Accurate multidisciplinary identification of nanophase iron minerals in simulated pedogenic environment

S.K. BANERJEE[1], R.L. PENN[2], T. BERQUÔ[1], Y. GUYODO[3] AND R. POPA[4]

[1]Department of Geology & Geophysics and the Institute for Rock Magnetism, University of Minnesota-Twin Cities, Minneapolis, MN, U.S.A. (banerjee@umn.edu)
[2]Department of Chemistry, University of Minnesota-Twin Cities, Minneapolis, MN, U.S.A. (penn@chem.umn.edu)
[3]Laboratoire des Sciences du Climat et de l'Environnement (UMR 1572, CEA/CNRS), Gif-sur-Yvette, France (yohan.guyodo@lsce.cnrs-gif.fr)
[4]Department of Marine Biology, University of Southern California, Los Angeles, CA, U.S.A. (rpopa@usc.edu)

We have begun an inter-disciplinary investigation (solid state chemistry, low temperature magnetism, Mössbauer effect and microbiology) to test chemical reactivity and environmental controls in simulated pedogenic transformations of nanophase (1-100 nm) iron oxyhydroxides and oxides of controlled size, crystallinity and impurity, in the presence or absence of iron-reducing bacteria (IRB). Pedogenic nanophase magnetite/maghemite end-products found in modern and ancient soils developed over loess (windblown silt deposits) parent materials in temperate climates are currently assumed to be proxies of annual rainfall (alone). We are testing and calibrating this abiotic model as well as comparing it with IRB-mediated magnetite formation since the latter (microbial type and concentration) could represent length of summer season and hence provide a new parameter, seasonality, for numerical climate model benchmarks.

Our research to date has led to a comparison of known synthesis techniques to produce monodisperse ferrihydrite (Fh) of different crystallinity, nanogoethite (Gt) and magnetite (Mt).High resolution transmission electron microscopy (HRTEM), x-ray absorption fine structure (XAFS) and Mössbauer spectra were used for sample characterization. Magnetometry and Mössbauer spectra at low temperatures (to 2.5K) and high field (to 5Tesla) have allowed cross-checked grain-size determinations. These two latter methods, used in conjunction, have proven to be rapid and reliable tools for granulometry, and for discovery of oriented aggregation in grain growth, adsorbed species on the surface and for core/shell distinction in these nanophase materials. Examples of data from iron oxyhydroxide precursors and their microbial conversion product of nanophase magnetite will be presented.

Nanoparticle-mediated processes and the Ostwald step rule

ALEXANDRA NAVROTSKY

NEAT ORU & Thermochemistry Facility, University of California, Davis, CA 95616, USA (anavrotsky@ucdavis.edu)

There is increasing recognition that many processes which involve crystallization or phase separation do not occur by classical nucleation and growth but rather by the aggregation of pre-existing nanoparticles of 2-3 nm size. Such particles may, because of a competition between the energetics of polymorphism and surface energetics, have structures of phases which are metastable when coarse-grained. Furthermore, within a given composition, it appears generally true that the more metastable a structure in the bulk, the lower its surface energy. The classical Ostwald step rule observes that, during crystallization, a series of metastable phases is often visited on the way down to the final appearance of the most stable crystals. As the figure shows, the correlation between metastability and decreasing surface energy may offer a rationalization of the Ostwald step rule. Nanoparticles of metastable phases may be more stable thermodynamically, as well as having lower energy barriers and smaller critical nuclei, than nanoparticles of the final stable phase. The crossover in stability between polymorphs may occur at much larger particle sizes than the "critical nucleus" for crystallization.