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Exploring effects of nanoscale exsolution on magnetic properties in the hematite-ilmenite series

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Magnetic properties of minerals in the hematite-ilmenite series vary considerably with absence or presence of exsolution, amount of exsolution, and size of exsolution. Phases in this series include R3 paramagnetic ilmenite, R3c paramagnetic titanohematite, CAF canted-antiferromagnetic hematite, and metastable R3 ferrimagnetic ferrian-ilmenite. CAF hematite is weakly magnetic. Ferrimagnetic ferrian-ilmenite can be strongly magnetic, if preserved by rapid cooling, but has a maximum Curie T of 280C. Slowly cooled, highly exsolved members of the series, have lamellae with thicknesses from several microns to 1-2 nm, equivalent to a single unit cell as shown by TEM [1-3]. Atomic simulations of lamellar contacts [4] showing “contact layers” between ilmenite and hematite in lamellar intergrowths has led to the theory of “lamellar magnetism” [5, 2].

Typical to all samples is high coercivity, and thermal stability, from 590-650C, producing strong and stable remanent magnetizations. The nanoscale exsolution lamellae would classically be considered to be superparamagnetic, too small to retain a magnetic memory. However, detailed rock-magnetic measurements show that in some composition ranges the nanoscale exsolution lamellae are magnetically ordered. Magnetic ordering may be affected by the high strain between the host and lamellar phases reflecting the different lattice parameters of the two phases. All nanoscale lamellae are coherent, whereas the larger lamellae are incoherent. The abundance of exsolution effects the total magnetic moment [3]. In addition there are major differences in magnetic properties where the host is paramagnetic ilmenite or CAF hematite.

References

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Synchrotron-based studies of nanoparticulate iron oxyhydroxide growth and metal uptake

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Iron oxyhydroxide minerals are present in many natural systems as dispersed and/or aggregated nanoparticles. However, the processes by which iron oxyhydroxides grow from nanosized to bulk particles is not well understood. Additionally, the effects of particle size and particle growth on contaminant sequestration, especially via particle aggregation, may have significant implications for contaminant sequestration and mobility. A suite of synchrotron-based techniques including X-ray absorption fine structure (XAFS) spectroscopy, small- and wide-angle X-ray scattering (SAXS/WAXS), and X-ray diffraction (XRD) was employed to study the growth of iron oxyhydroxide particles over a size range of 5-80 nm. Initial 5-nm particles were synthesized using a microwave synthesis technique; subsequent aging of these particles in suspension at 90°C over the course of 32 days resulted in batches with average particle sizes ranging from 10-80 nm in effective diameter. Further particle characterization was conducted using BET surface area analysis, laser light scattering, and transmission electron microscopy.

The growth of iron oxyhydroxide particles under these conditions occurs in two distinct stages: 1) rapid growth from 10-60 nm over the first 4 days followed by 2) slower growth from 60-80 nm over the next 28 days. XRD and WAXS data show a transition, primarily during the second stage, from a poorly-ordered phase (e.g. ferrihydrite) to well-crystalline goethite (α -FeOOH). SAXS data indicates that the initial population of 5-nm particles decreases directly over time and is replaced by significantly larger particles with a broad size distribution. In conjunction with TEM analysis, these trends suggest that the first stage of growth occurs primarily via oriented aggregation of 5-nm particles, while the second stage includes ripening-based growth and structural rearrangement into goethite.

XAFS spectroscopy analysis of sorption products featuring As(V), Cu(II), Hg(II), and Zn(II) show differences in both metal surface complex speciation and uptake as a function of particle size at the nanoscale, possibly due to changing proportions of binding sites (e.g. edges, corners) and an evolution of the particle morphology from oblong (5-nm) to tabular/acicular (25- and 75-nm) with time.