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http://hotel.telemuseum.se/vaxholmsshembygd/ytterby_gruva.htm



Ytterby Mine, near Stockholm, where the rare earths (oxides of the lanthanide elements) were first discovered.

Wherefore Gadolinium?

Magnetism of the Rare Earths

Mike Jackson
IRM

In 1794, the Finnish chemist Johan Gadolin, investigating an unusual mineral specimen from Sweden, discovered what he believed was a new element. Although he could not have imagined it, his discovery provided the basis for the best susceptometer calibration standards available today, as well as the strongest permanent magnets. But that is getting ahead of the story.

What's in a Name?

Chemists of classical Greece defined an *earth* as a substance that could not be broken down by the heating methods then available, and that classification scheme was still in use in the 18th

century. (Early in the 19th century Sir Humphrey Davy showed that the earths were not in fact elements, but oxides of metallic elements.) Gadolin classified his new "element" as an earth, and named it Ytterbia, for the village of Ytterby where the sample was discovered, near Stockholm. The same mineral specimen yielded a second new earth in 1803, named Ceria after the asteroid Ceres, which had been discovered in 1801. (Ceres, you may recall, provided Gauss with one of his early mathematical/scientific triumphs, when he applied his method of least squares to establish accurate orbital parameters from a very limited set of observations, and thereby enabled a quick re-discovery of the asteroid after its initial disappearance behind the sun.)

Subsequent work showed that Ytterbia and Ceria each actually contained several different *rare earths*. In the mid 1800s Carl-Gustav Mosander isolated two new elements in Ytterbium, to which he gave the derivative names Terbium and Erbium, and two others in

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Cerium, which he named Didymium (from the Greek for 'twin') and Lanthanum (from the Greek *lanthanein*, 'to lie hidden'). These in turn were further resolved into their actual elemental constituents with the advent of absorption and emission spectroscopy around 1860. Gadolin's Ytterbia was ultimately found to contain most of the heavy rare earth elements (REEs): Holmium (#67, named for Stockholm), Thulium (#69, for Thule, an early name for Scandinavia), Dysprosium (#66, from the Greek *dysprositos*, 'hard to get at'), Lutetium (#71, for Lutetia or Lutece, the ancient name for Paris, where a number of these elements were first isolated), and of course Gadolinium (#64) and Ytterbium (#70). From Mosander's Didymium came the light REEs Samarium (#62, for the mineral Samarskite, named in turn for a Russian mining official called Samarski), Praseodymium (#59, 'green twin'), Neodymium (#60, 'new twin'), and Europium (#63).

Rare earths are not as rare as originally thought. The Earth's crust contains more cerium (the most abundant REE) than tin, cobalt or beryllium; lanthanum and neodymium are more than three times as abundant as lead. The least abundant of the stable rare earth elements are thulium and lutetium, but they are still 100 times more abundant than gold. Promethium (#61, for Prometheus, who stole fire from the gods) was not isolated until the 20th century; it has a half-life of less than 20 years for all known isotopes, and essentially does not occur in nature (at least not in the earth's crust; it has been identified in the spectra of stars such as HR465 in Andromeda.)

Ferromagnetism in Rare-Earth Metals

Ferromagnetism is a relatively rare property among the elements, occurring only in the transition metals Fe, Ni, and Co, and in the lanthanides (REEs). Neutron-diffraction studies in the 1960's showed that magnetic ordering in the rare earths is generally far more interesting (i.e., complicated) than the simple collinear ferromagnetism of substances like iron, in which all the atomic magnetic moments are resolutely and monotonously parallel. The REEs collectively exhibit an astonishing bestiary of magnetically-ordered states, and even individual REEs undergo chameleon-like transformations, ordering in a variety of

REEs

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Titanomaghemite in ocean floor basalt: low-temperature / high field hysteresis loops

This project is part of my PhD studies under the supervision of Prof. N. Petersen. The objective was to determine saturation magnetization M_s at 0 K and the mechanism controlling magnetic stability (or coercivity H_c) of natural titanomaghemites in ocean basalts.

In total, 13 samples of ocean basalt of different age and titanomaghemite oxidation state were studied (3 samples with low, 7 samples with medium, and 3 samples with high oxidation state titanomaghemite). Magnetic hysteresis loops were measured at temperatures ranging from 300 K to 10 K. Additionally, thermomagnetic curves at different magnetic fields were measured in this temperature range. Magnetic Force Microscope (MFM) techniques were used to image magnetic structures in titanomaghemite grains of two selected samples.

The samples were selected from a set of 80 samples I had studied previously in Munich that show high M_s and low H_c values for 0-8 Ma (weakly oxidized) and 40 to 120 Ma (highly oxidized) old basalts, but low M_s and high H_c for 8 – 40 Ma old or medium oxidized ocean basalts. Low M_s values for the latter samples can be explained by a model with differential oxidation of Fe in the octahedral and tetrahedral sites of the spinel lattice. Determination of M_s at 0 K allows testing of this hypothesis, as the number of Fe cations in octahedral sites minus the number in tetrahedral sites can then directly be calculated, if the content of titanomaghemite in the samples is determined microscopically. The high magnetic stability for these samples can be explained by internal stress arising from the oxidation process. It is an interesting observation that these samples often show ratios of saturation remanence to saturation magnetization M_{rs}/M_s exceeding 0.5, apparently ruling out uniaxial anisotropy and (magnetostrictive) stress control. However, M_{rs}/M_s can be erroneously overestimated, if the maximum field applied does not saturate the sample.

For all samples, hysteresis loops between 10 K and 450 K were measured with the μ -VSM (maximum field 1.7 T). The 7 samples (8 – 40 Ma old) with high coercivity were also measured with the MPMS between 300 K and 10 K. The maximum field of this instrument (5 T)

was sufficient to saturate the samples, and M_{rs}/M_s ratios below the critical threshold of 0.5 were obtained at room temperature. Thus, it can be concluded that M_{rs}/M_s ratios above 0.5 are an artifact, and that ratios for these ocean basalts are not in contradiction to uniaxial anisotropy and stress control of coercivity. Hysteresis parameters for 16 Ma old sample 572D-34-1(99-100) (ODP code) determined at different temperatures are representative for medium oxidized titanomaghemite (see figure).

For the medium oxidized samples, M_s shows a clear decrease with lower temperatures, while H_c increases. Control of magnetic stability by (uniaxial) shape anisotropy can therefore be ruled out, as this would imply a linear relationship between H_c and M_s . On cooling, most of the samples reach M_{rs}/M_s ratios above 0.5 at temperatures between 250 K and 150 K. This might be interpreted as a change from stress control to control by magnetocrystalline anisotropy.

Two of the samples showed not only a decrease of SIRM applied at 300 K with cooling to 10 K in zero-field, but also a self-reversal of the remanence at 80 K. On warming the sample up to 300 K again, this behaviour was perfectly reversible.

The MFM observations of a slightly oxidized and a medium oxidized sample suggest stress-related magnetic structures. It remains unclear, if this observation is due to stress introduced in the polishing procedure or reflects the natural magnetic state of the grains.

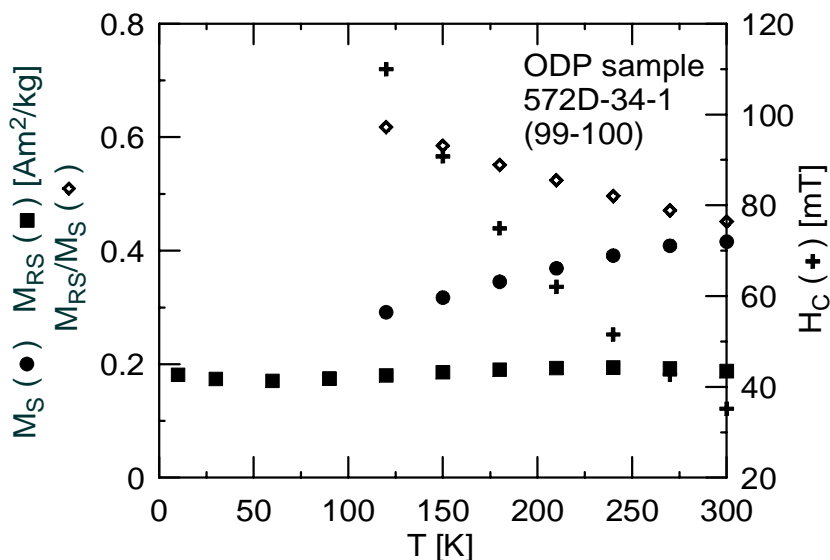
Using the MPMS for hysteresis measurements is rather uncommon and therefore I want to concentrate on the results of these measurements. The unique advantage of these instruments are the high magnetic fields which can be applied. For best results, the instrument had to be operated in “no overshoot mode” rather than in the much faster “hysteresis mode”. Although basalts give a strong magnetic signal, and the MPMS is a very sensitive instrument, good results were obtained only for samples >5 mg. Samples >20 mg were excellent and samples <2 mg showed considerable problems in high magnetic fields: the results were too high, the fit parameter for the SQUID response curve decreased significantly and the maximum in the SQUID response curve was shifted significantly away from the sample position. Both samples which initially showed that problem were remeasured successfully with bigger rock chips.

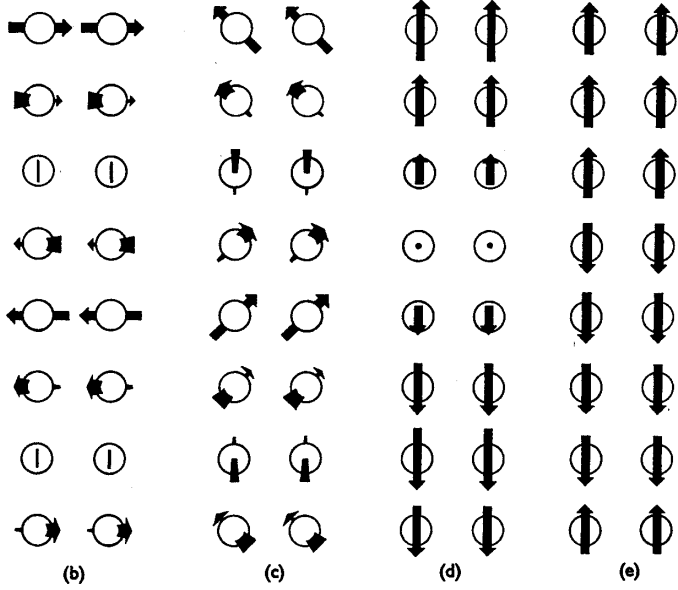
Another interesting aspect of hysteresis curves with high fields at low temperatures is the non-linearity between paramagnetism and magnetic field. Linearity is only a good assumption for $H/T \ll 1$ T/K. My MPMS hysteresis curves to 5 T below 100 K are significantly affected. The non-linearity can be accounted for by using a Brillouin function rather than a linear fit for paramagnetism. Three points have to be taken into account:

- to measure enough points above the saturation of the ferrimagnetic

VF Reports

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Various forms of ferromagnetic ordering found in lanthanide metals: helical antiferromagnetism (b); helical or conical ferromagnetism (c); modulated antiferromagnetism (d); and 4-3-4-3 ferromagnetism. From Magnetism in Solids, by D. H. Martin, Iliffe Books Ltd., London, 1967.

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.

Anisotropy

Borradaile, G. J., and Lagroix, F., 2000, **Thermal enhancement of magnetic fabrics in high grade gneisses:** *Geophysical Research Letters*, v. 27, no. 16, p. 2413-16.

AMS and AARM ellipsoids are non-coaxial in the Kapuskasing Zone granulites. AARM is due to the preferred orientation of magnetite which mostly postdates the silicate fabric. The AMS combines contributions of magnetite and the silicates. Heating does not increase the bulk susceptibility, but it improves the clustering of both AMS and AARM axes. The orientation-distribution of AARM is most enhanced and therefore heating emphasizes the magnetite subfabric. Heating does not clarify the interpretation of the silicate fabric in this study, but it does change the samples' AMS in such a way as to reveal the magnetite subfabric which can otherwise be detected only by more tedious AARM measurements.

de Wall, H., 2000, **The field-dependence of AC susceptibility in titanomagnetites: implications for the anisotropy of magnetic susceptibility:** *Geophysical Research Letters*, v. 27, no. 16, p. 2409-11.

Titanomagnetite-bearing rocks from the Riedheim dike (SW-Germany) have varying composition (T_c of 128 to 440° C) and strong ac field-dependence of susceptibility (in ac fields of 30 and 300 A/m). The parameter $\chi_{Hd}[\%] = [(\chi_{300A/m} - \chi_{30A/m}) / \chi_{300A/m}] * 100$ ranges from 4.1 to 26.5, and $\log \chi_{Hd}$ varies linearly with T_c . The anisotropy factor P' of AMS is significantly enhanced in the higher ac field, while the shape factor (T) appears to be insensitive to the field amplitude. The principal axes of the AMS-ellipsoids remain unchanged in orientation.

Hrouda, F., Hanak, J., and Terzijski, I., 2000, **The magnetic and pore fabrics of extruded and pressed ceramic models:** *Geophysical Journal International*, v. 142, no. 3, p. 941-7.

Ceramics were used as a model to investigate the pore fabric originated during ductile deformation. The magnetic anisotropy was used to measure the pore fabric after pore saturation by a ferromagnetic fluid. The ductile deformation of the ceramics was investigated by measuring the magnetic anisotropy of dry specimens. The character and symmetry of the pore fabric are compatible with those of the deformations forming the fabric of the ceramics: in the linearly extruded ceramics, the pore fabric is dominantly prolate, while in the pressed ceramics it is dominantly oblate.

Carriers and Origins of NRM

Bardot, L., and McClelland, E., 2000, **The reliability of emplacement temperature estimates using palaeomagnetic methods: a case study from Santorini, Greece:** *Geophysical Journal International*, v. 143, no. 1, p. 39-51.

Palaeointensity experiments were carried out to assess the origin (pTRM, CRM, or a combination of both) of the low- T_b component in 24 pyroclastic samples, seven of which passed stringent reliability tests. These values demonstrated, for six of the samples, that the low- T_b component was of thermal origin and therefore could be used to estimate of emplacement temperature (T_e). In the other 17 samples, valuable information was gained about the characteristics of the magnetic alteration that occurred during the palaeointensity experiments, allowing assessment of the reliability of T_e estimates in these cases.

McEnroe, S. A., and Brown, L. L., 2000, **Palaeomagnetism, rock magnetism and geochemistry of Jurassic dykes and correlative redbeds, Massachusetts, USA:** *Geophysical Journal International*, v. 143, no. 1, p. 22-38. The intrusions fall into three chemical types: high TiO_2 quartz-normative (Holden); low TiO_2 quartz-normative (Ware); and high Fe_2O_3 quartz-normative (Pelham-Loudville). The characteristic magnetizations unblock between 550° C and 580° C, with Curie temperatures in a discrete interval between 560° C and 580° C. The dominant remanence in the diabases is carried by oxidation-exsolved titanomagnetite occurring as euhedral grains, as fine needles or dust in the matrix, as devitrified glass, and as fine magnetite-ilmenite-silicate symplectite.

Otofujii, Y., Uno, K., Higashi, T., Ichikawa, T., Ueno, T., Mishima, T., and Matsuda, T., 2000, **Secondary remanent magnetization carried by magnetite inclusions in silicates: a comparative study of unremagnetized and remagnetized granites:** *Earth and Planetary Science Letters*, v. 180, no. 3, p. 271-85.

In Cretaceous granitic rocks of northeast Japan, the NRM of remagnetized rocks is stronger (0.3-1.7 A/m) than that of unremagnetized rocks (<0.5 A/m). Hysteresis properties indicate that the unremagnetized rocks contain MD grains whereas the remagnetized rocks have a mixture of MD and SD grains. Optical examination shows common titanomagnetite grains >30 μm with ilmenite lamellae in both sets of rocks; the remagnetized ones also contain numerous pure-magnetite grains <10 μm . SEM/EDA studies show that these fine grains occur as discrete particles within actinolitized parts of primary hornblende, suggesting formation from Fe ions released during the alteration.

Warnock, A. C., Kodama, K. P., and Zeitler, P. K., 2000, **Using thermochronometry and low-temperature demagnetization to accurately date Precambrian paleomagnetic poles:** *Journal of Geophysical Research*, v. 105, no. B8, p. 19435-53.

A new study of the Glamorgan Gabbro using LTD and modern thermochronometric methods shows that the HbA component is a primary TRM carried by SD magnetite. The new pole

position is not significantly different from the published pole, but the cooling history suggests a 1015 ± 15 Ma magnetization age, older than previously thought (980 Ma), producing a better fit in Rodinia supercontinent reconstructions. The refined HbB pole (29.9° N, 169.9° E) is carried by MD magnetite and pyrrhotite. The new age for HbB is 220 Myr younger than the previous estimate, raising questions concerning the ages of similar poles from the Grenville Province.

Zwing, A., and Bachtadse, V., 2000, **Paleoposition of the northern margin of Armorica in Late Devonian times: paleomagnetic and rock magnetic results from the Frankenstein Intrusive Complex (Mid-German Crystalline Rise)**: *Journal of Geophysical Research*, v. 105, no. B9, p. 21445-56. Stepwise thermal and AF demagnetization isolate four components (A, B, Cn and Cr) of magnetization. Component A is a recent viscous overprint with high T_{UBS} that can be explained by the presence of multidomain magnetite. Component B is carried by hematite and is considered to be a late Carboniferous remagnetization. Components Cr and Cn, found in 110 samples from 20 sites, are antiparallel and pass a class C reversal test. Their primary origin is further supported by a contact test. Cr and Cn have maximum unblocking temperatures of up to 580° C and occasionally over 600° C, indicating magnetite and hematite to carry the characteristic remanent magnetization.

Extraterrestrial Magnetism and Impacts

Courtilot, V., Gallet, Y., Rocchia, R., Feraud, G., Robin, E., Hofmann, C., Bhandari, N., and Ghevariya, Z. G., 2000, **Cosmic markers, $^{40}\text{Ar}/^{39}\text{Ar}$ dating and paleomagnetism of the KT sections in the Anjar area of the Deccan large igneous province**: *Earth and Planetary Science Letters*, v. 182, no. 2, p. 137-56. Anomalous Ir concentrations are confirmed in sediments within the traps, with up to three thin and patchy enriched layers. No Ni-rich spinels were found. Three flows underlying the Ir-bearing sediments are dated at 66.5 Ma, and two overlying flows at 65 Ma. Magnetic analyses uncovered clear reversed primary components in the upper flows, and more disturbed normal components in the lower flows, with evidence for an additional reversed component. These findings are compatible with the occurrence of the K/T impact at the paleontological K/T boundary, and of Deccan trap volcanism straddling the boundary and starting before the impact. There is no indication contradicting the view that the bulk of Deccan trap volcanism occurred over only three chrons.

Kletetschka, G., Taylor, P. T., Wasilewski, P. J., and Hill, H. G. M., 2000, **Magnetic properties of aggregate polycrystalline diamond: implications for carbonado history**: *Earth and Planetary*

Science Letters, v. 181, no. 3, p. 279-90. Carbonados are aggregate polycrystalline diamonds. Their origin is uncertain, but several hypotheses have been proposed, ranging from extraterrestrial to crustal, and mantle provenance. Magnetic studies combined with acid leaching indicates that the magnetic carriers are distributed at the vitreous surface and associated pores, and that the carbonado interior is essentially devoid of magnetic carriers. The formation of the magnetic carriers is thus closely linked with the origin of the smooth surface, perhaps during the hypervelocity ejection of carbonados into the Earth's atmosphere.

Senftle, E., Thorpe, A. N., Grant, J. R., Hildebrand, A., Moholy-Nagy, H., Evans, B. J., and May, L., 2000, **Magnetic measurements of glass from Tikal, Guatemala: possible tektites**: *Journal of Geophysical Research*, v. 105, no. B8, p. 18921-5.

Glass nodules found at the archeological site at Tikal, considered as possible tektites, contain very little Fe^{3+} as detected by Mössbauer spectroscopy. The Curie constants are similar to those found for tektites but show some intra-specimen variation, reflecting inhomogeneity in the iron concentration. The Fe^{2+} calculated from the Curie constants accounts for most of the iron. The magnetic properties resemble those of Muong Nong type tektites and suggest that the Tikal glass specimens are tektites of the Muong Nong type.

Magnetic Field Records and Paleointensity Methods

Baksi, A. K., and Hoffman, K. A., 2000, **On the age and morphology of the Reunion Event**: *Geophysical Research Letters*, v. 27, no. 18, p. 2997-3000. New $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations on lavas from two sequences on Reunion Island, along with available K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$ and astrochronological analyses, indicate an age of 2.15-2.13 Ma for the normal polarity Reunion "Event". Although the possibility cannot be completely ruled out, at present there is no convincing evidence supporting the contention of a short duration of normal polarity some 70-90 kyr later.

Brachfeld, S., Acton, G. D., Guyodo, Y., and Banerjee, S. K., 2000, **High-resolution paleomagnetic records from Holocene sediments from the Palmer Deep, Western Antarctic Peninsula**: *Earth and Planetary Science Letters*, v. 181, no. 3, p. 429-41. These sections provide the first high-resolution record of field behavior at high southern latitudes. The upper 25 m represents continuous sedimentation over the past 9000 yr, and display a stable, single-component remanent magnetization. Shipboard inclination measurements on split-core samples from three holes do not correlate well with each other, even though the intensities and susceptibilities correlate very well and the mean inclina-

tion for each hole is consistent with the expected GAD value. The correlation is dramatically better for u-channels taken from the centers of split cores. Consequently, the anomalous directions obtained from shipboard data can be attributed to coring-induced deformation and/or measurement artifacts in the split-core data.

Sarna-Wojcicki, A. M., Pringle, M. S., and Wijbrans, J., 2000, **New $^{40}\text{Ar}/^{39}\text{Ar}$ age of the Bishop Tuff from multiple sites and sediment rate calibration for the Matuyama-Brunhes boundary**: *Journal of Geophysical Research*, v. 105, no. B9, p. 21431-43.

Precise dating of sanidine from proximal ash flow and air fall can be used to derive an absolute age of the Matuyama -Brunhes (M-B) transition, identified stratigraphically close beneath the Bishop Tuff and ash at many sites in the western United States. Previous dates of the Bishop Tuff, obtained by others using conventional K-Ar and the fission track method on zircons, ranged from 650 ka to 1.0 Ma. A new age of 758.9 ± 1.8 ka was obtained by averaging results for individual sanidine crystals or groups of crystals.

Yokoyama, Y., and Yamazaki, T., 2000, **Geomagnetic paleointensity variation with a 100 kyr quasi-period**: *Earth and Planetary Science Letters*, v. 181, no. 1, p. 7-14.

A global paleointensity variation with a 100 kyr quasi-period was identified in a wavelet transform analysis of intensity records for the last 700 kyr in five sediment cores from a wide region of the Pacific Ocean. Because the variation does not correlate with that of magnetic properties of the sediments, it originated from a change in the geomagnetic field. The 100 kyr quasi-period of the field is close to those of Earth's orbital eccentricity and of late Quaternary paleoclimate. In particular, there is a correlation between the variations of the field intensity and climate with an 18 kyr time lag. While the geodynamo has widely been thought to be a self-sustained system, our results support the possibility of an external energy supply of the variation through orbital forcing or climate change.

Yu, Y. J., Dunlop, D. J., Pavlish, L., and Cooper, M., 2000, **Archaeomagnetism of Ontario potsherds from the last 2000 years**: *Journal of Geophysical Research*, v. 105, no. B8, p. 19419-33.

Thellier double-heating experiments yielded reliable paleointensity estimates for 49 of 65 specimens. AF and thermal demagnetization, $\chi(T)$, and hysteresis measurements indicate that magnetite of PSD grain size is the carrier of NRM. The paleointensity results follow a half-cycle sine curve, with a steady decrease between AD 90 and 885 and a monotonic increase between AD 1200 and 1900. The corresponding virtual axial dipole moments of the Earth's magnetic field that agree well with those from other parts of North America, except between AD 900 and 1400, when they are systematically lower. This discrepancy is probably caused by a

substantial non-dipole field in southwestern North America from the tenth to the fifteenth century, since secular variation studies using potsherds from Arizona and lake sediments from Minnesota show different inclination variations during that period.

Magnetic Microscopy and Spectroscopy

Garcia, J., Subias, G., Proietti, M. G., Renevier, H., Joly, Y., Hodeau, J. L., Blasco, J., Sanchez, M. C., and Berar, J. F., 2000, **Resonant “forbidden” reflections in magnetite**: *Physical Review Letters*, v. 85, no. 3, p. 578-81. Resonant x-ray scattering was used to investigate electronic fluctuations of the octahedral iron atoms in magnetite. We measured the (002) and (006) “forbidden” x-ray diffraction reflections permitted by the anisotropy of the iron anomalous scattering factor. The energy and azimuthal angle dependencies of these reflections, and the polarization analysis, clearly show p and d iron empty states ordering in magnetite at room temperature. Moreover, the octahedral iron atoms are electronically equivalent in a time scale lower than 10^{-16} sec. Therefore, magnetite should be considered as an itinerant magnet and not as a fluctuating mixed valence material.

Lacava, B. M., Azevedo, R. B., Silva, L. P., Lacava, Z. G. M., Neto, K. S., Buske, N., Bakuzis, A. F., and Morais, P. C., 2000, **Particle sizing of magnetite-based magnetic fluid using atomic force microscopy: A comparative study with electron microscopy and birefringence**: *Applied Physics Letters*, v. 77, no. 12, p. 1876-8.

Atomic force microscopy (AFM), transmission electron microscopy (TEM), and static magnetic birefringence (SMB) were used to unfold the particle size polydispersity profile of a magnetite-based magnetic fluid sample. The data obtained from different techniques were curve fitted using the lognormal distribution function, from which the mean particle diameter (D_m) and the standard deviation were obtained. In comparison to the TEM data, the AFM data show a reduction of D_m (about 20%) and an increase of σ (about 15%). In contrast, close agreement between the TEM and SMB data was found.

Modeling and Theory

Newell, A. J., and Merrill, R. T., 2000, **Nucleation and stability of ferromagnetic states**: *Journal of Geophysical Research*, v. 105, no. B8, p. 19377-91. Isothermal hysteresis and grain growth are simulated for cuboids with no internal stress or magnetocrystalline anisotropy, using a three-dimensional numerical micromagnetic model is combined with nucleation theory. The SD state becomes unstable at a pitchfork bifurcation, which has a jump in susceptibility but a continuous change in magnetic moment. This is a

generalization of curling mode nucleation. At any given grain size the lowest-energy state has SD-like stability in response to changes in magnetic field. A high-stability component of remanence is commonly observed in pseudo-SD grains. It has previously been assumed that the high stability must be due to SD-like regions in larger grains, but the micromagnetic simulations demonstrate that SD-like stability does not require a SD-like mechanism.

Newell, A. J., and Merrill, R. T., 2000, **Size dependence of hysteresis properties of small pseudo-single-domain grains**: *Journal of Geophysical Research*, v. 105, no. B8, p. 19393-403. A numerical micromagnetic model is used to calculate hysteresis loops as a function of grain size for two grain shapes (cube and cuboid with $X=1.5Y=1.4Z$). Magnetocrystalline anisotropy is ignored. The average M_r/M_s is calculated for a collection of randomly oriented grains. In the elongated grain it drops from 0.4 to 0.06 over a negligible size range, almost missing the usual PSD range altogether. Other hysteresis parameters, H_c , H_{cr} , and χ_0 , can only be calculated for a grain at a time. This is done for two magnetic field directions (close to the longest axis and close to the shortest axis). The single-grain values of H_c/H_s depend strongly on field direction, but it is clear that the average jumps rapidly from SD to MD values. In the size range studied ($L \leq 0.25 \mu\text{m}$), hysteresis parameters do not represent a typical grain size. Instead, they depend strongly on the size distribution.

Synthesis and Properties of Magnetic Minerals

Dumazet-Bonnamour, I., and Le Perche, P., 2000, **Colloidal dispersion of magnetite nanoparticles via in situ preparation with sodium polyoxyalkylene di-phosphonates**: *Colloids and Surfaces A*, v. 173, no. 1, p. 61-71.

Functionalized end-chain polymers were used to prepare stable aqueous magnetite colloidal dispersions. The magnetite nanoparticles were synthesized from coprecipitation of aqueous Fe^{3+} and Fe^{2+} ions in the presence of sodium polyoxyalkylene di-phosphonates. Transmission electron microscopy (TEM), dynamic light scattering (DLS), pyroanalysis techniques and isotherm determinations are reported to characterize the nanosized particles.

Nikiforov, M. P., Vertegel, A. A., Shumsky, M. G., and Switzer, J. A., 2000, **Epitaxial electrodeposition of Fe_3O_4 on single-crystal Au(111)**: *Advanced Materials*, v. 12, no. 18, p. 1351-3.

Magnetite (Fe_3O_4) is a very promising material for giant magnetoresistance devices. Here, the electrochemical deposition of epitaxial films of Fe_3O_4 on a Au(111) single crystal is reported. No thermal annealing is required to effect crystallization. It is shown that the

epitaxial film has a (111) out-of-plane orientation and two types of in-plane orientation.

O'Reilly, W., Hoffmann, V., Chouker, A. C., Soffel, H. C., and Menyeh, A., 2000, **Magnetic properties of synthetic analogues of pyrrhotite ore in the grain size range 1-24 μm** : *Geophysical Journal International*, v. 142, no. 3, p. 669-83.

Slow-cooled ‘non-ideal’ pyrrhotite is predominantly monoclinic but probably contains hexagonal pyrrhotite together with pyrite, and it may be a better analogue of pyrrhotite ore than ideal synthetic monoclinic pyrrhotite. Particles about 1 μm in size have a low M_s value of about 6 $\text{Am}^2 \text{kg}^{-1}$, indicating a lower concentration of ferrimagnetic monoclinic pyrrhotite than particles of about 6 μm and above (M_s of 12 $\text{Am}^2 \text{kg}^{-1}$). On the other hand, magnetization process parameters - H_c , M_{rs}/M_s , H_{cr} , χ , median destructive and inductive fields - follow well-behaved power law dependences on particle size, similar to monoclinic pyrrhotite. Domain patterns in the slow-cooled non-ideal pyrrhotite are similar to those observed in synthetic monoclinic pyrrhotite and in natural pyrrhotite particles in rocks.

Van der Zaag, P. J., Ijiri, Y., Borchers, J. A., Feiner, L. F., Wolf, R. M., Gaines, J. M., Erwin, R. W., and Verheijen, M. A., 2000, **Difference between blocking and Néel temperatures in the exchange biased $\text{Fe}_3\text{O}_4/\text{CoO}$ system**: *Physical Review Letters*, v. 84, no. 26, p. 6102-5. The blocking temperature T_B has been determined as a function of the antiferromagnetic layer thickness in the $\text{Fe}_3\text{O}_4/\text{CoO}$ exchange biased system. For CoO layers thinner than 50 \AA , T_B is reduced below the Néel temperature T_N of bulk CoO (291 K), independent of crystallographic orientation or film substrate ($\alpha\text{-Al}_2\text{O}_3$, SrTiO_3 , and MgO). Neutron diffraction studies show that T_B does not track the CoO ordering temperature and, hence, that this reduction in T_B does not arise from finite-size scaling. Instead, the ordering temperature of the CoO layers is enhanced above the bulk T_N for layer thicknesses $\leq 100 \text{\AA}$ due to the proximity of magnetic Fe_3O_4 layers.

phase to get a reasonable fit - additionally to the Brillouin function, the linear dependency between diamagnetism and magnetic field should be taken into account for the fit - one has to specify the ion to calculate the Brillouin function for (Fe^{2+} , Fe^{3+} or another paramagnetic ion, or even a mixture of those).

Not taking into account this effect leads to an overestimation of M_s and an underestimation of H_c . The same applies to μ -VSM measurements to 1.7 T at low

different ways in different temperature ranges.

All of the heavy rare-earth metals crystallize in a simple close-packed hexagonal form at low pressures. Gadolinium metal has the simplest magnetic behavior, with collinear ferromagnetism along the hexagonal c-axis below its Curie point (which, interestingly, is just at room temperature, i.e., 293 K) and Curie-Weiss paramagnetism at higher temperatures. Below the spin-reorientation temperature of 240 K, though, gadolinium's simple ferromagnetism becomes distorted: magnetic moments rotate away from the symmetry axis, into a "canted ferromagnetic" arrangement. Terbium and dysprosium also have relatively simple ferromagnetic ordering below their respective Curie points at 219 K and 85 K, with moments aligned in the basal plane (along the b-axis for Tb and the a-axis for Dy).

Above T_c , these two elements (and most REEs) do not immediately become disordered (i.e., paramagnetic), but instead slip into a curious antiferromagnetic state which persists up to Néel temperatures of 230 K and 179 K respectively, and which is quite different from the familiar antiferromagnetism of hematite and goethite. In the latter, the atomic magnetic moments of adjacent iron atoms are parallel but opposite in polarity, as if two antiparallel ferromagnetic materials were simultaneously occupying the same space, in an interpenetrating/interlocking arrangement - these are the magnetic sublattices. Terbium and dysprosium order in a more novel arrangement known as *helical antiferromagnetism*, in which all of the atomic moments in a particular basal-plane layer are parallel, and oriented at a fixed angle to the moments of adjacent layers. Thus in a transect along the c-axis the moments would be observed to rotate around the transect line in a screw-like or helical pattern. Over a volume containing more than a few layers, there is no net spontaneous magnetization, and hence the term antiferromagnetic is still applied.

temperature, where the effect is not so easy visible in the hysteresis curves and can lead to a serious error in the calculation of hysteresis parameters.

Yet, another effect at low temperatures was observed. From the paramagnetic signal above 100 K and utilizing the Brillouin function, a higher paramagnetic signal was calculated for temperatures below 100 K than observed by the measurements. M_{RS} is known for all temperatures, as it can be determined from hysteresis loops independently of the paramagnetic contribution. M_{RS}

Erbium below 19.5 K also exhibits a helical magnetic ordering, but each atom also has a component of magnetization parallel to the c-axis, and thus there is a net magnetic moment. This is termed *helical* or *conical ferromagnetism*. Above T_c erbium displays another novel arrangement known as *modulated antiferromagnetism*. The basal-plane components have the same helical organization as in the ferromagnetic state, but the c-axis components vary continuously in magnitude in a sinusoidal pattern from layer to layer, changing sign every seventh or eighth layer, and thus the net magnetization vanishes over volumes containing a few cycles or more. This ordering disappears at the Néel point of 80 K.

A related sort of sinusoidal antiferromagnetism occurs in thulium below its T_N of 56 K, differing from that of erbium by the absence of any transverse-component ordering. On cooling through its Curie point of 32 K, thulium displays yet another exotic new form of ordering known as *modulated ferromagnetism*. The sinusoidal variation in c-axis moments becomes an asymmetric square wave, with four layers of atoms having moments of one polarity, followed by 3 layers of opposite polarity, and continuing in a 4-3-4-3 sequence.

As intricate as these forms of magnetic ordering are in the heavy REEs, those in the lighter lanthanides are even more convoluted, and not all of them have been fully solved yet. Praesodymium and ytterbium are alone among the stable REEs in having no magnetically ordered states at temperatures down to 1 K.

Permanent Magnet Alloys

For sheer fun, it's hard to beat neodymium-iron-boron spherical magnets. Permanent magnet manufacturers, though, prefer to quantify the merit of their products in terms of the *energy product*, or BH_{max} . This is a measure of both "strength" and "hardness," and is simply the maximum value of the

shows an increase below some 50 K, which can not be attributed to titanomaghemite (see figure). The missing of paramagnetism as well as the increase of M_{RS} at low temperatures is explained by the transformation of paramagnetic minerals (hemoilmenites and/or Fe bearing silicates) into a magnetically ordered phase.

My research stay at the IRM was extremely beneficial to me and I would like to thank the IRM staff, postdocs and students for all their help.

product $B \cdot H$ on a hysteresis loop in the second quadrant; for a square loop it would equal the saturation remanence times the coercivity. Until the 1960's the best permanent magnets were alloys of cobalt and nickel with aluminum (Alnico), with maximum energy products of about 50 kJ m^{-3} . The first generation of rare-earth magnets, alloys of samarium and cobalt (SmCo_5 and $\text{Sm}_2\text{Co}_{17}$), improved on that mark by more than a factor of 3. Neodymium-iron-boron magnets ($\text{Nd}_2\text{Fe}_{14}\text{B}$) were introduced in 1984, and have attained maximum energy products exceeding 300 kJ m^{-3} .

To put that into more familiar terms, the saturation remanence (M_R) of neodymium-iron-boron is typically on the order of 10^6 A/m , twice the saturation magnetization (M_s) of magnetite. At the same time, these rare-earth alloys have coercivities (H_c) easily exceeding 10^6 A/m ($\mu_0 H_c \geq 2 \text{ T}$), comparable to those of the hard imperfect antiferromagnets hematite and goethite.

Alloys of the form RCO_5 , where R is a rare earth, are generally magnetically ordered with the cobalt moments antiparallel to those of the lanthanide atoms. For the heavy REEs, the net spontaneous magnetization is relatively weak and parallel to the rare earth magnetization; for the lighter REEs the cobalt moments are dominant and the net magnetization is strong (e.g., for the SmCo_5 magnets, $M_s=780 \text{ kA/m}$).

Similarly, in the Ne-Fe-B magnets, the magnetic moment is dominantly due to iron, while the lanthanide in effect provides the hardness. The enormous coercivities are apparently also related to microstructures resulting from the manufacturing process. The alloy is powdered and the particles are aligned in a strong magnetic field, pressed and sintered. The magnets are then coated to protect them from corrosion (they are in fact so eager to oxidize that the pair I recently bought came with the following warning: *these magnets are combustible*

Rare Earths

continued on page 7...

Gadolin, Johan

b. June 5, 1760, Turku (Åbo), Finland
d. August 15, 1852, Mynämäki (Virmo),
Finland

Both Gadolin's father and his (maternal) grandfather were professors of Physics at Åbo Akademi, in what is now Turku Finland (then part of Sweden). Gadolin upheld the family tradition (at least in part) by becoming a professor of chemistry there, after doing a thesis on the analysis of iron. Gadolin wrote in 1798 "Inledning till Chemien" (Introduction to chemistry) which is considered to be the first antiphlogistic textbook in Swedish. He is best known for his discovery of the first of the "rare earths," ytterbia, which was subsequently found to contain several lanthanide elements.

...Rare Earths

continued from page 6

and could ignite. They burn fast and hot (like magnesium) and the fumes are toxic. These temperatures could easily be reached when machining these magnets...).

In addition to their chemical vulnerability, they are quite brittle and susceptible to breakage, and they have relatively low thermal stability, with Curie points of about 200 C. Some care is thus required when handling Ne-Fe-B magnets. It should not be necessary to say that they can also inflict excruciating pinches on earlobes and nostrils, as was quickly discovered by two of our curious grad students.

Garnet Ferrites

As first conceived by Néel, ferrimagnets represent a special case of antiferromagnetism in which the sublattice magnetizations imperfectly cancel, so there is a net spontaneous magnetic moment. The familiar ferrimagnets magnetite and titanomagnetite are examples of *spinel ferrites*, in which the metal cations of one sublattice (the *A sublattice*) are each enclosed in a tetrahedral cage of four oxygen anions, and the *B sublattice* cations are each surrounded by six oxygens, forming the vertices of an octahedron. The magnetizations of the two sublattices generally have slightly different temperature dependences, leading to an interesting variety of possible net $M(T)$ functions (e.g. see the Visiting Fellow report by Jürgen Matzka in this issue.)

The rare earths are put to work in another sort of ferrimagnet, the *garnet ferrites*. (There are also *hexagonal ferrites*, but we won't consider them here.) Magnetic garnets have the composition $R_3Fe_5O_{12}$, where R is a rare-earth metal (or yttrium (#39), a sort of

distant cousin of the lanthanides). In addition to tetrahedral and octahedral sites, the garnets boast a dodecahedral site, and thus their structure contains three of the five "ideal" or "Platonic" solids (the others being, of course, the cube and the icosahedron, which to my knowledge have not yet been discovered in any magnetic site/coordination structure). The moments of the iron atoms in the tetrahedral sites are antiparallel to those in the octahedral sites, with a net moment of 5 Bohr magnetons per formula unit. The rare-earth atoms occupy the dodecahedral sites and, depending on which rare earth is involved, align either parallel or antiparallel to the net iron magnetization. The garnet ferrites have Curie points around 550° C.

Rare-Earth Oxides

Magnetism and chemistry are, of course, all about electrons. In the obsolete-but-still-appealing analogy of electrons as planets, there are both orbital and spin components of motion, and each of these contributes to the magnetic moment of an isolated atom or ion. When ions are combined in a crystalline solid, the story becomes more complicated as inter-ion electrostatic interactions begin to influence the behavior of the electrons.

The magnetism of the iron-group elements arises from the spins of unpaired electron in the 3d orbital. These elements are happy to shuck two electrons from their 4s orbital to become divalent cations (e.g., Fe^{2+}); they are also quite willing to part with a 3d electron and become trivalent. In either state, the 3d electrons are the outermost of the cation, and are exposed to relatively strong intracrystalline electric fields. In the planetary analogy, the result of the "crystal field" is to perturb the orbits to such an extent that they no longer contribute much to the net magnetic moment of the ion; the orbital moment is said to be *quenched*. Compounds of the iron-group elements thus have moments due primarily to the spins of the 3d electrons.

In the lanthanides it is the 4f electrons that account for the magnetism. As in the iron-group 3d electrons, a significant number of them can have unpaired spins, with a resultant atomic magnetic moment. In neutral REE atoms the number of 4f electrons ranges from 0 (La) to 14 (Yb and Lu), and the number of unpaired spins can be as large as 7. The lanthanides always (for reasons that are not clear to me) form trivalent ions by discarding their two 6s electrons and one 4f electron. The remaining 4f electrons are shielded from intracrystalline electric fields by a dense cloud of 5s and 5p electrons, so that, unlike the iron-group

elements, their orbital moments are not quenched. Thus both spin and orbital components are significant in REE magnetism, and the behavior of these elements in compounds more closely resembles that of free ions than is the case with iron. This screening also prevents the sort of "superexchange" coupling of magnetic moments that occurs in iron oxides, in which the coupling bridges through non-magnetic oxygen atoms by interaction of iron 3d and oxygen 2p orbital electrons. The REE oxides are thus quite 'pure' paramagnets.

Because of their relatively large net magnetic moment per ion, their chemical stability, and their pure paramagnetic behavior, REE oxides are the materials of choice for susceptometer calibration standards (they are also non-conducting, and therefore good for both AC and DC calibration). Several years ago at IRM, Jim Marvin settled on Gd_2O_3 for calibrating the LakeShore low-field AC susceptometer. More recently Quantum Design supplied us with a Dy_2O_3 standard to go with our new MPMS high-field DC / low-field AC instrument.

Wherefore Gadolinium

Rare earth elements have assumed an important role in geochemistry, but are unlikely to do so in geophysics, because any magnetic signal they generate is almost invariably swamped by that of the far-more-abundant iron-group elements. They are not really rare, nor are they exactly earths, but they have indisputably put an interesting new spin on magnetism.

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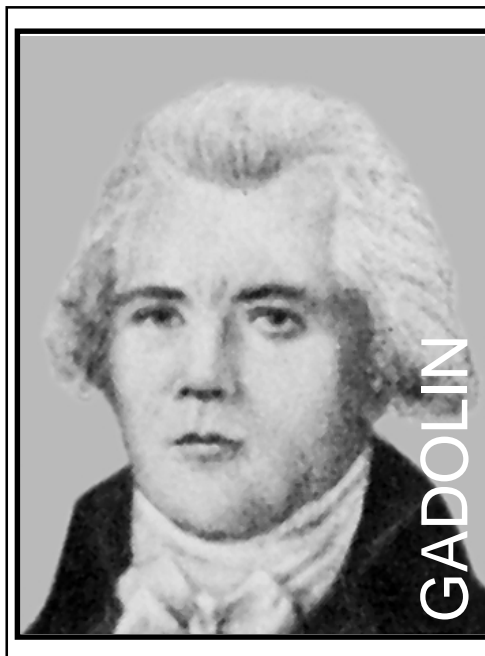
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