

Rock magnetism and magnetic mineralogy used in sedimentary series

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## **1.** Historical aspects

Mankind's interest in magnetism began as a fascination with the curious attractive properties of **the mineral lodestone**, a naturally occurring form of magnetite.

Called loadstone in early usage the name derives from the old English word load, meaning "way"; the **loadstone** was literally **a stone which showed a traveller the way**.

# -> No accurate records of the earliest observations before the Greek philosophers wrote about lodestone around 800 BC and its properties were known to the Chinese by 300 BC.

- The attractive forces of lodestone were ascribed to metaphysical powers. Some early philosophers even believed lodestone to possess a soul.

- False conceptions persisted well into the 19th century. For example there is a view that electrical and magnetic forces were related to invisible fluids.



One of the greatest of the ancient Greek city-colonies in Asia Minor was the seaport of Ephesus, at the mouth of the river Meander in the Persian province of Caria (Anatolia, Turkey).

In the fifth century BC the **Greek** state of Thessaly founded a **colony** on the Meander close to Ephesus called **Magnesia**, which after 133 BC was incorporated into the **Roman empire** as **Magnesia ad Maeandrum**.

In the vicinity of Magnesia the Greeks found lodestones, known after by **the Latin word** *magneta* from which the term magnetism derives.



The power of a magnet, i.e. its ability to align consistently north–south was recognized in the **Han dynasty**, **between 300 and 200 BC**, the Chinese fashioned a rudimentary compass out of lodestone.

It consisted of a spoon-shaped object, whose bowl balanced and could rotate on a flat polished surface. Not used for navigation !!



Si Nan, the world's first compass, took the form of shu'o (a spoon). By placing the magnetic shu'o on the bronze earth-plate one could rotate it by hand.

When the body of the shu'o becomes still, its handle will point to the south.

In the Song Dynasty (960-1279), Shen Kuo described the floating compass, suspended in water, a technique that minimized the effect of motion on the instrument.

Shen Kuo (1031-1095) was a scientist of the Song Dynasty.

Excelling in many fields of study, he was a mathematician, **astronomer**, meteorologist, **geologist**, zoologist, botanist, pharmacologist, agronomist, ethnographer, encyclopedist, poet, general, diplomat, hydraulic engineer, inventor, academy chancellor, finance minister, and governmental state inspector.

He was the head official for the Bureau of Astronomy in the Song court, as well as an Assistant Minister of Imperial Hospitality.



This enabled the compass to be used for sea navigation for the first time and its use soon spread to the Arab world, and then onto Europe (first reference of such compass in Europe by **Alexander Neckam**, an English monk, in 1187). The European mariners are more interested by the north direction.

#### The Earth magnetism

In 1269, a Frenchman, Pierre de Maricourt (better known as Petrus Peregrinus) described the pole locations of a lodestone compass, how the opposite magnetic poles of a compass attract each other, and how similar poles repel.

These observations were wroted by Peregrinus in the form of a letter on the properties of the lodestone which was entitled « **Epistola de Magnete** ».

He found that the magnetic poles always occurred in pairs of opposite signs. He thus discovered the dipolar nature of the magnet.

The northward pointing pole has been named the magnet's *north pole*. That means the Earth's pole in the northern Arctic region is really a magnet's south pole because it attracts the compass magnet's north pole.



In 1492, Cristopher Columbus, during his first travel to the West Indies, observed a growing misalignment between the magnetic north direction and the North Star between the spanish and the carribean coastlines.

This is one of the first documented observation of the magnetic declination change with changing longitude.



Magnetic declination corresponds to the angle between magnetic and geographic North Pole directions.

During two centuries, the magnetic declination were mapped all around the world.

Toward the end of the 16th century, Mercator recognized that the magnetic declination was the principal error during the realization of cartographic maps. The first observation of magnetic declination appears to have been made in China by the Buddhist astronomer Yi-Xing about A.D. 720 (Needham, 1962). However, knowledge of declination did not travel to Europe with the compass.

Although the Chinese records reveal at least nine measurements of declination from A.D. 720-1280.



Fig. 1.3. Variation of magnetic declination with time in China between A.D. 720 and 1829. Error bars represent the range within which the declinations lie as quoted by Chinese texts. After Smith and Needham (1967).

In 1544, Georg Hartmann, a German monk, discovered that a magnetic needle has a vertical inclination from the horizontal plan and this is called now magnetic inclination.



Fig. 1.1. The main elements of the geomagnetic field. The deviation, D, of a compass needle from true north is referred to as the *declination* (reckoned positive eastwards). The compass needle lies in the magnetic meridian containing the total field F, which is at an angle I, termed the *inclination* (or dip), to the horizontal. The inclination is reckoned positive downwards (as in the northern hemisphere) and negative upwards (as in the southern hemisphere). The horizontal (H) and vertical (Z) components of F are related as given by (1.1.1) to (1.1.3). From Merrill *et al.* (1996).



The publication in 1600 by William Gilbert, physician to Queen Elizabeth I, of his results of experimental studies in magnetism in a treatise entitled **De Magnete**. It's a summation of the knowledge of his time and of his own magnetic experiments.

He is considered as the father of science of magnetism.



**FIGURE 1.4**  $\blacktriangleright$  William Gilbert (1540–1603) produced the first scientific book about magnets and the Earth's magnetic field.

In an impressive series of experiments Gilbert discovered that a small magnetic needle is always pointing north-south while moved over the surface of a piece of lodestone cut as a sphere and called « **Terrella or little Earth** ».

He was the first to describe the Earth's main field as a giant magnet with a horizontal field at the Earth's equator and with two oppositely directed vertical fields at the Earth's poles.



**FIGURE 1.5** A dipole field pattern is superposed on Gilbert's picture of the Great Earth Magnet of 1600 in which he shows how magnets would naturally arrange about the surface.

Gilbert suggested that *"magnus magnes ipse est globus terrestris"* (the Earth globe itself is a great magnet) and that this was the reason compasses point north.

Between 1697 and 1701, in a time of significant English maritime expansion, **Edmund Halley** (more famous for his prediction of the return of the large comet that now bears his name) was commissioned to captain the ship *Paramour* in two voyages through the Atlantic Ocean, **mapping the magnetic field direction** for navigational purposes.

He produced the first chart of the full magnetic declination pattern for a major region of the Earth.





FIGURE 1.6 ► This 1701 chart of magnetic declination contours for the Atlantic Ocean was produced by Edmund Halley, who is more famous for his prediction of the orbit for a comet that bears his name. The plotted declinations are inaccurate because of the difficulty in obtaining longitude at sea during the years of Halley's voyage.

#### Physical origin of the magnetism

In 1777, a French military engineer, Charles Augustin Coulomb showed that the magnetic repulsion between magnetic poles and also their attraction varied inversely with the square of the distance (r) using a magnetic instrument called a « torsion balance ».



Coulomb law is also transposed for electricity by replacing the magnetic needle by two charged metal spheres (named q1 and q2). He shows that **the strength of electric forces also decreased like the inverse square of the distance**.

In 1800, Allesandro Volta (1745-1827) developed the voltaic pile, the ancestor of the electric battery.

The pile consists of a number of discs of zinc and copper separated by pieces of wet cloth and arranged in a vertical column.

This was the first device to produce a continuous flow of electric charge, an electrical current generated by a chemical process.





**Hans Christian Oersted** (1777-1851) showed accidentally that there is a connection between electricity and magnetism.

In 1820, Oersted's equipment included a magnetic compass, as well as an electric battery and a thin metal wire, and that one demonstration involved heating the wire by an electric current from the battery. Most probably it was only by accident that the wire passed over the compass or near it. Accidentally or not, whenever the wire was connected to the battery and a current flowed, the magnetic needle moved, and whenever the current ceased, it returned to its old position.







Discovery of what we called now electromagnetism

In several publications made between 1820 and 1828, the French scientist **André-Marie Ampère** (1777-1836) says that the basic feature was the force between electric currents.

When two currents flowed in the same direction along parallel wires, the wires attracted, and when the currents flowed in opposing directions, they repelled each other. The force between two parallel electric currents is inversely proportional to the distance between them and proportional to the intensity of the current circulating in each wire.

André-Marie Ampère has also suggested that iron atoms contained small circulating currents responsible of the magnetism. This idea was really important at that time because he is talking about ferromagnetism.





**Michael Faraday** (1791-1897) showed in 1831 that the magnetic field lines converge to the point where the magnetic field is strong and spread out where the magnetic field is weak.

This could be translated for a magnetic dipole by magnetic field lines that **spread out from the S pole, arch around its middle and converge again near the N pole.** 



These conclusions made for a magnetic dipole could be extrapolated by placing a large magnetic dipole in the center of the Earth.

**Carl Friedrich Gauss** (1777-1855) mentioned that the magnetism was related to magnetic charges which are opposite at the poles.

In **1893**, **James Clerk Maxwell** proposed mathematical equations that remains the best physical description of electricity and magnetism.

Finally, the present age of geomagnetism arrived with the extensive publication of a book entitled Geomagnetism by **Sydney Chapman** in **1940**. He applied the Maxwell's mathematics to the natural processes of the upper atmosphere and magnetic storms originating from solar mechanisms.





**FIGURE 1.9** James Clerk Maxwell (1831–1879) devised the mathematical formulation for the physics of electricity and magnetism that is still in use today.

**FIGURE 1.10** Sydney Chapman (1888–1970) was an early space-science pioneer and father of modern geomagnetic studies.

Geomagnetism corresponds to the natural fields within and around the Earth.

The field measurements correspond to a summation of all the natural fields that are at the place of measurement. There are many different sources of magnetic fields.

A **magnetic field** can be defined by the control that is exerted on certain substances near a magnet or a steady electric current. Of course, the word "near" is relative to the strength of the magnet or current.

At the place where a field exists, this control is measured by the force, having both a strength and a direction. The strength of this magnetic field decreases with the cube of the distance from the magnetic source.



**FIGURE 1.14**  $\blacktriangleright$  The strength of a field originating at a dipole magnet is shown to decrease rapidly with distance away from the magnet.

Two units were used for measuring how strong a magnetic field can be: **gamma** ( $\gamma$ ) and **SI unit** is the **Tesla** (T).

1 x 10<sup>-6</sup> T = 1 gamma

The Earth's main field varies from about 60,000 gammas in polar regions to about half this size near the equator.



**FIGURE 1.16** The size of magnetic fields originating from various sources. Note that the gamma (nanotesla) scale is logarithmic (meaning that each step upward is 10 times larger than the step below).

#### Introduction

The primary objective of paleomagnetic research is to obtain a record of past configurations of the geomagnetic field.

Paleomagnetism is a science with many applications in several domains such as the geomagnetism, tectonic, paleogeography, paleontology or sedimentology.

Thus, understanding paleomagnetism demands some basic knowledge of the geomagnetic field. We will begin by defining common terms used in geomagnetism and paleomagnetism,

#### Some basic defintions

#### 1) the magnetic field

Magnetic fields, like gravitational fields, cannot be seen or touched.

We know of the existence of magnetic fields by their effect on objects such as magnetized pieces of metal, naturally magnetic rocks such as lodestone, or temporary magnets such as copper coils that carry an electrical current.

Electric currents make magnetic fields, so we can define what is meant by a "magnetic field" in terms of the electric current that generates it.



Figure 1.1: a) Distribution of iron filings on a flat sheet pierced by a wire carrying a current i. b) Relationship of magnetic field to current for straight wire. [Iron filings picture from Jiles (1992).]

Figure 1.1a is a picture of what happens when we pierce a flat sheet with a wire carrying a current i.

When iron filings are sprinkled on the sheet, the iron filings line up with the magnetic field produced by the current in the wire. A circle tangential to the field is shown in Figure 1.1b, which illustrates the *right-handrule*.

If your right thumb points in the direction of (positive) current flow, your fingers will curl in the direction of the magnetic field.

The *magnetic field H* is perpendicular to both the direction of current flow and to the radial unit vector **r** in Figure 1.1b. The magnitude of **H** is proportional to the strength of the current i.

In the simple case, the magnitude of **H** is given by Ampere's law:  $\mathbf{H} = \mathbf{i} / 2\pi \mathbf{r}$  (in Am<sup>-1</sup>).

#### 2) The magnetic moment

If we bend the wire into a loop with an area  $\pi$  r<sup>2</sup> that carries a current i (Fig. 1.2a) the current loop creates the magnetic field shown by pattern of the the iron filings.

This magnetic field is the same as the field that would be produced by a magnet with a **magnetic moment M** (Fig. 1.2b) created by the current *i* and depending also on the area of the current loop (the bigger the loop, the bigger the moment):

 $\mathbf{M} = \mathbf{i} \, \mathbf{\pi} \, \mathbf{r}^2 \, (\text{in } \mathbf{A}\mathbf{m}^2)$ 

The moment created by a set of n loops (Fig. 1.2c) is the sum of the *n* individual loops so  $\mathbf{M} = \mathbf{n} \mathbf{i} \mathbf{\pi} \mathbf{r}^2$ .



Figure 1.2: a) Iron filings show the magnetic field generated by current flowing in a loop. b) The magnetic field of a current loop with current i and area  $\pi r^2$  is the same as one produced by a magnet with moment  $\mathbf{m}$ . c) The magnetic field of loops arranged as a solinoid is the sum of the contribution of the individual loops. [Iron filings pictures from Jiles (1992).]



Figure 1.1 (a) A magnetic dipole constructed from a pair of magnetic charges. The magnetic charge of the plus charge is *m*; the magnetic charge of the minus charge is –*m*; the distance vector from the minus charge to the plus charge is *I*. (b) A magnetic dipole constructed from a circular loop of electrical current. The electrical current in the circular loop is *I*; the area of the loop is *A*; the unit normal vector *n* is perpendicular to the plane of the loop. (c) Diagram illustrating the torque *Γ* on magnetic moment *M*, which is placed within magnetic field *H*. The angle between *M* and *H* is θ; *Γ* is perpendicular to the plane containing *M* and *H*.

**Magnetic field**, **H**, in a region is defined as the force experienced by a unit positive magnetic charge placed in that region. An experiment is to observe the aligning torque on a **magnetic dipole moment M** placed in a magnetic field (Figure 1.1c).

The aligning torque  $\Gamma$  is given by the vector cross product where  $\theta$  is the angle between **M** and **H** as in Figure 1.1c and  $\hat{\Gamma}$  is the unit vector parallel to  $\Gamma$  in Figure 1.1c.

 $\Gamma = M \times H = MH \sin \theta \hat{\Gamma}$ 

We can notice that the magnetic field is represented by the letter H or B but it is largely admitted that H is the magnetic field and B is the magnetic induction related to the magnetic field using the following equation:

 $\mathsf{B}=\mu_0~(\mathsf{M}+\mathsf{H})$ 

where  $\mu_0$  is known as the « **permeability of free space** » and corresponds to  $4\pi \times 10^{-7}$  henries/m (or H/m in SI unit) and **M** is the magnetization.

Parameter	SI unit	cgs unit	Conversion	
Magnetic moment (m)	$\mathrm{Am}^2$	emu	$1 \text{ A m}^2 = 10^3 \text{ emu}$	
Magnetization $(\mathbf{M})$	${\rm Am^{-1}}$	$ m emu~cm^{-3}$	$1 \text{ Am}^{-1} = 10^{-3} \text{ emu cm}^{-3}$	
Magnetic Field $(\mathbf{H})$	$\mathrm{Am}^{-1}$	Oersted (oe)	$1 \text{ Am}^{-1} = 4\pi \ge 10^{-3} \text{ oe}$	
Magnetic Induction (B)	Т	Gauss (G)	$1 T = 10^4 G$	
Permeability		1974 - 12		
of free space $(\mu_0)$	${\rm Hm^{-1}}$	1	$4\pi \ge 10^{-7} \text{ Hm}^{-1} = 1$	
Susceptibility $(\chi)$				
total $(\frac{\mathbf{m}}{\mathbf{H}})$	$m^3$	${ m emu} { m oe}^{-1}$	$1 \text{ m}^3 = \frac{10^6}{4\pi} \text{ emu oe}^{-1}$	
by volume $(\frac{\mathbf{M}}{\mathbf{H}})$	178	$\rm emu\ cm^{-3}\ oe^{-1}$	$1 \text{ S.I.} = \frac{1}{4\pi} \text{ emu cm}^{-3} \text{ oe}^{-1}$	
by mass $(\frac{\mathbf{m}}{m}, \frac{1}{\mathbf{H}})$	m <sup>3</sup> kg $^{-1}$	emu g $^{-1}$ o e $^{-1}$	$1 \text{ m}^3 \text{kg}^{-1} = \frac{10^3}{4\pi} \text{emu g}^{-1} \text{ oe}^{-1}$	
$H = \text{kg m}^2 \text{A}^{-2} \text{s}^{-2}, \ 1 \text{ emu} = 1 \text{ G cm}^3, \ B = \mu_o(H + M), \ 1 \text{ T} = \text{kg A}^{-1} \text{ s}^{-2}$				

Table 1.1: Conversion between SI and cgs units.

From Tauxe, 2005

#### 3) magnetic intensity or magnetization

The magnetization **M** (in the literature, J is also used instead of M) of a material submitted to a magnetic field **H** corresponds to a magnetic moment (**m**) per unit volume ( $Am^{-1}$ ) or per unit mass ( $Am^2kg^{-1}$ ) -> remember that m is in  $Am^2$ 

The magnetization corresponds to the total magnetization, which is the sum of two contributions:

#### M = Mi + Mr

where **Mi** is the **induced magnetization** represented by the equation :

#### $Mi = K \times H$

The induced magnetization is parallel to the magnetic field and a fucntion of the **bulk magnetic susceptibility K** (unitless) which represents the magnetization capacity of a substance submitted to a magnetic field. This magnetization disappears when the external magnetic field is stopped.

A material could possess a **remanent magnetization Mr** which is permanent even in the absence of an external magnetic field.

This remanent magnetization contains the paleomagnetic field which has affected the material in the past. This means that the direction of the geomagnetic field is recorded at the time of the magnetic mineral formation by the remanent magnetization.

#### 4) What are the different magnetization types: diamagnetism, paramagnetism and ferromagnetism

The classical theories of both diamagnetism and paramagnetism first appeared in 1905 in a paper by Paul Langevin (1872-1946). Diamagnetism is a property of all materials.

Fig. 2.1. Atomic magnetic moments in a solid. Moment orientation is random (a) and it varies from one instant to the other (b). The net magnetic moment is zero. In the presence of an external magnetic field H (c), a fraction of the moments is aligned with the field and the solid acquires an induced magnetization  $J_i$ 







#### 4.1.) Diamagnetism

The lowest response is called diamagnetism. It arises from the interaction of an applied magnetic field and the motion of electrons orbiting the nucleus.

It gives rise to a small induced magnetization in the opposite direction to the applied field, we said that it is antiparrallel.

For our purpose, the effect is so small that it can almost always be neglected. It is typically a hundred times smaller than paramagnetism and a hundred thousand times smaller than ferromagnetism.

Some materials present only a diamagnetic behaviour and correspond to all the organic molecules, water, acids, Pd, Zn, Cu, the aluminosilicates, kaolinite, the nobel gases (He, Ar, ...), ... etc.

The most important minerals in the sedimentary series, which have a diamagnetic behaviour are: quartz, halite and calcite. The rocks composed by a majority of this minerals will have a negative magnetic susceptibility (MS).



On a diagram plotting the **magnetization** (**M**, as ordinate) in fucntion of the **magnetic field** (**H**), we can notice that the MS is negative.

Diamagnetic minerals are independent of the temperature  $(T^{\circ}C)$  and have no remanence.

Quartz	-0,58 x 10 <sup>-8</sup> m³/kg
Calcite	-0,48 x 10 <sup>-8</sup> m³/kg
Eau	- 0,90 x 10 <sup>-8</sup> m³/kg
Kaolinite	-1,9 x 10 <sup>-8</sup> m³/kg

#### 4.2.) Paramagnetism

The paramagnetic materials placed in a magnetic field acquire a positive and parralell induced magnetization

When the applied magnetic field is removed, the magnetization returns to zero such as for the diamagnetic particles. These particles doesn't retain any remanence.

Paramagnetic minerals are those containing iron: most of the clay minerals (chlorite, smectite, illite, glauconite), siderite, ilmenite, biotite and pyrite. The rocks composed by a majority of these minerals will have a moderately positive MS.



On a diagram showing the evolution of the magnetization against the applied magnetic field, we can notice that MS is positive.

The paramagnetic minerals are dependent of the evolution of the temperature following the Curie law.

If the T° remains very low or the magnetic field is very high, the MS of paramagnetic particles is independent of the applied magnetic field. In these conditions, MS is proportionnal to the iron content.

## 4.2.) Paramagnetism

Dolomite	1.1 x 10 <sup>-8</sup> m³/kg
Chalcopyrite	3 x 10⁻ <sup>8</sup> m³/kg
Smectite	5 x 10 <sup>-8</sup> m³/kg
Montmorillonite	13 x 10 <sup>-8</sup> m³/kg
Illite	15 x 10 <sup>-8</sup> m³/kg
Pyrite	30 x 10 <sup>-8</sup> m³/kg
Lepidocrocite	50-69 x 10 <sup>-8</sup> m³/kg
Nontronite (Fe-rich)	65-86 x 10 <sup>-8</sup> m³/kg
Biotite	5-95 x 10⁻ <sup>8</sup> m³/kg
Siderite	100 x 10 <sup>-8</sup> m³/kg

Some of the common paramagnetic minerals present in the sedimentary series

#### 4.3.) Ferromagnetism (sensu lato)

The term ferromagnetism sensu lato corresponds to the materials possessing a remanent magnetization (Mr) even in the absence of an external magnetic field.

The interaction between the magnetic moments of atoms of a great numbers of domains produces a strong magnetization depending of the global position of all the magnetic moments in the ferromagnetic substances.

Four behaviour classes are represented from the highest to the smallest magnetization:





- ferromagnetism (sensu stricto) (the magnetic moments are parrallels and have the same intensities such as for iron). A remanence is present.

- **ferrimagnetism** (the magnetic moments are opposed and have different intensities such as magnetite and the monoclinic pyrrhotite). A remanence is observed.

- **antiferromagnetism** (the magnetic moments are opposed and parrallels such as for ilmenite and ulvospinel). No remanence observed.

- canted antiferromagnetism (the magnetic moments are opposed and subparrallel as for hematite) and a remanence is observed.

#### 4.3.) Ferromagnetism (sensu lato)

**Fig. 2.7.** Domain arrangement in a polycrystalline ferromagnetic material formed in the absence of a magnetic field. Each domain is spontaneously magnetized in its own easy direction



Fig. 2.8. Progressive spin moment rotation through a domain wall



The ferromagnetic minerals (s.l.) are rich in iron such as the iron oxides and hydroxides (magnétite, hématite, goethite, ulvospinel et titanomagnétite) and iron sulfides (pyrrhotite and greigite). Rocks composed by a majority of these minerals will have a positive and strong MS.

# The ferromagnetic minerals are characterized by a spontaneous magnetization and the existence of a magnetic ordering temperature.

A related term of the spontaneous magnetization is **the saturation magnetization** that could be measured in laboratory and corresponds to the maximal magnetization obtained for a given magnetic field. Above this field, there is no more increasing magnetization with an increasing magnetic field.

The saturation magnetization is T° dependent and independ ent of the particle size.



Big difference between ferromagnetic and paramagnetic susceptibility: the magnetization of ferromagnetic minerals is saturated for moderate magnetic field and for high TC.

	Hsat (Tesla)	T°range (C)	MS 10 <sup>-8</sup> m³/kg
Paramagnetic	> 10	<< 100	~ 50
Ferromagnetic	~ 1	~ 300	1000 -10 000



For the **ferromagnetic** (s.s.), canted antiferromagnetic and ferrimagnetic minerals, a temperature increase induces a thermal expansion which will progressively destroy the alignment of the magnetic moments. They are completely destroyed at the **Curie T**° (critical T° different for each mineral).

Above the Curie T°, these minerals will have a paramagnetic behaviour. In general, the process is reversible during the cooling.

For the **antiferromagnetic minerals**, the absence of resulting magnetic moment cannot achieved a Curie T°.

In that case, the alignment of the magnetic moment is completely destroyed at the **Néel T**° Above this critical T°, they have a paramagnetic behaviour.

Ms returns back to zero at the Curie T° as indicated by the diagram with the Curie T° of 575°C for magnetite.

Oxides	Composition	Type of magnetism	T℃ ( <b>Curie</b> or Néel)	Ms (10 <sup>3</sup> Am <sup>-1</sup> )
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	ferrimagnetic	575-585	480
Ulvospinel	Fe <sub>2</sub> TiO <sub>2</sub>	AFM	-153	
Hematite	aFe <sub>2</sub> O <sub>3</sub>	canted AFM	675	2.5
Ilmenite	FeTiO <sub>2</sub>	AFM	-233	
Maghemite	γFe <sub>2</sub> O <sub>3</sub>	ferrimagnetic	590-675 (~ 600)	380
Jacobsite	MNFe <sub>2</sub> O <sub>4</sub>	ferrimagnetic	300	77
Trevorite	NiFe <sub>2</sub> O <sub>4</sub>	ferrimagnetic	585	51
Magnesioferrite	MgFe <sub>2</sub> O <sub>4</sub>	ferrimagnetic	440	21

Sulfides	Composition	Type of magnetism	T℃ ( <b>Curie</b> ou Néel)	Ms (10 <sup>3</sup> Am <sup>-1</sup> )
Pyrrhotite	Fe <sub>7</sub> S <sub>8</sub>	ferrimagnetic	320	~ 80
Greigite	Fe <sub>3</sub> S <sub>4</sub>	ferrimagnetic	~330	~ 125
Troilite	FeS	AFM	305	

FM: ferromagnetic type AFM: antiferromagnetic type – no remanence Canted AFM: canted antiferromagnetic type Ms: saturation magnetization at ambient T°C

Oxyhydroxides	Composition	Type of magnetism	T℃ ( <b>Curie</b> or Néel)	Ms (10 <sup>3</sup> Am <sup>-1</sup> )
Goethite	αFeOOH	AFM, weak FM	~ 120	2
Lepidocrocite	γFeOOH	AFM (?)	-196	
Feroxyhyte	δFeOOH	ferrimagnetic	~ 180	
Metals & Alliages				
Iron	Fe	FM	765	1715
Nickel	Ni	FM	358	484
Cobalt	Со	FM	1131	1422
Awaruite	Ni <sub>3</sub> Fe	FM	620	120
Wairauite	CoFe	FM	986	235

FM: ferromagnetic type AFM: antiferromagnetic type – no remanence Ms: saturation magnetization at room T°C



Figure 2.1 (a) Magnetization, J, versus magnetizing field, H, for a diamagnetic substance. Magnetic susceptibility, χ, is a negative constant. (b) J versus H for a paramagnetic substance. Magnetic susceptibility, χ, is a positive constant. (c) J versus H for a ferromagnetic substance. The path of magnetization exhibits hysteresis (is irreversible), and magnetic susceptibility, χ, is not a simple constant.
### 5) The Magnetic Susceptibility (MS)

The **magnetic susceptibility** is a measure of the capacity of a rock to be magnetized when placed in a magnetic field. This capacity is related to their constituents so **it's a function of the magnetic mineralogy**, **and the concentration and size of their magnetic grains**.

The MS have a range of values from negative ones (for quartzites for example) to very high positive values (>  $10^{-5}$  m<sup>3</sup>/kg) for iron ores. The measured MS corresponds to the contribution of the three different group of magnetic minerals (dia-, para- and ferromagnetic).

We can use the **volumic** (on a standard volumic cylinder of 10 cm<sup>3</sup>) or the **massic** MS (samples weighted with a precision of 0.01 g) susceptibility.

$$X_{vol} = (V_0/V_s) \times X_{tot} \times 10^{-6} \times c$$

$$X_{mass} = (V_0/m_s) \times X_{tot} \times 10^{-6} \times c$$

where  $X_{vol}$  is the volumic MS  $X_{mass}$  is the massic MS  $V_0$  is the standard volume of 10 cm<sup>3</sup>  $V_s$  is the volume of the sample  $m_s$  is the mass (g) of the sample c is an automatically determined coefficient of correction

and  $X_{meas}$  is the MS of the samples  $X_{hold}$  is the MS of the plastic holder

$$X_{tot} = X_{meas} - X_{hold}$$

- In low-field (< 1 mT), the different contributions (dia-, para- and ferromagnetic s.l.) are independent of the intensity of the applied magnetic field. MS in low-field is thus constant (linear) and integrate all the minerals of the rock.

MS is called **low-field magnetic susceptibility or X<sub>LF</sub>** and corresponds to the general MS measurements.

- In high-field (0.1–3 T), the ferromagnetic grains are dependent of the intensity of the applied field and will tend to the saturation (nonlinear). When saturated, the ferromagnetic minerals will not participate in the MS any more. The MS in high-field integrates only the dia- and paramagnetic contributions.

MS is called high-field magnetic susceptibility or X<sub>HF</sub>

So, we can calculate the ferromagnetic susceptibility ( $X_{Ferro}$ ) using the equation below

 $X_{Ferro} = X_{LF} - X_{HF}$ 

Practically in the sedimentary series, we can measure the MS :

- in laboratory equipment using rock chips (for silicoclastic or carbonate rocks) or with parrallelipipedic rock fragment used to make thin sections

- directly on the field using a portable susceptibilimeter

Apparatus for measuring the Magnetic Susceptibility (MS), the Anisotropy of the Magnetic Susceptibility (ASM) and thermomagnetic susceptibility measurements (TMS) at the Geological Survey of Belgium



Measuring unit Control with the thermomagnetic sensor of the thermo

Control Unit (CS3) of the thermomagnetic sensor

# Model MFK1-A Spinner Kappabridge with a CS-3 Furnace apparatus produced by AGICO

We must notice to prevent against metallic interference during the measurements, the apparatus is placed on a wood table and wood chairs are used.

# SM-30 Susceptibilimeter of Zhinstruments used at the GSB



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MEASURED ROCK Sensivity of 1 x 10<sup>-7</sup> SI units



MS2K – probe de Bartington instruments



Sensivity < 2 x 10<sup>-5</sup> SI units



# 6) A first approach on the magnetic mineralogy using the thermomagnetic susceptibility measurements (TSM)

To obtain some information on the magnetic grains for a size not frequently > 1  $\mu$ m but decreasing down to 30 nm, optical microscopy are not useful anymore. Only more elaborated techniques such as the use of the SEM or TEM equipments are really useful but need to proceed to magnetic extraction.

Some methods of rock magnetism study are very sensitive to the composition and grain size of the magnetic minerals (hysteresis loops – see next chapter). Other techniques dealing with the Curie temperature are only dependent of the composition (e.g. OReilly, 1984).

To determine the Curie T<sup>°</sup>, the most used method consists to measure the evolution of the **induced magnetization in a high field against the temperature** ( $^{\circ}$ C) that will be reported as a **thermomagnetic curve** (e.g. Housden et al., 1988).

In a similar way, we can measure the variation of the magnetic susceptibility in function of the temperature evolution (from negative T° to positive T°).

### These techniques will give the first insights in term of magnetic mineralogy.

The bulk susceptibility in low field is typically measured in the range between ambient T<sup>o</sup>up to 700°C (with a furnace in argon gas environment) and between ambient T<sup>o</sup> down to -192°C (with a cryogenic module using liquid nitrogen).

The induced magnetization (M) in high field is realized in the same range of  $T^{\circ}$ .

-> The analysis of the thermomagnetic curves gives usually the Curie T°as the only quantitative parameter.

-> The reversibility or not of the curves during heating and cooling phases could only be examined qualitatively.



Fig. 1. High-field induced thermomagnetic curve for sample STA-14, showing irreversible alteration but similar values of magnetisation  $M_i(T)$  at 100 °C. Alteration factors R100 and IP are explained in the text.

A method developped by Sherwood et al. (1993) suggests to measure a parameter related to the alteration and the change of mineralogical composition in order to determine the relation between alteration and paleointensity variations.

The alteration is defined by the ratio R100 of the induced magnetization (Mi) corresponding to the Mi values during heating and cooling phases.

For example:

an alterated sample STA-14 but the ratio R100 is close to 1 which is quite good but we can that the curves are really different (two CT values during heating and only one during cooling).

This problem is solved by the AGICO product (software) that determine a similar parameter of alteration (A40). This parameter corresponds to the ratio of the MS value at  $40^{\circ}$  during heating and cooling phases.

A second parameter is used: the ratio **A(max)** indicates the T° for which the difference between MS value during heating and cooling phases is the most important (maximum).



Givetian sample from the Pic de Vissoux section



**PB38** shows a TSM curve characterized by higher positive TSM values (>15) with a clear drop in the curve with a Curie T° close to 320°C. This could reveals the presence of probably pyrrhotite (?). The presence of a small peak around 500°C and the highest TSM values during cooling indicate the formation of new ferrimagnetic mineral resulting from unstable paramagnetic grains at T°>400°C.

### Givetian sample from the Pic de Vissoux section



**PB44** shows a TSM curve characterized by positive TSM values (>7) with a small drop in the curve close to the Curie T° of 580°C corresponding to magnetite minerals. The cooling curve has higher TSM values (>40) which indicates the creation of ferromagnetic s.l. minerals.

This profile reveal the presence of magnetite (?) grains in the sample.

### Givetian sample from the Pic de Vissoux section



**PB58** shows a TSM curve characterized by higher positive TSM values (= 15) with a clear drop in the curve with a Curie T<sup> $\circ$ </sup> close to 320<sup> $\circ$ </sup>C. This could reveals the presence of "pyrrhotite – Ti-rich magnetite or Ti-rich hematite". The presence of a small drop also close to Curie T<sup> $\circ$ </sup> of 680<sup> $\circ$ </sup>C could indicate the presence of hematite grains in the sample.

This profile reveal the presence of hematite grains in the sample and another ferromagnetic s.l. phase.

### Givetian sample from the Sourd d'Ave section



### 7) Magnetic mineralogy using hysteresis loops

In addition to the Curie temperature and saturation magnetization, ferromagnetic minerals can retain a memory of an applied field once it is removed. This behavior is called **hysteresis or magnetic hysteresis** and a plot of **the variation of magnetization with magnetic field is called a hysteresis loop**.

### **Description of a hysteresis loop:**

- when a ferromagnetic material (s.l.), at an initial demagnetized state, is placed in an applied magnetic field (H or B), the sample will follow the magnetization curve from the origin as indicated in the diagram.

- (**part a of the curve**) if the magnetic field increase from zero, the magnetization will increase linearly at the beginning. So if the magnetic field is removed (return to zero), the process is reversible and M came back also to zero. The slope of this part of the curve correspond to the initial magnetic susceptibility or the low-field magnetic susceptibility ( $X_{LF}$ ).

- if the magnetic field continues to increase, the slope of the curve will increase also (**part b of the curve**) and at that point if the magnetic field is stopped the M will not return to zero but M will follow the way c (**part c of the curve**) and a **Isothermal Remanent Magnetization (IRM)** will be given by the value Mr.

- a new increase of the magnetic field above the end of the part b of the curve will **tend to the saturation** (characterized by the **point d on the curve**). After that point, the magnetization will never increase again with an increasing magnetic field. A **saturation magnetization Ms** will be given for a saturated magnetic field (Hsat or Bsat).

- by reducing the magnetic field to zero, the magnetization will decrease (and follow the **part e of the curve**) to the saturation remanent magnetization Mrs. When applying a magnetic field in the opposite direction, M will continue decreasing to zero. **This point corresponds to the coercive force Bc.** 



Fig. 2.5. Initial magnetization curve and hysteresis loops (M-B loops) for a ferromagnetic substance.

- a new decrease of the magnetic field value, the sample will reach again the saturation magnetization for a negative magnetic field (-Hsat or –Bsat). On this curve, there is a point where the removal of the magnetic field implies that magnetization will return directly to zero at the origin. This point corresponds to the remanence coercivity Mrs.

- the hysteresis curve is reversible and symmetric during a new cycle of increasing H. Again the saturation magnetization for the same positive magnetic field (Hsat) is achieved and a **complete hysteresis loop** is obtained.

- If the real saturation magnetization of all the magnetic minerals is not achieved, the real hysteresis loop could be higher but the samples need necessarily to be placed in a higher magnetic field using more powerfull magnetometers allowing to produce a magnetic field of 2.5 T for example instead of 500 mT (J-Coercivity meter) or 1 T (AGF Magnetometer of Princeton) in common magnetometers.









Figure 8.6: Hysteresis loops of end-member behaviors: a) diamagnetic, b) paramagnetic, c) superparamagnetic (data for submarine basaltic glass), d) uniaxial, single domain, e) magnetocrystalline, single domain, f) "pseudo-single domain".



Figure 8.7: Hysteresis behavior of various mixtures: a) magnetite, and hematite, b) SD/SP magnetite (data from Tauxe et al. 1996), c) another example of SD/SP magnetite.

It's also possible to determine the **high-field magnetic susceptibility** ( $X_{HF}$ ) from the slope of the hysteresis curve at high-field. The high-field curve slope is normalized by the sample mass and then converted in a high-field magnetic susceptibility  $X_{HF}$  (m<sup>3</sup>/kg) multiplying it by the magnetostatic constant ( $\mu_0 = 4\pi \times 10^{-7} \text{ T/Am}^{-1}$ ).

The  $X_{HF}$  is only controlled by the dia- and paramagnetic contributions so it's possible to calculate the **ferromagnetic susceptibility** ( $X_{Ferro}$ ) by subtracting the high-field MS from the low-field MS that includes all the magnetic contributions (dia-, para- and ferro-) through the following equation:

$$X_{Ferro} = X_{LF} - X_{HF}$$

The ferromagnetic susceptibility deals only with the ferromagnetic s.l. contribution.

#### CHANNELL AND McCABE: MAGNETIC HYSTERESIS IN LIMESTONES



Hysteresis loops diamagnetic slopes

Figure 2. Hysteresis loops from Maiolica limestone showing (a) diamagnetic slopes and (b) the same data after slope correction.



#### CHANNELL AND McCABE: MAGNETIC HYSTERESIS IN LIMESTONES

Hysteresis loops paramagnetic slopes

Figure 3. Hysteresis loops from Maiolica limestone showing (a) paramagnetic slopes and (b) the same data after slope correction.



Hysteresis loops ferromagnetic slopes

Figure 8. Hysteresis loops for white (above) and pink (below) Scaglia limestone. Color codes from Munsell color chart.

### **IRM curve**

A remanence acquired by short-term exposure to a strong magnetic field, generated by an electromagnet and usually at room-temperature, is an **isothermal remanent magnetization (IRM)**.

IRM is the form of remanence produced in hysteresis experiments and is acquired by ferromagnetic grains with coercive force less than the applied field.

If the field used to impart an IRM is sufficient to achieve saturation, we speak of **saturation isothermal remanence magnetization (SIRM)**, which is equivalent to Mrs.

 $\rightarrow$  [**Be warned**, however, that the acronym SIRM is often used to represent the remanence acquired by a sample after exposure to the highest field available to a particular investigator. This is usually on the order of 1 T and may, or may not, actually reach true saturation. The coercivity spectrum obtained by incremental IRM acquisition is a powerful - and popular - laboratory technique].

An instrument can measure the field dependence of both induced and remanent magnetization simultaneously in one experiment (Burov *et al.,* 1986; Jasonov *et al.,* 1998). This so-called **coercivity meter** is based on simple induction principles when a 1 cm<sup>3</sup> sample (powder or parallelipipedic rock stick) housed on a nonmagnetic rotation disk is spun between the pole tips of an electromagnet (*see next slide*).

IRM coercivity spectra are extremely well documented, allowing spectral analysis and modeling (Robertson and France, 1994; Eyre, 1996; Kruiver *et al.*, 2001; Egli, 2003).

# The J-Meter Coercivity Spectrometer allows measuring magnetic hysteresis loop, IRM acquisition spectrum and viscosity spectrum in 6 minutes.

The main element of the J-meter is a **pulse magnetometer.** A sample moving at a high speed is placed near the rim of a 50 cm diameter plexiglas disk which rotates 18 times/sec through the pole pieces of an electromagnet.

Both the induced and remanent magnetization are measured during each rotation of the disk.

**Induced magnetization for hysteresis loops are measured with a set of pick-up coils.** The magnetic field is continuously changed and monitored, and the induced magnetization is measured inside the electromagnets by a first induction coil and the **remanent magnetization is measured outside the electromagnets** by a second induction coil. A large number (up to 10,000 readings) of remanent and induced magnetization values may be recorded in one run up to the maximum field (Bmax = 500 mT) and to the corresponding backfield.

The remanence channel offers a sensitivity of 2 x  $10^{-3}$  Am<sup>-1</sup> and induced magnetization is measured down to 2 x  $10^{-2}$  Am<sup>-1</sup>.

The J meter is called a coercivity spectrometer because it is particularly well suited to measuring the IRM acquisition curve with sufficient sensitivity and resolution to take the derivative which defines the coercivity spectrum.

To finish each measurement, the magnetic field is cut to zero and the viscous demagnetization is monitored for 100s, mostly following a log(time) relationship but with perturbations determined by the grain size distribution of the finest grains.

A suite of analysis programs have been developed to determine hysteresis parameters and Sratios, and to characterize coercivity and viscosity spectra.



The J-Meter Coercivity Spectrometer allows measuring magnetic hysteresis loop, IRM acquisition spectrum and viscosity spectrum in 6 minutes.

(RMI, Dourbes)





### 8) Day Plot diagrams

Four hysteresis parameters (Ms, Mrs, Bc, Bcr) were deduced and calculated from the hysteresis loop. *Ms* and *Mrs* were obtained after correction of the high-field slope.

The **« Day plot »** diagrams allow to determine the grain size of the ferromagnetic grains (magnetite, titanomagnetite ..) which can be distributed in four different magnetic domains.

A magnetized ferromagnetic particle is subdivided into small regions in which the magnetization is uniform but the magnetization vector within each region is different from their neighbours. **These regions are called** *magnetic domains and separated by domain walls*.

Four main magnetic domains were defined:

- mineral grains containing one magnetic monodomain are **single-domain** (**SD**) particles, characterized by finegrained sizes (**50-100 ηm for magnetite**) with an homogeneous magnetization,

- mineral grains containing many domains are called **mutidomain** (MD) particles, characterized by coarsegrained sizes (around 1 µm for magnetite)

- mineral grains containing several domains are called **pseudo-single-domain** (**PSD**) particles, characterized by intermediate grained sizes (> 100 ηm for magnetite) with a strong remanence,

- **superparamagnetic particle** (**SP**), for ultra-fine grained particles (**around 30 ηm for magnetite**). The rock will present an unstable remanence close to paramagnetism and a strong MS value.



Fig. 2.16. Magnetic domains; a in a single domain grain (SD) all spin moments are mutually parallel; b,c a multi-domain grain (MD) is subdivided into a certain number of magnetized domains to minimize magnetostatic energy, which is further reduced if closure domains (d) are formed along the surface of the grain



Take in mind that magnetic mineralogy is frequently associated to mixtures of minerals or mixtures of different grain sizes particles of magnetite for example.

The Day Plot diagram (Mrs/Ms ratio vs Bcr/Bc ratio) was originally published by Day et al. (1977) and subdivided into three different regions related to specific domains : SD, PSD and MD.



**Figure R15** The Day plot classifies hysteresis curves in terms of the grain size sensitive quantities  $M_{rs}/M_s$  and  $B_{cr}/B_c$ . For magnetite and titanomagnetites the shown grain size classes have been originally defined in Day *et al.* (1977) and recently revised by Dunlop (2002a). The indicated theoretical trends for mixtures are taken from Dunlop (2002a) and Lanci and Kent (2003). While in case of the extensive quantities  $M_{rs}$  and  $M_s$  normalization is necessary to remove the volume dependence, using the ratio of the intensive quantities  $B_{cr}$  and  $B_c$  intends to remove dependencies of these quantities upon mineral composition. Exemplary hysteresis loops are shown inset. Loops are centered on the respective  $M_{rs}/M_s$  and  $B_{cr}/B_c$  values. Black: calculated synthetic loops. Gray: hysteresis loops of synthetic magnetite samples measured with an alternating gradient field magnetometer (maximum field 300mT).

The domain limits have been updated by Dunlop (2002) and correspond to :

(1) a MD domain defined for Mrs/Ms ratio  $\leq$  0.05 and a Bcr/Bc ratio  $\geq$  5.0,

(2) a SD domain defined for Mrs/Ms ratio  $\geq$  0.5 and a Bcr/Bc ratio  $\leq$  2.0,

(3) a new domain appears in relation with the SP particles for  $0.1 \le Mrs/Ms \le 0.5$  and Bcr/Bc > 100.



Figure 2. Theoretical Day plot curves calculated for magnetite using the equations developed in section 2. Detailed explanations of individual curves are given in the text. Numbers along curves are volume fractions of the soft component (SP or MD) in mixtures with SD grains.



**Figure 2.7** Day plot illustrating the effect of a binary mixture of single-domain (SD) and multidomain (MD) particles. The samples involved are lake sediments from Minnesota. (Modified from Dunlop, 2002b.)





Figure 14. Logarithmic plot of (a) hysteresis data from Figure 13, and (b) these hysteresis data compared with data from varicolored Scaglia, Ammonitico Rosso, and Corniola limestones (R is the linear correlation coefficient).



### Magnetic mineralogy

### 9) Magnetic mineralogy

The main magnetic minerals (iron and titanium bearing minerals) are reported on the ternary diagram on the right.

Three solid solution series are common in igneous rocks:

- between magnetite and ulvospinel corresponding to **titanomagnetite series**.

- between hematite and ilmenite corresponding to **titanohematite series**.

- between ferropseudobrookite and pseudobrookite corresponding to pseudobrookite series (allways paramagnetic)



Fig. 2.6. FeO-TiO<sub>2</sub>.-Fe<sub>2</sub>0<sub>3</sub> ternary system showing the three principal solid solution series found in igneous rocks. Members of the pseudobrookite series are all paramagnetic above liquid oxygen temperatures and therefore have little significance for remanence. Approximate Curie (or Néel) temperatures for various values of mole function x and y (at 0.1 intervals) are indicated for the titanomagnetite and titanohematite series respectively. After Merrill and McElhinny (1983).

**Table 2.2.** Properties of common ferromagnetic minerals Symbols:  $T_c(T_n) = \text{Curie}$  (Néel) temperature;  $J_s = \text{saturation magnetization}$ ;  $B_c = \text{maximum coercivity}$ 

Mineral		$T_{\rm c} \left( T_{\rm n} \right) (^{\circ}{\rm C})$	J <sub>s</sub> (kA m <sup>-1</sup> )	<i>B</i> <sub>c</sub> (T)
Oxides				
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	575	480	0.3
Maghemite	γ-Fe <sub>2</sub> O <sub>3</sub>	590 – 675	380	0.3
Hematite	a-Fe <sub>2</sub> O <sub>3</sub>	675	2.5	1–5
Goethite	α-FeOOH	60 - 130	2	>5
Sulfides				
Pyrrhotite	FeS <sub>1+x</sub>	≤320	80	0.5–1
Greigite	Fe <sub>3</sub> S <sub>4</sub>	330	125	0.03

### **Magnetic mineralogy**

a)

### Magnetite

For each unit cell there are four tetrahedral sites (A) and eight octahedral sites (B). To maintain charge balance with the four oxygen ions ( $O^{2-}$ ), there are two Fe<sup>3+</sup> ions and one Fe<sup>2+</sup> ion.

In sediments, magnetite often occurs as a detrital component, but it can also be produced by bacteria or authigenically during diagenesis.

#### Titanomagnetite

They can occur as primary minerals in igneous rocks. It should be noted that natural titanomagnetites often contain impurities (usually Al, Mg, Cr).

These impurities also affect the magnetic properties.

Substitution of 0.1 Al<sup>3+</sup> into the unit cell of titanomagnetite results in a 25% reduction in *Ms* and a reduction of the Curie temperature by some 50 °C.





Fe304 (magnetite)



Figure 4.1: a) A magnetite octahedron. b) Internal crystal structure. Big red dots are the oxygen anions. The blue dots are iron cations in octahedral coordination and the yellow dots are in tetrahedral coordination.  $Fe^{3+}$  sits on the A sites and  $Fe^{2+}$  and  $Fe^{3+}$  sit on the B sites.

### Le magnétisme des roches

### In soils or in sediments, magnetite can be produced by magnetotactic bacteria



Figure 6.13: Photomicrographs of bacterial magnetites produced by magnetotactic bacteria. a) Intact magnetosome in living bacterium. (Fassbinder et al., 1990.) b) Chains recovered from ODP Site 1006D in the Bahamas (Hounslow in Maher and Thompson, 1999).



Chains of magnetosomes extracted from magnetotactic bacteria (60x35 nm)
#### Hematite

Hematite has a corundum structure. It is rhombohedral with a pseudocleavage and tends to break into flakes.

Hematite occurs widely in oxidized sediments and dominates the magnetic properties of red beds. It occurs as a high temperature oxidation product in certain igneous rocks. Depending on grain size, among other things, it is either black (specularite) or red (pigmentary).

#### **Goethite** (antiferromagnetic)

It occurs widely as a weathering product of iron-bearing minerals and as a direct precipitate from ironbearing solutions.

It is metastable under many conditions and dehydrates to hematite with time or elevated temperature. Dehydration is usually complete by about 325°C.

It is characterized by a very high coercivity but a low Néel temperature of about 100-150°C.



Figure 6.3: Hematite. a) photograph of specularite. b) Crystal structure of hematite. c) same as b) but rotated 90°.

#### **Iron-sulfides**

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There are two iron-sulfides that are important to paleomagnetism: greigite (Fe_3S_4) and pyrrhotite (Fe_7S_8-Fe_{11}S_{12}).
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These are ferrimagnetic and occur in reducing environments. They both tend to oxidize to various iron oxides leaving paramagnetic pyrite as the sulfide component.

The Curie temperature of monoclinic pyrrhotite (Fe7S8) is about 325℃



Figure 6.11: Thermomagnetic curves for a) monoclinic b) hexagonal and c) mixture of a) and b) pyrrhotite. (After Dekkers, 1988)

### Le magnétisme des roches



Gravity core from the Black Sea with limic (black greigite banding) and marine sapropel (Eemian) sequences. (© 2009, Max Planck Institute for Marine Microbiology)

#### Le magnétisme des roches



SEM images from uplifted Late Miocene (6 to 10 million year-old) sediments from New Zealand (from a webblog).

Pyrite is often found in marine sediments, and it often has the 'framboidal' texture that you can see in the image above, where the cubic pyrite crystals are arranged into larger spheres ('framboid' is derived from 'framboise', the French for raspberry).

Pyrite formation occurs in the anoxic lower regions of the sediment column, where sulphate-reducing bacteria extract energy from buried organic matter by converting sulphate (SO4) to sulphide (H2S), which then reacts with detrital iron minerals to form pyrite. Firstly, one of the detrital iron minerals being dissolved during this process is magnetite; if sulphate reduction is intense enough, the concentration of magnetite within the sediment can be reduced by an order of magnitude or more.

#### Summary of the main magnetic characteristics of the different ferromagnetic *s.l.* minerals

Magnetite	$\rm Fe_3O_4$
Density = 5197 kg m <sup><math>-3</math></sup>	Dunlop and Özdemir [1997]
Curie temperature = $580^{\circ}$ C	Dunlop and Özdemir [1997]
Saturation Magnetization = 92 $Am^2kg^{-1}$	O'Reilly [1984]
Anisotropy Constant = $-2.6 \text{ Jkg}^{-1}$	Dunlop and Özdemir [1997]
Volume susceptibility = $\sim 1 \text{ SI}$	O'Reilly [1984]
Typical coercivities are 10's of mT	O'Reilly [1984]
Verwey transition: 110-120 K	Özdemir and Dunlop [1993]
Cell edge = $0.8396$ nm	Dunlop and Özdemir [1997]

Maghemite	$\gamma \mathrm{Fe_2O_3}$
Density = $5074 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Curie temperature = $590-675^{\circ}C$	Dunlop and Özdemir [1997]
Saturation Magnetization = $74 \text{ Am}^2 \text{kg}^{-1}$	Dunlop and Özdemir [1997]
Anisotropy Constant = $0.92 \text{ Jkg}^{-1}$	Dunlop and Özdemir [1997]
Verwey transition: suppressed	Dunlop and Özdemir [1997]
Breaks down to $\alpha \text{Fe}_2\text{O}_3$ : between 250 $\rightarrow$ 750°C	Dunlop and Özdemir [1997]

Hematite	$ m lpha Fe_2O_3$
Density = $5271 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Néel temperature = $675^{\circ}C$	O'Reilly [1984]
Saturation Magnetization = $0.4 \text{ Am}^2 \text{kg}^{-1}$	O'Reilly [1984]
Anisotropy Constant $= 228 \text{ Jkg}^{-1}$	Dunlop and Özdemir [1997]
Volume susceptibility = $\sim 1.3 \ge 10^{-3} \text{ SI}$	O'Reilly [1984]
Coercivities vary widely and can be 10's of teslas	Banerjee [1971]
Morin Transition: $\sim 250-260$ K (for $> 0.2 \ \mu m$ )	O'Reilly [1984]

TM60	$Fe_{2.4}Ti_{0.6}O_4$
Density = $4939 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Curie temperature = $150^{\circ}$ C	Dunlop and Özdemir [1997]
Saturation Magnetization = $24 \text{ Am}^2 \text{kg}^{-1}$	Dunlop and Özdemir [1997]
Anisotropy Constant = $0.41 \text{ Jkg}^{-1}$	Dunlop and Özdemir [1997]
$ m Coercivity \sim 8 \ mT$	Dunlop and Özdemir [1997]
Verwey transition: suppressed	Dunlop and Özdemir [1997]
Cell edge = $0.8482$ nm	Dunlop and Özdemir [1997]

Pyrrhotite	$\mathrm{Fe}_{7}\mathrm{S}_{8}$
$Density = 4662 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Monoclinic:	
Curie temperature $= \sim 325^{\circ}C$	Dekkers [1989a]
Hexagonal:	
Curie temperature $= \sim 270^{\circ}$ C	Dekkers [1988]
Saturation Magnetization = $0.4 \sim 20 \text{ Am}^2 \text{kg}^{-1}$	Worm et al. [1993]
Volume susceptibility = $\sim 1 \ge 10^{-3} \rightarrow 1 \text{ SI}$	Collinson [1983];O'Reilly [1984]
Anisotropy Constant = $20 \text{ Jkg}^{-1}$	O'Reilly [1984]
Coercivities vary widely and can be 100's of mT	O'Reilly [1984]
Has a transition at $\sim$ 34 K	Dekkers et al. [1989]
	Rochette et al. [1990]
Hexagonal pyrrotite: transition near $200^{\circ}$	(2) (2)(2)
Breaks down to magnetite: $\sim 500^{\circ}\mathrm{C}$	Dunlop and Özdemir [1997]

Greigite	$\rm Fe_3S_4$
Density = $4079 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Maximum unblocking temperature = $\sim 330^{\circ}$ C	Roberts [1995]
Saturation Magnetization = $\sim 25 \text{ Am}^2 \text{kg}^{-1}$	Spender et al. [1972]
Anisotropy Constant = $-0.25 \text{ Jkg}^{-1}$	Dunlop and Özdemir [1997]
Coercivity $60 \rightarrow > 100 \text{ mT}$	Roberts [1995]
Has high $M_r/\chi$ ratios ~ 70 x 10 <sup>3</sup> Am <sup>-1</sup>	Snowball and Thompson [1990]
Breaks down to magnetite: $\sim 270-350^{\circ}C$	Roberts [1995]

Goethite	$\alpha$ FeOOH
Density = $4264 \text{ kg m}^{-3}$	Dunlop and Özdemir [1997]
Néel temperature: $70 \rightarrow 125^{\circ}C$	O'Reilly [1984]
Saturation Magnetization = $10^{-3} \rightarrow 1 \text{ Am}^2 \text{kg}^{-1}$	O'Reilly [1984]
Anisotropy Constant = $0.25 \rightarrow 2 \text{ Jkg}^{-1}$	Dekkers [1989]
Volume susceptibility = $\sim 1 \ge 10^{-3} \text{ SI}$	Dekkers [1989]
Coercivities can be 10's of teslas	0. <b>2</b> 2 5 <b>4</b>
Breaks down to hematite: $250 \rightarrow 400^{\circ}C$	

## The end – stay magnetized

Thank you so much for not sleeping