2.8.21

Advances in characterizing nanophase materials and composites

D.G. RANCOURT

Department of Physics, University of Ottawa, Ottawa, Canada (dgr@physics.uottawa.ca)

The non-destructive physical characterization of solid materials that contain nanoclusters, nanoparticle aggregates, or nanostructures, from single phase synthetic samples to natural multi-phase composites such as soils and aquatic sediments, presents special challenges that are both experimental and theoretical. Experimental in that the particular (diffraction, spectroscopy, microscopy, or bulk response) method may not allow resolution or contrast/detection with nano-divided matter. Theoretical in that the measured response (diffractogram, spectrum, image, or signal) may require special treatment or analysis using tailored theoretical methods before it can be interpreted.

Part of the mandate of our Lake Sediment Structure and Evolution (LSSE) group is to develop such methods in areas of high need for natural and laboratory aquatic sediment geochemistry. Our main and recent achievements will be presented and include: (1) longstanding and ongoing developments in ^{57}Fe Mössbauer spectroscopy methodology, (2) significant recent advances in mineral magnetometry for dealing with composites that contain superparamagnetic (i.e., nano-size) particles having arbitrary distributions of supermoment and primary particle mass, and (3) exact X-ray diffraction (XRD) pattern simulation methods for arbitrary structure nanoparticles. The Mössbauer work includes: signal to noise optimization methods, lineshape theory for correlated multi-dimensional distributions of hyperfine parameters (required for the cryogenic spectra of most Fe oxyhydroxides), *ab initio* electronic structure predictions of hyperfine parameters for various coordination environments, and the first search and match identification algorithm and database for natural substances. The mineral magnetometry method (equilibrium measurements) provides the first exact treatment of nanoparticles having arbitrary distributions of the relevant primary particle characteristics and allows analysis of coexisting diamagnetic, paramagnetic, ferrimagnetic and ferromagnetic phases (in press, *Am.Mineral.*).

The XRD simulations are based on the exact Debye sum approach, rather than the usual crystallographic Bragg peak analyses (Scherrer, Williamson-Hall, etc.) that are expected to break down in the nanometer and Angstrom limits and that require an underlying crystal structure. Our simulator allows: any type of structure (crystalline to amorphous) and any spatial distribution of intra-particle (including surface and surface region) defects, intra-sample particle to particle variations, and all the usual powder diffractometer settings.

Examples of applications will focus on key results that could not easily have been obtained without these advances.

2.8.22

Controls on calcium phosphate cluster formation

E. VALSAMI-JONES[1], P.F. SCHOFIELD[1], N.J. TERRILL[2] AND C.M. MARTIN[3]

[1] Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK (evj@nhm.ac.uk; pfs@nhm.ac.uk)
[2] Diamond Light Source, Rutherford Appleton Laboratory, UK (nick.terrill@diamond.ac.uk)
[3] CLRC Daresbury Laboratory, UK (c.m.martin@dl.ac.uk)

Calcium phosphate cluster formation leads to the nucleation of apatite. Apatite controls phosphorus availability in the geosphere and is also an important biomineral (e.g. bone, tooth). Formation of apatite at the atomic scale is believed to take place via the formation of a $Ca_3(PO_4)_2$ precursor. Very little is currently known about the nature and evolution (in saturated aqueous solutions) of this precursor, and how this may be affected/controlled by the presence of organic species. Using the materials processing beamline, 6.2, at Daresbury Synchrotron Radiation Source for in-situ simultaneous small- and wide- angle X-ray scattering (SAXS/WAXS) experiments, we were able to to monitor apatite nucleation from supersaturated solutions at times scales of up to 30 minutes and at 10 second resolution. Our aim was to test the influence of a range of organic ligands (citrate, oxalate, osteocalcin) on nucleation and growth. Our preliminary observations suggest that organic ligands affect both the onset and the rate of crystal formation and growth, as well as the settling properties of apatite nucleating from a supersaturated solution (Figure 1). We discuss our results in the context of the precipitating apatite, as a proxy for bioapatites.

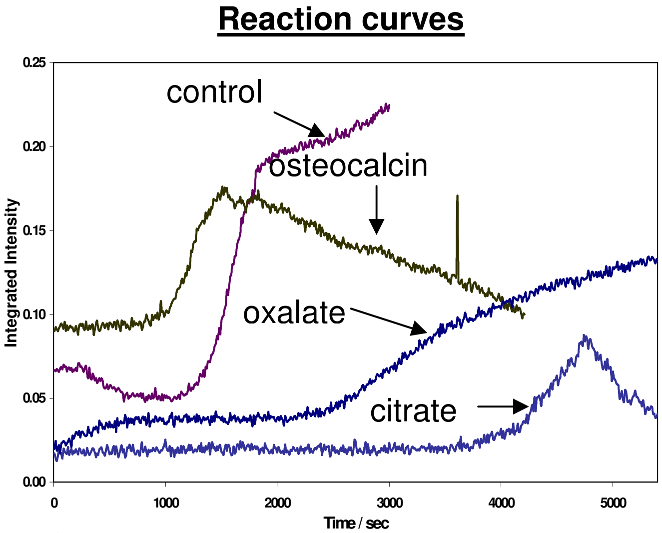

Figure 1. Intensity of scattering as a function of time for four solutions supersaturated with apatite: control, citrate (10^{-4}M), acetate (10^{-4} M) and osteocalcin (10^{-6} M).