The ageing of sesquioxide gels. I. Iron oxide gels.

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Summary. The gels prepared by adding ammonium hydroxide rapidly to ferric chloride solutions to various pH values are shown to consist of amorphous material and crystalline goethite; no other iron oxide was definitely identified in the present experiments, although this does not preclude other oxides being present in gels prepared under slightly different conditions. The goethite grows as acicular crystals on ageing at all pH values, but the rate of growth is greater at higher pH values. The exothermic peaks appearing on differential thermograms of such gels are apparently due to coalescence of extremely minute hematite particles to give larger particles, the sharpness of the peak indicating to some extent the size of the original hematite particles. These observations are related to data for other iron oxides, and the morphology of ferric oxide polymorphs under the electron microscope is considered.

THE brown iron oxide gel is of considerable interest in pedology because of its occurrence in some soils (Mackenzie, 1949), as well as in bog-iron ores (Kurnakov and Rode, 1928). It is known to be present only in systems in dynamic equilibrium (Kurnakov and Rode, 1928), but it may, because of its reactivity and large surface area, have a disproportionate influence on soil properties. The conditions for its formation and stability have been previously examined (Mackenzie, 1952*a*, 1957), but there is still much contradictory evidence upon certain factors, such as the mineralogical constitution of the gel. The electron diffraction studies of Weiser and Milligan (1940) and Milligan (1952) suggest that the ions are arranged in approximately the same configuration as in hematite, but the electron diffraction pattern quoted by Mackenzie (1952*a*) bears a closer resemblance to the X-ray diffraction pattern of β-$Fe_2O_3.H_2O$. On ageing, Weiser (1935) and Milligan (1952) found the washed gels to go to hematite, while Gheith (1952) obtained goethite. Mackenzie (1957) found mixtures of goethite and hematite on ageing in the mother-liquor, the rate of ageing being more rapid at higher pH values.

In view of these discrepancies it may be that the preparative conditions, &c., are critical for these gels; consequently, the characteristics of one carefully prepared and well-characterized gel are of some interest.

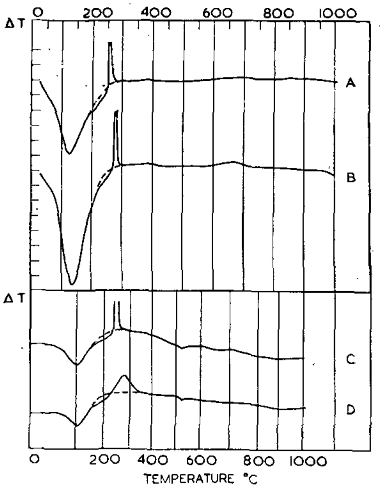
Experimental.

Materials. Two ferric oxide gels were prepared by adding a 9 N ammonium hydroxide solution dropwise to solutions of 5g. anhydrous ferric chloride in 250 ml. water until the pH, as measured by a glass electrode, reached in one instance pH 5, and in the other pH 10. A.R. chemicals were used throughout. The gels were allowed to settle for two hours, filtered off on Buchner funnels and washed free from Cl^- with distilled water. The bulk of each gel was then re-suspended in distilled water and brought to its initial pH value (pH 5 or 10) with NH_4OH or HCl, the remainder being divided into two parts, one of which was re-suspended in distilled water in a polythene container and retained for electron-optical study while the other was dried at 105° C. and ground to −100-mesh for differential thermal, X-ray, and infra-red examination. The suspensions at pH 5 and pH 10 were allowed to stand at room temperature at these pH values for 60 days, when they were again washed free from salts on the Buchner funnel and divided up into three portions, the bulk of the material being re-suspended at the original pH value. This final portion was washed free from salts after 155 days, part retained for electron-optical examination, and part dried and ground as previously. This gave in all six samples of material: (1) gel brought to pH 5 unaged; (2) gel aged at pH 5 for 60 days; (3) gel aged at pH 5 for 155 days; (4) gel brought to pH 10 unaged; (5) gel aged at pH 10 for 60 days; (6) gel aged at pH 10 for 155 days.

Methods. A Siemens electron microscope was used for the electron-optical studies, the suspension being dried out on the carrier after ultrasonic dispersion. X-ray examination of selected samples was carried out on a Hilger HRX unit, using Co-$K\alpha$ radiation. The apparatus used for differential thermal analysis has been previously described (Mackenzie, 1952*b*). Infra-red absorption spectra were obtained on a Grubb Parsons double-beam spectrometer.

Results.

The gels change in colour somewhat on ageing. The colours of the samples used for differential thermal analysis were checked against a Munsell Soil Colour Chart, and it was found that all the aged gels were yellowish red (5 YR: 4/6) while the unaged gels were dark reddish brown, the pH 5 gel being somewhat denser in colour (5 YR: 3/4) than the pH 10 gel (5 YR: 3/3).



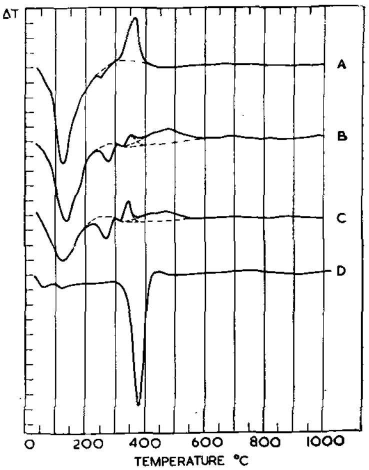


FIG. 1. Differential thermal curves for: *A*, pH 5 gel, unaged (250 mg. sample); *B*, pH 5 gel, aged for 60 days (250 mg. sample); *C*, pH 5 gel, unaged (15 mg. sample on sensitive apparatus); *D*, pH 5 gel, aged for 155 days (15 mg. sample on sensitive apparatus).

FIG. 2. Differential thermal curves for: *A*, pH 10 gel, unaged (250 mg. sample); *B*, pH 10 gel, aged for 60 days (250 mg. sample); *C*, pH 10 gel, aged for 155 days (200 mg. sample); *D*, goethite, Příbram, Czechoslovakia (350 mg. sample).

The differential thermal curves show the trends previously noted (Mackenzie, 1957). Thus, the unaged pH 5 gel shows a large endothermic peak at 125° C., which increases in size on ageing for 60 days, a shoulder at about 200° C., and a very strong exothermic peak at 257° C., which broadens and moves to a higher temperature on ageing (curves *A* and *B*, fig. 1). Insufficient of the 155-day aged sample was available for determination of a conventional differential thermal curve. However, on a very sensitive apparatus using only 15 mg., curve *D* (fig. 1) was obtained, indicating a continuation of the trend of movement and broadening for the exothermic peak; the endothermic peaks cannot be compared since the samples were evacuated before the determination, thus upsetting the water régime. Curve *C* (fig. 1) for the unaged pH 5 gel obtained on this same apparatus has been inserted for comparison purposes.

The relationships for the pH 10 gel are rather more complex. The unaged gel shows a large endothermic peak at 125° C., followed by a very small peak at about 250° C., suggesting the presence of goethite, and a strong exothermic peak at 365° C. (curve *A*, fig. 2). On ageing, the initial large endothermic peak decreases markedly in size (as would be expected if crystallization, with a reduction in surface area, were taking place), the goethite peak increases in size and moves to a slightly higher temperature, and the exothermic peak for the unaltered gel decreases in size and moves to a higher temperature (480° C.) (curves *B* and *C*, fig. 2). In addition, however, a sharp exothermic peak develops at about 350° C. and, in parallel with the goethite peak, increases in size with time of ageing.

The curves for all these gels indicate that they contain small amounts of goethite, the broken lines in figs. 1 and 2 indicating the approximate base-lines. The full interpretation of the curve will be considered later in the light of other evidence.

X-ray examination indicated that the original gels were amorphous. On ageing the goethite pattern appeared, this being strongest for the 155-day aged pH 10 gel. The latter specimen on heating to 300° C. in the differential thermal apparatus gave a pattern indicative of fine-grained hematite in addition to a broad band at about 4 Å.; heating to 385° C. and 600° C. caused the disappearance of this band and induced progressively better crystallization of the hematite.

The infra-red absorption spectra indicated that both the unaged gels (pH 5 and pH 10) were amorphous and showed strong bands due to sorbed water. The pH 5 gel after ageing for 60 days showed incipient goethite formation, but the material was still largely amorphous; the 60-day aged pH 10 gel, on the other hand, gave well-defined bands of goethite at 11·23 μ and 12·60 μ, but still showed the presence of amorphous material and sorbed water (band at 5·13 μ). Both the unaged and aged pH 10 gels had unassigned bands near 6·6 μ and 7·5 μ, which might be associated with sorbed NH_4^+ or CO_3^{2-}.

The electron-optical study revealed that the unaged pH 5 gel consisted largely of a 'pepper' of very fine particles (fig. 3*a*). The size of these particles is difficult to determine at all accurately, but they appear to be less than 40 Å. across and to fall within a remarkably small size range. In addition to this fine pepper there are also some small black specks, of irregular outline, up to about 0·04 μ across; most of these are undoubtedly clumps of the finer particles, but whether some represent minute crystals it is difficult to determine. Close examination also

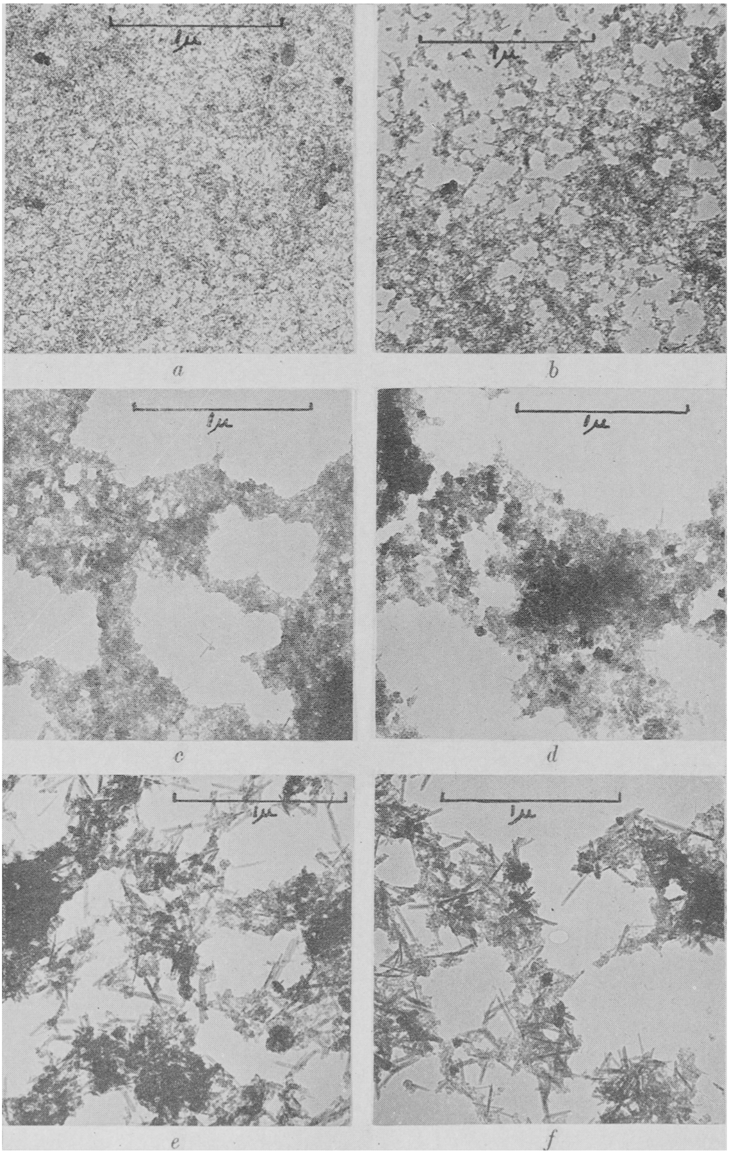


Fig. 3. Electron micrographs of precipitated ferric oxides: *a*, pH 5, unaged; *b*, pH 5, aged for 60 days; *c*, pH 5, aged for 155 days; *d*, pH 10, unaged; *e*, pH 10, aged for 60 days; *f*, pH 10, aged for 155 days.

reveals a tendency to the formation of extremely fine needles of the order of 0·06 μ long by about 40 Å. (i.e. single particle cross-section) wide. The electron diffraction pattern for this particular sample is very diffuse, in agreement with the small particle size, but bands appear in the regions associated with goethite.

The same gel aged for 60 days shows a much more pronounced tendency for the particles to clump together into aggregates of quite variable size, up to about 0·2 μ across (fig. 3*b*). Individual particles seem larger than in the unaged gel, being up to about 80 Å. across. There is no incontrovertible evidence of plates, but needles are much more apparent, their size being up to about 0·12 μ long by about 80 Å. across. They are still, therefore, very small. The electron diffraction pattern is very sharp and is essentially that of goethite, but the presence of some hematite cannot be entirely excluded.

On ageing for 155 days, clumping of the particles is particularly observable; needles are rather more clearly visible, but do not seem to be very much larger than at 60 days (fig. 3*c*). Individual particles are difficult to identify, but seem to be 80–100 Å. across. The electron diffraction pattern, although again essentially that of goethite, is rather diffuse—which may be accounted for by rather more gel material being in the field chosen.

The unaged pH 10 gel resembles the pH 5 gel aged for 155 days in that the particles tend to clump closely together (fig. 3*d*). The individual particles seem to be rather similar to, or only slightly larger than, those in the unaged pH 5 gel (i.e. 40–60 Å.). The dense black 'particles' (about 0·04–0·08 μ across), which often have a roughly hexagonal outline, appear usually to be but a collection of the primary particles closely packed together; again, it is difficult to decide whether or not some are true crystals of, for example, hematite. The usual acicular crystals, about 0·08 μ long by about 40 Å. across, are obvious throughout the gel, and the electron diffraction pattern, as before, indicates largely goethite. The diffuseness of the pattern indicates the very fine nature of the material: the pattern is, if anything, clearer than that for the unaged pH 5 gel.

After ageing for 60 days the material is largely composed of long acicular crystals of about 0·25 μ in length and up to 0·02 μ in thickness (fig. 3*e*). The length is remarkably uniform, but the thickness varies somewhat. A fair amount of residual gel is still visible, but the number of dense black aggregates has decreased considerably. Again, the electron diffraction pattern indicates essentially goethite, in agreement with X-ray data.

The needles in the 155-day aged pH 10 gel are even larger than previously, being up to about 0·4 μ in length and generally about 0·02 μ in thickness (fig. 3*f*). There are still considerable patches of unaltered gel, but the clumping is particularly noticeable. The electron diffraction pattern indicated goethite, the lines being quite spotty owing to the large crystal size. This gel was also examined under the electron microscope after heating to 220° C., 300° C., 385° C., and 600° C. in the differential thermal analysis apparatus, these temperatures being chosen from the characteristics of the differential thermal curve (*C*, fig. 2). The electron micrograph of the material heated to 220° C. was very similar to fig. 3*f*, but there appeared to be rather fewer needles and a greater number of dense clumps—probably because of the drying and grinding procedure undergone by this sample. Small particles about 50–100 Å. across, but of indefinite shape, could also be detected. The samples heated to 300° C. (fig. 4*a*) and 385° C. showed a progressive decrease in the number and size of needles and a progressive breakdown of the clumps into particles of 50–100 Å. across. In the 385° C. material only a few needles were observable, and these were about 0·07 μ long by about 50 Å. thick. Needles are very much more numerous again in the material heated to 600° C. (fig. 4*b*) and, on close examination, are seen to be non-uniform along their length. Length and thickness vary, maximum length being about 0·20 μ and thickness about 0·015 μ. The original solid aggregates are now completely broken down into a network

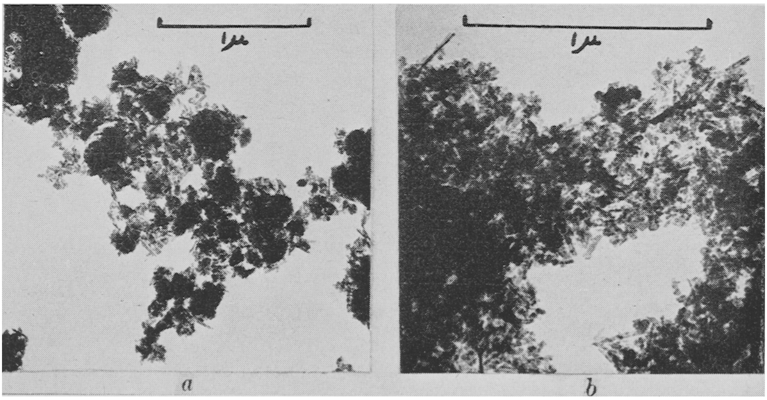


FIG. 4. Electron micrographs of 155-day aged pH 10 gel heated to: *a*, 300° C.; *b*, 600° C.

of these needles and small particles of about 50–200 Å. across. Some of the larger of these particles tend to show a hexagonal outline. The electron diffraction patterns of these samples show the presence of goethite along with hematite at 220° C., but only hematite at temperatures above this: the dense background also disappears above 220° C., indicating that the amorphous material has apparently crystallized to hematite by 300° C.

Apart from the unaged pH 5 gel where the particles are smaller, all the needle sizes quoted above are within the size range observed by Fricke and Weitbrecht (1943) for goethite prepared from gel at 100° C. in 2 N KOH (Glemser, 1937)—namely, 0·096–0·470 μ long by 82–165 Å. wide. Parallel orientation of the needles as observed by Fricke and Weitbrecht (1943) is nowhere observable; on the contrary the needles in the above-described gels are oriented in all directions and at times tend to form a criss-cross mat (see fig. 3*f*). The conditions of formation must, therefore, have some influence upon this factor.

Discussion.

The data presented above indicate the predominance of goethite as a crystalline component in all phases of this gel. In the early stages there *may* be small amounts of hematite, which would account for the black specks noted particularly in the unaged pH 10 gel, but this is doubtful, and later these are not observable. Ageing causes the primary particles to come together to form needles, which in the early stages may be seen to consist of primary particles cemented together in a row rather than true crystals (fig. 3*a*—this may not show up clearly in reproduction). Longer ageing leads to true acicular crystals. Ageing is more rapid at high pH values, but also occurs quite measurably even at pH 5 at room temperature. The acicular crystals are undoubtedly goethite and presumably the elongation is [001], since growth in this direction is apparently continuous and it is in this direction that macroscopic fibres of goethite are elongated. In view of the similarity of primary particle cross-section and needle width, growth originally would appear to occur by accretion of gel material on the (001) face, a similar situation to that observed by Méring and Oberlin (1957) for $Mg(OH)_2$ precipitates (cf. the observations of Bagno, Longuet-Escard, and Mathieu-Sicaud (1951) for $Ni(OH)_2$). The particles of $Mg(OH)_2$ observed by Méring and Oberlin (1957) differ from those of goethite in being platy and not acicular; on the other hand, the $Mg(OH)_2$ particles forming in the hydration hulls round partially decomposed dolomite particles are clearly acicular

(Meldau and Robertson, 1953), but there is no information as to direction of elongation or direction of growth.

In view of the fact that all samples described above contain goethite, the thermal reactions are of considerable interest. It is impossible to state definitely what is the constitution of the primary particles of the gel; that they are largely amorphous even to electrons is evidenced by the heavy background on most of the electron diffraction patterns. Nevertheless, since they tend to coalesce into needles very rapidly, it seems likely that their structure (which must necessarily be very rudimentary) is closely akin to that of goethite. The exothermic peak on the differential thermal curves for these gels is thus rather surprising since the goethite→hematite change is an oriented transformation with no intermediate stable amorphous phase and no heat evolution would be expected. Some goethite is observable on all the curves (figs. 1 and 2), as indicated by the dotted lines, but these small peaks obviously do not represent the dehydration of all the gel and can be accounted for by the amount of acicular crystals in each sample. In addition, hematite was observed by electron diffraction at 220° C. (i.e. before the goethite peak) for the 155-day aged pH 10 gel. One must therefore conclude that the very small primary particles lose their water entirely during the period of the low-temperature endothermic peak giving minute particles of hematite, which later coalesce with evolution of heat to give particles of sufficient size to diffract X-rays (for previous explanations of the exothermic effect see Fricke and Hüttig, 1937, and Mackenzie, 1957).

For the 155-day aged pH 10 gel, X-ray examination indicated that the particles of hematite at 300° C. were very small, but were progressively larger at 385° C. and at 600° C. (fig. 4). The growth of hematite needles and of somewhat larger particles in the sample between 385° C. and 600° C. would account for the result for the material heated to 600° C. and for the somewhat broad exothermic peak on the differential thermal curve at about 480° C.; there seems to be little on the electron micrographs which would account for the apparent growth of the particles between 300° C. and 385° C. The basic particles in the 385° C. sample seem slightly larger, but there is not as much difference as one might expect. On the other hand, there are many needles at 300° C. (fig. 4*a*), but virtually none at 385° C. It may be, therefore, that the needles at 300° C. are actually aggregates of extremely minute hematite particles pseudomorphous after goethite (goethite is known to be absent at this temperature) and that these coalesce into hematite crystals of about the same size as the ground-mass between 300° C. and 385° C. This would accord with the obvious relationship between the size of the goethite peak and the sharp exothermic peak at about 350° C. (fig. 2). The particles involved in this recrystallization are clearly very much smaller than those involved in the recrystallization between 385° C. and 600° C.—a fact which would explain both the position and the shape of the 480° C. peak. The shift in exothermic peak temperature and increase in breadth of the exothermic peak on ageing support this interpretation, since under such conditions the particles tend to be larger and to cover a wider range of particle size.

It is interesting to consider whether this interpretation can apply to the β-$Fe_2O_3.H_2O$ differential thermal curve, which shows a strong exothermic peak at 450° C. (Mackenzie, 1957). Electron micrographs of this material (fig. 5*a*) show beautiful crystals shaped rather like wheat grains, which on heating to 250° C. retain their outline but consist only of an extremely thin honeycombed skeleton, rather like a sponge (fig. 5*b*).[1] From X-ray evidence (Mackenzie, 1957) this skeleton must be largely hematite (although small amounts of residual β and of γ-Fe_2O_3 may also be present). The exothermic peak could then be accounted for as in the above gels by the coalescence of the extremely minute particles in the β-$Fe_2O_3.H_2O$ pseudomorph into discrete crystals of hematite. With such a mechanism it is clearly incorrect to conclude that all samples giving exothermic peaks belong to the same family, as was previously suggested (Mackenzie, 1952).

The increase in the size of the low-temperature endothermic peak on ageing of the pH 5 gel for 60 days remains to be explained. Close examination of the shape of this peak on curves *A* and *B*, fig. 1, indicates that on curve *A* the exothermic reaction for the coalescence of the fine particles (i.e. the exothermic peak) commences before all the water is removed, the endothermic peak thus being truncated by the superposition of the commencement of the exothermic peak. In curve *B*, on the other hand, the first peak is symmetrical, indicating complete dehydration before recrystallization. This is in accordance with what would be expected from the primary particle size of the gels.

The fact that the crystalline portion of the gels here studied consists largely of goethite is no indication that all brown gels are necessarily

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[1] Decompositions leaving a mosaic have previously been observed—e.g. the dehydration of gypsum and some other sulphates and the decarbonation of zinc carbonate may be cited as examples (Meldau, 1956); on the other hand, many minerals, such as chrysotile, dehydrate without passing through this phase (R.H.S. Robertson, private communication).

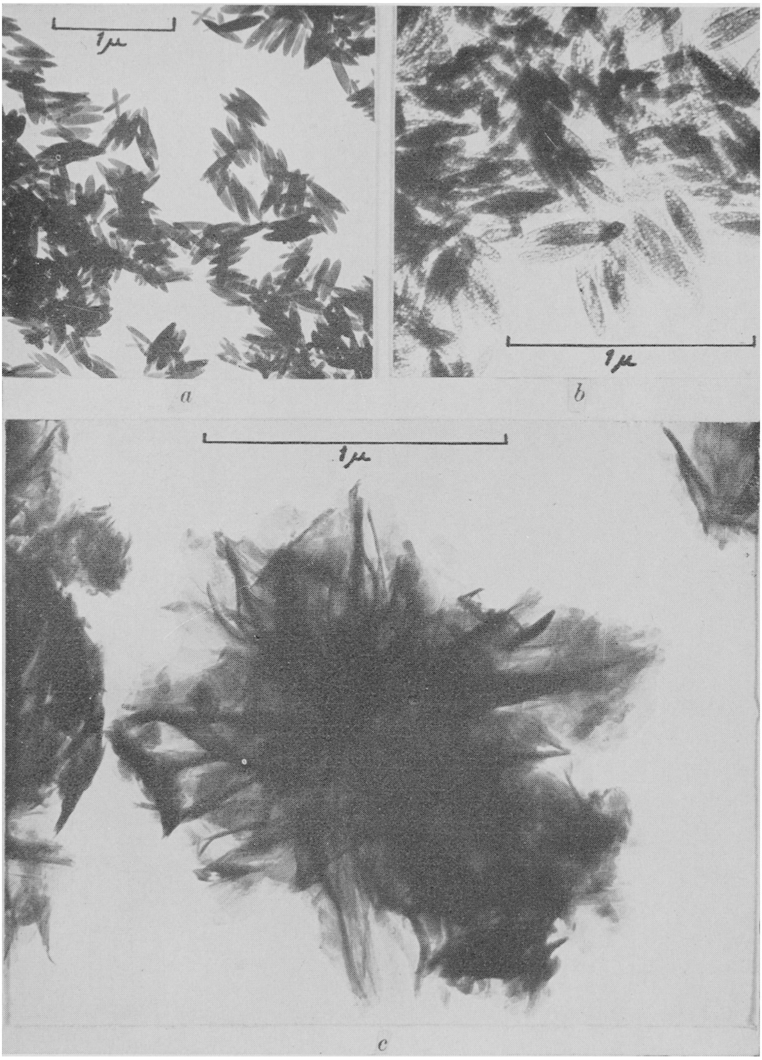

FIG. 5. Electron micrographs of: *a*, β-$Fe_2O_3.H_2O$; *b*, β-$Fe_2O_3.H_2O$ heated to 250° C.; *c*, γ-FeOOH.

of this constitution. Thus, there is no similarity between the electron diffraction pattern of this gel and that of β-$Fe_2O_3.H_2O$, as was observed for a previous gel. The preparative conditions may, therefore, easily determine the rudimentary structure of the primary particles and the explanation for the exothermic peak given above would be in accord with the fact that all such gels give similar exothermic effects irrespective of the constitution of their primary particles.

The morphology of the goethite crystals noted above is in conformity with its habit in macroscopic form and also with the acicular crystals previously observed in synthetic goethite by Fricke and Weitbrecht (1943) and in a mixture of lepidocrocite and goethite by Meldau (1957).[1] The electron diffraction pattern for the latter sample (fig. 2*f* in Meldau, 1957) is anomalous, as crystals of both goethite and lepidocrocite can be clearly observed on the electron micrograph (fig. 1*f* in Meldau, 1957), and may have been due to the field chosen for diffraction containing much uncrystallized gel.

The crystal morphology of most members of the hydrated ferric oxide series would thus appear to be clear. Thus, goethite (α-FeOOH) forms acicular crystals (fig. 3*f* is typical); β-$Fe_2O_3.H_2O$ occurs as very regular crystals, which look rather like wheat grains (fig. 5*a*), and which on heating to 250° C. retain their outline but appear to consist of a skeletal mosaic (fig. 5*b*); very thin and very flexible plates that show pronounced crumpling (fig. 5*c*) normally characterize lepidocrocite (γ-FeOOH), but Fricke and Weitbrecht (1943) claim that it may also occur in acicular form.[2] The shape of 'δ-$Fe_2O_3.H_2O$' cannot at present be determined: the sample examined by Meldau (1957) had dehydrated into hematite (as evidenced by the electron diffraction pattern) under the conditions inside the electron microscope.

The morphology of the anhydrous forms is not yet known with any certainty. Watson and Freeman (1956) associate maghemite (γ-Fe_2O_3) with a platelet structure. An unidentified iron oxide of hexagonal outline has been reported by the same authors, and a chain-forming iron oxide of very small particle size has been observed by von Ardenne

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[1] The crystals of yellow hydrated iron oxide used as a paint pigment are of the same shape (Anon., 1956), and are also presumably goethite. In contrast, the particles of goethite observed by Robertson (1958) in electron-micrographs of a clay from Kenya are not acicular but are of the type noted in the ground-mass of the gels described above, the particle size being about 60–150Å. across. The differential thermal curve for this goethite is consistent with such a small particle size, the endothermic peak occurring at about 200° C. (Mackenzie, 1958), but no reason can currently be suggested as to why this material has not aged to give acicular crystals.

[2] This observation of Fricke and Weitbrecht might be explicable on the basis of contamination of the lepidocrocite sample with some goethite. Their photographs of lepidocrocite are somewhat reminiscent of those obtained by Meldau (1957, fig. 1*f*) for a sample containing both minerals.

(1940). Hematite (α-Fe_2O_3) has been shown above to grow from a pepper of small particles to small needles. The growth of hematite crystals and the morphology of authentic samples of maghemite and magnetite (Fe_3O_4) therefore deserve further study.

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Note added in proof. It is possible that the rearrangement of Fe^{3+} in the oxygen-hydroxyl lattice, believed by Francombe and Rooksby (*Clay Min. Bull.*, in press) to occur during the dehydration of goethite to hematite, may contribute to the exothermic peak. The extent of the contribution of this factor is, however, uncertain, since the largest exothermic peaks occur with the gels of the smallest particle size where crystal growth would be expected to be predominant.