

NANOPHASES IN THE MINERAL WORLD: THE UNIQUE CASE OF FERRIHYDRITE *

M. O. Figueiredo^{1,2}, T. P. Silva^{1,2}, J. P. Veiga¹

¹ Department of Materials Science & EN, FCT-UNI, Campus de Caparica, 2829-516 Caparica.

² LNEG, Unit of Mineral Resources and Geophysics, Apt. 7586, 2721-866 Alfragide, Portugal

Minerals are usually well crystallized entities but recent studies have disclosed the strong dependence of their chemical properties from particle size. Differences in surface and near-surface atomic structure of nano-sized mineral phases comparatively to the bulk crystal structure imply significant variations in the geochemical behaviour, strongly reflected in the kinetics of biogeochemical reactions in soils.

The exclusively nano-sized natural ferric oxyhydroxide - ferrihydrite - is a singular case in the mineral world. With an approximate ideal formula $5Fe_2O_3 \cdot 9H_2O$, ferrihydrite is characteristic of red pre-soils formed by loose weathered rock plus mineral debris (regoliths) being commonly designated as "2-line" or "6-line" on the basis of the broadened maxima observed in the X-ray diffraction pattern. The bio-mineralization of ferrihydrite as the inorganic iron core of the protein ferritin in biological systems has increased the importance of studying the magnetic properties of this mineral phase that has no crystalline counterpart formed in the laboratory.

Synthetic nanocrystalline "6-line" ferrihydrite was recently studied through methods based on atomic-pair distribution functions [1] disclosing the occurrence of icosahedral clusters formed by twelve octahedra centred by an inner tetrahedron, all filled by Fe^{3+} ; however, a former Mössbauer study undertaken at 4.2 K in natural ferrihydrite was inconclusive about the existence of 4-coordinated iron [2], thus suggesting that the tetrahedral cation may well be Si^{4+} .

The edge features of X-ray Absorption Near-Edge Spectra (XANES) configure a powerful means of assessing the electronic state and formal valence of cations (particularly transition metal ions) and their coordination environment. Accordingly, a XANES study has been undertaken at the Fe K-edge of ferrihydrite-rich regoliths to ascertain the hypothetical presence of tetrahedral iron [3]. Comparison with data collected from well crystallized iron oxide and hydroxide minerals where $Fe^{3+/2+}$ ions occur in octahedral and tetrahedral coordination is described and the results so far obtained are discussed.

[1] F.M. Michel et al., The structure of ferrihydrite, a nanocrystalline material, *Science*, 316, 1726 (2007).

[2] E. Murad and U. Schwertmann, The Mössbauer spectrum of ferrihydrite and its relations to those of other iron oxides, *American Mineralogist*, 65, 1044, (1980)

[3] M.O. Figueiredo, T.P. Silva and J.P. Veiga, Oxidation state and coordination of iron in red pre-soils: first results from a Fe K-edge XANES study on regoliths from Santiago Island, Cape Verde, *Geophysical Research Abstracts*, 10 (EGU General Assembly, 2008).

* From a talk delivered by M.O. Figueiredo at the International Seminar on the Microscopy of the Nanoworld, held at Cantanhede Portugal (December 10-12, 2010)