Nanoscale haematite–ilmenite lamellae in massive ilmenite rock: an example of 'lamellar magnetism' with implications for planetary magnetic anomalies

S. A. McEnroe,^{1,3} R. J. Harrison,² Peter Robinson^{1,3} and Falko Langenhorst⁴

¹Geological Survey of Norway, N7491 Trondheim, Norway. E-mail: Suzanne.mcenroe@ngu.no

²Department of Earth Sciences, Cambridge University, Cambridge, UK

³University of Massachusetts, Amherst, MA, USA

⁴Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

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SUMMARY

Massive, nearly 'pure', haemo-ilmenite layers from historic ore deposits in Rogaland, Norway contain very few silicates or other oxides and typically produce remanence-dominated magnetic anomalies. These rocks are ideal for evaluating the magnetic properties of fine exsolution intergrowths and the larger titanohaematite lamellae in the host ilmenite grains. A typical bulk composition, Ilm 84, exsolved at high temperature to produce host ilmenite Ilm 94 and micron-sized haematite lamellae Ilm 23 as measured by electron microprobe (EMP). Subsequent undercooling of the ilmenite and the micron-scale haematite lamellae led to metastable nucleation of nanoscale lamellae down to unit-cell scale, leaving depleted hosts between lamellae with compositions of Ilm 98 and Ilm 15-13 as measured by TEM-EDX. Samples have high coercivities, and average NRM values of 25 A m^{-1} , which typically show \sim 2 per cent saturation in the NRM state. The amount of magnetization in these samples is too high to be solely accounted for by a spin-canted AF moment in the haematite. Based on Monte Carlo simulations of haematite-ilmenite interfaces at the atomic scale and on measured rock-magnetic properties, we predict that the magnetization is carried by a ferrimagnetic substructure produced at the contacts of the very fine-scale titanohaematite and ilmenite exsolution lamellae.

Key words: exsolution microstructures, geomagnetism, haematite–ilmenite series, mineralogy, planetary anomalies, rock magnetism.

1 INTRODUCTION

During the course of interpreting an aeromagnetic survey over the Proterozoic South Rogaland Anorthosite Province, Norway, large remanence-controlled negative magnetic anomalies were noted over the Åna Sira anorthosite and the Tellnes haemo-ilmenite ore deposit-one of the largest actively mined ilmenite deposits in the world (McEnroe et al. 1996; McEnroe 1997; Korneliussen et al. 2000). The Tellnes norite contains ~ 28 per cent haemoilmenite (ilmenite with fine-scale haematite exsolution lamellae) together with plagioclase, orthopyroxene, clinopyroxene (containing exsolved magnetite), olivine, minor biotite, hornblende, magnetite and sulphides. The origin of the remanence-dominated anomaly was initially puzzling, because the dominant multidomain (MD) magnetite grains were expected to contribute an induced component to the magnetic response, whereas the haemo-ilmenite was expected to carry a predominant paramagnetic component from the ilmenite host and a minor spin-canted antiferromagnetic moment from the haematite lamellae. Based on these assumptions,

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we first suggested that pseudo-single-domain (PSD) magnetite exsolved from the clinopyroxene grains could be the controlling factor in the magnetic response of the deposit. To investigate this possibility further, the bulk magnetic properties of over 500 samples were measured (McEnroe *et al.* 1996) and the magnetic and chemical properties of a subset of these were examined in detail (McEnroe *et al.* 2000, 2001b, 2002). The remarkable conclusion was that the large and stable magnetic remanence was carried both by PSD magnetite in pyroxene, and by the highly exsolved discrete haemo-ilmenite grains.

A detailed analysis of the phase-transformation behaviour and thermodynamics of the ilmenite-haematite solid solution, using a combination of experimental and computational techniques, laid the basis for the development of the concept of 'lamellar magnetism', in which a stable ferrimagnetic substructure occurs at the coherent interfaces of haematite and ilmenite exsolution lamellae with ilmenite and haematite hosts, respectively (Harrison & Becker 2001; McEnroe *et al.* 2001a; Robinson *et al.* 2002a). This concept has revolutionized thinking concerning the possible magnetic moments in exsolved phases. The lamellar magnetism theory was founded on studies of over 700 samples from igneous and metamorphic rocks that cover significant geographic areas of Sweden, Norway, USA and Canada. The rock properties of these samples demonstrated an intense and highly stable magnetization (McEnroe 1995, 1997; McEnroe & Brown 2000; McEnroe et al. 1996, 1998, 2001a,b; Robinson et al. 2001). These insights led to the present detailed study of the magnetic and mineralogical properties of the Frøytlog ore samples, consisting nearly entirely of haemo-ilmenite with abundant exsolution. Such rocks offer a unique opportunity for making investigations of lamellar magnetism caused by the large number of contact interfaces between ilmenite and haematite exsolution lamellae and hosts, and because, in contrast to the Tellnes norite, they are not complicated by the presence of other magnetic phases. Samples were also obtained for rock-magnetic studies from numerous other massive haemo-ilmenite-rich layers and ore deposits hosted by the anorthosites-these are the focus of additional studies.

1.1 Geology

The Mid-Proterozoic Egersund anorthosite–norite complex is within the Sveconorwegian Province of the Baltic shield in south Norway (see the review by Ashwal 1993). These igneous rocks, dated to ~930 Ma (Schärer *et al.* 1996), intrude rocks regionally metamorphosed to granulite facies around 980 Ma (Bingen & Van Breemen 1998). This province is dominated by three bodies of 'massif-type' anorthosite–leuconorite, and by the large (230 km^2) Bjerkreim–Sokndal norite–mangerite–quartz mangerite layered complex that intruded and cooled at an initial pressure of 5 kbar (Wilson *et al.* 1996). The anorthosites contain a variety of oxide-rich mineral deposits. In particular, the Åna-Sira anorthosite hosts numerous historic ilmenite- and magnetite-rich deposits (Korneliussen *et al.* 2000).

Frøytlog is a historic ore deposit mined in the late 1800s, located in the northwestern part of the Åna-Sira massif (Duchesne 2001). The worked deposit is in a massive cumulate layer with a maximum thickness of 2 m and an extension of 150 m. There is modal layering into nearly monomineralic haemo-ilmenite layers, and layers with a substantial amount of plagioclase and rare magnetite. All the ilmenite is coarse-grained haemo-ilmenite and is in coexistence with plagioclase and minor plenonaste. The samples described here are from the nearly 'pure' haemo-ilmenite layers.

1.2 Crystal structure and magnetic properties of the ilmenite-haematite solid solution

The magnetic properties of the ilmenite-haematite solid solution, and lamellar magnetism in particular, are determined by a complex interplay between the processes of cation ordering, magnetic ordering and subsolvus exsolution. Hence, some knowledge of the phase relations and crystallography of this system is required before the magnetic properties of natural samples can be understood. The reader is referred to Harrison (2000) and Harrison & Becker (2001) for a more detailed review.

Haematite (Fe₂O₃) has the corundum structure with space group $R\bar{3}c$. The structure is based on an approximately hexagonal closepacked arrangement of oxygen anions, with Fe³⁺ cations occupying two-thirds of the octahedral sites in layers parallel to (001) (Fig. 1a). Ilmenite (FeTiO₃) adopts a related structure (space group $R\bar{3}$), with Fe²⁺ and Ti partitioned on to alternating α and β layers (Fig. 1b). The solid solution contains a mixture of Fe²⁺, Fe³⁺ and Ti. Fe³⁺ is distributed equally over the α and β layers at all temperatures and bulk compositions, whereas Fe²⁺ and Ti are partitioned into α and β in ilmenite-rich compositions at low temperatures ($R\bar{3}$) and become randomly distributed over both layers at high temperatures ($R\bar{3}c$).

Haematite has a canted antiferromagnetic structure with a Néel temperature, $T_{\rm N} = 675 \,^{\circ}\text{C}$ (Fig. 1a). The sublattice spins lie within the basal plane but are rotated by a small angle about [001], producing a weak parasitic magnetic moment perpendicular to the alignment of the spins (Dzyaloshinsky 1958). End-member ilmenite has an antiferromagnetic structure with spins parallel to [001] and a Néel temperature of around 60 K (Fig. 1b). Disordered intermediate ilmenites are antiferromagnetic, with a similar magnetic structure to



Figure 1. Crystal and magnetic structure of (a) haematite (Fe₂O₃) and (b) ilmenite (FeTiO₃).



Mole fraction FeTiO₃

Figure 2. Summary of phase relations in the ilmenite–haematite solid solution at 1 atm: $R\bar{3}c$, cation disordered; $R\bar{3}$, cation ordered; P, paramagnetic; CAF, canted antiferromagnetic; FM, ferrimagnetic; AF, antiferromagnetic; SP, superparamagnetic; SG, spin glass. Closed circles are T_{od} for the $R\bar{3}c$ to $R\bar{3}$ phase transition (Harrison *et al.* 2000a; Harrison & Redfern 2001). End-member T_c and SP, SG and AF fields are taken from Ishikawa *et al.* (1985). The miscibility gap is taken from Ghiorso (1997). The dashed line shows the metastable extension of the magnetic ordering transition for intermediate compositions quenched from above the miscibility gap. The positive deviation from the straight line is caused by the onset of cation ordering in quenched samples containing more than ~40 per cent ilmenite.

end member haematite. Ordered intermediate ilmenites are strongly ferrimagnetic, since the concentration of Fe on the α and β layers is unequal (Ishikawa & Akimoto 1957, 1958a,b; Ishikawa 1958; Ishikawa & Syono 1963; Harrison 2000). The presence of a miscibility gap in the solid solution means that ordered ferrimagnetic ilmenite is metastable at low temperatures, and is only produced as a result of rapid cooling (Fig. 2). It can play no role in the magnetic behaviour of the slowly cooled exsolved samples considered in this study.

The equilibrium phase diagram for the solid solution at 1 atm is shown in Fig. 2. The position of the magnetic and cation ordering phase transitions are known with some certainty, and are well constrained by experimental data (Harrison *et al.* 2000a; Harrison & Redfern 2001; Ishikawa *et al.* 1985). The miscibility gap, however, is poorly constrained by experimental data and estimates of its position made using different thermodynamic approaches vary considerably (e.g. Burton & Kikuchi 1984; Burton 1984, 1985, 1991; Ghiorso 1997; Harrison *et al.* 2000b; Harrison & Becker 2001). All thermodynamic models predict the presence of a miscibility gap below 700–800°C, separating a paramagnetic haematite-rich

phase $(PR\bar{3}c)$ from a paramagnetic ilmenite-rich phase $(PR\bar{3})$. At lower temperatures, the haematite-rich limb of the miscibility gap approaches the magnetic ordering transition, causing the $PR\bar{3}c$ phase to become canted antiferromagnetic (CAF $R\bar{3}c$). Under equilibrium conditions, magnetic ordering in the haematite-rich phase leads to the eutectoid reaction $PR\bar{3}c \rightarrow CAFR\bar{3}c + PR\bar{3}$, and a pronounced widening of the miscibility gap (Fig. 2). Estimates of the temperature of the eutectoid reaction vary between $\sim 390^{\circ}C$ (Ghiorso 1997; Harrison & Becker 2001) and 525 °C (Burton 1985), while estimates of its position vary between 25 per cent and 30 mol per cent ilmenite (Ilm 25-30). We have chosen the miscibility gap of Ghiorso (1997) in Fig. 2, since this is the only one where experimental constraints on the position of the miscibility gap were taken into account. The exact position of the solvus is not of fundamental importance to the concept of lamellar magnetism. The equilibrium state at low temperatures consists of an intergrowth of CAF $R\bar{3}c$ and $PR\bar{3}$ phases, with compositions that diverge toward pure haematite and pure ilmenite, respectively. The size distribution and spatial arrangement of these phases is a complex function of the cooling history.

1.3 Lamellar magnetism

Harrison & Becker (2001) adapted the thermodynamic model of Harrison *et al.* (2000b) to take into account magnetic exchange interactions between neighbouring Fe cations. They were then able to perform a comprehensive investigation of the interaction between cation ordering, magnetic ordering and exsolution in the ilmenite– haematite solid solution. This work and that by McEnroe & Brown (2000) and McEnroe *et al.* (2001a,b) provided the first insights into the magnetic properties of exsolved ilmenite–haematite samples and laid the foundation for lamellar magnetism theory (Robinson *et al.* 2002a). The key aspects of this theory are outlined below.

Fig. 3 shows a 28-layer section of a 40-layer Monte Carlo simulation cell performed at 500 K and a bulk composition of 25 mol per cent ilmenite. During the simulation, the chemical and magnetic interactions between cations and spins are modelled using pair interaction energies out to third nearest neighbours. The distribution of the cations and orientations of their magnetic moments (either left or right in this case) are varied until thermodynamic equilibrium is achieved (i.e. the free energy is minimized). Instantaneous snapshots of the equilibrium structure can then be examined. Cations are shaded according to their chemistry and orientation of magnetic moment (see the caption). The upper and lower parts of Fig. 3 correspond to essentially pure antiferromagnetic haematite (layers of Fe³⁺ with alternating left and right spins). In the centre is a lamella of essentially pure paramagnetic ilmenite (layers of Ti alternating with layers containing equal numbers of Fe²⁺-spin left and Fe²⁺-spin right). The cation layers at the interface between ilmenite and



Figure 3. Snapshot of the distribution of cations and magnetic spins in a Monte Carlo simulation performed at 500 K and a bulk composition of 25 mol per cent ilmenite (Harrison & Becker 2001). 28 layers out of the 40-layer simulation are shown. Atoms correspond to Fe^{3+} with 5 μ_B pointing to the right, Fe^{3+} with 5 μ_B pointing to the left, Fe^{2+} with 4 μ_B pointing to the right, Fe^{2+} with 4 μ_B pointing to the left, Ti with no magnetic moment (see legend). A colour version of this figure is available on-line at http://www.blackwell-synergy.com. See the text for further details.

haematite contain a mixture of Fe²⁺ and Fe³⁺. These layers do not correspond to the chemistry of either haematite or ilmenite, and are referred to as 'contact' layers (Robinson *et al.* 2002a). Contact layers were observed in all simulations performed within the low-temperature $CAF R\bar{3}c + PR\bar{3}$ stability field.

A stable ferrimagnetic moment is caused by the characteristic arrangement of cations and spins at the interface between haematite and ilmenite. The simulations indicate that an ilmenite lamella of any thickness is bordered on both sides by a layer of Ti followed by a contact layer. In general, an ilmenite lamella contains n Ti layers (where n > 1), (n - 1) Fe²⁺ layers, and two contact layers. This makes a total of (2n + 1) layers, which is an odd number. In the antiferromagnetic haematite host, any two layers separated by an odd number of intervening layers will be magnetized in the same direction. Therefore, the Fe³⁺ layers immediately adjacent to the ilmenite lamella have the same magnetization direction (Fig. 3). The two contact layers are coupled antiferromagnetically to the host, so they are magnetized in the same direction as each other, but in the opposite direction to the adjacent haematite layers (Fig. 3). If we begin with a haematite host containing an even number of layers (which is a necessary requirement for an antiferromagnetic starting material), then an odd number of layers will remain after insertion of the ilmenite lamella. This contributes a net magnetization of M_{hem} to the supercell, where M_{hem} is the sublattice magnetization of a single Fe³⁺ layer. There are two contact layers, each with a magnetization $M_{\rm con}$ opposed to the net moment of the haematite layers, yielding a net ferrimagnetic moment of $M = (2M_{con} - M_{hem})$.

This mechanism is capable of generating a significant ferrimagnetic moment per formula unit. The size of the moment will depend on several factors, including the bulk composition, the composition of the haematite and ilmenite phases, the composition of the contact layers, the surface area-to-volume ratio of the lamellae, and whether the lamellae are magnetically in or out of phase (Robinson et al. 2002a). Although the model of Fig. 3 shows a lamella of pure ilmenite in a pure haematite host, there would not be very significant differences if both the ilmenite and haematite were impure solid solutions, as would be expected in a natural intergrowth. Solid solutions would also provide the necessary chemistry to allow still more lamellar growth, or nucleation of a new generation of finerscale lamellae, at a lower temperature. A net moment of the order of 0.3 $\mu_{\rm B}$ pfu is a typical value achieved in the Monte Carlo simulations. The most magnetic mineral in nature is magnetite (Fe_3O_4) with a net moment of 4 $\mu_{\rm B}$ pfu. To compare these values on the basis of quasi-equal volumes, it is conventional to multiply the ilmenite magnetization by four-thirds. Therefore, magnetizations up to 10 per cent of the saturation magnetization of magnetite (i.e. 48 000 A m⁻¹) are easily obtainable in systems exsolved on the length scale of the simulations (1–10 nm).

2 MINERALOGY AND IMAGING

2.1 Optical observations

Detailed observations were made on polished thin sections in reflected light. The samples consist of ferrian ilmenite host grains with 1–3 μ m thick haematite exsolution lamellae parallel to (001), and with second and subsequent generations of haematite lamellae also parallel to (001). Approximately 14 per cent of the grains are composed of optically visible haematite lamellae. The largest firstgeneration haematite lamellae may be up to 100 μ m long. These lamellae contain finer ilmenite exsolution down to the optical limit



Figure 4. SEM backscatter image of ilmenite (dark) with multiple generations of very fine (001) haematite exsolution lamellae (white) from Frøytlog ore deposit. The scale bar is 2 μ m.

of the microscope (~0.2 μ m). Second-generation haematite lamellae are also visible in the ilmenite host and these are generally free of optically visible ilmenite. Haematite lamellae in the ilmenite host with thicknesses of ~0.3 μ m were imaged (Fig. 4) on a scanning electron microscope (SEM). A local low-temperature alteration of haemo-ilmenite to haematite + rutile is present in a few sections.

2.2 TEM imaging and energy filtering

2.2.1 TEM operating conditions

To investigate the possibility that exsolution lamellae exist on a much finer scale than can be resolved using the SEM, we performed a detailed characterization using conventional and energy-filtered transmission electron microscopy (TEM). Observations were made using a JEOL 3010 TEM at the Institut of Mineralogy, University of Münster, equipped with a post-column Gatan imaging filter (GIF). The microscope was equipped with a LaB₆ cathode and operated at 297 kV. A detailed description of the methods can be found in Golla & Putnis (2001) and McEnroe *et al.* (2001a).

To prove that the nanometre-scale features seen in the TEM images are caused by exsolution and to obtain a better estimate of the minimum length scale of chemical heterogeneity, we obtained high spatial resolution element distribution maps using electron energy loss spectroscopy (EELS). When electrons pass through the sample they lose energy by a number of interaction processes such as ionization of the elements present. Ionization generates characteristic X-rays, which can be analysed using conventional energy-dispersive X-ray analysis (EDX). Alternatively, one can measure the intensity of transmitted electrons as a function of their energy loss to give an electron energy loss spectrum. The EELS spectrum consists of a number of ionizations edges corresponding to Ti, O and Fe. Using a post-column Gatan imaging filter it is possible to select electrons from a specific energy-loss window and refocus them into an image of the sample. The energy-loss window is chosen to coincide with the characteristic ionization edge of the element of interest. An approximate correction for the background inelastic scattering can be made by dividing the resulting image by one formed using an energy window immediately in front of the ionization edge (a so-called 'jump-ratio' image). The result is a qualitative elemental distribution map with a spatial resolution approaching 1 nm or less.

2.2.2 TEM images

Fig. 5 shows a series of bright-field images illustrating the different scales of exsolution observed in the sample as a whole. Fig. 5(a) is centred on a relatively thick ($\sim 1 \mu m$) exsolution lamella of haematite. These large haematite lamellae are semi-coherent with

the ilmenite host and are themselves exsolved on a very fine scale. A more detailed image is shown in Fig. 6. The haematite contains discrete exsolution lamellae of ilmenite with thicknesses varying from around 40 nm (0.04 μ m) down to around 4 nm (0.004 μ m). The coarser ilmenite precipitates have curved interfaces and composition planes deviating significantly from (001). They are fully



Increasing distance from hematite lamella

ilmenite ppts

Figure 5. Series of bright-field TEM images showing the different length-scales of exsolution observed in the sample as a whole. Scale bar = 100 nm.



Figure 6. Bright-field TEM image of a different region of the haematite lamella from Fig. 5(a) containing a range of differently sized ilmenite precipitates. Scale bar = 200 nm.



Figure 7. Bright-field TEM image of the ilmenite host containing fine-scale haematite precipitates. Scale bar = 100 nm.

coherent with the host, shown by the dark patches of strain contrast surrounding the lamellae and the absence of dislocations at the precipitate–host interface. The \sim 4 nm thick ilmenite precipitates are coherent and relatively straight, but several do appear to be kinked (see the magnified region of Fig. 6). In regions where no discrete lamellae are visible the haematite has developed a very fine-scale mottling, indicative of chemical heterogeneity on a unit-cell length scale.

Immediately adjacent to the large haematite lamellae, the ilmenite host appears to be homogeneous (Fig. 5a). The ilmenite develops a finely mottled texture with increasing distance from the haematite lamellae (Fig. 5b), which in turn develops into discrete fine-scale precipitates of haematite (Fig. 5c). A more detailed image is shown in Fig. 7. The lower part of Fig. 7 consists of well-defined discrete haematite precipitates with thicknesses of the order 10 nm (0.01 μ m) surrounded by homogeneous ilmenite host. The precipitates are fully coherent and oriented parallel to (001) of the ilmenite host. The upper part of Fig. 7 illustrates the gradual transition from discrete lamellae with thicknesses of the order 4 nm to fine-scale mottling.

2.2.3 High-resolution elemental maps

Fig. 8 shows jump-ratio images of the large haematite exsolution lamella from Fig. 6. The images were formed using the Ti ionization edge, so Ti-rich areas appear bright and Ti-poor areas appear dark. Fig. 8(a) shows the edge of the haematite lamella (lower right-hand side) and the ilmenite host (upper left-hand side). Note the homogeneous nature of both host and lamella close to the interface. Fig. 8(b) shows one of the larger (30–40 nm) curved ilmenite precipitates, while Figs 8(c) and (d) show the finer (4–8 nm) precipitates. Fig. 9 shows Ti jump-ratio images of the coarse and fine haematite

precipitates within the ilmenite host from Fig. 7. Compositional heterogeneities on a length scale of 2 nm and below are clearly visible in Fig. 8(b). To put this in perspective, the unit cell parameter of ilmenite perpendicular to (001) is 1.4 nm (corresponding to just six individual cation layers). The presence of compositional heterogeneities on this scale has been shown to have a profound impact on the magnetic properties of the solid solution (Harrison & Becker 2001; Robinson *et al.* 2002a).

3 MINERAL ANALYSES

3.1 Electron microprobe operating conditions

Compositional data were collected on a Cameca SX-50 electron microprobe at the Bayerisches Geoinstitut set at an accelerating potential of 20 keV, a beam current of 15 nA, and a typical beam diameter of 1 μ m. Counting times of 30 s per element were used. Corrections for differential matrix effects were done using the Cameca online PAP correction routine. The analytical precision is estimated at ± 0.1 weight per cent for oxide components present at the 1 weight per cent level. Analytical precision on typical values of 0.5 weight per cent V_2O_3 and Cr_2O_3 is estimated to be ± 0.06 weight per cent at the 95 per cent confidence level. In addition there is believed to be a systematic overestimate of V_2O_3 in ilmenite of $\sim+0.1$ weight per cent caused by Ti K β -V K α interference.

3.2 TEM-EDX and TEM-EELS operating conditions

The TEM observations reveal several generations of exsolutions with sizes down to the nanoscale level. This suggests that the microprobe measurements are overlap analyses of ilmenite host or coarse haematite lamellae with corresponding nanoscale exsolutions. Such overlap analyses can be avoided when employing a TEM equipped with an energy-dispersive X-ray detector. To obtain such pure quantitative analyses of the oxides, we thus performed measurements with a ThermoNORAN spectrometer, attached to the PHILIPS CM20 FEG scanning TEM at the Bayerisches Geoinstitut, University of Bayreuth. The EDX spectrometer is equipped with an ultrathin NORVAR window and a germanium detector. This analytical configuration allows the simultaneous detection of k lines of light (e.g. oxygen) and heavy elements.

To quantify the mineralogical compositions, we calibrated the $k_{X/Fe}$ factors for the elements *X* contained, and performed an absorption correction (Langenhorst *et al.* 1995). The $k_{X/Fe}$ factors were determined according to the parameterless correction method (Van Cappellen 1990), using homogeneous, well-characterized standards such as garnet, pyroxene and perovskite. The relative errors in *k* factors are 1–3 per cent and represent systematic errors in the quantification. Relative statistical errors expressed as a 1 σ deviation are 0.5–1 per cent for major elements (O, Fe, Ti in ilmenite) and 2–3 per cent for minor elements (Mg in ilmenite, Ti in haematite). Trace elements with a concentration smaller than 1 at per cent are only regarded as detected; these EDX data are distinctly less precise than the microprobe data.

X-ray absorption was corrected on the basis of the principle of electroneutrality, requiring the quantification of oxygen (Van Cappellen & Doukhan 1994). Where necessary, i.e. in the case of nanoscale exsolutions, the beam was focused in nanoprobe mode down to its minimum spot size of 1 nm. Otherwise, the beam sizes were adapted to the size of exsolution-free areas, hence minimizing carbon contamination and electron beam damage.



Figure 8. Ti jump-ratio images of the haematite lamella from Fig. 6 (dark) containing fine-scale ilmenite precipitates (bright).



Figure 9. Ti jump-ratio image of the ilmenite host (bright) containing fine-scale haematite precipitates (dark) from an area similar to that shown in Fig. 7.

To complete the analyses and to test the quality of EDX results, we also determined the Fe³⁺/ Σ Fe ratio in the oxides, using a Gatan parallel electron energy-loss spectrometer (PEELS 666) attached to the PHILIPS TEM. The determination of the Fe³⁺/ Σ Fe ratio is based on the white line intensities at the Fe L₂₃ edge; these intensities have been calibrated for minerals in the high-spin state (Van Aken et al. 1998). Fe L_{23} ELNES spectra were measured in diffraction mode with convergence and collection semi-angles of $\alpha = 8$ and $\beta = 2.7$ mrad and an energy dispersion of 0.1 eV per channel. The energy resolution defined as the width of the zero-loss peak at half maximum was \sim 0.8–0.9 eV. Spectra were corrected for dark current and channel-to-channel gain variation. To extract the pure singlescattering core-loss signal an inverse power-law background was subtracted and multiple-scattering contributions were removed by the Fourier-ratio technique (Egerton 1996). Errors in the Fe³⁺/ Σ Fe ratio are of the order of 0.05.

3.3 Electron microprobe analyses, tables and formulation

Electron microprobe (EMP) analyses are presented in Tables 1(a) and (b). Analyses represent the bulk compositions of hosts with lamellae at a scale too fine to resolve on the EMP, but certainly abundant, based on the TEM work. Analyses labelled 't' are from traverses, those labelled 's' are from selected spot analyses. Session 1 analyses are numbered 19 or below; session 2 analyses are numbered 30 or above (with separate symbols in Figs 11 and 12).

Electron microprobe analyses were formulated on the basis of a stoichiometric formula with two cations and three oxygens. In doing this, trace amounts of Na₂O were deleted before formulation. Following the estimation of the Fe³⁺/Fe total based on stoichiometry, weight percentage analyses were back-calculated to include oxygen related to Fe₂O₃. Cations were recast into percentages of end members in $R^{2+}R^{4+}O_3$ and $R^{3+}_2O_3$, totalling 100 per cent and also into plotting parameters.

3.4 TEM-EDX and TEM-EELS analyses, tables and formulation

14 TEM-EDX analyses were completed in two separate ion-thinned areas, 1 and 2. Analyses are reported in atomic per cent, including oxygen normalized to 100 per cent, in Tables 2(a) and (b), for ilmenite and for haematite, respectively. In each table, analyses of host areas between lamellae are labelled 'H' and attempted analyses of ultra-fine lamellae are labelled 'L' (separate symbols in Figs 11 and 12). Six analyses in Table 2(a) are from host ilmenite mostly in areas where haematite lamellae have separated, one (30-9L) is from a small ilmenite lamella hosted in a coarse haematite lamella where overlap may have influenced the analytical result, and one (30-14L), from its composition, is judged to show significant overlap with some haematite. Four analyses in Table 2(b) are from areas in large haematite lamellae that are the hosts for small ilmenite lamellae and two analyses (30-6L and 30-8L) are from a single small haematite lamella in an ilmenite host that gives unexpected results, especially in Mg content. At this point we believe the analytical results give a very good indication of single-phase host compositions in highly exsolved areas, but there is much more uncertainty concerning exact compositions of fine exsolution lamellae, requiring some speculation based on chemography.

Structural formulae of TEM–EDX analyses were normalized to two cations, and appropriate Fe²⁺ was changed to Fe³⁺ to reach a charge balance with three oxygens. One ilmenite analysis area (30-1H) was measured by the EELS technique to obtain a Fe³⁺/Fe total ratio of 0.03, which compares with a ratio of 0.016 based on stoichiometry. One haematite analysis area (30-2H) was measured by the EELS technique to obtain a Fe³⁺/Fe total ratio of 0.82, which compares with a ratio of 0.92 based on stoichiometry. Cations were recast into percentages of end members in two groups, $R^{2+}R^{4+}O_3$ and $R_2^{3+}O_3$, totalling 100 per cent and into plotting parameters.

3.5 Interpretation of analytical results

3.5.1 Microprobe results

The EMP analyses represent compositions achieved during the earliest and coarsest phases of exsolution, and include the compositions of fine later lamellae below the microprobe resolution. An important insight into the initial nucleation, growth and re-equilibration of the coarsest lamellae is provided in Fig. 10, which shows cations per

formula unit for the analyses in Table 1(b) plotted against traverse distance. Fig. 10(a) shows Ti, Fe³⁺ and Mg. Ti and Fe³⁺ are complementary throughout, but note that the most Ti-rich and Fe³⁺-poor ilmenites lie at the borders of the haematite lamella. This pattern is consistent with an initial exsolution equilibrium involving a more Ti-poor ilmenite, which was then depleted in haematite component by local diffusion into the adjacent haematite lamellae, producing a profile exactly as predicted on theoretical grounds by Harrison & Putnis (1999; their Fig. 21). Furthermore, such a pattern of relative haematite abundance exactly fits the pattern of abundance of very fine lamellae illustrated in Figs 5 and 7. Ti behaviour is shown on an enlarged scale in Fig. 10(b). Although the pattern is barely detectable in the Mg profile of Fig. 10(a), it is striking at the enlarged scale in Fig. 10(c). Fig. 10(d) shows the superb co-variation of Cr, V and Al, all being highest in haematite, next highest in ilmenite far from haematite contacts and lowest in ilmenite in contact with the haematite lamella as a result of diffusional depletion into the haematite.

An important matter is to determine the bulk composition of the ilmenite solid solution before exsolution took place. XRF analysis of the bulk haemo-ilmenite rock after correction for 4.98 per cent plagioclase An 45 and 2.1 per cent intermediate Mg–Fe spinel, gives a good ilmenite formula with a composition close to the tie lines between probe analyses of coarse ilmenite hosts and haematite lamellae (see below) and showing the following proportions of end members: 16.9 per cent MgTiO₃, 66.2 per cent FeTiO₃ and 0.5 per cent MnTiO₃, giving 83.6 per cent $R^{2+}R^{4+}O_3$ (i.e. 83.6 per cent 'ilmenite'); and 15.8 per cent Fe_2O_3 , 0.3 per cent Cr_2O_3 and 0.3 V_2O_3 , giving 16.4 per cent $R_2^{3+}O_3$ (i.e. 16 per cent 'haematite').

Based on the above considerations, the original ilmenite composition at the outset of coarse haematite exsolution is not directly recorded in the probe data and probe compositions near Ilm 88-89 should represent material, including fine exsolution lamellae, produced at intermediate stages of exsolution, which was too far from haematite contacts to be entirely cleared out in later stages of exsolution. The most ilmenite-enriched, haematite-poor compositions should represent the final equilibrium at a coarse scale between the ilmenite host and the haematite lamellae. For this composition we chose the eight most ilmenite-rich analyses with Ti contents between 0.940 and 0.949, and a mean of 0.943. For these analyses the significant end members of ilmenite include 17.3-19.0 per cent MgTiO₃, 74.8-76.6 per cent FeTiO₃, 0.4-0.6 per cent MnTiO₃ and 0-0.1 per cent ZnTiO₃, giving 94.0-94.9 per cent R²⁺R⁴⁺O₃ (i.e. 94-95 per cent 'ilmenite'); and 4.5–5.7 per cent Fe₂O₃, 0.1–0.3 per cent Cr₂O₃ and 0.2–0.4 per cent V_2O_3 , giving 5.1–6.0 per cent $R_2^{3+}O_3$ (i.e. 5– 6 per cent 'haematite').

For haematite there are five analyses, two fairly ilmenite-rich (session 2) with Ti contents of 0.276 and 0.283, and three less ilmenite-rich (session 1) with Ti contents of 0.230–0.243. The two ilmenite-richer compositions might be taken as bulk compositions more representative of initial compositions when haematite was nucleated, and the three more ilmenite-poor compositions might be taken as those of lamellae that have had more opportunity to re-equilibrate at a lower temperature. For the Ti-rich haematite group the significant end members include 3.1-3.6 per cent MgTiO₃, 23.9-25.1 per cent FeTiO₃ and 0–0.1 per cent MnTiO₃, giving 27.6–28.4 per cent R²⁺R⁴⁺O₃ (i.e. 28 per cent 'ilmenite'); and 69.6–70.5 per cent Fe₂O₃, 1.0 per cent Cr₂O₃, 0.8 V₂O₃ and 0.1-0.2 per cent Al₂O₃, giving 71.7–72.4 per cent R²⁺O₃ (i.e. 72 per cent 'haematite'). For the Ti-poor haematite group the significant end members include 1.8-2.3 per cent MgTiO₃, 21.0-21.9 per cent FeTiO₃ and

Table 1(a).	Electron probe analyses and	d structural formulae of	of ilmenite hosts and haematite lamellae.
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	Ilmenite host					Coarse haematite lamellae				
Wt per cent	17t	18t	19t	2s	4s	40s	11t	1s	3s	41s
SiO ₂	0.011	0.004	0.006	0	0	0.015	0	0.011	0	0.006
TiO ₂	51.562	51.540	51.472	51.655	51.043	48.189	11.640	12.230	11.721	14.28
ZrO_2						0.032				0
Al_2O_3	0	0	0	0.013	0.009	0	0.113	0.106	0.155	0.095
Cr ₂ O ₃	0.265	0.281	0.275	0.174	0.156	0.222	1.597	1.046	1.052	0.966
V_2O_3	0.365	0.315	0.331	0.238	0.335	0.269	0.874	0.791	0.806	0.786
$Fe_2O_3^1$	5.881	5.587	4.889	5.511	6.839	11.664	74.938	74.006	75.260	72.886
MgO	5.090	5.021	4.959	5.246	5.038	4.258	0.456	0.590	0.549	0.940
FeO ¹	37.010	37.150	37.221	36.784	36.608	35.524	9.599	9.934	9.542	11.140
MnO	0.235	0.203	0.222	0.291	0.287	0.225	0	0.028	0.019	0.014
ZnO	0.049	0.050	0	0.036	0.025	0.022	0.046	0	0	0.016
CaO	0	0.003	0	0	0.011	0.006	0	0.004	0	0.003
Na ₂ O	0.019	0	0	0.016	0.012	0.028	0.028	0.012	0.003	0.005
Total	100.487	100.154	99.375	99.964	100.365	100.454	99.291	98.758	99.107	101.137
C :	0.0002	0.0001	0.0001	Cations p	er three O a	atoms	0	0.0002	0	0.0002
51	0.0002	0.0001	0.0001	0 0 4 5 4	0 0226	0.0004	0 2204	0.0003	0 2222	0.0002
11 7:	0.9402	0.9430	0.9489	0.9454	0.9326	0.8870	0.2304	0.2431	0.2323	0.2759
	0	0	0	0.0004	0.0003	0.0004	0.0025	0.0022	0.0048	0 0028
AI Cr	0 0050	0 0054	0 0053	0.0004	0.0003	0.0043	0.0033	0.0033	0.0048	0.0028
V	0.0050	0.0054	0.0055	0.0034	0.0050	0.0043	0.0332	0.0218	0.0219	0.0190
v Fe ³⁺	0.0071	0.0001	0.0003	0.0040	0.0005	0.0055	1 4843	1 4714	1 /018	1 4002
Ma	0.1075	0.1023	0.0902	0.1009	0.1230	0.2140	0.0170	0.0232	0.0216	0.0360
Fe^{2+}	0.1840	0.1621	0.1613	0.1903	0.1624	0.1334	0.0179	0.0232	0.0210	0.0300
Mn	0.0048	0.0042	0.0046	0.7464	0.0450	0.0047	0.2115	0.2174	0.0004	0.2374
Ca	0.0040	0.0000	0.0040	0.0000	0.0003	0.0007	0	0.0000	0.0004	0.0001
Zn ²	0.0009	0.0009	0	0.0007	0.0004	0.0002	0.0009	0.0001	0	0.0003
Total	1.9999	2.0000	2.0000	2.0000	2.0000	2.0000^{3}	1.9999	1.9999	2.0000	2.0000^{3}
			Calcu	lated perce	entages of e	nd members	5			
FeSiO ₃	0.02	0.01	0.01	0	0	0.04	0	0.03	0	0.02
FeZrO ₃						0.04				0
MgTiO ₃	18.40	18.21	18.13	19.03	18.24	15.54	1.79	2.32	2.16	3.60
FeTiO ₃	75.04	75.59	76.31	74.84	74.36	72.64	21.13	21.94	21.03	23.92
MnTiO ₃	0.48	0.42	0.46	0.60	0.59	0.47	0	0.06	0.04	0.03
CaTiO ₃	0	0.00	0	0	0.03	0.01	0	0.01	0	0.01
ZnTiO ₃	0.09	0.09	0	0.07	0.04	0.03	0.09	0	0	0.03
Sum	94.03	94.32	94.91	94.54	93.26	88.79	23.01	24.36	23.23	27.61
Fe ₂ O ₃	5.37	5.12	4.51	5.05	6.25	10.74	74.22	73.57	74.59	70.46
Cr_2O_3	0.25	0.27	0.27	0.17	0.15	0.22	1.66	1.09	1.10	0.98
V_2O_3	0.36	0.31	0.33	0.23	0.33	0.26	0.92	0.84	0.85	0.81
Al_2O_3	0	0	0	0.02	0.02	0	0.18	0.17	0.24	0.14
Sum	5.98	5.70	5.11	5.47	6.75	11.22	76.98	75.67	76.78	72.39
Total	100.01	100.02	100.02	100.01	100.01	100.01	99.99	100.03	100.01	100.00
				Plo	tting ratios					
2Ti/*	0.9402	0.9431	0.9490	0.9454	0.9326	0.8877	0.2302	0.2431	0.2323	0.2760
Cr/*	0.0025	0.0027	0.0027	0.0017	0.0015	0.0022	0.0166	0.0109	0.0109	0.0098
V/*	0.0036	0.0031	0.0033	0.0023	0.0033	0.0026	0.0092	0.0084	0.0085	0.0081
Al/*	0	0	0	0.0008	0.0002	0	0.0017	0.0017	0.0024	0.0014
Mg/R ²⁺	0.1957	0.1931	0.1910	0.2013	0.1956	0.1750	0.0778	0.0954	0.0930	0.1304
Mg/#	0.1840	0.1821	0.1830	0.1903	0.1824	0.1554	0.0179	0.0232	0.0216	0.0360

Notes: t, analysis in traverse; s, spot analysis. ${}^{1}Fe_{2}O_{3}$ and FeO back-calculated after determining the stoichiometric formula. ${}^{2}Analysed$ trace amounts of Na₂O were ignored in the formula calculation. ${}^{3}Sum$ represents the total of figures rounded to five decimal places—figures above this are rounded to four places and do not give same sum. ${}^{*}2Ti + R^{3+}$; # $R^{2+} + (R^{3+}/2)$.

0–0.1 per cent MnTiO₃, giving 23.0–24.4 per cent $R^{2+}R^{4+}O_3$ (i.e. 23–24 per cent 'ilmenite'); and 73.6–74.6 per cent Fe₂O₃, 1.1–1.7 per cent Cr₂O₃, 0.8–0.9 per cent V₂O₃ and 0.2 per cent Al₂O₃, and giving 75.7–77.0 per cent $R_2^{3+}O_3$ (i.e. 76–77 per cent 'haematite').

The above interpretation of the compositions of micrometre-scale haematite for IIm 23 and ilmenite for IIm 94 is strongly supported by the following. The mode of haematite estimated in Fig. 4 is 14.6 per cent. The XRF bulk composition IIm 83.6 factored into amounts of IIm 23 and IIm 94, yields 14.6 per cent haematite and 85.6 per cent

Table 1(b). Electron probe analyses and structural formulae on a traverse across ilmenite and a haematite lamella.

Wt per cent	30t	31t	32t	33t	34t	35t	36t	37t	38t	39t
SiO ₂	0	0	0.013	0	0	0.011	0.002	0.011	0	0.004
TiO ₂	50.156	51.546	51.806	14.554	52.170	50.602	50.043	49.100	51.821	51.899
ZrO ₂	0.003	0	0.014	0.015	0	0.014	0	0	0	0.038
Al ₂ O ₃	0	0	0	0.125	0	0.002	0.011	0	0.004	0
Cr ₂ O ₃	0.209	0.118	0.124	0.992	0.152	0.180	0.178	0.174	0.158	0.136
V_2O_3	0.315	0.221	0.240	0.805	0.184	0.275	0.290	0.281	0.244	0.213
$Fe_2O_3^1$	9.433	6.960	6.068	71.471	5.609	8.181	9.222	10.856	6.225	5.900
MgO	4.782	4.958	4.860	0.807	4.815	4.695	4.679	4.666	4.797	4.823
FeO ¹	36.280	37.173	37.693	11.603	38.000	36.903	36.371	35.664	37.780	37.810
MnO	0.257	0.293	0.043	0.291	0.253	0.230	0.279	0.227	0.258	0.280
ZnO	0.037	0.047	0	0.036	0.068	0	0.006	0	0	0
CaO	0.003	0	0.006	0	0.010	0.010	0	0	0	0
Na ₂ O	0	0.012	0.035	0.016	0	0	0.011	0	0.001	0
Total	101.475	101.332	101.067	101.456	101.261	101.103	101.092	100.979	101.288	101.103
				Cations p	per three O	atoms				
Si	0	0	0.0003	0	0	0.0003	0.0001	0.0003	0	0.0001
Ti	0.9094	0.9339	0.9409	0.2833	0.9459	0.9208	0.9112	0.8957	0.9396	0.9425
Zr	0.0001	0.0002	0.0002	0	0.0002	0	0	0	0.0005	
Al	0	0	0	0.0038	0	0.0001	0.0003	0	0.0001	0
Cr	0.0040	0.0023	0.0024	0.0203	0.0029	0.0035	0.0034	0.0033	0.0030	0.0026
V	0.0061	0.0043	0.0047	0.0167	0.0037	0.0053	0.0057	0.0055	0.0047	0.0041
Fe ³⁺	0.1711	0.1262	0.1103	1.3922	0.1018	0.1489	0.1680	0.1992	0.1130	0.1072
Mg	0.1719	0.1780	0.1750	0.0312	0.1731	0.1694	0.1689	0.1688	0.1725	0.1737
Fe ²⁺	0.7315	0.7488	0.7613	0.2512	0.7662	0.7467	0.7366	0.7226	0.7618	0.7636
Mn	0.0053	0.0060	0.0047	0.0010	0.0052	0.0047	0.0058	0.0047	0.0053	0.0057
Ca	0.0001	0	0.0003	0.0002	0.0003	0.0003	0	0	0	0
Zn ²	0.0007	0.0008	0	0	0.0012	0	0.0001	0	0	0
Total ³	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
			Calcu	ulated perce	entages of o	end membe	ers			
FeSiO ₃	0	0	0.03	0	0	0.03	0.01	0.03	0	0.01
FeZrO ₃	0.01	0	0.02	0.02	0	0.02	0	0	0	0.05
MgTiO ₃	17.19	17.80	17.50	3.12	17.31	16.94	16.89	16.89	17.25	17.37
FeTiO ₃	73.14	74.88	76.08	25.10	76.62	74.63	73.65	72.23	76.18	76.30
MnTiO ₃	0.53	0.60	0.47	0.10	0.52	0.47	0.58	0.47	0.53	0.57
CaTiO ₃	0.01	0	0.03	0.02	0.03	0.03	0	0	0	0
ZnTiO ₃	0.07	0.08	0	0	0.12	0	0.01	0	0	0
Sum	90.95	93.36	94.14	28.36	94.60	92.12	91.14	89.62	93.96	94.30
Fe ₂ O ₃	8.56	6.31	5.51	69.61	5.09	7.45	8.40	9.96	5.65	5.36
Cr_2O_3	0.20	0.11	0.12	1.02	0.15	0.17	0.17	0.17	0.15	0.13
V_2O_3	0.30	0.21	0.23	0.84	0.18	0.27	0.28	0.27	0.24	0.21
Al_2O_3	0	0	0	0.19	0	0.01	0.03	0	0.01	0
Sum	9.06	6.63	5.86	71.66	5.42	7.90	8.88	10.40	6.02	5.70
Total	100.01	99.99	100.00	100.02	100.02	100.02	100.02	100.02	99.98	100.00
ATT: //				Plo	otting ratios	0.05		0.00.00		
2Ti/*	0.9094	0.9336	0.9413	0.2834	0.9459	0.9208	0.9113	0.8960	0.9396	0.9430
Cr/*	0.0020	0.0011	0.0012	0.0102	0.0015	0.0017	0.0017	0.0017	0.0015	0.0013
V/*	0.0030	0.0021	0.0023	0.0084	0.0018	0.0027	0.0028	0.0027	0.0008	0.0021
Al/*	0	0	0	0.0019	0	0.0001	0.0002	0	0.0001	0
Mg/R ²⁺	0.1890	0.1907	0.1859	0.1100	0.1830	0.1839	0.1853	0.1884	0.1836	0.1842
Mg/#	0.1719	0.1780	0.1750	0.0312	0.1731	0.1694	0.1689	0.1688	0.1725	0.1737

Notes: t, analysis in traverse. ${}^{1}Fe_{2}O_{3}$ and FeO back-calculated after determining stoichiometric formula. ${}^{2}Analysed$ trace amounts of Na₂O were ignored in the formula calculation. ${}^{3}Sum$ represents the total of figures rounded to five decimal places—figures above this are rounded to four places and do not give same sum. ${}^{*}2Ti + R^{3+}$; $\# R^{2+} + (R^{3+}/2)$.

ilmenite. Because of the very similar molar volumes of haematite and ilmenite, mol per cent and volume per cent are almost directly comparable.

3.5.2 TEM-EDX results

Compositions of ilmenite and haematite measured by TEM-EDX also show remarkably little variation provided ilmenite lamellar

analyses 30-9L, 30-14L, and haematite lamellar analyses 30-6L and 30-8L are put aside for further discussion. One ilmenite host analysis has a Ti per formula unit of 0.963, and the other five have Ti of 0.980–0.987 (average of 0.983), which can safely be taken as the composition of the most highly exsolved ilmenite hosts. Significant end members in these five analyses include 19.2–20.9 per cent MgTiO₃, 76.5–78.6 per cent FeTiO₃ and 0.5–0.9 per cent MnTiO₃, giving 96.9–99 per cent $R^{2+}R^{4+}O_3$ (i.e. 97–99 per cent 'ilmenite')

Table 2(a). TEM-EDX analyses and structural formulae of ilmenite.

		Are	ea 1		Area 2			
At per cent	30-1H	30-3H	30-4H	30-5H	30-9L	30-11H	30-12H	30-14L
0	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
Si	0.07	0.12	0.10	0.09	0.05	0.00	0.12	0.09
Ti	19.74	19.61	19.63	19.69	18.36	19.62	19.25	18.73
Al	0.05	0.07	0.03	0.07	0.00	0.03	0.01	0.00
Cr	0.01	0.04	0.02	0.02	0.05	0.04	0.01	0.01
V	0.06	0.05	0.04	0.11	0.03	0.00	0.17	0.10
Mg	3.84	4.01	4.18	3.91	4.50	3.89	3.77	4.05
Fe	16.04	15.96	15.86	15.96	16.94	16.32	16.54	16.83
Mn	0.09	0.13	0.14	0.15	0.06	0.10	0.13	0.19
Total	100.00	100.00	100.00 Cations	100.00 s per three O a	100.00 toms	100.00	100.00	100.00
Si	0.003	0.006	0.005	0.004	0.003	0	0.006	0.004
Ti	0.987	0.980	0.981	0.984	0.918	0.981	0.963	0.937
Al	0.003	0.004	0.002	0.004	0	0.001	0.000	0.000
Cr	0.001	0.002	0.001	0.001	0.003	0.002	0.000	0.001
V	0.003	0.003	0.002	0.005	0.001	0	0.009	0.005
Fe ³⁺	0.013	0.017	0.023	0.014	0.154	0.035	0.053	0.113
Mg	0.192	0.201	0.209	0.196	0.225	0.195	0.189	0.202
Fe ^{Tot}	[0.802]	[0.798]	[0.793]	[0.798]	[0.847]	[0.816]	[0.827]	[0.842]
Fe ²⁺	0.789	0.781	0.770	0.784	0.693	0.781	0.774	0.729
Mn	0.009	0.007	0.007	0.008	0.003	0.005	0.006	0.010
Total	2.000	2.001	2.002	2.000	2.000	2.000	2.000	2.001
			Calculated pe	rcentages of e	nd members			
FeSiO ₃	0.3	0.6	0.5	0.4	0.3	0	0.6	0.4
MgTiO ₃	19.2	20.1	20.9	19.6	22.5	19.5	18.9	20.2
FeTiO ₃	78.6	77.2	76.5	78.0	69.0	78.1	76.8	72.5
MnTiO ₃	0.9	0.7	0.7	0.8	0.3	0.5	0.6	1.0
Sum	99.0	98.6	98.6	98.8	92.1	98.1	96.9	94.1
Fe ₂ O ₃	0.65	1.00	1.15	0.7	7.70	1.75	2.65	5.65
Cr ₂ O ₃	0.05	0.1	0.05	0.05	0.15	0.1	0	0.05
V_2O_3	0.15	0.15	0.1	0.25	0.05	0	0.45	0.25
Al_2O_3	0.15	0.2	0.1	0.2	0	0.05	0	0
Sum	1.0	1.45	1.4	1.2	7.9	1.9	3.1	5.95
Total	100.0	100.1	100.0 Plotting	100.0 ratios summ	100.0 ations	100.0	100.0	100.1
2Ti/*	0.990	0.985	0.986	0.988	0.921	0.981	0.969	0.940
Cr/*	0.001	0.001	0.001	0.001	0.002	0.001	0	0.001
V/*	0.002	0.002	0.001	0.003	0.001	0	0.005	0.003
A1/ *	0.002	0.002	0.001	0.002	0	0.001	0	0
Mg/R^{2+}	0.194	0.204	0.212	0.198	0.244	0.199	0.195	0.215
Mg/#	0.192	0.201	0.209	0.196	0.225	0.195	0.189	0.202
*	1.994	1.989	1.990	1.992	1.994	2.000	1.988	1.993
#	1	1.001	1	1	1	1	1	1.001
Fe ⁼	0.016	0.025	0.029	0.018	0.182	0.043	0.064	0.134
Fe ^E	0.03							2.101
R ⁴⁺	0.990	0.986	0.986	0.988	0.921	0.981	0.969	0.941
R ³⁺	0.020	0.029	0.028	0.024	0.158	0.038	0.062	0.119
R ²⁺	0.990	0.986	0.986	0.988	0.921	0.981	0.969	0.941

Notes: H, analysis of ilmenite host between fine lamellae; L, analysis of fine lamella; * $2Ti + R^{3+}$; $\#R^{2+} + (R^{3+}/2)$; Fe⁼, Fe³⁺/Fe total as calculated from stoichiometry; Fe^E, Fe³⁺/Fe determined by EELS.

and 0.7–1.8 per cent Fe₂O₃, 0.05–0.15 per cent Cr_2O_3 , 0–0.25 per cent V_2O_3 and 0.05–0.2 per cent Al_2O_3 , giving 1–1.9 per cent $R_2^{3+}O_3$ (i.e. 1–2 per cent 'haematite').

 $R^{2+}R^{4+}O_3$ (i.e. 13–15 per cent 'ilmenite'); and 82.7–84.9 per cent Fe_2O_3, 0.65–0.8 per cent Cr_2O_3, 0.55–0.85 per cent V_2O_3 and 0.1–0.45 per cent Al_2O_3, giving 84.5–86.8 per cent $R_2^{3+}O_3$ (i.e. 85–87 per cent 'haematite').

One haematite host analysis has a value of Ti per formula unit of 0.131 and the other three have Ti values of 0.143–0.150. Together these appear to represent the compositions of the most highly exsolved haematite hosts. Significant end members in these four haematites include 1.2–1.8 per cent MgTiO₃, 11.7–13.4 per cent FeTiO₃ and 0–0.2 per cent MnTiO₃, giving 13.2–15.5 per cent

3.5.3 Plots of combined results showing Mg fractionation

Robinson *et al.* (2001, 2002b) have shown that the ilmenite content of members of the haematite–ilmenite series can be expressed

Table 2(b). TEM-EDX analyses and structural formulae of haematite.

		Area 1		Area 2			
At per cent	30-2H	30-7H	30-6L	30-8L	30-10H	30-13H	
0	60.00	60.00	60.00	60.00	60.00	60.00	
Si	0.14	0.09	0.14	0.02	0.11	0.03	
Ti	2.96	3.01	2.60	2.45	2.85	2.61	
Al	0.18	0.15	0.16	0.03	0.04	0.15	
Cr	0.32	0.26	0.31	0.26	0.31	0.31	
V	0.22	0.29	0.22	0.25	0.33	0.28	
Mg	0.28	0.36	1.04	0.73	0.28	0.24	
Fe	35.90	35.81	35.48	36.25	36.06	36.35	
Mn	0	0.03	0.05	0	0.01	0.03	
Total	100.00	100.00	100.00	100.00	100.00	100.00	
		Cations	s per three O a	toms			
Si	0.007	0.004	0.007	0.001	0.005	0.001	
Ti	0.148	0.150	0.130	0.122	0.143	0.131	
Al	0.009	0.008	0.008	0.002	0.002	0.007	
Cr	0.016	0.013	0.016	0.013	0.016	0.015	
V	0.011	0.014	0.011	0.013	0.017	0.014	
Fe ³⁺	1.654	1.656	1.691	1.727	1.669	1.699	
Mg	0.014	0.018	0.052	0.037	0.014	0.012	
Fe ^{Tot}	[1.795]	[1.791]	[1.774]	[1.813]	[1.803]	[1.817]	
Fe ²⁺	0.141	0.135	0.083	0.086	0.134	0.118	
Mn	0	0.001	0.002	0	0.000	0.002	
Total	2.000	1.999	2.000	2.001	2.000	2.000	
F 6:0	0.7	Calculated per	rcentages of er	nd members	0.5	0.1	
FeSiO ₃	0.7	0.4	0.7	0.1	0.5	0.1	
$Mg11O_3$	1.4	1.8	5.2	3.7	1.4	1.2	
FeliO ₃	13.4	13.1	/.6	8.5	12.9	11.7	
Mn I 1O ₃	0.0	0.1	0.2	0	0.0	0.2	
Sum	15.5	15.4	13.7	12.3	14.8	13.2	
Fe_2O_3	82.7	82.8	84.55	86.35	83.45	84.95	
Cr_2O_3	0.8	0.65	0.8	0.65	0.8	0.75	
V_2O_3	0.55	0.7	0.55	0.65	0.85	0.75	
AI_2O_3	0.45	0.4	0.4	0.1	0.1	0.35	
Sum	84.5	84.55	86.3	87.75	85.2	86.8	
Total	100.0	100.0 Plot	100.0 ting ratios sun	100.0	100.0	100.0	
2Ti/*	0 149	0 151	0.131	0.122	0.144	0 131	
Cr/*	0.008	0.007	0.008	0.007	0.008	0.008	
V/*	0.000	0.007	0.006	0.007	0.000	0.008	
A1/*	0.000	0.004	0.000	0.007	0.005	0.000	
$M\sigma/R^{2+}$	0.000	0 117	0 380	0 301	0.001	0.004	
Mg/#	0.014	0.018	0.052	0.037	0.014	0.012	
********	1 986	1 991	1 986	1 999	1 990	1 998	
#	1.000	1 000	1 000	1.001	1 000	1 000	
" Fe ⁼	0.921	0.925	0.953	0.953	0.926	0.935	
Fe ^E	0.921	0.723	0.755	0.755	0.720	0.755	
R ⁴⁺	0.02	0 154	0 137	0 123	0 148	0 132	
R ³⁺	1 600	1 601	1 726	1 755	1 704	1 736	
\mathbf{R}^{2+}	0 155	0 154	0 137	0 1 2 3	0 148	0 132	
IX.	0.155	0.154	0.157	0.125	0.140	0.132	

Notes: * $2Ti + R^{3+}$; # $R^{2+} + (R^{3+}/2)$; Fe⁼, Fe³⁺/Fe total as calculated from stoichiometry; Fe^E; Fe³⁺/Fe determined by EELS.

as values of the ratio $2\text{Ti}/(2\text{Ti} + \text{R}^{3+})$ (shown as Ti/* in Tables 1 and 2) and then plotted against other ratios, allowing insight into element fractionations between hosts and lamellae. Features previously noted elsewhere in ilmenite with exsolved haematite (Robinson *et al.* 2001) are concentrations of Mg and Mn in ilmenite and concentrations of Cr, V and Al in haematite. Fig. 11 is such a plot using $2\text{Ti}/(2\text{Ti} + \text{R}^{3+})$ versus Mg/($\text{R}^{2+} + [\text{R}^{3+}/2]$) (shown as Mg/# in Tables 1 and 2), which mainly illustrates the fractionation of Mg and Fe²⁺ between ilmenite and haematite. Because all of the Mg ratios are fairly low, the Mg ratio is shown in an inverted right triangle with

an exaggerated scale, so that we only see from the base (on the left) to 25 per cent of the distance toward the MgTiO₃ (geikielite) apex. Particularly striking in Fig. 11 is the fractionation of Mg against Fe^{2+} in ilmenite versus the ilmenite component in haematite, which makes up approximately 23–28 per cent of the haematite in the probe analyses and 13–15 per cent in the TEM analyses.

Expressed as the absolute ratio Mg/R^{2+} in the chosen ilmenites (Tables 1 and 2), the EMP values are 0.191–0.201 from session 1 and 0.183–0.191 from session 2, and the TEM values are 0.192–0.209. In contrast, as expressed in the absolute ratio Mg/R^{2+} in chosen



Figure 10. Results from a \sim 30 µm microprobe traverse across ilmenite with one haematite lamella. Analytical spot diameter 1 µm, spot spacing 3 µm. (a) Ti, Fe³⁺ and Mg per formula unit. (b) Ti per formula unit at an enlarged vertical scale. (c) Mg per formula unit at an enlarged scale. (d) Cr, V and Al per formula unit.

haematites, the EMP values for three Ti-poor haematites (session 1) are 0.078–0.095, EMP values for two Ti-rich haematites (session 2) are 0.110–0.130 and TEM values for four analyses are 0.090–0.117.

Fig. 11 brings into focus questions concerning phase equilibria and analytical accuracy. The dashed tie line connects the compositions of probe analyses in session 1. Compared with this tie line, the haematite probe analyses from session 2 are essentially on it, but the ilmenite probe analyses from session 2 all consistently lie on the Mg-poor side of it. The explanation for this may be that the session 2 analyses came from a different part of the section where Mg/Fe fractionation was weaker, perhaps because of coarse equilibration at a slightly higher temperature.

The TEM analyses of ilmenite hosts lie essentially on the dashed line in Fig. 11 or slightly to the Mg-rich side of it; the latter deviation, however, is within the error limits. These compositions were produced by separation of fine-scale haematite exsolution lamellae. The TEM analyses of haematite hosts lie well on the Mg-rich side of the tie line, and cannot be rationally explained by separation of ilmenite lamellae from the probe-composition hosts. Simple construction shows that the required ilmenite lamellar composition would be near the geikielite value of 0.075, suggesting weaker fractionation, and hence at a higher temperature than the original exsolution. The systematic overestimation of the Mg content in TEM analyses might be simply a problem in modelling and fitting the background in the low-energy range of the EDX spectrum, where the Bremsstrahlung has a significant contribution.

The TEM analyses of fine ilmenite and haematite exsolution lamellae, represented by X symbols in Fig. 11, are more difficult to understand. Because there was a strong fractionation of Mg and Fe^{2+} during the high-*T* coarse exsolution, there should have been an even stronger fractionation during low-*T* fine exsolution. For a haematite host, one would expect the contained fine ilmenite lamellae to be enriched in Mg relative to the coarse ilmenite hosts, and this fractionation could have been enhanced close to fine coherent lamellar contacts where evident lattice strain could be substantially



Figure 11. Combined plot of EMP and TEM–EDX analyses of the ilmenite and the haematite according to the ratios $2\text{Ti}/(2\text{Ti} + \text{R}^{3+})$, a measure of ilmenite proportion, and Mg/(R2++ [R3+/2]), a measure of the geikielite proportion. The dashed tie line connects microprobe analyses of session 1. The solid line in the lower right-hand corner is the haematite–geikielite edge of the extended triangle ilmenite–haematite–geikielite.

reduced by substitution of smaller Mg for Fe^{2+} in ilmenite. At the same time, with fine lamellar analyses, some analytical overlap with the haematite host might be expected, thus reducing the Ti content. The two analyses labelled as ilmenite lamellae show an increase in Mg combined with a decrease in Ti that may fit this explanation.

For an ilmenite host, one would expect the contained fine haematite lamellae to be impoverished, not enriched, in Mg relative to the coarse haematite hosts. Possibly, the high-Mg contents are a result of beam broadening and X-ray production in the surrounding ilmenite host, though this is not reflected by any increased Ti, as might be expected in this case. The two analysis points thus do not show attributes easily related to beam overlap, and, in fact, show higher absolute Mg/R^{2+} ratios than any of the ilmenites.

Fig. 11 also brings into focus the fact that Mg must play a significant role in the phase relations during exsolution, and strongly suggests that this substitution must influence the size and shape of the ilmenite-haematite two-phase fields. This third component means that the $PR\bar{3}c \rightarrow CAF + PR\bar{3}$ reaction (shown at 390°C in Fig. 2, and 520°C on the Burton diagram) is probably expressed as a triangular three-phase region in the three-component system, in which the $R\bar{3}c$ phase is not collinear between the AF and R3 phases. This is a subject for future investigations and such considerations might help explain the variation in the analytical results.

3.5.4 Plots of combined results showing Cr and V fractionation

Figs 12(a) and (b) compare the fractionations of Cr and V between ilmenite and haematite in all the analyses. In these cases both elements are at a low level and differences between probe and TEM results are clearly caused by the different precision and spectral resolution of methods. Besides the lower precision of EDX analy-



Figure 12. (a) Combined plot of EMP and TEM–EDX analyses of ilmenite and haematite according to the ratios $2Ti/(2Ti + R^{3+})$, a measure of the ilmenite proportion, and $Cr/(2Ti + R^{3+})$, a measure of the Cr_2O_3 eskolaite proportion. (b) Combined plot of EMP and TEM–EDX analyses of ilmenite and haematite according to the ratios $2Ti/(2Ti + R^{3+})$, and $V/(2Ti + R^{3+})$, a measure of the V_2O_3 karelinite proportion.

ses, the overlap of Ti K_{β} and V K_{α} and of V K_{β} and Cr K_{α} peaks in EDX spectra is much more severe than for WDS electron probe analyses. In these figures the vertical axis is the same as in Fig. 11 and is a measure of ilmenite fraction from 0 to 1. The horizontal axis in Fig. 11(a) is a measure of the atomic fraction of Cr substitution but with a very exaggerated scale extending only to 2 per cent of the Cr₂O₃ (eskolaite) end-member in the lower right-hand side. The horizontal axis in Fig. 11(b) is a measure of the atomic fraction of V substitution, but with a very exaggerated scale extending only to 1 per cent of the V_2O_3 (karelinite) end-member in the lower right-hand side.

In Fig. 12(a) the Cr content of TEM analyses of ilmenite is less than the Cr content of the microprobe analyses, as expected for fractionation during haematite separation, but the Cr content of TEM analyses of haematite is less than the Cr content of the microprobe analyses, which is not expected and probably indicates a problem in the deconvolution of overlapping Ti, V and Cr peaks. In line with this suggestion, the V content of TEM analyses of haematite is less than the V content of the microprobe analyses, which is unexpected (Fig. 12b). The V content of TEM analyses of ilmenite is scattered and similar to the V content of the microprobe analyses. However, unlike in Fig. 11, there seems to be little difference in Fig. 12 between TEM analyses of hosts (diamonds) and of lamellae (X symbols), so that whatever problem affected the Mg analyses seems to have had little effect on Cr and V. With these reservations, the diagrams show the already well-known fractionation of Cr and V into haematite during exsolution, with Cr showing stronger fractionation and V weaker.

3.5.5 Summary of analytical results and their significance

It is instructive to compare the results of EMP and TEM analyses displayed in Fig. 11 with the compositions predicted in the lowtemperature parts of the equilibrium phase diagrams of Harrison & Becker (Fig. 2) and of Burton (1991); in particular, the compositions suggested for the three-phase reaction $PR\bar{3}c \rightarrow CAFR\bar{3}c + PR\bar{3}$. For Fig. 2 the predicted values at 390 °C are IIm 31 \rightarrow IIm 25 + IIm 86. For Burton the predicted values at 520 °C are IIm 28 \rightarrow IIm 14 + IIm 83. The XRF bulk composition of the Frøytlog sample at IIm 83.6 lies outside the temperature range of the high-*T* two-phase field of Burton, but just inside for Fig. 2, though not sufficiently inside to account for the observed proportions of ilmenite host and coarse haematite lamellae.

We tentatively interpret the coarse EMP analyses of haematite at Ilm 28-27 or Ilm 24-23 and ilmenite at Ilm 94-95 as compositions derived by high-T exsolution in the $PR\bar{3}c + PR\bar{3}$ field and re-equilibration down to its low-temperature limits, which later exsolved at a much finer scale. The differences between these natural compositions, if correctly interpreted, and the compositions in the phase diagrams have several potential sources: (1) unrecognized errors in the phase diagrams; (2) effects of non-binary components, of which Mg is the most important; and (3) effects of approximately 5 kbar greater pressure during the exsolution of the natural samples. There is presently no sound basis for speculation on the effects of pressure on these equilibria, except that atomic interactions could become stronger, promoting widening of the miscibility gap. Such widening, if it occurred, would move the intersection of the $PR\bar{3}c$ solvus limb with the magnetic ordering curve to lower ilmenite compositions and higher temperatures, also increasing the eutectoid temperature. Other things being equal, movement of this intersection to the Ilm 23 composition from Frøytlog would raise the eutectoid temperature to 455 °C.

The patterns of finer lamellae in the TEM images suggest that the exsolution at finer scale took place in a series of nucleation events controlled by different degrees of oversaturation in the $CAF + PR\bar{3}$ field caused by variable compositions metastably preserved in composition gradients left over from the coarser exsolution cycles. Specifically, the coarsest of the fine lamellae occur furthest from old phase boundaries (Figs 5 and 7), whereas evolved compositions close to old phase boundaries yielded only the finest of lamellae

or mottling, indicating nucleation and growth at lower temperature. The most exsolved haematite and ilmenite host compositions at Ilm 15–13 and Ilm 98–99 should represent CAF and $R\bar{3}$ compositions derived by equilibration after nucleation of fine to very fine lamellae, below the temperature of the equilibrium eutectoid reaction. Taken as conjugate margins of the low-T solvus, this would indicate that it is considerably asymmetric toward higher Ti compared with either of the phase diagrams. However, without accurate compositions of fine lamellae, there is no proof that the haematite and ilmenite TEM host compositions were reached at the same temperature. Comparisons with Fig. 2, would suggest lower-T exsolution and re-equilibration, in ilmenite hosts than in haematite, perhaps related to greater ease of diffusion. If true, then fine haematite lamellar compositions would be expected to be significantly less than Ilm 15-13. Demagnetization temperatures (see below) would suggest Ilm 10-8 but not so low as Ilm 1.5, which would be conjugate to Ilm 98 in Fig. 2. The two TEM compositions allow one to postulate that the compositions of the equilibrium three-phase reaction for Frøytlog bulk chemistry may have been Ilm 20–16 for CAF haematite and Ilm 94 for $PR\bar{3}$ ilmenite.

The results given here compare fairly closely with results obtained from a Swedish granulite sample containing coarsely exsolved grains dominated by haematite hosts, but also with ilmenite hosts (McEnroe *et al.* 2001a). EMP analyses gave IIm 25–24 for most haematite-rich areas and IIm 88–93 for most ilmenite-rich areas. TEM gave IIm 16 for areas between fine ilmenite lamellae and IIm 88 for areas between fine haematite lamellae.

On crystal-chemical grounds, one might predict some shrinkage of the haematite–ilmenite two-phase field on the basis of approximately 20 per cent substitution of Mg for Fe²⁺ in the ilmenite, because the ionic radius of Mg is very close to Fe³⁺ compared with Fe²⁺. The positions of the analysis points in Fig. 11 may also hint at a three-phase reaction $PR\bar{3}c \rightarrow CAF + PR\bar{3}$ in which the $R\bar{3}c$ phase, represented by probe analyses of haematite, lies on the Fe-rich side of $CAF + R\bar{3}$ tie lines. Such an effect would be a consequence of broadening of the $CAF + PR\bar{3}$ two-phase field by Mg substitution, rather than shrinkage as postulated above. With only the $R\bar{3}c$ phase and CAF compositions approximately represented by the analyses and no fully reliable analyses of the $R\bar{3}$ phase within lamellae, this remains subject to speculation.

A final and important point concerning the approximately 20 per cent geikielite component in the ilmenite is that the atomic composition of the ilmenite Fe layers is what determines the magnetic moment of lamellar magnetism in each lamella of ilmenite in a haematite host or each lamella of haematite in an ilmenite host (Robinson *et al.* 2002a). With 20 per cent substitution of Mg, which is not a paramagnetic ion, we should expect a 20 per cent reduction in the magnetic moment per lamella. Similar substitutions of paramagnetic ions with lower magnetic moments for Fe³⁺ in the haematite layers, for example Cr³⁺ and V³⁺, should slightly weaken interlayer superexchange, but should not directly influence the magnetic moments of individual lamellae.

4 ROCK-MAGNETIC PROPERTIES

4.1 Experimental and analytical methods

Magnetic experiments were carried out at the Geological Survey of Norway (NGU) and the Institute for Rock Magnetism (IRM), University of Minnesota. NRM measurements were made on a JR5 magnetometer. Both alternating field and thermal demagnetization



Figure 13. Normalized intensity plot for thermal demagnetization from 0 to $650 \,^{\circ}\text{C}$.

were measured in incremental steps, AF to a maximum field of 100 mT and thermal demagnetization to a maximum temperature of 670 °C, with an error of $\pm 10^{\circ}$ C, in a MMTD60 thermal oven. Room-temperature susceptibilities were measured in a Bartington AC bridge. Measurements on hand samples for susceptibility, NRM, and density were made at the Petrophysical Laboratory at NGU. A thermomagnetic curve was measured on a horizontal Curie balance at NGU. At the IRM, hysteresis properties, both at room temperature and at elevated temperatures, were measured in a maximum field of 2 T (micromagnetometer, or vibrating sample magnetometer, Princeton Applied Research). Low-temperature remanence measurements were made on a Quantum Design (MPMS2) Squid magnetometer. The frequency and temperature dependence of susceptibility were measured with the MPMS2 at frequencies between 0.1 Hz and 1 kHz, in the temperature range 10-300 K, in fields of 279 A m⁻¹. Low-temperature measurements have an error of <0.01 K and temperature hysteresis measurements have a possible error of 10°C (M. Jackson, pers. comm.).

4.2 NRM and susceptibility

NRM directions are west to northwest and steeply negative, with an average declination of 293°, and an inclination of -67°, a direction similar to the surrounding anorthosites (Brown & McEnroe, in review) There is a limited range of initial NRM intensities from 21.5 to 30 A m⁻¹, with an average of 25 A m⁻¹. Bulk susceptibility measurements showed little variation with a mean value of 7.2 × 10^{-3} SI. Koenigsberger ratios (*Q*) are high, with an average value of 78, indicating that remanent magnetization dominates over the induced magnetization. Hand samples from the massive ilmenite-rich part of the deposit have average susceptibility and NRM values of 10.8×10^{-3} SI and 27 A m⁻¹, respectively. *Q* values range from 24 to 97. Samples have an average density of 4.6 g cm⁻³. Petrophysical measurements on other massive haemo-ilmenite ore samples from this region gave similar results to the Frøytlog deposit (McEnroe *et al.* 1996).



Figure 14. Normalized intensity plots show normalized alternating field demagnetization on the Frøytlog sample (Fr) and a sample from the Swedish Granulite Region (SW).

Progressive demagnetization, either thermal or alternating field, reveals high magnetic stability. Fig. 13 shows a typical thermal demagnetization curve for the haemo-ilmenite samples. A slight increase in intensity occurs just above room temperature with the removal of a small normal component. At higher temperatures a small but distinct increase is evident between 550 and 580°C. Between 600 and 605 °C 95 per cent of the NRM is lost. The remaining 5 per cent is spread over 45-650 °C, with 0.5 per cent remaining above this temperature. During the thermal run the NRM direction changes by only a few degrees, which is shown by a slight steepening in inclination, producing a more negative remanent vector typical of other massive haemo-ilmenite deposits in Rogaland. The slight increase observed between 550 and 580°C, might be the removal of a CAF moment from the bulk of the haematite (Ilm 14-11). Such a CAF moment would theoretically lie at 90° to the stronger moment of lamellar magnetism produced by contact layers on very fine, volumetrically less abundant, more Ti-poor haematite (Ilm 10-8).

AF demagnetization shows high magnetic stability with median destructive fields (MDFs) of 75-80 mT (Fig. 14). As with the thermal demagnetization, there is little directional change with AF demagnetization. Though these samples show a high magnetic stability, it is not as high as the samples studied by McEnroe & Brown (2000), McEnroe et al. (2001a,b) and Hargraves (1959), which all have bulk compositions significantly richer in haematite. The haematite-rich samples produce large numbers of fine-scale ilmenite lamellae within an antiferromagnetic haematite host. The magnetism associated with the interfaces between the haematite host and ilmenite lamellae will only be destroyed by demagnetizing the haematite host itself. This is extremely difficult if, as is usually the case in these samples, the host is effectively in the single-domain state. In contrast, the ilmenite-rich samples studied here produce large numbers of fine-scale haematite lamellae within a paramagnetic ilmenite host. We think the lamellar magnetism of the small isolated haematite lamellae in the paramagnetic ilmenite host is more easily demagnetized than when haematite is the host.



Figure 15. Hysteresis plots from massive haemo-ilmenite showing a change in hysteresis loops from 25° C (a) to 500° C (b). The horizontal axis denotes the applied field (*H*) in tesla; the vertical axis represents magnetization in A m² kg⁻¹.

4.3 Thermomagnetic curve

A thermomagnetic curve was measured on a chip in an applied field of 1 T, while the sample was heated at $\sim 20^{\circ}$ C min⁻¹ in air. Saturation magnetization (J_s) was measured as a function of temperature (T) from 30 to 650°C. The curve is nearly reversible upon cooling. A Néel temperature, determined as the average from the heating and cooling curves, is 595 ± 5°C. The nearly reversible heating and cooling legs indicate little oxidation or reduction occurred during the experiment. This measurement is within the ±10°C error of the thermal demagnetization measurements.

4.4 Hysteresis measurements

Hysteresis loops (Fig. 15) were measured at room temperature on 16 massive haemo-ilmenite samples in a maximum field of 1.5 T. Variations in hysteresis properties are likely to be caused by the amount and size of haematite exsolution, and the percentage of silicates in the different sample chips used. All hysteresis loops have a large paramagnetic corrections, samples have an average room-temperature saturation magnetization (M_s) of 266 mA m² kg⁻¹, and a saturation remanence (M_{rs}) of 44 mA m² kg⁻¹. These sam-

ples have average ratios of coercivity of remanence to saturation of 3.74, reflecting the influence of the paramagnetic ilmenite host at room temperature and an $M_{\rm rs}/M_{\rm s}$, average of 0.172. The saturation magnetization measured from the most oxide-rich sample at Frøytlog, has an $M_{\rm s}$ value of 210 mA m² kg⁻¹. When adjusted for density this yields an $M_{\rm s}$ values of 955 A m⁻¹. The average of all 16 haemo-ilmenite samples is 1205 A m⁻¹.

Elevated-temperature hysteresis loops were measured on two Frøytlog samples to understand better how the magnetic properties may be varying with temperature. $M_{\rm rs}/M_{\rm s}$ values increase to 0.5 by 300°C, and to a maximum of 0.84 at 560°C. This is followed by a decrease to 0.66 at 580 °C and to 0.32 at 600 °C. With increasing temperature a compositional control on the hysteresis parameters is assumed, with the more haematite-rich lamellae dominating the response at higher temperatures. The finest TEM analyses of haematite indicate little variation in composition around Ilm 15-13. However, these analyses are of hosts of fine ilmenite lamellae and not of haematite lamellae themselves, which could be more haematite-rich than anything analysed, and possibly have a strong control on the hysteresis behaviour. However, because many of the imaged nanoscale haematite lamellae show highly strained coherent interfaces, other controls, such as stress (Merrill 1968) and defects at the interfaces and contact regions, should be considered.

4.5 Low-temperature remanence measurements

Low-temperature measurements were made with a MSPS2 to determine the temperature of the transitions in the ilmenite host and haematite lamellae, and to detect the presence of any fine-grained magnetite.

A saturating field of 2.5 T was applied at room temperature and then the sample was cooled in a zero field to 19 K with remanence measured every 5 K. During this run neither the Morin transition for haematite, nor the Verwey transition, for magnetite were observed. Though there are abundant haematite lamellae in the sample, the Morin transition is suppressed by either the Ti content (up to 15 per cent) in haematite, or by the high strain observed in the coherent lamellae, and/or the very small size of the lamellae.

At 19 K a saturation remanence of 2.5 T was applied and then warmed in a near zero field at 5 K steps up to 300 K. Upon warming, a small transition occurs by \sim 40 K (Fig. 16) arising from the change from spin glass structure of the near-end-member ilmenite at low temperatures to the antiferromagnetic structure at higher temperatures (Ishikawa *et al.* 1985). Upon further warming a major decrease in remanence occurs between 60 and 75 K, coincident with the Néel temperature of near-end-member antiferromagnetically ordered ilmenite (Ishikawa & Akimoto 1957). With continued warming to room temperature little change in remanence occurs. The low-temperature SIRM experiments did not indicate that magnetite was part of the assemblage, consistent with other experiments.

4.6 Frequency-susceptibility measurements

Alternating current susceptibilities were measured for seven frequencies between 1 and 1000 Hz, over the temperature range of 5-300 K using a Quantum Design MPMS2 susceptometer. At room temperature there is a large paramagnetic contribution from the ilmenite host. This contribution results in an increase in susceptibility with lower temperatures (Fig. 17). However, there is little dispersion in the susceptibility measurements with decreasing temperature until \sim 110 K. The dispersion in the frequency measurements increases to \sim 10 per cent at 70 K. Below this temperature both the absolute



Figure 16. Low-*T* saturation remanence acquired at 19 K and warmed to room temperature in a zero field. The first derivative is shown as open circles. A Verwey transition was not observed in any sample.



Figure 17. Experimental frequency and temperature dependence of susceptibility for sample 004-3 in the temperature range of 10-300 K measured with MPMS. The in-phase component of susceptibility is shown for seven frequencies from 0.1 to 1000 Hz.

value of the susceptibility, and the dispersion in the measurements decrease, and by 30 K there is no dispersion evident. The peak height is depressed with higher frequencies, while there is no shift in the peaks with temperature.

Of interest here are the temperatures at which this dispersion is observed. The maximum frequency dependence is measured at \sim 70 K, just below the magnetic ordering (Néel) temperature of the host ilmenite (\sim IIm 97), of \sim 80 K. We believe this frequency dependence is related to the ordering of the ilmenite. In end-member and ilmenite-rich compositions there is a second ordering near 40 K that corresponds to a spin-glass structure, as described by Ishikawa *et al.* (1985). When a small amount of Fe_2O_3 is added to $FeTiO_3$ the Fe^{3+} ions in the Ti^{4+} layers align the moments on the adjacent Fe^{2+} ions in parallel, resulting in forming ferrimagnetic clusters. These clusters will behave superparamagnetically at temperatures near the spin-glass transition temperature (Ishikawa *et al.* 1985).

The overall shapes of the curves in Fig. 17 are related to the ilmenite host. The peak in dispersion of susceptibility should be just below the antiferromagnetic ordering. For end-member ilmenite, Ishikawa *et al.* (1985) showed a difference in the shape and temperature of the dispersion in susceptibility as long-range antiferromagnetic ordering occurs. This difference was a result of the orientation of the crystal. When measured parallel to the *c*-axis, a sharp peak occurs at 38 K, but when measured perpendicular to the *c*-axis a broad shaped peak, at a maximum of temperature of 50 K, occurs. Because our sample is not a single crystal, but made up of numerous imperfectly oriented haemo-ilmenite grains, it is likely that we are measuring the effects of both orientations and our data are showing a combination of these peaks.

It is not known whether the nanometre-scale haematite lamellae and associated contact regions between the haematite and ilmenite are adding to the dispersion near the antiferromagnetic ordering temperature, however, a contribution may be expected. In addition, if any of the very small haematite lamellae are behaving as superparamagnetic grains, then they will have to order when the ilmenite host orders magnetically. These lamellae will no longer be superparamagnetic because they are coupled to the ordered ilmenite. The ilmenite–haematite contact regions are also coupled to the ilmenite host and would also have to order when the host ilmenite orders.

5 DISCUSSION

5.1 Stability of remanence

The high magnetization coupled with the very high magnetic stability shown in these samples is typical of 'single-domain' and smaller particles of this solid solution series (McEnroe *et al.* 1997, 1998, 2001a,b; McEnroe & Brown 2000; Harrison *et al.* 1998). This behaviour has been found only in highly exsolved mineral phases, and is not expected in multidomain-sized grains lacking exsolved structures such as those described by Dunlop & Kletschka (2001). Studies on exsolved haemo-ilmenite and titanohaematite specimens, on average, show \sim 2 per cent saturation in the NRM state. This points critically to the fact that unexsolved titanohaematite and haematite will not behave in the same manner as the highly exsolved phases of the same composition. We believe this is a natural consequence of lamellar magnetism defined by a ferrimagnetic substructure produced by the development of contact layers between ilmenite and adjacent haematite (Harrison & Becker 2001; Robinson *et al.* 2002a).

5.2 Acquisition of remanence by haemo-ilmenite

When a *CAF* haematite is exsolved from a *PR* $\overline{3}$ ilmenite host, or when the *CAF* phase is produced by the eutectoid reaction *PR* $\overline{3}c \rightarrow CAFR\overline{3}c + PR\overline{3}$, it immediately acquires an NRM and is below its unblocking temperature. With slow cooling and equilibrium behaviour, acquisition of remanence for compositions more Ti-rich than ~IIm30 would take place below the eutectoid reaction, where compositions of the *CAF* phase on the left-hand side of the *CAF* $R\overline{3}c + PR\overline{3}$ field are all below their respective Néel temperatures (Fig. 2). These exsolved specimens obtained a magnetization by CRM, not TRM because the haematite lamellae are produced by a chemical reaction (i.e. exsolution) at a temperature well below their thermal blocking temperatures. This behaviour suggests an effective mechanism for acquisition of a chemical remanent magnetization.

The actual process of exsolution is governed by the phase diagram, and mechanisms by which exsolution lamellae nucleate and grow. Once nucleated in ilmenite, haematite lamellae must grow by inward diffusion of Fe³⁺ ions and outward diffusion of Fe²⁺ and Ti4+ ions, and once nucleated in haematite, ilmenite lamellae must grow by inward diffusion of Ti⁴⁺ and Fe²⁺ and outward diffusion of Fe³⁺ ions. The diffusion distance depends on diffusion rates that in turn are controlled by temperature. The EMP profile and TEM line scans and images show many stranded profiles. In the Rogaland region, slow cooling rates permitted cycles of exsolution to occur at low temperature, where slow diffusion rates set a limit on the size the lamellae could grow. Eventually, extensive areas between lamellae become too far from lamellar boundaries for diffusion to be effective, and these areas began to retain host compositions that were too precipitate-rich compared with the equilibrium value at these lower temperatures. Finally, these interlamellar areas become so oversaturated with the precipitate component that new, inevitably finer, lamellae nucleated and a new cycle of lamellar growth began.

Despite differences in temperatures and minor differences in compositions of the Harrison & Becker (Fig. 2) and Burton phase diagrams, they both contain the same essential features that can be used to explain the thermal acquisition of chemically controlled lamellar magnetism. In both diagrams, the greatest potential for creating a high proportion of fine lamellae comes when the haematite $PR\bar{3}c$ phase, which had evolved to the equilibrium three-phase composition or had been trapped metastably at a higher Ti composition, breaks down to a large amount of CAF $R\bar{3}c$ haematite plus a smaller amount of $PR\bar{3}$ ilmenite. In this reaction, the potential for a highlamellar yield is enhanced if the actual nucleation takes place during undercooling to a temperature considerably below the threephase temperature. Once bulk compositions of hosts and lamellae are settled on the CAF and $PR\bar{3}$ limbs, the potential for additional high-proportion lamellar yields is greatly reduced. These factors are illustrated by the following examples.

(1) $PR\bar{3}c \text{ IIm } 24 \rightarrow CAFR\bar{3}c \text{ IIm } 13 + PR\bar{3} \text{ IIm } 98 \text{ yields}$ 87 per cent haematite and 13 per cent ilmenite lamellae.

(2) $PR\bar{3}c \text{ Ilm } 28 \rightarrow CAFR\bar{3}c \text{ Ilm } 13 + PR\bar{3} \text{ Ilm } 98 \text{ yields}$ 82 per cent haematite and 18 per cent ilmenite lamellae.

(3) $CAF R\bar{3}c \text{ IIm } 18 \rightarrow CAF R\bar{3}c \text{ IIm } 13 + PR\bar{3} \text{ IIm } 98 \text{ yields}$ 94 per cent haematite and 6 per cent ilmenite lamellae.

(4) $PR\overline{3}$ Ilm 94 $\rightarrow CAFR\overline{3}c$ Ilm 13 + $PR\overline{3}$ Ilm 98 yields 95 per cent ilmenite host and 5 per cent haematite lamellae.

(5) $PR\overline{3}$ IIm 96 $\rightarrow CAFR\overline{3}c$ IIm 13 + $PR\overline{3}$ IIm 98 yields 98 per cent ilmenite host and 2 per cent haematite lamellae.

In addition to a favourable lamellar yield proportion, development of an intense lamellar magnetism requires that the lamellae should be very abundant per unit volume, and hence as fine as possible. It also requires that the lamellae be magnetized in-phase with each other, an effect that is best achieved when the basal planes of many grains are oriented parallel to the external magnetizing field.

SEM and TEM observations bearing on the $PR\bar{3}c + PR\bar{3}$ twophase field, and the $CAF + PR\bar{3}$ two-phase field, both suggest that there were multiple cycles of diffusion-limited growth followed by nucleation of new finer lamellae. For each nucleation event followed by growth in the $CAF + PR\bar{3}$ field, the *CAF* phase will be chemically magnetized, even though the exsolution process is thermally controlled. Re-equilibration with compositional adjustments toward progressively lower ilmenite content in the haematite is probable and may account for the limited compositional differences measured on the TEM. In addition to the haematite produced, however, one must be aware of compositional adjustments to the lamellar composition during the growth process, tending to change the haematite lamellar composition towards progressively lower ilmenite content. Thus, the measured composition range of the remanence-bearing *CAF* titanohaematite may not include the most ilmenite-rich compositions originally formed near the nuclei of the coarsest lamellae.

The thermal demagnetization results, suggest preservation of one dominant haematite composition demagnetizing by 605°C. At this point it cannot be said which part of the thermal demagnetization is from the haematite lamellar contacts in the ilmenite hosts, and which part is from the haematite hosts with lamellar ilmenite. When thermal demagnetization, Néel temperature results and TEM analyses are applied to the synthetic haematite curves of Ishikawa & Akimoto (1958a,b) a contradiction is evident. Thermal results suggest preservation of a haematite with a composition of ilmenite 10-8 (595-605°C), whereas the TEM nanoprobe composition is in the range Ilm 15-13. TEM analyses were not possible on the smallest haematite lamellae, and these may have slightly lower ilmenite contents that could account for the remaining 5 per cent of remanence unblocking at temperatures above 605 °C. Based on the Ishikawa & Akimoto curve, our TEM compositions should unblock at temperatures of only 545-560°C. A possible explanation for the high unblocking temperatures of the dominant Ilm 15-13 composition may be the abundance of highly strained coherent haematite lamellae. Another possibility is that the finest haematite lamellae not presently accessible analytically, have a higher haematite to ilmenite ratio, thus raising the demagnetization temperature. It may be these finest lamellae that also produce the dominant part of the lamellar magnetism.

The difference between the acquisition temperature of lamellar magnetism, and the higher demagnetization temperature during short-term thermal experiments, is extremely important to recognize. Acquisition, for these ilmenite-rich compositions, must take place within the stability field of $CAF + PR\overline{3}$ at a temperature at or below the eutectoid, indicated at 390 °C in Fig. 2, though possibly at higher temperatures in natural circumstances. The short-term experiments measure the demagnetizations of CAF haematite hosts and lamellae at higher than eutectoid temperatures, in Frøytlog mainly at 595-605°C, where these compositions are metastable in equilibrium with $PR\bar{3}$ ilmenite and should eventually be resorbed. While resorption is avoided, the thermal demagnetization curves show remarkable stability to very high temperatures, unlike the typical lower-temperature fall-off of magnetite. Therefore, the long-term thermal stability of lamellar magnetism is limited by the eutectoid temperature, and higher temperatures can only be preserved when Ti-poor haematite compositions are retained metastably.

Images of the natural samples show coarse lamellae exsolved at high *T* under conditions of rapid diffusion, down to nanometre-scale lamellae, exsolved at low *T* under conditions of slow diffusion. Production of a lamella involves first nucleation and then growth. A highly exsolved grain involves repetition of these events thousands of times, possibly over millions of years, while the orientation of the Earth's magnetic field probably changed. What happens to lamellar magnetism from initiation of magnetization at nucleation through an extended period of lamellar growth? This is deduced from layer models (Robinson *et al.* 2002a) and is surprising. When an ilmenite or haematite lamella thickens, it thickens by addition of two layers at a time. This shifts the adjacent contact layer by two layers, placing it in a new position exactly *in-phase* magnetically with its earlier position and still locked magnetically to adjacent haematite. Once orientation of a lamella moment is established during nucleation, it will not change significantly, i.e. 'lamellar magnetism is forever'. What happens to lamellar magnetism during later nucleations after the first generation is well established? Will new lamellae magnetize in response to Earth's changing magnetic field, or to the local field created by earlier lamellae? If the Earth's field dominates, then lamellae might attempt to record changing orientation; if the field of older lamellae dominates, either parallel or antiparallel, then magnetic orientation might remain the same, but the intensity would increase or decrease. With antiparallel magnetization of later lamellae and the correct proportions of lamellar yields, the material might undergo self-reversal. These questions and speculations show that lamellar magnetism has much promise for future research.

5.3 Intensity of NRM

The classic interpretation for a single-domain titanohaematite of composition Ilm 8-10, would be an antiferromagnetic structure with a weak parasitic ferromagnetism. Given the small modal proportion of haematite, this weak ferromagnetism is too small to account for the magnitude of NRM in these rocks. Though large NRM intensities are known from MD-size haematite grains because they are efficient carriers of TRM and are easily saturated (Uyeda 1958; Syono et al. 1962; Dunlop & Kletschka 2001), unlike MD haematite, the samples discussed in this paper have high coercivities, are not saturated and the magnetization is a CRM not a TRM. Based on density measurements and bulk composition estimates, the titanohaematite content in the samples is ~ 14 per cent. Even if one attributed all the magnetization to a 'saturated MD-type haematite phase' this value would only be 350 A m⁻¹, far lower than the haemo-ilmenite average M value of 1200 A m⁻¹. An alternative mechanism is necessary to account for the magnetization.

As discussed earlier, ordered ilmenites are ferrimagnetic with a high saturation magnetization over the composition range IIm 50–80. However, compositions in this range have low Curie temperatures ($250 > T_c > 0^\circ$ C), and could not account directly for the high-temperature stability of the NRM. TEM chemical analyses demonstrate that the ilmenite-rich component of the intergrowth is IIm 98, i.e. a bulk composition that is paramagnetic at room temperature.

At this point, the lamellar magnetism concept outlined earlier becomes compelling, because it has many of the characteristics required to explain the magnetic properties of these highly exsolved samples. The high unblocking temperatures are caused by the unblocking of the haematite lamellae, possibly made higher than predicted by coherence strain at the interfaces. The magnitude of the lamellar magnetic moment depends greatly on the changes in composition, cation distribution and spin structure that occur across the interface. The ilmenite-rich samples studied here have a lower net magnetization than more haematite-rich material because the amount of lamellae produced was less. As shown above, the maximum proportion of fine lamellae will be produced by the $PR\bar{3}c \rightarrow CAF + R\bar{3}$, reaction by breakdown of $R\bar{3}c$ compositions produced during earlier exsolution. These samples show a lower coercivity than samples dominated by haematite hosts, possibly because the moment is locked in place only by exchange interaction with the paramagnetic ilmenite host, rather than with a singledomain haematite host (McEnroe & Brown 2000; McEnroe et al. 2001a).

5.4 Implications for planetary anomalies

Hemo-ilmenite samples have high coercivity, with typical MDFs of 75 mT or greater. These MDFs are not as high as samples that contain haematite hosts with exsolution lamellae, which typically exceed 100 mT. High coercivity samples usually retain a magnetic direction on a geological timescale (i.e. hundreds of millions to billions of years). When evaluating the magnetic response of a rock in relation to magnetic anomalies NRM and susceptibility values are the two most important magnetic parameters. From these two parameters the Koenigsberger ratio (Q value) is calculated by dividing the NRM by the induced magnetization (susceptibility x ambient field). For our calculations we used a value of 50 027 nT (corresponding to a magnetizing force of 39.9 A m⁻¹) for the local magnetic field.

In areas where Q values are <1, the magnetic response mainly arises from the induced magnetization of the rocks. In areas with Q values >1, the remanent magnetization, i.e. the magnetization remaining after removal of an applied field, is the dominant contributor to the anomaly, provided the remanence directions are reasonably consistent. Where Q > 10 and NRM directions are consistent, the NRM overwhelmingly dominates the magnetic response of the rock, far exceeding the induced response. All the massive haemo-ilmenite samples have NRM values that are an order of magnitude higher than susceptibility values with resulting Q values all >10. The average Q value is 77. The aeromagnetic signature over the massive haemoilmenite deposits and enclosing Åna Sira anorthosite is dominantly a negative magnetic anomaly (McEnroe et al. 2001b) reflecting the regional Proterozoic remanent vector of NW and steeply upward. The properties of relatively high coercivity and NRMs coupled with low susceptibility account for the magnetic response of these rocks. Based on the magnetic response of the samples discussed in this paper, haemo-ilmenite, even just as an accessory phase, should be considered as an important magnetic mineral, especially on planets that no longer have a present-day magnetic field. This conclusion has been reached previously (McEnroe 1997; McEnroe et al. 2001a,b; McEnroe & Brown 2000) for members of this solid solution series and it is reiterated here.

6 CONCLUSIONS

This study has important implications for the magnetism of exsolved phases. Prolonged cooling, over millions of years, can produce the necessary conditions for continued nucleation, exsolution and growth cycles leading to a complex microstructure and little significant coarsening of the lamellae. In these rocks we attribute the high magnetization to the numerous haematite-ilmenite interfaces with ferrimagnetic contact regions. The hypothesis of lamellar magnetism, produced by contact layer interaction is not yet proven but is compelling. The strongest evidence is that thermal unblocking is at high temperature and occurs abruptly between 600 and 605 °C, a temperature characteristic of titanohaematite. The fact that the haematite compositions at the finest scale that could be measured by TEM-EDX are too Ti-rich for such temperatures on the theoretical curve may indicate an effect of coherent strain on the lamellar interfaces, or that the ultra-fine lamellae contributing the most to lamellar magnetism are actually less Ti-rich. The high-coercivity properties are attributed to fine-scale microstructures of ilmenite and haematite lamellae within ilmenite and haematite hosts. The coherent lamellae all show highly strained interfaces that may play an important role in thermal unblocking and coercivity. The magnitude of the NRM is too large to be caused solely by a spin-canted haematite and we put forth the concept of lamella contact interaction as the primary source for magnetization of the NRM.

Too often the magnetic response of deep crustal rocks is assumed to reflect MD-magnetite. It is important that a high-coercivity phase, such as a nanoscale exsolution intergrowth of titanohaematite and ilmenite, is capable of acquiring strong and highly stable NRM that can persist to temperatures higher than significant unblocking of magnetite, if not to the Curie temperature of the magnetite, and that the NRM is stable for billions of years. The highly exsolved near-end-member ilmenites studied here, such as their haematite counterparts, are important sources of magnetism for magnetic anomalies at depth in the Earth and in other planets. For very cold planetary bodies, there could be an additional contribution to the primary magnetic phases from Ti-rich ferrimagnetic ilmenites with very low Curie temperatures.

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