NATURAL NANOMATERIALS: REAPRISING THE ELUSIVE STRUCTURE OF THE NANOSIZED MINERAL FERRIHYDRITE THROUGH X-RAY ABSORPTION SPECTROSCOPY AT THE IRON K-EDGE

M.O. Figueiredo[1,2], T.P. Silva[1,2], J.P. Veiga[1]

[1]*CENIMAT / I3N, Fac. Sciences and Technology, New University of Lisbon (FCT-UNL), 2829-516 Caparica, Portugal.*
jpv@fct.unl.pt
[2]*LNEG, Unit of Mineral Resources and Geophysics, Estrada da Portela, 2721-866 Alfragide, Portugal*

Ferrihydrite is a nanocrystalline natural oxyhydroxide with nominal formula $5Fe_2O_3.9H_2O$. This nanomineral is characteristic of red pre-soils (regoliths) being commonly designated as "2-line" or "6-line" on the basis of the broadened maxima observed in the X-ray diffraction pattern. It is ubiquitous in near-surface environments, acting as a natural filter of inorganic contaminants through sorption reactions, and is frequently found in acid mine drainage areas where it is a precursor of goethite, α-FeO(OH), and hematite, α-Fe_2O_3. Biomineralization of ferrihydrite as the inorganic iron core of ferritin - the protein mainly involved in iron storage in biological systems - enhanced the importance of studying the magnetic properties of this mineral nanophase that up to now has no crystalline counterpart produced in the laboratory.
The atomic arrangement of ferrihydrite was recently approached by the atomic pair-distribution function (PDF) method, disclosing the probable occurrence of icosahedral clusters formed by twelve octahedra centred by an inner tetrahedron, all filled by Fe^{3+}, in the nanomineral. However, a former Mössbauer study undertaken at 4.2 K in natural ferrihydrite had been inconclusive about the existence of 4-coordinated iron ions.
The edge features of X-ray Absorption Near-Edge Spectra configure a powerful means of assessing the formal valence of 3d transition metal ions and their coordination environment. Accordingly, a XANES study at the Fe *K*-edge of ferrihydrite in regoliths from Cape Verde Islands was undertaken to ascertain the hypothetical presence of tetrahedral iron. The analysis of pre-edge features and the comparison with similar data collected from well crystallized iron oxide and hydroxide minerals where $Fe^{3+/2+}$ ions occur in octahedral and tetrahedral coordination are described. The results are weighed against recently published Mössbauer data on ordered ferrimagnetic ferrihydrite, showing that the hypothesis of minor ferric iron staying in tetrahedral coordination can not be entirely discarded.

Keywords: Nanominerals; Ferrihydrite; XANES; Fe *K*-edge.

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