NEW EVIDENCE FOR A TUBULAR STRUCTURE OF $\beta$-IRON(III) OXIDE HYDROXIDE – AKAGANEITE

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Abstract. A biological method for the preparation of ultrathin transmission electron microscopy (TEM) sections has been used successfully to examine the fragile mineral akaganéite. TEM exposures reveal a tubular structure for akaganéite. The existence of such a structure has been debated for over a decade. The tubular structure may have been active in prebiotic polymerization reactions on the young Earth.

1. Introduction

Fourteen years ago K. J. Gallagher (1970) published a paper in Nature entitled ‘The Atomic Structure of Tubular Subcrystals of $\beta$-iron(III) Oxide Hydroxide’. Based on nitrogen adsorption measurements and previous results by Watson et al. (1962) he proposed a detailed superstructure of $\beta$-iron(III) oxide hydroxide, or akaganéite (the name of the natural mineral). The general formula for this compound is $\beta$-FeOOH or even $\beta$-FeOOH · Cl$_n$ since it normally contains a small amount of Cl$^-$ (2–6%; Keller, 1970). Watson and coworkers carried out electron microscopy studies on sectioned crystals of synthetic $\beta$-FeOOH · Cl$_n$ embedded in methyl methacrylate. The minute crystals of this oxide hydroxide are isostructural with the manganate mineral hollandite. They are somatoids, i.e. crystals of regular internal structure but of more or less irregular external shape. Watson et al. observed that longitudinal sections of the somatoids showed striations with repeating distances of about 60Å. Cross-sections displayed a mottled pattern. Their interpretation of the observations was that the $\beta$-FeOOH · Cl$_n$ consisted of bundles of rods. They also thought that there was some evidence to support the view that the rods or subcrystals might be hollow, with internal and external diameters of about 30Å and 60Å respectively. Gallagher’s measured mean pore diameter was 28.2Å. The proposed hollow subcrystal structure of $\beta$-FeOOH · Cl$_n$ was suggested to have interesting applications in ion-exchange, chromatography, and catalysis etc. For commercial reasons, there has been considerable interest in studies of akaganéite for some years. However, data based on BET nitrogen adsorption measurements (after Braunauer et al., 1938) by Paterson and Tait (1977) and electron microscopy studies by Galbraith and coworkers have cast doubt on the existence of the tubular structure suggested by Gallagher. In a series of elegant articles (Baird et al., 1978; Galbraith et al., 1979, 1980) Galbraith et al. present evidence that features such as mottling and striations were due to radiation damage in the electron microscope. They concluded that the previously observed structures were artifacts and that $\beta$-FeOOH · Cl$_n$ somatoids are crystallographically homogenous.
Naono et al. (1982) also presented evidence that the crystals of \( \beta \)-FeOOH \( \cdot \) Cl\(_n\) are subject to damage on heating and that the damage produces large holes or channels.

The tubular structure discussed here must not be confused with the small 5 \( \times \) 5 \( \text{Å} \) tunnels inherent in the hollandite type primary structure of akaganéite (MacKay, 1960, 1962). These tunnels may be accessible to small exchangeable anions and neutral molecules such as Cl\(^-\), F\(^-\), OH\(^-\), H\(_2\)O. The presence of the halogen ions (normally 5.4–6.3 wt % chloride) is necessary for the formation of the \( \beta \)-iron(III) oxide hydroxide (MacKay, 1960, Keller, 1970). Once formed about 1/3 of the halogen ions may be removed by washing with water. It does not seem possible to remove a remainder of about 2% Cl\(^-\) by weight of the mineral and still maintain the hollandite structure of \( \beta \)-FeOOH \( \cdot \) Cl\(_n\) (Keller, 1970).

It is the aim of this paper to elucidate geochemical processes that maybe took place some 4 \( \times \) 10\(^9\) yrs ago. The paper describes low temperature hydrothermal geochemistry systems, i.e. temperatures not much higher than 100 °C. Above these temperatures we know that akaganéite will transform easily into goethite and/or hematite in water. The systems described are purely aquatic where the substances formed will never be subject to pressures lower than at least 1 atm depending on the water depth. If the original atmosphere of the Earth was like that of Venus today the minimum pressure would instead have been more than perhaps 60–90 atm. The secondary minerals, in this case akaganéite, that form in aquatic systems will never be dehydrated or removed from the aqueous solution (i.e. the mother liquid). Therefore, in a low-temperature geochemists view, surface analysis techniques such as BET measurements are rather meaningless since they include high dehydration temperature (> 100 °C), low pressure (10\(^{-3}\)–10\(^{-5}\) Torr) and the absence of water. Nevertheless BET measurements were carried out in an initial stage of this study (see Section 2).

2. Reappraisal of the Akaganéite Structure

My own previous work has shown (Holm et al., 1982, 1983) that the yellowish brown precipitate in samples of Red Sea brine consist solely of akaganéite. In an effort to explain the unusual distribution of amino acids reported by Ingman and Dowler (1980) studies of the uptake of amino acids by synthetic \( \beta \)-FeOOH \( \cdot \) Cl\(_n\) were carried out. The results suggested that amino acids are bound efficiently by the iron oxide hydroxide above pH 3. The deduction was that this new evidence together with results of my own BET and thermogravimetric (TG) measurements on dry powder \( \beta \)-FeOOH \( \cdot \) Cl\(_n\) (unpublished data) support a reappraisal of the akaganéite superstructure. The BET measurements show that the specific area of akaganéite varies significantly with the dehydration temperature. Decreasing the temperature from e.g. 110 °C to 80 °C doubles the specific surface area from 30 m\(^2\)/g to 60 m\(^2\)/g. XRD measurements after BET adsorption determinations reveal that the powder characteristics have changed (the akaganéite peaks almost disappear). TG measurements show that some lattice water of \( \beta \)-FeOOH \( \cdot \) Cl\(_n\) is bound very loosely and is lost in the temperature region of about 40–60 °C. Naono et al. (1982) found that the water content