normal kaolinite. This may indicate Al substitutes for Si in the kaolinite and that high-charge kaolinite is preferentially attracted to TiO_2. More likely some amorphous Al–Si complex is present. The Fe content of the TiO_2-rich particles is quite variable and determines, to a large extent, how much TiO_2 can be removed by magnetic methods.

In nature, individual TiO_2 pellets presumably precipitate from solution. It is less clear how large aggregates form in the presence of kaolinite. They may all be altered ilmenite and rutile; however, large aggregates which are composed of Ti pellets always contain some Si and Al which is not always on the surface.

Sedimentary chert and phosphate (apatite) consist of densely packed aggregates of small particles or crystallites and in this respect resemble anatase grains. Chert and apatite may precipitate as individual spherical to subspherical particles which may eventually coalesce or they may be deposited as an amorphous gel-like mass which crystallizes into a granular aggregate. Both also form by replacing other minerals. It seems likely that anatase froms similarly. Phosphate grains can form in a clay-rich environment by replacing the clay. The resulting grains contain considerable trapped clay and amorphous material (Weaver and Wampler, 1972). It is possible that much of the Al and Si associated with the TiO_2 aggregates, other than the surface coating of kaolinite, is amor-

phous material resulting from incomplete replacement of kaolinite and mica particles.

TiO_2 is insoluble at pH values above 2.5 and therefore immobile in the environment in which most kaolinites form. $Ti(OH)_4$ is not precipitated until a pH of 5 is reached and, based on studies of weathered basalt, Sherman (1952) and Loughman (1969) concluded that Ti is released as $Ti(OH)_4$ which when dehydrated precipitates as crystalline TiO_2. Both $Ti(OH)_4$ and $TiO(OH)_2$ form gelatinous precipitates which Weiser and Milligan (1939) concluded were agglomerates of extremely minute crystals of oxides or simple hydroxides which hold large amounts of water by adsorption or capillary forces. The initial precipitate is X-ray amorphous, consisting of very small crystals, but after aging at room temperature the crystals grow larger and X-ray peaks for anatase are obtained.

Thus, Ti can apparently behave similarly to Si and precipitate as an amorphous hydrous oxide gell which, with time, converts to a granular aggregate of small crystals. This is a reasonable origin for the anatase aggregates which occur in the kaolinite deposits, and probably for the anatase in most sediments.

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