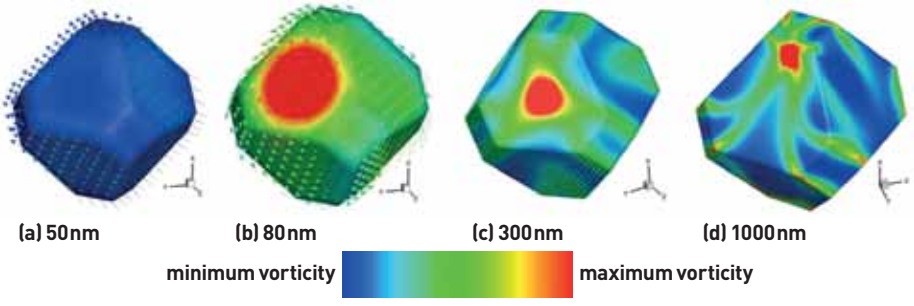
The role of magnetic interactions in natural systems

Inter-particle magnetic interactions between crystals in natural systems strongly affect their magnetic response. In the Bullerwell Lecture 2011, Adrian Muxworthy discusses how these interactions affect our ability to recover from rocks information about the ancient geomagnetic field behaviour, plate tectonics and palaeogeography, and how magnetotactic bacteria utilize interactions to improve navigational efficiency.



1: Magnetic domain structures in cubo-octahedral grains of magnetites obtained using micromagnetic modelling. The magnetization is coloured according to vorticity that highlights non-uniform structures. Grains smaller than 80nm are in the single domain (SD) state. Above 80nm a vortex state is nucleated. This vortex state persists for a large range of grain volumes with more complex states starting to emerge above 1000nm. When SD particles are smaller than a critical (blocking) volume (~30nm for magnetite at room-temperature) they are no longer magnetically stable because thermal energy can easily overcome the energy barrier that prevents domain switching. Such particles have superparamagnetic behaviour; they retain no magnetic remanence. All these domain-states are common in Nature though only non-interacting stable SD grains carry a reliable magnetic remanence; magnetically interacting SD grains also do not reliably record the field.

In the material science world it is possible to construct systems with limited or well-understood magnetic interactions, in striking contrast to Nature where we find complex magnetic systems that are far from ideal magnetic recorders. However, the contribution and understanding of these magnetic interactions have largely been ignored by the mineral-magnetic and palaeomagnetic community because the problem is highly nonlinear; in many natural systems it is argued that the role of magnetic interactions is limited. Nonetheless, in recent years, with the development of new instruments and synthesis techniques by the material science community and the great advances in computational hardware, it is now possible to try to understand these systems.

In this article I give an overview of the types of different interactions found in natural systems, and how we study them. I present data from a number of studies and finally will discuss how magnetic interactions found in living organisms can enhance navigational capability.

Magnetic domain states

Magnetic interactions between particles depend on the magnetic states of the particles. The smallest magnetic grains have near-uniform magnetization as all their atomic magnetic moments are aligned parallel to each other: such structures are termed single domain (SD) (see figure 1a). In larger grains the magnetic structure breaks up into discrete regions separated by magnetic domain walls, and are termed multidomain (MD) (figure 1d). Small MD grains, above the SD/MD threshold size (~100nm for magnetite) display SD-like characteristics though they have non-uniform magnetizations, and are often referred to as pseudo-single domain (PSD). Small PSD grains commonly have "vortex" structures, consisting of a curling outer region with a central core (figures 1b and 1c).

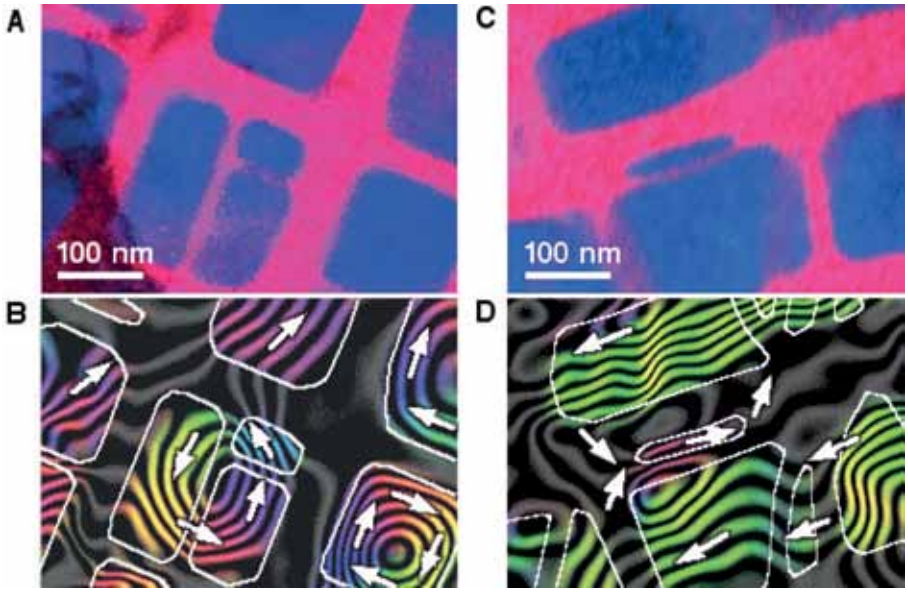
Dynamic and static interactions

In systems of interacting grains, both superparamagnetic (SP) grains, that do not retain magnetic remanence and stable domain states (i.e. SD, PSD and MD grains), contribute to the interaction field. The magnetic interaction field generated by a stable grain is constant during the rotation or structural change of a neighbouring grain's internal magnetic structure. This makes it possible to treat magnetic interaction fields arising from stable domain states grains as effectively static (Spinu and Stancu 1998), and for modelling purposes we can treat the interaction field like a variable "external" magnetic field (Dunlop and West 1969).

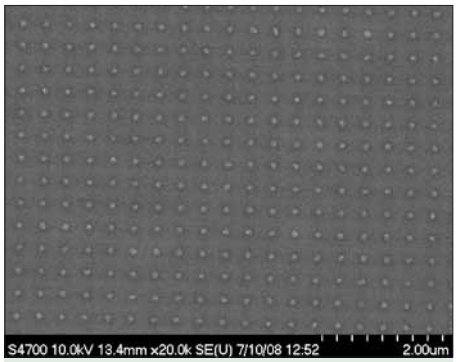
For interacting SP grains, the situation is more complicated. The behaviour of an assembly of SP particles falls into one of three regimes depending on the inter-particle interactions (Dormann *et al.* 1997): (i) a pure SP case (non-interacting), (ii) an SP state modified by interactions, and (iii) a glass collective state. The properties of state (iii) are close to those of spin glasses with a phase transition. This state is not fully understood and there is no simple model for the collective state. There are models for state (ii); these dynamic interactions are qualitatively different from static ones, as dynamic systems are not in thermodynamic equilibrium and hence cannot be directly modelled using Boltzmann statistics. Several approaches have been developed to address this problem (Dormann *et al.* 1988); these models demonstrate that the effect of interactions due to SP grains is to increase their relaxation time due to thermal fluctuations.

Understanding the effect of interactions

To try to quantify the contribution of interactions to natural magnetic systems, both experimental and numerical approaches have



2: Two areas of a finely exsolved titanomagnetite sample from Mount Yamaska, Quebec. In A and C the blue regions show magnetite blocks which are separated from each other by paramagnetic ulvöspinel. B and D show the corresponding magnetic phase contours measured using electron-holography from the same regions. In B, three adjacent magnetite-rich regions combine to form a "super vortex"; and D shows a small region that is magnetically antiparallel to its larger neighbours. (From Harrison *et al.* 2002)



3: Scanning electron microscope image of EBL-produced thin-film sample DK0124 which has a dot diameter of 74nm and separation of 300nm. Each thin-film contains millions of near-identical magnetite dots. (From Krása *et al.* 2011)

been taken. The principal areas are direct observations of static magnetic interactions in rocks, synthesis of ideal samples combined with electron-beam lithography, and numerical modelling.

Recent improvements in advanced transmission electron microscopy (TEM) techniques, in particular the method of off-axis electron holography, allow direct imaging of the magnetic fields within and between crystals on nanometric scales (Dunin-Borkowski *et al.* 1998). Because the image is constructed from the shift in phase that occurs when the electron beam passes through a magnetic field, the technique also images the static magnetic fields between magnetic crystals. The resolution of the TEM and the ability to image inter-grain magnetic fields makes this a significant improvement on previous methods such as Bitter pattern imaging, magneto-optical Kerr (MOKE) microscopy and magnetic force microscopy (MFM), when studying inter-grain magnetic interaction fields, though the other methods all have their benefits.

In a pioneering study, Harrison *et al.* (2002) examined the magnetic structure in a finely exsolved titanomagnetite from Mount Yamaska, Quebec, one of the Monterigian Hills of Cretaceous age. The sample consisted of areas of magnetite blocks separated from each other by paramagnetic ulvöspinel (figure 2a). The magnetic structures in individual grains displayed inter-grain coherent magnetic structures, the so-called "super-vortex" states, similar to the vortex state seen in the PSD (figure 1b). By examining samples of a similar size, it is clear that the interaction fields are sufficient to enable grains above the single-domain/vortex transition size, to be in a SD-like state.

Subsequent studies have examined magnetic structures in synthetic rocks and meteoritic samples (Church 2011, Lappe *et al.* 2011), and have examined magnetic interactions across phase boundaries. One of the main benefits of this technique is the direct crossover with micromagnetic models (see below).

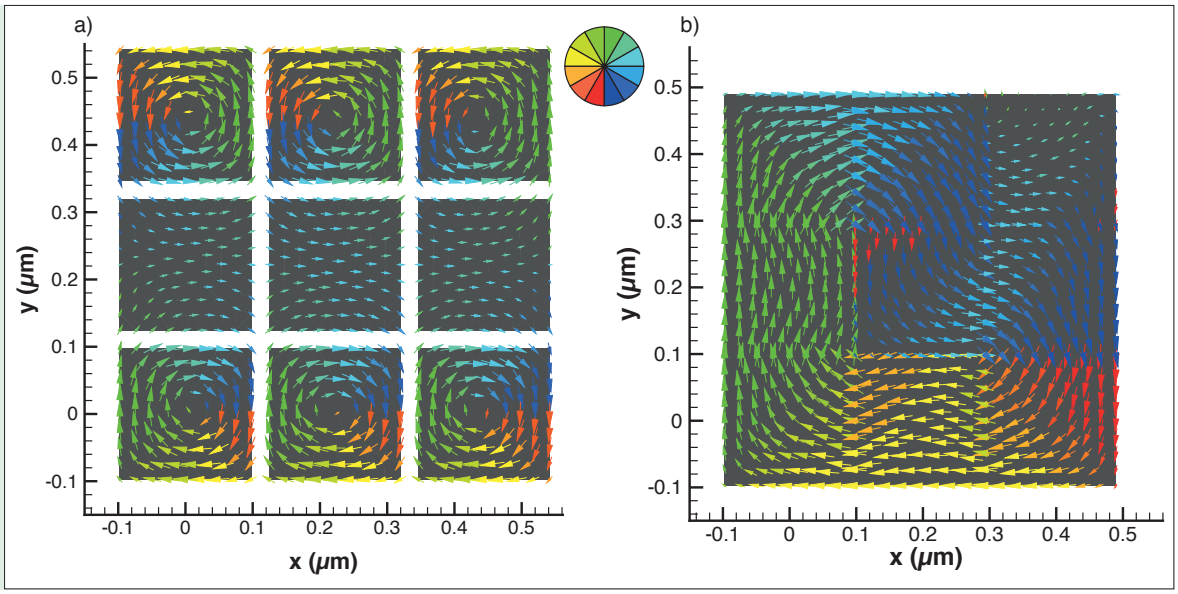
Experimentally quantifying the role of interactions in bulk samples is particularly difficult in small crystals of commonly occurring magnetic minerals like magnetite, because it is necessary to control accurately the size and shape of the crystals, plus the inter-grain spacing. Conventionally, samples with small crystals are grown through various aqueous and hydrothermal techniques, which produce stoichiometrically (in terms of chemical purity) perfect crystals with normal or log-normal grain distributions and uncontrolled inter-grain spacings. As small magnetic crystals behave like "mini-bar-magnets", the mobile crystals tend to clump together to form clusters. Such clusters are not representative of the magnetic minerals found in rocks, which tend to grow within the matrix and are not free to cluster.

Several techniques have been developed for synthesizing crystals that are fixed and not free to rotate. For example, the glass-ceramic method (Worm and Markert 1987) produces fixed crystals in silica matrix, i.e. they are essentially synthetic rocks; however, there are still problems with this technique. It is difficult to obtain narrow grain size distributions, and it can also be difficult to maintain even stoichiometry across this grain-size distribution, plus such samples are thought to contain very high levels of internal dislocations, higher than is found naturally in rocks. Such samples are thus not ideal for testing all aspects of inter-grain interactions.

The only method that has been shown to control stoichiometry, grain size and spacing in the synthesis of magnetic minerals is electron beam lithography (EBL). Starting with a thin film of material, EBL is used to produce arrays of near-identical particles with accurately controlled spacing (figure 3). These samples are ideal for testing various theories and the contribution of magnetic interactions to palaeomagnetic experiments. However, production of EBL samples has proved to be exceptionally difficult, with only two separate projects successfully managing to make samples for palaeomagnetic investigation (King *et al.* 1996, Krása *et al.* 2009). The only mineral to be as yet successfully synthesized that is of interest to the geophysicist is magnetite.

These studies have shed much light on the behaviour of both isolated PSD grains, and interactions between such grains. They have shown that while interacting particle assemblages may have unfavourable rock magnetic parameters, e.g. from hysteresis, which are commonly used to discriminate between "reliable" and "unreliable" recorders, they are still able to retain palaeomagnetically meaningful palaeodirectional information (Krása *et al.* 2011).

Numerical modelling is a valuable technique for understanding the theoretical basis of palaeomagnetic data. Magnetic states of interacting assemblages and individual PSD and MD grains are determined by a complex interplay of nonlinear, short and long-range interactions, plus variations in temperature. For this reason, analytic theories have not been able to provide predictive models to determine the accuracy of palaeomagnetic recordings. Instead, numerical models that solve Brown's

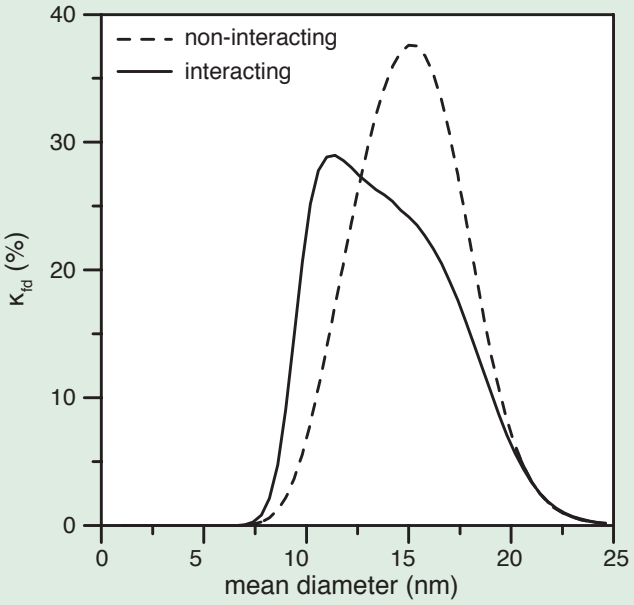


4: A numerical 3D micromagnetic model of nine magnetite grains: (a) "Small-field interacting state" – the grains experience small interactions fields but the majority of grains are in a vortex state. (b) "High-field interacting state" – when the grains are touching, a "super-vortex" magnetic structure forms, causing all the grains to display more uniform magnetic structures than seen in (a). (Redrawn from Evans *et al.* 2006)

(1963) micromagnetic equations are employed to understand these complex systems theoretically. Over the past 25 years these models have yielded a wealth of insight into the magnetic structures and behaviour of non-uniform magnetic structures within crystals covering more than an order of magnitude in size, e.g. for magnetite cubo-octahedral grains of length 0.01 to 1 μm. For example, the vortex structures shown in figure 1 were first predicted by numerical models, before being observationally verified.

In the last ten years, these models have also been applied to the study of magnetic interactions in assemblages of SD and PSD grains (Muxworthy *et al.* 2003, Muxworthy and Williams 2005). They have shown some paradoxes: interacting SD grains become more multidomain-like in character, while interacting PSD grains can become more SD-like in character, by forming super-vortex structures (figure 4). These model predictions have been confirmed on the microscopic scale, and also in the bulk-magnetic parameters.

Currently numerical micromagnetic algorithms can only determine static magnetic interaction fields, as thermofluctuations have yet to be fully implemented in models for natural systems, though this line of development is currently active and thermally activated micromagnetic models should be working within the next year or two. This makes current and previous calculations for dynamic interactions reliant on assumptions in micromagnetic models, such as those used in the calculations presented in figure 9, or approximated theories like those of Dormann *et al.* (1988). As dynamic systems are in non-equilibrium they are unlikely to retain a palaeomagnetically meaningful magnetic remanence, but they can still contribute to the magnetic signature of sample; this is particularly important in environmental magnetic studies where the signature is often used as a proxy. Using a variation of the model described in Dormann *et al.* (1988), Muxworthy (2001) showed that in weakly interacting SD assemblages the role of dynamic magnetic interactions is to supress a very common environmental parameter referred to as the frequency dependency of magnetic susceptibility, κ_{fd} (figure 5). The effect of interactions is to reduce κ_{fd} in absolute value and move the peak to smaller grain sizes. This partially explains why large values of κ_{fd}, which are theoretically possible, are rarely seen in natural samples.



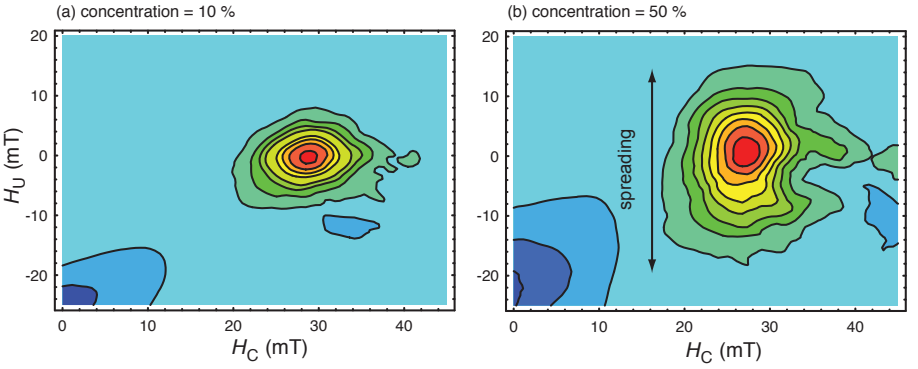
5: Results of a numerical model for the frequency dependency of magnetic susceptibility (κ_{fd}) versus mean grain size for an assemblages of SD magnetite particles with a mixture of dynamic and static interactions. It is seen that the effect of weak interactions is to reduce κ_{fd}. (Redrawn from Muxworthy 2001)

Magnetic interactions in rocks

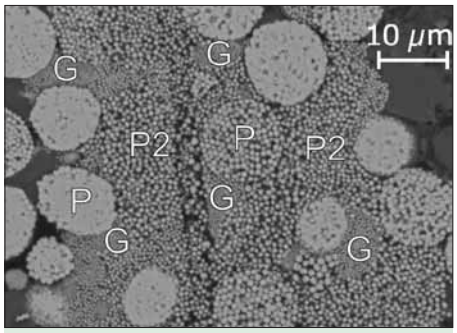
As it is not possible to examine every palaeomagnetic sample under the microscope, diagnostic bulk measurements that can identify the presence of magnetic interaction fields are required. There have been several approaches for assessing this, two of which are described below. However, differentiating between intergrain magnetostatic interactions and internal magnetic interactions between domains, i.e. multidomain behaviour, is particularly difficult as the magnetic responses of the two systems are often similar.

Traditionally, people have used Henkel plots (Henkel 1964) or its modern modification the deltaM curve, which are constructed from remanence acquisition curves for the same sample in two magnetic states (demagnetized and reversely magnetized). DeltaM plots work particularly well in the material science world, where synthetic samples have narrow grain size distributions of SD grains; however, natural systems rarely have such assemblages and these simple plots do not yield sufficient discriminatory usefulness when working with natural samples.

To better quantify the behaviour of natural systems, first-order reversal curves (FORC) measurements were developed in the late 1990s (Pike *et al.* 1999, Roberts *et al.* 2000), and have recently become common as the machines required to measure them have become readily available. FORC measurements map out the



6: Two numerically simulated FORC diagrams for assemblages of identical SD magnetite particles with cubic magnetocrystalline anisotropy. (a) The concentration of particles is 10% and (b) the concentration is 50%. Increasing the concentration increases the levels of inter-grain interactions resulting in spreading in the *y*-axis. As a first-approximation the *x*-axis is related to the coercivity (magnetic stability) distribution of the assemblage and the *y*-axis is a measure of magnetostatic interactions. (Redrawn from Muxworthy *et al.* 2004)



7: Back-scattered electron microscope images illustrating microtextures of authigenic greigite (G, Fe_3S_4) and pyrite (P, P2, FeS_2) in mudstone samples from New Zealand. Such samples' magnetic remanences were found to be unreliable and their FORC diagrams indicative of high levels of magnetic interactions. (From Rowan and Roberts 2006)

internal structure of a hysteresis loop, and provide a distribution of magnetic responses from a sample (figure 6). It has been shown that as a first-approximation, the *x*-axis represents the coercivity (magnetic stability) distribution of particles within a sample, and the *y*-axis is a measure of magnetostatic interactions (Muxworthy and Williams 2005).

The FORC method in itself does not distinguish between internal interactions, i.e. multi-domain behaviour, and inter-grain interactions: both cause spreading in the vertical axis; however, experience of handling natural magnetic systems tells us that usually the position of the peak of the distribution for MD grains lies near to the *y*-axis origin, and that of SD grains and PSD grains a little further from the vertical axis origin. Distributions with large spreads in the *y*-axis, where the peak of the distribution is far from the *y*-axis, are indicative of interacting SD grains (Muxworthy *et al.* 2004).

Combining theory and experiment

Neither numerical nor experimental approaches are able to answer uniquely the contribution of magnetic interactions to the palaeomagnetic signal, but a holistic approach can tell us where strong magnetic interactions are present. On a practical level such a holistic approach will involve a combination of scanning electron microscope (SEM) analysis including analytical analysis, and thorough mineral magnetic analysis using FORC diagrams in combination with thermomagnetic measurements. For example, such an approach was used successfully in the study of mudstones from New Zealand (Rowan and Roberts 2006), whose palaeomagnetic signal in some strata was dominated by interacting, authigenic iron sulphides (greigite, Fe_3S_4) (figure 7). The greigite-dominated signals were found to be unreliable. Once the results from such samples had been removed from the data set, the tectonic interpretation of the palaeomagnetic study could be made successfully (Rowan and Roberts 2006).

Magnetic interactions for navigation

Magnetotactic bacteria produce chains of magnetic crystals (magnetosomes) that usually consist of magnetite (Fe_3O_4) or greigite (figure 8). These magnetosome chains are found in both unicellular bacteria and in larger multicellular magnetotactic prokaryotes (MMP) (Faivre and Schüler 2008). The primary purpose of magnetosomes is thought to be navigation (magnetotaxis), therefore natural selection should ensure that magnetosomes provide a strong magnetic signal to maximize their efficiency (Kopp and Kirschvink 2008). The magnetic state that best exhibits this quality is the stable SD state. To maximize the magnetic signal from a magnetosome, the magnetosome should be just below or at the critical SD to PSD/MD grain size threshold. The exact threshold is dependent on many factors such as grain morphology. Determining the critical stable SD size range as a function of morphology is important for determining magnetosome function and possible magnetotaxis efficiency.

It is common to assess the domain state of magnetosome crystals by plotting their length versus grain-elongation axial-ratio (AR; short-axis/long-axis or width/length) on domain state phase diagrams (Thomas-Keprta *et al.* 2000), initially determined analytically by Evans and McElhinny (1969). They calculated the SP to stable SD critical size and the SD to PSD/MD critical size as functions of AR for individual particles of magnetite. Subsequently, both the SP to stable SD transition size (Winklhofer *et al.* 1997, Muxworthy and Williams 2009) and the SD to MD transition size (Fabian *et al.* 1996, Witt *et al.* 2005, Muxworthy and Williams 2006) have been re-examined and revised for individual magnetite particles through application of the numerical micromagnetics.

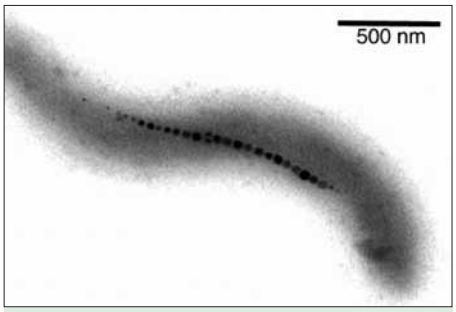
Muxworthy and Williams (2006) argued that it is flawed to compare magnetosome sizes with critical grain size boundaries derived for individual crystals because magnetosomes very often occur in magnetostatically interacting chains (Faivre and Schüler 2008). Muxworthy and Williams (2006, 2009) performed calculations for the critical thresholds for magnetically interacting magnetite rectangular cuboids, and demonstrated that for cube-shaped grains, interactions within chains increases the stable SD to MD threshold size for magnetite from ~70 nm to a maximum of ~200 nm (figure 9).

Interactions also decrease the SP/SD size for cube-shaped magnetite grains from ~26 nm to a minimum of ~12 nm for a thermal relaxation time of 60 s. Muxworthy and Williams (2006, 2009) showed that magnetostatic interaction fields are sufficient to cause the largest observed magnetite magnetosome crystals found in living bacteria (length = 250 nm [AR = 0.84]; Lins *et al.* 2005) to be in a stable SD state; without magnetostatic interactions they would be in a MD state and would have a far lower magnetotaxis efficiency.

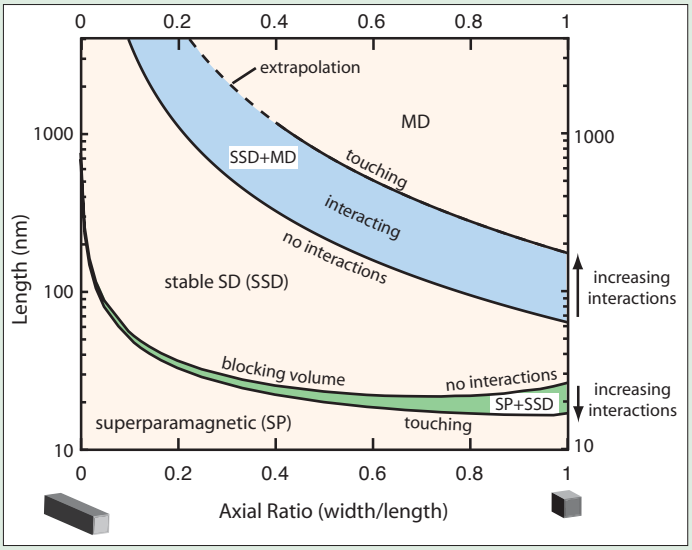
Magnetofossils and early life

When magnetotactic bacteria decease, they are one of the few bacteria that regularly leave an inorganic trace of their existence; the chains of magnetosomes often remain partially intact and are referred to as magnetofossils. Magnetofossils have been identified in pre-Cambrian rocks ~2 Ga in age (Chang *et al.* 1989), and have been suggested as evidence for extraterrestrial life (Friedmann *et al.* 2001).

One of the criteria for identifying magnetic crystals as magnetofossils is the presence of complete or partially broken chains. It is assumed that the magnetofossils were used for magnetotaxis, for which we assume that the magnetic crystals were in a SD state. Examining martian meteorite ALH84001, Friedmann



8: Transmission electron micrograph of an unstained cell of *Magnetospirillum magnetotacticum*, showing chain of magnetite magnetosomes. (From Bazylinski and Frankel 2003)



9: Stable single-domain ranges for individual grains and chains of interacting magnetosome crystals. Using the format of Evans and McElhinny (1969), length (long-axis) rather than volume is plotted versus AR for various grain spacing/length ratios. The figure considers the effects of interactions in chains on the stable SD range: interactions cause the SD-to-SP boundary to decrease and the SD-to-MD boundary to increase. The use of the length makes for easier comparison with Evans and McElhinny (1969), but the figure is a little more complicated to understand because on moving horizontally across the figure the volume of the grains changes, i.e. there is a change both in shape and volume contributing to the critical boundaries. (Modified from Muxworthy and Williams 2009)

et al. (2001) identified chains of magnetite, which they postulated may be magnetofossils of former magnetotatic bacteria; however, reconstructing the chains of magnetite using micromagnetic models (Muxworthy and Williams 2006) clearly demonstrated that the magnetic interactions between grains were insufficient to push the magnetic crystals into the SD stability field. The magnetic crystals were in MD states, making it unlikely that they are the remnants of magnetosomes used for magnetotaxis in an early martian magnetic field.

Conclusions

In rocks and other environmental samples, the contribution of magnetic interactions to the magnetic signals is generally thought to be undesirable; however, magnetic interactions appear to affect some magnetic remanences more than others. For example, thermoremanences acquired by igneous rocks during cooling the Earth's magnetic field, appear to be less effected by interactions than a chemical remanent magnetization carried in sedimentary rock dominated by authigenic minerals. It is, therefore, important to consider the type of magnetic remanence being carried by a rock, when estimating the degree of magnetic interactions in it. It is also important to consider the type of information that is being recovered. Generally, directional data is less affected by magnetic interactions than palaeointensity data (the recovery of the ancient field intensity).

There are clear cases in Nature where the role of magnetic interactions is beneficial. In particular in magnetotactic bacteria, that have been shown to have optimal magnetosome morphology and inter-grain magnetic interactions to maximize magnetotaxis. Their remains (magnetofossils) have been used to identify early life, and are excellent recorders of the geomagnetic field, as the highly interacting chains paradoxically individually behave like "ideal non-interacting" grains.

What areas of magnetic interactions are still to be truly understood? Magnetically interacting systems are highly nonlinear so every case is unique, but there are several key areas of research were the contribution of magnetic interactions is poorly understood. First, the role of magnetic interactions during thermoremanence acquisition has yet to be fully understood. There have been experimental and numerical attempts to quantify the contribution of interaction to thermoremanence acquisition, but as yet the results are not entirely conclusive. Second, relating the interaction fields observed with electron microscopes or calculated in numerical models to bulk magnetic parameters. In the first two cases, the number of crystals examined is of the order of 10 to 100 particles, whereas bulk measurements are made on potentially millions of particles. To resolve this gap, there are two possible solution paths: increase numerical model size through a combination of increased CPU power and quicker algorithms; and test the models on ideal samples such as those produced by EBL, which can be examined under a microscope, modelled and magnetically measured like a bulk sample. ●

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References

Bazylinski D A and Frankel R B 2003 Biologically controlled mineralization in prokaryotes, *Revs Mineralogy and Geochemistry* **54** 217–247.
Brown W F Jr 1963 *Micromagnetics* **18** (John Wiley, New York).
Chang S B R *et al.* 1989 *Precambrian Res.* **43** 305–315.
Church N 2011 *Magnetic properties of iron–titanium oxides and their nanoscale intergrowths* (PhD, University of Cambridge).
Dormann J L *et al.* 1988 *J. Phys. C: Solid State Phys.* **21** 2015–2034.
Dormann J L *et al.* 1997 *Adv. Chem. Phys* **98** 283–494.
Dunin-Borkowski R E *et al.* 1998 *Science* **282** 1868–1870.
Dunlop D J and West G F 1969 *Rev. Geophys.* **7** 709–757.
Evans M E *et al.* 2006 *J. Geophys. Res.* **111** doi:10.1029/2006JB004454.
Evans M E and McElhinny M W 1969 *J. Geomag. Geoelect.* **21** 757–773.
Fabian K *et al.* 1996 *Geophys. J. Int.* **124** 89–104.
Faivre D and Schüler D 2008 *Chem. Rev.* **108** 4875–4898.
Friedmann E I *et al.* 2001 *Proc. Natl Acad. Sci. USA* **98** 2176–2181.
Harrison R J *et al.* 2002 *Proc. Natl Acad. Sci. USA* **99** 16556–16561.
Henkel O 1964 *Phys. Stat. Sol.* **7** 919–924.
King J G *et al.* 1996 *Geophys. Res. Lett.* **23** 2847–2850.
Kopp R E and Kirschvink J L 2008 *Earth Sci. Rev.* **86** 42–61.
Krása D *et al.* 2009 *J. Geophys. Res.* **114** B02104.
Krása D *et al.* 2011 *Geophys. J. Int.* **185** 167–180.
Lappe S *et al.* 2011 *Geochem. Geophys. Geosyst.* **12** Z1235 doi:10.1029/2011GC003811.
Lins U *et al.* 2005 *Appl. Environ. Microbio.* **71** 4902–4905.
Muxworthy A R 2001 *Geophys. J. Int.* **144** 441–447.
Muxworthy A and Williams W 2005 *J. Appl. Phys.* **97** doi:10.1063/1.1861518.
Muxworthy A R and Williams W 2006 *J. Geophys. Res.* **111** B12S12.
Muxworthy A R and Williams W 2009 *J. Royal Soc. Inter.* **6** 1207–1212.
Muxworthy A R *et al.* 2003 *J. Geophys. Res.* **108** 2517.
Muxworthy A R *et al.* 2004 *Geophys. J. Int.* **158** 888–897.
Pike C R *et al.* 1999 *J. Appl. Phys.* **85** 6660–6667.
Roberts A P *et al.* 2000 *J. Geophys. Res.* **105** 28461–28475.
Rowan C J and Roberts A P 2006 *Earth Planet. Sci. Lett.* **241** 119–137.
Spinu L and Stancu A 1998 *J. Magn. Magn. Mater.* **189** 106–114.
Thomas-Keprta K L *et al.* 2000 *Geochim. Cosmochim. Acta* **64** 4049–4081.
Winklhofer M *et al.* 1997 *J. Geophys. Res.* **102** 22695–22709.
Witt A *et al.* 2005 *Earth Planet. Sci. Lett.* **233** 311–324.
Worm H-U and Markert H 1987 *Phys. Earth Planet. Inter.* **46** 263–270.