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Natural Nanomaterials: Reappraising the Elusive Structure of the Nano-sized Mineral Ferrihydrite through X-Ray Absorption Spectroscopy at the Iron K-Edge

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Abstract. Ferrihydrite is natural ferric oxyhydroxide occurring exclusively nanocrystalline. With ideal formula $5 \text{Fe}_2 \text{O}_3 \cdot 9 \text{H}_2 \text{O}$, ferrihydrite is quite abundant in sediments, weathering crusts and mine wastes, being characteristic of red pre-soils formed by loose weathered rock plus mineral debris (regoliths) and commonly designated as “2-line” or “6-line” on the basis of the broadened maxima observed in the X-ray diffraction pattern. Synthetic nanocrystalline “6-line” ferrihydrite was recently studied through methods based on atomic-pair distribution functions disclosing the possible occurrence of icosahedral clusters formed by twelve octahedra centred by an inner tetrahedron, all filled by Fe^{3+} ions. However, Mössbauer studies were inconclusive about the existence of 4-coordinated iron, thus suggesting that the tetrahedral cation may well be Si^{4+} . In view of such structural uncertainty, a XANES study at the Fe K-edge was undertaken on ferrihydrite from a regolith to ascertain the occurrence of tetrahedral iron. Comparison with data collected from well crystallized iron oxide and hydroxide minerals where $\text{Fe}^{3+/2+}$ ions occur in octahedral and tetrahedral coordination is described and the results so far obtained are discussed, showing that supplementary study is needed on the elusive structure of ferrihydrite.

Introduction

The Problematic of Ferrihydrite. Recent developments in Materials Science unveiled the strong dependence of chemical properties from particle size, disclosing a large span of innovative applications for nanomaterials.

Minerals are natural materials and usually well crystallized entities. However, differences in surface and near-surface atomic structure of nano-sized minerals comparatively to the bulk crystal structure imply significant variations in the geochemical behaviour [1], strongly reflected in the kinetics of biogeochemical reactions occurring in soils.

Ferrihydrite (natural ferric oxy-hydroxide with nominal formula $5 \text{Fe}_2 \text{O}_3 \cdot 9 \text{H}_2 \text{O}$) is a unique case in the mineral world because it is present exclusively nanosized and up to now no stable crystalline counterpart could be produced in the laboratory. It is the typical precursor of more stable iron oxide minerals [2], being characteristic of red pre-soils formed by loose weathered rock plus mineral debris – the so-called regoliths, very common in volcanic regions – and building up a peculiar link towards the biological world. In fact, the bio-mineralization of ferrihydrite as the inorganic iron core of ferritin – a protein common in biological systems which molecules comprise a thin hollow spherical protein shell enclosing a poly-nuclear iron core of ferrihydrite [3-5] – enhanced the need for deepening the structural study of this nanosize mineral phase.

The structural models first proposed for ferrihydrite based on X-ray and electron nanodiffraction data pointed towards a distorted double hexagonal closest packing of anions with iron ions filling octahedral and tetrahedral sites [6-8]. The presence of tetrahedral ferric iron could not be unequivocally proven using Mössbauer spectroscopy [9] but X-ray absorption spectroscopy may decisively clarify these structural doubts through the analysis of the pre-edge details from iron K-edge absorption spectra [10].