

Analytical transmission electron microscope characterisation of thermally aged two-line ferrihydrite co-precipitated with phosphorous

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The nanocrystalline mineral ferrihydrite (Fh) is a poorly ordered iron oxyhydroxide. It is identified and named according to the position and number of Bragg reflections in a powder X-ray diffraction pattern; the two 'end members' give 2- and 6-lines (2LFh and 6LFh). The exact structure of Fh is still a matter of debate [1, 2].

It has recently been shown that thermal ageing of citrate adsorbed 2LFh (at 175 °C) results in structural ordering and an increase in ferrimagnetic behaviour [3].

Electron energy loss spectroscopy (EELS) performed in the transmission electron microscope (TEM) can be used to determine both valence and co-ordination of iron in minerals by analysis of the Fe- $L_{2,3}$ energy loss peak. This method however should be used with caution for Fh since we have shown that it is sensitive to the high-energy electron beam of the TEM [4, 5].

We present here new TEM-EELS data which shows that the electron-beam induced sample alteration previously reported for 6LFh [4, 5] is driven by preferential oxygen loss. Additionally we present TEM-EELS characterisation of 2LFh co-precipitated with phosphorous pre and post thermal aging. We will focus on assessing the co-ordination and valence of the iron in the mineral as structural ordering develops.

- [1] Rancourt *et al.* (2008) *Am. Miner.* **93**, 1412–1417.
[2] Manceau (2009) *Clay Miner.* **44**, 19–34. [3] Michel *et al.* (2010) *P.N.A.S* **107**, 2787–2792. [4] Pan *et al.* (2006) *Micron* **37**, 403–411. [5] Pan *et al.* (2010) *Ultramicroscopy* "In Press, Corrected Proof" doi:10.1016/j.ultramic.2010.01.008

Water-oxide interfacial thermodynamics, aqueous growth control and confinement effects of nanostructured metal oxides and oxyhydroxides

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Ultra-divided systems such as colloidal and nanoparticle dispersions are generally unstable with regard to the size and number of their constituents because the solid-solution interfacial tension, acting as a driving force, leads to a reduction of the surface area to minimize the dispersion free enthalpy. Surface energy minimization induces an increase in the average particle size as a result of the decrease of the surface area at constant volume. Thus, these dispersions are usually considered thermodynamically unstable. However, they can be thermodynamically stabilized if, by adsorption, the interfacial tension of the system becomes very low. This phenomenon, well known for microemulsions, is quantitatively demonstrated for transition metal oxide nanoparticles. When the pH of precipitation is sufficiently far from the point-of-zero-charge and the ionic strength sufficiently high, the ripening of nanoparticles is avoided and their size can be monitored over one order of magnitude. A model based on Gibbs adsorption equation leads to an analytical expression of the water-oxide interfacial tension as a function of the pH and the ionic strength of the dispersion/precipitation medium. The stability condition, defined by a 'zero' interfacial tension, corresponds to the chemical and electrostatic saturation of the water-oxide interface. In such a condition, the density of charged surface groups reaches its maximum, the interfacial tension its minimum and further adsorption forces the surface area to expand and consequently, the size of nanoparticles decreases and metastable phases can be stabilized^[1,2].

Such ideas will be demonstrated on the controlled aqueous chemical growth of various oxide minerals such as *Akaganeite*, *Boehmite*, *Cassiterite*, *Hematite*, *Maghemite*, *Magnetite*, *Manganite* and *Zincite* in solution and by heterogeneous nucleation and growth as vertically oriented nanorod-arrays onto various substrates without template, surfactant, or applied field. In addition, size effect on the surface acidity (i. e PZC) of oxide^[3] will also be presented.

- [1] Vayssieres (2005) *Int. J. Nanotechnol.* **2**, 411–439.
[2] Vayssieres (2007) *Int. J. Nanotechnol.* **4**, 750–775.
[3] Vayssieres (2009) *J. Phys. Chem. C* **113**, 4733–4736.