Lectures in Paleomagnetism, 2005
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Citation:
http://earthref.org/MAGIC/books/Tauxe/2005/

May 31, 2005

Chapter 6

Magnetic Mineralogy

Suggested Reading
For background:
Chapter 3 in Evans and Heller (2003)
To learn more:
Chapter 3 in Dunlop and Özdemir (1997)

6.1 Introduction

An essential part of every paleomagnetic study is a discussion of what is carrying the magnetic remanence and how the rocks got magnetized. For this, we need some knowledge of what the important natural magnetic phases are, how to identify them, how they are formed, and what their magnetic behavior is. In this lecture, we will cover a brief description of geologically important magnetic phases. Useful magnetic characteristics of important minerals can be found in Table 6.1.

Because iron is by far the most abundant transition element in the solar system, most paleomagnetic studies depend on the magnetic iron species: the iron-nickels (which are particularly important for extra-terrestrial magnetic studies), the iron-oxides such as magnetite, maghemite and hematite, the iron-oxyhydroxides such as goethite, and the iron-sulfides such as greigite and pyrrhotite. We are concerned here with the latter three since iron-nickel is very rare in terrestrial paleomagnetic studies.

6.2 Iron-oxides

Two solid solution series are particularly important in paleomagnetism: the ulvöspinel-magnetite and ilmenite-hematite series as shown on the ternary diagram in Figure 6.1. The apices of the ternary diagram are Fe^{2+} on the lower left, Fe^{3+} on the lower right and Ti^{4+} on the top. The oxides with these species are FeO (wustite), Fe_2O_3 (hematite or maghemite depending on structure) and TiO (rutile). Every point on the triangle represents a cation mixture or solution that adds up to one cation (hence the fractional formulae). Each of the solid arrows in Figure 6.1 (labelled Titanomagnetite and Hemoilmenite) represent increasing substitution of titanium into the crystal lattices of magnetite and hematite respectively. The amount of Ti substitution in titanomagnetites is denoted by "x", while substitution in the hemoilmenites is denoted by "y". Values for x and y range from 0 (magnetite or hematite) to 1 (ulvöspinel or ilmenite).

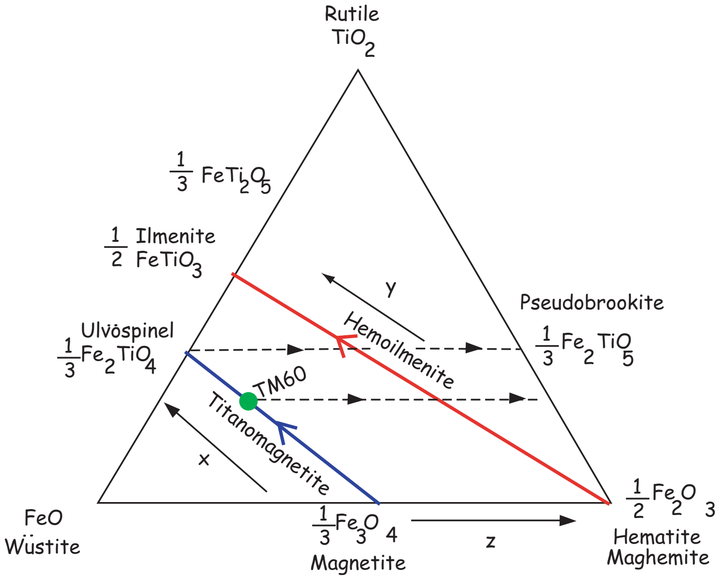

Figure 6.1: Ternary diagram for iron-oxides (modified from O'Reilly [1984]). The dashed lines with arrows indicate the direction of increasing oxidation (z). The solid lines are solid solution series.

Titanomagnetites $\mathbf{Fe}_{3-x}\mathbf{Ti}_x\mathbf{O}_4$

In earlier lectures on rock magnetism, we learned a few things about magnetite. As mentioned in Lecture 4, magnetite (Fe_3O_4) has an inverse spinel structure (AB_2O_4). The oxygen atoms form a face-centered cubic lattice into which cations fit in either octahedral or tetrahedral symmetry. 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^{3+} ions and one Fe^{2+} ion. Fe^{3+} has five unpaired spins, while Fe^{2+} has four. As discussed earlier, each unpaired spin contributes one Bohr magneton ($\mathbf{m}_b$). The divalent iron ions all reside in the octahedral lattice sites, whereas the trivalent iron ions are split evenly between octahedral and tetrahedral sites: $Fe^{3+}|Fe^{3+}Fe^{2+}|O_4$. The A and B lattice sites are coupled with antiparallel spins and magnetite is ferrimagnetic. Therefore, the net moment of magnetite is (9-5=4) $\mathbf{m}_b$ per molecule (at 0 K).

Titanomagnetites can occur as primary minerals in igneous rocks. Magnetite, as well as various members of the hemoilmenite series, can also form as a result of high temperature oxidation. In sediments, magnetite often occurs as a detrital component, but it can also be produced by bacteria or authigenically during diagenesis.

Substitution of Ti^{4+}, which has no unpaired spins (see Lecture 3), has a profound effect on the magnetic properties of the resulting titanomagnetite. Ti^{4+} substitutes for a trivalent iron ion. In order to maintain charge balance, another trivalent iron ion turns into a divalent iron ion. The end members of the solid solution series are:

magnetite	ulvöspinel
$Fe^{3+}\|Fe^{3+}Fe^{2+}\|O_4$	$Fe^{2+}\|Fe^{2+}Ti^{4+}\|O_4$
$x = 0$	$x = 1$

Ulvöspinel is antiferromagnetic because the A and B lattice sites have the same net moment. When x is between 0 and 1, the mineral is called a titanomagnetite. If x is 0.6, the mineral is called

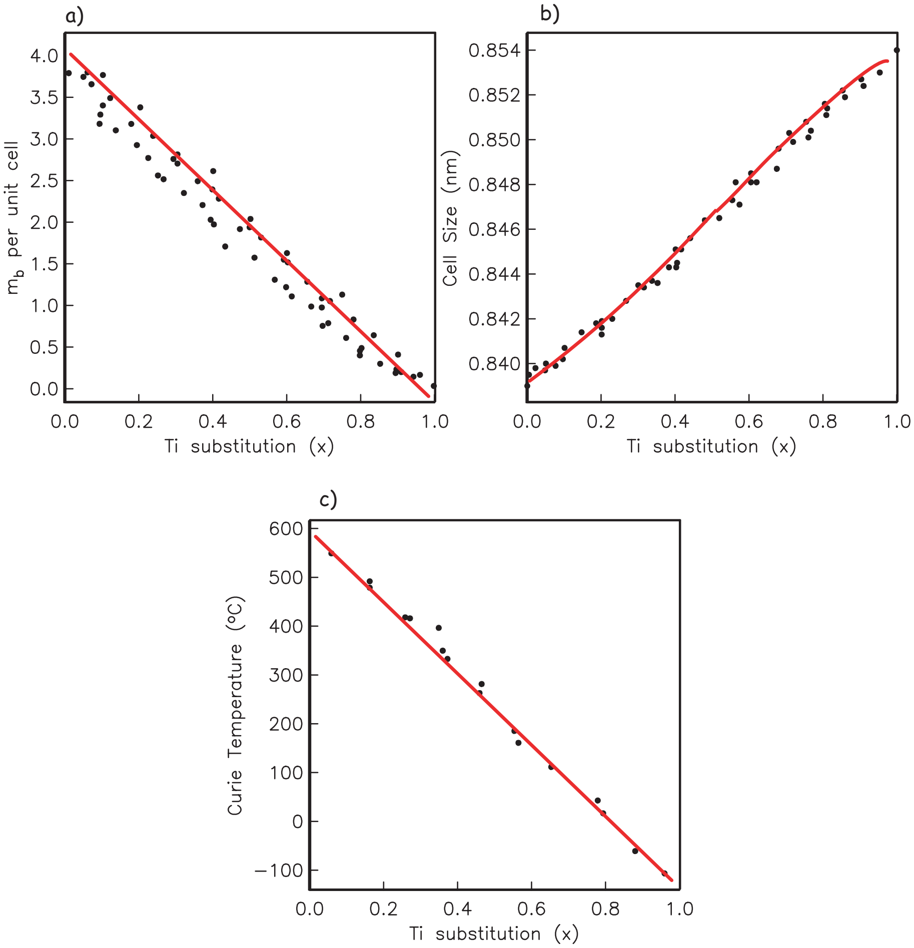

Figure 6.2: Variation of intrinsic parameters with titanium substitution in the titanomagnetite lattice. X is the degree of substitution from 0 (no Ti) to 1 (100% substitution). a) Variation of the magnetization expressed as Bohr magnetons per unit cell. b) Variation of cell lattice size. c) Variation of Curie temperature. (Data compiled by O'Reilly [1984].)

TM60.

The profound effect of titanium substitution on the intrinsic properties of titanomagnetite is illustrated in Figure 6.2. Because Ti^{4+} has no unpaired spins, the saturation magnetization decreases with increasing x (Figure 6.2a). The cell dimensions increase with increasing x (Figure 6.2b). As a result of the increased cell dimension, there is a decrease in Curie Temperature (Figure 6.2c). There is also a slight increase in coercivity (not shown).

The large M_s of magnetite (see Table 6.1) means that for deviations from equant grains as small as 10%, the magnetic anisotropy energy becomes dominated by shape. Nonetheless, aspects of the magnetocrystalline anisotropy provide useful diagnostic tests. The magnetocrystalline anisotropy constants are a strong function of temperature. On warming to ∼-100°C from near absolute zero, changes in these constants can lead to an abrupt loss of magnetization, which is known loosely as the *Verwey transition* (see Lecture 4). Identification of the Verwey transition suggests a remanence that is dominated by magnetocrystalline anisotropy. Furthermore the temperature at which it

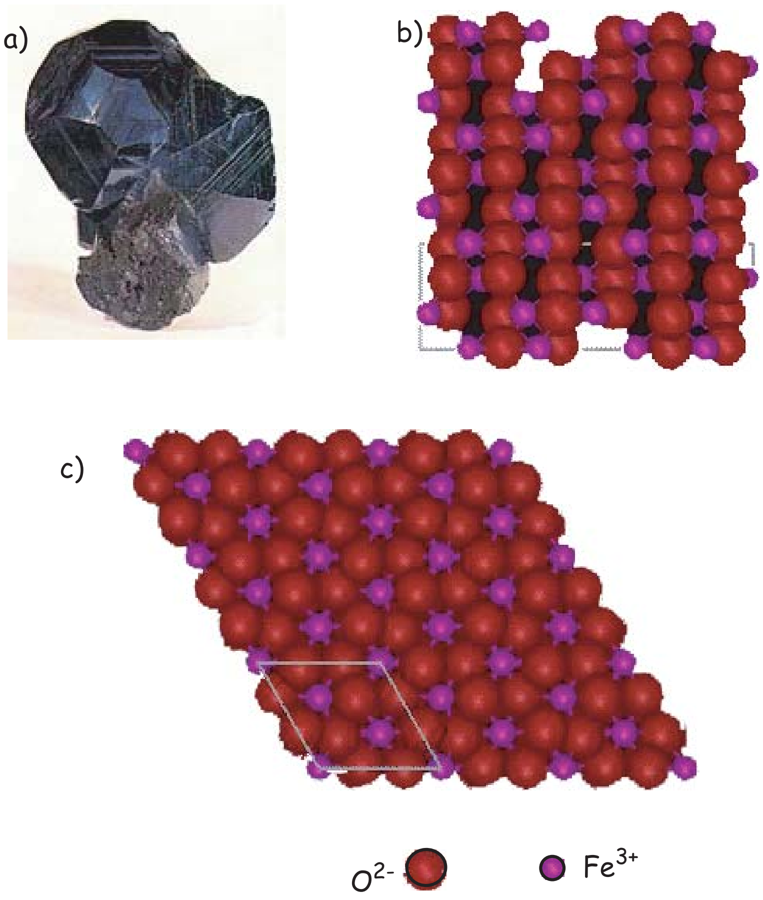

Figure 6.3: Hematite. a) photograph of specularite. b) Crystal structure of hematite. c) same as b) but rotated 90°.

occurs is sensitive to oxidation and the transition can be completely supressed by maghemitization (see Dunlop and Özdemir [1997]).

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^{3+} into the unit cell of titanomagnetite results in a 25% reduction in M_s and a reduction of the Curie temperature by some 50°C. Substitution of Mg^{2+} into TM60 also results in a lower saturation magnetization with a reduction of some 15%.

6.2.1 *Hematite-Ilmenite* $Fe_{2-y}Ti_yO_3$

Hematite has a corundum structure (see Figure 6.3). It is rhombohedral with a pseudocleavage (perpendicular to the c axis) and tends to break into flakes. It is antiferromagnetic, with a weak parasitic ferromagnetism resulting from either spin-canting or defect ferromagnetism (see Lecture 3). Because the magnetization is a spin canted antiferromagnetism, the temperature at which this magnetization disappears is called the Néel Temperature instead of the Curie Temperature which is *sensu strictu* only for ferromagnetic minerals. The Néel temperature for hematite is approximately

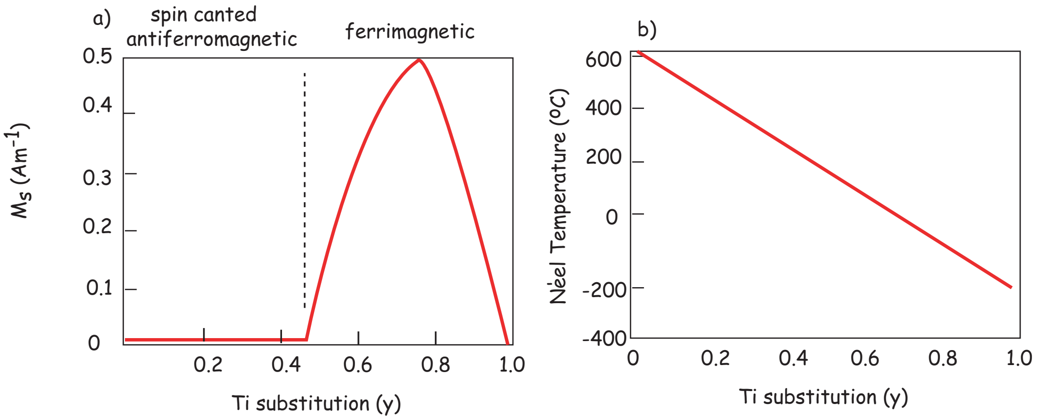

Figure 6.4: Variation of properties with Ti substitution in the titanohematite series. a) Variation of saturation magnetization. b) Variation of Nèel Temperature. (Redrawn from Butler, 1992).

685°C.

Above about -10°C (the *Morin transition*), the magnetization is constrained by aspects of the crystal structure to lie perpendicular to the c axis or within the basal plane. Below the Morin transition, spin-canting, but disappears and the magnetization is parallel to the c axis. This effect could be used to demagnetize the grains dominated by spin-canting: it does not affect those dominated by defect moments. Most hematites formed at low-temperatures have magnetizations dominated by defect moments, so the remanence of many rocks will not display a Morin transition.

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). Diagnostic properties of hematite are listed in Table 6.1.

The substitution of Ti into the lattice structure of αFe_2O_3 has an even more profound influence on magnetic properties than for magnetite. For $y = 0$ the magnetization is spin-canted antiferromagnetic, but when $y = 0.45$, the magnetization becomes ferrimagnetic (see Figure 6.4a). For small amounts of substitution, the Ti and Fe cations are distributed equally among the cation layers. For $y > 0.45$, however, the Ti cations preferentially occupy alternate cation layers. Remembering that the Ti^{4+} ions have no net moment, we can imagine that antiparallel coupling between the two sub-lattices results in ferrimagnetic behavior, as opposed to the equal and opposite style of anti-ferromagnetism.

6.2.2 Solid solution series

Above about 600°C, there is complete solid solution between magnetite and ülvospinel as well as between hematite and ilmenite along the two tracks in Figure 6.1. As the temperature goes down, ilmenite and titanohematite can exolve out of the crystals forming crystals with Ti-rich and Ti-poor lamellae (see Figure 6.5). Exolution is inhibited if the crystals cool rapidly so there are many metastable crystals with intermediate values of x or y in nature. A very common composition for magnetites in the ocean crust is 60% substituted with Ti. This is called TM60 (green dot in Figure 6.1.

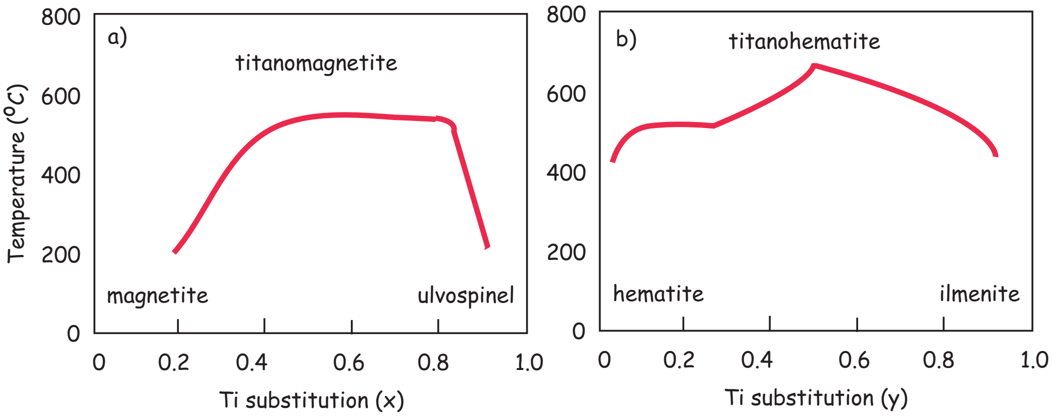

Figure 6.5: Phase diagrams for FeTi oxides. The composition is indicated by x or y. There is complete solid solution above the solid lines. Exolution begins as the temperature cools below the solid curves. a) Titanomagnetite series. b) Titanohematite series. (Redrawn from Dunlop and Özdemir, 1997).

Titanohematite particles with intermediate values of y have interesting properties from a paleomagnetic point of view. There is a solid solution at high temperatures, but as the temperatures drop the crystals exsolve into titanium rich and poor lamellae (see Figure 6.6). Figure 6.4 shows the variation in saturation magnetization and Néel temperature with Ti substitution. For certain initial liquid compositions, the exolution lamellae could have bands Ti-rich bands alternating with Ti-poor bands. If the Ti-rich bands have higher magnetizations, yet lower curie temperatures than the Ti-poor bands, the Ti-poor bands will become magnetized first. When the curie temperature of the Ti-rich bands is reached, they will become magnetized in the presence of the demagnetizing field of the Ti-poor bands, hence they will acquire a remanence that is antiparallel to the applied field. Because these bands have higher magnetizations, the net NRM will also be anti-parallel to the applied field and the rock will be *self-reversed*. This is fortunately very rare in nature.

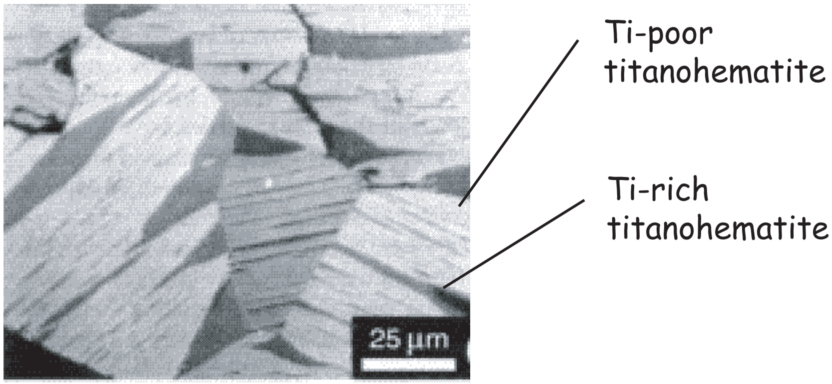

Figure 6.6: Photomicrograph of titanohematite exolution lamellae. Dark bands are Ti-rich (high magnetization, low T_c), light grey bands are Ti-poor (low magnetization, high T_c). (Modified from Maher and Thompson, 1999.)

6.2.3 Oxidation of (titano)magnetites to (titano)maghemites

Many minerals form under one set of equilibrium conditions (say within a cooling lava flow) and are later subjected to a different set of conditions (sea-floor alteration or surface weathering). They will tend to alter in order to come into equilibrium with the new set of conditions. Because the new conditions are often more oxidizing than then original conditions, compositions tend to move along the dashed lines in Figure 6.1. The degree of oxidation is represented by the parameter z.

While the solid solution between magnetite and ulvöspinel exists in principle, intergrowths of these two minerals are actually quite rare in nature because the titanomagnetites interact with oxygen in the melt to form intergrowths of low Ti magnetite with ilmenite. This form of oxidation is known as “deuteric” oxidation.

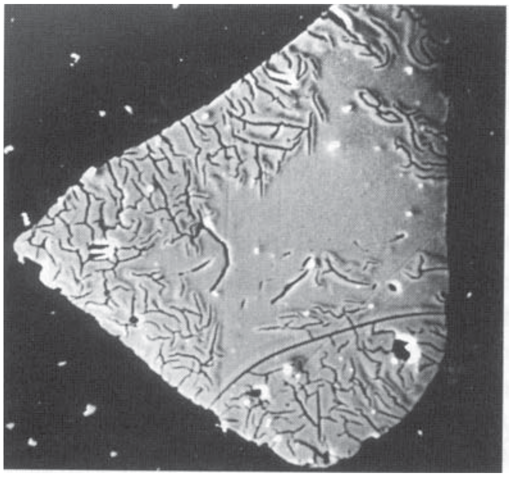

Figure 6.7: A magnetite crystal ($\sim 30\ \mu$m) undergoing maghemitization. Because of the change in volume, the crystal begins to crack. (From Gapeyev and Tsel’movich, 1988).

Low temperature oxidation will tend to transform a single phase spinel (titanomagnetite) into a new single phase spinel (titanomaghemite) by diffusion of Fe^{2+} from the lattice structure of the (titano)magnetite to the surface where it is converted to Fe^{3+}; titanomaghemite is a “cation-deficient” inverse spinel. Figure 6.7 shows a magnetite crystal in the process of becoming maghemite. The conversion of the Fe^{2+} ion means a loss in volume which results in characteristic cracking of the surface. There is also a loss in magnetization, a shrinkage of cell size and along with the tightening unit cell, an increase in Curie Temperature. These trends are shown for TM60 in Figure 6.8. Maghematization results in a much reduced Verwey transition (see Figure 6.9).

The (titano)maghemite structure is metastable and can invert to form the isochemical, but more stable structure of (titano)hematite, or it can be reduced to form magnetite. The two forms of Fe_2O_3 are distinguished by the symbols γ for maghemite and α for hematite. Inversion of natural maghemite is usually complete by about 350°C, but it can survive until much higher temperatures (for more details, see Dunlop and Özdemir, 1997). Also, it is common that the outer rim of the magnetite will be oxidized to maghemite, while the inner core remains magnetite.

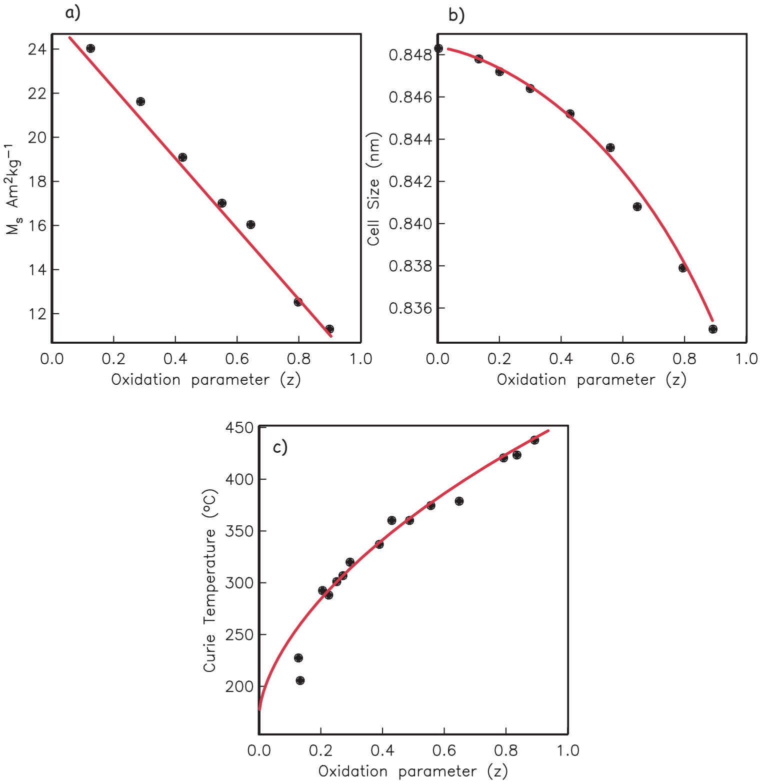

Figure 6.8: Variation of intrinsic parameters with oxidation in TM60. z is the degree of oxidation. a) Variation of the magnetization. b) Variation of cell lattice size. c) Variation of Curie temperature. (Data compiled by Dunlop and Özdemir [1997].)

6.3 Iron-oxyhydroxides and iron-sulfides

Of the many iron oxyhydroxides that occur in any abundance in nature, goethite (αFeOOH)is the most common magnetic phase. It is antiferromagnetic with what is most likely a defect magnetization. It occurs widely as a weathering product of iron-bearing minerals and as a direct precipitate from iron-bearing 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. Diagnostic properties of goethite are listed in Table 6.1.

There are two iron-sulfides that are important to paleomagnetism: greigite (Fe_3S_4) and pyrrhotite (Fe_7S_8-$Fe_{11}S_{12}$). 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 (Fe_7S_8) is about 325°C (see Figure 6.11a; Table 6.1). Monoclinic pyrrhotite undergoes a transition at $\sim$ 35 K, so low temperature measurements can be diagnostic for this phase (see Figure 6.10). Hexagonal pyrrhotite undergoes a structural transition from an imperfect antiferromagnet to a ferromagnet with much higher saturation magnetization at about 200°C. During a thermomagnetic experiment, the expansion of the crystal results in a large peak in magnetization just below the Curie Temperature (see Figure 6.11b). Mixtures of monoclinic and hexagonal pyrrhotite result in the behavior sketched in see Figure 6.11c. The

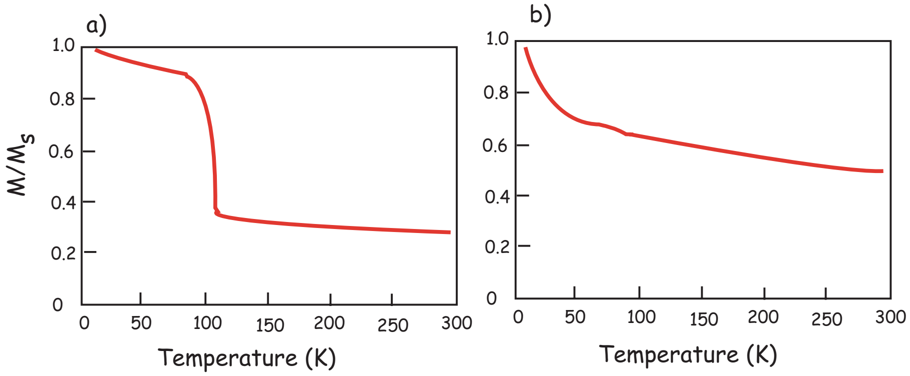

Figure 6.9: Effect of maghemitization on Verwey transition. a) Saturation remanence acquired at 10 K observed as it warms up for 37 nm soichiometric magnetite. b) Same but for partially oxidized magnetite. (Data from Özdemir et al., 1993).

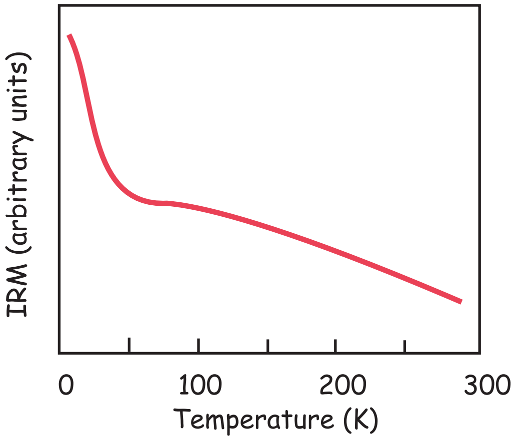

Figure 6.10: Low-temperature transition in monoclinic pyrhotite. (After Snowball and Torrii, 1999).

maximum unblocking temperature of greigite is approximately 330°C. Other diagnostic properties of greigite and pyrrhotite are listed in Table 6.1.

6.4 Occurence and alteration of FeTi oxides in igneous rocks

The composition and relative proportions of FeTi oxides, crystallizing from a silicate melt depend on a number of factors, including the bulk chemistry of the melt, oxygen fugacity and the cooling rate. The final assemblage may be altered after cooling. FeTi oxides are generally more abundant in mafic volcanic rocks (e.g. basalts) than silicic lavas (e.g., rhyolites). FeTi oxides can be among the first liquidus phases ($\sim$ 1000°C) in silicic melts, but in mafic lavas they generally are among the last phases to form ($\sim$1050°C), often with plagioclase and pyroxene.

Although there is considerable variability, the Ti (ulvöspinel) content of the titanomagnetite crystallizing from a melt generally is lower in more silicic melts (see solid black lines in Figure 6.12). Titanomagnetites in tholeiitic lavas generally have $0.5 < x < 0.8$ with an initial composition near

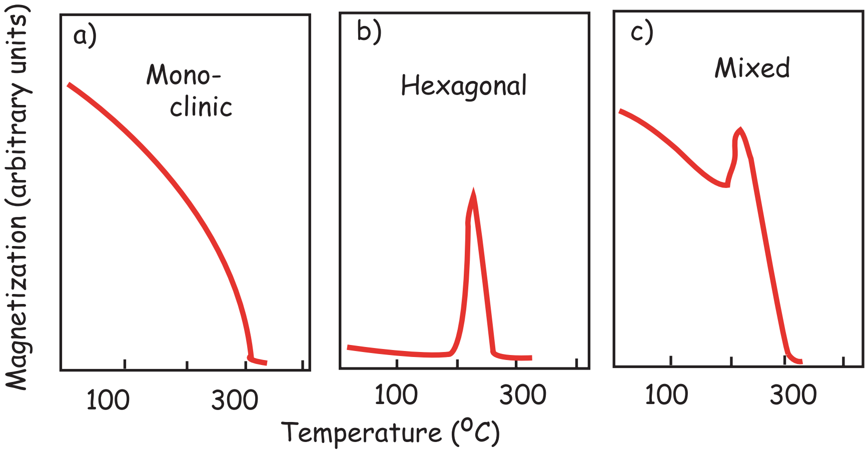

Figure 6.11: Thermomagnetic curves for a) monoclinic b) hexagonal and c) mixture of a) and b) pyrrhotite. (After Dekkers, 1988)

TM60 (x=0.6) characteristic for much of the oceanic crust. The range of rhombohedral phases (dashed red lines) crystallizing from silicate melts is more limited, $0.05 < y < 0.3$ for most lavas.

The final magnetic mineral assemblage in a rock is often strongly influenced by the cooling rate and oxygen fugacity during initial crystallization. As a first approximation, we distinguish slowly cooled rocks (which may undergo solid state exsolution and/or deuteric oxidation) from those in which the oxide minerals were rapidly quenched. As mentioned before, FeTi oxides in slowly cooled igneous rocks can exhibit exolution lamellae with bands of low and high titanium magnetites if the oxygen fugacity remains unoxidizing. This reaction is very slow, so its effects are rarely seen in nature.

The typical case in slowly cooled rocks is that the system becomes more oxidizing with increasing differentiation during cooling and crystallization. For example, both the dissociation of magmatic water and the crystallization of silicate phases rich in Fe will act to increase the oxidation state. This will drive compositions to higher z values (see Figure 6.1). The final assemblage typically consists of ilmenite lamellae and a nearly pure magnetite host because adding O_2 drives the reaction $Fe_2TiO_4 + O_2 \rightleftharpoons Fe_3O_4$ to the right. This process is known as *oxyexsolution*. Under even more oxidizing conditions, these phases may ultimately be replaced by their more oxidized counterparts (e.g., hematite, pseudobrookite).

Weathering at ambient surface conditions or mild hydrothermal alteration may lead to the development of cation deficient (titano)maghemites. This can either occur by addition of oxygen to the spinel phase with a corresponding oxidation of the Fe^{2+} to Fe^{3+} to maintain charge balance, or by the removal of some of the octahedral iron from the crystal structure.

6.5 Magnetic mineralogy of soils and sediments

Igneous rocks are the ultimate source for the components of sedimentary rocks, but biological and low-temperature diagenetic agents work to modify the igneous components and have a significant effect on magnetic mineralogy in sediments. As a result there is a virtual rainbow of magnetic mineralogies found in sediments. (Titano)magnetite coming into the sedimentary environment from an

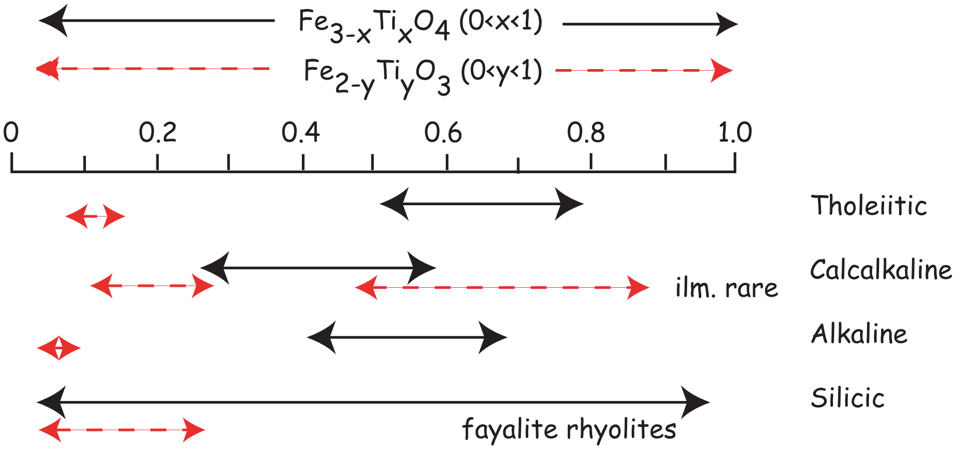

Figure 6.12: Occurence of FeTi oxides in igneous rocks. (Data from Frost and Lindsley, 1991).

igneous source may experience a change in pH and redox conditions that make it no longer the stable phase, hence may alter. Also, although the geochemistry of seawater is generally oxidizing with respect to the stability field of magnetite, pronounced changes in the redox state of sediments often occur with increasing depth as a function of the breakdown of organic carbon. Such changes may result in locally strongly reducing environments where magnetite may be dissolved and authigenic sulfides produced. Indeed, changes down sediment cores in the ferrimagnetic mineral content and porewater geochemistry suggest that this process is active in some marine sedimentary sequences. For example, dissolution of magnetite and/or production of non-magnetic sulfides may be responsible for the oft-seen decrease in various bulk magnetic parameters (e.g., magnetic susceptibility, IRM, ARM, etc.) with depth.

Some of the more spectacular magnetic minerals found in sediments are biogenic magnetites produced by magnetotactic bacteria (see Figure 6.13). The sizes and shapes of bacterial magnetite, when plotted on the Evans diagram from Lecture 3, suggest that magnetotactic bacteria form magnetite in the single domain grain size range - otherwise extremely rare in nature. It appears that bacterial magnetites are common in sediments, but their role in contributing to the natural remanence is still poorly understood.

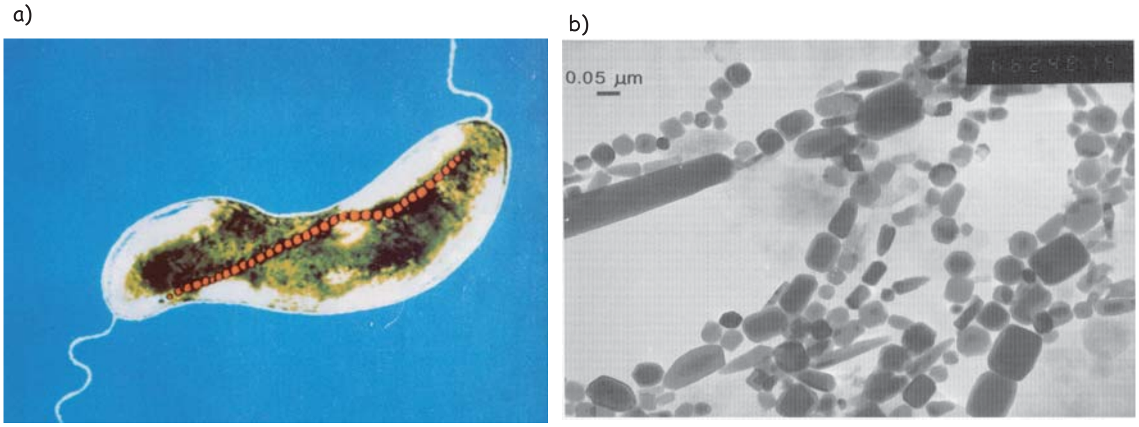

Figure 6.13: Photomicrographs of bacterial magnetites produced by magnetotactic bacteria. a) Intact magnetosome in living bacterium. (Fassbinder et al., 1990.) b) Chains recovered from ODP Site 1006D in the Bahamas (Hounslow in Maher and Thompson, 1999).

Table 6.1: Physical properties of magnetic minerals.

Magnetite	Fe_3O_4
Density = 5197 kg m^{-3}	Dunlop and Özdemir [1997]
Curie temperature = 580°C	Dunlop and Özdemir [1997]
Saturation Magnetization = 92 Am^2kg^{-1}	O'Reilly [1984]
Anisotropy Constant = -2.6 Jkg^{-1}	Dunlop and Özdemir [1997]
Volume susceptibility = $\sim$ 1 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	γFe_2O_3
Density = 5074 kg m^{-3}	Dunlop and Özdemir [1997]
Curie temperature = 590-675°C	Dunlop and Özdemir [1997]
Saturation Magnetization = 74 Am^2kg^{-1}	Dunlop and Özdemir [1997]
Anisotropy Constant = 0.92 Jkg^{-1}	Dunlop and Özdemir [1997]
Verwey transition: suppressed	Dunlop and Özdemir [1997]
Breaks down to αFe_2O_3: between 250→ 750°C	Dunlop and Özdemir [1997]
TM60	$Fe_{2.4}Ti_{0.6}O_4$
Density = 4939 kg m^{-3}	Dunlop and Özdemir [1997]
Curie temperature = 150°C	Dunlop and Özdemir [1997]
Saturation Magnetization = 24 Am^2kg^{-1}	Dunlop and Özdemir [1997]
Anisotropy Constant = 0.41 Jkg^{-1}	Dunlop and Özdemir [1997]
Coercivity $\sim$ 8 mT	Dunlop and Özdemir [1997]
Verwey transition: suppressed	Dunlop and Özdemir [1997]
Cell edge = 0.8482 nm	Dunlop and Özdemir [1997]
Hematite	αFe_2O_3
Density = 5271 kg m^{-3}	Dunlop and Özdemir [1997]
Néel temperature = 675°C	O'Reilly [1984]
Saturation Magnetization = 0.4 Am^2kg^{-1}	O'Reilly [1984]
Anisotropy Constant = 228 Jkg^{-1}	Dunlop and Özdemir [1997]
Volume susceptibility = $\sim 1.3 \times 10^{-3}$ 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]

Table 1 - continued

Goethite	αFeOOH
Density = 4264 kg m^{-3}	Dunlop and Özdemir [1997]
Néel temperature: 70 → 125°C	O'Reilly [1984]
Saturation Magnetization = $10^{-3} \rightarrow 1$ Am^{2}kg^{-1}	O'Reilly [1984]
Anisotropy Constant = $0.25 \rightarrow 2$ Jkg^{-1}	Dekkers [1989]
Volume susceptibility = $\sim$ 1 x 10^{-3} SI	Dekkers [1989]
Coercivities can be 10's of teslas	
Breaks down to hematite: 250 → 400°C	
Pyrrhotite	Fe_7S_8
Density = 4662 kg m^{-3}	Dunlop and Özdemir [1997]
Monoclinic:	
Curie temperature = $\sim$ 325°C	Dekkers [1989a]
Hexagonal:	
Curie temperature = $\sim$270°C	Dekkers [1988]
Saturation Magnetization = 0.4 -$\sim$ 20 Am^{2}kg^{-1}	Worm et al. [1993]
Volume susceptibility = $\sim$ 1 x $10^{-3} \rightarrow 1$ SI	Collinson [1983];O'Reilly [1984]
Anisotropy Constant = 20 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°	
Breaks down to magnetite: $\sim$ 500°C	Dunlop and Özdemir [1997]
Greigite	Fe_3S_4
Density = 4079 kg m^{-3}	Dunlop and Özdemir [1997]
Maximum unblocking temperature = $\sim$ 330°C	Roberts [1995]
Saturation Magnetization = $\sim$ 25 Am^{2}kg^{-1}	Spender et al. [1972]
Anisotropy Constant = -0.25 Jkg^{-1}	Dunlop and Özdemir [1997]
Coercivity 60$\rightarrow>$ 100 mT	Roberts [1995]
Has high M_r/χ ratios $\sim$ 70 x 10^3 Am^{-1}	Snowball and Thompson [1990]
Breaks down to magnetite: $\sim$ 270-350°C	Roberts [1995]

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