The ageing of sesquioxide gels.

II. Alumina gels.

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Summary. Aluminium oxides occur widely in soils and are of considerable pedological significance. The ageing of alumina gels, prepared from aluminium chloride and ammonia, into crystalline hydroxides has been investigated using thermal, X-ray, infra-red, and electron-microscope techniques. At room temperature ageing is more rapid at high pH values. The structure of the original gel particles appears to resemble boehmite and ageing causes the formation of bayerite with small amounts of gibbsite. The morphology of the various mineral types is considered and a mechanism of ageing suggested.

HYDRATED aluminium oxides and alumina gels are of great interest in pedology because of their wide occurrence either alone or as mixed gels with silica. Relatively little investigation of mixed gels has so far been carried out, but the thermal behaviour of pure alumina gels and their products of ageing has been previously discussed (Mackenzie, 1957).[1] In view of the results then obtained and those reported on iron oxide gels in the first paper of this series (Mackenzie and Meldau, 1959), it was considered that a combined thermal, electron-optical, and infra-red study might provide information of value in pedological studies.

When iron oxide gels were investigated, relatively little information on their morphology was available; the position regarding alumina gels, however, is rather different. This is largely because of the effect of ageing upon their adsorptive properties for enzymes and viruses, which has

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[1] For a review of earlier information on alumina hydrates, see Milligan and McAtee (1952).

inspired a number of electron microscope investigations (see, e.g., Sawa-mura, 1952; Souza Santos, Vallejo Freire, and Souza Santos, 1953; Watson *et al.*, 1955; Suzuki, 1958, 1959; Moscou and van der Vlies, 1959). An excellent review of such morphological studies has been given by the last-named authors; details need not be reported here but relevant points will be brought out in discussion.

The gels used in this investigation were prepared from aluminium chloride and ammonium hydroxide at low temperatures and were, of course, highly hydrated. Since they were well washed before investigation the electron-optical results should not be affected by the various disturbing factors recently discussed by Shabalina, Derevyankin, and Kuznetsov (1960). Gels prepared from aluminium sulphate were avoided because of the possible formation of basic sulphates, particularly at lower pH values (Weiser, Milligan, and Purcell, 1941; Mackenzie, 1957).

Not only were the gels when freshly prepared very fine, but on ageing at room temperature they showed rather curious structural features which add considerably to previous knowledge as described by the above investigators.

Experimental.

Materials. A 9 N solution of ammonium hydroxide was added drop-wise to two solutions of 3 g anhydrous aluminium 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. Both precipitates were washed free from salts on a Buchner funnel after standing for 2 hours. Because of filtration difficulties, the pH 10 gel was left standing overnight and further washed the following day. As is noted below, this slight ageing affected the results, although it did not obscure the trends. Ageing was then allowed to occur at room temperature (*c.* 18° C) at the initial pH value and under exactly the same conditions as for iron oxide gels (Mackenzie and Meldau, 1959). Four samples in all were obtained: gel brought to pH 5 unaged; gel aged at pH 5 for 60 days; gel brought to pH 10 unaged; and gel aged at pH 10 for 60 days. The pH values were adjusted by NH_4OH or HCl as required. A.R. chemicals were used as far as possible. In order to elucidate some of the peculiar features observed with the pH 10 gel, another pH 10 gel was prepared and examined under the electron microscope at periods varying from less than 2 hours after preparation to 4 months. Results obtained for these two gels will be considered together.

Methods. As for iron oxide gels (Mackenzie and Meldau, 1959), the
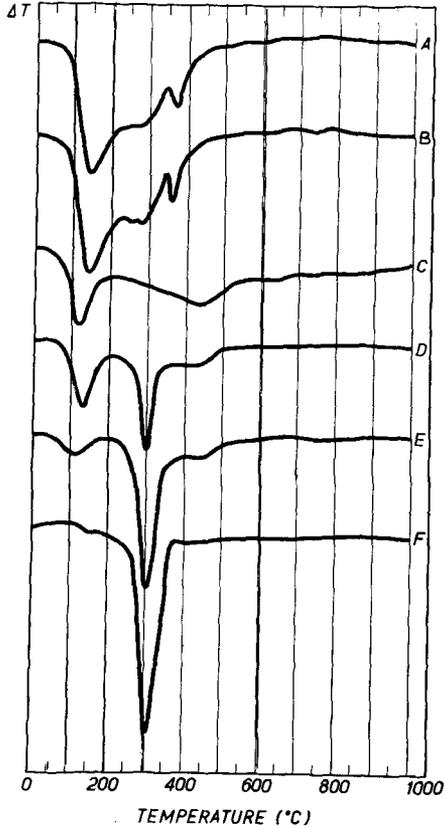
FIG. 1. Differential thermal curves for: *A*, pH 5 gel unaged (200 mg sample); *B*, pH 5 gel aged 60 days (200 mg sample); *C*, pH 10 gel unaged (170 mg sample); *D*, pH 10 gel aged overnight at pH 10 and then 4 days at pH 7 (200 mg sample); *E*, pH 10 gel aged for 2 days (200 mg sample); *F*, pH 10 gel aged for 60 days (150 mg sample).

gels were examined by electron-optical, X-ray, differential thermal, and infra-red absorption methods. Stereographic electron-micrographs were obtained from several preparations and attempts were made to obtain single-crystal diffraction patterns.

Results.

The differential thermal curves (fig. 1) are somewhat similar to those previously described (Mackenzie, 1957), but it would appear that the unaged pH 5 gel is even more poorly crystalline than usual (curve *A*),

perhaps because of more rapid precipitation. The apparent endo-thermic peak at 370° C may be due to a trace of ammonium chloride occluded in the gel, or to an exothermic reaction at 345° C. This gel aged for 60 days (curve B) does not appear to have altered appreci-ably, apart from the development of a very small peak at 280° C, which is probably due to the formation of a small amount of bayerite. The unaged pH 10 gel (curve C) gives a curve identical with those pre-viously described (Mackenzie, 1957) showing only the presence of poorly crystalline boehmite. The sample left overnight—i.e. 21 hours ageing— (curve D) showed the presence of bayerite (peak at 302° C) in addition to boehmite, while ageing for 2 days increases the bayerite content (peak at 307° C) tremendously (curve E), although there is still a considerable amount of unaltered material. After 60 days (curve F) the gel consists essentially of bayerite (peak at 310° C) but the very small dip at about 400° C suggests that even after this length of time some of the original boehmite is still present.

Infra-red spectra indicated that only amorphous gel, with a band due to adsorbed water at $6·13\mu$, was present in the pH 5 gel both in the original and aged states. The pH 10 gel aged for 21 hours gave an infra-red spectrum indicating in addition to gel, bayerite, and boehmite, a small proportion of gibbsite. For the pH 10 gel aged for 60 days, X-ray and infra-red absorption results agree in indicating bayerite with not more than 2 to 3 % of gibbsite; the infra-red data also showed the pre-sence of some unaltered gel. Bands at 6·5 to $7·5\mu$ were observed on several infra-red spectra; these may be due to the presence of ammonium compounds, and support the conclusion that the 375° C peak on the differ-ential thermal curve is due to a small amount of ammonium chloride.

The electron-micrograph of the fresh pH 5 gel (fig. 2a) shows a marked agglomeration of the primary particles into small aggregates of ill-defined shape but mostly in the rather narrow size-range 120 to 200 Å across. No true crystals could be observed in this gel. As in the iron oxide gel the individual particles are extremely small and it is difficult to delineate them sufficiently to estimate their size. This gel aged for 60 days (fig. 2b) again shows rounded particles, some of which now appear to be true crystals rather than the aggregates noted above; but in addition to these there are quite clearly visible a number of small rods about 0·04 to $0·08\mu$ long showing the definite commencement of crys-tallization. It seems probable that, as with the iron oxide gels, aggrega-tion of the individual gel particles into clumps precedes crystallization.

The fresh pH 10 gel (fig. 3a) is almost identical with the fresh pH 5 gel
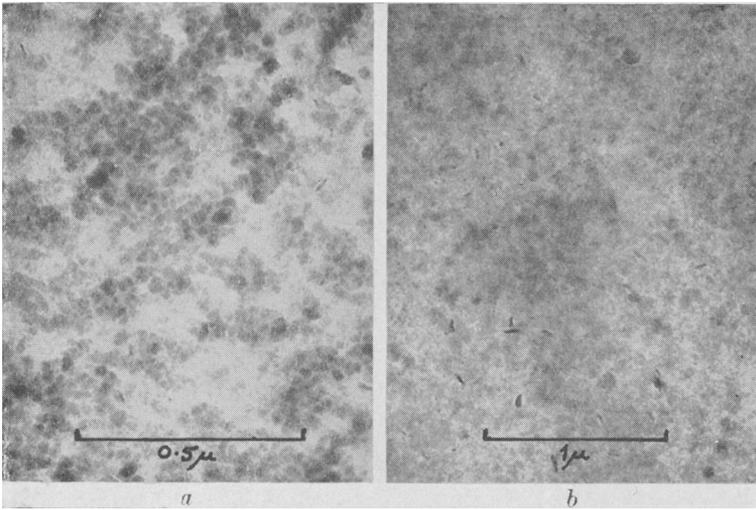
FIG. 2. Electron micrographs of pH 5 alumina gel: *a*, unaged; *b*, aged for 60 days.
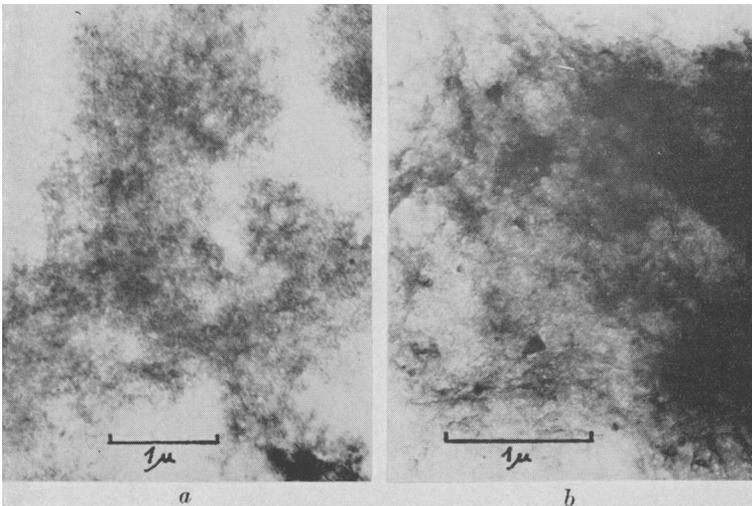

FIG. 3. Electron micrographs of pH 10 alumina gel: *a*, unaged; *b*, aged for 21 hours.

and stereo-micrographs of this preparation give it the appearance of a semi-transparent cumulus cloud—in other words, the individual gel particles must be extremely small and certainly less than 100 Å across. Micrographs (fig. 3b) and stereo-micrographs of the pH 10 gel aged for 21 hours show marked nuclei both triangular and rod-like in shape. These nuclei are up to about 0·2 μ long and 0·1 μ across. The bulk of the gel, however, shows the same features as the unaged gel with some fibrils which appear to be agglomerates of primary gel particles. These fibrils are small and do not show up well on reproduction. Stereo-micrographs of the gel aged for 2 days (fig. 4 a, b) show a very marked growth of triangular and rod-shaped particles in the gel matrix. A few of the triangular particles, which are up to about 0·7 μ across, tend to decrease in height towards their apices, but others towards the base (e.g. the large crystal in fig. 4) and generally their shape is that of a wedge of relatively uniform height standing on one of its triangular faces. Most of these particles also give the appearance of being platy parallel to the supporting film. The rod-shaped particles appear to be rectangular plates up to about 0·35 by 0·1 μ in size. The unaltered gel now appears to be largely in the form of fibrils. A few platy particles of rounded hexagonal nature are also seen, but these are infrequent. An interesting stereo-micrograph of this particular gel was obtained in which the supporting carbon film had ruptured and curled up until one part was virtually parallel to the electron beam; in this particular stereo the triangular faces of the particles were still uppermost. The appearance of the gel aged at pH 10 overnight and then in suspension at pH 7 for 4 days during its transit to Germany (fig. 4c), is very similar to that aged for 2 days, except that a number of hexagonal particles are quite clearly visible and the rod-shaped particles in this particular field are in an early stage of growth and appear to predominate over the tri-angular particles. One or two 'hour-glass' particles are also observed. After ageing for 60 days (fig. 5a) there is a marked difference in the appearance of the gel. The triangular particles are not so regularly shaped and have serrated edges; like the triangles in the earlier gels they appear to be wedge-shaped rather than pyramidal. No conical particles (*inter alia*, Watson *et al.*, 1955; Bye and Robinson, 1961) were observed in any of these preparations. 'Hour-glass' particles are observed and again a large number of rectangular particles, with here and there an occasional small hexagonal crystal. Stereo-micrographs of this gel (fig. 5 b, c) show that all the serrated roughly triangular particles appear now to be layered at right angles to the supporting film and parallel to the
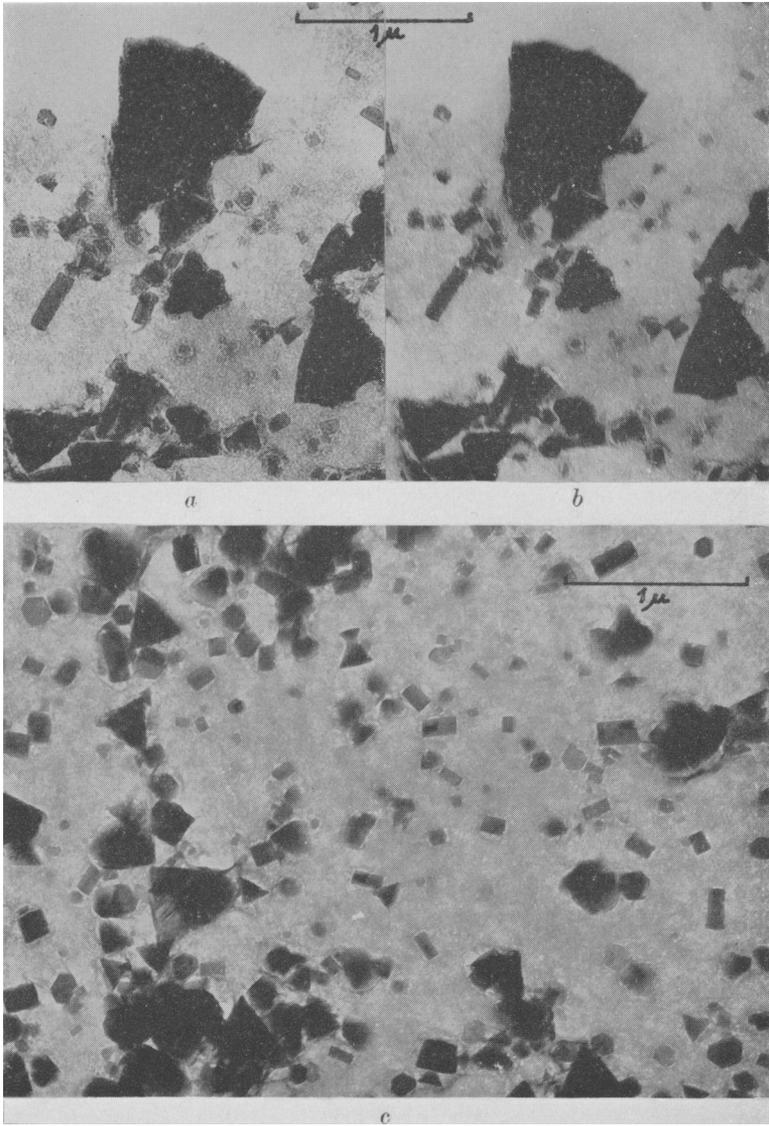
FIG. 4. Electron micrographs of pH 10 gel: *a* and *b*, stereographic micrographs of gel aged for 2 days; *c*, gel aged overnight at pH 10 and then 4 days at pH 7.
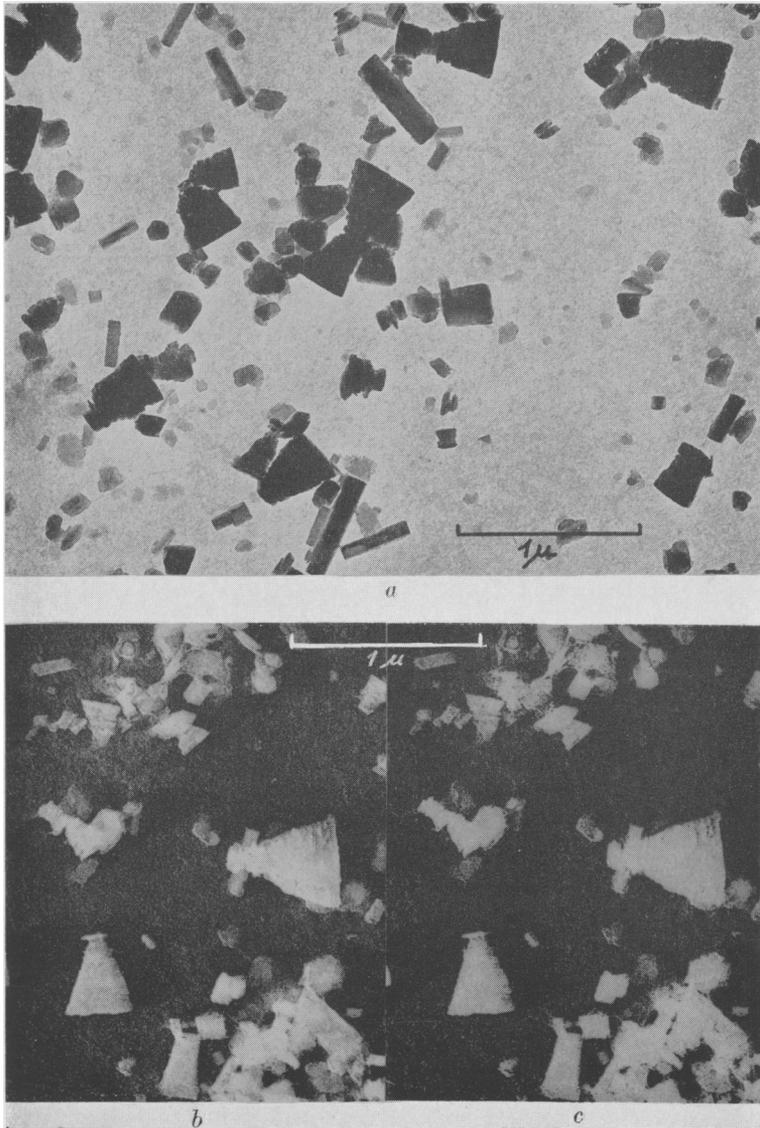
FIG. 5. Electron micrographs of pH 10 gel: *a*, aged for 60 days; *b* and *c*, stereographic micrographs of the same gel.

base of the wedge, and that, again, the rectangular particles are platy. On ageing for longer periods the crystals are appreciably larger but their shape is less definite and it may be that growth of one particle is affected by that of neighbouring particles. It should be mentioned that in all stages of ageing some original gel is still visible.

Discussion.

From the thermal, X-ray, and infra-red results it is clear that the main product of ageing of both gels is bayerite, although traces of gibbsite also appear and in the early stages of ageing the pH 10 gel contains fine and poorly crystalline boehmite. As described above, however, a number of different crystal shapes appear clearly in these gels and some correlation of crystal shape with mineral type is obviously desirable as a first step in the study of the mechanism of ageing. So little crystallization occurs in the pH 5 gel that it may for the moment be neglected and attention centred on the pH 10 gel, where a considerable variation is observed with ageing time in agreement with earlier work (Kraut and Humme, 1931).

Souza Santos, Vallejo Freire, and Souza Santos (1953), and Suzuki (1958), have described boehmite in hydrated alumina gels as occurring in the form of fibrils, while Moscou and van der Vlies (1959) described one of their preparations of boehmite as being 'composed of thin sheets which are agglomerated to larger fragments with a very airy structure'. Watson et al. (1955) have associated 'prisms' or rod-shaped particles (which they regard as being hexagonal in section) with gibbsite and all authors seem to agree that the serrated roughly triangular particles ('somatoids') and the 'hour-glass' particles consist of bayerite. Conical particles of bayerite have also been described by these authors, Bye and Robinson (1961) and others. On the other hand, well-crystallized gibbsite and boehmite (fig. 6 *a*, *b*) from Antrim laterites occur as roughly hexagonal particles with a tendency to rounded corners, and as diamond-shaped particles, respectively (Robertson and Meldau, unpublished). Suzuki (1958) describes the growth of a hexagonal particle of trihydrate —but it is uncertain whether he regards this as gibbsite or bayerite—and in a later paper (1959) also refers to rhombic particles as consisting of boehmite.

As mentioned above, small hexagons are visible on the electron micrographs of some of the samples of the pH 10 gel and are more common during the earlier periods of ageing than in the same gel aged for 60 days. Infra-red results suggest that there is more gibbsite in the former gel and it seems reasonable, therefore, to associate these hexagons with
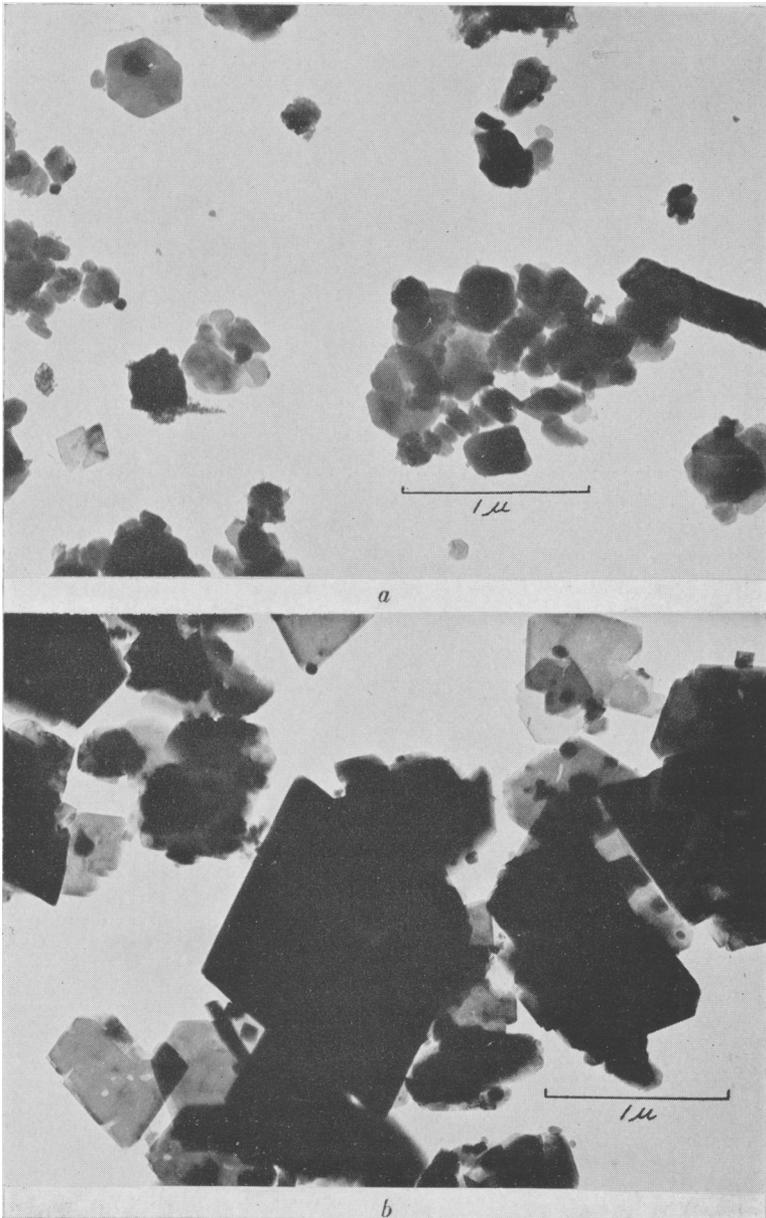
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FIG. 6. Electron micrographs of: *a*, gibbsite, and *b*, boehmite samples from Antrim laterites.

gibbsite. In addition the rod-shaped particles in these gels, as shown by the stereo-micrographs, are in fact platy and not hexagonal in section. Since they have the general appearance of those described by Watson *et al.* (1955) and others, it may be assumed that they have the same constitution. There is, however, far too great a proportion of these rectangular plates to triangular or serrated particles for them to be considered as gibbsite and consequently the attribution of these to gibbsite by Watson *et al.* (1955) would seem to be in error. It should be mentioned that these workers also observed platy hexagonal particles in their gels which were regarded as an early stage in the crystallization of gibbsite; this attribution would, on the above evidence, be correct.

In the gels aged for 21 hours and for 2 days, in addition to individual gel particles, quite a number of fibrils can be observed, these apparently consisting of agglomerations of individual gel particles. They have the appearance described in several of the papers mentioned above. In addition, it has been remarked that almost regular triangular or wedge-shaped particles layered parallel to the triangular faces appear during the early stages of this gel, but disappear later on when the serrated particles of somewhat similar shape, which seem to be layered parallel to the base of the wedge, appear. If the serrated particles are bayerite, as from all the evidence we must accept, then the nature of the wedge-shaped particles may be explained as follows. There is a marked similarity between these particles and the description quoted above by Moscou and van der Vlies (1959) for boehmite. Furthermore, the apical angle of several of these triangles is virtually identical with the apical angle on the diamond-shaped boehmite particles in fig. 6b. It would appear, therefore, that these particles are probably boehmite formed by agglomeration and perhaps recrystallization of gel particles; the rather open structure suggests that they are not highly crystalline.

Since the later stages of ageing of the gel, according to all the evidence available, consist essentially of bayerite with only a very small proportion of gibbsite (and a little unaltered gel), both the rectangular platy particles and the serrated particles apparently consist of bayerite. An attempt to prove this by single crystal electron diffraction patterns failed because of the small size of the crystallites involved. The only other possibility is that the rectangular platy particles belong to the third alumina trihydrate described by van Nordstrand, Hettinger, and Keith (1956) or to one of the variants of bayerite described by Schmäh (1946). From X-ray results, however, this seems unlikely.

Summing up all the evidence obtained during this study and assessing

it in conjunction with previous work on alumina hydrates, the fresh unaged particles in the pH 10 gel probably have essentially a boehmitic structure. On ageing, these particles agglomerate to form fibrils, also of boehmite, and some wedge-shaped particles, which are probably slightly better crystallized boehmite, although on stereo-micrographs they still have the very 'airy' structure described by Moscou and van der Vlies (1959). On further ageing the fibrils probably change into the rectangular platy particles of bayerite, while the triangles are converted into the serrated truncated triangular and 'hour-glass' particles, also of bayerite. The serrated truncated triangular particles on this basis are pseudo-morphs of bayerite after boehmite, consisting of assemblages of sheets with the basal plane of the bayerite at right angles to that of the boehmite. Such a mechanism is not improbable from the crystallographic aspect (Seifert, private communication), particularly if the triangular boehmite particles have water molecules occluded between their layers. This, in fact, might explain the rather open appearance of these wedges, since the water molecules would presumably be expelled, partially at least, in the high vacuum of the electron microscope, causing the triangular particles to expand somewhat, in a manner similar to the exfoliation of vermiculite.

The above mechanism is also in accordance with results from the pH 5 gel; the particles of bayerite observed in the aged gel have the general appearance of being younger variants of the rectangular platy particles.

The evidence presented above, therefore, is in agreement with previous observations that bayerite normally forms readily on the ageing of alumina gels, that ageing is more rapid at higher pH values, and that particles of at least five distinct shapes are formed. It does not support a previous suggestion that gibbsite occurs as rod-shaped particles, but it seems established from all the evidence that gibbsite crystallizes in hexagonal or roughly hexagonal platelets, boehmite can occur as primary gel particles (?), fibrils, wedge-shaped particles, or diamond-shaped particles, and bayerite as rectangular platelets or as serrated truncated triangles or 'hour-glass' particles, consisting of assemblages of sheets.

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