

# Striped domains of coarse-grained magnetite observed by X-ray photoemission electron microscopy as a source of the high remanence of granites in the Vredefort dome

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The characteristics of a coarse-grained high-remanence magnetite obtained from shocked Vredefort granite were investigated by X-ray magnetic circular dichroism (XMCD) analysis and X-ray absorption spectroscopy (XAS). The study utilized a spectroscopic photoelectron low-energy electron emission microscope (SPELEEM) and was conducted in the SPring-8 large-synchrotron radiation facility. It is generally believed that the strong and stable bulk remanence of Vredefort granites is due to the presence of minerals that have been strongly magnetized by either an impact-generated magnetic field or terrestrial lightning strikes. Although coarse-grained magnetite is traditionally characterized by weak coercivity and remanence, the specimen used in the present study exhibited high coercivity and an intense remanent magnetization. The presence of hematite lamellae observed on the partially oxidized magnetite specimen indicated an array of striped domains, intensifying a remanence and coercivity. We also conducted XAS and XMCD analyses on a natural lodestone permanent magnet produced by lightning strikes; while maghemite was found to be present, no magnetic domain structures were observed. Considering that the nucleation of hematite lamellae on magnetite/maghemite grains is due to oxidation, we attribute the intense remanent magnetization and magnetic hardening of Vredefort granites to post-impact hydrothermal activity.

**Keywords:** striped domain, coarse-grained magnetite, XMCD, lodestone, post-impact hydrothermal activity, lightning, hematite lamellae

## Introduction

The Vredefort dome is known as the largest and oldest ( $2023 \pm 4$  Ma) terrestrial impact structure. It is the deeply-exhumed remnant of the central uplift zone of a crater with an original diameter of  $\sim 250$  km (Reimold and Gibson, 1996; Gibson and Reimold, 2008) and exhibits strong aeromagnetic anomalies (Hart et al., 1995). Shocked Archean granitic rocks in the crystalline core

of the Vredefort crater exhibit anomalously strong natural remanent magnetization (NRM), but with random centimeter-scale orientation (Hart et al., 1995; Carporzen et al., 2005; Salminen et al., 2009). Previous researchers have hypothesized that the origin of these unique magnetic remanence properties is associated with very intense impact-generated small-wavelength magnetic fields that not only produce strong remanence, but also randomize the directions of the remanence (e.g., Hart et al., 1995; Cloete et al., 1999; Carporzen et al., 2005). This hypothesis has been rejected based on the observation of terrestrial lightning remagnetization in studies that utilized 10-m borehole paleomagnetic measurements (Carporzen et al., 2012) and artificial lightning experiments (Salminen et al., 2013). Salminen et al. (2013) found that lightning-induced enhancement of remanence is due to the secondary production of partially oxidized magnetite, implying the presence of post-impact alteration. To understand these unusual remanence properties of Vredefort rocks, it might be necessary to consider the effect of impact-generated hydrothermal fluids that flow through fractures in the rocks (e.g., Osinski et al., 2013; Quesnel et al., 2013; Yokoyama et al., 2015). Such fluids enhance the remanence of primary low-coercivity coarse-grained magnetite by high-temperature oxidation.

Lightning-induced remanent magnetization (LIRM) is capable of remagnetizing grains with relatively low magnetic coercivities. Verrier and Rochette (2002) described alternating-field (AF) demagnetization and clearly distinguished secondary variably-oriented LIRM from primary remanence in a high AF (Graham, 1961). Vredefort granitic rocks contain magnetite with two different grain sizes. The first size is often on the order of microns to millimeters and grains of this size are formed at about 3.0 Ga (e.g., Cloete et al., 1999; Nakamura et al., 2010). The second size is less than 1  $\mu\text{m}$  and grains of such size are formed within the interstices of the planar deformation features (PDFs) of quartz formed by impacts of 2.02 Ga (e.g., Cloete et al., 1999). Although it is generally believed that coarse-grained magnetites contain soft secondary components that are of “little geological interest” (Butler, 1992; Nakamura et al., 2010) showed that such magnetites embedded in biotite produce highly coercive and strong remanence, as determined by surface magnetic imaging using a scanning magneto-impedance magnetic microscope (**Figure 1A**). By Raman spectroscopy, they also found that a particular type of coarse-grained magnetite has lamellae of hematite. Salminen et al. (2013) succeeded in reproducing the unusual remanence properties by artificial lightning experiments, and showed that the source mineral was a coarse-grained partially oxidized magnetite with irregular magnetic microstructures and reduced grain size. They, however, undertook no further petrographic examination. Banfield et al. (1994) also proposed a relationship between the inter-grown nanometer-scale microstructure of massive-maghemite and the strong magnetic properties of the natural permanent magnet known as lodestone. It is well known that the magnetite-ilmenite intergrowths formed by the high-temperature oxidation of titanomagnetite, and not the multiple mineralogies, are what contribute to the highly stable remanence of a subdivision of minerals that include magnetite, maghemite, and non-magnetic

ilmenite (e.g., Davis and Evans, 1976; Tucker and O'Reilly, 1980). Harrison et al. (2002) showed that magnetic susceptibility and remanence can be substantially enhanced by the formation of small amounts of magnetite and/or maghemite. However, there has been no report on the magnetic domain structure of highly magnetized natural rocks.

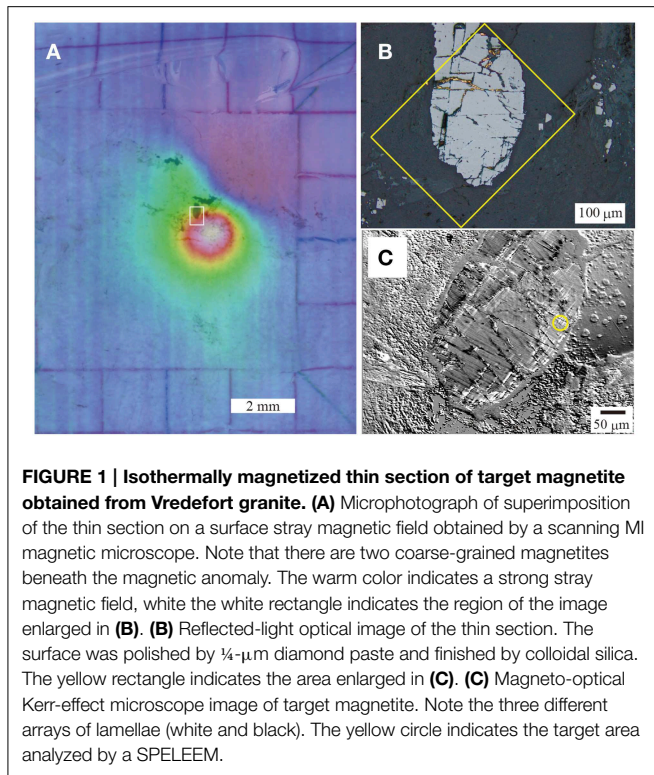
Almost all the Vredefort granitoid rocks with random and strong remanence that were examined by Carporzen et al. (2005) and Salminen et al. (2013) exhibited high-temperature metamorphism at  $>800^{\circ}\text{C}$  during post-impact event (e.g., Gibson and Reimold, 2008). This mechanism is capable of nearly or completely remagnetizing any remanence by subsequent cooling and/or post-impact hydrothermal activity (Salminen et al., 2009). We therefore investigated the effect of post-impact high-temperature metamorphism on the microtexture of magnetic minerals that have been strained or modified by a shock event or post-shock process. The investigation, which was undertaken at the SPring-8 facility, utilized X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) using a spectroscopic photoelectron low-energy electron emission microscope (SPELEEM). We also determined the crystallographic orientation of the minerals by electron backscatter diffraction (EBSD). This study was undertaken to address the question of why coarse-grained types of magnetite found in Vredefort rocks possess strong and high coercive remanence.

## Materials and Method

### Sample Description

The utilized shocked granite of 2.5 cm in diameter was drilled from an exposed crystalline basement of the Vredefort crater near Parys, South Africa, at  $26^{\circ}52.615'S$   $27^{\circ}25.277'E$ . The sample was provided by J. Salminen (University of Helsinki). The magnetic properties of the rock specimen had already been measured by J. Salminen, and comprised a density of  $2599\text{ kg/m}^3$ , bulk NRM intensity of 9.1 A/m, Königsberger ratio (defined as the ratio of the NRM to the product of the magnetic susceptibility and geomagnetic field) of 75, and Curie temperature of  $588^{\circ}\text{C}$  (which is equal to that of magnetite). Nakamura et al. (2010) examined the Raman spectroscopy of tip samples of thickness 1.0 and 1.5 mm and found the NRM intensities to be 13.1 A/m. They confirmed the presence of hematite lamellae on the host magnetite, which was embedded in chloritized biotite.

A thin section was made from the same tip sample examined by Nakamura et al. (2010) to examine the magnetic properties of the same grain by SPELEEM. Before the present experiments, the surface of the thin section was carefully polished using 1- $\mu\text{m}$ -diameter diamond paste. The specimen was then finished by buff polishing using colloidal silica slurry. The thin section was subjected to an impulse field of several hundred milliteslas in an out-of-plane orientation. We then rescanned the surface magnetic stray field on the thin section and detected the presence of highly coercive coarse-grained magnetites after 50-mT stepwise AF demagnetization using a scanning magneto-impedance (MI) magnetic microscopy (**Figure 1A**). The grain was also examined by reflected light microscopy (**Figure 1B**)



and magnetic Kerr-effect microscopy (**Figure 1C**), and this revealed three different orientations of lamellae. No fine-grained magnetites were found in the PDFs of the shocked quartz grain of the thin section, and this suggested that our coarse-grained magnetite was a major paleomagnetic carrier. This type of magnetite is unique and can be used to investigate the unusual magnetic properties of Vredefort granite. This enhances the reliability of using only one sample for this study.

### Spectroscopic Photoemission and low-energy electron microscope (SPELEEM)

The experiments were performed using a SPELEEM produced by ElmitecCreative Commons Attribution License (CC BY) and a soft X-ray beamline (BL17SU) at the SPring-8 facility. The SPELEEM achieved a high spatial resolving power by the use of magnetostatic lenses, with a spatial resolution of 22 nm. Three different excitation sources (highly brilliant circularly polarized soft X-ray, electron beam, and mercury lamp) were used to visualize the surface structure of the specimen. Circular-polarized soft X-rays were used to determine the spatially resolved chemical composition, the electronic states, and the magnetic domain structures of the specimen. The fine structure of the X-ray absorption spectrum (XAS) was used to analyze the mineral species and their spatial distribution. The XMCD effect was used to visualize the magnetic domain structures of the sample, and an electron beam was used to image the surface topological structure. The SPELEEM was used to simultaneously obtain information about the mineral species and their distribution as well as the magnetic domain structure and surface structure (Kotsugi et al., 2010, 2011).

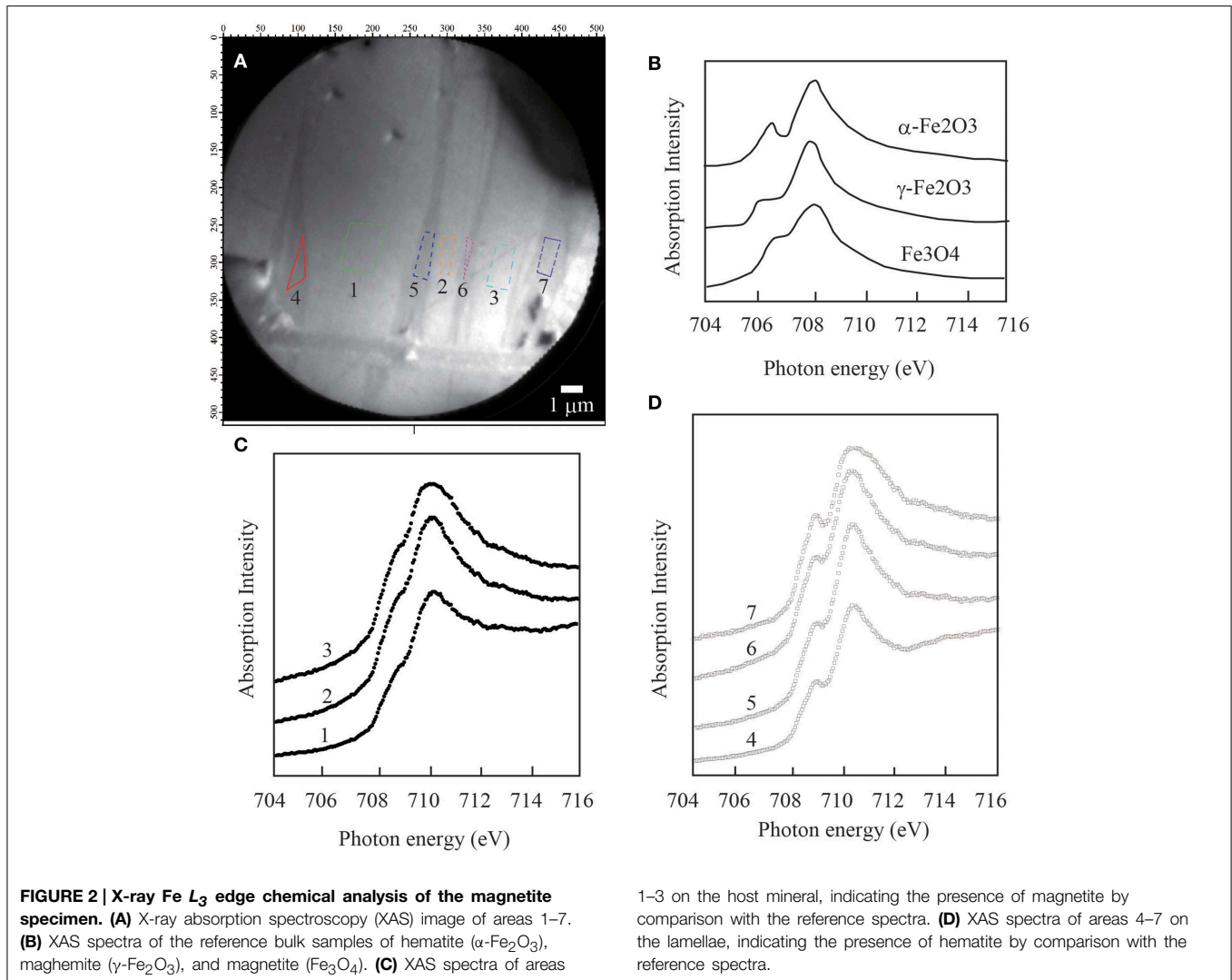
We analyzed the X-ray absorption spectrum at the Fe  $L_{3,2}$  absorption (706–712 eV) edge to determine the species of iron oxides, and used XMCD to visualize the magnetic domains. The XMCD-PEEM contrast was expressed as the intensity difference  $I_{\mu}(+) - I_{\mu}(-)$ , where  $I_{\mu}(+)$  and  $I_{\mu}(-)$  are respectively the image intensities determined by right-handed ( $\mu(+)$ ) and left-handed ( $\mu(-)$ ) circularly-polarized lights. This image treatment contrasts due to non-magnetic factors, namely, the topography and chemical composition. Because 3d transition metals (Fe, Co, and Ni) have  $L_{3,2}$  absorption-edges that experience  $2p \rightarrow 3d$  core electron transitions at 700–730 eV, magnetic information about the 3d electrons can be selectively obtained from the soft X-ray region. The Fe  $L_{3,2}$ -edge XMCD spectra of iron oxides such as magnetite exhibit three characteristic peaks with respect to the chemical environment (Pearce et al., 2006), namely, the Fe<sup>2+</sup> octahedral peak (negative peak,  $\sim 710.5$  eV), Fe<sup>3+</sup> tetrahedral peak (positive peak,  $\sim 711.5$  eV), and Fe<sup>3+</sup> octahedral peak (negative peak,  $\sim 712.5$  eV).

Furthermore, to determine the differences between the crystallographic orientations of magnetite and those of hematite crystals, we employed EBSD using a scanning electron microscope (HITACHI S-3400N) equipped with HKL Flamenco for EBSD data acquisition.

## Results

The SPELEEM was used to examine the remanence-carrying coarse-grained magnetite with lamellae, indicated by the yellow circle in **Figure 1C**. The chemical distribution of Fe on the Fe  $L_3$  absorption edge was determined, and the local XAS spectra were extracted from areas 1–7 indicated by the colored lines in the XAS-PEEM image in **Figure 2A** ( $I_{\mu}(+) - I_{\mu}(-)$ ). The green square (area 1), yellow square (area 2), and sky blue square (area 3) indicate regions within the host minerals; and the red triangle (area 4), blue square (area 5), violet triangle (area 6), and purple square (area 7) indicate portions of the lamellae. The corresponding X-ray absorption spectra of the host minerals are shown in **Figure 2C**, and those of the lamellae are shown in **Figure 2D**. **Figure 2B** shows the reference spectra of the Fe  $L_{3,2}$  absorption edge of the iron oxides obtained from previous works (e.g., Kuiper et al., 1993; Pearce et al., 2006; Signorini et al., 2006; Kuzmin and Chaboy, 2014; Piquer et al., 2014). By comparing the spectral shapes of the data obtained from the present study with the references, the materials in areas 1–3 were determined to be magnetite, and those in areas 4–7 were determined to be hematite. The noticeable energy shift of  $\sim 2$  eV observed between the present and reference data is due to the differing oxidation states, and such is not uncommon in magnetite (Waychunas et al., 1983; Okudera et al., 2012).

**Figure 3A** shows a clear image of the structure of the striped magnetic domain. The striped domains in the target magnetite have a horizontally sinuous pattern that is cut by the hematite lamellae that run perpendicular to the domain walls. The magnetic contrast of the magnetic domain structure is proportional to the cosine of the angle between the atomic magnetic moment and the incident light. Hence, the absence of a change in the contrast of the XMCD image indicates

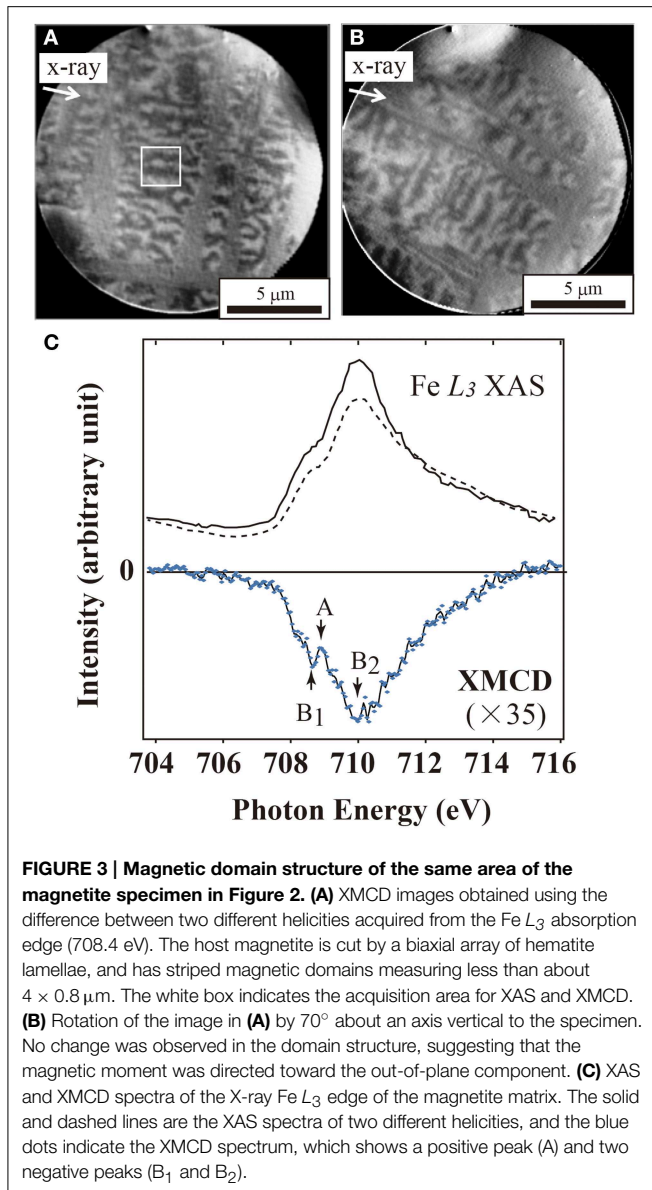


out-of-plane magnetization, while the observation of a change indicates in-plane magnetization. To further verify the out-of-plane orientation of the magnetization, the specimen was rotated by  $70^\circ$  about the vertical axis, while the same incident angle of the synchrotron radiation was maintained. As can be observed from **Figure 3B**, the brightness and contrast of the underlying striped magnetic domains revealed no change in the incident light of the synchrotron radiation, thereby indicating out-of-plane magnetization. The grayscale of the figure indicates the XMCD intensity. The dark portions of the image indicate upward-magnetization, and the white portions indicate downward-magnetization perpendicular to the surface. Owing to the difficulty of achieving saturated out-of-plane magnetization, it can be concluded that our magnetite possessed highly coercive and strong remanence.

**Figure 3C** shows the XAS and XMCD spectra of the magnetite region (white box) in **Figure 3A**. The XAS spectra of this region agree well with the reference spectra of the natural magnetite in **Figure 2C**. The XMCD was calculated as the difference between

two different helicities (**Figure 3C**). The XMCD difference spectrum (**Figure 3C**, bottom) shows the well-defined peaks on the  $L_3$  and  $L_2$  edges, as characteristic of magnetite (Goering et al., 2006). The two negative peaks on the  $L_3$  edge are mainly due to the octahedral Fe $^{2+}$  and Fe $^{3+}$  ions. The small positive peak in the middle is due to the tetrahedral Fe $^{3+}$  ions. The opposite signs of the XMCD peaks produced by the Fe cations at the octahedral and tetrahedral sites indicate antiferromagnetic coupling. The magnetite crystals are thus ferrimagnetic. The cause of the little differences between the positive tetrahedral Fe $^{3+}$  and negative octahedral Fe $^{2+}$  is unknown. According to Piquer et al. (2014), the shift of the energies of the absorption peaks in the magnetite XAS spectra is due to a single-phase non-stoichiometric Fe $_{3-x}$ O $_4$  oxide, and this modifies the structural arrangements at the Fe sites.

To compare the magnetic properties of the strongly magnetic Vredefort rocks with those of a lightning-created material (i.e., lodestone), we undertook the first ever XAS and XMCD analyses of natural lodestone (**Figure 4**), which has different



host mineralogy. Lodestone is a natural permanent magnet that attracts a paper clip (see **Figure 4A**), and the specimen used in this study was obtained from a magnetite ore, namely, a granitic pegmatites (Utah, USA, exact locality unknown). **Figures 4B,C** show a typical LEEM chemical component image and XMCD magnetic domain image of lodestone. Maghemite contained in a magnetite matrix cut by hematite lamellae was observed in the lodestone specimen (**Figure 4B**). The magnetite had a typical maze-like domain pattern (**Figure 4C**, bottom) and a characteristic disordered domain pattern (**Figure 4C**, upper). The XAS spectra of the  $L_3$  and  $L_2$  edges revealed the presence of maghemite (**Figures 4D,E**) (Brice-Profeta et al., 2005), and the XMCD spectra had two negative peaks (octahedral  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) and one positive peak (tetrahedral  $\text{Fe}^{3+}$ ). The XAS spectra of our Vredefort specimen were identical with those of the magnetite. However, the negative octahedral  $\text{Fe}^{2+}$  peak in

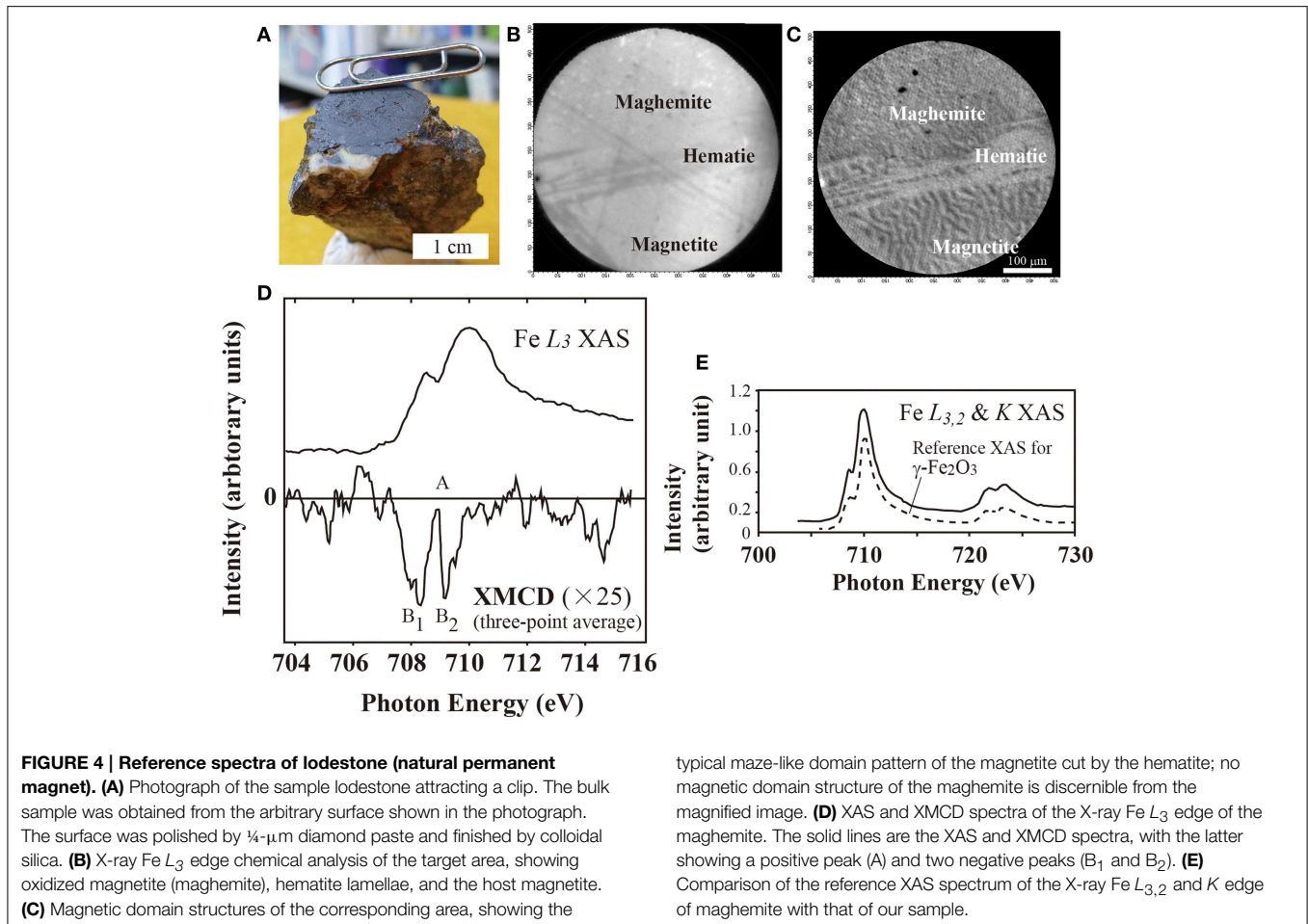
the XMCD spectra was lower than that of lodestone, and the corresponding magnetic contribution was comparable to that of the octahedral  $\text{Fe}^{3+}$ . The lower octahedral  $\text{Fe}^{2+}$  peak indicates partial oxidation of magnetite, and this suggests the presence of trace maghemite in the  $L_3$  spectrum of the host magnetite, as also observed by Salminen et al. (2013). The magnetic domain structure of our partially oxidized magnetites contained a striped domain cut by hematite lamellae. The domain structure differs from the maze-like domains of the host magnetites in lodestone.

The crystal orientations of the minerals (i.e., magnetite and hematite) were obtained by EBSD in the same region of the XMCD analysis. The observed Kikuchi patterns of the magnetite grain clearly indicated an inverse spinel pattern (**Figures 5A,B**), while the hematite lamellae were observed to have trigonal patterns (**Figures 5C,D**). **Figure 5E** is an equal-area diagram of the lower hemisphere, and it shows that the  $\langle 0001 \rangle$  direction on the  $c$ -axis of the hematite is perpendicular to the  $\{111\}$  plane of the magnetite. Although magnetization can be easily achieved in the  $\langle 111 \rangle$  direction of magnetite, the results of the XMCD analysis showed that the actual magnetization direction in the specimen was close to the hard  $\langle 100 \rangle$  axis.

## Discussion

By 10-m borehole paleomagnetic measurements, Carporzen et al. (2012) showed that terrestrial lightning strike was the cause of the unusual magnetic rock properties of Vredefort granites. They also found that the natural remanence directions and their 0.55-m magnetic anomaly vectors mostly lie along a great vertical circle and are consistent with the circular field expected for a current flowing horizontally in the northeastern direction. In addition, in the southeastern part of their study area, they observed a negative magnetic anomaly that extended concentrically around the center of the dome. This concentric magnetic anomaly has often been observed within an inner annular zone (e.g., Quesnel et al., 2013; Yokoyama et al., 2015), and it cannot be explained by only terrestrial lightning strike. Moreover, the inner annular zone might be a path for percolated post-hydrothermal fluids that flowed along fractures. Salminen et al. (2013) confirmed that the strong remanence of Vredefort granites was due to lightning strikes on the rocks, which previously contained partially oxidized magnetite within their microstructures. Our results also showed that coarse-grained magnetite in Vredefort granites contained an array of hematite lamellae, resulting from a partial oxidation. The presence of hematite lamellae might be prerequisite for the origin of high magnetization. It is therefore considered that preexisting partially oxidized magnetite in Vredefort granites intensify the remanence.

Our XMCD and XAS analyses showed that the hematite lamellae cut magnetic domains in the host magnetite. The opposite sense of the XMCD peaks produced by the Fe cations at the octahedral and tetrahedral sites indicated antiferromagnetic coupling of the cations (Monti et al., 2012). The grains of the host magnetite were divided into smaller grains measuring less than  $5 \times 10 \mu\text{m}$ . These smaller parallel-piped grains correspond to a pseudo-single domain of magnetite in terms of size

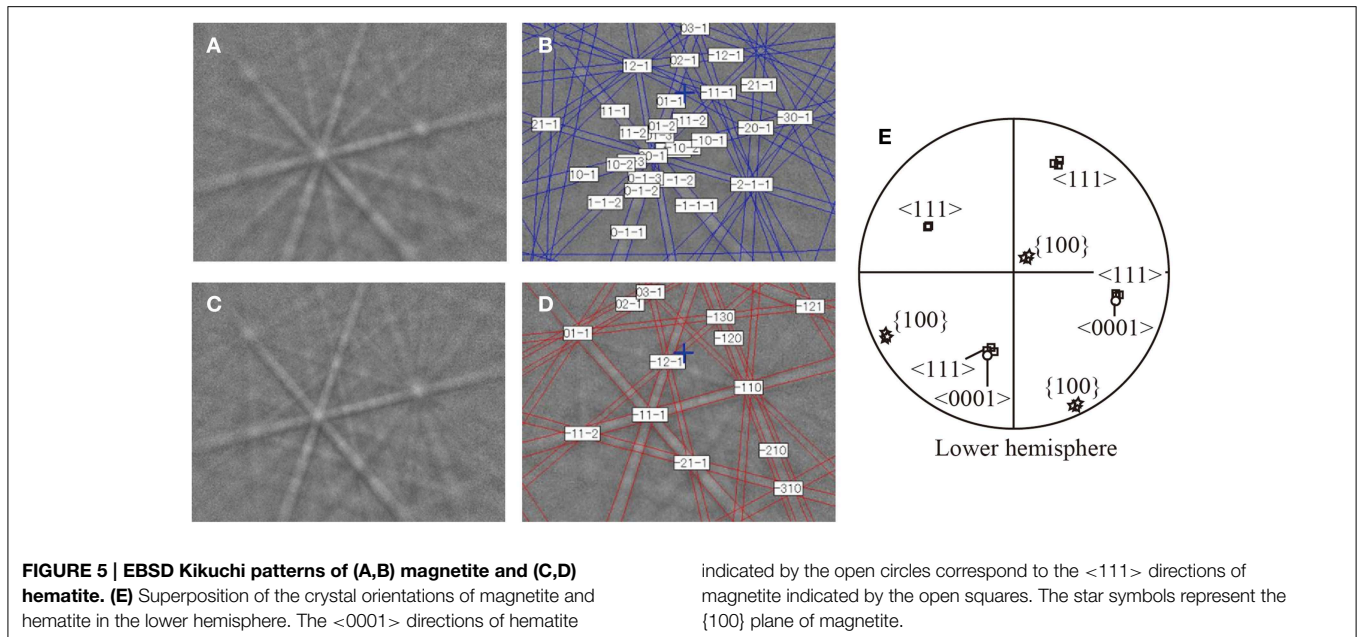


and shape (Butler and Banerjee, 1975). EBSD showed that the  $\{0001\}$  planes of hematite contact the plane parallel to the  $\{111\}$  planes of magnetite (the easily magnetized axes of magnetite and hematite are in the  $\langle 111 \rangle$  direction and  $\{0001\}$  plane). The subdivision of the host magnetite by a biaxial array of hematite yielded new and smaller striped domains with out-of-plane magnetizations. Kasama et al. (2006) reported that the out-of-plane magnetization of magnetite thin films are directly associated with the presence of structural defects and antiferromagnetic coupling. Incidentally, based on an annealing experiment performed on a magnetite thin film for 4 min in air at  $250^\circ\text{C}$ , Wei et al. (2006) showed that the appearance of striped domain structures was possibly caused by defect-related out-of-plane magnetization. Therefore, antiferromagnetically coupled hematite lamellae may immobilize the movement of striped domain walls. This suggests that the highly coercive and intense remanence of our coarse-grained magnetite is due to the presence of newly formed striped domains.

Yokoyama et al. (2015) reported the impact-induced hydrothermal alteration of the magnetic mineralogy of basalts obtained from an internal annular zone in the Vargeão impact structure in southern Brazil. This confirmed the formation of

new secondary magnetic carriers such as magnetite and hematite along a highly hydrated and oxidized fracture. They proposed that the interaction of a hydrothermal fluid with brecciated basalts at higher than  $200^\circ\text{C}$  account for the occurrence of magnetite and hematite under no equilibrium with the atmosphere in an internal annular zone. This suggests that the observed concentric aeromagnetic anomalies were due to localized hydrothermal alteration along concentric faults, which acted as conduits for fluid circulation through the impact structure. Such a concentric and negative aeromagnetic anomaly has been observed in the Vredefort dome (Muundjua et al., 2007). The magnetite sample used in this study was taken from the region in which the anomaly was found, and this implies the occurrence of hydrothermal alteration in the impact structure.

Magnetite generally transforms to hematite by oxidation at high temperatures. Below  $300^\circ\text{C}$ , magnetite oxidizes to the metastable phase known as maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) by the migration of Fe cations (e.g., Gallagher et al., 1968). At higher temperatures (roughly above  $600^\circ\text{C}$ ), the oxidation of magnetite always results in the formation of secondary hematite (Colombo et al., 1965). The granite used in this study must have experienced a reheating event due to the impact of a



meteorite. Based on the model of Ivanov (2005), the central part of the impact structure (of radius  $\leq 15$  km) would have been extensively heated above  $700^\circ\text{C}$ . Magnetites in the granite might have transformed into hematite by high-temperature oxidation induced by the impact of the meteorite (2.03 Ga). By *in situ* X-ray spectroscopy, McCarty et al. (2014) found a biaxial array of hematite lamellae in oxidized magnetite after heating to  $600^\circ\text{C}$ . We also found that our magnetite contained very dense hematite lamellae that run horizontally and vertically (see **Figures 2A, 3A**), and this suggests the occurrence of secondary high-temperature metamorphism. Furthermore, the presence of maghemite might indicate that our magnetite also experienced low-temperature oxidation such as induced by lightning strikes. Our XMCD spectra and the domain examination of our magnetite revealed the conversion of  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions and the presence of characteristic striped magnetic domains cut by biaxial hematite lamellae. As previously proposed by Salminen et al. (2009), these evidences of high-temperature oxidation suggest that Vredefort rocks have experienced hydrothermal alteration induced by an impact event, and hence the occurrence of impact-generated hydrothermal activity beneath the crater. It is posited that latter terrestrial lightning strikes on the hydrothermally oxidized magnetites intensified their magnetization.

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## Conclusion

Using a SPELEEM, we observed striped magnetic domains subdivided by hematite lamellae in a high-coercivity coarse-grained magnetite obtained from Vredefort granite. In addition, X-ray absorption spectra showed that the coarse-grained magnetite had been partially oxidized into maghemite, and XMCD analysis clarified the magnetic contribution of the octahedral  $\text{Fe}^{3+}$  ions. The array of hematite lamellae within the partially oxidized magnetite suggests that the rock has been affected by post-impact hydrothermal activity beneath the Vredefort crater. Latter terrestrial lightning strikes on the partially oxidized magnetite intensified its remanence.

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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