The relationship between exsolution and magnetic properties in hemo-ilmenite: Insights from Mössbauer spectroscopy with implications for planetary magnetic anomalies

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[1] Remanence properties of ilmenites with exsolved hematite have recently been the object of much study, because their high natural remanent magnetization (NRM) is greater than predicted for these two minerals. X-ray diffraction (XRD) and Mössbauer spectroscopy in conjunction with electron microprobe and NRM measurements were used to explore the possibility that single domain (SD) hematite lamellae in the ilmenite host could explain the observed remanence, and to determine if magnetite is present. XRD results show the presence of ilmenite and hematite. Mössbauer data show that only species assigned to hematite, ilmenite, and a small amount of tetrahedral Fe^{3+} are present. Magnetic properties at high and low T also indicate that the only magnetic minerals are ilmenite and hematite. Magnetic data suggest that ultra-fine hematite lamellae are magnetically ordered, and their resultant remanent magnetic anomalies may contribute significantly to magnetism on terrestrial planets, even those without present-day magnetic fields. *INDEX TERMS:* 3929 Mineral Physics: NMR, Mossbauer spectroscopy, and other magnetic techniques; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction; 5109 Physical Properties of Rocks: Magnetic and electrical properties; 5440 Planetology: Solid Surface Planets: Magnetic fields and magnetism. **Citation:** Dyar, M. D., S. A. McEnroe, E. Murad, L. L. Brown, and H. Schiellerup (2004), The relationship between exsolution and magnetic properties in hemo-ilmenite: Insights from Mössbauer spectroscopy with implications for planetary magnetic anomalies, *Geophys. Res. Lett.*, *31*, L04608, doi:10.1029/2003GL019076.

1. Introduction

[2] Occurrences of ilmenite with exsolved hematite (hemo-ilmenite) and hematite with exsolved ilmenite (ilmeno-hematite) are common, but until recently their magnetic properties have been largely ignored. Early studies on magnetic properties of the ilmenite-hematite solid solution were mostly made on synthetic samples [e.g., *Ishikawa and Akimoto*, 1958] with only a few on natural samples [*Hargraves*, 1959]. Recent studies coupling petrology, chemistry and magnetic properties on hemo-ilmenite or ilmeno-hematite show a large, stable NRM [*McEnroe and Brown*, 2000; *McEnroe et al.*, 2001a, 2001b, 2002]. It had been common to attribute high NRMs to undetected SD magnetite, but the recent work shows unblocking temperatures too high to be attributed to magnetite. A possible explanation for the high NRM values and coercivities involves the fine scale of exsolution lamellae.

[3] A key question is whether or not the abundant hematite lamellae that are smaller than the SD to superparamagnetic (SPM) transition of 0.3 μm, are interacting with the host to allow for magnetic ordering, or if these lamellae are behaving as superparagmagnets. In this study we use Mössbauer spectroscopy to investigate hemo-ilmenite cumulates both in a search for elusive SD magnetite and for magnetic ordering in the hematite lamellae from a few microns to 1–2 nm thick.

2. Samples

[4] The samples discussed here are from hemo-ilmenite deposits hosted by the Åna-Sira Anorthosite in Rogaland Norway. They represent primitive cumulates derived from melts saturated in ilmenite and plagioclase, of similar composition to that in the enclosing anorthosites ($\sim An_{50}$). The composition of the hemo-ilmenite is relatively primitive, with a geikielite component ($MgTiO_3$) of 15–22%. Numerous generations of Ti-hematite lamellae are present ranging in thickness from ~3 μm down to a few nanometers. Samples studied include 1007, from the Florklev hemo-ilmenite deposit, 1012 derives from the Vardåsen deposit, 1004 and 1009 from massive hemo-ilmenite layers

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in the Blåfjell-Laksedal norite pegmatite transecting the Åna-Sira Anorthosite, and 004-3 from the Frøytlog deposit. The last has been extensively studied for magnetic properties and chemically by EMP and TEM [*McEnroe et al.*, 2002].

3. Methods

[5] Compositional data were collected on a Cameca SX-50 electron microprobe (EMP) at the University of Massachusetts and the Bayerisches Geoinstitut using an accelerating potential of 15 keV and a beam current of 15 nA. Corrections for differential matrix effects were done using the online PAP correction routine. Analytical precision is estimated at ±0.1 wt.% for oxide components present at the 1 wt.% level.

[6] NRM measurements were made on a Molspin magnetometer at the University of Massachusetts. Both alternating field (AF) and thermal demagnetization were measured in incremental steps, AF to 100 mT, and thermal to 680°C, in a MMTD60 or Schonsted furnace. Core susceptibility was measured on a Bartington AC bridge. Hand samples were measured for susceptibility, NRM, and density at NGU. Hysteresis properties were measured on a Princeton Applied Research Micromagnetometer in fields up to 2 T and low-temperature remanence was measured on a Quantum Design (MPMS2) Squid magnetometer after saturation in a 2.5T field at the Institute for Rock Magnetism.

[7] X-ray diffraction (XRD) was carried out using CuK_α radiation on a Bruker D8 instrument equipped with a sample spinner and a diffracted-beam graphite monochromator. Powder specimens were step-scanned in 2θ-steps of 0.02° in the 2θ range 5–70° for 15 seconds per step. Peak positions were determined using a fit program described by [*Stanjek and Friedrich*, 1986] and mean coherence lengths were determined by the Scherrer formula after stripping the data of the $CuK_{\alpha 2}$ components using the Bruker "Diffrac" program.

[8] Samples were prepared for Mössbauer analysis by diluting the samples with sugar and grinding under acetone to avoid preferred orientation. Sample thicknesses were <1 mg Fe/cm^2, below the thin absorber approximation of *Long et al.* [1983], in order to avoid thickness effects. Spectra were acquired at 300 K and ±12 mm/s using a WEB Research Co. Mössbauer spectrometer and processed using WMOSS.

4. Results

4.1. Composition

[9] The dominant phase in all samples is a hemo-ilmenite with fine to ultra-fine exsolution. The host ilmenite varies from an Ilm_{94} to $Ilm_{98,}$ with up to 22% geikielite component.

[10] In all samples the hematite lamellae were difficult to analyze accurately by EMP because the lamellae are almost always narrower than the microprobe beam. Hematite analyses, with the least overlap with the ilmenite host, yielded compositions in the range of $Ilm_{28-23.}$. Sample 004-3 gave accurate TEM-EDX analyses on the larger hematite lamellae of Ilm_{15} [see *McEnroe et al.*, 2002]. Minor plagioclase ($An_{\sim 50}$) and rare Ca-poor pyroxenes ($En_{\sim 75}$) are present, but neither mineral contains enough Fe to contribute significantly to the Mössbauer spectrum. Though minor late stage magnetite could occur in the ore deposits, no phase with the composition of Fe_3O_4 (magnetite) was found by XRD, EMP or by TEM. The TEM analyses were made by two different TEMs at Bayreuth (Falko Langenhorst) and Münster (Richard Harrison).

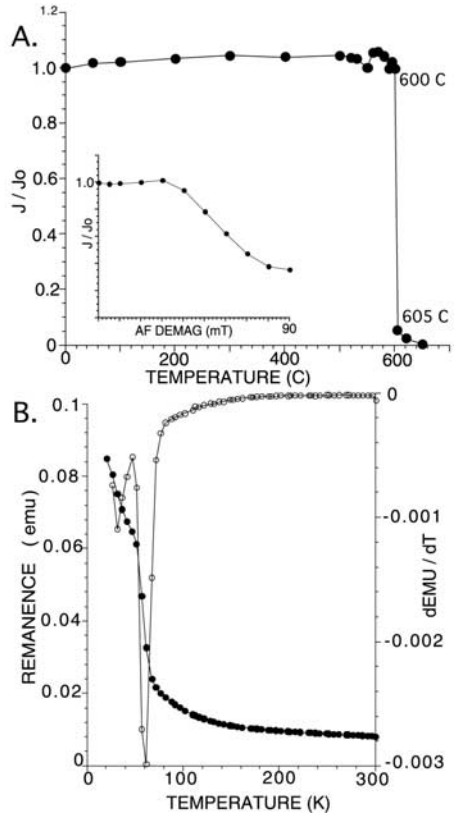

Figure 1. (A) Normalized intensity plot of thermal and AF demagnetization (insert) for sample 004-3. (B) Saturation remanence for sample 004-3 acquired at 19 K and warmed to room temperature in a zero field (solid circles). The derivative (open circles) plotted showing decay in remanence at 40 K and 60 K.

4.2. Magnetic Properties

[11] The hemo-ilmenite samples have average NRM values of 36 A/m. Susceptibility values are low with a mean of 8.5×10^{-3}S I. Thermal demagnetization shows high stability until 585 to 600°C, with rapid decay to less than 10% by 605°C (Figure 1A). In AF demagnetization median destructive fields were between 70 to 95 mT, with the high coercivity attributed to the SD lamellae that have internal exsolution microstructures.

[12] Hysteresis measurements made on sample chips give a range of the ratio of saturation remanence (Mr) to saturation magnetization (Ms) of 0.14 to 0.21 with an average of 0.18. Variability in Mr and Ms values is due to variable amounts of hematite exsolution and amount of silicates in each sample. When adjusted for density, the average Ms value is 1177 A/m. The average coercivity (Hc) value is 48 mT, significantly higher than Hc values of 2–14 mT for MD-size hematite crystals [*Halgedahl*, 1998]. Ratios of remanence of coercivity (Hcr) to Hc show

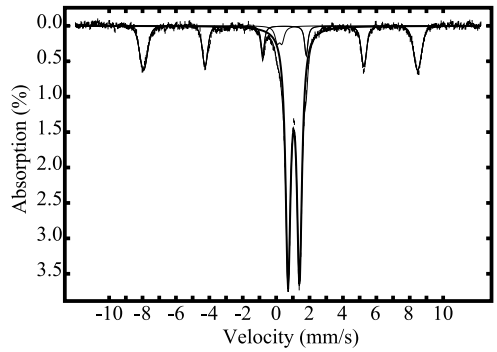

Figure 2. Mössbauer spectrum of sample 004-3 is typical of all those studied.

some variability with an average Hcr/Hc ratio of 4. Nearly reversible Ms-T measurements on sample chips yielded Néel Ts of 590–600°C, indicating that magnetite, a Ti-substituted magnetite, or a maghemite were not present, in good agreement with the thermal demagnetization results on larger core specimens.

[13] Low-T remanence measurements on a MPMS2 were made from 19 K to 300 K with samples showing similar behavior upon warming and cooling. A small transition occurs by ~40 K (Figure 1B), when the spin glass structure of the host ilmenite changes to a SPM structure [*Brown et al.*, 1993]. At ~60 K a major decrease in remanence occurs at the Néel temperature as ilmenite passes through from the SPM to the paramagnetic state. When a field was applied at room-T and samples were cooled to 19 K, no Morin transition was evident for the hematite.

[14] The behavior found in these samples is vastly different from that in unexsolved MD-size hematite grains (>15 μm), which can obtain a large thermal remanent magnetization (TRM) if it is blocked in or near its Néel T due to low self-demagnetization [*Dunlop and Kletetschka*, 2001].

4.3. X-Ray Diffraction

[15] The iron mineralogy of all samples appears to be quite similar, with ilmenite > hematite as principal constituents. Subtle differences indicate the presence of minor phases such as mica in 1004 and 1007. The purest sample studied was 1009, which showed only ilmenite and hematite. Neither maghemite nor magnetite was present. Average ilmenite and hematite mean coherence lengths in the [104] direction, here taken to represent mean particle size, were roughly 160 nm in all samples.

4.4. Mössbauer Spectroscopy

[16] Three considerations are relevant to interpret our Mössbauer results. First, asymmetry and line broadening are common occurrences in Mössbauer spectra of oxides due to contributions from factors including superparamagnetic relaxation, different kinds of magnetic excitations, cluster ordering, and surface effects. For these reasons, spectra are best described by hyperfine field distributions (HFDs); accordingly, such models are used here.

[17] Second, the value of the hyperfine field in an oxide depends in part upon crystallinity, which is usually expressed as inverse mean crystallite dimension as noted above. Previous workers have observed that grain sizes below 20 nm [*Kündig et al.*, 1966] may suppress the Morin transition, however our samples have hematite lamellae up to 3 μm with an average of 160 nm. Therefore, small grain size may be ruled out as a cause of the absent Morin transition.

[18] Third, the value of the hyperfine field in an oxide also depends upon substitution of iron by other cations. Al contents have the well documented effect of reducing the hyperfine field [*Murad and Schwertmann*, 1986; *da Costa et al.*, 2002]. Samples studied here have only minor Al contents (<0.19 wt% Al_2O_3), but they do have significant Ti contents, which, because Ti^{4+} is diamagnetic, would also act to depress the hyperfine field [*Morin*, 1950]. Therefore, the observed absence of a Morin transition in our samples is probably due to their high Ti contents.

[19] Spectra of all samples and their fits are nearly identical; an example is shown in Figure 2. Each spectrum has three components (Table 1).

[20] 1. A HFD site with $\Delta = -0.23$ mm/s and $\delta = 0.38$ mm/s represents hematite. Its hyperfine field of ~50.6 T at room temperature is lower than those observed for well-crystallized, chemically-pure hematites, but is attributed to the presence of diamagnetic Ti^{4+}, which would reduce the hyperfine field. This hematite sextet could also be fit with two subcomponents/sextets, but this resulted in nearly identical parameters, χ^2, and total probability distributions, as is typical of the Voigt-based/HFD fitting method. Thus there was no justification for using more than a single HFD for hematite, and the presence of other hyperfine phases could be ruled out.

[21] 2. A normal quadrupole doublet with $\delta = 1.05$ mm/s and $\Delta = 0.69$ mm/s corresponds to ilmenite.

[22] 3. Another, distinct doublet with $\delta = 0.23$ mm/s and $\Delta = 0.28$ mm/s has parameters typical of Fe^{3+} in tetrahedral coordination.

Table 1. Mössbauer Data on Hemo-ilmenites at 300 K

	1007.01.2	1012.01.1	1004.01.5	1009	004-3
γ, mm/s	0.20	0.20	0.20	0.20	0.20
z_0, mm/s	3.45	3.44	3.44	3.43	3.45
B_{hf}, T	50.7	50.5	50.6	50.4	50.7
δ_z, mm/s	0.18	0.18	0.18	0.18	0.19
δ_0, mm/s	0.38	0.38	0.38	0.38	0.38
ε_0, mm/s	−0.24	−0.23	−0.24	−0.24	−0.23
Area	27%	29%	24%	24%	30%
γ, mm/s	0.35	0.34	0.33	0.32	0.35
δ_0, mm/s	1.05	1.06	1.05	1.05	1.06
ε_0, mm/s	0.69	0.67	0.69	0.69	0.68
Area	69%	67%	70%	72%	66%
γ, mm/s	0.28	0.27	0.34	0.25	0.32
δ_0, mm/s	0.22	0.26	0.24	0.22	0.21
ε_0, mm/s	0.27	0.30	0.29	0.24	0.28
Area	4%	4.5%	6.5%	4%	4%
χ^2	11.3	8	2	6.3	1.4

Errors on γ, z_0, δ_z, δ_0, and ε_0, are roughly ±0.02 mm/s; for B_{hf} roughly ±0.5, and for areas ±0.5–3%. All δ values are relative to α-iron. γ = the full width at half maximum of the intrinsic Lorentzian. z_0 is the center of the hyperfine field Gaussian distribution. δ_z is the full width at half maximum of the HFD Gaussian. δ_0 is the value of δ when z = 0. ε_0 is the value of ε when z = 0. For these fits the values of h_2/h_3 and h_1/h_3 were constrained to be 2 and 3, respectively. Values for δ_1 and ε_1 were allowed to vary in these fits but remained at zero, suggesting the lack of any linear correlation between δ and Δ. For a detailed explanation of these parameters, see *Rancourt and Ping* [1991].

[23] The two quadrupole doublets have significantly different shifts and cannot be described as parts of one species with a HFD. If the third doublet were to represent superparamagnetic hematite (i.e., with grain sizes <20 nm), it would be expected to show a doublet with parameters of Fe^{3+} in octahedral coordination [e.g., *Zhou et al.*, 2001]. However, the feature observed in our spectra is very sharp and has parameters typical of tetrahedral Fe^{3+}. Magnetite particles <6–10 nm would result in collapse of magnetic hyperfine splitting [*Mørup and Topsøe*, 1976] creating a very broad ferromagnetic peak [*Zaitsev et al.*, 1999] that is not observed in any of the spectra acquired here.

[24] Magnetite with larger particles sizes would be apparent as two additional sextets in addition to those of hematite and ilmenite, as observed by *Waerenborgh et al.* [2002], but the magnetite sextets are clearly not visible here. Based upon these results, we can also rule out the presence of magnetite at any scale.

5. Discussion and Conclusions

[25] Samples in this study show strong magnetization and high coercivity. Based upon Mössbauer, microprobe, XRD, and low- and high-T remanence measurements, there is no evidence for magnetite in any sample. More surprisingly all the hematite lamellae appear to be magnetically ordered, even though many are smaller than the classic "lower limit" for SD hematite and should behave as superparamagnetic grains in the magnetization measurements. A possible explanation is that the fine-scale lamellae could be interacting with the host, producing a ferrimagnetic interaction at the atomic scale due to coupling in the contact layers between the host and exsolution as proposed by *Robinson et al.* [2002].

[26] Understanding how these ultra-fine lamellae are ordered is of fundamental importance to understanding rock magnetism throughout the solar system. Due to their high NRM values and coercivities, hemo-ilmenite and ilmeno-hematite-bearing rocks on Earth can create remanent-dominated anomalies. Because they are capable of retaining their magnetic signature for gigayears, they have the potential to create magnetic anomalies on any planet that once had a magnetic field but no longer does. Both our Moon and Mars show evidence of an ancient magnetic field, but the present magnetic anomalies are controlled by remanent, rather than induced components. On Earth, both induced and remanent components play an important role in magnetic anomalies, but induced components are commonly due to MD magnetite interacting with the Earth's ambient field.

[27] Although Mercury has a relatively weak magnetic field (~1% of Earth), high surface temperatures of up to 700 K would allow both near-and-end member magnetite, hemo-ilmenite and ilmeno-hematite to contribute to both induced and remnant anomalies. Though the contribution from induced anomalies would be smaller than those on Earth because of the weaker present-day magnetic field, there could be a Hopkinson effect that would create induced anomalies. There the remanent contribution to magnetic anomalies may be important if magnetic stability can be retained at the elevated temperatures. In short, hemo-ilmenite rocks with remanent anomalies may be of greater importance in understanding magnetism in our solar system than those involving magnetite.

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