Magnetic property characterisation focusing on soil and archaeological materials.



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Funded by the Horizon 2020 Framework Programme of the European Union • Properties of some magnetic minerals

• Formation of magnetic minerals

Magnetic characterisation methods

Examples

Element	Abundance (wt %)* in Earth's crust *Lutgens & Tarbuck 2000	Magnetic minerals	
		Magnetite	Fe ₃ O ₄
Oxygen	46.6	Maghaemite	γ–Fe ₂ O ₃
Silicon	27.7		
Aluminum	8.1	Haematite	$\alpha - Fe_2O_3$
Iron	5.0		
Calcium	3.6	Goethite	α-FeOOH
Sodium	2.8	$\begin{array}{llllllllllllllllllllllllllllllllllll$	
Potassium	2.6		hex. Fe_9S_{10}
Magnesium	2.1		
All other	1.5	Greigite	Fe ₃ S ₄

Iron resides amongst the most abundant elements in the Earth's crust and forms in combination with oxygen and sulphur magnetic minerals which are omnipresent in our environment.

Electrons = moving electric charges





Free atoms

orbit + spin momenta

Solids

often only spin momenta

Ferromagnetic s.l. minerals

uncompensated spin momenta in overlapping orbits

e – elementary

n – main quantum number of Hydrogen, *s* – spin quantum number of e^{-} , *m* – mass of e^{-} , charge, \hbar – reduced Planck constant



Magnetite

ferrimagnetic

• Fe₃O₄



 $M_{S} = 480 \ kA/m$

 $T_{C} = 585 \ ^{\circ}\text{C}$

- T_V = between -163 and -153 °C
- H_c = between 10 and 80 mT (size dependent)
- (Soils)
- Inside bacteria
- Baked clays
- Combustion product
- Lacustrine/marine sediments







ferric iron Fe³⁺ at tetrahedral (A) and octahedral (B) sites



ferrous iron Fe²⁺ at octahedral site



oxygen anions

Magnetite Fe₃O₄



Superexchange

Magnetic minerals

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄



Close packing of oxygen & iron

Superexchange

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄

Oxygen 2p orbital overlaps with both 3d orbitals of Fe³⁺ and Fe²⁺



Superexchange

Magnetic minerals

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄

Oxygen exchanges both outer 2p electrons with the iron ions



Superexchange

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄

2 parallel spins → violation of Pauli principle



Superexchange

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄

Solution: opposite spins of Fe- ions \rightarrow lattices with opposite magnetic moments





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Magnetic minerals

Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄



ferric iron Fe³⁺ at tetrahedral (A) and octahedral (B) sites



ferrous iron Fe²⁺ at octahedral site



oxygen anions

at tetrahedral sites, Fe³⁺ occurs only

at octahedral sites occur both, Fe³⁺ and Fe²⁺

whole crystal: spins of Fe³⁺ at A sites equal spins of Fe³⁺ at B sites -> resulting moment only from Fe²⁺

magnetic moments at A and B sites are unequal and antiparallel -> ferrimagnetism

4 uncompensated moments

 $4 \mu_B$



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ferric iron Fe³⁺ at tetrahedral (A) and octahedral (B) sites



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5 uncompensated moments

 $4 \mu_B$

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Magnetite Fe³⁺[Fe³⁺Fe²⁺]O₄



ferric iron Fe³⁺ at tetrahedral (A) and octahedral (B) sites



ferrous iron Fe²⁺ at octahedral site



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5 uncompensated moments

 $4 \mu_B$

Magnetite

• Fe₃O₄



 $M_{S} = 480 \ kA/m$

due to high thermal energy

loss of magnetic ordering

characteristic temperature for each mineral but depends on substitution degree

 $T_C = 585 \ ^{\circ}\text{C}$

 T_V = between -163 and -153 °C

- H_c = between 10 and 80 mT (size dependent)
- (Soils)
- Inside bacteria
- Baked clays
- Combustion product
- Lacustrine/marine sediments



Maghaemite

 γ -Fe₂O₃



$3.33 \mu_B$

ferrimagnetic

Oxidised magnetite

 $M_{S} = 380 \ kA/m$

 $T_C = 645 \ ^{\circ}\text{C}$ (depends on substitution)

 T_V = depending on oxidation degree

Metastable 250 – 750 °C Converts to haematite

- Soils
- Soil bacteria excretion
- Baked clays
- Lacustrine/marine sediments



Maghaemite

• γ-Fe₂O₃

Oxidation of 44 *nm* magnetite

at 30° and variable p_{O_2}

 $M_{S} = 380 \ kA/m$

 $T_C = 645 \ ^\circ \text{C}$ (depends on substitution)

 T_V = depending on oxidation degree

Metastable 250 - 750 °C Converts to haematite

- Soils
- Soil bacteria excretion
- Baked clays
- Lacustrine/marine sediments



<u>Haematite</u>

• α-Fe₂O₃

"antiferromagnetic"

 $M_{S} = 2.5 \ kA/m$

 $T_N = 680 - 690 \ ^{\circ}\text{C}$

- T_M = between -100 and 13 °C (size dependent)
- H_c size dependent
- Soils
- Baked clay
- Sediments



<u>Haematite</u>

• α-Fe₂O₃

• apparent antiparallel alignment of spins



 $M_{S} = 2.5 \ kA/m$

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<u>Haematite</u>

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<u>Haematite</u>

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Fe³⁺



Haematite

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- Imperfect antiparallel alignment of spins
- Holes in crystal lattice (defects)
 - \rightarrow weakly ferromagnetic behaviour





Haematite

 α -Fe₂O₃

 $M_{S} = 2.5 \ kA/m$

 $T_N = 680 - 690 \,^{\circ}\mathrm{C}$

 T_M = between -100 and - 13 °C (size dependent)

0

- H_c size dependent
- Soils
- Baked clay
- **Sediments**

- Imperfect antiparallel alignment of spins ٠
- Holes in crystal lattice (defects) ٠

\rightarrow weakly ferromagnetic behaviour



Temperature, $T(^{\circ}C)$

Özdemir & Dunlop 2006

Haematite

• α-Fe₂O₃

- $M_{S} = 2.5 \ kA/m$
- $T_N = 680 690 \ ^{\circ}\text{C}$
- T_M = between -100 and 13 °C (size dependent)
- H_c size dependent
- Soils
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- Imperfect antiparallel alignment of spins
- Holes in crystal lattice (defects)
 - \rightarrow weakly ferromagnetic behaviour



Summary

Magnetic minerals

Origin of magnetism

- Electrons carry a spin magnetic moment
- In crystals with uncompensated spins
- Ordering requires energy gain by spin coordination of electrons in <u>overlapping</u> orbitals.
- Only ions with uncompensated spins in highly eccentric orbitals (*e.g.* 3d for *Fe*³⁺) are possible sources of ferro-, ferri- or antiferromagnetism.







Diamagnetism ($\kappa < 0$)

- external magnetic field H causes distortion of electron-orbit (Lorentz force)
- precession of orbital plane around *H* direction (*Larmor-precession*)
- a second magnetic moment is created but opposite to H (Lenz rule)
- precession frequency depends on H
- in all materials
- weak, best observed in materials without a resulting spin momentum



Summary

Magnetic minerals



4 uncompensated moments







non-overlapping atomic orbitals

H = 0



thermal energy randomises spin alignment hence spin alignment depends on temperature

Temperature T





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Magnetic minerals

Ferromagnetism ($\kappa >> 0$)

- in materials with <u>unpaired spins</u> and <u>overlapping atom orbits</u> (close packing)
- electrons are exchanged between iron atoms either directly (ferromagnetism) or indirectly via interjacent oxygen atoms (superexchange – *e.g.* antiferromagnetism, ferrimagnetism)
- $\hfill\square$ materials exhibit a spontaneous magnetisation $\hfill M_s$ after field removal, due to uncompensated spin moments



Magnetic iron minerals

Basics of magnetism

Magnetite (Fe ₃ O ₄):	$M_{\rm s} = 480 \text{ kA/m}, T_{\rm c} = 580 ^{\circ}\text{C}, T_{\rm v} = -150 ^{\circ}\text{C}$ ferrimagnetic, in soils, bacteria, lacustrine/marine sediments, often partly oxidised, also in human and animal tissue, combustion product
Maghaemite (γ-Fe ₂ O ₃):	$M_{\rm s} = 380 \text{ kA/m}, (T_{\rm c} = 590-675 \ ^{\circ}\text{C})$ ferrimagnetic weathering product (fully oxidised magnetite, no Fe ²⁺ in lattice), common in soils and sedimentary rocks, combustion product
Haematite (α-Fe ₂ O ₃):	$M_{\rm s} = -2.5$ kA/m, $T_c = 675$ °C, $T_M = -15$ °C, imperfect antiferromagnet (weakly ferromagnetic) common in soils and sediments, red beds
Pyrrhotite (Fe ₇ S ₈):	$M_{\rm s} = ~80 \text{ kA/m}, T_{\rm c} = 320 ^{\circ}\text{C}$
Pyrrhotite (Fe ₉ S ₁₀):	ferrimagnetic above 200 °C, $T_c = 265$ °C in sedimentary metamorphic rocks, sulfide ores
Greigite (Fe ₃ S ₄):	$M_{\rm s}$ = ~ 125 kA/m, $T_{\rm c}$ = ~330 °C forms in aquatic enivronments (and soils) under unoxic conditions, in bacteria
Goethite (α-FeOOH):	$M_{\rm s} = ~2$ kA/m, $T_{\rm c} = 120$ °C imperfect antiferromagnet (weakly ferromagnetic), in soils and acquatic environments, lateritic weathering product
Siderite (FeCO ₃):	$T_{\rm N} = -235 \ ^{\circ}{\rm C}$ (antiferromagnetic, but paramagnetic @ room temperature) marine lacustrine, in soils probably

Properties of some magnetic minerals

• Formation of magnetic minerals

Magnetic characterisation methods

Examples

Formation

Dead vegetable and animal matter is decomposed by soil animals and microorganisms (such as worms, mollusca, bacteria, fungi), altered and incorporated into the soil. -> humification of organic matter.

Source material and products of weathering/humification are transported on and in the soil, either as solid particles or in solutions.

The soil constituents are then connected by cementing material, which is partly of biologic origin. This causes a new texture and granularity.



Formation

Pedogenesis = progressive transformation of bed rock into a soil



Formation



Formation





Simo Spassov

Formation



Baked materials

Formation


Formation

Source material contains "non"-magnetic iron

Magnetic minerals are generated during prolonged heat exposure at different p_{O_2}



Phylloscilicates (e.g. clays, micas, chlorites) Murad & Wagner 1998

- 1. Loss of physically adsorbed or intercalated water at 100-200 °C
- 2. Oxidation, where applicable, of divalent iron
- 3. Loss of structural hydroxyl at intermediate higher temperatures
- 4. Final structural breakdown combined with the formation of new phases close to 1000 $^{\circ}$ C
- 5. Vitrification.



Formation

Tournassat et al. 2015

FIGURE 1.1 From top to bottom: tetrahedral and octahedral sheets, TO (Kaol) and TOT layers (*cv*-Mt), and clay mineral particles. The Kaol layer structure was taken from the COD database (Gražulis et al., 2012). The *cv*-Mt structure was taken from Tsipursky and Drits (1984).



Formation

Source material contains "non"-magnetic iron

Magnetic minerals are generated during prolonged heat exposure at different p_{O_2}

Iron minerals

Murad & Wagner 1998 (and references therein)

Dehydroxylation under	200 - 320°C	310-485°C
oxidising conditions	$2 (\alpha, \gamma)$ -FeOOH $\rightarrow \gamma$ -Fe ₂ O ₃ + H ₂ O	$\rightarrow \alpha - Fe_2O_3$
reducing conditions	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$\rightarrow Fe_3O_4$

Presence of Al and Ti in clay can result in substituted maghaemite and haematite.

Formation

Source material contains "non"-magnetic iron

Magnetic minerals are generated during prolonged heat exposure at different p_{O_2}



Formation



Properties of some magnetic minerals

• Formation of magnetic minerals

Magnetic characterisation methods

Examples

Loops RT LT, Day, exchange bias, Pasha, FORC nur am rande Coercivity spectra analysis nur am rande



- H_c coercive force
- H_{cr} remanent coercive force
- M_s saturation magnetisation
- M_{rs} saturation remanence

Ratios $M_{\rm rs}/M_{\rm s}$ and $H_{\rm cr}/H_{\rm c}$ are indicators of the magnetic grain size



Hysteresis

Characterisation



Hysteresis

Characterisation



<u>Hysteresis</u>



Hysteresis

Characterisation



Magnetic hysteresis



Definition & Units

- $\vec{M} = \kappa \vec{H}$ H[A/m] and $M[A/m] \rightarrow \kappa$ dimensionless, refers to volume
- $M_i = \kappa_{ij} H_j$ 2nd degree Tensor

For practical use

Mass susceptibility
$$\chi_{mass} = \frac{\kappa}{\rho} = \frac{\kappa}{m_{sample}} V_{measurement}$$
 $[m^3/kg]$
Molar susceptibility $\chi_{molar} = M \cdot \chi_{mass}$ $[m^3/mol]$

Characterisation

DC susceptibility



Initial and high-field susceptibility are determined by fitting the M(H) curve.

General practice κ_{low} obtained from AC measurements, only κ_{hifi} used for interpretations.

Characterisation

AC susceptibility



from Nikolo, Am. J. Phys. 63, 1995

U measured with a phase separating lock-in amplifier $\rightarrow \kappa'$ and κ'' can be separated.

Characterisation

AC susceptibility

Real part

• Related to <u>reversible</u> magnetisation processes.

- Absorption of energy during magnetisation.
- Stays in phase with the driving oscillating field,
- Reflects the sensitivity of material to applied magnetising field *H*. "Magnetisability"
- is positive for antiferro-, ferro-, ferri-, paramagnetics
- is negative for diamagnetics



Characterisation

Imaginary part

 $\chi^{\prime\prime}$

AC susceptibility

- Due to <u>irreversible</u> magnetisation changes
- Dissipation of energy during magnetisation, e.g. due to:
 - irreversible domain wall movements
 - relaxation of SP grains
 - Spin lattice relaxation in paramagnets
 - eddy currents in conducting materials
- May be zero or positive, but never negative.
- $\chi'' < \chi'$
- If $\chi'' = 0 \rightarrow \chi_{ac} = \chi_{dc}$

Characterisation



AC vs. DC susceptibility

molecular Fe-Nb ferromagnet with a Curie temperature well below room temperature

Instruments measuring κ_{AC}

Producer	Т	H_{ac}	f	H _{DC-bias}
	[K]	[<i>A</i> / <i>m</i>]	[kHz]	[m <i>T</i>]
Bartington	73-1123	0.2	0.456 & 4.56	-
Agico	81-973	5-750	0.976, 3.904, 15.6	-
QD	0.5-1000	8-800	0.0001-1	0.5-7000
	Bulk, aniso	tropy, χ()	T), $\chi(f)$, $\chi(H)$	
	,			

KLY

www.agico.com

Characterisation

Instruments measuring κ_{AC}



	Producer	Т	H_{ac}	f	H _{DC-bias}
		[K]	[<i>A</i> / <i>m</i>]	[kHz]	[m <i>T</i>]
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(SAGA rnaTS) BaPtaguer 29-31 nHa2022 and Rock Magnetism

Instruments measuring κ_{AC}

[<i>K</i>] Bartington 73-1123	[<i>A</i> / <i>m</i>]	[kHz]	[m <i>T</i>]	
Bartington 73-1123	0.2			
Agico 81-973	5-750	0.456 & 4.56	-	
QD 0.5-1000	8-800	0.0001-1	0.5-7000	
Not-qd.de DC in function of T , H , Anisotropy in function of H AC χ', χ'' in function of T , H , f				



magnetic mineral identification

- small fields < 800 A/m (in reversible region of hysteresis loop)
- Initial slope changes are different for different magnetic minerals

Field dependence



Low temperature magnetisation

40 $[mAm^2kg^{-I}]$ 30 Magnetic properties in function of distance 20 $M_{1\,mT,20\,K}$ $6 - 8 \, cm$ 10 4 – 6 *cm* 2 - 4 cm0-2 cm0 50 100 150 200 300 250 Temperature [*K*] TUnpublished data from Ech-chakrouni & Spassov (2019)

Characterisation

Low temperature magnetisation

Characterisation $[mAm^2kg^{-l}K^{-l}]$ 0.3 Fully oxidised Partially oxidised magnetite = 0.2 maghaemite magnetite $T_V = 119 K$ dT0.1 **6 – 8** *cm* 4 – 6 *cm* 2-4 cm $T_V = 102 K$ 0-2 cm0.0 50 150 100 200 250

Temperature T [K] Unpublished data from Ech-chakrouni & Spassov (2019)

 $d(M_{1\,mT,\,20\,K})$





<u>ARM</u>

Characterisation

Anhysteretic remanent magnetisation

Steady field magnetisation and alternating field demagnetisation at once



Normalised SIRM vs remanent coercive force

Characterisation



Grain size & concentration





From Evans & Heller (2003)

Thermal demagnetisation of IRM



From Evans & Heller (2003)

Thermal demagnetisation of IRM



Characterisation



Table 5.1 Maximum coercivities and blockingtemperatures for some common ferromagnetic minerals

Ferromagnetic mineral	Maximum coercivity [T]	Maximum blocking temperature [°C]
Magnetite	0.3	575
Maghemite	0.3	≈350
Titanomagnetite (F	$e_{2} = Ti_{0}O_{4}$:	
x = 0.3	0.2^{-x}	350
x = 0.6	0.1	150
Pyrrhotite	0.5 - 1	325
Hematite	1.5 - 5	675
Goethite	> 5	80–120

Lowrie (2007)

Thermal demagnetisation of IRM

Characterisation



1. Magnetise in strong field, e.g. 2 T,

2. demagnetise with alternating fields

Decay of IRM

Remanent magnetisation decays over time

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

$$\begin{split} M_{eq} &= M(t \to \infty) \\ M_0 &= M(t=0) \\ \tau &= f(V, M_s, H_k, H_0) \text{ relaxation time} \end{split} \begin{array}{l} H_k &= \text{micro-coercivity assuming shape} \\ H_0 &= \text{external field} \\ V &= \text{lognormal distribution of volumes} \end{split}$$

Small grains, *e.g.* 30 – 40 nm magnetite/maghaemite or haematite loose their remanence quickly

Larger grains, i.e. single domain and multidomain do practically not loose their remanence.

Decay of IRM

Characterisation

