Today's Schedule

Magnetism of Solids
Exchange Forces and Magnetic Ordering in Minerals
Antiferromagnetism
Ferrimagnetism

Magnetic Minerals

Magnetic Characterization of Magnetic Minerals (Part I)

Paramagnetism: Molecular Field Theory and Exchange Interactions

Curie Law of Paramagnetism
\[ \chi = \frac{C}{T} \]

Curie-Weiss Law of Paramagnetism
\[ \chi = \frac{C}{T - \theta} \]

Assume a Molecular field acts on the magnetic ions ($H_m$ is very large)

Produced by interactions between electron 'neighbors':

Total field acting on an internal "molecular" moment:

\[ H = H_a + \lambda M \]

Ferromagnetism

Curie Temperature

$T < T_c$ Paramagnetism

$T > T_c$ Ferromagnetism

The interaction constant from Curie-Weiss Law can be:

$\theta = 0$ paramagnetism unpaired spins independent (Curie-Law)

$\theta > 0$ ferromagnetism unpaired spins align parallel

$\theta < 0$ antiferromagnetism unpaired spins align antiparallel

Magnetic Ordering Temperature ($T_c$, Curie Temperature)

Fe$_3$O$_4$: 580°C
Fe: 780°C
Ni: 358°C
Co: 1121°C

$T > T_c$ Curie-Weiss law

Magnetic Ordering Temperature

Magnetite octahedra from Cerro Huanaquino, Bolivia.

Magnetite 50 nm

Large magnetic moments in low magnetic fields (< 1 T) and high temperatures (300K)

Spontaneous (saturation) Magnetization ($M_s$, $B_s$ = 0)

Fe$_3$O$_4$: 480 kA/m
Fe: 1700 kA/m
Paramagnet: <1 A/m

Magnetic Ordering Temperature ($T_c$, Curie Temperature)

Fe$_3$O$_4$: 580°C
Fe: 780°C
Ni: 358°C
Co: 1121°C

$T > T_c$ Curie-Weiss law

Shape of M-H curve

Shape of M-T curve

Molecular Field Theory and Exchange Interactions

The interaction constant from Curie-Weiss Law can be:

$\theta = 0$ paramagnetism unpaired spins independent (Curie-Law)

$\theta > 0$ ferromagnetism unpaired spins align parallel

$\theta < 0$ antiferromagnetism unpaired spins align antiparallel

Ferromagnetism $T < T_c$

Paramagnetism $T > T_c$

Lowrie, 2007
**Weiss Molecular Field Theory of Ferromagnetism**

Start with Langevin Equation for M(T,H)

\[ M = M_0 L \left( \frac{\mu B}{kT} \right) \]

Assume a molecular field dependent on M

\[ H_x = wM \]

Total field \( H = H_x + H_m \)

Magnetization exists even when \( H_x = 0 \) and \( T < T_c \)

\[ M = M_0 L \left( \frac{\mu w M}{kT} \right) \]

\[ \alpha = \left( \frac{\mu w M}{kT} \right) \gg 1, \quad M(H = 0) = M_0 \]

**Antiferromagnetism**

\( T > T_c \)

\( x = \frac{C}{T - \theta} \)

**Ferromagnetism**

\( T < T_c \)

\( x = \frac{C}{T - \theta} \)

*Curie Temperature*

Slope of line at \( T = T_c = \) slope of Langevin Function at origin

\[ M = \frac{KT}{\mu w M}, \quad \frac{\partial M}{\partial \alpha} = \frac{KT}{\mu \mu w} \]

\[ \lim_{\alpha \to 0} L(\alpha) = \alpha / 3, \quad \frac{\partial M}{\partial \alpha} = M_0 / 3 \]

\[ T = \frac{\mu w M}{3k} \]

**Magnitude of Molecular Field at 0 K**

\[ H_m = wM_0 = \frac{3kT}{\mu \mu w}, \quad w \propto kT \]

Fe: \( T_c = 1063 \) K, \( \mu = 2.2 \mu_B \)

\( H \sim 10^6 \) A/m, \( B \sim 1000 \) T

Field is much larger than that produced by magnetic dipole-dipole interaction between spins \( (a = \) lattice spacing, \( \sim 0.3 \) nm)

\[ \frac{H_0}{a^3} \sim 10^9 \) A/m (0.1 T)
Ferromagnetism

Theory of Ferromagnetism must explain

Large magnetic moments in low magnetic fields (< 1 T) and high temperatures (300K)
Spontaneous (saturation) Magnetization (M≠0, B=0)

Fe₃O₄ 480 kA/m
Fe 1700 kA/m
Paramagnet <1 A/m

Weiss Domains: How to explain the demagnetized state
Magnetic Domains and Walls

Some ways to image domains
Bitter patterns
Magnetic Force Microscopy
Magneto optic Kerr effect

Quantum Theory of Magnetically Ordered Materials

The source of the molecular field is exchange interactions between overlapping electron orbitals resulting in:

1. Direct Exchange between neighboring electron spins
2. Superexchange between unpaired electrons spins couple through covalent interactions with intervening ligand (e.g. O2)

Exchange Forces

Exchange energy: energy related to the exchange of two electron spins (s) between atoms

\[ e_s = -2J \sum s \cdot s \]

\( J_{12} \) is the exchange integral (constant)
\( >0 \) ferromagnetic ordering
\( <0 \) antiferromagnetic ordering

Depends on degree of orbital overlap between electrons

\( \frac{r_s}{r_{3d}} \)
Small AF ordering
Larger values FM ordering
Still larger values dia/paramagnetism

Curie Temperature is related to strength of exchange integral

\[ J_{12} \propto k_B T_c \]

Exchange Energy: \( T=1403K \), Curie, 1972
Magnetically Ordered Materials

When the applied field is zero, the internal field is still present and leads to magnetic ordering and spontaneous magnetization.

### Table: Main Types of Magnetic Ordering

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetism</td>
<td>Fe, Ni, Co, NiFe, Gd</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>MnO, FeTiO₃</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>Fe₂O₃, MO•Fe₂O₄, where M=transition metal</td>
</tr>
</tbody>
</table>

### Antiferromagnetism

Two separate magnetic sublattices (A and B) with negative (antiparallel) magnetic superexchange coupling

- $M_B = -M_A$ at all temperatures
- $M_{AB} = M_A - M_B = 0$

Néel Temperature ($T_N$)

### Molecular Field Theory of Antiferromagnetism (Néel Theory)

Molecular Field “seen” by A and B ions on A and B sublattices

- $\lambda_{AB} = $ molecular field constant (>0)
- $H_A = -\lambda_{AB} M_A$
- $H_B = -\lambda_{AB} M_B$

Brillouin Functions

- $M_A(T) = M_{AB} B_{mag} \frac{\mu g H_A}{kT}$
- $M_A(T) = M_{AB} B_{mag} \frac{\mu g H_B}{kT}$
- $M_A(T) = |M_A(T) - M'_A(T)| = 0$

Egli, 1972; Dunlop and Özdemir, 1997

Applied Field $\perp$ to spin axis

$T > T_N$

$\chi = \frac{C}{T + \theta}$

$\chi(T > 0) > 0$

Applied Field $\parallel$ to spin axis

$T < T_N$
Antiferromagnetism

- Marcasite (FeS$_2$)
- Goethite (α-FeOOH)
- Goethite (α-FeOOH) - K = 393 K
- Goethite (α-FeOOH) - H = 0.5 defect

Ferrimagnetism

- Two separate magnetic sublattices (A and B) with negative (antiparallel) magnetic superexchange coupling
- Different numbers or kinds of cations or valence states on each sublattice + different site coordination
- $M_A = M_A$ at all temperatures
- $M_B = M_B - M_A > 0$
- $T < T_c$
- Similar magnetic properties to ferromagnetic materials ($M_B$ hysteresis, remanence)
- $T > T_c$
- $X = \frac{C}{T + \theta}$
- $M_s = (T_c - T)^\gamma$
- $\gamma = 0.3 - 0.5$
- Data from various sources

Antiferromagnetic Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$T_N$ (K)</th>
<th>$M_s$ (Am$^2$/kg)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite (FeTiO$_3$)</td>
<td>40</td>
<td>0</td>
<td>AFM</td>
</tr>
<tr>
<td>Ulvospinel (Fe$_3$TiO$_4$)</td>
<td>120</td>
<td>0</td>
<td>AFM</td>
</tr>
<tr>
<td>Hematite (α-Fe$_2$O$_3$)</td>
<td>948</td>
<td>0.4</td>
<td>canted</td>
</tr>
<tr>
<td>Goethite (α-FeOOH)</td>
<td>393</td>
<td>~0.5</td>
<td>defect</td>
</tr>
<tr>
<td>Lepidocrocite (γ-FeOOH)</td>
<td>52</td>
<td>~0.1</td>
<td>defect</td>
</tr>
<tr>
<td>Siderite (FeCO$_3$)</td>
<td>37</td>
<td>0.38</td>
<td>canted</td>
</tr>
<tr>
<td>Rhodocrosite (MnCO$_3$)</td>
<td>34</td>
<td>0.46</td>
<td>canted</td>
</tr>
<tr>
<td>Vivianite (Fe$_3$(PO$_4$)$_8$H$_2$O)</td>
<td>~12</td>
<td>0.06 (?)</td>
<td>defect?</td>
</tr>
<tr>
<td>Ferrihydrite (Fe$_6$O$_4$(OH)$_4$O)</td>
<td>~500</td>
<td>6-12</td>
<td>non-compensated</td>
</tr>
</tbody>
</table>

Ferrimagnetism

- Similar magnetic properties to ferromagnetic materials ($M_B$ hysteresis, remanence)
Molecular Field Theory of Ferrimagnetism

\[ M_a = \lambda_{AA} M_A - \lambda_{AB} M_B \]

Different combinations of AB, AA, BB interactions give rise to different types of \(M_s-T\) curves.

Cullity, 1972

Temperature Dependence of Magnetization

Ferrimagnetic Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( T_m (K) )</th>
<th>( M_s (Am^2/kg) ) at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>853</td>
<td>92</td>
</tr>
<tr>
<td>Maghemite ((\gamma)-Fe₂O₃)</td>
<td>863-948</td>
<td>73</td>
</tr>
<tr>
<td>Greigite (Fe₃S₄)</td>
<td>Unknown, &gt;593</td>
<td>59</td>
</tr>
<tr>
<td>Pyrrhotite (Fe₇S₈)</td>
<td>593</td>
<td>20</td>
</tr>
<tr>
<td>Jacobsite (MnFe₂O₄)</td>
<td>673</td>
<td>77</td>
</tr>
<tr>
<td>Trevorite (NiFe₂O₄)</td>
<td>713</td>
<td>51</td>
</tr>
<tr>
<td>Daubreelite (FeCr₂S₄)</td>
<td>~170</td>
<td>~30 (at 70 K)</td>
</tr>
<tr>
<td>e-Fe₂O₃</td>
<td>~510</td>
<td>~15</td>
</tr>
<tr>
<td>Feroxyhyte ((\delta)-FeOOH)</td>
<td>440-460</td>
<td>~12</td>
</tr>
</tbody>
</table>

Data from various sources.

Nickel-Iron Vanadates (NiFe₃₋ₓVₓO₄)
Variation as a function of composition (O’Handley, 2000)

Titanomaghemite (Fe₃₋ₓTiₓO₄)
Variation as a function of oxidation (Readman and O’Reilly, 1972)
Summary

Magnetic Ordering in Solids
- Diamagnetism: No unpaired e⁻
- Paramagnetism: Unpaired e⁻, disordered and fluctuating
- Ferromagnetism: All unpaired e⁻ spins aligned parallel
- Antiferromagnetism: Unpaired e⁻ aligned antiparallel
- Ferrimagnetism: Unpaired e⁻ aligned antiparallel but don’t fully cancel out

Magnetic Mineralogy

Sources of magnetic minerals
- Igneous and metamorphic processes
- Soil formation and diagenesis
- Cosmic dust
- Biomineralization
- Industrial pollution
- Archaeological materials

Transformation of magnetic phases
- Chemical weathering
- Low/high temperature oxidation
- Dissolution/precipitation
- Biogenic formation/alteration

Magnetic minerals follow the rock cycle

Magnetic Minerals can undergo significant chemical/physical changes after formation
Physical/Chemical changes can destroy primary remanence or produce new remanence

Ternary diagram for iron-oxides

Most Important Magnetic Phases
- Fe-Ti oxides
- Fe-sulfides
- Fe-oxyhydroxides

Magnetic Mineralogy

Magnetite and Titanomagnetites (Fe₃₋ₓTyO₄)
Hematite and Titanohematites (Fe₂₋TyO₃)
Maghemite and Titanomaghemites

Chemical Change
- Exsolution
- High temperature oxidation, T>600 C (oxy-exsolution)
- Low temperature oxidation (titanomaghemites)

Magnetic Oxyhydroxides, Sulfides, and Fe-Ni

Tauxe, 2008
Titanomagnetites

Solid Solution Series (T>600°C)
- Cubic minerals
- Spinel crystal structure

\[ \text{Fe}_{x+Ti_{1-x}}O \]
\[ (1-x)\text{Fe}_x\text{O} \cdot x\text{Fe}_\text{Ti}O \]

Spinel Crystal Structure

Spinel is the Mg-Al member of the larger spinel group of minerals.

\[ \text{MgAl}_2\text{O}_4 \]

A-sites: tetrahedral coordination
B-sites: octahedral coordination

Superexchange Interactions in Spinels

Superechange between unpaired electrons spins couple through covalent interactions with intervening ligand (e.g. O²⁻)

Bond angles in Magnetite
- Angles near 90° are unfavorable for superexchange interactions
- AB, BB, and AA interactions

Crystal Structure of Magnetite

Unit cell contains 32 O²⁻ anions arranged in a face-center cubic network
- Two types of cation sites
  - A-sites: tetrahedral coordination (8 sites per unit cell)
  - B-sites: octahedral coordination (16 sites per unit cell)

General Structural Formula: \( (A)[B]_8O_{16} \)

Butler, 1992; Walz, 2002
**Magnetite**

\[
\text{Fe}_3\text{O}_4 \quad (\text{Fe}^{3+},\text{Fe}^{3+},\text{Fe}^{2+})\text{O}_4^{2-}
\]

In magnetite, there are 16 Fe\(^{3+}\) and eight Fe\(^{2+}\) cations per unit cell

\[
\begin{align*}
\text{Fe}^{2+} & : S=2, \mu = 4 \mu_B \\
\text{Fe}^{3+} & : S=5/2, \mu = 5 \mu_B
\end{align*}
\]

What's the magnetic structure of Magnetite?

**Ferromagnetism** (all spins are aligned)

**Ferrimagnetism** (A and B sites are AF coupled)

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Spin Moment</th>
<th>Coupling</th>
<th>Spin Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferromagnetic</td>
<td>All spins aligned</td>
<td>(Fe(^{3+})),[Fe(^{3+}),Fe(^{3+})],O(^4)</td>
<td>(5+5)-4=6 \mu_B</td>
</tr>
<tr>
<td>Ferrimagnetic</td>
<td>(Fe(^{3+})),[Fe(^{3+}),Fe(^{2+})],O(^4)</td>
<td>(5+4)-5=4 \mu_B</td>
<td></td>
</tr>
</tbody>
</table>

\[\overset{\text{~4.1} \mu_B}{\text{Observed value}}\]

**Verwey Transition in Magnetite**

Change in lattice symmetry at \(T_v=121 \text{ K}\)

- Monoclinic Magnetite
- Cubic

Saturation IRM (SRM) given at 10 K
Measurement on warming to 300 K

**Maghemite (\(\gamma\)-Fe\(_2\)O\(_3\))**

Isochemical with hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) but maintains the inverse spinel structure of magnetite.

Convert all Fe\(^{2+}\)\(\rightarrow\)Fe\(^{3+}\) and maintain charge balance

\[
(\text{Fe}^{3+}),[\text{Fe}^{3+},\text{Fe}^{3+}],\text{O}^4 \rightarrow (\text{Fe}^{3+}),[\text{Fe}^{3+},\text{Fe}^{3+}],\text{O}^4
\]

\[
\text{[Fe}^{3+}\text{]_4[Fe}^{3+}\text{]_2[\text{Fe}^{2+}\text{]_2[\text{O}_4]]}
\]

\[M_s (300K)= 74.3 \text{ Am}^2/\text{kg}\]

\(T_v \sim 863-948 \text{ K} (590-675 \text{ °C})\)

No Verwey like transition

Maghemite is oxidized to maghemite by changing the valence state of two thirds of the original Fe\(^{2+}\) to Fe\(^{3+}\) while simultaneously removing one third of the original Fe\(^{2+}\) from the B sublattice.

**Magnetite**

Temperature dependence of the sublattice magnetizations

- Curie Temperature: \(853 \text{ K} (580 \text{ °C})\)
- Saturation Magnetization at \(23 \text{ °C}\)
  - \(74.3 \text{ Am}^2/\text{kg}\)
  - \(480 \text{ kA/m}\)

Magnetite is oxidized to maghemite by changing the valence state of two thirds of the original Fe\(^{2+}\) to Fe\(^{3+}\) while simultaneously removing one third of the original Fe\(^{2+}\) from the B sublattice.
Maghemite ($\gamma$-Fe$_2$O$_3$)

$\gamma$-Fe$_2$O$_3$ is metastable and typically inverts to $\alpha$-Fe$_2$O$_3$ (hematite) when heated to $T > 300°$ C

Synthetic maghemite

D=0.47 $\mu$m
Axial ratio 9:1

Synthetic maghemite

D=0.025 $\mu$m

Inversion to $\alpha$-Fe$_2$O$_3$

Dunlop, 1988

Synthetic maghemite $D \approx 0.025$ $\mu$m

Özdemir, 1990

Synthetic maghemite $D \approx 0.47$ $\mu$m

Axial ratio 9:1

Tc=645°C

Differential thermal analysis (DTA) heated in O$_2$.

Cation Distribution and Magnetization in Titanomagnetites

Distribution of cation between A and B sites and the exchange coupling between/within sublattices control intrinsic magnetic properties (e.g., $M_s$ and $T_c$) of titanomagnetites

Normal spinel: similar cations occupy the same sublattice

Inverse spinel: different cations occupy the same sublattice

Generalized Cation Distribution Formula for Titanomagnetites

$(Fe^{3+}_{x}Fe^{2+}_{1-x})_2[Fe^{3+}_{1-2x}Fe^{2+}_{2x}Ti^{4+}]_bO_4^-$

$b$: distribution parameter (no. of A-site Fe$^{3+}$)

$x$: compositional parameter

For example (x=0, Magnetite)

$b=0$: normal spinel $(Fe^{3+})_2[Fe^{3+},Fe^{2+}]_bO_4^-$(A-site)

$b=1$: inverse spinel $(Fe^{3+})_2[Fe^{3+},Fe^{2+}]_bO_4^-$(B-site)

Crystal Chemistry in Spinels: Cation Site-Preference for transition metal ions in A and B Sites

Certain cations have a preference for occupying a particular coordination site

$(Fe^{3+})_x[Fe^{3+},Fe^{2+}]_bO_4^-$(A-site)

$(Fe^{3+})_x[Fe^{3+},Ti^{4+}]_bO_4^-$(B-site)

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$(Fe^{3+})_x[Fe^{3+},Ti^{4+}]_bO_4^-$(B-site)

Variation in saturation magnetization

(Bohr magnetons pfu at 0K)

$\mu = 6(1-x) - 2b$
Magnetic Properties of Titanomagnetites

In the titanomagnetite series (Fe₃₋ₓTₓO₄),

\[ \text{Ti}^{4+} \text{ substitutes for } \text{Fe}^{3+} \text{ as Ti content increases.} \]

The ionic substitution is

\[ 2\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{Ti}^{4+} \]

Saturation Magnetization at 300 K

Data from various sources

Natural titanomagnetites can also contain Al³⁺, Mg²⁺, Mn²⁺

Lattard et al., 2006

Hematite: Fe₂O₃

Canted Antiferromagnetism

Weak ferromagnetism

Curie Temperature: 948 K (675 ºC)
Saturation Magnetization at 300 K
0.5 Am²/kg
2 kA/m

Morin Transition

Spin-flop transition

Dunlop and Özdemir, 1997; Butler, 1992

Magnetic Properties of Titanomagnetites

Different combinations of AB, AA, BB interactions give rise different types of Mₛ-T curves

Temperature dependences of the sublattice magnetizations are not always the same, but all go to 0 as \( T \rightarrow T_c \).

P-type behavior in TM60

Dunlop and Özdemir, 1997

Hematite: Fe₂O₃

Morin Transition

Spin-flop transition

Dunlop and Özdemir, 1997; Özdemir et al., 2008
Titanohematites: Fe$_{2-y}$Ti$_y$O$_3$

**Phase diagram for titanohematites**
Both end-members have rhombohedral crystal structures and are antiferromagnetic below $T_N$.

**Ordered Phase:** Fe$^{3+}$ uniquely distributed within the A layer and Ti$^{4+}$ within the B layer.

**Magnetic Structure**

**Compositions around y=0.5** have the property of self-reversed thermoremanent magnetization:
Applied a field in the positive direction and cool through Curie temperature an negative remanence is produced.

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**Primary Fe-Ti oxides**

Originally crystallized from igneous melts:
~1-5% by volume, crystallize $T>1300^\circ$C $> T_c$.

Cooling rate has major impact on grain size and microstructure:
extrusive volcanic rocks: TM grain sizes < 50 μm, many <1μm
intrusive igneous rocks: TM grain sizes > 100μm.

Composition of the melt:
Mafic magmas (enriched in Fe, low Si)
Basalts and Gabbros
TM's: 0<x~0.8, Ferrimagnetic, $T_c$ 10°C
TH's: 0.8<y~0.95, Paramagnetic, $T_c$ > 0°C

Felsic magmas (higher in SiO2)
rhyolites, granites
TM's: x~0
TH's: 0 < y~0.8

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**Magnetic Inclusions in Paramagnetic Silicate Minerals**

Ti-poor TM (< 1μm) can be exsolved from silicate minerals.

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Tauxe, 2008

Dunlop and Özdemir, 1997; Lagroix et al., 2004
Chemical Change

Quench by rapid cooling (volcanic rocks)
- single phase composition

Exsolution by slow cooling (>10^6 yr) igneous intrusions
- multiphase compositions

Hemoilmenite
- two-phase composition

Important Changes
- Magnetic properties due to change in composition
- Decrease in effective magnetic grain size

Chemical Change and Exsolution (T>500°C)

Magnetic properties due to change in composition
Decrease in effective magnetic grain size

Chemical Change

Ilmenite-Hematite Exsolution in granulites from S. Sweden

Lamellar Magnetism

Exsolution in Titanohematites

Lamellar magnetism is associated with boundary layers between the exsolved phases.

Monte Carlo simulation of cation ordering and resulting magnetic signal of hematite-rich and ilmenite-rich phases in exsolved titanohematite

Robinson et al. (2002)
Slow Cooling and Oxy-Exsolution

Oxidation that occurs during original cooling of an igneous rock is deuteric oxidation.

Solid solution between magnetite and ulvospinel exists in principle, intergrowths of these two minerals are rare.

Natural titanomagnetites interact with oxygen in the melt to form intergrowths of low Ti magnetite with ilmenite (deuteric oxidation).

Titanomagnetite grain displaying typical high temperature oxidation texture (i.e. produced during cooling).

Titanomagnetite (brown) is sub-divided by ilmenite (pale brown). Some lamellae and patches of hematite are also present (width of image =320μm).

Optical photomicrograph of ilmenite lamellae within titanomagnetite grain; note the symmetry of the ilmenite planes that are parallel to (111) planes of the host titanomagnetite.

Low-Temperature (T<300°C) Titanomaghemites

Weathering at ambient surface conditions
Hydrothermal alteration
Ocean floor basalts

Maghemization
No change in crystal structure (spinel)
Convert all Fe²⁺→Fe³⁺ & maintain charge balance

Phases are called cation-deficient spinels (non-stoichiometric TM)

\[
(Fe^{2+}_{x}Fe^{3+}_{1-x})_{1/2}\left(Fe^{2+}_{(1-x/3)}Fe^{3+}_{x/3}\right)_{1/2}Tl^{4+}_{9-x}O_{8+x}^{-}\delta
\]

0 ≤ \(\delta\) ≤ (1 + x) / (9 + x)

Oxidation parameter: 0 ≤ z ≤ 1, z=9δ

For x=0: z=0 → magnetite
z=1 → maghemite

Consequences of Maghemization

Titanomagnetite (x = 0.6) is the dominant primary FeTi oxide in oceanic pillow basalts (upper 0.5 km of oceanic crust).

During seafloor weathering, titanomagnetites oxidize to maghemite.

Titanomaghemite is one of the most abundant FeTi oxides in the earth’s crust.

A magnetite crystal (~ 30 μm) undergoing maghemitization. Because of the change in volume, the crystal begins to crack. [From Gapeyev and Tsirlinovich, 1988.]
Ocean-Floor Basalts

If titanomaghemites are heated, by burial beneath later flows on the seafloor for example, they become unstable and ‘invert’.

Temperature dependence of magnetization
Inversion of titanomaghemite
\[ \text{intergrowth of Fe-rich TM and Ti-rich ilmenite} \]

Other Common Magnetic Phases

Goethite (\(\alpha\)-FeOOH)
Common weathering product and precursor to hematite in sediments and soils.

Saturation Magnetization
\[ \approx 0.1 \text{ Am}^2/\text{kg} \]
\[ 1-2 \text{ kA/m} \]

Néel and Curie Temperature

Thermomagnetic heating curve (strong field)

Step-wise thermal demagnetization of thermoremanent magnetization (TRM)

Weak ferromagnetism has a \(T_c = T_N\)
Iron-Sulfides: Pyrrhotite

Monoclinic pyrrhotite (Fe₇S₈): Ferrimagnetic
Tc=593 K (320°C)
Ms=20 Am²/kg (80 kA/m)

Hexagonal pyrrhotite (Fe₉S₁₀): Structural transition from an imperfect antiferromagnet to ferrimagnet at about 200°C.

Fe cations are FM coupled within c-planes and AF coupled between layers via S²⁻ ions.

“Besnus” Transition (T=34 K) in Monoclinic Pyrrhotite

Transition “34K is diagnostic of the presence of monoclinic pyrrhotite
Physical Origin of transition is likely related to crystallographic transformation

Iron-Sulfides: Greigite (Fe₃S₄)

Crystal Structure: Cubic, Inverse spinel
Magnetic Structure: Ferrimagnetic

Tₜ unknown but must be T> 603 K (330°C)
Chemically unstable at high T and decomposes at T<Tₜ

High-temperature hysteresis data (measured in air)

Iron-Sulfides: Greigite (Fe₃S₄)

Tₜ unknown but must be T> 603 K (330°C)
Chemically unstable at high T and decomposes at T<Tₜ

High-temperature hysteresis data (measured in air)
Iron-Sulfides: Greigite (Fe$_3$S$_4$)

No low-Temperature transition

Coarse grained SD/PSD/MR samples

Nanophase Unblocking behavior

Greigite and Pyrrhotite occur in reducing environments and both tend to oxidize to various iron oxides leaving paramagnetic pyrite as the sulfide component.

Magnetic Mineral Identification: Part 1

Different Approaches:

Imaging
Diffraction
Magnetic Characterization

Looking for changes in magnetic behavior at characteristic temperatures (2-1000 K)

High-Temperature (>300 K) methods

Most magnetic minerals that carry stable remanence (SD/PSD) are small (< 10 μm) and in low concentrations (< 1%)

The challenge is to associate a particular component of NRM (identified from partial demagnetization) with a particular ferrimagnetic mineral.
Imaging Magnetic Minerals

Exsolved magnetic & ilmenite in an igneous rock

Detrital titanomagnetites from Chinese loess.

Hematite rosettes on a smectite grain.

Industrial pollutant ("fly-ash")

Interstellar Dust Particle (IDP)

Just looking at your samples in a microscope can help explain a LOT about the magnetic behavior of your samples.

The shape, grain-size, texture, and associated non-magnetic minerals all give clues to the magnetic mineralogy in a sample and their origins.

Frequently used modes of imaging:

Scanning Electron Microscopy (SEM)
Electron MicroProbe Analysis (EMPA)

Better spatial resolution (~0.1 µm), observation of 3D morphology of grains, and ability to measure composition (EDS) and crystal structure (via EBSD)

EDS: Energy-dispersive X-ray spectroscopy, EBSD: Electron backscatter diffraction

Imaging Magnetic Minerals

Exsolved magnetic & ilmenite in an igneous rock

Detrital titanomagnetites from Chinese loess.

Hematite rosettes on a smectite grain.

Industrial pollutant ("fly-ash")

Interstellar Dust Particle (IDP)

Frequently used modes of imaging:

Transmission Electron Microscopy (TEM)
Synchrotron Radiation

Best spatial resolution (0.1-5 nm), ability to measure composition (EDS or EELS), and crystal structure (SAED).

EELS: electron energy loss spectroscopy, SAED: selected area electron diffraction
Magnetic Characterization of Minerals

Characteristic Temperature Changes

All FM minerals have a Curie or Neel point.

One of the ways we characterize samples is by heating them up and determining these key temperature transitions.

Vibrating sample magnetometer

Typical Strong-field (~1 T) thermomagnetic experiment.

Measurement of \( M(T) \) in whole rock samples.

Experiment measures induced magnetization in a very strong field.

Peak shows temperature of maximum curvature, interpreted as the Curie temperature.

Examples of thermomagnetic curves

Standard Experimental practice is to measure thermomagnetic curves during a heating and cooling cycle.

Heating in air (not typically recommended)
Heating in vacuum, or inert gas (N\(_2\), Ar) to reduce effects of oxidation

The Curie temperature is the same on both heating and cooling (~575°C). This is termed reversible behavior.

No (likely) chemical alteration occurred during heating and cooling cycle.

Examples of thermomagnetic curves

The Curie temperature of ~200°C is observed with reversible behavior.

Could be either titanomagnetite (x~0.55) or titanohematite (y~0.5)

(Optical microscopy shows that titanohematite is the dominant magnetic phase in the sample.)

Magnetic Characterization of Minerals

Identification of Magnetic Minerals by thermomagnetic analysis is complicated by two main factors

1. Each magnetic mineral has its own unique Curie (or Neel) temperature, but different minerals can have the same \( T_c \) or \( T_n \) (solid solution series titanomagnetites and titanohematites)

2. Chemical alteration of samples can occur during thermomagnetic analysis (heating samples up to 500-700°C)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( T_c ) or ( T_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite (FeO)</td>
<td>580°C</td>
</tr>
<tr>
<td>TM60</td>
<td>120</td>
</tr>
<tr>
<td>Pyrrhotite (Fe7S8)</td>
<td>320</td>
</tr>
<tr>
<td>Maghemite (γ-Fe2O3)</td>
<td>600°</td>
</tr>
<tr>
<td>Greigite (Fe3S4)</td>
<td>350° (?)</td>
</tr>
<tr>
<td>Hematite (α-Fe2O3)</td>
<td>675</td>
</tr>
<tr>
<td>Goethite (α-FeOOH)</td>
<td>120</td>
</tr>
</tbody>
</table>

Normalized \( M(T) \) dependences for five common magnetic minerals

Titanomagnetites

Butler 1992
Magnetic Characterization of Minerals

Examples of thermomagnetic curves

Non-reversible behavior

Usually indicates a change in the magnetic mineralogy has occurred during heating (oxidation, reduction, crystallographic change).

This sample contains intergrowths of Fe$_7$S$_8$ and Fe$_9$S$_{10}$

The change 225-320°C is a transition from antiferromagnetism to ferrimagnetism in the Fe$_9$S$_{10}$

Irreversible Behavior: Titanomaghemites

For example, TMAGH→Fe-rich TM + Ti-rich ilmenite

Characteristic irreversible thermomagnetic curve of a partially oxidized TM60 (Özdemir and O'Reilly, 1982)

Irreversible Behavior: \( \gamma \)-FeOOH→\( \gamma \)-Fe$_3$O$_4$→\( \alpha \)-Fe$_3$O$_4$

"Irreversible" Behavior: Sluggish (reversible) phase transformations producing thermal hysteresis

Figure 15.8. Vacuums thermomagnetic curves (\( H_0 \) = 550 mT) characteristic of (a) iron (karnasite or \( \alpha \)-Fe), and (b) non-nickel containing \( \alpha \)-FeNi, showing the sluggish karnasite \( \rightarrow \) torberite \( \rightarrow \) \( \alpha \)-FeNi transformation. (After Nagata et al., 1971) [Reproduced by permission of Kluwer Academic Publishers]

Özdemir and Dunlop, 1993

Dunlop and Özdemir, 1997
**Magnetic Characterization of Minerals**

Examples of thermomagnetic curves

Some samples have more than one magnetic phase

Curie temps at 580°C and 680°C are due to magnetite and hematite respectively.

This is a nice example where you can see a mineral with a large Ms (magnetite) and a low Ms (hematite).

Sometimes, the stronger Ms mineral swamps the signal, making it hard to detect the presence of other magnetic phases.

Often, you need to combine information from different kinds of experiments.

**Magnetic Characterization of Minerals - Susceptibility**

Paramagnetism has a $1/T$ dependence.

So the $\chi_{100}$ should be twice as large as $\chi_{10}$.

Diamagnetism is independent of $T$.

Susceptibility experiments measure induced magnetization in a very weak field.

**Magnetic Characterization of Minerals**

Examples of thermomagnetic curves

Identification of the ferromagnetic minerals in a pelagic limestone by determination of their Curie temperatures in concentrated extracts.
Problems with Paramagnetism and high-field measurements

Susceptibility Measurements

Magnetic Characterization of Minerals

ISO THERMAL REMANENT MAGNETIZATION (IRM)

The magnetization acquired during exposure to a short-lived magnetizing field.

Usually at room T and in large fields.

Low-coercivity minerals

Saturation <300 mT ferrimagnets
Fe₂O₄, γ-Fe₂O₃

High-coercivity minerals

Saturation >1000 mT Open loop to high fields ‘imperfect’ Antiferromagnets α-Fe₂O₃, α-FeOOH

High-field thermomagnetic (Ms) and NRM unblocking Temperature curves

High-Field Results: T_c ~150°C, unoxidized TM60
NRM unblocking: T_B >300°C, oxidized TM60

Why discrepancy between High-field results and NRM results?

Dust on Snow (Red Mountain Pass, San Juans CO)

Kent and Gee, Science, 1994
Isothermal Remanent Magnetization

Imparting IRMs in the Lab

ASC Impulse Magnetizer

The magnetic field is produced by discharge of energy from a capacitor bank through a coil surrounding the sample cavity. The capacitor bank is first charged to the desired voltage (corresponding to the desired field). It is then discharged through the coil very quickly ($B_{\text{max}} \sim 2$ T).

Electromagnets

$B_{\text{max}} \sim 2$ T

Superconducting Magnets

$B_{\text{max}} \sim 5-20$ T

Highest magnetic field for a continuous field magnet (Guinness World Record)

- 45 T
- 36.2 T
- 60 T
- 90 T
- 33.8 T

National High Magnetic Field Laboratory [www.magnet.fsu.edu](http://www.magnet.fsu.edu)

- Electromagnets
- Superconducting Magnets

IRMs can be very useful in the lab.

IRM Acquisition: Samples can be exposed to progressively higher fields and the resulting magnetization can be measured.

The magnitude of the IRM is sensitive to the magnetic mineralogy, concentration, and grain size of the assemblage.

Maximum IRM is known as SIRM (saturation IRM) or $M_r$.

Isothermal Remanent Magnetization

IRM Demagnetization

After saturation has been reached, the sample can be turned around and subjected to increasingly large backfields.

A some point the back-field strength will be strong enough to flip half of the moments in a sample, resulting in a net moment of zero. This is the Coercivity of Remanence ($H_{\text{cr}}$).

Sometimes people use a term called $H_{\text{co}}$, which is the field required to impart half the SIRM.

The acquisition of IRM is one of the many tools we use to characterize the magnetic minerals in a sample.

Coercivity of Remanence ($H_{\text{cr}}$).

IRM = 50% $M_r$

$\mu_0 H_{\text{cr}} = \mu_0 H_{\text{cr}}^{\text{IRM}}$

$H_{\text{cr}}^{\text{IRM}}$

IRM Demagnetization

Back-field Curve

IRM demagnetization
IRM Acquisition and Demagnetization Curves

Cisowski plot: simultaneously graphs the acquisition curve together with the AF or DC demagnetization curve as a function of field

Slope of Henkel plot = -2
Crossover point for Cisowski plot = 0.5

Wohlfarth (1958) Relationships for Non-interacting SD grains

\[ M_{\text{SD}}(H) = M_{\text{IRM}}(H) - 2 M_{\text{MD}}(H) \]
\[ M_{\text{MD}}(H) = M_{\text{IRM}}(H) - M_{\text{HA}}(H) \]

Slope of Henkel plot = -2
Crossover point for Cisowski plot = 0.5

Jackson, 2007

Coercivity Analysis (IRM acquisition curves)

Coercivity in AFM phases like hematite and goethite is much larger than that observed in ferrimagnetic phases like (titanom)agnetite.

During IRM acquisition, it is more difficult to saturate AFM phases than magnetite.

(titanom)agnetite: \( H_{\text{cmax}} \approx 300 \) mT
Hematite/goethite: \( H_{\text{cmax}} > 1 \) T.

So the point at which an IRM curve reaches a plateau tells you something about the mineralogy in a sample.

Non-saturation of the defect moment of goethite and fine-grained hematite up to 57 T (Rochette et al., 2005)

Room-Temperature

IRM acquisition curves up to 57 T

Goethite powders

Rock samples
RR, RD: goethite
TO: fine-grained hematite

Anomalous decrease in between 34=39 T is due to field reversal between the two coils used.
**Magnetic Characterization - IRM and Coercivity Analysis**

In (a) we see an IRM experiment that is rapidly magnetized up to ~200-250 mT. At this point, the acquisition of IRM slows down considerably, but does not plateau (even by 800 mT). This is evidence for the presence of hematite or goethite. It does not exclude the presence of magnetite.

A Curie temperature of 580°C is evident, but there is no indication of hematite (680°C) or goethite (120°C).

**Magnetic Characterization - IRM and Coercivity Analysis**

(b) thermal demagnetization experiment for the IRM acquired in (a).

This experiment measures the remaining magnetization after the sample is heated in zero field to progressively higher temperatures. Most of the remanence is gone by the Curie temperature of magnetite (580°C).

However, a portion of the magnetization is still present at temps >580°C. This is the remanence held by hematite.

**Magnetic Characterization - IRM and Coercivity Analysis**

(c) strong-field thermoremanent experiment for the same sample.

We see a Curie temperature around 580°C (and also near 425°C), but no sign of a Curie temperature associated with hematite or goethite.

This highlights the need for complementary experiments!

**Magnetic Characterization - IRM and Coercivity Analysis**

Combining thermal and isothermal Magnetizations

3D IRM Test:

- Acquisition of 3-component IRM ("Triaxial" IRM)
  1. Apply 2 T field along z-axis
  2. Apply 0.4 T along y-axis
  3. Apply 0.12 T along x-axis

Thermal demagnetization of a 3-axis IRM. Each component is plotted separately.

- 2 T field: AFM phases (hematite/goethite)
- 0.4 T field: (titanom)agnetite
- 0.12 T field: MD magnetite

Curve is dominated by a phase with a $T_{max} = 550-600°C$ and coercivity < 0.4 T, but > 0.12 T [PSD Magnetite]

Small fraction of a high coercivity (>0.4T) mineral with a maximum unblocking temperature > 650°C [Hematite]

Butler 1992
Examples of the identification of magnetic minerals by acquisition and subsequent thermal demagnetization of IRM.

Hematite is present in both (a) and (b), because SIRM requires fields \( > 1 \text{T} \) and thermal demagnetization of the hard fraction persists to \( T = 675^\circ\text{C} \).

In (a) the soft fraction that demagnetizes at \( T = 575^\circ\text{C} \) is magnetite.

In (b) no magnetite is indicated but pyrrhotite is present in all three fractions, shown by thermal unblocking at \( T = 300-330^\circ\text{C} \).