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Oxidation of Pseudo-Single Domain Fe_3O_4 Particles and Associated Magnetic Response Examined by Environmental TEM and Off-Axis Electron Holography

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In order to interpret palaeomagnetic measurements reliably, the mechanisms that induce magnetic remanence in naturally occurring magnetic recorders and those that can subsequently alter it must be fully understood. Whilst some mechanisms, such as thermoremanent magnetisation (TRM) acquisition, are well known, there is also a broad class of mechanisms that come under the heading of chemical remanent magnetisation (CRM). The latter mechanisms can result in either the acquisition or the alteration of remanence and occur frequently in nature, but are still poorly understood [1]. Current models of CRM processes only exist for the smallest uniformly-magnetised single domain (SD) grains. However, magnetic signals from rocks are often dominated by larger grains that contain non-uniform pseudo-SD (PSD) magnetisation states. In contrast to larger, more weakly magnetic multi-domain grains, PSD grains often exhibit magnetic recording fidelities that are similar to those of SD grains. However, there is very little understanding of their CRM properties [2].

Magnetite (Fe_3O_4) is the most magnetic naturally occurring mineral on Earth [3], carrying the dominant magnetic signature in rocks and providing a critical tool in paleomagnetism. The oxidation of Fe_3O_4 to other iron oxides, such as maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3), is of particular interest as it influences the preservation of remanence of the Earth's magnetic field by Fe_3O_4. During oxidation, the inverse spinel ferrite Fe_3O_4 reacts with oxygen to form the Fe^{2+} cation deficient phase γ-Fe_2O_3, which can then further oxidise to form hexagonally-close-packed α-Fe_2O_3 [4].

Spherical aberration (C_S) correction combined with environmental transmission electron microscopy (ETEM) enables the detailed investigation of localised chemical reactions under gas atmospheres with an interpretable spatial resolution that can reach the sub-Ångstrom level [5]. Off-axis electron holography permits nanometre-scale imaging of magnetic induction within and around materials as a function of applied field and temperature [3, 6]. The complementary use of these advanced TEM techniques can be used to reveal local changes in magnetisation in minerals as they alter during *in situ* heating in a controlled oxidising atmosphere. Such experiments can provide direct information about the relationship between magnetic domain structure and chemical alteration features, phase boundaries and crystalline microstructure.

In the present study, synthetic Fe_3O_4 particles with sizes in the PSD range (< 300 nm) were heated *in situ* in an ETEM to a temperature of 700 °C in 8 mbar of O_2. Oxidation of the Fe_3O_4 particles was investigated using bright-field and dark-field imaging, nano-diffraction, and electron energy-loss spectroscopy (EELS). Close examination of an individual Fe_3O_4 particle (Fig. 1a) revealed surface degradation and the formation of additional nanoparticles after heating (Fig. 1b). Corresponding EEL spectra revealed features close to the Fe 2p *L*-edge (Fig. 1c, d), acquired using an energy resolution of

~ 0.5 eV before and after *in situ* heating (Fig. 1c, d, arrowed), that are in good agreement with the presence of Fe_3O_4 (Fig. 1c) and α-Fe_2O_3 (Fig. 1d) [7], respectively. The associated alteration in CRM exhibited by individual Fe_3O_4 particles was investigated using off-axis electron holography (Fig. 2a), in the form of reconstructed magnetic induction maps (Fig. 2b).

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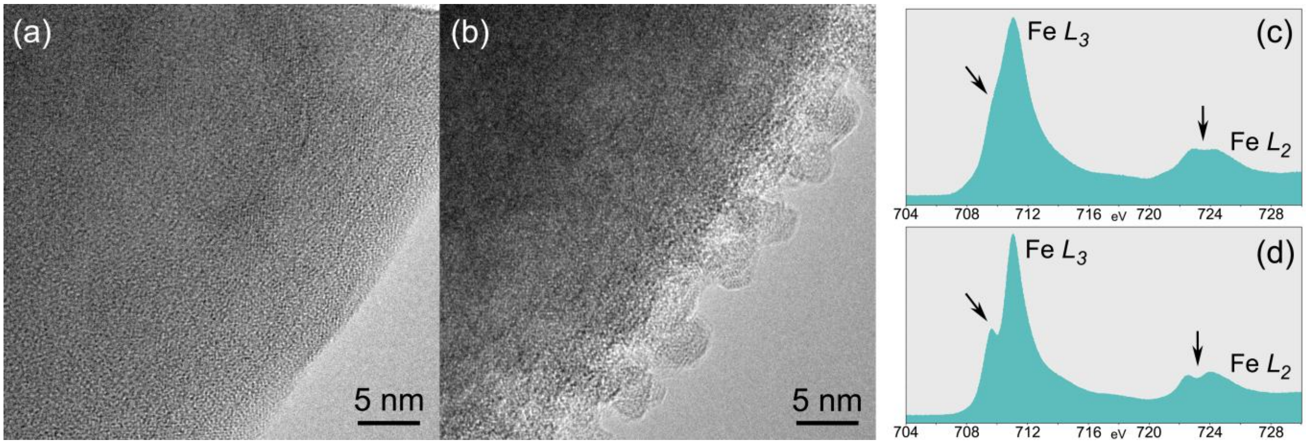

Figure 1 (a, b) Bright-field TEM images of the surface of an individual Fe_3O_4 particle acquired (a) before and (b) after *in situ* heating to 700 °C in 8 mbar of O_2 in an ETEM. (c, d) EEL spectra acquired close to the Fe 2p *L*-edge (c) before and (d) after *in situ* heating, revealing fine features (arrowed) that are characteristic of the presence of Fe_3O_4 and α-Fe_2O_3, respectively.

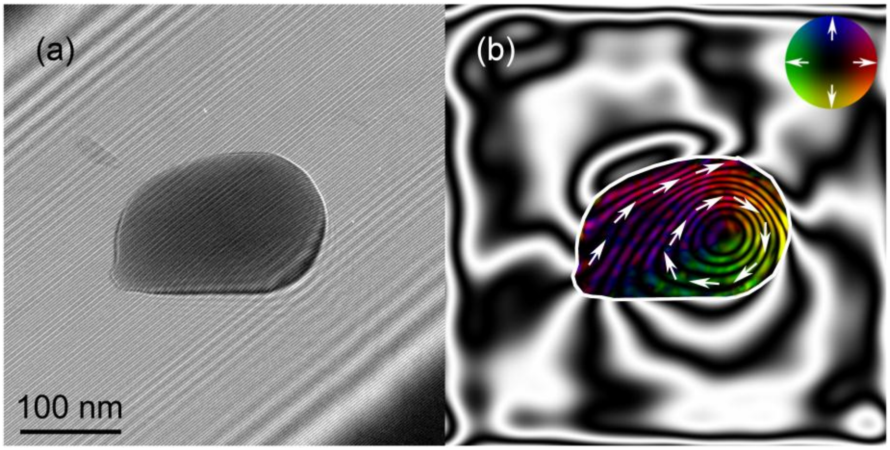

Figure 2 (a) Off-axis electron hologram of an individual Fe_3O_4 particle in the PSD size range (~ 200 nm) acquired in magnetic field-free conditions and (b) the corresponding magnetic induction map determined from the magnetic contribution to the phase shift reconstructed from holograms similar to that shown in (a), revealing the PSD nature of the particle, which contains both a magnetic vortex and a stray magnetic field similar to that expected for a SD particle.