Practical Magnetism XI: The low temperature AC susceptibility of multidomain (titano)magnetite, an addendum on its amplitude dependence

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While nominally about the low temperature frequency-dependence of (titano)magnetite susceptibility, the article in the previous IRMQ issue (32-4) also included observations of amplitude dependence in multidomain (MD) grains, and relative discussion. One relevant aspect was omitted, however, dealing with the relation between in-phase, $\chi'$, and out-of-phase, $\chi''$, of amplitude dependent susceptibility, warranting a short addendum. Behind that omission, is the observation that most articles published on the topic are somewhat incomplete: for example, of the two most in-depth studies of titanomagnetite low temperature susceptibility, Carter-Stiglitz et al. (2006) reported on both frequency and amplitude dependence of titanomagnetite, but only for the in-phase susceptibility, whereas Church et al. (2011) strictly reported on frequency dependence of both in-phase and out-of-phase, but not on their amplitude dependence. Likewise, Jackson et al. (1998) dealt with the amplitude dependence of in-phase AC susceptibility of titanomagnetite only at room temperature. It is therefore sometimes difficult to appreciate the larger picture, which is what I tried to amend with the IRMQ:32-4 review (Bilardello, 2003), yet inevitably some aspects escape.

For the frequency-dependence of AC susceptibility, Néel demonstrated that for assemblages of grains with a distribution of relaxation times there is a relation between the in-phase and out-of-phase, which follows the "$\pi/2$" law ($\chi''_{\text{visc}} = -\pi/2 \times \frac{\partial \chi'}{\partial \ln(f)}$), see IRM:32-4). The "$\pi/2$" law can be shown to be related to the viscous decay of remanence, and is further applicable to thermal activation energies (Mullins and Tite, 1973), and allows estimating with reasonable precision the viscous component of susceptibility ($\chi''_{\text{visc}}$). In a similar manner, Rayleigh (1887) investigated the change of magnetization in very weak-fields, exploring the relation between in-phase and out-of-phase susceptibility where there is amplitude dependence (between room temperature and ~100-150 K). The delayed response and corresponding out-of-phase susceptibility in certain materials arises from irreversible magnetization changes driven by the AC field, which is typically on the order of 200-300 A/m. Such low-field hysteresis has been documented in a handful of minerals, namely in multidomain pyrrhotite, hematite, and intermediate composition titanomagnetites, and was already covered by Mike Jackson (2003) in the IRMQ:13-4. But does a similarly reasonable approximation for the hysteretic component of susceptibility exist?
The Dove Basin drill sites, particularly Site U1537, appear to have a reliable reversal stratigraphy for the last 3.3 Ma that has been useful for paleo-investigations (Reilly et al., 2021a; Warnock et al., 2022; Weber et al., 2022) and ongoing work has pointed to potential for relative paleointensity reconstructions over some time intervals (Reilly et al., 2021b). While preliminary work indicates the Pirie Basin Site U1538 holds a high resolution and well defined paleomagnetic record for the last glacial interval, its paleomagnetic record becomes more complex at depth. Lithologic and physical property variations are remarkably similar between the Dove and Pirie Basin sites, allowing for detailed stratigraphic correlation for the last ~1.5 Ma (Bailey et al., 2022). This correlation suggests a thick interval of normal polarity during the reverse polarity zone, C1r.1r, at Site U1538 and ambiguity in the assignment of the Matuyama-Brunhes boundary (Figure 1). These differences cannot be explained by coring disturbance.

The goal of my IRM visiting fellowship was to better characterize the remanence carriers at Sites U1537 and U1538 from correlative intervals to see if the paleomagnetic differences could be attributed to differences in the magnetic mineralogy. To do so, I collected low temperature data on the Quantum Designs MPMS3 and room temperature data on the Lakeshore 8600 VSM. In general, U1538 samples had a less well defined Verwey Transition ($T_v$) and higher coercivities than U1537 samples. For example, Sites U1537 and U1538 last interglacial period (~125 ka) samples from ~26.8 m on the Bailey et al. (2022) correlated depth scale are presented in Figure 2. While both sites have similar lithology and provenance, the rock magnetic properties are clearly different. The Site U1537 sample shows much greater loss of its room temperature saturation isothermal remanent magnetization (RTSIRM) after low temperature cycling (LTC) to 10 K (20% loss) than the Site U1538 sample (6% loss), indicating a stronger $T_v$. This is also reflected in the difference of the $\delta T_v$ parameter (Moskowitz et al., 1993) calculated from the Field Cooled (FC) and Zero Field Cooled (ZFC) curves. The sites also show a large difference in their Coercivity of Remanence ($H_c$) values and DC Demagnetization (DCD) curves, with the Site U1538 sample having $H_c$ values more than 2 times higher than the Site U1537 sample. This coercivity difference is also clearly reflected in hysteresis loops and first order reversal curves (FORCs), which show that Site U1537 is dominated by vortex state behavior, while Site U1538 has greater contribution from fine-grained, potentially single domain particles. This is seen in higher $M_r / M_s$ and greater spread along the $H_c$ axis on the FORC diagram (Figure 2).

Data collected during this IRM visiting fellowship indeed demonstrate that despite similar sedimentologic properties, there are large differences between the remanence carriers in the Dove and Pirie Basin drill cores. Dove Basin Site U1537 generally has a signature consistent with magnetite in a domain state typical for detrital particles in marine sediments, while Pirie Basin often has magnetic minerals with a higher coercivity. Ongoing work
will compare these detailed rock magnetic data collected during this visiting fellowship to sediment magnetic data collected on discrete cube samples collected at 1.5 m intervals, high temperature thermal demagnetization of laboratory magnetizations, and geochemical data to better understand the nature, trends, and processes of the remanence carriers at each site. In turn, these data will help highlight the opportunities and challenges in using paleomagnetic methods to constrain the chronology of these important paleoclimate archives.

Acknowledgements

I am grateful to the captain, crew, IODP staff, and scientific team that made IODP Expedition 382 successful, particularly fellow Expedition 382 paleomagnetists, Lisa Tauxe and Stefanie Brachfeld, who have been integral to this work. All samples and data were provided by IODP. I thank Dario Bilardello and the IRM staff for welcoming me and assisting me during my visiting fellowship. This work is supported by NSF OPP-ANT Award 2302832.

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Using field-dependent magnetic susceptibility to quickly characterize magnetic mineralogy for submarine basalts

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Oceanic basalts are a database of Earth’s magnetic field records. To decipher this information, ocean drilling expeditions are often necessary to collect samples. For oceanic basalts on Earth, the expected magnetic carriers are in the compositional space defined by four endmembers – magnetite, ulvöspinel, hematite and ilmenite (Fig.1). The magnetite-ulvöspinel solid solution is expected to be found in fresh submarine basalts while the ilmenite-hematite series represents oxidized ones. Additional complexities may arise due to compositional heterogeneity from exclusion, and mineral structure variations within the same composition (Zhou et al., 2000; Özdemir 1987; Furuta 1993). Due to these complexities, it may be difficult to figure out whether alternating field (AF) or thermal demagnetization methods are better for a given sample a priori during either shipboard or onshore measurements. It is therefore desirable to have a fast, non-destructive pre-screening method to choose the best demagnetization method. During this IRM visit, I explored whether measuring the field dependence of magnetic susceptibility (MS) could be used to screen oceanic basalt samples for this purpose.

Measured MS values can depend on the amplitude and the frequency of the applied magnetic field (Bilandello 2023; Jackson et al., 1998; Ustra et al., 2018). Room-temperature field dependence of MS can be measured using a Kappabridge MFK2-FA susceptibility-meter, which is available on the JOIDES Resolution scientific drilling vessel as well as in the Stanford Paleomagnetism Lab. I studied basalts collected during International Ocean Discovery Program (IODP) Expedition 391: Walvis Ridge Hotspot (Sager et al., 2022). At Stanford, in addition to field-dependent MS measurements, I obtained thermomagnetic curves to determine the thermal stability of magnetic carriers as well as the Curie or Néel temperatures of magnetic minerals. Further rock magnetic characterization was conducted at the Institute for Rock Magnetism. Using the LakeShore VSM 8600, I measured hysteresis loops, backfield remanence curves, and conducted FORC measurements. Using the Quantum Design MPMS-3, I also obtained low-temperature AC magnetic susceptibility data with varying field amplitude and frequency.

Here, I show example results from two basalts with distinguished field dependence behaviors. The magnetic field dependence is calculated as $\chi_{Hd} = (\chi_{300 A/m} - \chi_{30 A/m})/\chi_{30 A/m}$.

Sample B7151 ($\chi_{Hd} = 50\%$, IODP# 391-U1577A-23R-4-W 4-6) exhibits high field dependence (Fig. 2a-c). Peaks around 50-80 K in the imaginary susceptibility are observed, indicative of titanomagnetite (Bilandello 2023). Its Curie temperature is around 85 °C (Fig. 2c) (Petrovský and Kapička, 2006). These features indicate that the magnetic carrier is titanomagnetite with a composition of Fe$_{3-x}$Ti$_x$O$_4$ ($x=0.65$) (Lattard et al., 2006, Liloiva et al., 2012). In contrast, sample B2861 ($\chi_{Hd} = 1\%$, IODP# 391-U1578A-34R-2-W 26-28) is almost field-independent.

![Figure 1. FeO-Fe$_2$O$_3$-TiO$_2$ ternary diagram. The shaded regions show the possible mineralogies that can be found in terrestrial submarine basalts. Point size represents the MS field dependence of individual minerals, reported in Clark 2016.](image1)

![Figure 2. Magnetic susceptibility measurements of samples B7151 and B2861. Shown are the (a,d) real and (b,e) imaginary components of low-temperature susceptibility data acquired on the MPMS-3. Color differences in data points indicate variation in field amplitude and while shape differences indicate variation in frequency. Thermomagnetic curves (measured at 200 A/m and 976 Hz with MFK2-FA) acquired for (c) B7151 and (f) B2861 are also shown.](image2)
dependent at room temperature (Fig. 2d-f). In low temperature susceptibility curves, the first peak around 180 K is indicative of the ilmenite-hematite solid solution (Lattard et al., 2006). The increasingly large frequency dependence around 250-300 K also indicates hematite (Fig. 3b).

Our hysteresis parameters generally show that field-dependence of MS appears to be correlated with lower $M_r/M_s$ and higher $B_{cr}/B_c$ values. This behavior may reflect fresh titanomagnetite-dominated samples with higher field dependence. Oxidation would likely produce finer titanomaghemite or ilmenite-hematite grains that are field-independent. In conclusion, we found that room-temperature field dependence of MS values can be used to crudely infer the mineralogy of oceanic basalts and help select appropriate demagnetization methods. Field-dependent samples are associated with fresh Ti-rich magnetite with very low Curie temperatures, so AF demagnetization should be used. Field-independent samples are more oxidized and may respond well to either AF or thermal treatment.

Acknowledgements
I would like to thank Maxwell Brown for arranging the visit and navigating low-temperature magnetic measurements, Peter Solheid and Dario Bilardello for helping with experiments and instructions for data processing. I would also like to thank the U.S. Science Support Program and the Expedition 391 Scientists and Staff for making this study possible. Finally, I would also like to express my gratitude to my supervisor Sonia Tikoo.

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Shock and FORC: Magnetic Domain Response of Shocked and Oxidized Magnetite with Temperature

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Magnetite is the most widely occurring ferrimagnetic mineral, however the study of shock-related effects on its magnetic properties is still recent. Research of shocked magnetite suggests that for shock pressures above 5 GPa, up to 90% of magnetic susceptibility is lost. Shock-related physical deformation has a strong impact on the magnetic susceptibility, mineral structural-transition temperatures, and domain sizes of magnetite (Reznik et al., 2016). In nature, shock pressures preserved in impact rocks often range from 5 to 35 GPa, and locally even above 60 GPa where melting is observed, such as in Chixculub (Morgan et al., 2017). Shockwave-derived fractures and crystal lattice defects cause a reduction in magnetic domain size, from multi-domain (MD), to pseudo-single domain (PSD). The mechanism behind the latter feature is that dislocations increase magnetic wall-pinning, and thus promote relative magnetic grain size reduction (Lindquist et al., 2015). Kontny et al. (2018) found that post-shock thermal treatment (up to 700°C) increases magnetic susceptibility and reduces Hopkinson Peak Ratio (HPR), signifying a domain size increase.

A recent study of naturally shocked magnetite from the Chixculub impact structure (Mendes et al., in press) reports pre-impact martitization of otherwise pure and stoichiometric magnetite in the basement. After being exposed to high temperatures during a $k$-T experiment in an argon atmosphere, the hematite is replaced by newly formed, mottled textured magnetite. This newly formed magnetite is interpreted to comprise small SD-SP magnetic grains. The increase in susceptibility associated...
with magnetite formation causes irreversibility in the \( k-T \) signal, with the same shape as the pure magnetite experiencing deformation annealing (Kontny et al., 2018). Just and Kontny (2012) also report this transformation for non-shocked but hydrothermally altered magnetite-bearing granite, where \( k-T \) curves related to hematite to magnetite (hem-mt) transformation having a very similar signal to those from both non-oxidized shocked magnetite, and botch shocked and oxidized granitoids from the Chicxulub.

In the frame of my fellowship, I aimed to isolate these two natural and experimental phenomena and its effects on domain sizes of magnetite. I investigated the evolution of hysteresis, IRM components and first-order reversal curve (FORC) diagrams at different high-temperature steps in laboratory-shocked magnetite, natural oxidized magnetite, and natural oxidized and shocked magnetite from the Chicxulub peak ring. A total of nine samples were used in this study: seven pure magnetite ore samples shocked at increasing pressures (non-shocked “initial” MD sample, 1, 3, 5, 10, 20 and 30 GPa), and two natural magnetite samples: Soultz-sous-Forêts granite (“2533”), and Chicxulub impact crater peak-ring basement (“1100”). I used a LakeShore 8600 Series VSM instrument to measure hysteresis, Direct Current Demagnetization (DCD) and FORC diagrams in sequence, for each mass normalized sample at each temperature step. Temperature step increments were made using an ASC furnace with controlled atmosphere. For ore samples I performed 5 measurements, at room temperature (RT), and after heating to 540, 560, 580 and 700°C, while in natural samples I added the 600 and 650°C steps. The temperature steps were all made in a controlled inert Ar-gon atmospheric chamber.

RT measurements for the non-shocked “Initial” and Soultz 2533 samples, as well as “Low-shock” 1 and 3 GPa samples show typical diagrams for MD grains, and coercivities ranging from 13.5 mT to 20.1 mT. At 5 GPa (the Hugoniot Elastic Limit of magnetite) coercivities increase to ~33.2 mT, and the horizontal and vertical spread of the FORC signal increases strongly, but a PSD state lobe peak distribution is not yet well defined. At “high-shock” (10, 20 and 30 GPa, and Chicx. 1100), samples show a further increase of coercivities, ranging from 34.6 mT to 50.1 MT, and FORC signals define a standard PSD/V state, with intense closed-contour peak lobe shape, and broad horizontal and vertical dispersion.

With temperature, “Low-shock” and initial non-oxidized samples do not show any change in domain size or coercivity. For samples above 5 GPa, we observe a shift of the lobe peak signals towards lower coercivities accompanied by a systematic decrease of average coercivity with temperature and a continuous enlargement of the vertical low-coercivity elongation around the origin (Fig. 1a, represented by sample 20 GPa). This is very clear when observed in a horizontal FORC diagram (Fig. 2a), and total MD-SD FORC signal area is calculated (Fig. 2b). We observe that No and Low shock samples (represented by Initial in Fig. 2b) show no variation of FORC features, whilst the high shock samples (represented by 20 GPa in Fig.1, 2) show a clear leftward progression of the peak position towards a MD+PSD composite distribution (Fig. 2b, 20 GPa, black arrow), and a decrease in SD-MD mixture signal area (as described in Reznik et al., 2016). The mean coercivities also shift systematically towards lower values with temperature, with final values being 12.0 to 17.7 mT lower than RT values. These results provide a step by step observation of post-shock thermal annealing and domain-wall unpinning, leading to a more MD composition.

The oxidized, non-shocked sample Soultz 2533 shows a two-stage evolution from RT to 560°C, where there are barely any changes in magnetic properties, retaining a bulk/rock MD behavior (Fig. 1b, 2a). After 560°C, the hematite content decreases from 10.7% to 3.1%, and mean coercivity increases from 18.2 to 43.2 mT. A large ridge in the FORC diagrams is formed, and a large increase of signals are observed in the horizontal FORC, combined with a large increase in the SD-MD area (Fig. 1b, 2b). I interpreted this as the previously postulated formation of magnetite from hematite in an argon atmosphere.

In Chicxulub, I observed a mix of the previous two phenomena, where the shocked magnetite with PSD behavior tends to lower coercivity (Fig 1c; Fig. 2a at origin), but existing hematite also transforms to magnetite.

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**Figure 1:** FORC diagrams of sample evolution with temperature. a) evolution of “high shock” samples; b) evolution of Hem-Mt transformation in sample Soultz 2533; c) evolution of Hem-Mt transformation and annealing in sample Chicxulub 1100.
(contribution from 7.1% to 0%), leading to a formation of low-coercivity SD-SP magnetite and associated ridge, and an increase in MD-SD area. (Fig. 2b). The mean coercivity increases from 34.6 mT to 51.7 mT. I interpreted this as evidence that when both shock and oxidation occur in a sample, the hemo-magnetite transformation masks annealing as the dominant phenomenon. Only FORCs, the most sensitive method to small scale domain changes can clearly distinguish between the two effects.

These findings are important even outside of impact craters, as martitization is a ubiquitous process in surface rocks. The formation of new SD magnetite in non-oxidizing or inert atmospheres as a temperature response may cause an overprint of paleomagnetic directions and other properties in natural samples, creating the need for an extra layer of scrutiny in interpretations. It may also be a process for overprinting natural remanent magnetization.

References


RAC News!

The IRM welcomes new RAC members Claire Nichols (Oxford University), Wyn Williams (University of Edinburgh), and Ioan Lascu (Smithsonian Institution).

We thank former RAC chair Julie Bowls (University of Wisconsin-Milwaukee), Karl Fabian (Norwegian University of Science and Technology), and Sonia Tikoo (Stanford University) for their service to the IRM, and are grateful to Roger Fu (Harvard University) for becoming the new RAC chair!
Current Articles

A list of current research articles dealing with various topics in the physics and chemistry of magnetism is a regular feature of the IRM Quarterly. Articles published in familiar geology and geophysics journals are included; special emphasis is given to current articles from physics, chemistry, and materials-science journals. Most are taken from ISI Web of Knowledge, after which they are subjected to Procrustean culling for this newsletter. An extensive reference list of articles (primarily about rock magnetism, the physics and chemistry of magnetism, and some paleomagnetism) is continually updated at the IRM. This list, with more than 10,000 references, is available free of charge. Your contributions both to the list and to the Current Articles section of the IRM Quarterly are always welcome.

Archeomag


Environmental Magnetism


Rong, S. W., J. Wu, J. Liu, Q. Li, C. P. Ren, and X. Y. Cao (2023), Environmental Magnetic Characteristics and Heavy Metal Pollution Assessment of Sediments in the Le’an River, China, Minerals, 13(2), doi:10.3390/min13020145.


Fundamental and Applied Rock Magnetism


Extraterrrestrial and Planetary Magnetism and Petrology


Geomagnetism, Paleointensity and Records of the Geomagnetic Field


Magnetic Fabrics and Anisotropy


Magnetic Microscopy and Tomography


Magnetic Mineralogy and Petrology, Other


Paleomagnetism


Wang, S., et al. (2023), New Middle Jurassic Paleomagnetic and Geochronologic Results From the Lhasa Terrane: Contributions to the Closure of the Meso-Tethys Ocean and Jurassic True Polar Wander, Geophysical Research Letters, 50(7), doi:10.1029/2023gl103343.

Stratigraphy
A short re-cap for all those that have just arrived: in externally-applied time-varying magnetic fields $H(t) = H_0 \cos(\omega t)$, where $H_0$ is the amplitude and $\omega$ the angular frequency, the magnetization of many materials varies in phase with the field: $M(t) = M_0 \cos(\omega t)$, and thus the ratio $M(t)/H(t)$ does not vary with $t$, but maintains a constant value, equal to $M_0/H_0 = \chi$, where $\chi$ is generally used for mass-normalized susceptibility and $k$ for volume-normalized. However, in certain materials, including those with low-field hysteresis, the magnetization lags behind the time-varying applied field: $M(t) = M_0 \cos(\omega t - \Delta t) = M_0 \cos(\omega t - \delta)$, where $\Delta t$ is the time lag, and $\delta$ is referred to as the phase shift, lag, or the phase. $M$ can be decomposed into in-phase (“real”) and 90° out-of-phase (“imaginary” or “quadrature”) components: $M = M_0 \cos(\omega t) + M_0 \sin(\omega t)$, where $\tan(\delta) = M' / M_0$ and $M_0^2 = M'^2 + M''^2$. Accordingly, AC susceptibility $\chi$ is a complex quantity, with $\chi'' = -i \omega \chi'$, where $\chi'$ is the in-phase and $\chi''$ is the out-of-phase response.

Moving on, weak-field hysteresis was first measured and described by Rayleigh (1887), inspired by the discovery of (strong-field) hysteresis by Ewing (1886), and his speculations about what may occur when $\partial M / \partial H$ approaches zero. Rayleigh, supposing that the limit of linearity cannot be constrained within fields of $-4$ A/m ($500 \mu$T), and indeed Jackson (2003) notes that the threshold of nonlinearity varies strongly with mineralogy and grain size: magnetite generally behaves linearly in fields up to 1000 A/m (~125 mT) or more, but the limit is much lower (101-103 A/m, ~126-129 $\mu$T) for such important minerals as pyrrhotite, titanomagnetite and hematite (e.g., Worm, 1991; Worm et al., 1993; Hrouda, 2002), all of which generate significant quadrature signals in typical instrumental AC fields.

Going back to the posit from above, a reasonable approximation for the hysteretic component $\chi''_{hyst}$ was derived by Jackson et al. (2003) from the definitions of the in-phase and quadrature components of the AC Rayleigh loops above ($\chi' = \chi_0 + aH_0$ and $\chi'' = 4aH_0/3\pi$), so that $\chi''_{hyst} = (4H_0/3\pi) \partial \chi'/\partial H_0 = (4/3\pi) \partial \chi'/\partial (\ln(H_0))$, or the “4/3$\pi$” law.

While the “4/3$\pi$” law is suitable for SP-SSD assemblages below room temperature and thermally-activated processes in MD (titanomagnetite below the Verwey transition in magnetite) or 100-150K in different compositions of titanomagnetites, the “4/3$\pi$” law is applicable to titanomagnetites above those same temperatures, MD pyrrhotite above the Besnus transition (34 K), and MD hematite above the Morin transition (250 K).

Figures 2-8 report results from a series of synthetic MD titanomagnetite samples of compositions ranging from $x = 0.05$ (TM05) to $x = 0.78$ (TM78), in $Fe_{3-x}Ti_xO_y$. The samples were single crystal rods produced by B.J. Wanamaker at Lawrence Livermore National Laboratories (LLNL), and described in Wanamaker and Moskowitz (1994), or by J.M. Honing (Purdue University) and described in Kakol et al. (1991a,b;1994) and Moskowitz et al. (1998), as specified on the plots. The LLNL samples were examined under optical microscope, scanning electron microscope, electron microprobe, thermomagnetic analysis, and Laue back-reflection camera, and determined to be single crystal, single phase, and chemically homogeneous except for a small gradient in Ti/Fe along the growth dimension due to the different melt-solition distribution coefficients of these species. These sample rods were cut into discs by Wanamaker and Moskowitz (1994), but were subsequently ground into powders by Carter-Stiglitz et al. (2006), who made the measurements reported here.

For the Purdue samples, the titanium distribution and actual composition were verified for each crystal using a microprobe electron analyzer and by energy dispersive x-ray analysis. Single crystals were reannealed under the appropriate CO-CO$_2$ gas mixture to monitor the oxygen fugacity and attain the ideal oxygen-to-cation ratio for each specimen. Samples were subsequently ground into spheres of 1.5 - 2 mm diameter. After completion of the measurements, each sphere was cut open to check the Ti composition using the microprobe analyzer, and found to be homogeneous within instrumental resolution. These samples were used by the Purdue group for a number of publications on magnetic properties, magnetocrystalline anisotropy, and cation distributions in titanomagnetites (e.g., Kakol et al., 1991ab; 1994).

In each figure, the left-hand panels show the frequency-dependent in-phase (top) and out-of-phase (bottom) susceptibilities measured in “maximum” field amplitudes of 199.9 or 238.8 A/m, depending on the specific protocol used (data from the Rock Magnetic Bestiary), including the $\chi''_{visc}$ parameter calculated from the “4/3$\pi$” law.

For the frequency dependence of all samples there is a reasonable agreement between $\chi'$ and $\chi''_{visc}$ below ~150 K, and particularly for the TM05 and TM55 samples, whereas for the other samples the measured out-of-phase component is somewhat higher; $\chi''_{visc}$ does a very good job at replicating the low temperature MD peak, the subject of the IRMQ:32-4 article, in both position and magnitude, which Church et al. (2011) attributed to an “internal” domain-wall pinning regime. Note how all samples possess some, albeit inconsistent throughout the series, frequency dependence at ~250 K, associated with the magnetic after effect caused by diffusional reorientation of interstitial Fe$^{2+}$ defects (Walz et al., 1997). This
frequency dependence is most prominent in $\chi''$ but not replicated by $\chi''_{\text{visc}}$, indicating that it is not due to a thermally activated process. Furthermore, the TM35 sample, and less so the TM41 sample, possess a kink in $\chi''$ at 140 and 180K, respectively, which are accompanied by an increase in $\chi''_{\text{visc}}$ at the same temperatures, and subsequent frequency dependence of both, with slight “sagging” of $\chi''$, though this is mitigated by the continued upward trend towards room temperature (more below on these features).

The right-hand panels report the amplitude-dependent susceptibilities acquired at 1 Hz frequencies: $\chi'$, top, and $\chi''$, bottom, and including the $\chi''_{\text{hyst}}$ calculated from the $1/4/3\pi^2$ law. Above a certain relaxation temperature, ranging from $\sim$100K to $\sim$150K and increasing with titanium content, all samples exhibit amplitude dependence residing in low field hysteresis. Above these temperatures, $\chi''_{\text{hyst}}$ provides a reasonable approxima-
tion for χ''', at least in providing a broad indication of its magnitude. The “4/3χ'''' law does not replicate the peak observed in χ'', for the sole reason that this is not a hysteretic process and thus amplitude dependent (note that the temperature of the peaks does not vary with amplitude), but is in fact the “internal domain-wall pinning” thermally activated feature that is so well captured by the frequency-dependence and the “π/2'''' law. A clear amplitude-dependence is also observed concomitant with the features in frequency dependence described above for TM35 and TM41 (at and above 140K and 180K, respectively). In fact, inspecting the series, sample TM05 also exhibits amplitude dependence of χ'' above 180K, with a clear relaxation (“sagging”) of the susceptibility between 180K and room temperature. Except for at 300K, in this temperature range there is an obvious mismatch between χ'' and χ''_hyst, implying that χ'' does not reside (entirely?) in low-field hysteresis. A similar disagreement is promi-
component around 200K for TM28, TM35 and TM41, and less prominently in TM05, TM16 and TM55. Excluding oxy-
exsolution of the titanomagnetite into magnetite and il-
menite (e.g., Lagroix et al., 2004; Bowles et al., 2013; Jackson and Bowles, 2014) based on the sample charac-
terization described above, the relaxation of susceptibility observed is likely associated with the change in the domi-
nant microcrystalline anisotropy constant $K_1$ with temper-
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Figure 6: TM41-Purdue: Frequency (left-hand side) and amplitude (right-hand side) dependence of a synthetic multidomain tit-
nomagnetite crystal of composition x = 0.41 (TM41), acquired at an AC field amplitude of 199.9 A/m and frequency of 1 Hz, respectively. Note the frequency-dependence <100 K associated with the thermal activation of domain walls and the agreement below this temperature of the measured $\chi''$ and the calculated $\chi''_{\text{visc}}$ peaks. Likewise, note the agreement of the $\chi''$ and the calculated $\chi''_{\text{hyst}}$ above that temperature, other than the mismatch around 200K, associated with low-field hysteresis. The peak in $\chi''$ instead is related to thermal activation, is not amplitude-dependent, and is thus not replicated by the $\chi''_{\text{hyst}}$ curves. A kink/peak at ~180K and relaxation of susceptibilities above this temperature is observed. See text for details.

Figure 7: TM55-Purdue: Frequency (left-hand side) and amplitude (right-hand side) dependence of a synthetic multidomain tit-
nomagnetite crystal of composition x = 0.55 (TM55), acquired at an AC field amplitude of 238.8 A/m and frequency of 1 Hz, respectively. Note the frequency-dependence <150 K associated with the thermal activation of domain walls and the very good agreement below this temperature of the measured $\chi''$ and the calculated $\chi''_{\text{visc}}$ peaks. Likewise, note the reasonable agreement of the $\chi''$ above 150K, peaking around 250K, and the calculated $\chi''_{\text{hyst}}$ associated with low-field hysteresis. The peak in $\chi''$ instead is related to thermal activation, is not amplitude-dependent, and is thus not replicated by the $\chi''_{\text{hyst}}$ curves. See text for details.

At higher Ti-substitutions, e.g., TM78 in figure 8, the samples lose all frequency-dependence. One domi-
nant susceptibility peak is present at 250K in both $\chi''$ and $\chi''$, but the latter is not replicated by $\chi''_{\text{visc}}$, implying that it is not due to a thermally activated process. Instead, the $\chi''$ peak is nicely reproduced by $\chi''_{\text{hyst}}$, indicat-
ing that it resides in low-field hysteresis. It is somewhat unfortunate that these TM-series data were acquired at coarse (10K) intervals, preventing pin-pointing the peak-temperatures other than by curve-fitting. In any case, for these stoichiometries the ordering temperature of the titanomagnetite decreases to below room temperature, so that the sharp drop in $\chi'$ represents the Curie temperature of TM78.

For completeness, and preventing another addendum, I end with reporting the variation of titanomagnetite Curie temperatures with composition of Lattard et al. (2006) (Fig. 9).

Figure 8: TM78-Purdue: Frequency (left-hand side) and amplitude (right-hand side) dependence of a synthetic multidomain titanomagnetite crystal of composition $x = 0.78$ (TM78), acquired at an AC field amplitude of 199.9 A/m and frequency of 1 Hz, respectively. Note the lack of frequency-dependence at low temperature, with susceptibility curves being flat <200K. Likewise, note the reasonable agreement of the $\chi''$ above 200K, peaking around 250K, and the calculated $\chi''_{\text{visc}}$ associated with low-field hysteresis. The sharp drop at ~260K is the Curie temperature for this stoichiometry. See text for details.

Figure 9: Variation of Curie temperature with titanomagnetite compositional parameter $x$ from Lattard et al. (2006).

Acknowledgments
I thank Nathan Church for the discussions around his titanomagnetite samples/data, which, although not included here, have helped me sort out and better understand data included in the IRM’s Rock-Magnetic Bestiary. I also thank Bruce Moskowitz for his careful proofreading of my IRMQ manuscripts and useful suggestions.

References
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Funding for the IRM is provided by the National Science Foundation, the W. M. Keck Foundation, and the University of Minnesota.

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