

ROCKMAGNETISM AND PALEOMAGNETISM

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Summary

Paleomagnetic data allow establishment of the movement of tectonic blocks over Earth as a function of geologic time. Paleolatitude and the amount of vertical rotation can be

measured directly, while paleolongitude must be inferred from other constraints like the continuation of geologic structures. The amount and the timing of vertical axis rotation also provide important constraints for geodynamic models within orogenic zones. By comparing paleomagnetic and hotspot reference frames, hot-spot motion and “true polar wander” can be assessed. Magnetostratigraphy, which uses the Geomagnetic Polarity TimeScale (GPTS), is an important way to date sedimentary rocks. Rock magnetism provides the theoretical basis for the physical interpretation of paleomagnetic data. This is achieved by numerical simulations, laboratory experiments of acquisition, and stability of remanences, or careful physical analysis of observations. Magnetic properties of rocks, in particular of sedimentary rocks and soils, vary as a function of (paleo)climate and (paleo)environment, aspects that are advantageously used in environmental magnetism to establish mineral–magnetic proxy parameters.

1. Introduction

The disciplines of paleomagnetism, rock- or mineral magnetism, and environmental magnetism are closely related. They are closely related to geomagnetism as well, which is treated elsewhere (see *Magnetic Field of the Earth; Magnetohydrodynamics of the Earth's Core*). Paleomagnetism studies the permanent magnetic moments or remanent magnetizations recorded in rocks—referred to as natural remanent magnetization (NRM)—as a function of space and (geological) time, thereby concentrating on the directional information contained in the rocks. While the geomagnetic field is quite variable on short timescales it can be described by a geocentric axial dipole (GAD) field, when averaged over a sufficient amount of time. The GAD hypothesis is the basic hypothesis underlying paleomagnetism. Paleodeclinations can be interpreted in terms of tectonic rotation and paleoinclinations can be related to paleolatitude.

NRM resides in “magnetic minerals” which represent only a small fraction of the total rock volume (from 1 ppm to 1%). While paleomagnetism focuses on the analysis of NRM directions, rock magnetism or mineral magnetism investigates the magnetic properties of these magnetic carriers. Rock-magnetic theories form the physical basis of paleomagnetism.

In environmental magnetism the magnetic properties of natural and anthropogenic materials are used as proxy parameters for many environmental processes. Examples are paleoclimate analysis, paleoceanographic studies, provenance studies of sediments, studies of anthropogenically induced pollution, and archeological investigations. It is based on the same mineral–magnetic principles as paleomagnetism and relies as well on the theoretical foundations provided by rock magnetism.

1.1. Paleomagnetism

Paleomagnetism requires, in principle, access to outcrops, in contrast to a series of other geophysical techniques. Paleomagnetic samples are usually obtained by drilling with portable drills and hollow drill bits. Drill plugs are removed from the rock after their orientation has been noted. The essence of any paleomagnetic investigation is the separation and recognition of the primary NRM component from the total NRM in the set of samples under study. The primary NRM is acquired during or shortly after its

formation: the direction and intensity of the local geomagnetic field is locked into the rock and, in principle, may last forever. Once formed, however, rocks are not closed systems and can undergo various geologic processes like diagenesis, compaction and burial, deformation, metamorphism, and weathering. Hence, during the complete geologic history of a rock, secondary NRM components can be added later to the primary component which itself can also be (partially) erased, for instance by physical removal of its mineral carriers or by so-called viscous resetting. Therefore, in virtually all rocks the NRM is a composite consisting of the primary NRM component and secondary component(s) acquired later in the geological history. The primary NRM component is routinely established by stepwise progressive demagnetization, or subjection of a sample to increasingly higher alternating magnetic fields or temperatures.

Paleomagnetism has been very successful in setting the stage for the development of the concept of plate tectonics by proving that continental drift is a reality. Plate tectonics (see *Tectonic Processes*) constitutes the cornerstone of the modern earth sciences. Its importance for earth sciences is equivalent to that of concept of evolution for the biological sciences.

1.2. Rock Magnetism

Rock magnetism involves research into the magnetic properties of the magnetic minerals in rocks and the stability of remanence. The discipline is linked to fine-particle magnetism, but predominantly studies magnetic material of natural origin and occurring in low concentration (magnetic grain interaction is less important). Experimental data can be either acquired from natural material or from synthetics. The natural magnetic minerals are regarded as better analogues for the processes in rocks but usually behave less ideally than the synthetic counterparts. The natural magnetic minerals are comprised mainly of oxides and sulfides of iron. Metallic iron is extremely rare in crustal and upper-mantle rocks. The most important terrestrial magnetic mineral is magnetite (Fe_3O_4).

On the atomic scale, magnetism arises from the uncompensated spin moment of the outermost electrons orbiting around a nucleus. In quantum mechanics, electrons are assigned an orbital moment and a spin moment. The orbital moments of electrons generally cancel out in crystalline solids. In most minerals by far, the outermost unpaired electrons behave independently of each other, yielding a paramagnetic spin configuration. In crystalline solids that contain transition elements in large amounts, the atomic nuclei are sufficiently close to each other to have the orbits of the outermost electrons overlapping with each other. In this situation, the uncompensated spins may line up and their individual magnetic moments can be added to get macroscopic magnetism, caused by long-range exchange coupling or collective ordering of atomic magnetic moments in the crystal lattice of the magnetic mineral. This situation can occur in metals, oxides and sulfides. In nature, the transition element of most interest is iron.

Only minerals with collective ordering, those with a ferro-, ferri-, or antiferromagnetic structure, can possess remanent magnetization (Figure 1). Long-range exchange

coupling only exists below the Curie or Néel temperature. Above this temperature, collective magnetic ordering is overcome by thermal energy and the mineral becomes paramagnetic. Magnetite has a Curie temperature of 578° C with only a small pressure dependence, so at depths $>\sim 20$ km below Earth's surface, depending on the prevailing geotherm, remanent magnetism cannot exist.

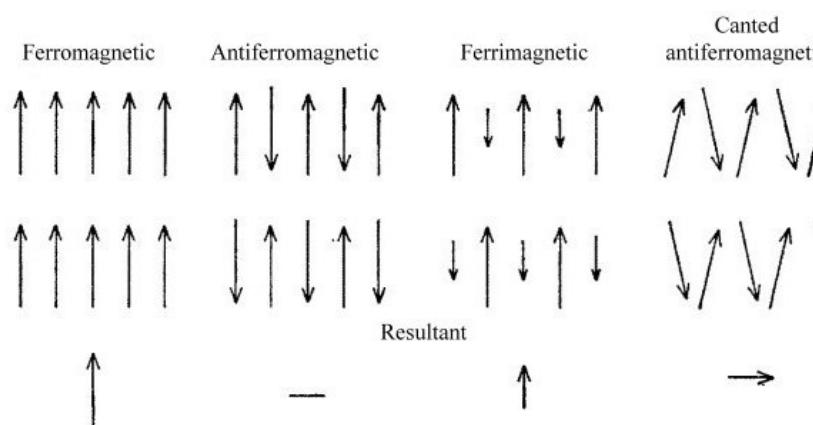


Figure 1. Types of collective spin ordering

Determination of the magnetic mineralogy yields clues regarding the origin of the NRM, essential to a proper geophysical and geological interpretation of paleomagnetic data. Rock-magnetic research has provided and still is providing paleomagnetism and environmental magnetism with the necessary theoretical formulations and methodology.

1.3. Environmental Magnetism

The sensitivity of magnetic properties to small changes in grain size and concentration is used in environmental magnetism to establish proxy parameters for many purposes. All rocks and soils contain iron oxides and/or iron sulfides in trace amounts or more. The mineral-magnetic methods can therefore be applied to all of them. Samples are certainly not restricted to hard rocks and unconsolidated sediments: environmental magnetic data are also acquired from soils, dusts, organic tissues, or peats. The magnetic properties of samples allow the magnetic mineralogy, the concentration of magnetic grains, and the size of these grains to be deduced. This information, in turn, is used as proxy parameters for several environmental purposes, including provenance analysis of sedimentary basins, paleoceanographic studies, paleoclimate studies, and pollution assessment.

Mineral-magnetic techniques are sensitive, require little sample preparation, are rapid, often grain-size indicative, and usually nondestructive. The techniques involve bulk properties which makes them complementary to geochemical micro-analytical techniques. Measurements include the field- and temperature-dependence of various types of induced and remanent magnetizations. Apart from processes in the provenance area and at the depositional site, also the pathway between those two places has a crucial impact on the magnetic properties. The underlying causal relations between observed mineral-magnetic properties and the processes that led to those properties, are becoming increasingly better understood, and the extended use of such properties as proxy parameters for many processes is foreseen.

2. Theoretical and Methodological Foundation

To arrive at a geophysically and geologically meaningful interpretation of paleomagnetic data, the NRM must be: (a) a reliable recorder of the geomagnetic field, and (b) stable over geological time. To satisfy criterion (a), the rock should ideally be isotropic and contain a random assembly of magnetic grains, because remanent magnetism is tied to crystallographic properties and the shape of individual magnetic particles through the easy directions. Magnetism is thus anisotropic by nature. This excludes most metamorphic rocks as well as severely deformed rocks from paleomagnetic observation. Criterion (b) implies that the primary NRM must have a long relaxation time. The NRM in rocks is metastable because any magnetic moment tends to align itself to an ambient magnetic field that represents the minimum energy configuration. For example, when the geomagnetic field reverses its direction, the magnetic vector that is recorded by each grain will try to align itself to the new field configuration. The time needed to conform to the new field configuration is related to the height of the energy barrier between the old and new configuration in each individual magnetic particle. If this occurs rapidly (from less than a second to days, i.e., on a laboratory timescale), the relaxation time of a sample is said to be short (and the NRM viscous). If it occurs slowly or is negligible with respect to geological time, the relaxation time is said to be long (and the NRM stable).

2.1. Rock and Mineral Magnetism

The number of different ferromagnetic and ferrimagnetic minerals in natural rocks is, fortunately, limited. In practice we only have to consider iron oxides, ironoxyhydroxides, and some iron sulfides. The widespread occurrence of magnetic sulfides in terrestrial rocks is only recently appreciated. Most natural magnetic minerals are ferrimagnets or antiferromagnets; only metallic iron is ferromagnetic.

The iron oxides form solid solutions between magnetite (Fe_3O_4) and ulvöspinel (Fe_2TiO_4), and between hematite ($\alpha\text{-Fe}_2\text{O}_3$) and ilmenite (FeTiO_3). Substitution of Ti for Fe is most common but also Al, Cr, Mg, and Mn substitution for Fe is possible. Titanomagnetites crystallize in the spinel structure. They can oxidize completely to titanomaghemitites thereby retaining this structure. Their formula can be written as $\text{Fe}_{(3-x)}\text{Ti}_{xR3(1-R)}\text{O}_4$, where denotes a cation vacancy. R expresses the oxidation degree and varies between zero and $8/(9 + x)$, while x takes values between zero and 1.285 depending on the mechanism by which the oxidation proceeds. If this occurs via the addition of oxygen mechanism, x varies between 0 and 1. If the oxidation is progressing via the preferential removal of Fe^{2+} from the spinel, x may take values >1 . Completely oxidized magnetite, maghemite ($\gamma\text{-Fe}_2\text{O}_3$), is thermodynamically metastable with respect to hematite, but nonetheless fairly common in rocks. Its thermal stability is quite variable with common inversion temperatures at 300–400° C, but maghemite may persist up to even 900° C. In maghemite, Al and Ti can substitute for Fe. The hematite-ilmenite series crystallizes in the corundum structure. In hematite, Al and Ti can substitute for Fe, and in goethite ($\alpha\text{-FeOOH}$), mainly Al substitution may occur. The

magnetic iron sulfides pyrrhotite (Fe_7S_8 - $\text{Fe}_{11}\text{S}_{12}$) and greigite (Fe_3S_4) are relatively pure and substitution is often negligible.

In addition to the external temperature and field conditions, the properties of magnetic minerals are determined by intrinsic material properties that differ among the magnetic minerals, and by the volume of the magnetic particles. Different volumes lead to different magnetic domain states that profoundly influence magnetic properties and stability (see section 2.1.2). The more common natural magnetic minerals are listed in Table 1, along with some iron-bearing minerals that are not magnetic under ambient conditions but may transform into magnetic minerals on heating. Their occurrence may therefore have important paleomagnetic and environmental magnetic implications. With the exception of titanomagnetite, the magnetic minerals listed in Table 1 are usually referred to as “minor magnetic minerals.”

Mineral	Formula	T_C, T_N (C)	M_s^a	Structure ^b
Magnetite-ulvöspinel	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$	578° – 155°	480	Fi
Magnetite-hercynite	$\text{Fe}_3\text{O}_4\text{-FeAl}_2\text{O}_4$	578° – 339°	480	Fi
Magnetite-jacobsite	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{MnO}_4$	578° – 350°	480	Fi
Magnetite-chromite	$\text{Fe}_3\text{O}_4\text{-Fe}_2\text{CrO}_4$	578° – 30°	480	Fi
Hematite-ilmenite	$\alpha\text{-Fe}_2\text{O}_3\text{-FeTiO}_3$	675° – 170° Afm-Fi ^c	~2.5	canted
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	645° ^d	380	Fi
Goethite	$\alpha\text{-FeOOH}$	120°	0.2–2	Afm
Akagenéite	$\beta\text{-FeOOH}$	26°	very small	Afm
Bernallite	$\text{Fe}(\text{OH})_3$	154° Afm ^e	very small	canted(?)
Feroxyhite	$\delta'\text{-FeOOH}$	177°	large	Fi
Pyrrhotite	$\text{Fe}_7\text{S}_8\text{-Fe}_{11}\text{S}_{12}$	325°	~80	Fi-Afm ^f
Greigite	Fe_3S_4	350°? ^g	~125	Fi
Iron	Fe	770°	1715	Fo
Lepidocrocite	$\gamma\text{-FeOOH}$	–196°	—	Afm ^h
Siderite	FeCO_3	–238°	—	Afm ^h
Ferrihydrite	$\text{Fe}_5\text{HO}_{8.4}\text{H}_2\text{O}$	–158° – 248° ^g	—	Spe ^{h,i}

^a M_s values at room temperature (per unit volume, kAm^{-1}). For solid solution series, the iron-rich endmember value is given. If no value is possible, a dash is shown.

^b Fo, ferromagnetic; Fi, ferrimagnetic; Afm, antiferromagnetic; Spe, speromagnetic.

^c Above the Morin transition, hematite has a canted antiferromagnetic structure, which results in a macroscopic magnetic moment. In addition it possesses a variable “defect” magnetization that is insensitive to the Morin transition. The magnetic structure becomes ferrimagnetic with increasing Ti content. As in the titanomagnetite solid-solution series, high Ti content yields Curie temperatures below room temperature.

^d Most maghemites invert to hematite before their Curie temperature is reached.

^e The magnetic structure of bernallite is not known with certainty.

^f Only monoclinic pyrrhotite (Fe_7S_8) is ferrimagnetic at room temperature, while the other pyrrhotite structures become ferrimagnetic on heating above ~200° C.

^g On heating, greigite decomposes before it reaches its Curie temperature. Therefore, the temperature listed should be regarded with great caution.

^h The last three minerals listed are paramagnetic at room temperature but they order magnetically at low temperatures, so their presence can be demonstrated with magnetic methods. Furthermore, on heating a sample above room temperature these paramagnetic minerals chemically alter into magnetic minerals.

ⁱ Speromagnetism is characterized by short-range antiferromagnetic spin coupling. On longer ranges the magnetic ordering is random. The range of ordering temperatures of ferrihydrite is related to its crystallinity.

Table 1. Common natural magnetic minerals, chemical formulae, Curie or Néel temperatures (T_C and T_N), saturation or spontaneous magnetizations (M_s), and magnetic structures below T_C or T_N

2.1.1. Intrinsic Magnetic Properties

Intrinsic magnetic properties include the spontaneous or saturation magnetization (M_s), the Curie temperature (T_C), the Néel temperature (T_N), and for some magnetic minerals, temperatures at which magnetic transitions occur. Ferromagnetism arises from direct exchange coupling between neighboring Fe atoms/ions. In oxides and sulfides—schematically seen as consisting of alternate layers of metal (Fe) ions and oxygen ions—the orbital structure of the oxygen (or sulfur) ions dictates that spin directions in adjacent Fe layers are antiparallel, giving rise to ferrimagnetism or antiferromagnetism. This mechanism is called superexchange. Curie temperatures, determined by thermomagnetic analysis (Figure 2), are mineral specific although solid solution complicates the interpretation of a thermomagnetic run. Substitution of Fe by other cations will generally lead to a reduction of the Curie temperature. On heating, either in air, in vacuum, or in an inert atmosphere, chemical alteration of the sample may occur as well. Repeated thermomagnetic runs serve to distinguish between chemical alteration and magnetic behavior, which is in principle reversible on cooling.

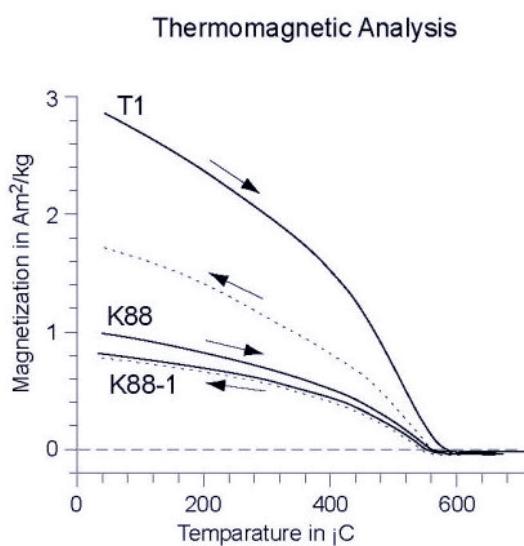


Figure 2. An example of thermomagnetic analysis of a magnetite-bearing fly ash. Heating (cooling) curves are solid (dotted) lines. Sample T1 is distinctly nonreversible: the magnetite oxidizes on heating (in air) which results in a cooling curve that is clearly

below the heating curve. Sample K88 is much more reversible, the second thermomagnetic run (K88-1) being completely reversible.

Magnetite, hematite, and pyrrhotite show so-called magnetic transitions, changes in magnetization and/or magnetic behavior at discrete temperatures. This property can be used to diagnose their occurrence in rocks. In magnetite the so-called Verwey transition occurs at ~120 K. Magnetically, it is detected by an abrupt change in remanent magnetization, coercive force, or susceptibility at that temperature. Substitution of Ti or Al for Fe, and/or a low degree of uniform oxidation lower the temperature at which the magnetic transition occurs. A high degree of oxidation or surficial oxidation of grains may suppress the transition completely. Well-crystallized hematite can be recognized by the so-called Morin transition, which occurs at ~20° C. Substitution of Al lowers the transition temperature, and substitution of Ti suppresses the transition already at a low degree of substitution. In case of rather poorly crystallized material—the rule in natural samples—the transition is characterized by a fairly broad temperature interval rather than a narrow temperature range. Pyrrhotite shows a magnetic transition at 34 K.

The height of the anisotropy barrier between easy directions determines the magnetic stability of individual grains. Apart from being dependent on temperature and field conditions, the anisotropy is a function of material properties, grain shape, and grain volume. A higher temperature reduces the magnetic stability by increased thermal jostling of the electron spins that make up the magnetic structure. At and above the Curie temperature, no barrier exists. The classic example of anisotropy due to shape (with a single easy direction) is the compass needle, which is always magnetized along its long axis and never otherwise. This is because the long-axis configuration of the electron spins yields the smallest number of “free” magnetic poles (only at the tips of the needle) which represents the lowest energy configuration. Magnetocrystalline anisotropy due to crystal structure can have more easy directions. Lattice imperfections (dislocations, vacancies, stacking faults, twin planes, inclusions) also add to the energy barriers because they pin down a certain spin structure. When mixed anisotropies occur, the uniaxial term dominates quickly. By inserting values for common magnetic minerals at ambient temperature, it becomes evident that the fields corresponding to anisotropy, H_K , (~50 mT to over 1 T) exceed typical intensity values of the geomagnetic field (~50 µT) by at least three orders of magnitude. Reversals of the geomagnetic field will thus not affect NRMs that reside in SD particles.

2.1.2. Relaxation Time and Domain State

The concept of relaxation time is central to (paleo)magnetic stability. Its basic principles are described in the following analytical equations; a complete description requires a numerical approach for solving. The magnetization M evolves towards the thermal equilibrium magnetization M_{eq} in a small (Earth-like) field H_0 according to:

$$M(t) = M_0 e^{-t/\tau} + M_{eq}(1 - e^{-t/\tau}) \quad (1)$$

M_0 = magnetization at time $t = 0$. The thermal equilibrium magnetization is:

$$M_{eq} = M(\infty) = M_s \tanh\left(\frac{\mu_0 V M_s H_0}{kT}\right) \quad (2)$$

The relaxation time τ is:

$$\frac{1}{\tau} = \frac{1}{\tau_0} e^{-E_b/kT} = \frac{1}{\tau_0} \exp\left[-\frac{VK}{kT}\right] = \frac{1}{\tau_0} \exp\left[-\frac{\mu_0 M_s V H_K}{2kT}\right] \quad (3)$$

τ_0 ($\approx 10^{-9}$ s) is the atomic reorganization time, the interval between successive thermal excitations. E_b is the magnetic energy or blocking energy of the ensemble and kT the thermal energy. V is the grain volume, K the anisotropy constant and H_K the microscopic coercivity. The relaxation time is thus determined by the ratio of the blocking energy and the thermal energy. τ changes dramatically as a function of temperature, (microscopic) coercivity, grain volume, and saturation magnetization. A rock sample generally contains a continuum of τ 's and for paleomagnetism only the long τ 's, preferably comparable to the life-time of Earth (4.56 Ga), are of interest. SD grains have such long relaxation times.

Relaxation times and magnetic properties gradually change as a function of domain structure. With increasing grain size, four types of magnetic domain state are distinguished: SP, SD, PSD, and MD. SP grains ($<\sim 0.030$ μm) have short relaxation times ($\tau < \sim 150$ s); paleomagnetically stable NRMs therefore do not reside in SP grains. Their presence in rocks, however, does influence the magnetic properties of the rock. The SD grain-size range in magnetite ranges from ~ 0.03 to ~ 0.50 μm , depending on the shape of the particles. The transition between SD and MD grains is smooth and gradual. It is traditionally referred to as PSD, because PSD grains have properties similar to those of SD grains, including long relaxation times. In magnetite the upper threshold of the PSD range is ~ 10 – 20 μm . The largest grains ($>\sim 10$ – 20 μm) with many conventional magnetic domains are referred to as MD. The relaxation times of PSD and MD grains decrease with increasing grain size, although at present only approximate trends are known.

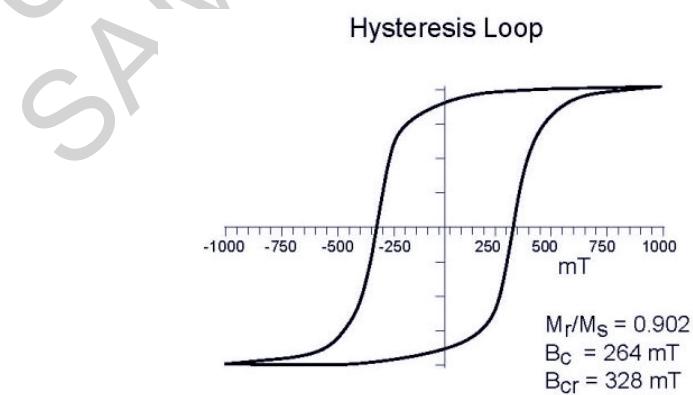


Figure 3. Example of a hysteresis loop for hematite, measured with an alternating gradient magnetometer up to peak fields of 1 T

The squareness of the loop indicates a single-domain structure.

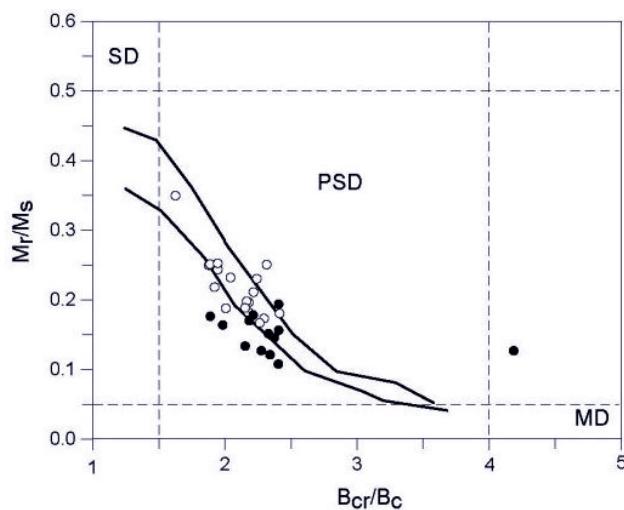


Figure 4. “Day plot” of $M_r:M_s$ and $B_{cr}:B_c$ ratios

The solid lines represent the experimental calibration for titanomagnetite. The data points shown are from Icelandic lavas with stable (open circles) and unstable (closed circles) NRM behavior.

Information on the grain size (domain state) is obtained from magnetic hysteresis loops (Figure 3). A hysteresis loop displays the response of a sample to an applied magnetic field, which is measured in that applied field. Hysteresis loops are indicative of magnetic mineralogy. As a rule of thumb, ferrimagnetic minerals saturate in fields up to ~0.5 T. For minerals that owe their magnetic properties to imperfect antiferromagnetism (hematite, goethite), much higher fields are needed. However, hysteresis loops are particularly sensitive to subtle changes in grain size as well which complicates the interpretation of results from natural samples. Classically, the ratios of $M_r:M_s$ and $B_{cr}:B_c$ are plotted on a so-called “Day plot” (Figure 4) in which SD, PSD, and MD fields are distinguished. Ratios usually fall in a narrow band which has been experimentally calibrated for (titano)magnetite grains of known size so that information indicating grain size can be extracted.

A magnetic parameter that is often used in paleomagnetism and environmental magnetism is the low-field or initial susceptibility (χ_{in}), the magnetic moment of sample in low external magnetic fields, up to ~10 times the strength of the geomagnetic field. Importantly, measurement of χ_{in} does not interfere with the NRM present in the sample, so it can be done along with paleomagnetic demagnetization of the sample set. χ_{in} is very sensitive to minute changes in the content of (maghemitized) magnetite, because they have very high χ_{in} values. SP particles are characterized by distinctly higher values than larger particles of the same magnetic material, a property termed superparamagnetism.

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Biographical Sketch

Mark J. Dekkers, is a lecturer in Geophysics at Utrecht University (Netherlands). He got his PhD from Utrecht University in 1988. He was a post-doctoral researcher at Utrecht University from 1988 to 1989, after which he spent a year working at the Laboratoire de Géophysique Interne et Tectonophysique in Grenoble (France). From 1991 to 1996 he was research fellow of the Royal Netherlands Academy of Sciences and Arts. In 1992 he was a visiting scholar at Scripps Institution of Oceanography (La Jolla, California, USA). In 1996 he was appointed lecturer in Geophysics at Utrecht University. His main research interests are in the area of rock-, paleo-, and environmental magnetism focusing on acquisition mechanisms of the natural remanent magnetization (NRM) of sedimentary rocks and the influence of later geological processes on the NRM. He employs a variety of mineral-magnetic, microscopical, and geochemical techniques to characterize the magnetic mineralogy to improve the interpretation of the NRM in terms of variations of the geomagnetic field and to improve the use of magnetic proxy parameters for (paleo)environmental and paleoclimatic purposes.