Direct visualisation of the thermal demagnetisation of pseudo-single domain magnetite particles

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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 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.

Experimental

- Fe_3O_4 particles (~ 150 to ~ 250 nm in diameter), in powder form or embedded within a silicate matrix, were heated from room temperature to 600˚C in an FEI Titan HOLO TEM (Figure 1), operated at 300 kV.
- Off-axis electron holograms were acquired at 300 kV in Lorentz mode with an electron biprism operated typically at 90 V (Figure 2).
- The direction of magnetization in each particle was initially reversed at room temperature *in situ* in the TEM by tilting the sample by ±75° and turning on the conventional microscope objective lens to apply a magnetic field of > 1.5 T.
- 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 50 or 100 °C intervals during *in situ* heating from 100 to 550 °C or 600 °C using single or double tilt DENSsolutions heating holders (Figure 3), and again upon cooling.
- The mean inner potential, acquired in a separate experiment, was subtracted to construct the magnetic induction maps representative of the magnetic remanence.

Figure 1 FEI Titan HOLO TEM with C_S correction on the objective lens and equipped with 3 biprisms and Lorentz lens for electron holography of magnetic fields, as well as a 11 mm pole piece gap for tilting to ± 75º.

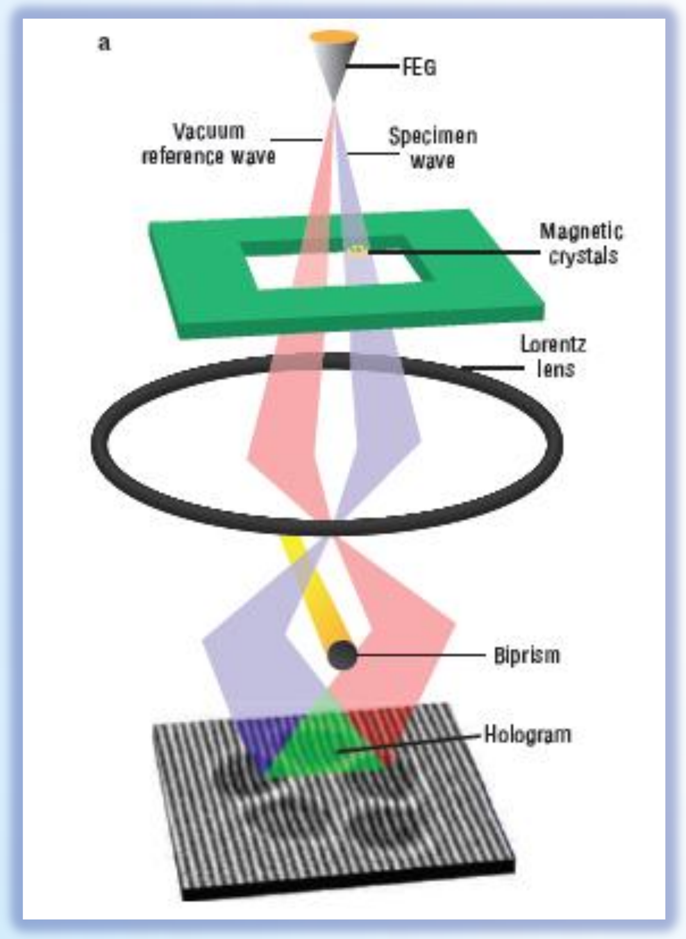

Figure 2 Schematic diagram of the setup for off-axis electron holography. Application of a voltage to the biprism induces an overlap of the specimen and reference electron waves, resulting in interference fringes[1].

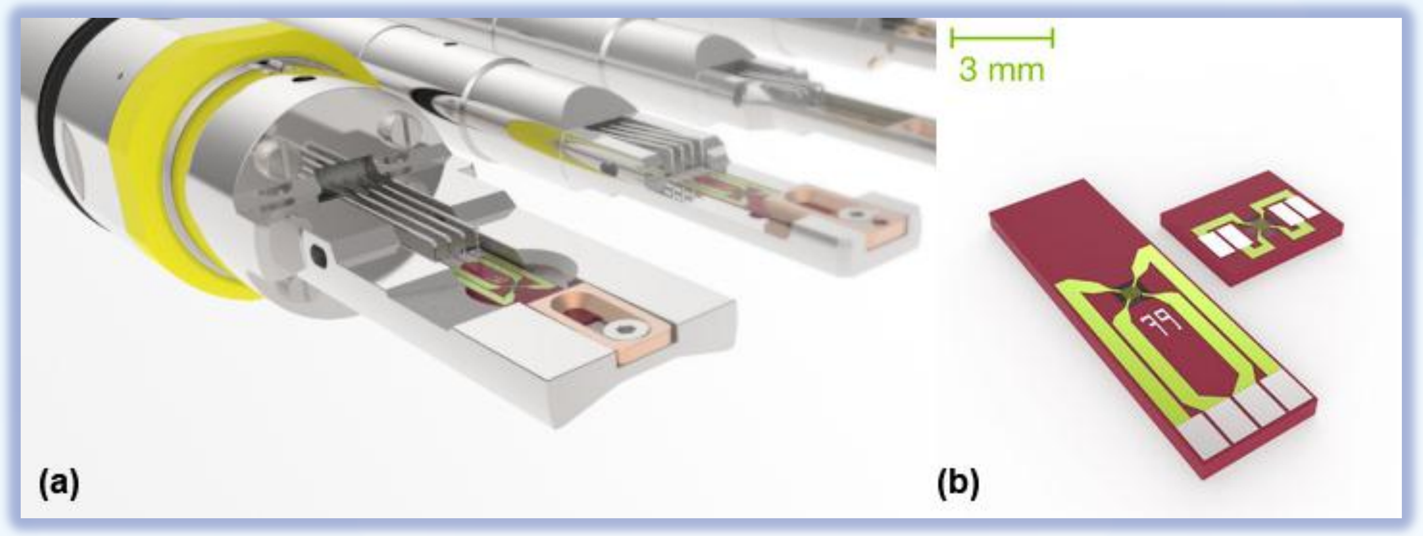

Figure 3 Images of DENSsolutions (a) *in situ* single-tilt TEM heating holder; and (b) EMheaterchips™.

Results

Figures 4 - 7 show the effect of heating and cooling on the room temperature saturation isothermal remanent magnetisation (SIRM) of several Fe_3O_4 grains, either in powder form (Figs 4 – 6) or embedded within a silicate matrix (Fig. 7). Their thermomagnetic behaviour is visualised in a series of magnetic induction maps, which were reconstructed from the magnetic contribution to the total phase shift, after subtraction of the mean inner potential contribution.

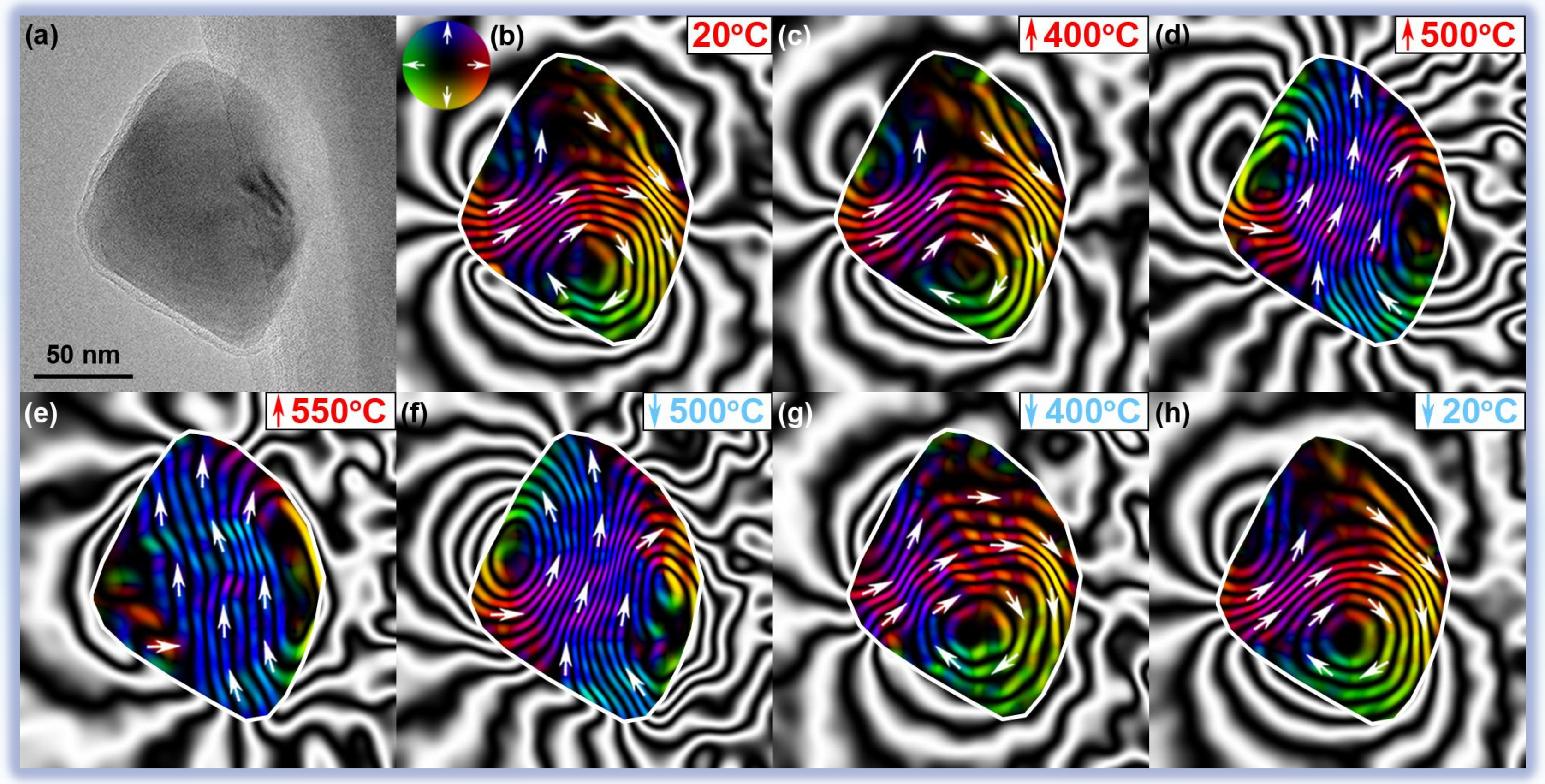

Figure 4 (a) Bright-field TEM image of an individual Fe_3O_4 particle (~ 150 nm in diameter). (b-h) Magnetic induction maps reconstructed from holograms taken at (b) room temperature; and during *in situ* heating to (c) 400˚C; (d) 500˚C; (e) 550˚C; as well as upon subsequent cooling to (f) 500˚C; (g) 400˚C; and (h) room temperature.

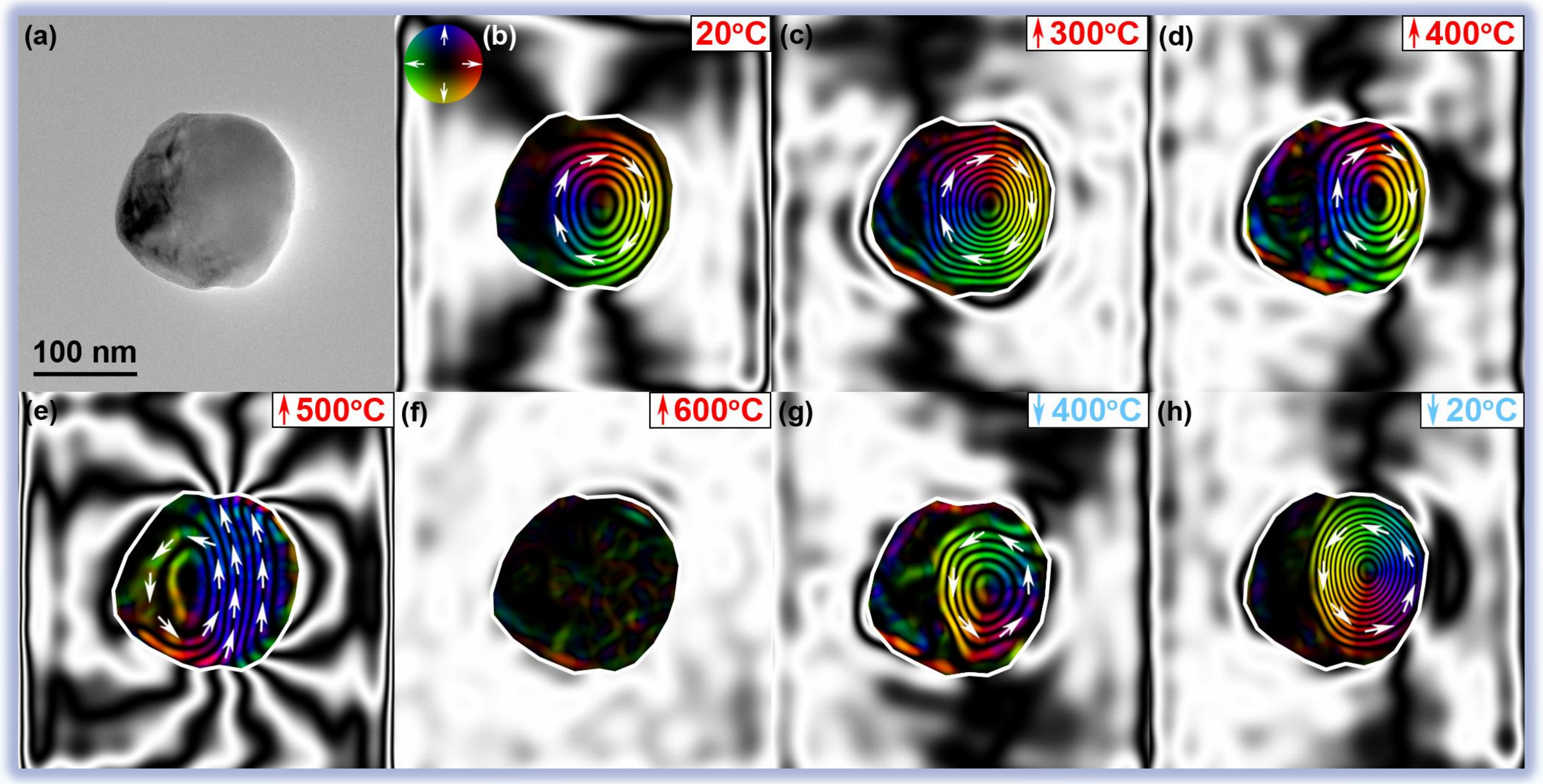

Figure 5 (a) Bright-field TEM image of an individual Fe_3O_4 particle (~ 180 nm in diameter). (b-h) Magnetic induction maps reconstructed from holograms taken at (b) room temperature; and during *in situ* heating to (c) 300˚C; (d) 400˚C; (e) 500˚C; (f) 600˚C; as well as upon subsequent cooling to (g) 400˚C; and (h) room temperature.

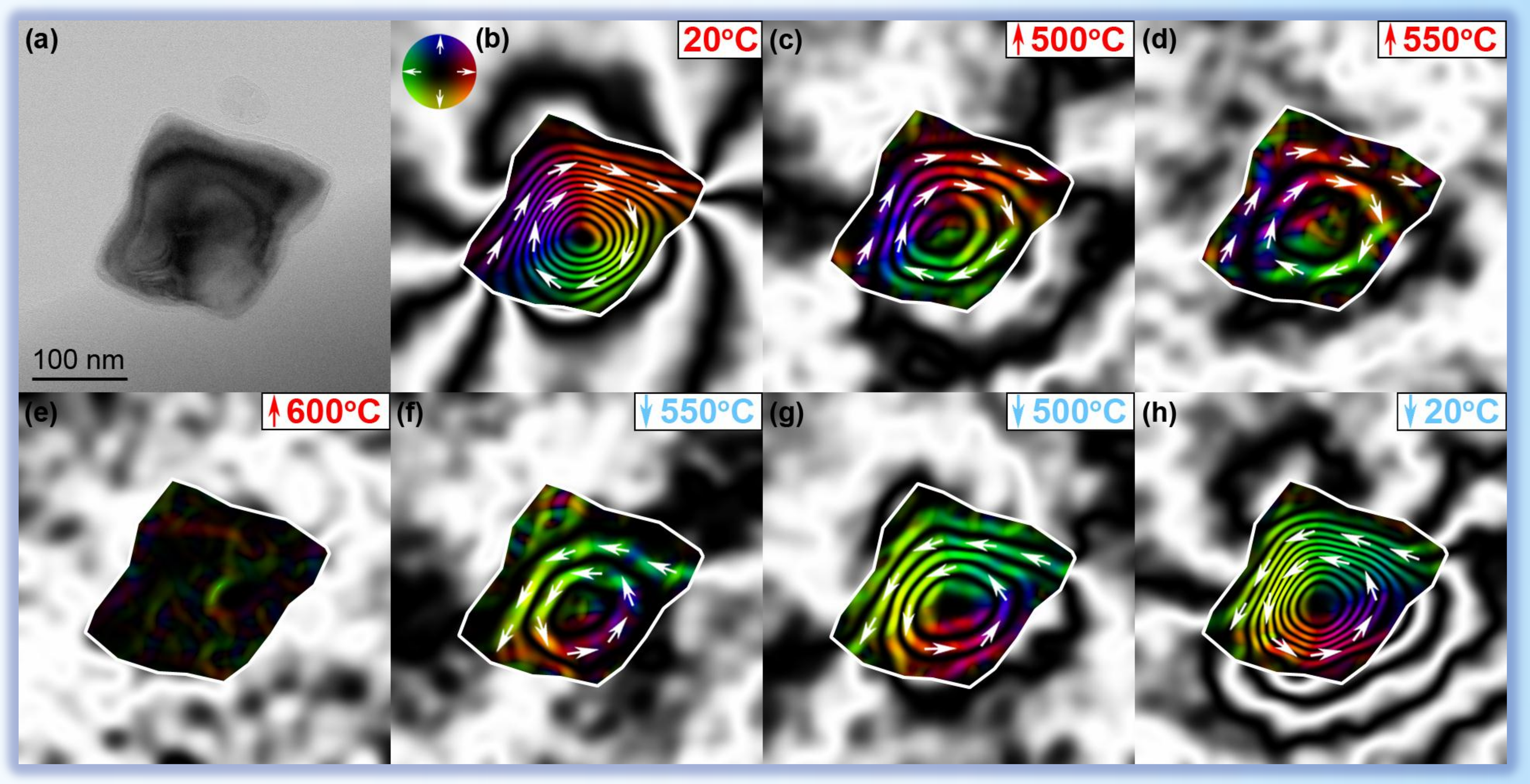

Figure 6 (a) Bright-field TEM image of an individual Fe_3O_4 particle (~ 250 nm in diameter). (b-h) Magnetic induction maps reconstructed from holograms taken at (b) room temperature; and during *in situ* heating to (c) 500˚C; (d) 550˚C; (e) 600˚C; as well as upon subsequent cooling to (f) 550˚C; (g) 500˚C; and (h) room temperature.

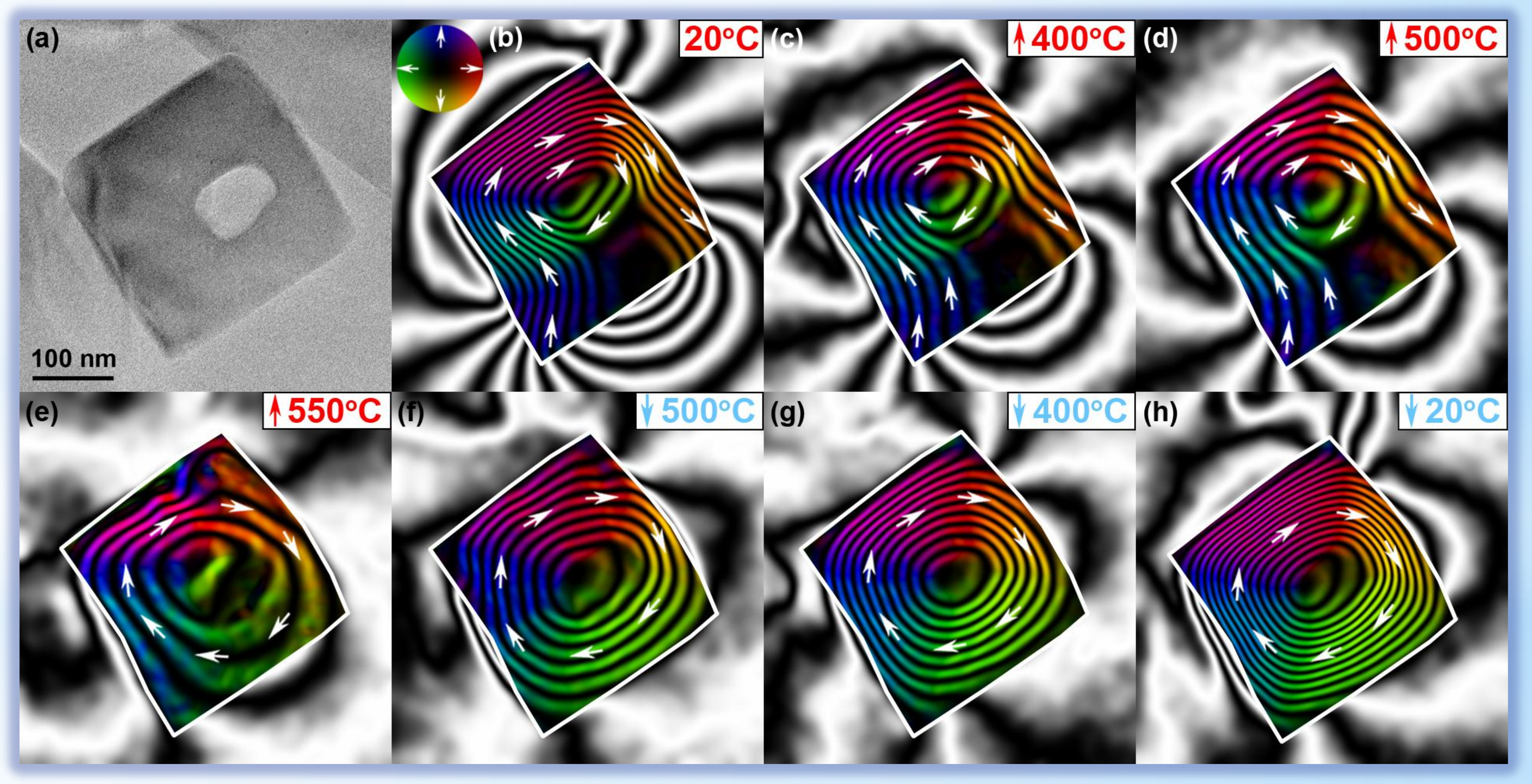

Figure 7 (a) Bright-field TEM image of an individual Fe_3O_4 particle (~ 400 nm in diameter). (b-h) Magnetic induction maps reconstructed from holograms taken at (b) room temperature; and during *in situ* heating to (c) 400˚C; (d) 500˚C; (e) 550˚C; as well as upon subsequent cooling to (f) 500˚C; (g) 400˚C; and (h) room temperature.

Discussion and Conclusions

- This *in situ* TEM and off-axis electron holography investigation provides a visualised representation of the effect of temperature on the SIRM of PSD Fe_3O_4 particles.
- Figs. 4b – 2h demonstrate the effect of increasing temperature from 20˚C to 550˚C, where the Fe_3O_4 grain's PSD vortex state transforms to a SD domain as it approaches its Curie temperature (T_C), ~585˚C, which then recovers its original PSD state upon cooling.
- The Fe_3O_4 grain in Fig. 5 exhibits a similar behaviour to Fig. 4, transforming from a vortex state to SD just below the T_C. However, after heating to above the T_C, the Fe_3O_4 grain acquires a vortex structure flowing in the opposite direction upon cooling.
- The larger Fe_3O_4 grain (Fig. 6) retains its vortex state up to 550˚C before demagnetising above the T_C. It acquires a vortex structure flowing in the opposite direction upon cooling.
- The Fe_3O_4 grain in Fig. 7 exhibits a horse-shoe shaped magnetic domain state, as well as a stray magnetic field. Upon heating to just below the T_C, the domain state transforms to a vortex state, which magnetic intensity increases upon cooling back to room temperature.
- Hence, critical insight into the effect of temperature is presented, having significant implications for the field of palaeomagnetism and reliable interpretation of associated data, with particle size playing a key role in their thermomagnetic behaviour.

References

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