β-Ferric oxyhydroxide—akaganéite.

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[Taken as read 8 November 1962.]

Summary. A new mineral, akaganéite, has been found in limonite deposits and has been shown to be identical with synthetic β-FeOOH. It contains no chlorine. The micro-morphology of β-FeOOH as it occurs as akaganéite and as it is produced by a solid-state transformation from $FeCl_2.4H_2O$, by the hydrolysis of dilute $FeCl_3$ solutions, and by the hydrolysis of very concentrated $FeCl_3$ solutions, has been studied, chiefly by electron microscopy and diffraction. Some modes of colloidal association of the particles of β-FeOOH are described.

THE structure and some of the properties of β-FeOOH have been described in our first communication[1] and although at that time no reference to the natural occurrence of the material had been found, this was then expected. β-FeOOH has recently been discovered as a mineral by Dr. M. Nambu of Sendai University, Japan (priv. comm., 1961) and was named akaganéite by him, after the locality, the Akagané mine, Iwate Prefecture, Japan. The mineral was identified from its X-ray diffraction powder pattern, which matched very closely the data published by the present author who showed the unit cell to be tetragonal with the space group $I4/m$ and cell dimensions a 10·48 Å and c 3·023 Å. The mineral was an apparent limonite, and seemed to derive from the metamorphosis of pyrrhotine through ferrous sulphate,[2] the sequence of the layers encountered being: massive pyrrhotine; ferrous sulphate + goethite + akaganéite; goethite + akaganéite; goethite + hydrohematite; black soil. It appears then that the title *Limonite is goethite* (qualified in the text) of the short communication by W. T. Holser (1953) should be modified.

Dr. Nambu gives two analyses of akaganéite, the first made in 1957, the second (in parentheses) in 1959: Fe_2O_3 78·23 % (80·98), FeO 0·82 (0·23), SiO_2 3·10 (3·57), Al_2O_3 1·21 (1·40), Na_2O 0·62 (0·82), K_2O 0·19 (0·29), H_2O^+ 10·20 (9·71), H_2O^- 4·96 (2·55), sum 99·33 (99·55). These

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[1] Min. Mag. 1960, vol. 32, p. 545.

[2] It is curious, as akagané means red gold, that August Strindberg believed that this process generated gold (see letter to Jollivet-Castelot, 15 Apr. 1896, quoted by M. Caron and S. Hutin in The Alchemists, p. 94, 1961).

analyses correspond as closely as may reasonably be expected for this class of mineral with the formula FeOOH (Fe_2O_3 89·90, H_2O 10·10 %). It is, however, significant that the material contains no chlorine but has instead some 3·5 % SiO_2+1·3 % Al_2O_3. This would be equivalent to one Al or Si atom to every 11 or 12 Fe atoms. The hypothesis formed earlier that chloride or fluoride ions are necessary for the formation of the structure is clearly disproved, although the role of silica is uncertain and it may well be present as a second phase. Prof. H. Zocher (priv. comm., 1961) reports that he has prepared β-FeOOH from ferric nitrate, although mixed with some α-FeOOH.

FIG. 1. Electron micrograph of crystals of akaganéite.

R. Van Tassel (1959) has also briefly reported the occurrence of β-FeOOH as a mineral, this time in association with goethite and delvauxite in phosphate-rich breccia in limestone.

K. C. Chandy (1961) has encountered β-FeOOH in the heavy mineral fraction of the natural coke from a borehole in the Jharia coalfield, India.

A sample of akaganéite (from Dr. Nambu) has been examined by electron microscopy and by selected area electron diffraction, and single

FIG. 2. Electron micrograph of a mat showing two texture axes for the β-FeOOH crystals composing it, which had transformed in the solid from $FeCl_2.4H_2O$.

crystal patterns have confirmed the identification. The crystals (fig. 1) have dimensions approximately 2500 × 250 Å and most are lying on the specimen film on their {100} faces. The direction of the elongation is [001]. The material is better crystallized than any obtained synthetically.

FIG. 3. Electron micrograph of a sheet of β-FeOOH fibres produced by a solid transformation from $FeCl_2.4H_2O$.

Formation from $FeCl_2.4H_2O$.

When lemon-yellow crystals of $FeCl_2.4H_2O$ are allowed to oxidize in the air they become brown with the formation of β-FeOOH. X-ray powder photographs show this. Electron microscopic examination provided further information on the process and shows that the β-FeOOH is in the form of sheets (figs. 2, 3, and 4). Although there is good orientation of the β-FeOOH fibres into mats, the orientation of the fibres about the texture direction (in the plane of the sheets) is not highly ordered.

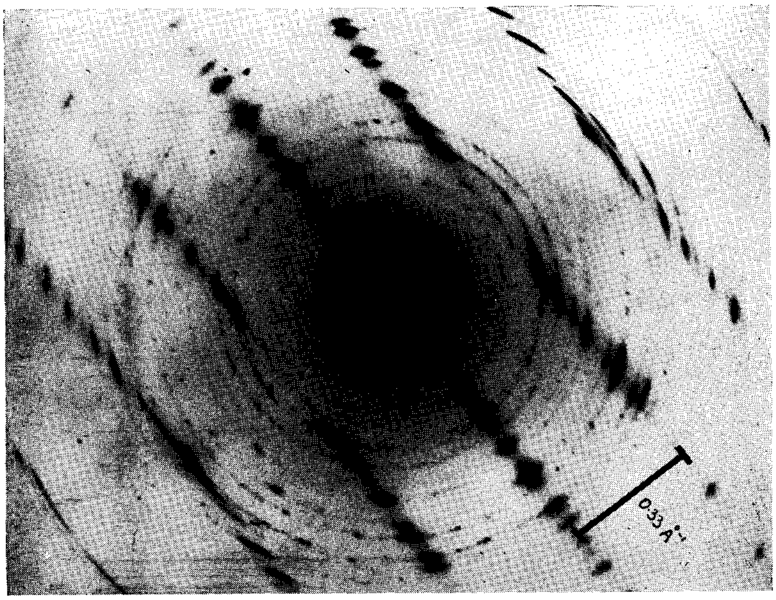


FIG. 4. Electron diffraction pattern from the area shown in fig. 3.

No very close connexion between the structures of $FeCl_2.4H_2O$ (Penfold and Grigor, 1959) and of β-FeOOH can be seen and it is possible that $FeCl_2.4H_2O$ is not the immediate precursor of β-FeOOH. $FeCl_2.2H_2O$ and FeOCl are other possibilities. Sometimes the textures are crossed and there are two texture axes. Further experiments would be necessary to sort out the intermediate steps in the process.

Occurrence as somatoids.

The somatoids (fig. 5) obtained by the hydrolysis of dilute ferric chloride solutions have been further examined. These somatoids of β-FeOOH (Kohlschütter and Egg, 1925, define the word somatoid) are spindle-shaped quasi-single crystals 2000–5000 Å long and 200–1000 Å in diameter, which aggregate as single-layer schiller sheets in which their longer axes (c-crystallographic axes) are perpendicular to the plane of the sheet and their a-axes are also aligned parallel to each other so that the spindles are azimuthally oriented. The diffraction photograph obtained from a small area of a sheet is reproduced in fig. 6. Fig. 7 shows part of such a schiller sheet or raft and it is evident that the packing tends to be square and not hexagonal as would be expected for closest packing. The effects of the tetragonal symmetry of the crystal structure, therefore, persist for a considerable distance into the water surrounding each somatoid and decisively influence its contacts with neighbouring somatoids. This effect of the extension of the oxide structure into the solution perhaps explains the role of the oxide coating in the slip casting of metals and ceramics.

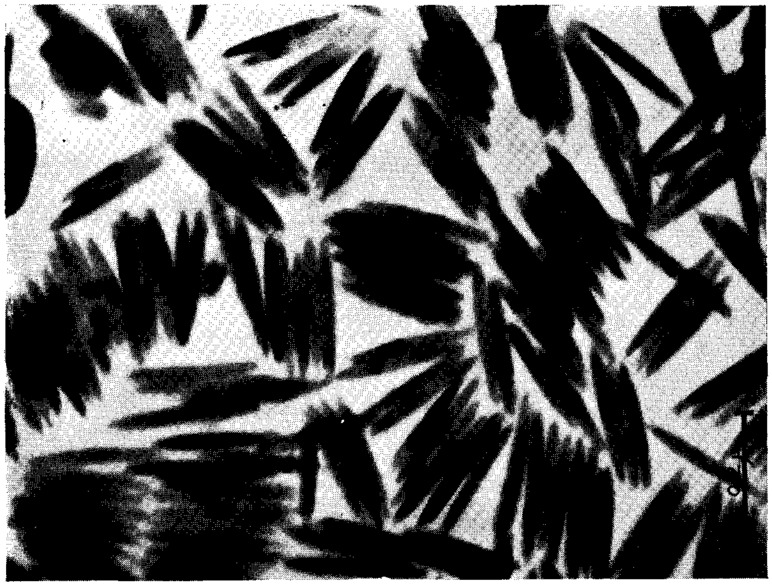


FIG. 5. Somatoid particles of β-FeOOH showing parallel association.

Somatoids of β-FeOOH have recently been examined by Watson, Heller, and Schuster (1960) whose results are in general agreement with those reported here and earlier except for one observation. Fig. 8 is reproduced from Watson, Heller, and Schuster's paper and represents a thin cross-section of a raft of somatoids which had been embedded in butyl methacrylate. This should be contrasted with fig. 7 taken by the present author for free material. Diffraction from single somatoids shows that they have a preference for lying on the specimen film on {100} planes but the round cross-section seems unequivocally demonstrated in fig. 7. We believe, from an examination of the sub-structure of the somatoids, that the unit particles making up the somatoids are rods elongated parallel to [001]. Lamellae, as originally proposed by Watson, Heller, and Schuster, would be inconsistent with the crystal symmetry and would lead to anisotropic sharpening of the diffraction spots. As a result of private correspondence with Dr. J. H. L. Watson and further experiments these discrepancies have been removed and it is agreed that the differences in cross-section are real and are due to differing rates of crystallization. A 2 % (by weight) solution of $FeCl_3$ left to hydrolyse at room temperature for 6 months showed particles which

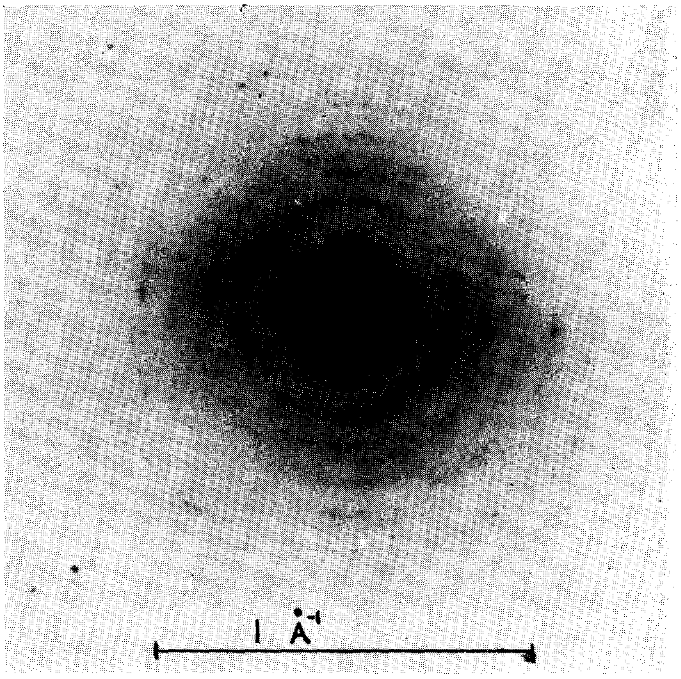
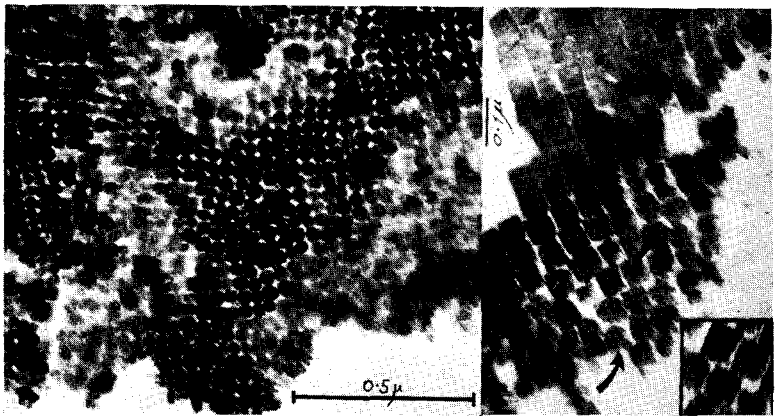
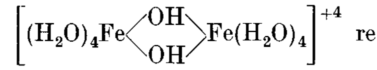


FIG. 6. Diffraction pattern from a schiller sheet (beam perpendicular to the sheet) showing the preferred azimuthal orientation of the somatoid particles composing it.

were appreciably squarer in cross-section than those which were found in a solution hydrolysed at 40° C for 24 hours.



FIGS. 7 and 8: FIG. 7 (left). Electron micrograph of a schiller sheet or raft of somatoids (particles viewed end on) showing square packing and nearly circular cross-section. (Particles grown at 40–50° C.) FIG. 8 (right). Micrograph by Watson, Heller, and Schuster of a microtome section of a schiller sheet of β-FeOOH particles showing square cross-section. (Particles grown at room temperature.)

The unit particles mentioned, the long rods, perhaps 25 Å square in cross-section, which make up the somatoid particles, appear to be held together by normal crystal forces and not colloidal forces. There is no degree of freedom in the positioning of the subparticles and the somatoids are not tactoids (discussed below). We would suggest, as a hypothesis, that there exist in the solution complexes of hydrated Fe^{+++} ions that are chains of linked octahedra. These could be extensions of the binuclear ion  $\left[(H_2O)_4Fe\overset{OH}{\underset{OH}{<>}}Fe(H_2O)_4\right]^{+4}$ reported by Mulay and Selwood (1955). These authors write: 'hydrous ferric oxide owes its subnormal magnetic moment to the presence of diamagnetic $Fe_2(OH)_2^{+4}$ built into its structure' although in fact the structure of β-FeOOH was not known at the time they wrote. Sillén (1959) has reviewed the question of the hydrolysis of ferric salts and agrees that polynuclear complexes may occur. In this connexion it should be noted that the reported structures of $Fe(OH)_3$ have all proved illusory. In particular, the cubic cell with a 5·71 Å quoted in Crystal Data (Fordham and Tyson, 1937) is in fact that of NaCl. We believe also that the 'standard' X-ray diffraction pattern of Watson, Heller, and Schuster does not supersede that given earlier (Mackay, 1960) as the seven weakest lines appear to be due to impurities ($FeCl_2.2H_2O$?).

β-FeOOH *as tactoids.*

We have examined a tactosol of β-FeOOH prepared by Professor H. Zocher in the following way:

> 25 g $FeCl_3.6H_2O$ were dissolved in 25 g water and, after cooling to about 0° C, 27 ml of a 29 % solution of ammonia in water (also cooled) were added with vigorous stirring. The precipitate was washed 5–6 times with centrifugation until peptization began. The wet precipitate was heated at 50° C for 3 weeks. The paste, 10 times diluted, formed tactosol at the bottom of the vessel after strong centrifugation.

Tactoids (spindle-shaped anisotropic liquid droplets about 0·2 mm long and 0·1 mm in diameter) were observed optically with a polarizing microscope. They are regions in which spontaneous orientation of rod-like particles occurs and their shape (Bernal and Fankuchen, 1941) can be described in terms of an anisotropic surface tension with two tensions σ_1 and σ_2 corresponding to the two principal radii of curvature r_1 and r_2 at any point of the surface of the drop by a relationship $\sigma_1/r_1+\sigma_2/r_2 =$ constant. If $\sigma_1 = \sigma_2$ this equation can be elegantly integrated to give an unduloid, which is a surface of constant Gaussian curvature, and if the tensions are different the shape will nevertheless be fairly similar although exact calculation has to be replaced by numerical or graphical methods.

Some of the tactosol was greatly diluted with water and examined with the electron microscope. It was found to be made up of prismatic crystals of very uniform size (fig. 9) about 60 × 500 Å. It was not found possible to obtain diffraction pictures from single particles but parallel aggregations of 5 to 10 particles diffracted as a texture showing the long axis to be [001]. Ordinary X-ray powder photographs showed marked selective line broadening due to the particle shape, the 002 reflexion being much sharper than the others. The tactosol was sheared between two glass plates and the resulting thin smear was dried. Flakes of this could be examined by ordinary and by small angle X-ray diffraction techniques and proved to have the crystallites aligned parallel to the flow direction. The ordinary diffraction pictures showed strong preferred orientation effects and a pair of equatorial spots near the origin corresponded to the rod diameter.

The colloidal properties of β-FeOOH are thus shown to be of considerable complexity and undoubtedly will have a bearing on the formation of deposits of hydrated iron oxides.

FIG. 9. Electron micrograph of the minute crystals of β-FeOOH occurring in a tactosol.

Acknowledgements. During the period of this work the author was in receipt of a research grant from the Department of Scientific and Industrial Research for which assistance he is most grateful. He also wishes to acknowledge the collaboration of Prof. Zocher who introduced him to many colloidal phenomena during a month's visit to Birkbeck College. Some of the micrographs were taken by Mr. J. F. Kerridge and Mr. J. Phillips also provided photographic assistance. Thanks are also due to Dr. Nambu for his sample of akaganéite.

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