

Dynamic exsolution of titanomagnetites and their associated magnetic response examined by complementary environmental TEM and off-axis electron holography

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In order to reliably interpret palaeomagnetic data, the mechanisms that induce magnetic remanence and those that can subsequently alter it must be fully understood. Whilst some mechanisms, e.g., thermoremanent magnetisation (TRM) acquisition, are well known, there is a broad class of remanence acquiring or altering mechanisms termed chemical remanent magnetisation (CRM) and thermochemical remanent magnetisation (TCRM), that are poorly understood, yet frequently occur in nature [1]. Currently, models of CRM processes only exist for the smallest, uniformly magnetised grains, termed single domain (SD). However, the magnetic signal from rocks is often dominated by slightly larger grains containing non-uniform magnetisation states and these are termed pseudo-SD (PSD) grains. In contrast to the largest and weakly magnetic multi-domain grains, PSD grains often exhibit magnetic recording fidelities similar to SD grains yet there is very little understanding of their CRM properties [2].

Magnetic properties of naturally occurring basalts strongly depend on grain size and chemical composition of their ferrimagnetic constituents - the titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$, $0 \leq x \leq 1$). However, the magnetic properties of titanomagnetites may be affected by low temperature exsolution into separate ulvospinel (Fe_2TiO_4) and magnetite (Fe_3O_4) phases [3]. This two-phase intergrowth is a common feature in titanomagnetites found in basic rocks from hypabyssal and plutonic environments. The intergrowth structure generally consists of a 3D framework of ulvospinel-rich lamellae with interlamellar magnetite-rich blocks. This microstructure only develops on a small scale due to the slowness of the kinetic processes involved in unmixing of titanomagnetites, typically in the temperature range between 500-600°C. Consequently, the exsolution of titanomagnetites in the PSD size range has a marked effect on their corresponding magnetic remanence [4].

The latest advanced transmission electron microscopy (TEM) techniques like off-axis electron holography and environmental TEM (ETEM) allows for the imaging of magnetisation on nanometre scales as minerals alter during *in situ* heating under controlled oxidising/reducing atmospheres. Off-axis electron holography provides nanoscale imaging of the induction field produced by the magnetic structures in the samples as function of applied field and temperature [5,6]. The imaging can be done in a controlled atmosphere, allowing for direction observation of the magnetic structure on a sub nanometre scale as titanomagnetites chemically alter through exsolution. Hence, domain images and how they relate to the chemical alteration features, phase boundaries and the crystalline structure can be directly visualised.

In this context, titanomagnetite grains of varying degrees of oxidation state and Ti content have been synthesised within a glass-ceramic matrix. Samples were heated to 1400°C in a gas-mixing furnace under a controlled CO/CO₂ atmosphere for 15 hours until molten and subsequently quenched, following a previously reported method [7]. To promote nucleation of titanomagnetite grains, the samples were reheated to 750°C for 3 hours and again quenched. The size and crystal structure of the PSD titanomagnetite grains (< 1.5 μm) were confirmed by complementary secondary electron microscopy (SEM) (Figure 1a) and X-ray diffractometry (XRD) (Figure 1b), respectively. In order to understand exsolution of synthetic PSD titanomagnetite grains (Figure 2)

and the associated alteration of the CRM, examination of the samples whilst heating *in situ* within the ETEM, along with imaging their magnetic response using electron holography, is presented.

References

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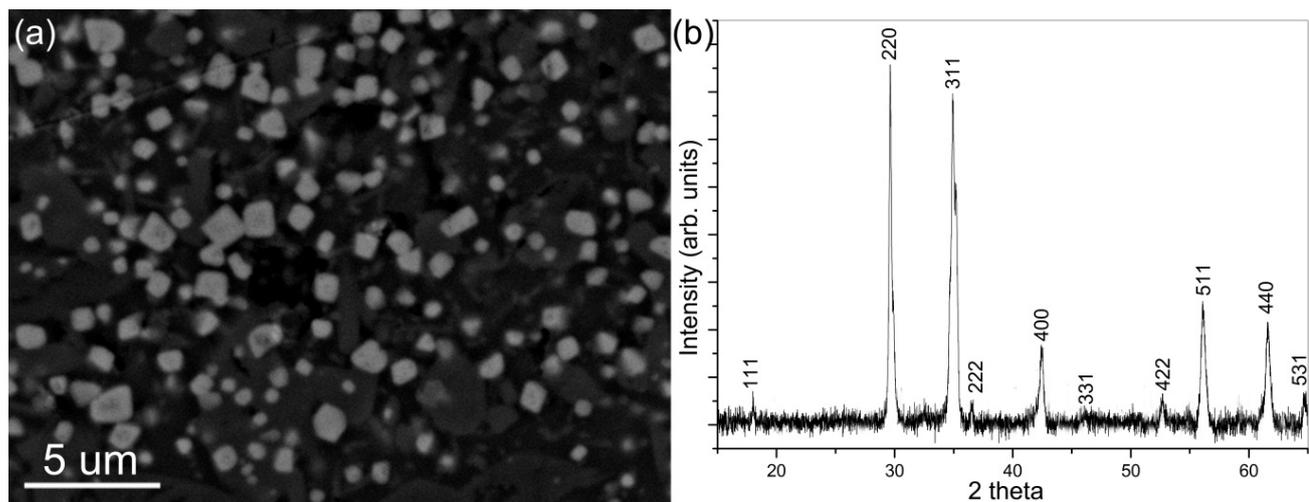


Figure 1. (a) SEM image of titanomagnetite grains (< 1.5 μm diameter) dispersed in a glass matrix. (b) Associated XRD pattern of the synthetic titanomagnetites, indexed to Fe₂TiO₄ (JCPDS 73-1724).

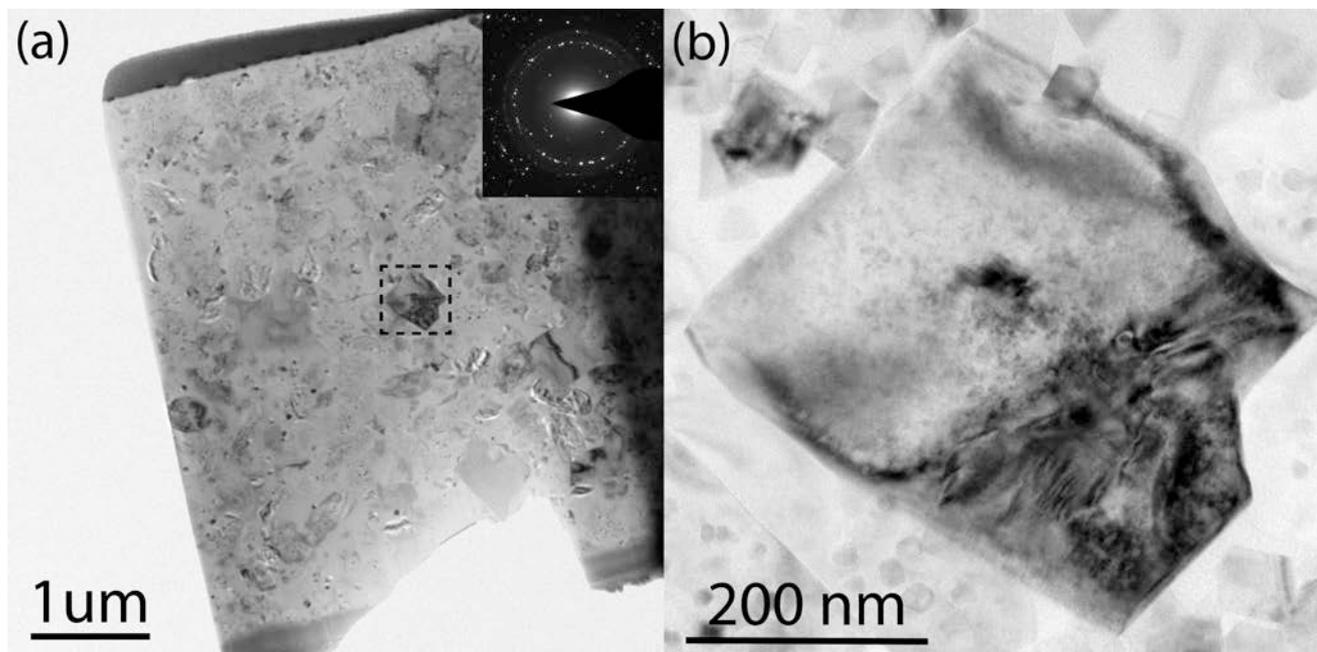


Figure 2. Bright field diffraction contrast TEM images of (a) titanomagnetite grains of various sizes dispersed within a glass matrix and SAED (inset); and (b) an individual titanomagnetite grain in the PSD size range ~ 400 nm (outlined in (a)).