The role of hematite-ilmenite solid solution in the production of magnetic anomalies in ground- and satellite-based data

Gunther Kletetschka a,b,*, Peter J. Wasilewski b, Patrick T. Taylor c

2 samples studied:
- titanohematite with exsolved ferrian ilmenite lamellae from Wilson Lake, Labrador
- ferrian ilmenite with exsolved titanohematite lamellae from Allard Lake, Quebec

Allard lake sample:
- the remnant magnetization (RM) is carried by very fine lamellae of titanohematite within the ferrian ilmenite host
- smaller ilmenite lamellae within titanohematite

Kletetschka et al. 2002
Magnetic properties

- A spinning electron behaves as a minute magnet.
- The most important elements producing a magnetic response are those with unshared electrons (not involved in bonding) in 3d orbitals:
  - Ti, V, Cr, Mn, Fe, Co, Ni and Cu (Z=22 to 29)
  - Magnetic moments are the result of the spin of single, unpaired electrons
  - Magnetic moments are proportional to the number of such electrons
Magnetic properties

- An electron can spin in only 2 directions
- The maximum number of electrons in any given orbital (e.g. 2s) is **two**
- These electrons must have opposite spin directions
- A spinning electron behaves as a minute magnet
- Complete filling of orbitals \((s^2, p^6, d^{10})\) prevents any magnetic response in pure calcite, albite, quarz, apatite...
- Next page: elements such as Cr, Mn and Fe (or their ions with valence +2, +3) may induce strong magnetism in solids
<table>
<thead>
<tr>
<th>Z, Element, Ions</th>
<th>Number of 3d electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 Sc Ti³⁺, V⁴⁺</td>
<td>1 unpaired</td>
</tr>
<tr>
<td>22 Ti Ti²⁺, V⁴⁺</td>
<td>2 unpaired</td>
</tr>
<tr>
<td>23 V V²⁺, Cr³⁺, Mn⁴⁺</td>
<td>3 unpaired</td>
</tr>
<tr>
<td>24 Cr Cr²⁺, Mn³⁺</td>
<td>4 unpaired</td>
</tr>
<tr>
<td>25 Mn Mn²⁺, Fe³⁺</td>
<td>5 unpaired</td>
</tr>
<tr>
<td>26 Fe Fe²⁺, Co³⁺</td>
<td>2 paired, 4 unp’d</td>
</tr>
<tr>
<td>27 Co Co²⁺</td>
<td>4 paired, 3 unp’d</td>
</tr>
<tr>
<td>28 Ni Ni²⁺</td>
<td>6 paired, 2 unp’d</td>
</tr>
<tr>
<td>29 Cu Cu²⁺</td>
<td>8 paired, 1 unp’d</td>
</tr>
<tr>
<td>30 Zn Zn²⁺, Cu²⁺</td>
<td>10 paired, 0 unp’d</td>
</tr>
</tbody>
</table>
Magnetic properties

- Many minerals have a structure with a *random arrangement* of magnetic dipoles from these unpaired electrons
- Placed in a magnetic field, these minute dipoles align themselves with the field
  - this behavior is called “paramagnetism”
  - E.g. olivine, augite
- The resulting magnetic attraction to an external field is weak
- The magnetization is not permanent
- Can be used in ore separation: the magnetic susceptibility of many silicate minerals is proportional to their FeO+MnO content
Magnetic properties

- In some solids, the overlap of orbitals among neighbors results in alignment of the dipoles.
- Domains exist containing large numbers of paramagnetic atoms with their dipole moments well aligned.
- Placed in a magnetic field, all domains tend to become aligned.
- The material exhibits strong attraction to the external field.
  - This behavior is called “ferromagnetism”
  - E.g. metallic iron

![Diagram of magnetic domains](image)

(a) Unmagnetized domains

(b) Magnetized domains
Magnetic properties

- In a **ferromagnetic** solid such as Fe
  - The domains remained aligned after the field disappears
  - E.g. an iron nail can be magnetized by running a permanent magnet over it)

- When the material is heated above its **Curie temperature**, these domains lose their dipole alignment
But not every Fe-rich mineral displays magnetism.

In pyrite, FeS$_2$, the 6 nearest neighbor sulfide anions result in a crystal field where the energy splitting keeps the 6 “d” electrons paired in a “low spin configuration”.

Pyrite of ideal chemistry is thus **diamagnetic** (i.e. no unpaired electrons). It is not magnetized even in the presence of a strong, external field.
Magnetic properties

- In other solids, the ionic spin moments are antiparallel (i.e. opposite), but non-equal: **ferrimagnetism**

- This results in permanent magnets
  - The magnetite-ulvospinel series Fe$_3$O$_4$ - Fe$_2$TiO$_4$
  - Pyrrhotite Fe$_{1-x}$S
  - Two cases where Fe$^{2+}$, Fe$^{3+}$ are both present

- In magnetite (an inverse spinel):
  - Equal amounts of Fe$^{3+}$ ions (5 unpaired electrons) occupy in two different lattice sites (CN=4 and CN=6).
  - Their opposing spin directions cancel the magnetic susceptibility they could impart to the solid.
  - The Fe$^{2+}$ ions (in CN=6) have lesser magnetic moments (only 4 unpaired electrons) but their spins do not cancel each other’s
  - Above 580°C (its Curie temperature), magnetic ordering disappears in magnetite.
Magnetic properties

- The hematite-ilmenite solid solution members $\text{Fe}_2\text{O}_3 - \text{FeTiO}_3$ show a different situation.

- In this series, the orientation of magnetic dipoles of individual $\text{Fe}^{3+}$ ions (or $\text{Fe}^{2+}$) ions alternate regularly between layers, throughout the structure, and nearly cancel each other. However, the dipoles are slightly inclined, so there is a weak, net magnetism.
“Sublattice” refers to an array of sites (e.g. tetrahedral or octahedral) within a structure. As you may suspect, changing the degree of cation ordering, or exsolving end-members during cooling, in structures containing (Fe, Mn, Cr) $^{2+}$ or $^{3+}$ affects their magnetism.

<table>
<thead>
<tr>
<th>Type</th>
<th>Arrangement</th>
<th>Lattice</th>
<th>Resultant</th>
</tr>
</thead>
<tbody>
<tr>
<td>true ferromagnetic (Fe, Ni, Co)</td>
<td>alignment within lattice</td>
<td><img src="up" alt="Up" /> <img src="up" alt="Up" /> <img src="up" alt="Up" /> <img src="up" alt="Up" /></td>
<td><img src="up" alt="Up" /></td>
</tr>
<tr>
<td>antiferromagnetic</td>
<td>sublattices, A &amp; B, aligned but antiparallel, equal</td>
<td><img src="up" alt="Up" /> <img src="down" alt="Down" /> <img src="up" alt="Up" /> <img src="down" alt="Down" /></td>
<td>(none)</td>
</tr>
<tr>
<td>Hematite below 10°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ferrimagnetic</td>
<td>sublattices, A &amp; B, aligned antiparallel, unequal</td>
<td><img src="up" alt="Up" /> <img src="down" alt="Down" /> <img src="up" alt="Up" /> <img src="down" alt="Down" /></td>
<td><img src="up" alt="Up" /></td>
</tr>
<tr>
<td>Magnetite-ulvospinel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>canted antiferromagnetic</td>
<td>sublattices, A &amp; B, canted equal</td>
<td><img src="up" alt="Up" /> <img src="down" alt="Down" /> <img src="up" alt="Up" /> <img src="down" alt="Down" /></td>
<td></td>
</tr>
</tbody>
</table>
phase diagram for the hematite-ilmenite system 
(Fe$_2$O$_3$ - FeTiO$_3$)

H = titanohematite
IL = ferrian ilmenite
HIL = disordered hematite-ilmenite solid solution

Wilson = hematite-rich sample
Allard = ilmenite-rich sample

The heavy dotted line represents the metastable exsolution of the HIL phase.

The titanohematite grains acquires magnetization before exsolution occurs.

As the temperature decreases, exsolution of ilmenite lamellae starts and the magnetization is locked in place.

Note how the \textit{Curie temperature} (dashed line $T_c$) depends on the titanohematite composition (the Fe content is crucial).

The Curie temperature is always within the field of ordered cations. The magnetism is lost if the cations are disordered in the structure.
Hematite (Fe$^{3+}_2$O$_3$) vs Magnetite (Fe$^{2+}$Fe$^{3+}_2$O$_4$)

Hexagonal
Space Group: R -3c
a = 5.038  c = 13.772  z = 6

G = 5.25

Usually contains some Ti:
- substitution of Fe$^{2+}$Ti$^{4+}$ for 2Fe$^{3+}$

Isometric
Space Group: F d3m
a = 8.396  z = 8

G = 5.18

Usually contains some Ti:
- solid solution between magnetite and ulvospinel (TiFe$^{2+}_2$O$_4$)
- substitution of Ti$^{4+}$ for Fe$^{3+}$ in octahedral site coupled with the substitution of Fe$^{2+}$ for Fe$^{3+}$ in tetrahedral site
Hematite
\((Fe^{3+}2O_3)\)
\(FeO_6\)
octahedra sharing faces and edges.

Magnetite
\((Fe^{2+}Fe^{3+}_2O_4)\)
Yellow: octahedral sites
Orange: tetrahedral sites