

## 1.6.12

### Probing the reactivity of iron oxides at the nanoscale: Magnetite with water and small organic molecules

D.J. VAUGHAN<sup>1</sup>, R.S. CUTTING<sup>1,2,3</sup>,  
C.A. MURYN<sup>2</sup> AND G.T. THORNTON<sup>2,4</sup>

<sup>1</sup>Williamson Research Centre for Molecular Environmental Science, and Department of Earth Sciences, Manchester University, Manchester M13 9PL, UK  
(David.Vaughan@man.ac.uk)

<sup>2</sup>Department of Chemistry, Manchester University, Manchester M13 9PL, UK (C.Muryn@man.ac.uk)

<sup>3</sup>Advanced Materials Research Institute, Northumbria University, Newcastle-upon-Tyne, NE1 8ST, UK  
(richard.cutting@unn.ac.uk)

<sup>4</sup>Department of Chemistry, University College London, London WC1E 6BT, UK (g.thornton@ucl.ac.uk)

Application of a combination of scanning probe microscopic and spectroscopic methods under highly controlled conditions is the key to understanding the reactivity of many mineral surfaces at the nanoscale, whether it be of small particles or larger crystals. The (111) surface of Fe<sub>3</sub>O<sub>4</sub> (magnetite) provides an excellent example for detailed study. Our work shows that carefully prepared surfaces can exhibit four different kinds of termination, only one of which exposes both (uncapped) iron and oxygen atoms.

In addition to imaging freshly prepared magnetite surfaces, the reactivities of such surfaces have been explored using Scanning Tunneling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) following exposure to H<sub>2</sub>O, HCOOH, C<sub>5</sub>H<sub>5</sub>N and CCl<sub>4</sub>. These studies enable both the validation of models of surface structure and the investigation of the mechanisms of reaction. The surface that exposes (uncapped) both iron and oxygen atoms is the most reactive to all of these molecules. The other surfaces exhibit reactive behaviour that relates to the presence of point defects.

Variable temperature STM studies, along with XPS and UPS investigations, of the reaction of magnetite with water vapour show limited reactivity at low exposures. Under higher water vapour exposures (100L of H<sub>2</sub>O) and isothermal isobaric conditions, the magnetite surface undergoes extensive hydroxylation. Spectra obtained at different pH<sub>2</sub>O show that both pressure and exposure level influence the onset of extensive dissociation of water on interaction with Fe<sub>3</sub>O<sub>4</sub>.

## 1.6.13

### Nanometer-scale texture and magnetic frustration in exsolved magnetite inclusions in clinopyroxene

J.M. FEINBERG<sup>1</sup>, G.R. SCOTT<sup>2</sup>, P.R. RENNE<sup>1,2</sup>  
AND H.R. WENK<sup>1</sup>

<sup>1</sup>University of California, Berkeley, U.S.A.  
(feinberg@eps.berkeley.edu)

<sup>2</sup>Berkeley Geochronology Center, California, U.S.A.

To successfully unravel the behavior of the Earth's ancient magnetic field, it is important to identify and characterize the minerals that record it. Magnetite inclusions in pyroxene and plagioclase have been noted as the carriers of stable magnetic remanence in slowly cooled rocks such as gabbros, anorthosites, granulites, and diorites. These needle-shaped inclusions have average dimensions of 1 by 1 by 50 microns and are inferred to be products of exsolution, forming epitaxially within their host silicate. Multiple mechanisms have been proposed to explain the high coercivities frequently associated with these inclusions (e.g., extreme shape anisotropy, and crystal defect pinning of magnetic domain boundaries). To evaluate these mechanisms, the microstructure within inclusions in clinopyroxene crystals was imaged using atomic and magnetic force microscopy (AFM and MFM).

AFM images of magnetite inclusions from clinopyroxene crystals with coercivities >80 mT show a second, nonmagnetic phase forming a network of walls within the inclusion with thicknesses <20 nm parallel to {100} of magnetite. The remaining magnetite is partitioned into orthogonal parallelepipeds with sides 50-200 nm long, creating a nano-scale boxwork texture. The nonmagnetic phase was also observed using an analytical transmission electron microscope and is rich in Fe, Ti, and Cr with a spinel structure. This internal segmentation is the product of a second, lower temperature stage of exsolution. The temperature and duration over which this oxide exsolution event occurred are not well constrained. These segmented inclusions exhibit a unique kind of stable magnetic domain state, whereby individual boxes of magnetite act as single domains whose directions are strongly influenced by those of neighboring boxes and are stabilized by the surrounding nonmagnetic phase. The distribution of magnetization directions among adjacent boxes generates a geometrically induced magnetic frustration, which in turn increases the coercivity. Thus, the magnetic field required to change the magnetization direction in any single magnetite block must be large enough to overcome 1) the magnetic energies internal to the block and 2) the magnetostatic energy from all neighboring blocks. In short, the magnetic stability that makes these inclusions useful to paleomagnetic studies is an outgrowth of the nanometerscale mineral texture within them.