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Lamellar magnetism and exchange bias in billion-year-old titanohematite with nanoscale ilmenite exsolution lamellae: I. Mineral and magnetic characterization

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SUMMARY

Recent high-resolution aeromagnetic surveys in South Norway have revealed numerous remanent anomalies over Mesoproterozoic metamorphic rocks. Studies on the nature of the minerals that are the remanent carriers has led to discoveries of titanohematite samples with unusual magnetic properties caused by nanoscale exsolution lamellae with their related lamellar magnetism. Here we focus on a rock unit dominated by quartz-plagioclase-biotite granulite containing titanohematite grains with a strong lattice-preferred orientation parallel to regional foliation. When samples with their natural remanent magnetization (NRM), acquired nearly 1 billion years ago, are cooled to 10 K and hysteresis loops measured, these loops show bi-modal exchange bias caused by the magnetism induced within the ilmenite by antiferromagnetic coupling with the adjacent lamellar NRM. By contrast when the samples are cooled in a strong magnetic field (1.5 Tesla), this results in unimodal lamellar magnetism, and, below the $T_{\rm N}$ of ilmenite it adopts a consistent negative orientation, giving rise to unimodal negative exchange bias of >500 mT. The results presented here cover the chemical and magnetic properties, Mossbauer results and transmission electron microscopy of the titanohematite and ilmenite lamellae. Initial magnetic experiments indicated the shifts found in the exchangebias experiments were directly related to the orientation of the sample to the applied field and the initial state of the NRM. In most samples with these unusual magnetic properties, ilmenite lamellae could not be seen in an optical or a scanning electron microscope. However magnetic experiments gave proof of the presence of ilmenite, later confirmed by Mössbauer spectroscopy. Several attempts were made to identify ilmenite in TEM studies, finally successful in showing ilmenite lamellae parallel to (001) of hematite with thicknesses ~ 1.2 to 1.7 nm and aspect ratios 7–13. Here we compare new TEM images and the magnetic behaviour of these samples to the MOD2 samples that previously showed extraordinary exchange bias properties, and investigate further the nature of these magnetic minerals.

Key words: Magnetic mineralogy and petrology; Rock and mineral magnetism.

1 INTRODUCTION

The samples considered here were discovered by exploring the oxide mineralogy in areas of distinct negative remanent aeromagnetic anomalies, where the natural remanent magnetization (NRM) contribution is greater than the induced magnetization to the bulk signal. With the recent launch of the SWARM satellites, there is renewed interest in the nature of crustal magnetism because these satellites will map the magnetic response of the earth's crust at a resolution never achieved before. Though much of the continental crust has an induced magnetic signature there are parts of the crust, which are dominated by remanence. Understanding of why some minerals with fine exsolution microstructures contribute strongly to the remanent component of magnetic anomalies is still in its infancy. The samples discussed here, are from Mesoproterozoic amphibolite-facies metamorphic rocks in the Modum area, South Norway. The anomalies are associated with reversely magnetized rocks, that is those having NRMs with steep negative inclinations acquired ~ 1 billion

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years ago. The Koenigsberger ratios (NRM/induced magnetization) or Q values range from 17 to 313 with an average of 124 (n = 46), clearly indicating that the rock responses are completely dominated by remanence.

In this region, as a result of ancient sediment deposition under oxidizing conditions and later Sveconorwegian (~1092 Ma) amphibolite-facies regional metamorphism (Bingen *et al.* 2008), the NRMs in these metamorphic rocks are commonly carried by titanohematite with ilmenite and rutile exsolution lamellae, creating a very stable remanence attributed to 'lamellar magnetis' (Robinson *et al.* 2002, 2004, 2013). The extraordinarily high Q values indicate that the nature and geometry of these present-day anomalies are due to a memory acquired nearly 1 billion years ago and retained to the present.

By studying minerals and their intergrowths, which have faithfully retained a record of the earth's field over hundreds of millions of years, we found new insights into magnetic behaviour, which have applications for modern-day memory systems. Earlier work on titanohematite with extremely fine ilmenite exsolution lamellae many <10 nm thick from the Modum area provided the largest magnetic exchange bias, 1.34 Tesla (T), ever measured in any material, natural or synthetic (McEnroe et al. 2007a). This was also the first report of significant exchange bias in a natural mineral. Meiklejohn & Carter (1959) and Nagata & Uyeda (1959) showed a minor shift in natural hemo-ilmenite samples. Since then there have been few studies on exchange bias in natural minerals, and these were focused on the origin of self-reversal, which also led to research on synthetic analogs of ilmenite-rich compositions in the hematite-ilmenite (Fe₂O₃-FeTiO₃) solid solution (Uyeda 1957; Lawson et al. 1981; Nord & Lawson 1989; Hoffman 1992; Goguitchaichvili & Prevot 2000; Prevot et al. 2001; Lagroix et al. 2004; Harrison et al. 2005; McEnroe et al. 2007b; Burton et al. 2008; Robinson et al. 2010; 2012a,b, 2014a; Fabian et al. 2011, 2015). The first demonstration of shifted hysteresis loops was by Meiklejohn & Bean (1956) on Co nanoparticles coated with CoO at 950 mT. This still remains one of the largest shifts ever reported.

The onset of the exchange bias in the MOD2 sample occurred just below ~57 K, the magnetic ordering temperature, the Néel temperature, T_N , of ilmenite. Earlier TEM studies showed ilmenite lamellae, some thinner than ~1 nm, thus ~2/3 of the 1.4 nm thickness of one unit cell. A new set of high-resolution TEM images, presented here, provides added information on this unusual sample.

A theoretical basis for the exchange bias reported in the MOD2 sample was developed by Harrison *et al.* (2007). They demonstrated involvement of the Fe²⁺–Fe³⁺ contact layers necessary between the ilmenite lamellae and titanohematite host, a key feature of lamellar magnetism (Robinson *et al.* 2002, 2004, 2006), and showed that exchange bias occurs only in association with ilmenite lamellae containing odd numbers of Fe layers and even numbers of Ti layers, where each atomic layer is ~0.23 nm thick. In this arrangement lamellae would be composed of: one Fe layer and two Ti layers (0.69 nm), three Fe layers and four Ti layers (1.61 nm), five Fe layers and six Ti layers (2.53 nm), etc. For comparison, a unit cell of ilmenite has six layers and thickness 1.4 nm. The two Fe²⁺–Fe³⁺ contact layers associated with each lamella are not counted in the above tally, and it is not known whether their thickness would, or would not, show as parts of lamellae in TEM images.

By field-free cooling a natural MOD2 titanohematite sample to below 57 K, the T_N of ilmenite, and then measuring a hysteresis loop, it was discovered that the ilmenite magnetization that was created and coupled to the lamellar remanent magnetization produced bimodal exchange bias. This was then used as a direct proof that lamellar magnetism carries the NRM in MOD2 (Fabian *et al.* 2008). It was then shown by Shcherbakov *et al.* (2009) that the observed exchange signal could be modelled by high magnetocrystalline anisotropy in ilmenite pinning domain walls in the surrounding AF titanohematite.

A remaining serious challenge was to understand how the magnetic moment, including the lamellar moment, in the titanohematite host, considered to be parallel to the (001) basal plane, could be coupled to the ilmenite magnetic moment, which is considered to be parallel to the *c*-crystallographic axis, 90° from the basal plane. Later neutron diffraction experiments on the MOD2 sample showed that the magnetic moments of the hematite near contact layers were bent $\sim 30^{\circ}$ out of the basal plane (Harrison *et al.* 2010). This result was understandable below $T_{\rm N}$ of ilmenite, however, it was not expected that the same angle would be recorded also at room temperature. This provided clear evidence that the room temperature lamellar NRM influenced the direction of acquisition of magnetization of the coupled ilmenite lamellae when passing through their Néel temperature at \sim 57 K. This key discovery provided a good explanation for the NRM hysteresis results discussed by Fabian et al. (2008) and is employed extensively here. Following the findings given here, Paper II in this series describes the importance of the NRM orientation and placement in a Magnetic Property Measurement System (MPMS), and how this effects the exchange coupling and most particularly the ability to predict exchange bias. These added experiments involved fields up to 5 T and temperatures down to 5 K. Paper III uses these additional results to develop crystalmagnetic models to try to explain the origin of the varied exchange bias, tied to EBSD measurements, and the role of lattice-preferred orientation.

2 NATURE OF THE SAMPLES

An aeromagnetic map of the negative magnetic anomalies of the Modum area is shown in Robinson et al. (2014b, their fig. 1). The MOD-22 and MOD2 sample localities were discovered by groundmagnetic traverses as follow-up work to a new high-resolution aeromagnetic survey. Over the MOD22 locality there is a narrow 14m-wide negative anomaly of 1750 nT below local background. The body that produces the anomaly is marked by a zone of vertical dark grey layers, which in thin section, are dominated by quartz and plagioclase with minor amounts of biotite and scattered opaque grains. The opaque grains are dominantly titanohematite with traces of rutile, minor ilmenite and very rare magnetite. These layers were originally deposited as sediments and subsequently metamorphosed to upper amphibolite facies. Electron microprobe (EMP) analyses showed varied compositions of titanohematite, summarized in Table 1. Analyses were influenced locally to an uncertain extent by overlap with the rutile lamellae.

Six MOD22 samples were analysed by EMP. Bulk titanohematite compositions, range from 11 to 23 per cent FeTiO₃. In terms of mean-median compositions, the samples fall in three groups with % FeTiO₃ of 13–14, 17, and 20. For each of the six samples analysed, we selected four simplified compositions: a typical composition on the Fe-rich side of the analytical cluster, the mean, the median, and a typical composition on the Ti-rich side of the analytical cluster. These compositions, in order of increasing per cent FeTiO₃ are:

Mod22-22: 12.2, 12.9, 12.9, 13.7; **Mod22-52b:** 12.2, 12.9, 12.6, 14.7.

Mod22-51b: 12.6, 14.1, 14.3, 15.7; **Mod22-42a:** 11.0, 17.2, 17.2, 19.4.

| Table 1. | Represen | tative EMI | ^o analyses | cation fo | ormulae a | nd end n | nembers (| of MOD2 | 2 sample | s. | | | | | | | | | | | | | |
|----------|------------------------------------|-------------|-----------------------|---|-----------|----------|-----------|---------|----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|----------|---------|--------|
| | | 22 22 | 22 | 22 | 52A | 52A | 52A | 52A | 51B | 51B | 51B | 42 | 42 | 42 | 42 | 12c | 12c | 12c | 12c | 4A | 4A 4 | A A | 4A |
| | ř. | Min. Med | ian Mean | Мах | Min. | Median | Mean | Max | Min. N | Md = Mn | Max | Min. N | fedian | Mean | Max | Min. N | ledian N | fean] | Max N | din. M | edian M | ean N | Лах |
| | SiO ₂ (| 0.00 0.0 | 49 0.000 | 0.039 | 0.025 | 0.028 | 0.006 | 0.026 | 0.028 | 0.018 | 0.011 | 0.019 | 0.034 | 0.000 | 0.008 | 0.000 | 0.008 | 000.0 | 0.050 (|).066 (| 039 0 | 031 0 | .068 |
| - | TiO ₂ (| 6.200 6.5 | 80 6.46(| 7.480 | 6.130 | 6.380 | 6.570 | 7.720 | 6.270 | 7.180 | 8.020 | 5.430 | 8.880 | 8.620 1 | 1.140 | 7.220 | 8.220 | 8.350 1 | 2.740 8 | 8.820 10 | .160 10 | 410 13 | .630 |
| | ZrO ₂ | 0.0 0.0 | 86 0.17 <i>1</i> | 0102 | 0.150 | 0 165 | 0.075 | 0111 | 0.003 | 0.060 | 0.130 | 0 121 | 0.005 | 0.152 | 0.117 | 0.058 | 0.023 | 0.000 | 0.000 | 0000 | 0 108 | 0.85 0 | 990 |
| - | ChO, 0 | 0.209 0.2 | 47 0.300 | 0.232 | 0.193 | 0.219 | 0.268 | 0.254 | 0.217 | 0.158 | 0.255 | 0.147 | 0.530 | 0.162 | 0.192 | 0.159 | 0.147 | 7110 | 0.157 (|) 565 (| 477 0 | 583 0 | 515 |
| | V103 (| 0.0 000.0 | 38 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.043 | 0.000 | 0.000 | 0.004 | 0.027 | 0.000 | 0.000 | 0.000 | 0000 | 000 | 0.059 (| 0000 | 000 | 000 | 000 |
| | Fe, O ₃ 85 | 8.135 87.1 | 49 87.33 | 85.141 | 88.014 | 87.549 | 87.056 | 84.896 | 87.621 | 86.125 | 84.343 | 39.312 8 | 2.245 8 | 3.300 7 | 8.645 8 | 5.760 8 | 3.896 8 | 3.758 7: | 5.203 82 | 2.233 79 | .936 79 | 312 73 | 372 |
| Wt% | FeO 5 | 5.537 5.8 | 86 5.79' | 6.729 | 5.412 | 5.770 | 5.787 | 6.878 | 5.634 | 6.412 | 7.101 | 4.813 | 7.855 | 7.685 | 9.993 | 6.322 | 7.330 | 7.364 1 | 1.362 8 | 3.005 5 | 036 9 | 303 12 | .221 |
| Oxides | MnO (| 0.00 0.0 | 23 0.000 | 0.013 | 0.059 | 0.000 | 0.000 | 0.053 | 0.016 | 0.000 | 0.003 | 0.007 | 0.088 | 0.000 | 0.023 | 0.041 | 0.006 | 0.069 | 0.000 (| 0.000 (| 0000 | 033 0 | 052 |
| | MgO (| 0.022 0.0 | 17 0.00' | 0.017 | 0.018 | 0.000 | 0.016 | 0.000 | 0.012 | 0.018 | 0.060 | 0.048 | 0.046 | 0.037 | 0.001 | 0.000 | 0.024 | 0.039 | 0.023 (| 0000 (| 0.082 0 | 035 0 | 036 |
| - | CaO | | | | | | | | | | | | | | | 0.000 | 0.000 | 0.004 | 0.015 | | | | |
| |) Ouz | 0.00 0.0 | 40 0.00 | 0.000 | 0.042 | 0.000 | 0.112 | 0.047 | 0.000 | 0.038 | 0.016 | 0.000 | 0.000 | 0.000 | 0.011 | 0.184 | 0.041 | 000.0 | 0.103 (| 0.005 (| 003 0 | 000 | 000. |
| | NiO | | | | | | | | | | | | | | | 0.000 | 0.000 | 000.0 | 0.003 | | | | |
| - | Tot Fe ³⁺ 10(| 0.249 100.1 | 15 100.084 | 99.753 | 100.052 | 100.110 | 99.890 | 99.985 | 99.932 | 100.008 | 99.948 | 6 668.60 | 9.801 9 | 9.956 10 | 0.130 9 | 9.841 9 | 9.820 9 | 9.930 9. | 9.855 99 | 9.784 99 | .840 99 | 791 99 | 1961 |
| - | Si (| 0.0000 0.0 | 013 0.000 | 0 0.001(| 0.0007 | 0.0007 | 0.0002 | 0.0007 | 0.0007 | 0.0005 | 0.0003 | 0.0005 | 0.000 | 0.0000 | 0.0002 | 0.0000 | 0.0002 | 0000.0 | 0.0013 (| 0.0017 0 | 0010 0 | 0008 0 | 0.0018 |
| - | Ë | 0.1227 0.1 | 304 0.128 | 30 0.1486 | 0.1216 | 0.1264 | 0.1305 | 0.1530 | 0.1245 | 0.1424 | 0.1589 | 0.1079 | 0.1760 | 0.1707 | 0.2198 | 0.1435 | 0.1631 | 0.1654 | 0.2515 (| 0.1749 (| .2010 0 | 2061 0 | .2686 |
| | Zr | | | | | | | | | | | | | | | 0.0007 | 0.0003 | 0000.0 | 0.0000 | | | | |
| | AI (| 0.0045 0.0 | 027 0.00 | 5 0.0032 | 0.0049 | 0.0051 | 0.0023 | 0.0034 | 0.0029 | 0.0019 | 0.0043 | 0.0038 | 0.0030 | 0.0047 | 0.0036 | 0.0030 | 0.0039 | 0.0052 | 0.0043 (| 0.0028 (| 0033 0 | 0026 0 | 0020 |
| - | Cr | 0.0044 0.0 | 051 0.000 | 0.0049 | 0.0040 | 0.0046 | 0.0056 | 0.0053 | 0.0045 | 0.0033 | 0.0053 | 0.0031 | 0.0110 | 0.0034 | 0.0040 | 0.0033 | 0.0031 | 0.0037 | 0.0033 (| 0.0118 0 | 0 6600' | 0121 0 | 0107 |
| Cats/2 | ^ | 0.0000 0.0 | 008 0.000 | 000000000000000000000000000000000000000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0009 | 0.0000 | 0.0000 | 0.0001 | 0.0006 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0000.0 | 0.0012 (| 00000 (| 0000 0 | 0 0000 | 0000 |
| . – | Fe ³⁺ | 1.7457 1.7 | 280 1.732 | 1 1.6927 | 1.7466 | 1.7360 | 1.7307 | 1.6838 | 1.7412 | 1.7091 | 1.6720 | 1.7763 | 1.6315 | 1.6505 | 1.5524 | 1.7052 | 1.6658 | 1.6603 | 1.4855 | 1.6321 1 | .5826 1 | 5714 1 | .4466 |
| | Mg (| 0.0008 0.0 | 007 0.000 | 0.000 | 0.0007 | 0.0000 | 0.0006 | 0.0000 | 0.0005 | 0.0007 | 0.0023 | 0.0019 | 0.0018 | 0.0015 | 0.0000 | 0.0000 | 0.0009 | 0.0015 | 0.0009 | 00000 (| 0032 0 | 0014 0 | 0014 |
| | ĨZ | 0.0000 0.0 | 000 0.000 | 000000000000000000000000000000000000000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0000.0 | 0.0001 (| 0000.0 | 0000 0 | 0 0000 | 0000. |
| | Fe ²⁺ (| 0.1219 0.1 | 297 0.12' | ⁸ 0.1487 | 0.1194 | 0.1272 | 0.1279 | 0.1516 | 0.1244 | 0.1414 | 0.1564 | 0.1064 | 0.1732 | 0.1692 | 0.2192 | 0.1397 | 0.1617 | 0.1622 | 0.2494 (| 0.1766 (| 0.1988 0 | 2048 0 | .2678 |
| | Mn (| 0.0 0000.0 | 005 0.000 | 000000000000000000000000000000000000000 | 0.0013 | 0.0000 | 0.0000 | 0.0012 | 0.0004 | 0.0000 | 0.0001 | 0.0001 | 0.0020 | 0.0000 | 0.0005 | 0.000 | 0.0001 | 0.0015 | 0.0000 (| 0000.0 | 0000 0 | 0007 0 | 0012 |
| | Zn (| 0.0000 0.0 | 008 0.000 | 000000000000000000000000000000000000000 | 0.0008 | 0.0000 | 0.0022 | 0.0009 | 0.0000 | 0.0007 | 0.0003 | 0.0000 | 0.0000 | 0.0000 | 0.0002 | 0.0036 | 0.0008 | 0000.0 | 0.0020 (| 0.0001 (| 0001 0 | 0 0000 | 0000 |
| | Ca (| 0.0000 0.0 | 000 0.000 | 000000000000000000000000000000000000000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0004 (| 0000.0 | 0000 0 | 0 0000 | 0000 |
| - | Sum | 2.0000 2.0 | 000 2.000 | 0 2.000(| 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 5.0000 | 2.0000 | 2.0000 2 | .0000 2 | 0000 2 | .0000 |
| | FeSiO ₃ (| 0.000 0.1 | 29 0.000 | 0.103 | 0.066 | 0.072 | 0.016 | 0.069 | 0.074 | 0.046 | 0.028 | 0.049 | 0.091 | 0.000 | 0.022 | 0.000 | 0.021 | 0000 | 0.130 (| 0.173 (| 0.104 0 | 081 0 | .179 |
| • | FeZrO ₃ | | | | | | | | | | | | | | | 0.075 | 0.030 | 0000 | 0.000 | | | | |
| | MgTiO ₃ (| 0.085 0.0 | 68 0.020 | 0.069 | 0.072 | 0.000 | 0.065 | 0.000 | 0.046 | 0.072 | 0.234 | 0.189 | 0.179 | 0.146 | 0.003 | 0.000 | 0.093 | 0.154 | 0.091 (| 0.000 | .320 0 | 135 0 | .140 |
| . • | NiTiO ₃ (| 0.000 0.0 | 00 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0000 | 0.006 (| 0000 | 0000 | 000 | 000 |
| • | FeTiO ₃ 11 | 2.187 12.8 | 41 12.77 | 14.764 | 11.871 | 12.643 | 12.771 | 15.092 | 12.370 | 14.094 | 15.616 | 0.589 1 | 7.228 1 | 6.922 2 | 1.901 | 3.896 1 | 6.124 1 | 5.222 2. | 4.812 17 | 7.483 19 | .777 20 | 403 26 | .599 |
| | MnTiO ₃ (| 0.000 0.0 | 51 0.000 | 0.029 | 0.133 | 0.000 | 0.000 | 0.118 | 0.036 | 0.000 | 0.007 | 0.015 | 0.197 | 0.000 | 0.051 | 0.091 | 0.013 | 0.154 | 0.000 | 0000 | 0000 | 073 0 | .116 |
| End . | ZnTiO ₃ (| 0.000 0.0 | 78 0.000 | 0.000 | 0.081 | 0.000 | 0.218 | 0.092 | 0.000 | 0.073 | 0.031 | 0.000 | 0.000 | 0.000 | 0.021 | 0.360 | 0.080 | 0000 | 0.200 (| 0.011 0 | 005 0 | 000 | 000. |
| Members | CaTiO ₃ (| 0.000 0.0 | 00 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.010 | 0.041 (| 0000 (| 0000 | 000 | 000. |
| - | Sum 12 | 2.272 13.1 | 68 12.80 | 14.965 | 12.222 | 12.715 | 13.068 | 15.371 | 12.525 | 14.286 | 15.917 | 0.841 1 | 7.695 1 | 7.069 2 | 1.998 1 | 4.422 1 | 6.361 1 | 5.541 2: | 5.280 17 | 7.667 20 | .206 20 | 692 27 | .035 |
| | Fe ₂ O ₃ 8'. | 7.284 86.4 | 02 86.60 | 84.635 | 87.330 | 86.801 | 86.535 | 84.192 | 87.059 | 85.456 | 83.602 8 | 38.813 8 | 1.576 8 | 2.527 7 | 7.622 8 | 5.261 8 | 3.290 8 | 3.013 7. | 4.277 81 | 1.604 75 | .131 78 | 569 72 | .330 |
| - | Cr ₂ O ₃ (| 0.218 0.2 | 57 0.319 | 0.243 | 0.201 | 0.228 | 0.280 | 0.265 | 0.226 | 0.165 | 0.265 | 0.154 | 0.552 | 0.169 | 0.199 | 0.166 | 0.154 | 0.185 | 0.163 (|).589 (| .496 0 | 607 0 | .534 |
| | V ₂ O ₃ (| 0.000 0.0 | 40 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.045 | 0.000 | 0.000 | 0.004 | 0.029 | 0.000 | 0.000 | 0.000 | 0.000 | 0000 | 0.062 (| 0000 | 0000 | 000 | 000. |
| | Al ₂ O ₃ (| 0.226 0.1 | 33 0.27 | 0.158 | 0.247 | 0.256 | 0.117 | 0.172 | 0.144 | 0.093 | 0.216 | 0.188 | 0.148 | 0.236 | 0.181 | 0.152 | 0.196 | 0.262 | 0.217 (| 0.140 (| 0.167 0 | 132 0 | .101 |
| - | Sum 8. | 7.728 86.8 | 32 87.19' | 85.035 | 87.778 | 87.285 | 86.932 | 84.629 | 87.475 | 85.714 | 84.083 8 | 39.159 8 | 2.305 8 | 2.931 7 | 8.002 8 | 5.578 8 | 3.639 8 | 3.459 7. | 4.720 82 | 2.333 79 | .794 79 | 308 72 | .965 |
| | Total 100 | 0.000 100.0 | 00 100.000 | 100.000 | 100.000 | 100.000 | 100.000 | 100.000 | 00.000 | 100.000 1 | 00.000 10 | 0.000 10 | 0.000 10 | 0.000 10 | 0.000 10 | 0.000 10 | 0.000 10 | 0.000 10 | 0.000 100 | 0.000 100 | 000 100 | 000 100 | .000 |
| | | | | | | | | | | | | | | | | | | | | | | | |

Table 2. Comparison of titanohematite EMP analysis results and inferred T_N values (left) with T_N based on magnetic measurements (right). Listed in order of increasing EMP XIIm.

| Sample | Fe-rich ^a | Mean | Median | Sample | Measured |
|----------------------------|----------------------|------|--------|-----------|-------------|
| MOD22-22 | | | | MOD22-22 | |
| $XIlm \times 100 (68)^b$ | 12.2 | 12.9 | 12.9 | | 8.0 |
| T _N °C | 607 | 602 | 602 | | 635 |
| MOD22-52b (68) | | | | MOD22-52 | |
| $XIlm \times 100$ | 12.2 | 12.9 | 12.6 | | 7.1 |
| $T_{\rm N}^{\circ}{\rm C}$ | 607 | 602 | 604 | | 641 |
| MOD22-51b | | | | MOD22-51b | |
| $XIlm \times 100 (53)$ | 12.6 | 14.1 | 14.3 | | 7.2 |
| $T_{\rm N}^{\circ}{\rm C}$ | 604 | 593 | 592 | | 640 |
| MOD22-12c | | | | MOD22-12c | |
| $XIlm \times 100 (106)$ | 15.2 | 16.8 | 16.5 | | 9.0 |
| $T_{\rm N}^{\circ}{\rm C}$ | 586 | 573 | 576 | | 629 |
| MOD22-42a | | | | MOD22-42a | |
| $XIlm \times 100 (35)$ | 11.0 | 17.2 | 17.2 | | 9.0 |
| $T_{\rm N}^{\circ}{\rm C}$ | 615 | 570 | 570 | | 629 |
| MOD22-4a | | | | MOD22-4a | |
| $XIlm \times 100 (98)$ | 17.8 | 20.7 | 20.0 | | 9.0 |
| $T_{\rm N}^{\circ}{\rm C}$ | 565 | 542 | 548 | | 629 |
| | | | | MOD22-6 | |
| $XIlm \times 100$ | | | | | 8.8 |
| $T_{\rm N}^{\circ}{\rm C}$ | | | | | 630 |
| | | | | MOD22-8 | |
| $XIlm \times 100$ | | | | | 8.8 |
| $T_{\rm N}^{\circ}{\rm C}$ | | | | | 630 |
| | | | | | (580-600) |
| | | | | | (15.9–13.2) |

^{*a*}Hematite-rich end of main cluster of analyses.

^bNumber of EMP analyses with acceptable sums.

Mod22-12c: 15.2, 16.8, 16.5, 17.8; **Mod22-4a:** 7.8, 20.7; 20.0, 23.2.

The composition data suggests that the more Ti-rich compositions include significant fine ilmenite exsolution lamellae, however, the compositions with the lowest Ti may, or may not include areas free of ilmenite exsolution. Magnetically inferred compositions of the titanohematite hosts (see below) indicate that from 6.4 to 16.6 per cent FeTiO₃ is retained in solid solution. The presence of the ultra-fine ilmenite lamellae (see below) was confirmed by magnetic measurements and Mössbauer spectroscopy on sample MOD22-22.

TEM investigations initially failed to demonstrate the presence of ilmenite lamellae in titanohematite in samples MOD22-6 and MOD22-22, and it was speculated that these lamellae might be too small to detect by conventional TEM methods. After numerous attempts, electron diffraction patterns and a dark-field image were obtained from titanohematite separates from sample MOD22-22 showing very fine ilmenite exsolutions ~ 1 nm thick parallel to (001). The successful TEM observations were made on titanohematite grains from the separates used for Mössbauer spectroscopy.

We were never able to resolve ilmenite lamellae in sample MOD22-6, though magnetic experiments consistently indicated the presence of ilmenite and distinctive exchange bias in all the samples measured. We speculated that the ilmenite lamellae, possibly only three layers thick, are so small that they would not show an ordered reflection. The EMP analyses likely reflect overlap between the titanohematite host and extremely fine ilmenite exsolution lamellae. The chemistry reported here on the MOD22 samples, is very similar to MOD2 samples that had a typical titanohematite bulk composition of 18 per cent FeTiO₃ with \sim 10 per cent FeTiO₃ remaining in solid solution and 8–9 per cent lamellae (McEnroe *et al.* 2007a). However, compared to titanohematites from other ig-

neous and metamorphic rocks we have studied (McEnroe & Brown 2000; McEnroe *et al.* 2001a,b, 2002, 2007b; Kasama *et al.* 2004; McCammon *et al.* 2009; Robinson *et al.* 2014b), the minor substitutions in the titanohematite are extremely limited, with maximum values of: wt.% Al₂O₃ 0.18; Cr₂O₃ 0.60; V₂O₃ 0.09, MnO 0.09 and MgO 0.09.

The above compositions and their interpolated titanohematite Néel temperatures were compared with titanohematite Néel temperatures measured on four samples as discussed later. The compositions and temperatures are listed in Table 2. By using measured and inferred compositions in terms of % FeTiO₃, and assuming the ilmenite lamellae have a composition of 98 per cent FeTiO₃, the inferred percentages of lamellae and hosts are as follows:

MOD22-22 Bulk mean EMP composition 12.9; MOD22-22 Magnetically inferred host 8;

5.4 per cent Ilmenite lamellae, 94.6 per cent Hematite host MOD22-52b Bulk mean EMP composition 12.9; MOD22-52b Magnetically inferred host 7.1;

6.4 per cent Ilmenite lamellae, 93.6 per cent Hematite host MOD22-51b Bulk mean EMP composition 14.1; MOD22-51b Magnetically inferred host 7.2;

7.6 per cent Ilmenite lamellae, 92.4 per cent Hematite host MOD22-12c Bulk mean EMP composition 16.8; MOD22-12c Magnetically inferred host 9.0;

8.8 per cent Ilmenite lamellae, 91.2 per cent Hematite host

MOD22-42a Bulk mean EMP composition 17.2; MOD22-42a Magnetically inferred host 9.0;

9.2 per cent Ilmenite lamellae, 90.8 per cent Hematite host MOD22-4a Bulk mean EMP composition 20.7; MOD22-4a Magnetically inferred host 9.0;

13.1 per cent Ilmenite lamellae, 86.9 per cent Hematite host



Figure 1. (a) NRM in A m⁻¹ plotted against susceptibility (SI). The shading represents density values, with the darkest shades indicating the highest densities. (b) Susceptibility (10^{-6} SI) plotted against density (kg m⁻³). The grey shading is indicating NRM intensity with darkest shading representing highest NRM values.

The fact that the EMP analyses are significantly higher in FeTiO₃ contents than the magnetically inferred host compositions implies that the titanohematite host contains substantial ilmenite exsolution lamellae at a scale finer than the electron probe beam at 1 μ m, so that EMP analyses represent overlap analyses between titanohematite and ilmenite lamellae. Because the rocks are of sedimentary origin, with titanohematite produced by high-grade metamorphism of earlier fine-grained sedimentary oxides, these oxides are not homogeneous and may contain variations in ilmenite content even within the same thin section, and in some, local occurrences of magnetite and rutile.

3 MAGNETIC PROPERTIES

3.1 NRM and susceptibility

NRM measurements on 1-inch paleomagnetic core samples were made on an AGICO JR-6 magnetometer and susceptibility on the same cores was measured with a sapphire susceptibility bridge (SI-2b). Though the amounts of oxide are small, the rock layers at the MOD22 location show a strong and stable NRM with a mean vector of declination 260° , inclination -67° , and intensity of 5.5 A m⁻¹. Intensities range from 2 to 23 A m⁻¹. In a plot of susceptibility against NRM (Fig. 1a) the highest NRM values plot in the region of low bulk susceptibility (<0.003 SI). Some samples contain a very small amount of magnetite. An estimate of the amount of magnetite for the sample with the highest susceptibility (0.0073/0.0347) is ~ 0.2 per cent, and even this estimate is too high, because it treats all susceptibility as if it were due solely to magnetite. Given that samples with higher NRMs have low susceptibility ($<3 \times 10^{-3}$ SI), and typical $T_{\rm N}$ above 575 °C (discussed below), magnetite clearly is not responsible for the high NRM values. The median susceptibility value for the 46 MOD22 samples is 1.29×10^{-3} SI, (average 1.86 $\times 10^{-3}$ SI). There is a good correlation between NRM and density values, with the highest NRMs all having densities significantly greater than the average of 2.81 g cm⁻³ (Fig. 1b). Titanohematite is the densest mineral in these rocks, which are mainly composed of quartz, feldspar and muscovite and is strongly correlated with the NRM. The orientation of the titanohematite crystals will also effect the intensity of NRM (Robinson *et al.* 2013). Numerous 'large' crystals are actually groups of crystals, likely geometrically related due to deformation-induced lattice-preferred orientation that is demonstrated by EBSD studies to be presented in Paper III. In addition to the effect of the lattice-preferred orientations on the NRM, the titanohematite grain orientations with respect to the Mesoproterozoic magnetizing field are also important in interpreting the magnetic exchange bias related to the NRM.

3.2 Room- and high-temperature experiments

The room-T hysteresis loops were measured on a Princeton vibrating sample magnetometer (VSM). MOD22 samples show a range of bulk coercivities (H_c) from 8 to 30 mT. In many samples the hysteresis loop remains open to fields above 200 mT indicating components with significantly higher coercivities than the bulk coercivity. Room-temperature hysteresis loops of MOD22-22 and MOD22-6 are shown in Figs 2(a) and (c). The hysteresis loop for MOD22-6 is clearly that of a titanohematite with a magnetic remanence (M_{RS}) to magnetic saturation (M_S) ratio of over 0.6, while MOD22-22 loop has a slightly lower ratio of 0. 53.

High-T magnetic measurements were made to obtain Néel temperatures on the host titanohematites, and to determine if magnetite were present in the sample. Dense quarter hysteresis loop measurements provide $M_{\rm S}(T)$, $M_{\rm RS}(T)$ and low-and-high field susceptibility χ_0 (*T*), and $\chi_{\rm HF}(T)$ from room temperature to 700 °C (Fabian *et al.* 2013). These measurements were made on a Princeton VSM with a furnace installed. Four samples were measured from the different layers in MOD22, (4a, 42a, 8 and 22), and one from MOD2. $M_{\rm S}(T)$ and $M_{\rm RS}(T)$ curves for samples 22–8 and 22–43 are shown in Fig. 3, together with their derivatives, from which ordering temperatures in the range 575–620 °C can be inferred. These coincide with the characteristic $T_{\rm N}$'s of titanohematites with compositions of ~IIm 10.3–16.6. This temperature range also contains the Curie temperature of magnetite at 580 °C. Fortunately, magnetite can be



Figure 2. Room-temperature symmetric hysteresis loop of MOD22-22 (a) and MOD22-6 (b) measured in a 1 T field. Hysteresis loops of field cooled (+1.5 T) samples measured at 10 K (c) MOD22-22 and (d) MOD22-6. Both samples show significant negative shift.

distinguished from titanohematite by its characteristic peak in highfield susceptibility $(\chi_{\rm HF})$ slightly above $T_{\rm C}$ (Fabian *et al.* 2013). Because such a peak in $\chi_{\rm HF}$ is absent in Figs 3(a) and (b) the observed ordering temperatures are not of ferrimagnetic origin but are AF, and can be related to the titanohematite. This explanation agrees well with the observation in Fig. 3(b) that different ordering temperatures are inferred from the $M_s(T)$ curve with steepest slope near 580 °C and the $M_{\rm rs}(T)$ curve with steepest slope near 610 °C. In a pure phase like magnetite, this discrepancy could not be explained, while it is not unusual if the phase has variable titanium content corresponding to a distribution of Néel temperatures. In such a case the steepest slope of $M_{\rm s}(T)$ marks the average $T_{\rm N}$, while the steepest slope of $M_{rs}(T)$ may be shifted towards the highest occurring $T_{\rm N}$. It is important to note that the lamellar moments of the contact layers do not have an individual ferrimagnetic structure, because they are not a separate phase, but are exchange coupled to the host titanohematite, so that they retain their magnetization to the $T_{\rm N}$ of the host.

In addition, four samples, 22–12C, 22–4a, 22–51B, and 22–6, were measured on an AGICO Kappabridge from 30 to 700 °C. Samples showed a range of titanohematite T_N from 575 to 640 °C. A temperature susceptibility measurement for MOD22-6 on warming from –196 to 20 °C is shown in Fig. 4. There is a steady increase in susceptibility from –196 to room temperature, with no abrupt change in magnetization to indicate a Verwey, or a Morin transition. With continued warming from 30 °C there is a strong increase in susceptibility with a peak at ~55 °C, followed by a rapid decrease

to 100 °C, then little decrease until approximately 625 °C. The bulk $T_{\rm N}$ of the titanohematite is interpreted to be ~630 °C, representing a composition of \sim ilm8.8. The distinctive susceptibility peak at 55 °C is also reminiscent of an AF ordering peak, or a phase transition. A peak at this temperature is also visible in the low-field slope in Fig. 3(a) where it can be seen that it reflects only changes to a very small fraction of M_s and M_{rs} . The source of this peak is unknown, however it may be due either to an intrinsic feature of titanohematite, a chrome-rich spinel with a component of Fe₂Cr0₄, or a mineral we have yet to identify. A chrome spinel of \sim composition Fe_{1.9}Cr_{1.1}0₄, would have a Curie temperature of \sim 55 °C (Francombe 1957). Though the peak shape and Curie temperature also resembles that of a titanomagnetite of composition TM70 (70 per cent ulvöspinel), the rocks are far too oxidized to contain a phase of this composition. Detrital grains of TM70, if they originally existed at all, would have oxy-exsolved to a magnetite with ilmenite oxy-exsolution lamellae during cooling from the amphibolite-facies regional metamorphism. A titanohematite with a very small fraction of chromian spinel may be consistent with some of our EMP analyses indicating up to $0.5 \text{ wt\% } \text{Cr}_2\text{O}_3$ (Table 1).

When we compare the high-temperature susceptibility measurements from the VSM with the Kappabridge measurements, for the purpose of estimating the Néel temperature (T_N) of the titanohematite the temperature uncertainty of the Kappabridge measurements is presumably lower, because the thermocouple sits inside the sample powder, whereas the sample on the VSM is a rock chip with variable size and thickness positioned several millimetres above the



Figure 3. High-temperature quarter hysteresis loops for samples MOD22-8 (a) and MOD22-43 (b) contain detailed information about titanohematite composition. After moderate smoothing, each data set (left) synchronously estimates $M_s(T)$, $M_{rs}(T)$, (top: orange, blue), $\chi_0(T)$, and $\chi_{HF}(T)$, (bottom: orange, blue). The derivatives dM_s/dT , dM_{rs}/dT (top: red, green) indicate position and distribution of ordering temperatures. The presence of any significant amount of magnetite can be excluded because it would generate a significant peak in $\chi_{HF}(T)$. To show the χ_{HF} curves these were multiplied by 10 for (a) and by 30 for (b). The $\chi_0(T)$ can be used to link the results to independent measurements made on the Kappabridge.



Figure 4. Sample was cooled to -196C and susceptibility was measured with warming to room temperature. The high temperature measurement was from 30 to 700 °C. There is no evidence for a Verwey transition at low temperature. The distinct peak at 55 °C is not identified, but may be due to Cr-rich magnetite-chromite solid solution, or an intrinsic property of the titanohematite with exchange coupled ilmenite lamellae, which is common in these samples. The T_N of titanohematite host is ~635 °C.

thermocouple. However, determining the exact position of the ordering temperature from initial susceptibility can be intrinsically inaccurate (Petrovsky & Kapicka 2006), also because the theoretically unique peak at the Curie temperature entangles with grain size dependent unblocking. Though the exact numbers will be different by some degrees, it is important to combine the complementary information from both of these data sets to estimate the compositions and to evaluate the magnetic properties at elevated temperatures. Given the above caveats, both methods yield useful temperatures that can give reasonable estimates of the amount of FeTiO₃ in solid solution in the titanohematite. These high-temperature data (Table 2) were used to estimate the approximate amount of FeTiO₃ in solid solution and thus estimate the amounts of ilmenite lamellae as described earlier.

3.3 Low-temperature magnetic experiments

Because of the remarkable low-temperature magnetic exchange bias found in the MOD2 sample (McEnroe *et al.* 2007a), similar experiments were made at the IRM, University of Minnesota, in fields up to 1.5 Tesla with a cyro-cooler installed in a Princeton VSM. The sample chips measured on the VSM were randomly oriented grains, however the rock has a strong foliation and there is presumed to be a preferred orientation of the titanohematite grains with in the samples. In addition an MPMS was used for low-T hysteresis measurements with fields up to 5 T, as reported in Paper II, and for measurements of frequency dependence of alternating current (AC) susceptibility reported here.

For one set of low-temperature (low-T) experiments the first loops were measured at 10 K after zero-field cooling (ZFC) from room temperature on rock chips that were in an initial 'NRM' state (no prior experiments). It has been shown that the NRM component in the measurement direction is reflected in the exchange bias distribution as determined from the hysteresis shape (Fabian *et al.* 2008). The direction and orientation of the lamellar NRM and the statistical magnetization in the NRM state have a strong effect on the shape and amount of shift in the resulting hysteresis loop. During the



Figure 5. Plotted are the maximum shift, (H_E), for each hysteresis loop with from 60 to 20 K for samples MOD2 (square), and for MOD22-6 from 60 to 10 K (circle). Here the H_E is measured by subtracting the lower branch from the upper branch of the hysteresis loop with the maximum difference representing the amount of shift. Because the sample was pretreated with a +1 T field, and then FC (+1 T) prior to measuring the hysteresis loops the resulting shift is in the negative field. Data for *H*_E for the MOD2 sample was originally published in McEnroe *et al.* (2007a).

hysteresis experiment part of the NRM properties are changed, and therefore this experiment cannot be repeated. We refer to these initial hysteresis measurements made at low-T as 'NRM' loops because the only treatment the sample has experienced is the ZFC to low-T (10 K), prior to the hysteresis measurement. This distinguishes them from samples that previously had a RT hysteresis measurement prior to cooling, or samples that have been field-cooled (FC) prior to measuring a hysteresis loops at low-T.

Figs 2(b) and (d) shows hysteresis loops measured after cooling in a +1.5 T field from RT to 10 K for samples MOD22-22 and MOD22-6. Both samples show a negative shift of more than 500 mT in stark contrast to the symmetrical RT loops (Figs 2a and b). MOD22-22 has a peculiar beak shape possibly due to the presence of a small amount of magnetite, which saturates at significantly lower fields than the ilmenite lamellae and associated contact layers. These field-cooled loops are in sharp contrast to hysteresis loops run above the T_N of ilmenite (57 K), which are symmetric.

To compare the low-temperature behaviour of MOD22 to MOD2, hysteresis loops were measured with warming in steps of 5° , from 10 to 60 K, after samples were first field-cooled in a positive field of 1.5 T. This resulted consistently in a strong negative magnetic exchange bias $(H_{\rm E})$ in both the MOD2 and MOD22 samples, with negatively shifted loops at temperatures below 57 K. The exchange bias $(H_{\rm E})$ values determined for MOD2 and MOD22 at each temperature are plotted in Fig. 5. A common method used to determine exchange bias field is by averaging the negative and positive coercivites. It is the irreversible portion of the hysteresis loop that is of interest here therefore we remove the reversible linear portion of the loop. We calculated the irreversible part by subtracting the upper branch of the hysteresis loop from the lower branch, which results in a curve where the maximum field is a good approximation of the exchange bias field. Using this method for a symmetric loop the field value at the maximum would be zero (no exchange bias field). Here the bias fields range from 0 to 1 mT at 55 K, to 750 mT for MOD22-22 at 10 K, whereas MOD2 is shifted by nearly 1 T at 20 K. Higher applied fields are necessary to saturate the ilmenite lamellae, and to give a true measure of the H_E , than what was used on the VSM.



Figure 6. (a) An untreated rock chip of MOD22-12c with the original natural lamellar NRM was placed at random in the instrument and cooled to 10 K before the hysteresis loop was measured. (b) The same sample was FC (+1.5T) from RT to 10 K. With the application of a strong field at RT a significant portion of the lamellar magnetism was oriented in the field direction and harden with cooling before reaching T_N of ilmenite. The FC hysteresis loop shows significant H_E however the resultant loop is not fully saturated. Experiment (a) necessarily took place before (b).

The strong positive field applied, and held during the field cooling from RT to 10 K, oriented most of the lamellar magnetic moments quasi-parallel to the field regardless of the strong tendency in crystals for remanence to lie in or close to the (001) basal plane. Thus, on cooling through T_N of ilmenite, the ilmenite magnetization takes a direction normal to (001) because it is coupled antiferromagnetically to the component of the positive lamellar magnetism that was normal to (001).

In a different set of experiments aimed at evaluating the effect of the NRM on the exchange coupling at low temperature, a set of sample chips were first cooled in absence of a field down to 10 K, well below T_N of ilmenite, before measurement of the hysteresis loop (Fig. 6a). The resulting 'NRM' loop is distinctly bimodal, with the dominant opening in a positive direction, and a slightly smaller opening in a negative direction. After these initial 'NRM' loops were measured, the samples were warmed back to RT well above the T_N of ilmenite, and a field of +1.5 T was applied causing the lamellar magnetism to obtain a strong orientation in a positive direction. The sample was then FC (+1.5 T) to 10 K, well below the T_N of ilmenite. Below 57 K the ilmenite acquires a negative magnetic moment by antiferromagnetic coupling to the strong positive lamellar moment



Figure 7. A rock chip of MOD22-6 cooled in field of +1.5T from room temperature to 10 K. The induced magnetization increases progressively until close to 57 K, the T_N of ilmenite. Beyond this there is a decline to ~40 K, beyond which increase resumes. The decline is interpreted as due to the onset of ilmenite magnetization antiferromagnetically coupled to the lamellar magnetism of hematite.

initially created at RT. This interaction during the field cooling results in a very large unimodal shifted loop (Fig. 6b).

Cooling samples in a strong magnetic field and measuring the moment with cooling also indicated the presence of ilmenite. Fig. 7 shows the magnetic moment plotted against temperature for a sample cooled in a field of positive 1.5 T from 300 to 10 K. In this measurement the induced magnetization increases progressively from room temperature until close to 57 K, the Néel T of ilmenite. This is followed by a decline interpreted as the effect of antiferromagnetically coupled ilmenite to ~40 K, below this temperature, there is an increase in the moment which we attribute to a further strengthening of lamellar magnetism in the contact layers.

To examine the possibility of superparamagnetic lamellae and to have an estimate of the blocking temperature of the AF ilmenite, AC susceptibility was measured from 300 to 5 K at seven frequencies from 1 to 999 Hz on MOD22-6 and is compared to the same measurements on MOD2. This data set (Fig. 8) shows a distinct susceptibility peak just above 55 K, in both in-phase, and out-ofphase susceptibility, interpreted as the magnetic blocking temperature of ilmenite lamellae. The data shows little dispersion at any temperature, which would be an indication of superparamagnetic behaviour. This data from MOD22-6 (Fig. 8a) and MOD 2 (Fig. 8b) was measured in the same conditions and at the same frequencies. The MOD2 sample contains abundant nanoscale ilmenite lamellae (Fig. 11). The two plots show nearly identical behaviour with a small but distinct, AF ordering peak just below 57 K that we attribute to the ilmenite lamellae. The lack of dispersion in the data, at all the frequencies measured is convincing evidence that there are no superparamagnetic grains or lamellae in the samples. In addition, the disappearance of the exchange bias on warming these samples to above 57 K, confirms that the magnetic ordering of ilmenite is the critical factor in producing this unusual magnetic behaviour.

3.4 Nature of magnetic coupling

The matter of magnetic coupling between the high-temperature lamellar NRM of titanohematite and the low-*T* magnetism of ilmenite is illustrated in Fig. 9. In order for the ilmenite to have a magnetic moment, and couple with the titanohematite host, it must consist of an odd number of Fe layers (Harrison *et al.* 2007), in this example, one layer. However, Fig. 9(a) shows that if the



Figure 8. Alternating current susceptibility on sample MOD22-6 (a) in the temperature range 300-5 K, and 300 to 10 K for MOD2 (b) both at seven frequencies from 1 to 999 Hz. Both samples have nanoscale ilmenite lamellae and have similar behaviours, showing a peak in susceptibility at all frequencies at ~55 K. This is interpreted as the magnetic blocking temperature for ilmenite lamellae. AC data for MOD2 sample was originally published in McEnroe *et al.* (2007a).

remanent magnetic moments of the contact layers are strictly parallel to (001) at room-temperature and below, and the ilmenite magnetic moments are perpendicular to (001) at T_N of ilmenite, then the lamellar NRM cannot influence the magnetic moment direction of the ilmenite lamellae on passing through T_N . The nature of the coupling determined by neutron diffraction studies (Harrison *et al.* 2010) showed that the remanent magnetic moments of the contact layers are tipped out of the basal (001) plane by about 30° (Fig. 9b). This tipping of the magnetic moment is present at low-*T*, where the coupling occurs, but also even at room *T*, and necessarily even at the



Figure 9. Theoretical diagrams showing two Fe atomic views of the nature of interface magnetic coupling between lamellar magnetism in a hematite host and a simple ilmenite lamella parallel to (001) with only a single Fe layer. Atomic views are parallel to a (1 - 2 0) plane of the unit cell, and show the 6-layer repeat of (001) layers. In (a) the lamellar magnetic moments are rigidly parallel to (001) and the ilmenite magnetic moments are rigidly normal to (001) so that coupling is theoretically not possible. In (b) the lamellar magnetic moments are tipped 30° from (001), based on Harrison *et al.* (2010), providing a lamellar component out of the (001) plane that can couple antiferromagnetically with ilmenite below T_N .

high *T*, where the lamellar remanence was acquired. Some tipping likely occurs also in the adjacent titanohematite layers, which are exchange coupled to the contact layers.

4 MÖSSBAUER SPECTROSCOPY

Mössbauer spectroscopy was used to characterize the magnetic phases using methods from Dyar *et al.* (2004). Approximately 20 mg of the powdered mineral separates of titanohematite were mixed with sugar, then placed in a sample holder confined by Kapton[®] tape. Mössbauer spectra were acquired from 295 K down to 4 K using a source of 40 mCi ⁵⁷Co in Rh on a SEE Co. (formerly WEB Research Co.) model WT302 spectrometer (Mount Holyoke College). Spectra were collected for 24 hr in 2048 channels and corrected for nonlinearity via interpolation to a linear velocity scale, which is defined by the spectrum of the 25 m Fe foil used for calibration. Mössbauer spectra were modelled using the Mex_Distd program, which was acquired from the University of Ghent cour-

tesy of E. DeGrave. The program uses Lorentzian line shapes and solves full Hamiltonians for isomer shift and quadrupole splitting. The program uses a line-shape-independent model for fitting the spectra. The program solves the full hyperfine-interaction Hamiltonian, producing a distribution of values for the hyperfine field and using quadrupole shift (Δ), centre shift (δ), magnetic field (kOe) and line width (Γ) as adjustable parameters.

A magnetic grain separate for Mössbauer spectroscopy was obtained from sample MOD22-22. The resulting pattern taken at room temperature, and its interpretation are shown in Fig. 10(a). The overall fit envelope (red line) is dominated by a typical absorption sextet of magnetic hematite that was fit with three subtly different distributions with $\delta = 0.37-0.39$ mm s⁻¹ and $\Delta = -0.23$ to -0.21 mm s⁻¹; these are shown by blue, green and brown curves having magnetic fields of 516, 507 and 491 kOe, respectively (Table 3). The multiple distributions suggest that this sample consists of hematite with varied grain sizes, which is not inconsistent with possible variations within different small layers or patches within the sample. The



Figure 10. Mössbauer spectra of a magnetic grain separate from core sample MOD22-22. The ilmenite doublet is best resolved in the 295 K spectrum in the top panel, which also illustrates the contribution from three different hematite distributions (shown in dashed purple, blue, and green lines). Data points are plotted as standard error bars, and the fit envelope is given as a thin red line. The bottom panel shows that the ilmenite doublet persists to *ca.* 75–60 K, at which point it magnetically orders such that its sextet is indistinguishable from those of the hematite.

Table 3. Mössbauer parameters for MOD22-22 magnetic separates. The sample is fit in Mexfieldd with Lorentzian distributions. Because multiple distributions were required to model hematite in this sample, broadening was not accounted for using QSD line shapes. The best fit was obtained using three hematite distributions and one distorted ilmenite distribution.

| | Hem1 | Hem2 | Hem3 | Ilm |
|-----------------------------|-------|-------|-------|------|
| $\delta (\text{mm s}^{-1})$ | 0.37 | 0.37 | 0.39 | 1.17 |
| $\Delta (\text{mm s}^{-1})$ | -0.23 | -0.23 | -0.21 | 1.02 |
| Field (kOe) | 516 | 507 | 491 | _ |
| $\Gamma (\text{mm s}^{-1})$ | 0.24 | 0.28 | 0.48 | 0.50 |
| Area (%) | 32 | 43 | 22 | 4 |
| χ^2 | | 3.3 | 2 | |

ilmenite doublet at 295 K has parameters of $\delta = 1.17 \text{ mm s}^{-1}$ and $\Delta = 1.02 \text{ mm s}^{-1}$ that are slightly higher than those of pure ilmenite (which would be $\delta = 1.07 \text{ mm s}^{-1}$ and $\Delta = 0.68 \text{ mm s}^{-1}$, *cf*. Dyar *et al.* (2006). Those differences likely reflect variations in the ilmenite crystal structure in such close proximity to hematite. There is no evidence in the Mössbauer spectra to suggest the presence of any other Fe-bearing phases such as spinel.

The sample was also measured at a range of temperatures down to 4 K, and the results are shown in Fig. 10(b). The ilmenite doublet orders magnetically over the temperature range from 75- to 50 K,

and the resultant sextet is overlapped by those of the hematite below those temperatures, making its contribution impossible to resolve separately. Moreover, at this low temperature, the small signal is split into a sextet so it is more difficult to resolve. For this sample and the temperatures studied, the ilmenite is best resolved in the 295 K spectra.

The room-temperature results show that 4 per cent of the total Fe in this sample is in ilmenite (Fe²⁺TiO₃) with an error estimate of ± 1.5 per cent (Dyar 1984). To understand these results properly, consider that every unit cell of end-member ilmenite contains six Fe²⁺ atoms per unit cell in a volume of 315.84 Å³, while every unit cell of end-member hematite contains 12 Fe³⁺ atoms in per unit cell volume of 301.20 Å³. Therefore, a 1:1 mixture of hematite and ilmenite would result in a distribution with 32 per cent of the total Fe in ilmenite, and 68 per cent in hematite (mole percentages 33.3 and 66.7).

To make use of the estimated 4 ± 1.5 per cent of total Fe in ilmenite, one must first calculate the proportion of Fe atoms in the bulk composition for this sample. Using 66 of the 68 EMP analyses, (excludes two Ti-rich outliers), the average composition with standard deviation is Ilm 12.9 \pm 0.5 (average as reported in Table 2). A chemical estimate of mole percents of ilmenite and hematite is made, according to the lever rule, by combining this chemical value 12.9, or 0.129 with error, with the estimated composition of the ilmenite phase at Ilm 98, or 0.98 (1.02 Fe atoms), and the hematite phase at Ilm 8, or 0.08 (1.92 Fe atoms). This calculation yields 5.4 ± 0.5 per cent ilmenite and 94.6 \pm 0.5 hematite on the basis of bulk composition.

Mössbauer %Fe (M_{Fe} Ilm) in ilmenite (M_{Fe} Ilm) relates to the bulk composition with its error limits ($B = 0.129 \pm 0.005$), the composition of the ilmenite phase (0.98) and the composition of the hematite phase (0.08) by the equation:

$$M_{Fe} Ilm = (B - 0.08) (2 - 0.98) / (2 - B) (0.98 - 0.08)$$

= 0.03 ± 0.003 (3 ± 0.3 per cent)
× [0.02968 if B = 0.129].

In process of constructing the equation, we took the average composition *B* as 200 atoms, including 12.9 atoms of Fe²⁺ and 2×87.1 atoms of Fe³⁺, giving at total of 187.1 Fe atoms. This also involved mole fractions of ilmenite and hematite, but these terms drop out in the final equation. The result of 3 ± 0.3 per cent fits within the broader error limits of the Mossbauer estimate, and is compatible with the chemical estimate of 5.4 ± 0.5 per cent ilmenite lamellae.

5 TRANSMISSION ELECTRON MICROSCOPY

From the hysteresis behaviour described above, and modelling related to lamellar magnetism, one might understand that ilmenite lamellae could be detected directly. A common route to phase identification in exsolved oxides is through X-ray diffraction or electron diffraction in the TEM. X-ray diffraction has proven inefficient at distinguishing exsolved phases from the host if the exsolved phase is minor. Because of more favourable diffraction geometry, TEM is generally much more successful at identifying minor phases. There has been extensive experience with identification and spatial resolution of ilmenite lamellae in hematite. This has been based on phase interface lattice strain in bright-field images and notably on the 003 Fe–Ti ordering reflection in ilmenite and its absence in hematite (Nord & Lawson 1989; McEnroe *et al.* 2007b), and dark-field



Figure 11. High-resolution TEM bright field images (a, c) and corresponding energy-filtered Ti element maps (b, d) at same scale prepared of MOD2 at University of Stuttgart. These images, of higher resolution than the one published by McEnroe *et al.* (2007a), demonstrate even more clearly the presence of ilmenite lamellae at least as thin as the 1.4 nm-thick unit cell. N.Y. Jin-Phillipp kindly provided the TEM images.

images taken through the 003 reflection. Spatial resolution can also be obtained in Fe and Ti element maps down to very fine scale (Golla & Putnis 2001; McEnroe *et al.* 2001b, 2002, 2007b; Kasama *et al.* 2009; Brownlee *et al.* 2010; Golla-Schindler & van Aken 2010).

The effectiveness of bright-field images and Fe-Ti element maps is illustrated in new images of the MOD2 sample (Fig. 11), which provide insights into size and shape characteristics in that sample. Many if not most of the lamellae are highlighted by shadows in bright-field images caused by coherent lattice strain between lamellae and host, but, at present, it is impossible to be sure if these show lamellar thicknesses including contact layers or without them. As noted above, critical lamellar thicknesses for magnetic exchange bias, not including contact layers would be 0.69, 1.61 and 2.53 nm. Aside from one large rutile lamella, one can see that the ilmenite lamellae occur in a wide range of sizes, and that the sizes are distributed in a way similar to other samples we have studied. The lamellae in each size range are surrounded by lamellar-free depletion zones, outside of which one finds lamellae of smaller sizes. This pattern has been interpreted as a product of several repeated cycles of nucleation and growth with gradually falling temperature. Measurement of the thicknesses of four sets of lamellae in an enlarged TEM image gave the results in nm: 30, 9.3, 4.7 and 2.3. By dividing by 0.23 nm (1 layer in ilmenite = 0.23 nm, 1 layer in hematite = 0.229 nm), these convert to 130, 40, 20 and 10 atomic layers, and further, to unit cells by dividing by 6. Adjacent to the thinnest measured lamellae one can see finer lamellae grading into very fine scale mottling that is not resolved as discrete lamellae. It seems entirely possible that this includes lamellae as thin as 0.69 nm that are not easily resolved by conventional TEM.

Samples of MOD22-22 were examined with a 200 kV Philips CM20 field emission gun transmission electron microscope at the

Bayerisches Geoinstitut. The sample was crushed under ethanol in a SiO_2 mortar and the dispersion placed on a lacey carbon film on Cu-grid (200 mesh). Dark-field TEM imaging and selected area electron diffraction were mainly employed to find lamellae of the ordered ilmenite phase within the titanohematite hosts. Earlier explorations of sample MOD22-6 discussed briefly below were made on a different instrument at Bayreuth.

Despite the strong magnetic evidence for ilmenite lamellae within the titanohematite hosts of the MOD22 samples, TEM methods similar to those used for the MOD2 sample failed to detect any ilmenite lamellae in earlier studies on the MOD22 samples. Specifically no ilmenite lamellae were observed in bright-field images, such as those obtained in Figs 11(a) and (c). In a few lattice images, very faint 003 reflections were observed that are characteristic of Fe-Ti ordered ilmenite, but attempts to obtain corresponding dark-field images, showing the spatial distribution of lamellae were unsuccessful. Small satellite diffraction spots thought to be a spinel structure phase, possibly magnetite were observed. It was speculated that magnetite might have been produced by reduction during ion thinning by argon bombardment, and further work was restricted to crushed grains. However, TEM evidence for very small amounts of magnetite in a few grains seems plausible. This is supported in hysteresis loops on one selected small completely natural rock fragment (MOD22-21b, candidate 2) reported in detail in Paper II.

Persistence concerning ilmenite was finally rewarded (Fig. 12), when dark-field TEM images were obtained through the thin edge of a powdered grain from sample MOD22-22, showing strong 1 -1 -1 reflections, characteristic of Fe-Ti ordered ilmenite, and forbidden in disordered hematite. One dark-field image with the 1 -1 -1 reflection (the lower right inset in Fig. 12) shows very abundant small lamellae parallel to (001). Measurements of the dark-field image,



Figure 12. A dark-field image with $\mathbf{g} = 1$ -1 -1 at the edge of a broken powdered grain of sample MOD-22-22. The diffraction spot of $\mathbf{g} = 1$ -1 -1 is one of the characteristic ones for Fe-Ti ordered ilmenite and forbidden for hematite. The inset at the upper left indicates the nearest zone axis, the inset at the lower right indicates the diffraction condition of the dark-field image.

with knowledge of the image orientation (see Appendix A), provide estimates that the lamellae are 1.3 to 1.68 nm thick (*c* of ilmenite is 1.4 nm) and have a common length along (001) of 12.5–17 nm, thus aspect ratios 7.4–13. So far there is no evidence in this sample of the range of coarser lamellae found in the MOD-2 sample, and it is at least possible that several of these samples, due to their composition and thermal history, contain only a single simple cycle of nucleation and growth.

5 CONCLUSIONS

The samples described here are from rocks that retained a remanent magnetization for nearly 1 billion years. This remanent magnetization creates a distinct ground-magnetic anomaly ~1700 nT below background. The average Koenigsberger ratio, Q = 124, for this rock body, clearly indicates that the response is completely dominated by the ancient NRM. The magnetic mineralogy is dominated by titanohematite with the nanoscale ilmenite lamellae, which explains the stable nearly billion-year memory retention. It also produces the highly unusual magnetic property of exchange bias shown by a shifted hysteresis loop below the 57 K ordering temperature of ilmenite. This feature requires two phases that are magnetically coupled (Shcherbakov & Sycheva 2005; Shcherbakov et al. 2009). Exchange bias will not be observed in a pure bulk antiferromagnetic, or ferrimagnetic mineral, but is observed in intergrowths of AFM and FM phases. In these intergrowths interface effects dominate the magnetic response when the phases become strongly exchangecoupled under temperature conditions where both become magnetized, below the lower of their Curie/Néel temperatures.

Shifted hysteresis loops in engineered materials are commonly in the range of 5–100 mT, but rarely were reported in natural materials. In MOD22 the horizontally shifted loops are associated with exchange coupling across a ferrimagnetic interface contact layer between AF nanoscale ilmenite lamellae and a canted AF titanohematite host. This new data shows bias fields of nearly 1 T, determined from the shift in hysteresis loops at 10 K. Though the H_E is less, the low-temperature magnetic behaviour is similar to that reported earlier on the MOD2 titanohematite with abundant nanoscale lamellae of ilmenite. The AF titanohematite with its moments in or near the basal plane, and nanoscale AF ilmenite with moments parallel to c, are coupled through a ferrimagnetic interface (Robinson *et al.* 2002) where the titanohematite moments are tilted approximately 30° out of the basal plane (Harrison *et al.* 2010). This interface coupling is responsible for these unusual magnetic properties. In the MOD22 samples the titanohematite host was characterized by EMP and TEM, however, the minor phase was very difficult to detect by conventional observation techniques (SEM, EMP and TEM). This was in contrast to the extensive magnetic evidence in the temperature range of 60–10 K for the presence of ilmenite lamellae.

The presence of ilmenite lamellae was further supported by the results of room and low-temperature Mössbauer spectroscopy, and eventually by the detection in a dark-field TEM image of fine Fe-Ti ordered ilmenite lamellae with thickness ~1 nm through the reflection 1 -1 -1. Such extremely small lamellae have a profound effect on the magnetic properties and through the associated contact layers create a strong natural magnetic remanence at room temperature that is implicated in significant magnetic exchange bias when samples are cooled below the Néel temperature of ilmenite. A key overall conclusion of Part I of this study is that the stable NRM of lamellar magnetism can be carried on the contacts of ilmenite lamellae \sim 1 nm thick when embedded in a magnetized hematite host, and that below $T_{\rm N}$ of ilmenite near 57 K, the ilmenite itself becomes magnetized and couples antiferromagnetically to the host. The observed exchange bias reported here is one of the largest known in any mineral, or synthetic material.

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REFERENCES

- Bingen, B., Davis, W.J., Hamilton, M.A., Engvik, A., Stein, H.J., Skår, Ø. & Nordgulen, Ø., 2008. Geochronology of high-grade metamorphism in the Sveconorwegian belt, S Norway: U-Pb, Th-Pb and Re-Os data, *Norwegian J. Geol.*, 88, 13–42.
- Brownlee, S.J., Feinberg, J.M., Harrison, R.J., Kasama, T., Scott, G.R. & Renne, P.R., 2010. Thermal modification of hematite-ilmenite intergrowths in the Ecstall ploton, British Columbia, Canada, *Am. Mineral.*, 95, 153–160.
- Burton, B.P., Robinson, P., McEnroe, S.A., Fabian, K. & Boffa Ballaran, T., 2008. A low-temperature phase diagram for ilmenite-rich compositions in the Fe₂O₃–FeTiO₃ system, *Am. Min.*, **93**, 1260–1272.
- Dyar, M.D., 1984. Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals, Am. Min., 69, 1127–1144.

- Dyar, D.M., McEnroe, S.A., Murad, E., Brown, L.L. & Schiellerup, H., 2004. The relationship between exsolution and magnetic properties in hemo-ilmenite: insights from Mössbauer spectroscopy, *Geophys. Res. Lett.*, **31** (4), L04608, doi:10.1029/2003GL019076.
- Dyar, M.D., Agresti, D.G., Schaefer, M., Grant, C.A. & Sklute, E.C., 2006. Mössbauer spectroscopy of Earth and planetary materials, *Ann. Revs. Earth planet. Sci.*, 34, 83–125.
- Fabian, K., Shcherbakov, V.P. & McEnroe, S.A., 2013. Measuring the Curie temperature, *Geochem. Geophys. Geosyst.*, 14, 947–961.
- Fabian, K., McEnroe, S.A., Robinson, P. & Shcherbakov, V.P., 2008. Exchange bias identifies lamellar magnetism as the origin of the natural remanent magnetization in ilmeno-hematite from Modum, Norway, *Earth planet. Sci. Lett.*, doi:10.1016/j.epsl.2008.01.034.
- Fabian, K., Miyajima, N., Robinson, P., McEnroe, S.A., Boffa Ballaran, T. & Burton, B.P., 2011. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: I. Fe-Ti order transition in quenched synthetic Ilm 60, *Geophys. J. Int.*, **186**, 997–1014.
- Fabian, K., Shcherbakov, V.P., McEnroe, S.A., Robinson, P. & Burton, B.P., 2015. Magnetic mean-field modelling of solid solutions: theoretical foundations and application to the hematite–ilmenite system, *Geophys. J. Int.*, 202, 1029–1040.
- Francombe, M.H., 1957. Lattice changes in spinel-type iron chromites, J. Phys. Chem. Solids, 3, 37–43.
- Goguitchaichvili, A. & Prevot, M., 2000. Magnetism of oriented single crystals of hemo-ilmenite with self-revered thermoremanent magnetization, *J. geophys. Res.*, **105**, 2761–2780.
- Golla, U. & Putnis, A., 2001. Valence state mapping and quantitative electron spectroscopic imaging of exsolution in titanohematite by energy fileted TEM, *Phys. Chem. Mins.*, 28, 119–129.
- Golla-Schindler, U. & van Aken, P.A., 2010. Electron energy-loss spectroscopy and energy-filtered transmission electron microscopy: nanoscale determination of Fe3+/Σ Fe ratios and valence-state mapping, in *Nanoscopic Approaches in Earth and Planetary Sciences*, Vol. 8, pp. 57–110, eds Brenker, F.E. & Jordan, G., EMU Notes in Mineralogy, The European Mineralogical Union and the Mineralogical Society of Great Britain & Ireland.
- Harrison, R.J., Kasama, T., White, T.A., Simpson, E.T. & Dunin-Borkowski, R.E., 2005. Origin of self-reversed thermoremanent magnetization, *Phys. Rev. Lett.*, 95, 268501.
- Harrison, R.J., McEnroe, S.A., Robinson, P., Palin, E.J. & Kasama, T., 2007. The mechanism of giant exchange bias (>1 T) in a natural intergrowth of Fe₂O₃-FeTiO₃, *Phys. Rev. B*, **76**, 174436-1–10.
- Harrison, R.J., McEnroe, S.A., Robinson, P. & Howard, C., 2010. Spin orientation in a natural Ti-bearing hematite: evidence for an out-of plane component, *Am. Min.*, **95**, 974–979.
- Hoffman, K.A., 1992. Self-reversal of thermoremanent magnetization in the ilmenite-hematite system—order-disorder, symmetry, and spin alignment, J. geophys. Res., 97, 10 883–10 895.
- Kasama, T., McEnroe, S.A., Ozaki, N., Kogure, T. & Putnis, A., 2004. Effects of nanoscale exsolution in hematite-ilmenite on the acquisition of stable natural remanent magnetization, *Earth planet. Sci. Lett.*, 224, 461–475.
- Kasama, T. *et al.*, 2009. The application of Lorentz transmission electron microscopy to the study of lamellar magnetism in hematite-ilmenite, *Am. Min.*, 94, 262–269.
- Lagroix, F., Banerjee, S.K. & Moskowitz, B.M., 2004. Revisiting the mechanism of reversed thermoremanent magnetization based on observations from synthetic ferrian ilmenite (y = 0.7), *J. geophys. Res.*, **109**, B12108, doi:10.1029/2004JB003076.
- Lawson, C.A., Nord, G.L., Jr., Dowty, E. & Hargraves, R.B., 1981. Antiphase domains and reverse thermoremanent magnetism in ilmenite-hematite minerals, *Science*, 213, 1372–1374.
- McCammon, C., McEnroe, S.A., Robinson, P. & Burton, B.P. 2009. Mössbauer spectroscopy used to quantify natural lamellar remanent magnetization in single-grains of ilmeno-hematite, *Earth planet. Sci. Lett.*, 288, 268–278.
- McEnroe, S.A. & Brown, L.L., 2000. A closer look at remanence-dominated anomalies: rock-magnetic properties and magnetic mineralogy of the Rus-

sell Belt microcline-sillmanite gneisses, Northwest Adirondacks Mountains, New York, *J. geophys. Res.*, **105**, 16 437–16 456.

- McEnroe, S.A, Harrison, R.J., Robinson, P., Golla, U. & Jercinovic, M.J., 2001b. Effect of fine-scale microstructures in titanohematite on the acquisition and stability of natural remanent magnetization in granulitefacies metamorphic rocks southwest Sweden: implications for crustal magnetism, J. geophys. Res., 106, 30 523–30 546.
- McEnroe, S.A., Robinson, P. & Panish, P.T., 2001a. Aeromagnetic anomalies, magnetic petrology and characterization of ilmenite-and magneticrich cumulates of the Sokndal region, Rogaland, Norway, *Am. Min.*, 86, 1447–1468.
- McEnroe, S.A., Harrison, R.J., Robinson, P. & Langenhorst, F., 2002. Nanoscale haematite-ilmenite lamellae in massive ilmenite rock: an example of "lamellar magnetism" with implications for planetary magnetic anomalies, *Geophys. J. Int.*, **151**, 890–912.
- McEnroe, S.A., Carter-Stiglitz, B., Harrison, R.J., Robinson, P., Fabian, K. & McCammon, C.C., 2007a. Magnetic exchange bias of more than 1 Tesla in a natural mineral intergrowth, *Nat. Nanotechnol.*, doi:10.1038/nnano.2007.292.
- McEnroe, S.A., Robinson, P., Langenhorst, F., Frandsen, C., Terry, M.P. & Boffa Ballaran, T., 2007b. Magnetization of exsolution intergrowths of hematite and ilmenite: mineral chemistry, phase relations, and magnetic properties of hemo-ilmenite ores with micron- to nanometer-scale lamellae from Allard Lake, Quebec, *J. geophys. Res.*, **112**, B10103, doi:10.1029/2007JB004973.
- Meiklejohn, W.H. & Bean, C.P., 1956. New magnetic anisotropy, *Phys. Rev.*, 102, 1413.
- Meiklejohn, W.H. & Carter, R.E., 1959. Exchange anisotropy in rock magnetism, J. Appl. Phys., 30, 2020, doi:10.1063/1.1735116.
- Nagata, T. & Uyeda, S., 1959. Exchange interaction as a cause of reverse thermo-remanent magnetism, *Nature*, 184, 890–891.
- Nord, G.L., Jr. & Lawson, C.A., 1989. Order-disorder transition-induced twin domains and magnetic properties in ilmenite-hematite, *Am. Min.*, 74, 160–176.
- Petrovsky, E. & Kapicka, A., 2006. On determination of the Curie point from thermomagnetic curves, J. geophys. Res., 111, B12S27, doi:10.1029/2006JB004507.
- Prevot, M., Hoffman, K.A., Goguitchaichvili, A., Doukhan, J.C., Shcherbakov, V. & Bina, M., 2001. The mechanism of self-reversal of thermoremanence in natural hemoilmenite crystals: new experimental data and model, *Phys. Earth planet. Inter.*, **126**, 75–92.
- Robinson, P., Harrison, R.J., McEnroe, S.A. & Hargraves, R.B., 2002. Lamellar magnetism in the hematite-ilmenite series as an explanation for strong remanent magnetization, *Nature*, **418**, 517–520.
- Robinson, P., Harrison, R.J., McEnroe, S.A. & Hargraves, R.B., 2004. Nature and origin of lamellar magnetism in the hematite-ilmenite series, *Am. Min.*, 89, 725–747.
- Robinson, P., Harrison, R.J. & McEnroe, S.A., 2006. Fe²⁺/Fe³⁺ charge ordering in contact layers of lamellar magnetism: bond valence arguments, *Am. Min.*, **91**, 67–72.
- Robinson, P., Fabian, K. & McEnroe, S.A., 2010. The geometry of ionic arrangements and magnetic interactions in ordered ferri-ilmenite solid solutions and its effect on low-temperature magnetic behavior, *Geochem., Geophys., Geosyst.*, **11**, Q05Z17, doi:10.1029/2009GC002858.
- Robinson, P., Harrison, R.J., Fabian, K. & McEnroe, S.A., 2012b. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic self-reversal and exchange bias, III. Magnetic interactions in samples produced by Fe-Ti ordering, *Geophys. J. Int.*, **188**, 1025–1047.
- Robinson, P., Harrison, R.J., Miyajima, N., McEnroe, S.A. & Fabian, K., 2012a. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic self-reversal and exchange bias, II. Chemical changes during quench and annealing, *Geophys. J. Int.*, **188**, 447–472.
- Robinson, P., Fabian, K., McEnroe, S.A. & Heidelbach, F., 2013. Influence of lattice-preferred orientation with respect to magnetizing field on intensity of remanent magnetization in polycrystalline hemo-ilmenite, *Geophys. J. Int.*, doi: 10.1111/j.1365-246X.2012.05692.x.

- Robinson, P., Langenhorst, F., McEnroe, S.A., Fabian, K. & Boffa Ballaran, T., 2014b. Ferroan geikielite and coupled spinel-rutile exsolution from titanohematite: interface characterization and magnetic properties, *Am. Min.*, **99**, 1694–1712.
- Robinson, P., McEnroe, S.A., Fabian, K., Harrison, R.J., Thomas, C. & Mukai, H., 2014a. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic selfreversal and exchange bias, IV. The fine structure of self-reversed thermoremanent magnetization, *Geophys. J. Int.*, **196**, 1375–1396.
- Shcherbakov, V.P., Fabian, K. & McEnroe, S.A., 2009. A mechanism of exchange bias for nanoparticles embedded in an antiferromagnetic matrix, *Phys. Rev. B*, **80**, 174419.
- Shcherbakov, V.P. & Sycheva, N.K., 2005. Three-dimensional modeling of biased hysteresis loops in the presence of exchange anisotropy at the boundary between ferro- and antiferromagnetic phases, *Izv-Phys Solid Earth*, **41**(6), 485–491.
- Uyeda, S., 1957. Thermo-remanent magnetization and coercive force of the ilmenite-hematite series, *J. Geomagn. Geoelectr.*, **9**, 61–78.

APPENDIX: MEASURING LAMELLAR THICKNESS USING FIG. 12

These notes provide background for understanding results from the dark-field TEM image and electron diffraction patterns of Fig. 12 for sample MOD22-2-2.

Fig. A1 shows an ilmenite unit cell, consisting of 6 cation layers parallel to (001) and normal to c, with one additional layer below the





Figure A1. Shows an ilmenite unit cell, consisting of 6 cation layers parallel to (001) and normal to c, with one additional layer below cell. Plane (1-1-1) is marked in red, two (001) planes are marked in blue, and a plane normal to (1 -1 -1) is marked in violet. Shows the distance 'w' (lamellar width) in relation to 't' (lamellar thickness). 'w' remains constant in any view parallel to the plane (1-1-1). Also shows angle calculations described in text.



Figure A2. Shows an ilmenite lamellae in three different views along the plane (1-1-1). In all of these the value 'w' remains constant, whereas 't' is correctly observed only in orientation A.

cell. The plane (1-1-1) is marked in red. Two of the (001) planes are marked in blue and a plane normal to (1 - 1 - 1) is marked in violet. The angle Ø between (1-1-1) and the *c* axis is easily calculated from the parameters for *c* and for *a*/2 sqrt 3, which are 13.772 Å and $(5.038/2) \times 1.73 \ 204 = 4.363$ Å. Using these tan Ø = 4.363/13.772 = 0.31 \ 680 and arc tan 0.31 \ 680 = 17.578°.

Fig. A2 shows three views all looking along (1 - 1 - 1). Part A looks exactly along the intersection between (1 - 1 - 1) and (001). This is a direction where the exact thickness (*t*) of a lamellae could be observed, as well as the width of a lamellae (*w*) along the image surface. Part B shows relationships as seen in the dark-field image of Fig. 12, in which the projection of the *c* axis makes an angle of ~35° with (1 - 1 - 1). Part C looks along (1 - 1 - 1) in a direction where one is also looking nearly normal to (001), in fact at an angle of 72.422°, rather than 90°. A very important property of all three of these views is that the distance w remains constant. In other words, if we maintain (1-1-1) parallel to the viewing direction, the observed distance *w* will remain the same. View A also shows the true thickness *t* and the relationship between *t* and *w*, where t = w sine 17.578°, or $t = w \cos 72.422°$.

With the information in Fig. A2, it is then possible to calculate t from any observations of w. Measurement of w was done directly

| Profile distance | True width | True thickness |
|------------------|------------|----------------|
| | 5.556 nm | 1.68 nm |
| | 4.166 nm | 1.26 nm |
| 10 nm | 5.74 nm | 1.73 nm |
| 15 nm | 8.61 nm | 2.60 nm |
| 5 nm | 2.87 nm | 0.866 nm |
| 6 nm | 3.44 nm | 1.04 nm |
| 7 nm | 4.02 nm | 1.21 nm |

on a large print of the dark-field image. The widest lamella was determined to be 5.56 nm. (The widest lamella was 0.4 cm, and the 50 nm scale bar is 3.6 cm. Thus 0.4/3.6 = 0.1111, and $0.1111 \times 50 = 5.556$ nm. A slightly narrower lamella was 0.3 cm. Thus 0.3/3.6 = 0.0833, and $0.0833 \times 50 = 4.166$ nm.) Applying the equation above relating *w* to thickness (*t*) we get t = 1.73 and 1.26 nm.

Another method to estimate thickness was to measure using the distance across the 1 - 1 - 1 electron diffraction peaks on an intensity profile run parallel to the projection of the crystallographic *c*-axis. One set of estimates across this gave distances of 10 and 15 nm, mainly emphasizing distances between troughs, and probably providing too high a proportion of ilmenite to hematite. Another set

True width (w) = Profile distance × sine 35° (0.574). True thickness (t) = True width × sine 17.578° (0.302).

These estimates indicate that we are indeed dealing with very thin lamellae, in fact perhaps so thin that ordering reflections might not be observed in many orientations, but in fact they are in some. In considering the number of layers in a lamellar thickness, there are two ways to calculate, with ilmenite layers only, or with ilmenite layers plus contact layers, where each layer is about 0.23 nm thick. An ilmenite with two Ti layers and one Fe layer is thus 0.69 nm thick, but with two contact layers becomes 1.15 nm. A lamella with three Ti layers and 2 Fe layers becomes 1.15 nm thick or with two contact layers becomes 1.61 nm. However, magnetic theory (Harrison et al. 2007) tells us that such a lamella with two Fe layers cannot produce the exchange bias that we know is present. A lamella with four Ti layers and three Fe layers becomes 1.61 or 2.07 nm thick. Likely the lamellae are of varied thickness, but there is presently no evidence in this sample of lamellae any thicker than these. The thicker parts may help with the diffraction, whereas the thinner parts could be dominant in the exchange bias.