[E4.2011] *In situ* transmission electron microscopy and off-axis electron holography of thermal demagnetisation in non-ideal palaeomagnetic recorders

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Summary. The thermomagnetic behaviour of magnetite (Fe_3O_4) particles in the pseudo-single domain (PSD) size range is investigated using off-axis electron holography. Magnetic induction maps, which are recorded at 100 ºC intervals during *in situ* heating up to 700 ºC, reveal the presence of vortex domain states in two individual Fe_3O_4 grains. Although one of the vortex states is shown to rotate or collapse into a single-domain state close to its unblocking temperature rather than remaining thermally stable, both grains recover their initial in-plane remanent intensities upon cooling. Our results therefore suggest that evidence for PSD behaviour should not preclude palaeomagnetic investigations.

Introduction. Magnetite (Fe_3O_4) is arguably the most important naturally occurring magnetic mineral on Earth due to its high abundance and strong, dominating magnetisation. The development of a full understanding of its thermal behaviour and magnetic recording fidelity is therefore crucial to the field of palaeomagnetism. Of the constituent magnetic minerals that are found in rocks, particles in the single domain (SD) grain size range (< 100 nm) are regarded as ideal palaeomagnetic 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)). In order to fully understand the thermomagnetic behaviour of these non-ideal palaeomagnetic recorders, it is necessary to examine the effect of temperature on their PSD magnetic domain states directly. The transmission electron microscopy (TEM) technique of off-axis electron holography permits nanometre-scale imaging of magnetic induction within and around materials as a function of applied field and temperature[1]. This is the only technique that is presently able to provide high-resolution images of magnetic domain states in nanometric grains. It has been applied in mineral magnetism for more than a decade[2,3] but has not previously been used to examine thermal behaviour in minerals above room temperature. Here, the first use of off-axis electron holography to examine local changes in remanent magnetization in PSD magnetite grains during *in situ* heating is presented.

Materials / Methods. Fe_3O_4 grains with diameters ranging from ~150 to ~250 nm were heated *in situ* in the TEM to 700 °C. Off-axis electron holograms were acquired at 300 kV in Lorentz mode in Titan 80-300 TEMs equipped with charge-coupled device cameras and electron biprisms. The direction of magnetization in each particle was initially reversed at room temperature *in situ* in the TEM by tilting the sample by ±30° or ±75° and turning on the conventional microscope objective lens to apply a magnetic field of > 1.5 T to the sample parallel to the direction of the electron beam. The objective lens was then turned off and the sample tilted back to 0° for hologram acquisition in magnetic-field-free conditions with the particles induced with a room temperature saturation isothermal remanent magnetisation (SIRM). Electron holograms were recorded with each particle magnetized in opposite directions, in order to determine the mean inner potential contribution to the phase. Holograms were then acquired in magnetic-field-free conditions at 100 °C intervals during *in situ* heating from 100 to 700 °C using Protochips or DensSolutions heating holders and again upon cooling. The mean inner potential contribution to the phase was subtracted from the phase image recorded at each temperature to allow the construction of magnetic induction maps representative of the magnetic remanence.

Results and Discussion. Figure 1 shows the effect of heating and cooling on the room temperature SIRM of a smooth-surfaced Fe_3O_4 grain (~200 nm in diameter, Fig. 1a), visualised in the form of a series of magnetic induction maps (Figs. 1b-d)[4]. The initial magnetic induction map (Fig. 1b) contains evenly-spaced magnetic contours from the surface to the centre of the grain, which flow in a counter-clockwise direction (denoted by arrows) and are indicative of a vortex state. The magnetic induction map shown in Fig. 1c demonstrates the effect of increasing the temperature to 500 °C, with a widening of the phase contours within the Fe_3O_4 grain that is suggestive of a reduction in the remanent magnetic

field. (Electron-beam-induced charging of the specimen is also visible outside the particle). The magnetic induction map in Fig. 1d shows the effect of cooling to 200 °C, with a narrowing of the magnetic contours demonstrating the recovery of the remanent magnetic field.

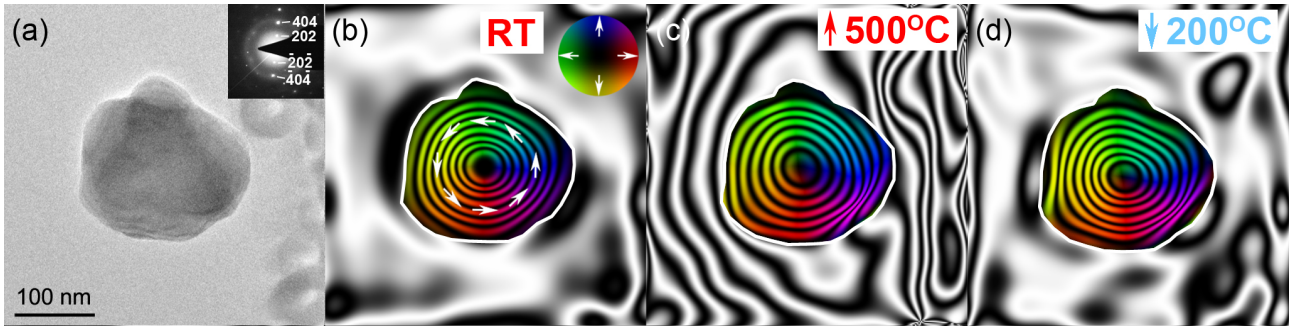

Figure 1 (a) Bright-field TEM image of an Fe_3O_4 particle (~200 nm diameter) and a selected area electron diffraction pattern (inset) indexed to Fe_3O_4 (JCPDS 75-449), shown alongside magnetic induction maps reconstructed from electron holograms taken (b) at room temperature, (c) during *in situ* heating to 500°C and (d) upon cooling to 200°C.

A different Fe_3O_4 grain (~180 nm in diameter, Fig. 2a) also exhibited a magnetic vortex state at room temperature, flowing in a clockwise direction (Fig. 2b). The magnetic phase contours in the vortex domain state again widen with increasing temperature and subsequently transform to a single domain state at 500 °C (Fig. 2c), before becoming fully demagnetised at 600 °C. The vortex structure is then recovered upon cooling to 400 °C, but with the magnetic contours flowing in an anti-clockwise direction (Fig. 2d).

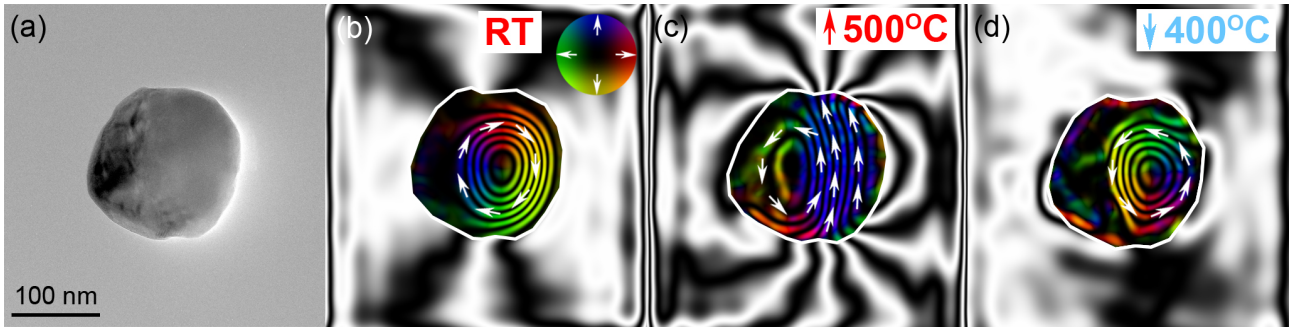

Figure 2 (a) Bright-field TEM image of an Fe_3O_4 particle (~180 nm diameter), shown alongside magnetic induction maps reconstructed from electron holograms taken (b) at room temperature, (c) during *in situ* heating to 500°C and (d) upon subsequent cooling to 400 °C.

Based on the present study, the directions of the vortex cores are unknown as they lie normal to the planes of the Fe_3O_4 grains. However, the key finding is that the vortex structure in the Fe_3O_4 grain shown in Fig. 1 is essentially stable during heating to a temperature close to the Curie temperature of ~585 °C and subsequently reversible upon cooling to room temperature. Therefore, in this instance, the magnetic structure preserves its in-plane directional recording information. In contrast, the Fe_3O_4 grain shown in Fig. 2 either experiences a rotation of the magnetic vortex with increasing temperature or a possible collapse into a SD state prior to reaching its unblocking temperature. Nevertheless, relaxation into a vortex state flowing in the opposite direction upon cooling confirms that the Fe_3O_4 grain palaeointensity like a uniaxial SD particle.

Conclusion. Our direct observations demonstrate visually, for the first time, the thermomagnetic stability of PSD magnetite grains. These findings imply that structures that initially appear to be non-ideal magnetic recorders are in fact likely to record palaeointensity information reliably and need not preclude palaeomagnetic studies.