**Visualized effects of oxidation and temperature on pseudo-single-domain $Fe_3O_4$ particles examined by environmental TEM and off-axis electron holography**

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Magnetic minerals in rocks record the direction and intensity of the ambient magnetic field during formation, providing, for example, varied information of the geomagnetic field and past tectonic plate motions. Magnetic carriers in the single domain (SD) grain size range (< 100 nm) are regarded as ideal paleomagnetic recorders because of their strong remanence and high magnetic stability, with potential relaxation times that are greater than the age of the Universe. However, magnetic signals from rocks are often dominated by small multi-domain grains that exhibit magnetic recording fidelities similar to those of SD grains (termed pseudo-SD (PSD)). To reliably interpret paleomagnetic signals from these PSD grains, mechanisms which induce and alter their magnetic remanence must be fully understood.

Magnetite ($Fe_3O_4$) is the most magnetic naturally occurring mineral on Earth, carrying the dominant magnetic signature in rocks and providing a critical tool in paleomagnetism [1]. The oxidation of $Fe_3O_4$ to other iron oxides, such as maghemite (γ-$Fe_2O_3$) and hematite (Φ#177;-$Fe_2O_3$), is of particular interest as it influences the preservation of remanence of the Earth's magnetic field by $Fe_3O_4$. Further, signals in $Fe_3O_4$ grains are acquired in the direction of the geomagnetic field as they cool below their Curie temperature ($T_C$) of ~ 580 °C. However, current understanding of the effects of oxidation and thermomagnetic behaviour of PSD remanence in $Fe_3O_4$ grains is restricted to bulk magnetic measurements and numerical models. Fortunately, the advanced transmission electron microscopy (TEM) techniques of off-axis electron holography and environmental TEM allow for magnetic imaging of nano-scale minerals during *in situ* heating under controlled atmospheres.

In the present study, synthetic $Fe_3O_4$ particles in the PSD size range (< 200 nm) were heated *in situ* in an environmental TEM to a temperature of 700 °C in 8 mbar of $O_2$ [2]. The oxidation of the $Fe_3O_4$ particles was monitored qualitatively using electron energy-loss spectroscopy (EELS). Fig. 1a shows a native smooth-surfaced $Fe_3O_4$ grain and complementary EELS analysis of the Fe 2p $L_{2,3}$ edge is in good agreement with that of pure $Fe_3O_4$ (Fig. 1b, blue spectra). Close examination of the EEL spectra after *in situ* heating revealed the development of pre-peaks (arrowed) close to the Fe 2p $L_{2,3}$ edge (Figs. 1b, red spectra) that are indicative of oxidation. The associated effect of oxidation on their magnetic remanence was investigated using electron holography, in the form of reconstructed magnetic induction maps, where the oxidised grains exhibited a change in remanent strength and direction (Fig. 1c,d). The thermomagnetic behaviour of $Fe_3O_4$ particles in the PSD size range is also investigated using electron holography (Fig. 2) [3-5]. Magnetic induction maps recorded during *in situ* heating to just below the $T_C$, reveal the thermal stability of several PSD $Fe_3O_4$ grains by visualizing their vortex domain states. The vortex states in small $Fe_3O_4$ grains are shown to rotate close to its $T_C$ (Fig. 2b-d), rather than remaining thermally stable as seen in the vortex states of larger $Fe_3O_4$ grains.

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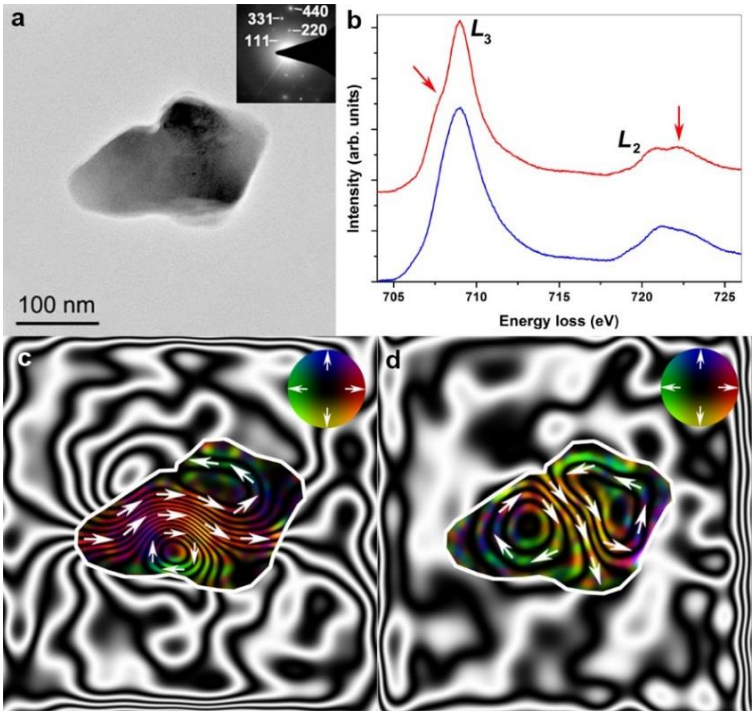


**Fig. 1** (a) TEM image of an $Fe_3O_4$ particle and (b) Fe edges of the EEL spectrum acquired before (blue) and after oxidation (red). (c,d) Magnetic induction maps of the particle (c) before; and (d) after oxidation.

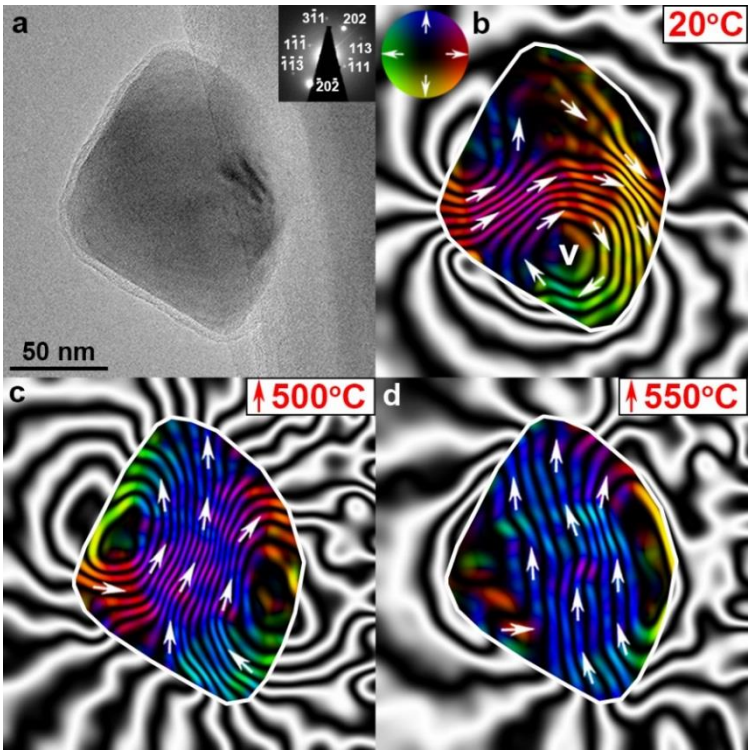


**Fig. 2** (a) TEM image of an $Fe_3O_4$ particle and magnetic induction maps taken (b) at 20°C; during *in situ* heating to (c) 500°C; and (d) 550°C.