

β -Ferric oxyhydroxide—akaganéite.

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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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 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 communication¹ 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

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



FIG. 1. Electron micrograph of crystals of akaganéite.

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 .

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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

crystal patterns have confirmed the identification. The crystals (fig. 1) have dimensions approximately $2500 \times 250 \text{ \AA}$ 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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

Formation from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

When lemon-yellow crystals of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 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 pro-

vided 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.

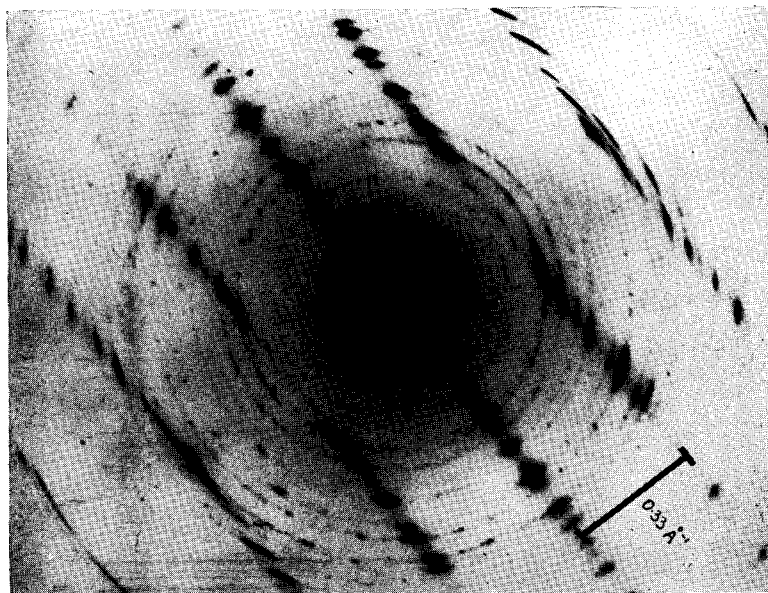


FIG. 4. Electron diffraction pattern from the area shown in fig. 3.

No very close connexion between the structures of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Penfold and Grigor, 1959) and of β -FeOOH can be seen and it is possible that $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is not the immediate precursor of β -FeOOH. $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ 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



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

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.

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

