

IRON SULFIDES

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General

Iron sulfides are generally quoted as minor magnetic minerals and the interest of paleomagnetists for this family of minerals progressively developed only during the last 10 – 15 years. This was due partly to the fact that their occurrence was originally believed to be restricted to peculiar geological environments (i.e. sulfidic ores, anoxic sulfate-reducing sedimentary environments) and partly to their metastability with respect to pyrite (FeS_2), which is paramagnetic. Magnetic iron sulfides were therefore not expected to carry a stable remanent magnetisation and to survive over long periods of geological time in sedimentary environments. However, their occurrence as main carriers of a remanent magnetisation stable through geological times has been increasingly reported in recent years from a large variety of rock types, primarily as a result of more frequent application of magnetic methods to characterize the magnetic mineralogy in paleomagnetic samples. The recognition of the widespread occurrence of magnetic iron sulfides as stable carriers of natural remanent magnetisations in rocks propelled specific researches on their fundamental magnetic properties.

Pyrrhotite: magnetic properties

Among magnetic iron sulfides, the pyrrhotite solid solution series (Fe_{1-x}S ; with x varying between 0 and 0.13) exhibits a wide range of magnetic behaviours. Stoichiometric pyrrhotite FeS (troilite) show a hexagonal crystal structure based upon the NiAs structure, with alternating c-planes of Fe and S (Figure 1). In each Fe-layer the Fe^{2+} ions are ferromagnetically coupled, while neighbouring Fe-layers are coupled antiferromagnetically to each other via intervening S^{2-} ions. The non-stoichiometric pyrrhotites are cation deficient. The increase of Fe deficiency affects both the crystallographic and magnetic structures: ordering of Fe vacancies leads to an alternation of partially and fully filled Fe layers, the

hexagonal structure distorts to monoclinic and the magnetic ordering turns from antiferromagnetic to ferrimagnetic. Pyrrhotite shows a strong magnetocrystalline anisotropy, with the easy directions of magnetisation confined in the crystallographic basal plane (the magnetic crystalline anisotropy constant K_1 is positive and estimated at ca. 10^4 J/m^3 , see Dunlop and Özdemir, 1997). The crystallographic c-axis perpendicular to the basal plane is the axis of very hard magnetisation.

The more Fe-rich, hexagonal, pyrrhotites (F_9S_{10} , and possible $\text{F}_{10}\text{S}_{11}$, $\text{F}_{11}\text{S}_{12}$) are antiferromagnetic at room temperature and are characterized by a λ transition at temperatures between ca. 180°C and 220°C , depending on composition, above which they exhibit ferrimagnetism. The λ transition represents a change in the vacancy ordering pattern of the crystal structure and is distinctive and diagnostic of hexagonal (Fe-rich) pyrrhotites. The Curie temperature for the different compositions of hexagonal pyrrhotites varies between 210°C and 270°C .

The most Fe-deficient pyrrhotite (F_7S_8) is monoclinic and ferrimagnetic at room temperature, with a Curie temperature of ca. 325°C . It has no λ transition, but it shows a diagnostic low-temperature transition in remanence and coercivity at 30 - 35 K (Rochette et al., 1990).

Natural pyrrhotite usually occurs as a mixture of superstructures of monoclinic and hexagonal types, which results in an intermediate overall composition. Magnetic properties of pyrrhotite and their dependence from grain size and temperature have been investigated in detail in a number of specific studies (e.g. Clark, 1984; Dekkers, 1988; 1989; 1990; Menyeh and O'Reilly, 1991; 1995; 1996; Worm et al., 1993; O'Reilly et al., 2000). Monoclinic ferrimagnetic pyrrhotite (F_7S_8) has a saturation magnetisation (J_s) of $18 \text{ Am}^2/\text{kg}$ at room temperature. The magnetic susceptibility of pyrrhotites is field independent in grains smaller than $30 \mu\text{m}$, however for larger grains the magnetic susceptibility (χ) and its field dependence increase with increasing grain size ($1 \times 10^{-5} - 7 \times 10^{-5} \text{ m}^3/\text{kg}$). Conversely, the coercivity

parameters all increase with decreasing grain size. The room temperature coercive force (H_c) ranges from 10 to 70 kA/m (i.e. 12 – 88 mT for coercive force expressed as magnetic induction B_c) and for synthetic powders with grain size in the range 1-24 μm , it could be fitted by a power-law dependence of the form $H_c \propto L^n$, where L is the particle size and $n = -0.38$ (O'Reilly et al., 2000). During hysteresis measurements and isothermal remanent magnetisation (IRM) acquisition experiments pyrrhotite powders approach complete saturation only in fields greater than 1 T, with the magnetic hardness increasing with decreasing grain sizes (O'Reilly et al., 2000).

In synthetic monoclinic pyrrhotites the critical size for the transition from the single domain SD to the multidomain MD state, with typical lamellar domains normal to the c-axis, is estimated at a mean value of ca. 1 μm . The micromagnetic structures of hexagonal synthetic pyrrhotites is far more complex than that of monoclinic pyrrhotites, with typical wavy walls and a significantly smaller size of the individual magnetic domains (O'Reilly et al., 2000).

The remanent magnetisation carried by pyrrhotites can be of prime importance for paleomagnetic studies, but various factors may complicate the paleomagnetic interpretation of the data obtained from the classical demagnetisation treatments. During alternating field (AF) demagnetisation pyrrhotite-bearing samples were reported to acquire significant gyromagnetic and rotational remanent magnetisation in fields higher than 20 mT (Thomson, 1990) and upon heating at temperatures greater than 500°C during thermal demagnetisation pyrrhotite transforms irreversibly to magnetite and, via subsequent further oxidation and heating, to hematite (Dekkers, 1990), producing new magnetic phases that may acquire new remanent magnetisations in the laboratory. Furthermore, self-reversal phenomena of pyrrhotite have been earlier reported under various laboratory experiments (Everitt, 1962; Bhimasankaram, 1964; Bhimasankaram and Lewis, 1966). Recent studies linked such

phenomena to crystal twinning (Zapletal, 1992) and/or to a close coexistence of pyrrhotite and magnetite crystals, the latter being nucleated from direct oxidation of the pyrrhotite grains during heating (Bina and Daly, 1994).

Greigite: magnetic properties

The iron sulfide greigite (Fe_3S_4) is the ferrimagnetic inverse thiospinel of iron and its crystalline structure is comparable to that of magnetite (Fe_3O_4) in which sulfur replace oxygen atoms. In the cubic close-packed crystal structure of greigite the tetrahedral A-sites are filled by Fe^{3+} ions and the octahedral B-sites are filled half by Fe^{3+} ions and half by Fe^{2+} ions (Figure 2).

Greigite is characterized by a high magnetocrystalline anisotropy (with a positive magnetic crystalline anisotropy constant K_1 estimated at ca. 10^3 J/m^3 , see Diaz Ricci and Kirschvink, 1992; Dunlop and Özdemir, 1997) and its magnetic easy axis is aligned along the $\langle 100 \rangle$ crystallographic direction. Basic magnetic properties at room temperature in synthetic greigite powders were systematically investigated by Dekkers and Schoonen (1996), indicating a minimum lower bound for the saturation magnetisation (J_s) of $29 \text{ Am}^2/\text{kg}$, a magnetic susceptibility (χ) between ca. 5×10^{-5} and $20 \times 10^{-5} \text{ m}^3/\text{kg}$ and intermediate coercivities (i.e. IRM acquisition curves saturate after application of fields $\geq 0.7 - 1 \text{ T}$).

Greigite is unstable during heating to temperature higher than ca. 200°C . As a consequence of such instability the magnetic susceptibility and the magnetisation in greigite-bearing sediments both undergo significant changes during heating (see Krs et al., 1990; 1992; Reynolds et al., 1994; Roberts, 1995; Horng et al., 1998; Sagnotti and Winkler, 1999; Dekkers et al., 2000): a major drop is generally observed between ca. 250°C and 350°C ,

reflecting decomposition of greigite in nonmagnetic sulfur, pyrite and marcasite, followed by a dramatic increase above 350-380°C and a subsequent decrease above 400-450°C, indicating progressive production of new magnetic phases (pyrrhotite, then magnetite/maghemite and finally hematite). Thermal decomposition of greigite precludes direct determination of its Curie temperature.

Greigite does not show any low temperature (5 – 300 K) phase transition (Roberts, 1995; Torii et al., 1996; Dekkers et al., 2000), though a broad J_s maximum peak value was observed at 10 K during cooling from 300 K to 4 K (Dekkers et al., 2000).

Typical for greigite are: low to intermediate coercivities, with spectra that partly overlap those of magnetite and pyrrhotite (i.e. for natural greigite-bearing sediments and synthetics greigite the published values for the coercivity of remanence (B_{cr}) ranges from 20 to 100 mT, while for the coercivity (B_c) varies from 13 to 67 mT), maximum unblocking temperatures in the range 270-380°C, the lack of low-temperature phase transitions and the presence of distinct stable single domain (SD) properties (i.e. Roberts, 1995). With regards to these latter properties, in particular, greigite-bearing sediments show: (a) SD-like hysteresis ratios, with M_{rs}/M_s often exceeding 0.5 (where M_{rs} is the saturation remanent magnetisation and M_s is the saturation magnetisation) and B_{cr}/B_c often lower than 1.5, (b) high values of the SIRM/k ratio (where SIRM is the saturation isothermal remanent magnetisation and k the low-field magnetic susceptibility), (c) a sensitivity to field impressed anisotropy and (d) a marked tendency for acquisition of gyromagnetic remanent magnetisation (GRM) and rotational remanent magnetisations (RRM). GRM and RRM acquisition in greigite-bearing samples has been investigated in the detail in several specific studies (Snowball, 1997a; 1997b; Hu et al, 1998; Sagnotti and Winkler, 1999; Stephenson and Snowball, 2001; Hu et al., 2002) that have shown that greigite has the highest effective gyrofield (B_g) reported so far for all magnetic

minerals (of the order of several hundred μT for a peak AF of 80 mT) and that gyromagnetic effects are powerful indicators for the presence of greigite in sediments.

GRM and RRM are effects due to the application of an AF on SD grains. They are produced whenever there is an asymmetry in the number of magnetic moments that flip in a particular sense during the AF treatment. In other words, such remanences appear in any system where a particular sense of flip predominates (Stephenson, 1980a; 1980b). RRM was explained in terms of a gyromagnetic effect associated with the irreversible flip of SD particles during rotation of the sample in an AF (Stephenson, 1985).

The typical SD properties of natural greigite grains may be explained by its intrinsic magnetic and crystalline structure, with the magnetocrystalline anisotropy dominating the magnetisation process. The theoretically estimated size range of stability for prismatic greigite SD grains extends well beyond that of magnetite, suggesting that elongated greigite crystals may be in a SD state even for very large sizes (up to several μm) (Diaz Ricci and Kirschvink, 1992). Moreover, direct magnetic optical observations indicated that the SD to two-domain transition in greigite may occur for grain sizes of 0.7-0.8 μm (Hoffmann, 1992) and that greigite usually occurs in framboidal aggregates of grains individually smaller than 1 μm (i.e. Jiang et al., 2001).

The maximum value for the M_{rs}/M_s ratio in SD grains with shape anisotropy is 0.5.

Conversely, if magnetocrystalline anisotropy controls the hysteresis behaviour and the $\langle 100 \rangle$ axis is the easy axis of magnetisation, it would be expected that M_{rs}/M_s would approach a value of 0.832 as B_{cr}/B_c approach unity. Under the same circumstances if $\langle 111 \rangle$ is the easy axis of magnetisation M_{rs}/M_s is predicted to approach 0.866 (O'Reilly, 1984; Dunlop and Özdemir, 1997).

A magnetic method for discriminating between greigite and pyrrhotite in paleomagnetic samples has been proposed by Torii et al. (1996), based on the thermal demagnetisation of a composite isothermal remanent magnetisation (IRM) and relying upon the instability and alteration of greigite during thermal heating at temperatures above 200°C.

Notwithstanding its metastable properties and magnetic instability, the importance of greigite for paleomagnetism and magnetostratigraphy has been particularly stressed in recent years since it has been widely recognized as a carrier of stable chemical remanent magnetisation in lacustrine and marine sediments, with ages ranging from the Cretaceous to the Present (e.g. Snowball and Thompson, 1990; Snowball, 1991; Hoffmann, 1992; Krs et al., 1990; 1992; Roberts and Turner, 1993; Hallam and Maher, 1994; Reynolds et al., 1994; Roberts, 1995; Roberts et al., 1996; Sagnotti and Winkler, 1999), as well as in soils (Fassbinder and Stanjek, 1994).

Fe-Ni sulfides

Smythite (Fe, Ni)₉S₁₁, Pentlandite (Fe, Ni)₉S₈ and other complex Fe-Ni sulfides were occasionally reported in sediments (i.e. Krs et al., 1992; van Velzen et al., 1993) in association with pure Fe sulfides, but their magnetic properties have not been studied in the detail so far.

Occurrences: formation, preservation, problems and potential for use in paleomagnetism

Troilite is common in meteorites and lunar rocks, but not on Earth.

Pyrrhotites are ordinary magnetic carriers in magmatic, hydrothermal and metamorphic rocks. Pyrrhotite in metamorphic rocks has been shown to acquire post-metamorphic partial thermomagnetic remanent magnetisation (pTRM) during the uplift of mountain belts and has been used as a thermometer for post-metamorphic cooling (thermo-paleomagnetism) and for dating and evaluation of exhumation rates through various reversals of the Earth magnetic field (i.e. Crouzet et al., 1999; 2001a; 2001b).

Pyrrhotite has also been recognized as the main remanence carrier in SNC (Shergotty-Nakhla-Cassigny type) Martian meteorites, and inferred as a main magnetic phase in the crust of Mars with significant implication for a proper evaluation of magnetic anomalies on such planet (Rochette et al., 2001).

Pyrrhotite and greigite occur also as authigenic phases in geologically young or recent sediments deposited under anoxic, sulfate reducing conditions (Figure 3).

The presence of magnetic iron sulfides in sediments is of special interest, since they have important implication for magnetostratigraphy and environmental magnetism. Reduction diagenesis and authigenesis can significantly affect the magnetic mineralogy of sediments (Karlín and Levi, 1983, Karlín, 1990a; 1990b; Leslie et al., 1990a; 1990b). In particular, magnetic iron sulfides can be produced through a number of different processes: (1) bacterially mediated synthesis of single-domain greigite, in form of magnetosomes produced by magnetotactic bacteria (Mann et al., 1990; Bazylinski et al., 1993) and/or (2) precipitation from pore waters and/or (3) dissolution of detrital iron oxides and subsequent precipitation of iron sulfides.

Authigenic growth of iron sulfides is a common and relatively well understood process in anoxic sedimentary environments with relatively high organic carbon contents (e.g. Berner, 1984; Leslie et al., 1990a; 1990b; Roberts and Turner, 1993). Authigenic magnetic iron sulfides (pyrrhotite and greigite) are intermediate mineral phases within the chemical iron

reduction series that eventually forms stable paramagnetic pyrite (FeS_2 ; Berner, 1969; 1970; 1984; Canfield and Berner, 1987). The process can be mediated by bacterial activity that reduces pore-water sulfate (SO_4^{2+}) to sulfide (S^-) associated with consumption of organic carbon during burial. Hydrogen sulfide (H_2S) then progressively reacts with detrital iron minerals to ultimately produce pyrite. Intermediate magnetic iron sulfides are metastable with respect to pyrite in the presence of excess H_2S . The major factors controlling pyrite formation and the preservation of the (magnetic) intermediate phases in marine sediments are the amounts of dissolved sulfate, reactive iron detrital minerals and decomposable organic matter (Berner, 1970; 1984). Intermediate magnetic iron sulfides may be preserved in all cases when the limited availability of sulfide, reactive iron and/or organic matter prevents completion of the processes that result in formation of pyrite. In normal marine environments, sulfate and reactive detrital iron minerals are practically unlimited and the major controlling factor on the pyritization process appears to be the availability of detrital organic matter (Kao et al., 2004). In this case, the small amounts of sulfide produced will rapidly react with dissolved iron; the rapid consumption of sulfide means that formation of intermediate greigite is favoured over pyrite. However, in some settings, organic carbon may have different sources and greigite has also been reported to form during later burial as a consequence of the diffusion of hydrocarbons and gas hydrates through permeable strata (Reynolds et al., 1994; Thompson and Cameron, 1995; Housen and Mousgrave, 1996).

Greigite is the more common magnetic iron sulfide in fine-grained sediments; pyrrhotite, however, has also been reported in various fine-grained sediments, often alongside greigite (Linssen, 1988; Mary et al., 1993; Roberts and Turner, 1993; Dinarès-Turell and Dekkers, 1999; Horng et al., 1998; Sagnotti et al., 2001; Weaver et al., 2002) (Figure 3). The relative abundance of reactive iron versus organic matter appears to be the controlling factor for the transformation pathway of initial amorphous FeS into greigite or into pyrrhotite (Kao et al., 2004). Compared to greigite, pyrrhotite is favoured by more reducing environments (i.e.

lower Eh) and higher concentration of H₂S, both implying a higher consumption of organic carbon (Kao et al., 2004). Even under appropriate diagenetic conditions, however, monoclinic pyrrhotite (Fe₇S₈) formation will be extremely slow below ~180°C, which makes it a highly unlikely carrier of early diagenetic remanences in sediments (Hornig and Roberts, 2006). The abundance of monoclinic pyrrhotite in regional metamorphic belts makes it a likely detrital rather than authigenic magnetic mineral in marginal basins in such settings (Hornig and Roberts, 2006).

During nucleation and crystal growth, authigenic greigite and pyrrhotite acquire a chemical remanent magnetisation (CRM) which contributes to the total natural remanent magnetisation (NRM) of the sediments. Authigenic formation of magnetic iron sulfides is generally believed to occur at the very first stages of diagenesis and natural remanent magnetisations carried by magnetic iron sulfides were used for detailed paleomagnetic studies, assuming they reflect primary components of magnetisation (e.g. Tric et al., 1991). However, many studies documented a significant delay between the deposition of the sediment and the formation of magnetic iron sulfides, implicating late diagenetic magnetisations. In particular, sediments bearing magnetic iron sulfides were often reported to carry chemical remanent magnetisations that are anti-parallel either to those carried by coexisting detrital magnetic minerals and of opposite polarity with respect to the polarity expected for the age of the rock unit (e.g., Florindo and Sagnotti, 1995; Hornig et al., 1998; Dinarès-Turell and Dekkers, 1999; Jiang et al. 2001; Weaver et al, 2002; Oms et al., 2003; Sagnotti et al., 2005; Roberts and Weaver, 2005). Such studies demonstrate that magnetic iron sulfides can carry stable magnetisations with a wide range of ages and that a syn-depositional age should not be automatically assumed.

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Captions

Figure 1

Sketch of the crystalline structure of stoichiometric troilite (FeS). The structure is basically hexagonal, with alternating layers of Fe²⁺ and S²⁻ ions. The c-axis of hexagonal symmetry is the axis of very hard magnetization and is perpendicular to the basal planes. Elemental magnetic moments are parallel within a particular cation basal plane. The alternating Fe²⁺ layers define the two magnetic sublattices with oppositely directed magnetic moments. In nonstoichiometric monoclinic pyrrhotite Fe₇S₈, the cation vacancies are preferentially located on one of the two magnetic sublattices, giving rise to ferrimagnetism.

Figure 2

Sketch of the ½ of a unit cell of greigite (Fe₃S₄). The crystalline structure of greigite is basically the same inverse spinel structure typical for magnetite (Fe₃O₄) in which S²⁻ ions substitute O²⁻ ions. Cations are both in tetrahedral (A-site) and octahedral (B-site) coordination with S²⁻ ions. In greigite the easy axis of magnetization is the <100> crystallographic axis.

Figure 3

- A) Back-scattered electron micrograph of an iron sulphide nodule from the Valle Ricca section, Italy (see Florindo and Sagnotti, 1995). The nodule shows evidence for multi-phase sulfidization and contains framboidal pyrite (Py) and greigite (G), which always occurs with finer crystal sizes than the co-occurring pyrite, and intergrown plates of hexagonal pyrrhotite (Pyrr) (Courtesy of Andrew P. Roberts and Wei-Teh Jiang).
- B) Back-scattered electron micrograph of a Trubi marl sample from Sicily (see Dinarès-Turell and Dekkers, 1999) showing framboidal pyrite (Py) filling foraminifera shells and

pyrrhotite (Pyrr) intergrown plates dispersed in the rock matrix (Courtesy of Jaume Dinarès-Turell).





