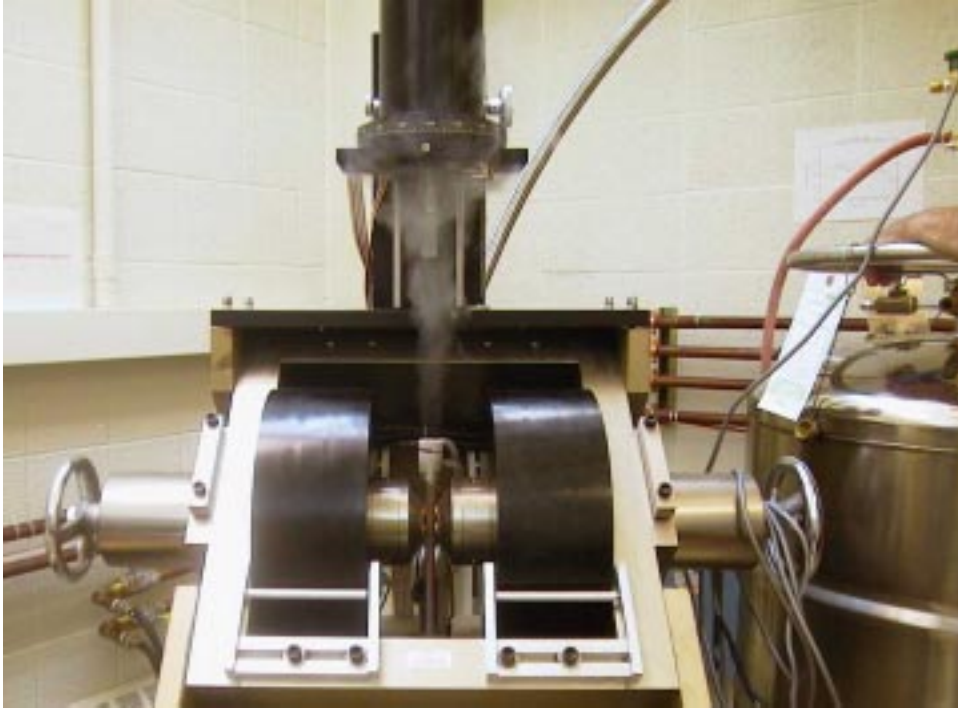# The IRM Quarterly

Spring 2000, Vol. 10, No. 1 Institute for Rock Magnetism

portrait by Stefanie Brachfeld

A swirling cloud of vapors condenses around a plume of helium at 4.2 K as it emerges from the cryostat of the new low-temperature VSM during rapid initial cooling. In routine operation the helium flow is reduced, and the plume is drawn off by a vacuum hose.

Cryosota

**Peat Solheid
Jim Marvin**

IRM

The moment Yossarian saw the MicroVSM he fell madly in love. With a cryostat that has a temperature range from 10 to 450 Kelvin, a magnet with a maximum field of 1.8 Tesla and the ability to automatically rotate the sample, who wouldn't?

Another addition to our low temperature instrumentation is installed and working beautifully. Now with several months of operation under our belts we can safely say this is one of the most useful and versatile instruments we have. Formally it is known as a MicroMag 3900 Vibrating Sample Magnetometer (VSM), but in keeping with *IRM* traditional nomenclature, we call it the cold MicroVSM. A conversion module from Princeton Measurements enabled us to reversibly transform our original

MicroMag Model 2900 Alternating Gradient Magnetometer (AGM), replacing the piezoelectric force probes with a vibration head, and the gradient coils with induction pickup coils. The VSM configuration is considerably more robust than the AGM, which is a tremendous advantage for low-temperature work. Of course, there's a catch: with a sensitivity range from 5×10^{-9} Am^2 (5 μemu) to 1×10^{-3} Am^2 (10 emu) it is about 2 orders of magnitude less sensitive than the AGM. This difference is significant for low-T measurements, where sample size is limited to roughly 50 mg due to the cryostat geometry. With the cryostat removed, however, the VSM can handle much larger samples (up to a few tens of grams) and in many cases actually produces better room-T (22° C) data than

the AGM, without the calibration and broken probe problems.

The heart of this instrument is its variable temperature cryostat. With an operating range of 10 to 473 K, and a speedy temperature slew rate of nearly 100 degrees/minute, measurements of hysteresis loops at 10 K increments are a snap. Samples can be either in the form of small chips affixed with vacuum grease to the sample holder or powders packed into one end of a gelcap and pushed onto a sample holder. For chips the maximum size is about 3 mm on a side and for powders, generally 50 to 100 mg is sufficient. The chip-and-vacuum-grease method allows measurements over the full temperature range, while gelcaps are limited to a maximum temperature of 373 K. Powders can be fixed in cement for measurements above 373 K. The temperature range of the cold MicroVSM overlaps and complements that of the companion hot MicroVSM (see *IRM Quarterly v. 5, n. 4, Winter 1995-96*), enabling excellent hysteresis measurements from 10 K to 1073K between the two instruments. The sometimes problematic range from room temperature to 423K on the hot MicroVSM is handled perfectly on the cold one.

With this new instrument, very high resolution investigations of temperature-dependent hysteresis properties are now practical. To measure a set of loops at 5K intervals from 10 to 300 K (nearly sixty loops!) takes only about 2 hours. Compare this to the MPMS, where a single loop takes about 2 hours, and you can begin to imagine how Yossarian felt. There are trade-offs, of course: remanence measurements are possible only for stronger (or more precisely, high-Q) samples, as the "zero" field is at best equal to the ambient lab field, and the operating range is limited to above 10 K. Therefore remanence measurements, loops at temperatures below 10 K and fields above 1.8 T are still in the MPMS domain, but for a large majority of studies of the temperature dependence of hysteresis properties the new MicroMag low-temperature VSM rocks!

For an example of the type of work that can be carried out during a visiting fellowship with this instrument have a look at Andrei Kosterov's VF report in this Quarterly.

Visiting Fellows' Reports

Magnetic hysteresis of pseudo-single-domain and multidomain magnetite below Verwey transition

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Magnetite has been extensively studied since it is the most important magnetic mineral in nature, and also because of its widespread applications in industry. It is therefore surprising to recognize how little is known about the magnetic hysteresis properties of its low-temperature phase, existing below the Verwey transition (119 – 123 K in stoichiometric material). Until now, only the behavior at the Verwey transition and immediately below it, down to 77 K, has been studied in some detail. For small PSD grains 60 to 250 nm in size a very limited set of hysteresis data is available for the temperature range below 77 K [*Schmidbauer and Schembera*, 1987; *Schmidbauer and Keller*, 1996].

The primary goal of my visit to IRM was therefore to carry out hysteresis measurements from 10 K to room temperature on multidomain (MD) and pseudo-single-domain (PSD) magnetite samples. I happened to be the first visiting fellow to use the newly-installed Princeton Measurements microVSM equipped with a cryostat. This instrument allows measuring hysteresis loops from 10 K onwards in just 5 minutes or less – great change compared with the few hours (!) required by the MPMS. Perhaps the only obvious drawback of the new instrument is that the maximal field for hysteresis loops is only 1.4 T. I tried also higher fields, up to 1.8 T, but there was no improvement using them because of the electromagnet pole saturation. These fields are not sufficient to truly saturate the low-temperature phase of magnetite.

The multidomain sample was crushed magnetite with the grainsize 100-150 μm, fully described by *Hartstra* [1982] (fraction of his sample HM4, hereafter referred as HM4L). Both SIRM warming and χ(T) curves of this sample display a sharp Verwey transition at 117.5 K suggesting a relatively small non-stoichiometry. One of the PSD samples was also a < 5 μm fraction of HM4 (referred to hereafter as HM4S; note in passing that room temperature hysteresis parameters suggest even smaller mean grainsize). Another two were the commercial magnetites from Wright (3006) and Pfizer (BK5099) companies with a mean grainsize around 1 μm. Verwey temperatures for these samples were found to be 122 K for HM4S, 110 K for 3006, and 95 K for BK5099 showing that the two latter samples have been noticeably oxidized. Hysteresis measurements have been performed after cooling down to 10 K either in zero magnetic field or in 1.5 T field.

Hysteresis properties below Verwey transition were found to depend strongly on the cooling history for both PSD and MD samples. For PSD samples (Fig. 1) M_{rs}/M_s ratios are lower after zero field cooling, as observed by *Schmidbauer and Keller* [1996]. However, in contrast to the results of that study, the M_{rs}/M_s ratios for the field-cooled (FC) samples show a relatively strong decrease between 15 and 80 K. After zero-field cooling (ZFC), M_{rs}/M_s does not vary much in this temperature range for samples HM4S and 3006, while for the sample BK5099 it has a distinct maximum at 30-35 K. Behavior of the coercive force in this temperature range is altogether dissimilar to that of Schmidbauer and Keller's sample, zero-field cooling resulting in higher coercive force than field cooling. Temperature dependences of coercive force show a trend opposite to that for M_{rs}/M_s: it decreases strongly for zero-field-cooled samples, remaining almost constant for the field-cooled ones. Moreover, coercive force of the three PSD samples was found to depend on whether the sample had been zero-field-cooled from a magnetized (SIRM at room T) or from a demagnetized initial state. Taken together, these results strongly suggest that below the Verwey transition a multitude of magnetic states may be available to PSD magnetite grains, and neither shape nor magnetocrystalline anisotropy exert full control over the hysteresis properties in this temperature range. Close to the Verwey transition both M_{rs}/M_s and H_c decrease significantly; curves corresponding to different cooling histories converge. Samples HM4S and 3006 show minima in both M_{rs}/M_s and H_c at 132-134 K and 122-124 K respectively, and for sample BK5099 M_{rs}/M_s and H_c flatten out at about 110 K. Bearing in mind that the isotropic point of magnetite does not shift down much with the increase of non-stoichiometry [*Kakol and Honig*, 1989; *Aragón*, 1992], previous identification of this anomaly with the isotropic point seems doubtful.

For the multidomain sample HM4L (Fig. 2) both M_{rs}/M_s ratio and coercive force are significantly higher after zero field cooling. This effect is most likely due to the fact that cooling in a strong magnetic field renders easy magnetization axes to be as close to the cooling

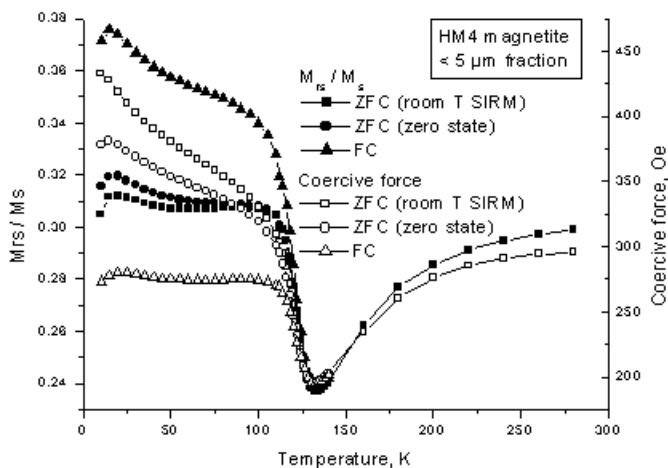**VF Reports**

Figure 1. *Variation of hysteresis parameters with temperature for the pseudo-single-domain sample HM4S.*
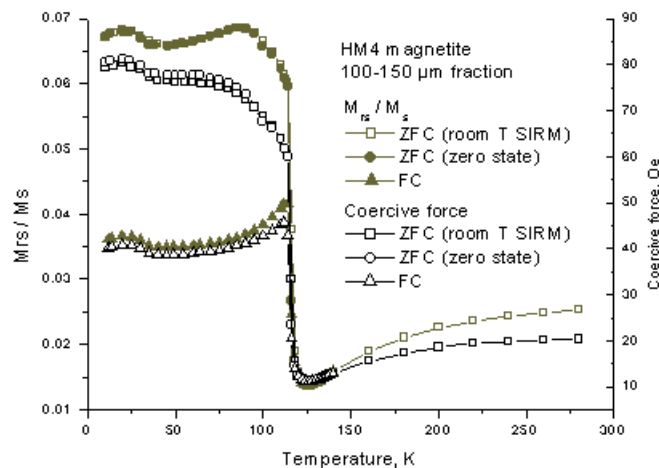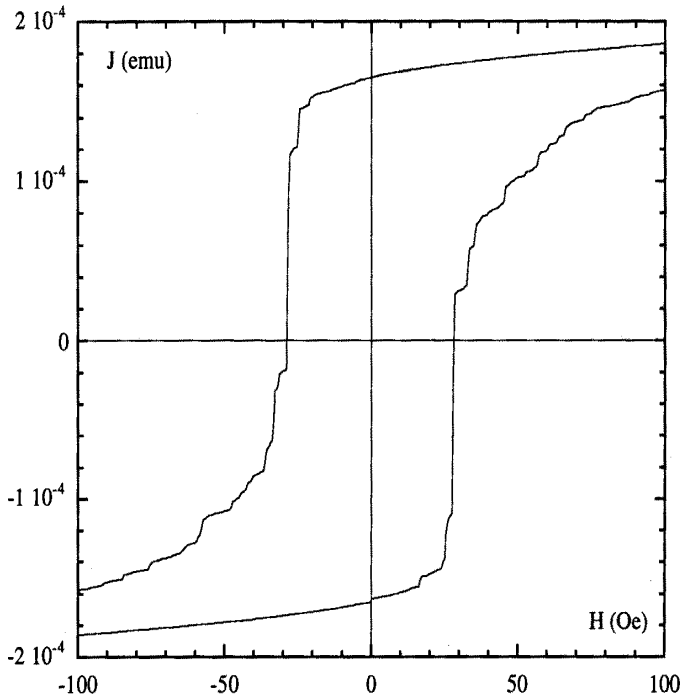

Figure 2. *Variation of hysteresis parameters with temperature for the multidomain sample HM4L.*

Barkhausen jumps (discontinuous changes in magnetization due to abrupt shifts of domain walls) visible in the hysteresis loop of a large hematite platelet. From "Barkhausen jumps in large versus small platelets of natural hematite," by Susan L Halgedahl, Journal of Geophysical Research, v. 103, p. 30,575-30589, 1998.

Current Abstracts

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 abstracts are culled from* INSPEC *(© Institution of Electrical Engineers),* Geophysical Abstracts in Press *(© American Geophysical Union), and* The Earth and Planetary Express *(© Elsevier Science Publishers, B.V.), after which they are subjected to Procrustean editing and condensation 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 5200 references, is available free of charge. Your contributions both to the list and to the Abstracts section of the* IRM *Quarterly are always welcome.*

Data Analysis

Borradaile, G. J., and Lagroix, F., 2000, **Magnetic characterization using a three-dimensional hysteresis projection, illustrated with a study of limestones**: *Geophysical Journal International, v. 141*, no. 1, p. 213-26.
Three hysteresis properties useful in characterizing the magnetic mineralogy of limestones (B_{cr}, B_c and the ratio M_r/M_s) have traditionally been plotted on a combination of 2D graphs. However magnetic discrimination and characterization of the limestones becomes much easier on a three-axis hysteresis projection. Using logarithmic scales, the regression surfaces through the data become almost planar and distinguish pelagic, shallow marine, shelf and remagnetized limestones on the basis of the slope and intercept of the associated regression surface.

Diagenesis and Magnetic Mineral Alteration

Moreau, M. G., and Ader, M., 2000, **Effects of diagenesis on magnetic mineralogy in a Jurassic claystone-limestone succession from the Paris Basin**: *Journal of Geophysical Research, v. 105*, no. B2, p. 2797-804.
The main carrier of magnetization is magnetite. Anhysteretic remanent magnetization (ARM) varies by a factor of 40, and the variations are linked to magnetite grain size. When carbonate content is high (>30%) and $\delta^{13}C \approx 0\%$, magnetite is characterized by small grain sizes. It appears that the oxidation of organic matter by sulfate reduction controls both $\delta^{13}C$ and magnetite grain size. H_2S produced during sulfate reduction causes partial dissolution of magnetite grains, with the finest magnetite grains being dissolved first.

Environmental Magnetism and Paleoclimate

Stockhausen, H., and Zolitschka, B., 1999, **Environmental changes since 13000 cal. BP reflected in magnetic and sedimentological properties of sediments from Lake Holzmaar (Germany)**: *Quaternary Science Reviews, v. 18*, no. 7, p. 913-25.
The concentration of magnetic minerals is very variable and zones exist where magnetic properties are dominated by paramagnetic minerals. Remanence is carried dominantly by titanomagnetite with grain sizes between a few microns and ≈25 µm. Initial magnetic susceptibility (κ) correlates positively with sediment accumulation rate and with non-arboreal pollen percentage. κ and organic carbon content show a negative correlation. The variations show a broad dependence on climatic conditions for times prior to significant human activities in the region, and two cooling events can be correlated with ice rafted debris events of the North Atlantic.

Extraterrestrial Magnetism

Christensen, P. R., Bandfield, J. L., Clark, R. N., Edgett, K. S., Hamilton, V. E., Hoefen, T., Kieffer, H. H., Kuzmin, R. O., Lane, M. D., Malin, M. C., Morris, R. V., Pearl, J. C., Pearson, R., Roush, T. L., Ruff, S. W., and Smith, M. D., 1999, **Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: evidence for near-surface water**: *Journal of Geophysical Research, v. 105*, no. E4, p. 9623-42.
The Thermal Emission Spectrometer (TES) instrument on the Mars Global Surveyor (MGS) mission has discovered a remarkable accumulation of crystalline hematite (α-Fe_2O_3) that covers an area with very sharp boundaries approximately 350 by 500 km in size. Particle diameters of hundreds of micrometers are permitted within the instrumental noise and natural variability of hematite spectra; particles <5-10 µm in diameter fail to match the TES spectra. Of the possible mechanisms for formation of coarse-grained, crystalline hematite, we prefer chemical precipitation from Fe-rich water on the basis of the probable association with sedimentary materials, large geographic size, distance from a regional heat source, and lack of evidence for extensive groundwater processes elsewhere on Mars.

Hargraves, R. B., Knudsen, J. M., Bertelsen, P., Goetz, W., Gunnlaugsson, H. P., Hviid, S. F., Madsen, M. B., and Olsen, M., 2000, **Magnetic enhancement on the surface of Mars?**: *Journal of Geophysical Research, v. 105*, no. E1, p. 1819-27.
The magnetic properties experiments on the Viking and Pathfinder missions indicate that the Martian soil and airborne dust are somewhat magnetic (average $\sigma_s = 4$ Am²kg⁻¹). Hematite is not sufficiently magnetic to yield the results obtained, and pyrogenetic titaniferous magnetite (TiMt) is probably not sufficiently abundant. We conclude that ferrous iron in the bedrock silicates must have been converted to maghemite (γ-Fe_2O_3) by some unknown oxidative mechanism; this "magnetic enhancement" should be incorporated in any process envisioned for the origin of Martian soil.

Instruments and Measurements

Hohne, R., Kleint, C. A., Pan, A. V., Krause, M. K., Ziese, M., and Esquinazi, P., 2000, **Torque magnetometry on thin magnetite films at low temperatures**: *Journal of Magnetism and Magnetic Materials, v. 211*, no. 1, p. 271-7.
Torque measurements at 130 K in the (110) plane allow us to evaluate the influence of shape and stress anisotropy in epitaxial Fe_3O_4 films grown by pulsed laser deposition on (001) MgO substrates. Field-cooled measurements performed at T=5 K show that the magnetic anisotropy is strongly influenced by the direction of the magnetic field applied above the Verwey temperature. In contrast to bulk magnetite we find smaller

abstracts

effective contributions of the magnetocrystal-line anisotropy. In zero-field-cooled films our measurements suggest a tendency to a preferential out-of-plane orientation of the magnetic easy axis, but the dominating shape anisotropy favours an in-plane orientation of the magnetization.

Magnetic Field Records and Paleointensity Methods

Valet, J. P., and Herrero-Bervera, E., 2000, **Paleointensity experiments using alternating field demagnetization**: *Earth and Planetary Science Letters, v. 177*, no. 1, p. 43-58.
After briefly reviewing current techniques for paleointensity, this paper investigates approaches relying on AF demagnetization. Measurements have been performed on at least eight samples from seven contemporary flows from Hawaii. AF techniques can be used with confidence provided that the whole spectrum of coercivities is involved in the field determination and exempt from any correction. This condition is necessary and sufficient to demonstrate the absence of alteration after heating. Because of the rapidity of such experiments, an approach combining AF and thermal experiments is certainly the best way to increase considerably the number of field determinations per lava flow and hence the overall quality of paleointensity studies.

Zanella, E., Gurioli, L., Chiari, G., Ciarallo, A., Cioni, R., De Carolis, E., and Lanza, R., 2000, **Archaeomagnetic results from mural paintings and pyroclastic rocks in Pompeii and Herculaneum**: *Physics of the Earth and Planetary Interiors, v. 118*, no. 3, p. 227-40.
The remanence associated with red pigments from murals at Pompeii has directions very close to those of the pyroclastic rocks from the Vesuvius AD 79 eruption. The remanence of the murals is shown, using X-ray analyses, to be carried by haematite. Murals in Thermae Stabianae, known to have been painted a few years before AD 79, yield an archaeomagnetic direction indistinguishable from that of a nearby kiln probably last used immediately prior to the eruption. The directions are also consistent with those of fine-grained pyroclastic rocks from the eruption. This study shows that murals can retain their remanent magnetization for centuries and demonstrates the viability of pictorial remanence as an archaeomagnetic tool.

Magnetic Microscopy and Spectroscopy

Bødker, F., Hansen, M. F., Koch, C. B., Lefmann, K., and Mørup, S., 2000, **Magnetic properties of hematite nanoparticles**: *Physical Review B, v. 61*, no. 10, p. 6826-38.
α- Fe_2O_3 particles with sizes of about 16 nm, studied by Mössbauer spectroscopy, magnetization measurements, and neutron diffraction, are weakly ferromagnetic at temperatures down to 5 K, with M_S only slightly higher than that of bulk hematite. Simultaneous fitting of Mössbauer spectra from 5 K to well above the blocking tempera-ture allowed estimation of the pre-exponential factor in Néel's expression for the relaxation

time, $\tau_0=(6\pm4)*10^{-11}$ s and the magnetic anisotropy energy barrier, $E_{bm}/k=590$ K.

Halgedahl, S. L., and Jun, Y., 2000, **Observed effects of mechanical grain-size reduction on the domain structure of pyrrhotite**: *Earth and Planetary Science Letters, v. 176*, no. 3, p. 457-67.
Bitter patterns observed on two mutually perpendicular surfaces of natural pyrrhotite grains, whose sizes were reduced mechanically in the laboratory, show that domain widths, the overall positions of surviving walls, and even many small-scale details in the shapes of curved walls were remarkably insensitive to thinning. These results lead to three conclusions. First, local energy minimum (LEM) domain states in pyrrhotite could be stable across a wide range of grain sizes and shapes. Second, defects that pin domain walls could inhibit LEM-LEM transitions by impeding the wall motions required for such transitions. Third, the defects which prevent walls from adjusting to thinning-induced changes in demagnetizing field appear to be densely and rather homogeneously distributed across a wall's surface, rather than being volumetrically rare.

Novak, P., Stepankova, H., Englich, J., Kohout, J., and Brabers, V. A. M., 2000, **NMR in magnetite below and around the Verwey transition**: *Physical Review B, v. 61*, no. 2, p. 1256-60.
NMR on ^{57}Fe nuclei was measured in two single crystals of magnetite between 4.2 and 135 K. All lines detected at 4.2 K also registered at temperatures up to the Verwey transition temperature T_V. The spectra are compatible with the space group Cc, which predicts 8 and 16 lines for iron on tetrahedral (A) and octahedral (B) sites, respectively. One of the Fe(A) lines is doubly degenerate for all $T<T_V$, which restricts the possible models of the Fe^{2+} and Fe^{3+} ordering on the B sites. Above T_V no remnant of the low-temperature spectrum was detected.

Van Lierop, J., and Ryan, D. H., 2000, **Mössbauer spectra of ferrofluids characterized using a many state relaxation model for superparamagnets**: *Journal of Applied Physics, v. 87*, no. 9, pt.1, p. 6277-9.
Using a many-state relaxation formalism, combined with an accurate expression for the relaxation time of single-domain ferromagnetic particles and a log-normal size distribution, we are able to fit Mössbauer spectra of two Fe_3O_4 ferrofluids, from 12 K, where a pure hyperfine field distribution is present, to 180 K, where a single broad line occurs due to high relaxation rates. Fits to the ferrofluid with a mean particle size of 4.5 nm yield an anisotropy energy (K) of $3.0\pm0.1*10^4$ J/m³ with the onset of magnetic relaxation at 30 ± 5 K while data for a mean particle size of 6.0 nm give $K=2.4\pm0.2*10^4$ J/m³ with magnetic relaxation starting at 55 ± 5 K. These blocking temperatures agree with those extrapolated from frequency dependent χ_{ac} data.

Magnetization Processes

Dunlop, D. J., and Ozdemir, I., 1999, **Effect of grain size and domain state on thermal demagnetization tails**: *Geophysical Research Letters, v. 27*, no. 9, p. 1311-14.
Thermal demagnetization of VRM and pTRM of 20- and 135- µm natural magnetites reveals a broad spectrum $f(T_{UB})$ of unblocking temperatures T_{UB}, both > and < T_B, the blocking temperature. In contrast, 0.04-µm SD grains demagnetize sharply at $T_{UB} \approx T_B$. High- and low-T_{UB} tails of $f(T_{UB})$ were wider for 135-µm MD grains than for 20-µm PSD grains. 10-mT alternating-field demagnetization rendered the VRM of the 20-µm magnetite more SD-like in subsequent thermal cleaning, selectively erasing both low- and high-T_{UB} tails of $f(T_{UB})$. Primary and secondary remanences are then cleanly separated, and non-linear Thellier paleointensity determination becomes linear. Because $(T_{UB})_{av}=T_B$ for PSD and MD as well as SD grains, the Pullaiah et al. (1975) paleothermometry method will work if $(T_{UB})_{av}$ values are used instead of $(T_{UB})_{max}$ values.

Dunlop, D. J., Ozdemir, O., Clark, D. A., and Schmidt, P. W., 2000, **Time-temperature relations for the remagnetization of pyrrhotite (Fe_7S_8) and their use in estimating paleotemperatures**: *Earth and Planetary Science Letters, v. 176*, no. 1, p. 107-16.
Time-temperature relations are well known for magnetite but are reported here for the first time for pyrrhotite. Data for each mineral separately yield independent estimates of paleotemperature if geologically reasonable estimates of heating time can be made. Paleotemperature can be estimated without geological input if data for both minerals are combined. Together with the age of remagnetization, determined from the paleomagnetic pole of the NRM overprint, these paleotemperature estimates can be used to infer the history of heating and uplift following burial. As a test case, the authors examine thermally acquired NRM overprints carried by pyrrhotite and magnetite in the Milton Monzonite of southeastern Australia.

Goguitchaichvili, A., and Prevot, M., 2000, **Magnetism of oriented single crystals of hemoilmenite with self-reversed thermoremanent magnetiza-tion**: *Journal of Geophysical Research, v. 105*, no. B2, p. 2761-80.
Ten large, single crystals of hemoilmenite ($yFeTiO_3(1-y)Fe_2O_3$) with y close to 0.54 were extracted from the self-reversed Pinatubo dacitic pumice erupted in 1991 and oriented with respect to the crystallographic c axis, which is the hardest magnetization axis. The directions of NRM, SIRM, and TRM all lie in the basal plane, regardless of the direction of the applied field. The pTRMs are approxi-mately reversed; that is, their direction is always more than 90° away from the applied field direction and most often close to 180°. In fact, pTRM directions are discretely distributed along three directions in the basal plane which are 60° away from each other. This distribution indicates that the magnetic anisotropy is of magnetocrystalline origin. The authors propose a self-reversal model based on negative exchange interactions in which the self-reversed TRM is carried by cation-ordered (ferrimagnetic) SD-like regions

dispersed within a cation-disordered (antiferromagnetic with weak ferromagnetism) MD matrix carrying a weak, normal TRM.

Jianbiao, D., Jian-Qing, W., Sangregorio, C., Jiye, F., Carpenter, E., and Tang, J., 2000, **Magnetic coupling induced increase in the blocking temperature of γ-Fe$_2$O$_3$ nanoparticles**: *Journal of Applied Physics, v. 87*, no. 10, p. 7397-9.
The magnetic properties of surfactant coated γ - Fe$_2$O$_3$ nanoparticles vary with pressure. With increasing pressure, the sample volume decreases, density increases, and a 55% density change has been achieved. The blocking temperature is increased from 50 to 80 K. Blocking temperature increases linearly with density, which is understood in terms of increased magnetic interactions between neighboring nanoparticles, which is due to the reduced average interparticle distance by the applied pressure.

Kletetschka, G., Wasilewski, P. J., and Taylor, P. T., 2000, **Unique thermoremanent magnetization of multidomain sized hematite: implications for magnetic anomalies**: *Earth and Planetary Science Letters, v. 176*, no. 3, p. 469-79.
In contrast to magnetite and titanomagnetite, hematite exhibits inverse grain size dependence, with MD hematite acquiring a relatively intense TRM in the geomagnetic field, comparable to submicrometer sized magnetite and only an order of magnitude less than SD magnetite. Consequently MD hematite remanence may be of significance as a source of magnetic anomalies at all scales. MD hematite is the only magnetic mineral having a TRM/SIRM ratio >>0.1 for TRM acquisition in the geomagnetic field. The differences in TRM behavior of magnetite and MD hematite are due to two factors. The first is the lesser influence of demagnetizing energy with respect to wall pinning energy, at temperatures almost up to the Curie temperature for hematite. The second is the greater importance of the magnetostatic energy in the applied field, which for hematite dominates the total energy at high temperatures.

Modeling and Theory

Gehring, G. A., 1999, **Conductivity and magnetism of magnetic oxides**: *Acta Physica Polonica A, v. 97*, no. 1, p. 175-84.
In a stoichiometric oxide the energy for magnetic ordering is due to superexchange. This depends on the virtual transfer of a d electron from the transition ion to the neighbouring oxygen. When the oxide is p-doped there are compensating holes on the oxygen or the transition ion becomes mixed valent. The oxide may then conduct. The same transfer integral enters both the expression for the antiferromagnetic superexchange and the band width of the mobile carriers. Thus materials with a large antiferromagnetic exchange energy will be expected to have a relatively wide conduction band in the doped state and hence to have a high conductivity. In this paper the difference is explored between the materials in which there is true antiferromagnetism and those

which are ferrimagnetic. In the antiferromagnets the carriers must destroy the magnetic order as they move. This behaviour is well known from the cuprates. In ferrimagnets the carriers may be able to move entirely on one sublattice. This occurs in Fe$_3$O$_4$ and probably in the doped garnets. In the case where motion is on one sublattice then doping does not destroy the magnetism and there is a relatively small magnetoresistance. An interesting feature is that unlike the cuprates the ferrimagnets do not become good metals at any doping but exhibit hopping conductivity.

Synthesis and Properties of Magnetic Minerals

France, D. E., and Oldfield, F., 2000, **Identifying goethite and hematite from rock magnetic measurements of soils and sediments**: *Journal of Geophysical Research, v. 105*, no. B2, p. 2781-95.
A sequence of experiments involving the acquisition of IRM in high (>2 T) fields, followed by orthogonal demagnetization and the cooling and heating of remanent magnetization (Mr) over the temperature range -196º C to +680º C, improves the basis for identifying the imperfect antiferromagnetic minerals hematite and goethite. Goethite can be unambiguously identified, often accompanied by hematite, in the majority of the samples studied. The rock magnetic tests are a much more sensitive basis for recognizing the presence of goethite in natural samples than are XRD analyses. The results suggest that goethite's contribution to the rock magnetic properties of soil and sediment samples may often have been underestimated.

Petrovsky, E., Alcala, M. D., Criado, J. M., Grygar, T., Kapicka, A., and Subrt, J., 2000, **Magnetic properties of magnetite prepared by ball-milling of hematite with iron**: *Journal of Magnetism and Magnetic Materials, v. 210*, no. 1, p. 257-73.
Hysteresis loops, isothermal remanence acquisition and temperature dependence of magnetic susceptibility are used to characterise magnetite powders prepared by ball-milling of stoichiometric mixture of hematite and iron in an inert atmosphere. Ball-milling of during periods ranging from 30 min up to almost 5 h yields magnetite which exhibits high magnetic hardness, characterised by coercive force three times higher than that typical for single-domain natural magnetites. However, the magnetite produced is unstable upon heating in air, reoxidising almost completely to hematite. Heating in an argon atmosphere causes enhancement of typical magnetic parameters, but decreases the magnetic hardness.

Tejada, J., Xixiang, Z., Kroll, E., Bohigas, X., and Ziolo, R. F., 2000, **Solid containing rotationally free nanocrystalline γ - Fe$_2$O$_3$: Material for a nanoscale magnetic compass?**: *Journal of Applied Physics, v. 87*, no. 11, p. 8008-12.
A nanocomposite material, containing 5-10 nm γ - Fe$_2$O$_3$ crystals that are free to rotate in a solid methanol polymer matrix, was prepared by freezing a ferrofluid and subjecting it to a magnetic field applied in alternate directions to

anneal the matrix. Before the field treatment, the solid displays magnetic behavior characteristic of an ordinary nanoscopic magnetic material. It is superparamagnetic above the blocking temperature (160 K) and hysteretic below, showing magnetic remanence and coercivity. After the field treatment to anneal the matrix, the same solid shows only Curie-Weiss behavior above and below the blocking temperature over the temperature range from 4.2 to 200 K and in response to applied magnetic fields as low as 1.59 kA/m. The data are consistent with a solid containing rotationally free, nanoscopic magnets encased in cavities of very small dimensions. The free rotation of the particles precludes the observation of magnetic relaxation phenomena that are characteristic of magnetic solids and ferrofluids. The present solid portends a class of magnetic materials with very little or no electrical and magnetic loss.

Zergenyi, R. S., Hirt, A. M., Zimmermann, S., Dobson, J. P., and Lowrie, W., 1999, **Low-temperature magnetic behavior of ferrihydrite**: *Journal of Geophysical Research, v. 105*, no. B4, p. 8297-303.
Two samples of six-line ferrihydrite (5Fe$_2$O$_3$·9H$_2$O) were precipitated from an Fe(III) solution. Scanning electron microscopy indicates that the grains have good crystallinity and variable grain size (<0.5 to 100 μm). Mössbauer spectra show a broad asymmetric doublet without split components between 150 K and 250 K. Hyperfine magnetic splitting can be observed at 130 K, and a sextet spectrum is apparent below 100 K. The in-phase mass susceptibility χ' has a value of $1.0*10^{-6}$ m^3 kg^{-1} at room temperature. At low temperatures, χ' is frequency-dependent, and increases with temperature from 10 K to a maximum at 90 K, decreasing smoothly at higher temperatures. The quadrature susceptibility peaks at 65 K. These characteristics suggest the presence of superparamagnetic grain sizes below 120 K. The temperature of the in-phase susceptibility peak increases with frequency from 86 K at 40 Hz to 94 K at 4000 Hz. Hysteresis loops, coercivity, and isothermal remanence at low temperature agree with the susceptibility measurements and suggest that ferrihydrite is antiferromagnetic with a parasitic ferromagnetic moment and a Néel temperature around 120 K.

field direction as possible. It is worth noting however that ZFC and FC states display the same temperature dependence of hysteresis parameters only below ~ 60 K. At higher temperatures, but below the Verwey transition itself, the ZFC curves decrease quite significantly, and the FC curves show a slight increase. This may indicate that from the point of view of magnetism, low-temperature structure formed on cooling through Verwey transition is in fact fully stable only well below the transition temperature. At the same time, the transition itself, as shown in hysteresis properties, is quite sharp and extends over 3-4 K at the most. Above the transition, ZFC and FC curves of both M_{rs}/M_s and H_c converge perfectly. Minima of M_{rs}/M_s and H_c occur at 124-126 K, again suggesting that they may not be directly related to the isotropic point.

I am particularly grateful to Jim Marvin and Peat Solheid who helped me run the instrument for the whole ten days of my stay, and to the IRM staff for their hospitality.

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Magnetic Properties at Low Temperature of Ferric Hydroxides

The main objective of my visit to the IRM was to examine the magnetic properties of lepidocrocite and poorly crystalline (2-line) and well-crystalline (6-line) ferrihydrite. These minerals are common in modern soils, and are generally identified with X ray diffraction (XRD) or spectroscopic techniques. A short summary of the results from the lepidocrocite and 2-line ferrihydrite are given below.

There is some controversy about the temperature at which lepidocrocite orders magnetically. Extremely well-crystalline samples order between 73 and 77 K (Johnson, 1969; Murad and Schwertmann, 1984); less well-crystalline phases are reported to have a lower Néel temperature. Mössbauer spectra of several lepidocrocites were examined as a function of temperature by DeGrave et al. (1986), and all underwent magnetic ordering between 50 and 60 K despite their varying degree of crystallinity.

Three sets of experiments were made with a synthetic, relatively well-crystalline sample of lepidocrocite. XRD and the Mössbauer spectrum suggest a pure sample. The in-phase and quadrature components of susceptibility were measured on the Lakeshore Susceptometer at five frequencies between 4 and 4000 Hz. Starting at 300 K, the in-phase susceptibility increases with decreasing temperature, reaching a peak value at 52 K, before decreasing at lower temperatures. No frequency dependence is observed, except near the ordering temperature. The quadrature component is small, ex-
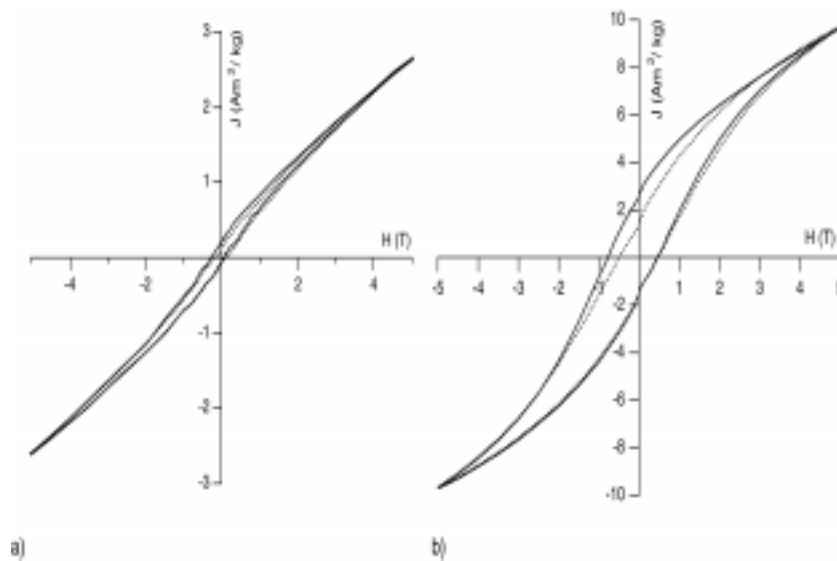

Figure 1. Hysteresis loops at 5K; solid line is FC loop and dashed line is ZFC loop; (a) lepidocrocite, and (b) 2-line ferrihydrite.

cept near the ordering temperature. As opposed to Murad and Schwertmann (1984), this result suggests that there is not a large temperature range over which lepidocrocite is superparamagnetic. A hysteresis loop was measured on the MPMS at 300 K and at 5 K after cooling in a field (FC) or zero field (ZFC). The magnetization at 300 K changes linearly as a function of the applied field, which indicates a pure paramagnetic sample. The ZFC curve displays a hysteresis symmetrical about the origin, and saturation is not reached at 5 T (Fig. 1a). Although lepidocrocite is antiferromagnetic, a defect moment appears to be responsible for the remanence below the Néel temperature. The FC curve is similar to the ZFC curve, except that it is shifted by 76 mT along the field axis (Fig. 1b). We interpret this shift as reflecting exchange coupling between antiferromagnetic and ferrimagnetic alignment within the sample. This interpretation is supported by the fact that the inverse susceptibility above the Néel temperature is not linear, but is comprised of two linear segments. The hysteresis loops of the 6-line ferrihydrite at 5 K behave similarly.

The same experiments were performed on three samples of 2-line ferrihydrite. The in-phase susceptibility is antiferromagnetic and has a peak at

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Barkhausen earned his doctorate in Göttingen in 1907, and four years later became a professor of electrical engineering in Dresden. In 1919, Barkhausen discovered that the quasi-continuous increase in magnetization of ferromagnetic materials in smoothly-increasing applied fields actually consists of discrete, discontinuous jumps. These Barkhausen jumps represent rapid shifts in domain walls that are unpinned by the external field and are forced through intermediate higher-energy positions before snapping into new local energy minimum locations. The Barkhausen effect is used to characterise stress-induced microstructure and fatigue in steel and other ferromagnetic alloys.

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approximately 60 K. It does not show frequency dependence, except where the quadrature component increases sharply at the ordering temperature. The room temperature magnetization curve displays no hysteresis and is nearly linear. The ZFC magnetization curve displays hysteresis at 5 K and is symmetrical about the origin. It is not saturated in a 5 T field (Fig. 1b). The FC magnetization curve is expanded in the field direction.

The equal magnetization values in the highest measured field suggest that this is not a minor loop, but reflects an exchange interaction.

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Magnetic mineralogy and grain size distribution of iron oxides in basaltic samples before and after CRM experiments

During my stay at the IRM I completed rockmagnetic experiments on samples I used for CRM experiments. The CRM experiments were carried out at Montpellier/France before I came to Minneapolis. A laboratory CRM or TCRM (depending on the type of experiment) was acquired in volcanic rocks as a result of oxidation of titanomagnetite at moderate temperature. After the (T)CRM experiment the Thellier method was used to determine the apparent paleointensity on those samples.

The concern was that the so-called 'high-temperature oxidation' in Nature might continue well below the Curie point of magnetite, as suggested by Grommé et al. (1969). If this is the case, the primary remanence is not a TRM but a TCRM. Consequently the paleointensity estimates obtained from Thellier experiments on titanomagnetite oxidized at 'high' temperature could be largely in error.

We were able to create a CRM (at a constant temperature of oxidation) or TCRM (at a very slowly decreasing temperature of oxidation) and to monitor the growth and characteristics of CRM for various oxidation times as long as 120 hours at temperatures between 400 and 500°C. Finally paleointensity measurements (q factor between 20 to 50) were obtained using temperature steps as small as 4°C with pTRM checks between each of them.

We demonstrated that the apparent paleointensity from CRM is lower than the actual magnetizing field B_{ox} and varies largely with the oxidation temperature (from $0.4B_{ox}$ at 400°C to $0.9B_{ox}$ at 500°C). If oxidation occurs during cooling (0.1 °C/min) between 560 and 400°C, the TCRM so acquired provides an almost correct apparent paleointensity ($1.1B_{ox}$). This suggests that the oxidation occurring during the initial flow cooling does not imply large errors in the paleointensity estimate even if oxidation continues well below 560°C. Some bias due to the continuation of oxidation during the paleointensity heatings may be the reason for the 10% overestimate of B_{ox}. The results also beautifully document the fact that chemical alteration during paleointensity experiments affects not only pTRMs but also the remanence left. This means that the usual interpretation of pTRM checks can be totally misleading.

The samples which were used for the (T)CRM experiments were basaltic samples with titanomagnetite of very high titanium content ($T_c \cong 40$-80 °C and therefore ~TM70). The chemical composition is estimated from low field $\kappa(T)$ Experiments. We suppose that during the heating process we are producing a crystallization remanence with exsolution of a low titanium iron oxide (close to magnetite) and a high titanium iron oxide (close to ulvöspinel or ilmenite). Hysteresis parameters show that the newly formed magnetic mineral is much smaller than the original titanomagnetite. Susceptibility measurements at high temperatures on the oxidized samples show that a mineral close to magnetite is formed. But what happens to the titanium? Is the other component really Ulvöspinel or Ilmenite or something close? Optical microscopy and SEM investigations do not show any change of the grains, although the samples were heated 32 hours at 400 °C and a change in magnetic parameters is visible by looking at the CRM. It might be that the resolution is not high enough to detect the exsolution lamella. At the IRM I performed low-temperature and high-temperature experiments (in both cases low field and high field) and tried to answer the question whether Ilmenite or Ulvöspinel is present in the oxidized samples. Low-temperature experiments were performed using the Lakeshore susceptometer (different fields and different frequencies) and the MPMS. Néel Points for Ilmenite or Ulvöspinel and the Verwey transition of magnetite could not be identified. Nevertheless, the high temperature experiments (Kappabridge and µVSM) show again that a magnetic mineral close to magnetite was formed.

All the experiments on the Lakeshore susceptometer, MPMS, Kappabridge and µVSM were done automatically so I had additional time to measure some other samples, which I brought to the IRM. These were samples I am using currently for absolute paleointensity determinations from Inner Mongolia/China. The experiments have been more or less standard experiments like measuring hysteresis loops, thermomagnetic curves in low and high fields or low temperature IRMs, and were performed to determine the carriers of remanent magnetization in the samples.

Finally I would like to thank everybody at the IRM for making the experiments possible, for fixing instruments (Jim Marvin postponed his vacation to repair a broken pump at the Lakeshore) and for the time they spent discussing the difficult results I received for my CRM samples.

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The *IRM* staff consists of **Subir Banerjee**, Professor/Director; **Bruce Moskowitz**, Associate Professor/ Associate Director; **Jim Marvin**, Senior Scientist; **Mike Jackson**, Senior Scientist and Facility Manager, and **Peat Solheid**, Scientist.

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