

THE LOCATION OF IRON-55, STRONTIUM-85 AND IODIDE-125 SORBED BY KAOLINITE AND DICKITE PARTICLES

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Abstract—The autoradiographic method at the electron microscope level has been applied successfully to locate the position of sorbed ions and compounds associated with kaolinite and dickite particles. For suitable isotopes, the limit of resolution was about $0.2 \mu\text{m}$ and would be conceivably less in the most favorable conditions.

Judged by the location of iodide-125 and strontium-85, the majority of positive sites and also the most reactive negative sites were situated at the edges of the clay particles. These conclusions were supported by normal electron microscope examination of mixtures of clay with charged gold and silver iodide sols.

Iron (III) ions, which have been shown to react with kaolinite by chemisorption mechanisms in 0.15 M systems and by both ion exchange and chemisorption in 0.01 M systems, were, in either case, located at edge-sites on the clay. When intentionally precipitated onto dickite, iron (III) hydroxides were distributed evenly over the clay surfaces. However, precipitation was probably initiated at the particle edges.

Minor exceptions to the above conclusions appeared to be caused by basal surface features such as fracture or stress lines, outgrowths or cavities, and if the clays had not been cleaned, by strongly associated impurities such as iron hydroxides.

INTRODUCTION

THE MAIN object of this work was to determine the location of iron (III) on kaolinite particles after (a) the iron had been sorbed from salt solutions of constant ionic strength and (b) it had been precipitated from the same solutions in the presence of the clay. Some of the characteristics of the sorption and precipitation reactions have been investigated previously (Fordham, 1970, and subsequent papers submitted to the same journal). At an ionic strength of 0.15 M, iron (III) was considered to be sorbed by two consecutive reactions — the first a reversible, weak chemisorption involving hydrolyzed iron-hydroxy ionic species, and the second an irreversible chemisorption. When the ionic strength was decreased to 0.01 M, a third mechanism of ion exchange of unhydrolyzed ions featured more prominently. Iron hydroxides intentionally precipitated in the presence of kaolinite have been identified as lepidocrocite in NaClO_4 systems and βFeOOH in NaCl systems, and their solubility products have been defined.

Autoradiography at the electron microscope level, frequently applied to biological but only rarely to non-biological materials, was employed in the present work. As will be seen, sufficient resolution was achieved with iron-55 to distinguish whether iron was sorbed on the basal planes or the

edges of the clay particles. Dickite suspensions were also examined, since better differentiation was expected with the larger dickite particles.

The same approach was applied with strontium-85 and iodide-125, with the aim of comparing the locations of ion exchange sites with those responsible for iron uptake. The results were supplemented by normal electron microscope examination of mixtures of clay with charged gold and silver iodide sols.

MATERIALS AND METHODS

General

The kaolinite used most frequently was a well-crystallized sample from St. Austell, Cornwall, United Kingdom. The less than $2 \mu\text{m}$ fraction was extracted to remove isotopically exchangeable native iron by the methods which have been described previously (Fordham, 1969), and stored suspended in 0.15 M NaCl solution. The clay had a cation exchange capacity of 4.7 meq/100 g oven-dry clay (ammonium acetate method) and a surface area of $18 \text{ m}^2/\text{g}$ after strong acid extraction and $15 \text{ m}^2/\text{g}$ after extraction by ascorbic acid-EDTA reagent.

Some comparisons were made with a kaolinite from Colombia, South America, kindly supplied by Prof. Dr. A. Weiss. It was treated ultrasonically

in water for 5 min (M.S.E., 60 W at 20 kcal/sec) and the dispersed material examined without further purification.

The dickite was a sample of API No. 15 from San Juanito, Mexico. It was ultrasonically dispersed in 1.0 M NaCl and only the very coarse fraction was separated after a few minutes settling, and discarded. Part of the remaining finer fraction was extracted by the same strong acid method applied to St. Austell kaolinite.

A stable negatively charged gold sol was prepared by adding sodium citrate to auric acid according to the directions of Turkevitch, Stevenson and Hillier (1951). The pH value of the sol was 4.9. Mixtures of gold sol and clay were obtained by adding 1 mg clay in aqueous suspension to 1 ml sol and diluting to 2 ml after sufficient HCl had been added to give a final pH value of 3.5. The suspension was shaken for 15 min and washed with water. Drops of aqueous suspension were dried on carbon-collodion coated grids for electron microscope examination.

Positively charged silver iodide was prepared by adding 1.5 ml 0.025 M KI dropwise with magnetic stirring to 500 ml deionised water containing 2 ml 0.025 M AgNO₃ and maintained at 90°. The thin yellow sol produced was stable for several hours but was used immediately after preparation. One ml of sol was added to an aqueous suspension containing 1 mg unfractionated dickite, and diluted to 3 ml after sufficient HNO₃ had been added to give a final pH value of 3.6. The suspension was shaken for 15 min in the dark, washed with water and finally air-dried in the dark on carbon-collodion coated grids.

Electron micrographs were obtained with a JEOL instrument, type JEM 6A, operating at 100 kV.

Autoradiographic technique

An excellent description of the principles and practice of autoradiography has been provided by Rogers (1967). The procedure employed in the present work was adapted from methods specified by Rogers and also Salpeter and Bachmann (1964).

In the initial stage of sample preparation the isotope was usually shaken with 0.5 mg clay in 2 ml of aqueous suspension. When iron-55 was used, NaClO₄ was added to give a final concentration of 0.15 M. This supporting electrolyte was omitted with strontium-85 and iodide-125 in order to promote greater exchange between the isotope and the sodium ions already present on the clay. Sodium chloride was contained in the radioactive

iodide-125 concentrate and this produced a concentration of about 0.003 M when added to the suspensions. The pH value was adjusted with NaOH or HClO₄ to be in the range 3.3–3.6 for sorption experiments and 4.0–4.5 for precipitation experiments. A small volume of bromine solution was added to iron systems to maintain oxidizing conditions. Other details such as isotope concentration and shaking time are listed with each illustration.

After shaking by end-over-end action, pH values were measured, as well as the distribution of isotope between solid and solution phases by counting both suspension and solution aliquots with a scintillation detector containing a well-type crystal. The separated clay was washed once with water, then resuspended in water and 4–5 drops of suspension placed on each of several collodion-coated glass slides. The samples on the slides were freeze-dried. A carbon layer of about 50 Å thickness was then applied by vacuum evaporation to provide a protective barrier against chemical reaction between the samples and an overlying film of nuclear emulsion.

Ilford L4 emulsion was applied in a constant temperature (20°) dark room. The emulsion was melted at 42° and diluted with water containing glycerol. The prepared slides were dipped individually into the emulsion and drained vertically for about 30 min in a container of 70 per cent relative humidity. Preliminary experiments showed that this procedure gave an emulsion thickness of about 1500 Å, judged by the purple interference color on test slides taken out of the dark room. Direct observation of the emulsion coating under the electron microscope confirmed that the film consisted of a close-packed monolayer of crystals of uniform size. After drying, the slides were sealed in slide boxes, together with a few grams of dried silica gel wrapped in gauze, and stored in black plastic bags at 2° during the period of exposure.

Following exposure, the process of gold latentification was applied as described by Salpeter and Bachmann (1964), and the samples were developed by the elon-ascorbic reagent prescribed by them. In some cases, *p*-phenylenediamine was used as developer. Subsequently, the emulsion was treated with Ilford rapid fixer. In brief, the developing and fixing procedure consisted of dipping the slides successively into the following solutions: Water: Gold (30 sec): Water: Elon (10 min): Water: Fixer (1 min): Water.

The developed sandwich (composed of collodion, sample, carbon and silver-gelatin) was

soaked for at least 30 min in water before being stripped almost completely from the slide onto the surface of water. To facilitate subsequent separation of the sample spots, the sandwich was rewound back onto the slide, and the loosely adhering film indented with a needle around each spot. The film was then completely detached from the slide by refloating and the areas around each spot separated. An electron microscope grid was placed over the spot and a small strip of filter paper positioned on top so that one end overlapped the edge of the film and could be wetted by capillary action. The entire ensemble was picked up from the water surface with a sintered glass plug under suction, air-dried, and the film cut around the grids, which were then ready for viewing.

A number of control slides, identical in all respects with the others except for the absence of radioisotope, were included in each experiment to check against spurious exposure produced by heat, pressure, light or chemical interaction between clay and emulsion. However, no such effects were ever observed.

Resolution

The resolution of the autoradiographs was dependent on a number of factors among which was the type of emulsion used. The spherical AgI crystals of L4 emulsion have a diameter of between 0.10 and 0.15 μm . They were close-packed on the surface of the specimen. A radioactive particle emitted by the isotope in the specimen may activate a small number of silver ions within the crystal. This process, in turn, catalyses the reduction of all the silver ions of the crystal during chemical development. Consequently, the developed silver grain, often in the shape of a twisted whorl, does not necessarily coincide with the position of the parent crystal, although it makes contact at some point with the original site of activation within the crystal. The resolution, therefore, was somewhat larger than the size of the undeveloped crystal. The contributions of other factors such as the energy of the particle emitted by the isotope can be taken into account. Calculations based on the examples given by Rogers (1967, p. 61) for tritium gave a value of about 0.18 μm for the overall resolution with L4 emulsion developed by gold-elon-ascorbic acid. Since the energy of the particles emitted by iron-55 (6 keV) was about the same as that of tritium (mean value of 5.5 keV), the resolution of autoradiographs with iron-55 was of the same order of magnitude.

RESULTS AND DISCUSSION

Iron-55

The results take the form of a series of autoradiographs and electron micrographs. The first autoradiograph (Fig. 1) shows the distribution of silver grains produced about a dickite particle containing iron (III) ions sorbed from 0.15 M NaClO_4 , at which ionic strength the main reactions were believed to be chemisorption processes. The majority of silver grains were located close to the edges of the particle, which was typical of the many particles examined in this and several other replicate preparations. Where significant exposure occurred on the basal planes, the silver grains were either in dense clusters or else oriented in contour patterns, such as might be expected if iron was sorbed at the edges of raised outgrowths (or cavities) upon the surface. The same distribution occurred whether or not this dickite sample was previously treated with iron-extracting reagents, indicating the absence of any iron hydroxide impurities associated with the surface or of any artifact produced during chemical pretreatment.

The corresponding autoradiographs with St. Austell kaolinite are shown in Fig. 2. There was again very strong preference for edge-sites. In comparison with the dickite, much less sorption occurred on the basal planes, which suggests that the basal surfaces of this kaolinite were uniform

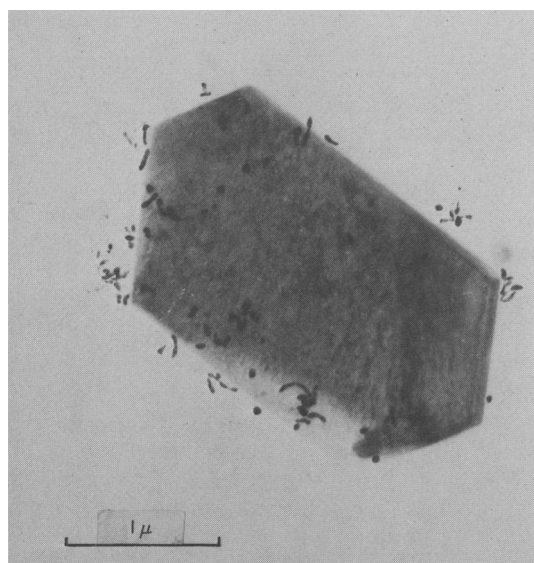


Fig. 1. Autoradiograph of iron-55 sorbed by dickite after 3 days at pH 3.2 from 0.15 M NaCl; about 0.001 per cent Fe_2O_3 deposited on clay; exposed 76 days; developed gold, elon-ascorbic acid.

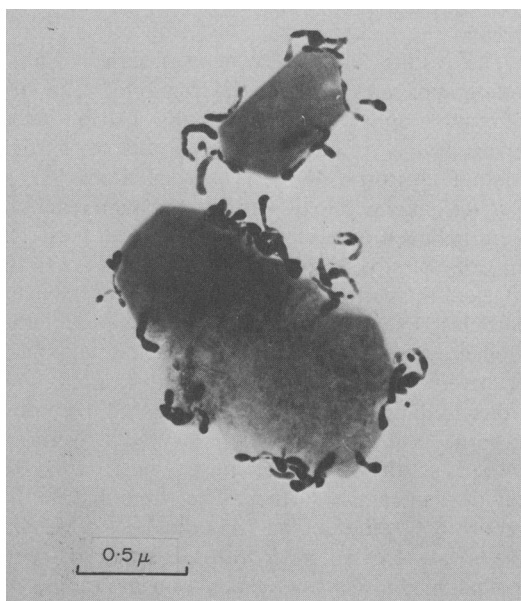


Fig. 2. Autoradiograph of iron-55 sorbed by St. Austell kaolinite after 7 days at pH 3.6 from 0.15 M NaCl; about 0.005 per cent Fe_2O_3 deposited on clay; exposed 37 days; developed gold, elon-ascorbic acid.

and free of defects. Preferred edge sorption was also shown by a South American kaolinite (Fig. 3) but, in this case, the silver grains were often concentrated in clusters. Groups of edge sorption sites may have arisen during ultrasonic treatment

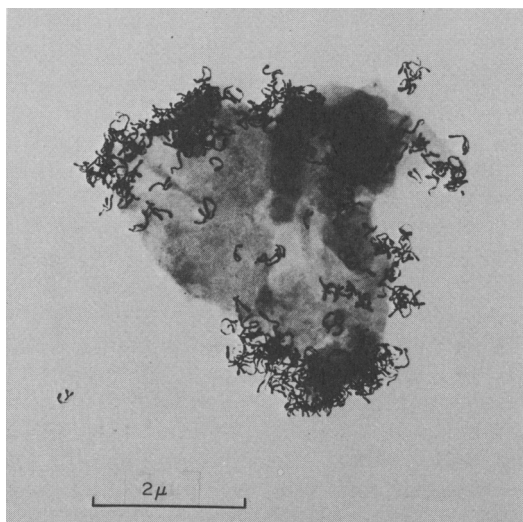


Fig. 3. Autoradiograph of iron-55 sorbed by South American kaolinite after 7 days at pH 3.7 from 0.15 M NaCl; about 0.005 per cent Fe_2O_3 deposited on clay; exposed 37 days; developed gold, elon-ascorbic acid.

(see methods) when the clay fragments were torn off larger particles. Alternatively, the clustering may be explained by the presence of smaller, reactive particles or impurities attached to the edges of the clay fragments, for this kaolinite sample was not cleaned by extractive procedures. An uneven and patchy surface was evident by normal electron microscope examination.

The results presented so far indicate some of the consequences to be expected from defects, impurities and other surface features, and stress the difficulties which might be encountered in clay studies by assuming that clay particles have an idealized structure and charge distribution.

When the ionic strength during the reaction of iron with St. Austell kaolinite was reduced to 0.01 M, the same strong preference for edge uptake was observed in subsequent autoradiographs (not illustrated). As both ion exchange and chemisorption of iron were considered to operate under these conditions, then the active sites of both processes were mainly located at the particle edges and, to some degree, at defects on the basal surfaces. The location of ion exchange sites was consistent with the strontium-85 results to be described later. It is conceivable that chemisorption of iron was feasible at 0.15 M ionic strength because of the close proximity of both positively and negatively charged edge-sites, though the fact that negatively charged gold particles held at the edges had no influence on iron chemisorption (Fordham, unpublished results) was not in favor of this proposition.

Precipitation of iron-55 onto the dickite at pH 4.5 in 0.15 M NaCl resulted in quite a different distribution of silver grains (Fig. 4) from that observed with samples containing sorbed iron. The grains, denoting the presence of iron hydroxides, were spread fairly evenly across the whole surface of the clay particles. Some degree of contouring could be detected and might be significant. The number of silver grains on the particle illustrated corresponded approximately to the number of AgI crystals present in the overlying emulsion before it was developed. Thus, most of the crystals were activated by radioactive emission, and at least one atom of iron-55 must have been within an area slightly larger than the cross-sectional area of one crystal. This condition was realized even if iron hydroxide was present as small discrete particles such as the spherical polymeric units, 70 Å in dia. each containing about 1200 iron atoms, suggested by Spiro and Saltman (1969). In this case, the surface density of the units was calculated

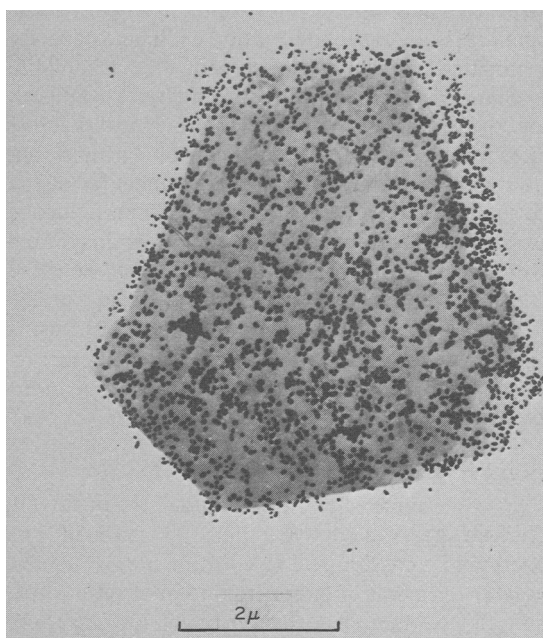


Fig. 4. Autoradiograph of iron-55 precipitated on dickite after 3 days at pH 4.5 in 0.15 M NaCl; about 0.07 per cent Fe_2O_3 deposited on clay; exposed 38 days; developed *p*-phenylenediamine.

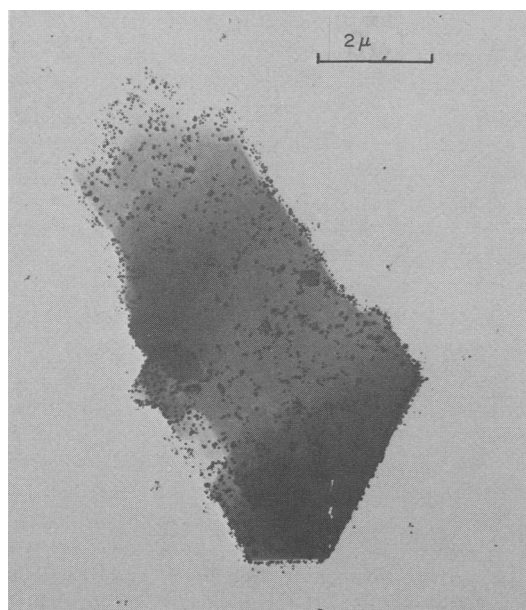


Fig. 5. Autoradiograph of iron-55 precipitated on dickite after 3 days at pH 4.0 in 0.15 M NaCl; about 0.01 per cent Fe_2O_3 deposited on clay; exposed 16 days; developed gold, elon-ascorbic acid.

from the total number of iron atoms precipitated ($55 \times 10^{14}/\text{mg}$ clay) and an assumed surface area of $5 \text{ m}^2/\text{g}$ to give an area of clay surface available to each polymer unit at least an order of magnitude less than the cross-sectional area of one AgI crystal.

A slightly different picture was obtained if iron was precipitated under conditions which only just exceeded the solubility product of iron hydroxide. The autoradiograph shown in Fig. 5 was produced from a suspension of pH value 4.0 and initially containing $1.5 \times 10^{-6} \text{ M}$ iron (III). The iron hydroxide was concentrated around the edges of the dickite particles, and the density on the basal planes was less than before. This situation could mean that precipitation was initiated at the edges of the particles, perhaps by a sorption process, and subsequently spread across the basal surfaces in a manner similar to that described for the growth of ammonium iodide on muscovite by Dunning and Savva (1968). There was no evidence to show whether or not the presence of negative charges on the basal surfaces of the clay was essential for the formation of hydroxide upon the surface.

The amount of iron hydroxide (less than 0.1 per cent Fe_2O_3) contained in these dickite samples would not be observed by normal electron micro-

scope procedures, except perhaps as dark smudges which could be interpreted in alternative ways. In previous work (Fordham, 1970), the smallest amount of Fe_2O_3 which could be detected by normal viewing was 4 per cent and this was only when the samples had been aged and contained crystalline hydroxides. Once iron hydroxides associated with the clay attained a certain degree of crystallinity, they no longer appeared to be attracted strongly to the clay surface.

Strontium-85

Radioactive strontium-85 has an energy of emission (15 keV) suitable for autoradiographic purposes, and some of the autoradiographs obtained are illustrated in Figs. 6 and 7. Some difficulty was experienced in preparing clay samples which retained adequate radioactivity (even in the absence of supporting electrolyte, only 0.5 per cent of the added carrier-free strontium-85 was sorbed by sodium saturated dickite, and 2 per cent by St. Austell kaolinite), and consequently the silver grain density over the particles was relatively low compared to background. Nevertheless, it is clear from the autoradiographs that strontium exhibited a preference for sites at the edges of both dickite and kaolinite particles. At first sight, this

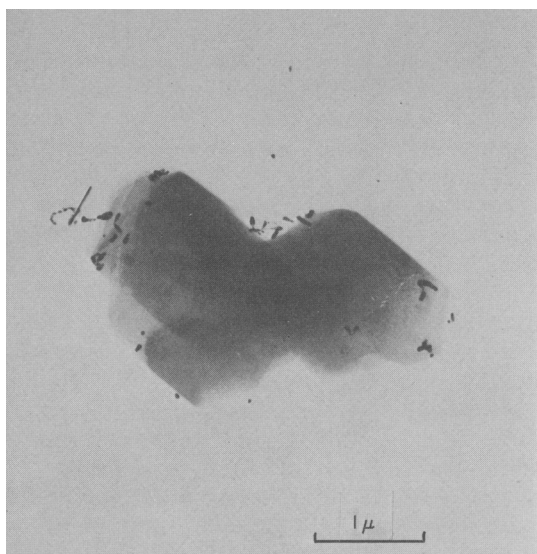


Fig. 6. Autoradiograph of strontium-85 sorbed on Naldickite after 22 hr at pH 3.4; about 0.004 meq. strontium sorbed per 100 g clay; exposed 127 days; developed gold, elon-ascorbic acid.

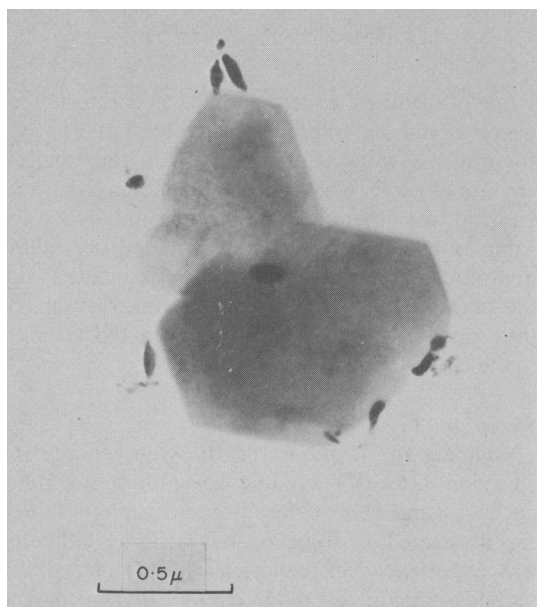


Fig. 7. Autoradiograph of strontium-85 sorbed on Na-kaolinite (St. Austell) after 23 hr at pH 3.3; about 0.06 meq. strontium sorbed per 100 g clay; exposed 132 days; developed gold, elon-ascorbic acid.

result appears contrary to the generally accepted view that cation exchange sites are located on the basal planes as a result of isomorphous replacement of lattice ions. However, it must be empha-

sized that the amount of strontium taken up was small relative to the total cation exchange capacity (estimated that about 1 per cent of the kaolinite exchange sites were occupied by strontium), and the results only indicated that the most reactive sites were located at the edges and gave no information about the disposition of the remainder of the cation exchange sites. There was some evidence from the orientation of those silver grains which were present on the basal planes that negative sites of equivalent energy existed at surface irregularities. Weiss and Russow (1963), using a macroscopic autoradiographic technique, reported that nickel-63 was sorbed on only one of the two basal surfaces of large kaolinite flakes.

Iodide-125

To determine the distribution of positively charged sites, radioactive iodide-125 was used. The energy of emission (35 keV) from this isotope is greater than that of either iron-55 or strontium-85, and the resolution correspondingly lower. There were no difficulties in obtaining sufficient radioactivity on the clays in the absence of supporting electrolyte, as 4 per cent was sorbed by St. Austell kaolinite and a surprisingly high 41 per cent by dickite. Despite the higher energy of iodide-125 emission, good autoradiographs were produced with kaolinite (Fig. 8). The sites of iodide uptake were almost exclusively around the edges of the particles, confirming the widely-held opinion

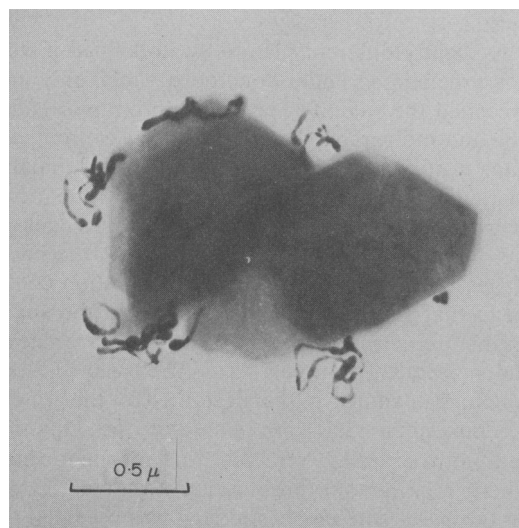


Fig. 8. Autoradiograph of iodide-125 sorbed on St. Austell kaolinite after 22 hr at pH 3.3; about 0.05 m-equiv iodide sorbed per 100 g clay; exposed 30 days; developed gold, elon-ascorbic acid.

(Schofield and Samson, 1954) that positive charges are located in this position. The silver grain density of dickite samples was extremely high when developed by the normal procedure even after short exposure times. Consequently, the autoradiographs (Fig. 9) were prepared without gold latensification. The resolution was much poorer than with the corresponding kaolinite samples. This difference was caused in part by the high radioactivity contained in the sample, which increased the statistical probability of hits being recorded on crystals in the emulsion at some distance from the source, whereas hits on crystals near the source cannot be registered more than once. However, the clay particles exhibited extensive blackening around the edges due to the accumulation of silver grains, and there can be no doubt that this was the location of most of the sorbed iodide. Because of the poor resolution, the sometimes appreciable silver grain density within the particle boundaries could not be interpreted with certainty. Even so, in many cases, there were strong indications from silver accumulation in specific areas or lines, that additional iodide uptake occurred on the basal surfaces, probably at structural defects rather than lattice substitutions.

Gold and silver iodide sols

Further evidence of the distribution of positive and negative sites was obtained by normal electron

microscope observation of mixtures of clays with both gold and silver iodide sols. Electron micrographs of negatively charged gold sol sorbed on St. Austell kaolinite (Fig. 10) were very similar to those illustrated by Thiessen (1942) and Follett (1965). The gold was concentrated almost without exception around the edges of the clay particles, confirming the location of positive charges indicated from iodide-125 autoradiographs and showing that the basal surfaces of this particular kaolinite were free of imperfections. In the case of dickite (Fig. 11), most of the gold was again sorbed around the edges but the distinction was not as prominent as for kaolinite. A significant amount was associated with the basal surfaces, in agreement with the observations made with iodide-125. This evidence of the presence of positive charges on the basal planes of a kaolin mineral could be important in the interpretation of the orientation of flocculated kaolin particles (see O'Brien, 1971).

In silver iodide-dickite mixtures, the positively charged sol formed a continuous aggregated layer over most of the clay particles. However, with perhaps 10 per cent of the particles, such as the one illustrated in Fig. 12, the basal surfaces were relatively clear and the sol present was associated with the edges. This observation supports the view



Fig. 9. Autoradiograph of iodide-125 sorbed on dickite after 22 hr at pH 3.3; about 0.5 m-equiv iodide sorbed per 100 g clay; exposed 8 days; developed elon-ascorbic acid.

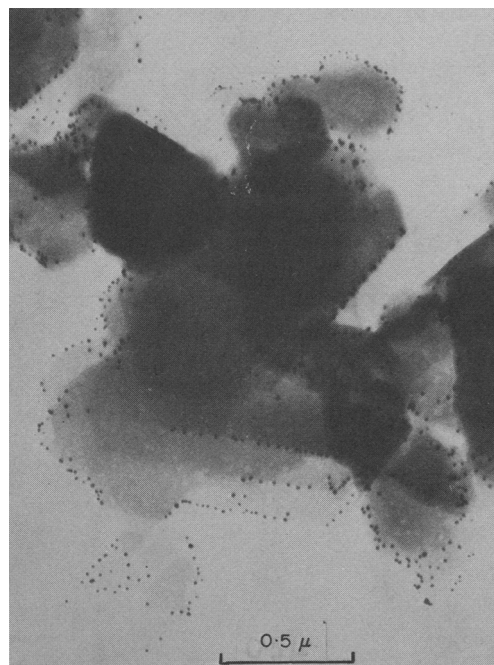


Fig. 10. Electron micrograph of freshly prepared gold sol sorbed on St. Austell kaolinite at pH 3.5.

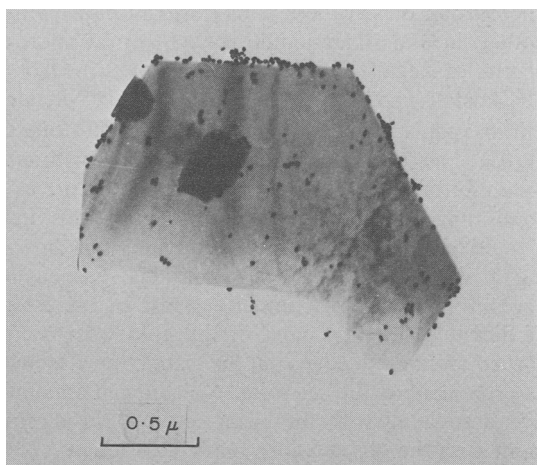


Fig. 11. Electron micrograph of aged (17 days) gold sol sorbed on dickite at pH 3.5.

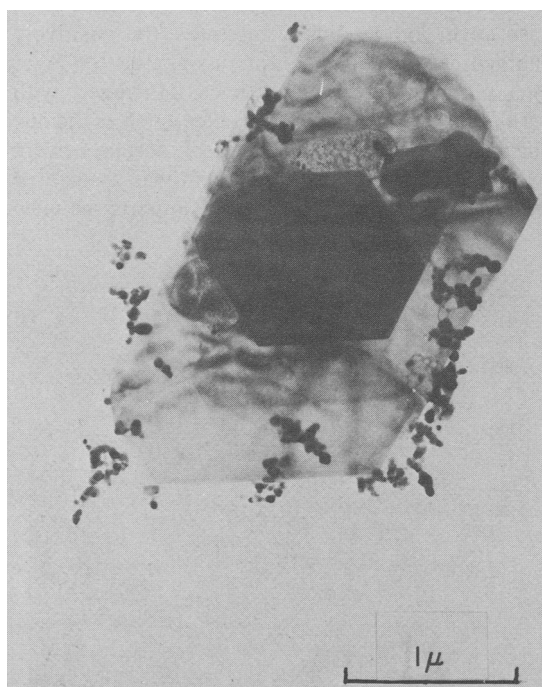


Fig. 12. Electron micrograph of freshly prepared AgI sol sorbed on dickite at pH 3.6.

that the most reactive negative sites were located at the edges of the clay particles. Uptake of silver iodide particles probably followed the same course as that proposed previously for iron hydroxides, namely, that edge sites and defect sites were occupied before the intervening spaces on the basal planes were filled. It is not essential

from the evidence presented to infer the presence of additional negative sites on the basal planes, for aggregation of AgI along the basal surface may be favored simply by van der Waals forces.

Okuda, Inoue and Williamson (1969) examined clay-AgI mixtures and found evidence for negative edge-charges on pyrophyllite and talc samples at pH 4. They suggested the charges were due to broken silica tetrahedral layers, although the silanol radical is not normally thought to dissociate in this pH region. In the case of dickite, they observed complete coverage of the basal planes such as was evident with the majority of dickite particles examined in the present work. Several other workers (Thiessen, 1942; Weiss and Russow, 1963) have made similar observations.

CONCLUSIONS

Regardless of whether iron (III) was sorbed by chemisorption or ion exchange processes, the sorbed ions were located mainly at the clay particle edges. There was some uptake on the basal planes, more evident on dickite than well-crystallized kaolinite, but this uptake appeared to be associated with surface irregularities.

When precipitated in the presence of dickite, iron hydroxides were distributed evenly over the clay surfaces. Precipitation was probably initiated at the particle edges.

When a small percentage of the exchangeable ions of kaolinite and dickite was replaced by strontium-85, the strontium ions were located at the particle edges, indicating that the most reactive cation exchange sites were in this position. There was some evidence that sites of equivalent energy existed at defects on the basal planes. These conclusions were consistent with the distribution of positively charged AgI sol when present in low concentrations.

Anion exchange sites, as observed by iodide-125 and negatively charged gold sol, were exclusively around the edges of the well-crystallized kaolinite. To a minor extent, they occurred as well on the basal planes of the dickite sample, again probably at defect sites.

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Résumé—La méthode autoradiographique au niveau du microscope électronique a été appliquée avec succès pour localiser la position des ions fixés sur les particules de kaolinite et de dickite ainsi que celle des composés associés à ces minéraux. Avec des isotopes convenables, la limite de résolution est environ de 0,2 μm ; on peut envisager de reculer considérablement cette limite dans les conditions les plus favorables.

Si l'on en juge par la localisation de l'iode-125 et du strontium-85, la majorité des sites positifs ainsi que les sites négatifs les plus réactifs sont situés sur les bords des particules d'argile. Ces conclusions sont étayées par l'examen normal au microscope électronique de mélanges d'argile et de sols d'or et d'iode d'argent chargés.

Les ions fer (III) pour lesquels on a pu montrer qu'ils réagissent avec la kaolinite par des mécanismes de chimisorption dans des systèmes 0,15 M et à la fois par adsorption physique et chimisorption dans les systèmes 0,01 M, sont, dans les deux cas, localisés sur l'argile sur les sites de bordure. Quand ils sont intentionnellement précipités sur la dickite, les hydroxydes de fer (III) sont distribués d'une façon uniforme sur les surfaces de l'argile. Toutefois, la précipitation débute probablement sur les bords des particules.

Des exceptions mineures à ces conclusions semblent dues à certaines caractéristiques de la surface basale, telles que des lignes de fracture ou de contrainte, des excroissances ou des trous, et, si les argiles n'ont pas été nettoyées, à des impuretés fortement associées comme les hydroxydes de fer.

Kurzreferat—Um die Position sorbierter Ionen und Verbindungen festzustellen, die mit Kaolinit- und Dickiteilchen assoziiert sind, wurde die autoradiographische Methode auf elektronenoptischer Ebene erfolgreich angewandt. Für geeignete Isotope betrug die Auflösungsgrenze 0,2 μ . Es ist denkbar, daß sie unter sehr günstigen Bedingungen noch herabgesetzt werden könnte.

Nach der Anordnung von Jod-125 und Strontium-85 zu urteilen, sind die Mehrzahl der positiven Austauschplätze und auch die reaktionsfähigen negativen Austauschplätze an den Seitenflächen der Tonteilchen gelegen. Diese Schlußfolgerungen wurden durch eine normale elektronenmikroskopische Untersuchung an Mischungen aus Ton mit geladenen Gold- und Silberjodid-Solen bestätigt.

Eisen(III)-Ionen, die—wie gezeigt wurde—mit Kaolinit in 0,15 m Systemen durch chemische Adsorptionsmechanismen und in 0,01 m Systemen sowohl durch physikalische als auch durch chemische Sorption reagieren, waren in beiden Fällen an den Austauschplätzen der Seitenflächen der Tonminerale angeordnet. Eisen(III)-hydroxide, die absichtlich auf Dickit ausgefällt wurden, waren gleichmäßig über die Tonoberflächen verteilt. Allerdings wurde die Fällung wahrscheinlich an den Seitenflächen der Teilchen ausgelöst.

Geringfügige Ausnahmen von obigen Schlußfolgerungen scheinen durch die Oberflächenausbildung der Basisflächen (z.B. durch Bruch- oder Druckzonen, Auswüchse- oder Hohlformen) und bei nicht gereinigten Tonen durch fest angelagerte Verunreinigungen (z.B. Eisenhydroxid) verursacht zu sein.

Резюме—Метод авторадииграфии на уровне электронного микроскопа с успехом применялся для определения положения сорбированных ионов и соединений ассоциированных с частицами каолинита и диккита. Для подходящих изотопов предел разделения равнялся примерно 0,2 μ и в более благоприятных условиях был бы значительно ниже.

Судя по положению иодида-125 и стронция-85 большинство положительных мест и большинство наиболее реактивных отрицательных мест находились у граней частиц глины. Эти выводы были подтверждены исследованием под нормальным электронным микроскопом смесей глины с заряженными золотом и серебром иодидными растворами.

Ионы железа (III), которые как было показано, реагируют с каолинитом механизмом хемосорбции в системе 0,15 M и как в физической адсорбции, так и в механизме хемосорбции

в системе 0,01 М находились в обоих случаях на краевых узлах глины. Но, очевидно, осаждение началось у граней частиц.

Но, исключения к этим выводам представляют поверхности с изломами, с линиями напряжения, с наростами или с впадинами или, если глину не очистили от сильносвязанных с ней примесей окиси железа.