## ERC Advanced Grant 2012

### **Research proposal (Part B section 1)**

# Nanopaleomagnetism: a multiscale approach to paleomagnetic analysis of geological materials

# NanoPaleoMag

#### **Cover Page:**

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- 60 months

#### Proposal summary

Paleomagnetism has played a pivotal role in developing our modern understanding of the Earth, and remains one of the primary tools used to study the structure and dynamics of the Earth and other planets. Nevertheless, numerous factors can be detrimental to the fidelity of magnetic information recorded by a rock. Some of the most interesting and controversial periods of Earth's history occur far beyond the current limits of our confidence in the paleomagnetic signals used to study them. NanoPaleoMag will solve this problem by dramatically increasing the range of materials that are suitable for paleomagnetic study, thereby opening up periods of Earth history that have hitherto defied conventional paleomagnetic analysis.

The dominant source of uncertainty stems from the over reliance on bulk rock measurements. Rocks are chemically, mineralogically, texturally and magnetically heterogeneous materials, with heterogeneity occurring at all length scales – from metres to nanometres. There is a pressing need, therefore, to push the spatial resolution of paleomagnetic studies beyond their current limits and to extend the analysis into three dimensions.

Adopting cutting-edge techniques from physics and materials science, NanoPaleoMag will perform paleomagnetic measurements at submicron length scales, enabling primary magnetic signals to be extracted from ancient and severely altered geological materials. 3D measurements of the volume, shape and spacing of all magnetic particles within a microscale region of interest will be made using a 'dual beam' focussed ion beam workstation. Combined with high-resolution paleomagnetic measurements and nanometre/nanosecond electron/X-ray magnetic imaging, NanoPaleoMag will, for the very first time, be able to characterise the magnetic properties of geological materials at fundamental length scales and time scales. The nanoscale measurements will enable me to capture the essential physics of the remanence acquisition process and to explore magnetic behaviour 'in silico', allowing predictions to be made that can be tested directly against experimental observations at all length scales. Sample-return missions to asteroids, comets, moons and planets will soon provide unprecedented opportunities for extraterrestrial paleomagnetism. NanoPaleoMag will provide the methodology and instrumentation needed to analyse these precious materials.

#### Section 1(c): <u>Extended Synopsis of the project proposal</u> (max 5 pages)

#### **1.** Objectives and state-of-the-art

Some of the most interesting and controversial periods of Earth's history occur far beyond the current limits of our confidence in the paleomagnetic signals used to study them...

#### 1.1. The promise and pitfalls of paleomagnetism

Paleomagnetism has played a pivotal role in developing our modern understanding of the Earth, and continues to be one of the primary tools used by Earth scientists to study the structure, dynamics and geological history of our planet. Despite the importance of paleomagnetic observations, however, numerous factors can be detrimental to the fidelity of magnetic information recorded by a rock. Ultimately, these factors restrict our confidence in geological theories that rely heavily on paleomagnetic evidence.

Paleomagnetic information is, like the magnetic information stored on a computer's hard drive, susceptible to data loss and corruption over time. The older the rock, the more complex is its geological history, and the more likely it is to have experienced conditions (e.g. metamorphic heating, exposure to geothermal fluids, groundwater and biogeochemical processes) that altered, or even destroyed, its primary magnetic information. Consequently, some of the most interesting and controversial periods of Earth's history occur far beyond the current limits of our confidence in the paleomagnetic signals used to study them. This problem is epitomized by the on-going debate surrounding the 'Snowball Earth', a controversial theory of Neoproterozoic low-latitude glaciation (when tropical glaciers reached sea level) that is based on highly disputed



Fig. 1. Electron holography image revealing the complex magnetic microstructure of an array of ~ 100 nm sized cubes of magnetite.<sup>1</sup>

paleomagnetic evidence. The problem of paleomagnetic reliability gets dramatically worse when it comes to extraterrestrial materials, such as meteorites, that predate the formation of the Earth itself.

This proposal sets out the scientific and technological basis for a multiscale approach to paleomagnetism, that tackles directly the issue of reliability and confidence in paleomagnetic measurements of such challenging samples. The approach adopts recent technological developments within the fields of solid state physics and materials science to provide a detailed chemical, microstructural and magnetic analysis of microscale regions of interest with nanoscale spatial resolution. The information obtained will be used to develop a comprehensive physical model of the sample that establishes a quantitative link between nanoscale and microscale magnetic behaviour. This integrated experimental and computational approach – which I call 'nanopaleomagnetism' – will allow me to quantify and interpret magnetic remanence carried by ancient or severely altered rocks, massively expanding the range of materials suitable for paleomagnetic study and thereby opening up entirely new avenues of scientific enquiry (see Section 1.5).

#### **1.2.** The root of the problem

A key tenet of this proposal is that the dominant source of uncertainty in traditional paleomagnetic studies stems from their over reliance on bulk rock measurements. Rocks are chemically, mineralogically, texturally and magnetically heterogeneous materials, with heterogeneity occurring at all length scales – from metres to nanometres (Fig. 1).<sup>1</sup> The most obvious failure of bulk measurements occurs in the study of meteorites, which are magnetically heterogeneous down to sub-mm length scales. Any attempt to unravel the magnetic history of such heterogeneous materials using bulk measurements is utterly futile.

#### **1.3.** Current state-of-the-art: micropaleomagnetism

<sup>&</sup>lt;sup>1</sup>Harrison RJ, Dunin-Borkowski RE, Putnis A (2002) Direct imaging of nanoscale magnetic interactions in minerals. Proc. Nat. Academy Sci., 99, 16556-16561.

The move from bulk measurements to spatially-resolved measurements is a current and necessary trend in paleomagnetism, often termed 'micropaleomagnetism'. The state-of-the-art is epitomised by the work of John Tarduno (University of Rochester) and Ben Weiss (M.I.T.). Tarduno's approach focusses on individual silicate crystals extracted from a bulk rock. Each crystal contains multiple inclusions of a magnetic mineral, such as magnetite. The elongated shape of the magnetic inclusions (which imparts high magnetic stability) and their encapsulation within a silicate host (which provides protection from chemical alteration) dramatically increases the likelihood that they carry a primary magnetic signal.<sup>2</sup> Weiss's approach is to perform spatially resolved measurements of magnetic remanence using a highly sensitive scanning magnetometer with spatial resolution of ~100  $\mu$ m. The scanning magnetometry technique creates a two-dimensional map of the stray magnetic field above a standard rock thin section, which can then be used to derive a two-dimensional model of remanent magnetisation via a mathematical inversion. This scanning approach is particularly suited to samples containing fine-scale magnetic heterogeneity, such as meteorites.<sup>3</sup>

#### 1.4. Going beyond the state-of-the-art: NanoPaleoMag

Micropaleomagnetism has provided a dramatic step forward in our ability to extract reliable magnetic information from the most challenging of geological samples. Nevertheless, micropaleomagnetism leaves many questions unanswered and, most critically, provides no information regarding the mineral magnetic processes that operate on length scales below  $\sim 100 \ \mu m$ . Research pioneered by the Harrison group has demonstrated that identifying and quantifying such nanoscale processes is absolutely essential if we are to have any confidence in the nature and fidelity of the magnetic signals recorded in geological materials (Fig. 1). There is a pressing need, therefore, to push the spatial resolution of micropaleomagnetic studies beyond their current limits and to extend the characterisation into three dimensions.

Adopting cutting-edge techniques from physics and materials science, NanoPaleoMag will perform paleomagnetic measurements at submicron length scales, enabling primary magnetic signals to be extracted from ancient and severely altered geological materials. 3D measurements of the volume, shape and spacing of all magnetic particles within a microscale region of interest will be made using a 'dual beam' focussed ion beam workstation. Combined with high-resolution paleomagnetic measurements and nanometre/nanosecond electron/X-ray magnetic imaging, NanoPaleoMag will characterise magnetic properties at fundamental length scales and time scales. In order to extract primary magnetic remanence, the method will target individual grains of a host silicate mineral containing multiple submicron magnetic inclusions. Such grains are common in both igneous and sedimentary rocks, as well as in extraterrestrial materials. A physical model that captures the essential physics of the remanence acquisition process will allow the magnetic properties of the sample to be explored 'in silico', allowing predictions to be made that can be tested directly against experimental observations at all length scales. When theory and observation are in quantitative agreement, and the nature of the remanence acquired has been confirmed down to the smallest length scale, it may finally be possible to have full confidence in paleomagnetic measurements of all geological materials, no matter how ancient or altered they are.

#### **1.5.** Future prospects for paleomagnetic research if the methodology proves successful

The case for NanoPaleoMag becomes compelling when studying ancient and highly altered rocks. The paucity of reliable precambrian paleomagnetic data places severe restrictions on our understanding of the early geological history of our planet. NanoPaleoMag could dramatically increase the range of materials that are suitable for paleomagnetic study, allowing us to begin filling the gaps in the paleomagnetic record of the early Earth. The availability of such data would enable us to address many outstanding geophysical questions, such as how do variations in heat flow at the core-mantle boundary impact long-period variations in the Earth's magnetic field? The need for NanoPaleoMag is most pressing in the study of extraterrestrial materials. Magnetic fields from a variety of sources played an important role in the evolution of the early solar system. Information about the origin and strength of such fields may be recoverable from extraterrestrial materials. Currently, such studies are limited to meteorites but in the longer term both NASA

<sup>&</sup>lt;sup>2</sup>Tarduno JA (2009) Geodynamo history preserved in single silicate crystals: Origins and long-term mantle control. Elements 5, 217-222.

<sup>&</sup>lt;sup>3</sup>Weiss BP, Lima EA, Fong LE, Baudenbacher FJ (2007) Paleomagnetic analysis using SQUID microscopy. J. Geophys. Res. 112, B09105.

and the ESA are committed to sample-return missions to asteroids, comets, moons and planets. Samplereturn missions will provide unprecedented opportunities for extraterrestrial paleomagnetism. It is essential, therefore, that we invest now in the development of the methodologies and instrumentation that will give us the capability to analyse these precious materials. The possibility of such missions providing samples of extraterrestrial soil also opens up the tantalizing prospect of performing nanoenvironmental magnetic studies on planets other than our own, such as Mars.

#### Section 2: Methodology

- 1. High-resolution scanning magnetic microscopy is used to obtain remanence data from a polished rock section with a spatial resolution < 1  $\mu$ m. A typical region of interest would consist of a ~100x100x100  $\mu$ m volume of a host silicate grain containing multiple submicron inclusions of primary magnetic particles.
- 2. The region of interest is physically extracted from the sample using Focussed Ion Beam (FIB) milling and in-situ lift out. A serial sectioning technique is used to slice through the entire region in a series of 20-200 nm steps. After each new slice, a high-resolution scanning electron microscope image, chemical map, and crystallographic orientation map are acquired from the top surface. The stacked images are used to construct a 3D tomographic model of the region, yielding precise information about volume, shape, spacing, crystallographic orientation and chemical composition of all magnetic particles within the sampled volume. This information is used to build a physical model of the region in Step 5.
- 3. Electron holography is performed on individual slices extracted from the region of interest to characterise the remanent states and microcoercivities of the magnetic particles contained within. Images are obtained with nanometre spatial resolution and as a function of temperature.
- 4. X-ray magnetic imaging is performed on the same slices to determine the hysteretic and dynamic behaviour of the magnetic particles. Stroboscopic techniques are used to provide magnetic information with sub-nanosecond time resolution, providing dynamic information that can be used to improve the models developed in Step 5.
- 5. A comprehensive 3D micromagnetic model of the region of interest is developed. A modular approach is employed so that, based on information gathered in Steps 1 to 4, the correct level of theory needed to capture the essential physics of the remanence acquisition process is used. The predictions of the model are compared directly to the experimental data collected in Steps 3 and 4, and used to provide a robust interpretation of the paleomagnetic data acquired in Step 1.

Each of the five steps corresponds to an individual Work Package (WP), outlined below. The proof-ofconcept studies illustrated in Figs. 2, 3 and 4 are a mixture of recent published and unpublished work done by the Harrison group.

#### Work Package 1: Bulk and micropaleomagnetic measurements

The two goals of WP1 are 1) to provide a quantitative analysis of the magnetic mineralogy of the bulk rock sample and 2) to provide micropaleomagnetic remanence data with submicron spatial resolution. The first goal will be achieved through the use of first-order reversal curve (FORC) diagrams, which act as a fingerprint of the magnetic mineralogy. The second goal will be achieved using a state-of-the-art CS1000 scanning magnetic microscope. The CS1000 utilises a combination of magnetic tunnel junction and giant magnetoresistive sensors to achieve both high sensitivity (down to 1 nT) and significantly greater spatial resolution (down to 100 nm) than the current generation of scanning microscopes. The feasibility of the scanning magnetic microscopy technique has been well established through the work of Weiss (Section 1.3).<sup>3</sup> Examples of images obtained with the CS1000 scanning magnetic microscope, along with a description of its technical specifications, are available online at http://www.micromagnetics.com.

#### Work Package 2: 3D spatial characterization at the mesoscale

The two main goals of WP2 are 1) to produce a 3D model of the magnetic particles contained within the region of interest and 2) to extract subsamples of the region of interest suitable for transmission electron microscopy and X-ray magnetic imaging. Both goals will be achieved using an existing Helios Nanolab



Figure 2. (a) The region of interest is milled from the thin section using FIB. (b) An in-situ box lift-out technique is then used to extract the region. (c) A high-resolution SEM image or EBSD crystallographic orientation map is acquired from the surface. (d) Successive slices (each in this case just 20 nm thick) are milled away from the sample surface, and the resulting stack of images are converted to segmentation maps. (e) The stack of segmentation maps is converted to a 3D tomographic reconstruction of the entire region of interest, revealing the volume, shape and spacing of all particles within it. da Silva Fanta, Lappe, Harrison, unpublished data.

facility within the host institution. The Helios Nanolab is a dual-beam instrument, combining a Focussed Ion Beam (FIB) Nanomill with a field-emission gun scanning electron microscope, incorporating both electron back-scattered electron diffraction (EBSD) and energy-dispersive X-ray (EDX) detectors for crystallographic

and chemical analysis of each remanence carrier. A 3D re multiple submicron inclusions of metallic Fe is shown in Fi grains found in primitive meteorites that we recently demonst remanence.<sup>4</sup> The serial sectioning technique yields precice crystallographic information that is required to build a com region of interest (WP5). The ability of the FIB to target sut studying heterogeneous geological materials, including sedim many possibilities for future research in other areas of geoscie

#### Work Package 3: Nanoscale imaging of magnetic and

#### chemical microstructures

The three main goals of WP3 are to 1) provide nanoscale resolution images of the magnetic domain states of particles in the region of interest, 2) measure the microcoercivity of individual particles as a function of temperature and 3) assess the primary/secondary nature of the magnetic particles through detailed microstructural analysis. WP3 builds on the P.I.s track record in the field of nanoscale imaging of magnetic minerals (Figs. 1, 3). I will employ a range of cutting-edge transmission electron microscopy (TEM) techniques, including off-axis electron holography<sup>1</sup>, to provide images of the magnetic



Fig. 3. Electron holography image revealing the range of nanoscale magnetic domain states within a subregion of the dusty olivine sample shown in Fig. 2.<sup>4</sup>

<sup>&</sup>lt;sup>4</sup>Lappe SLL, Church NS, Kasama T, Bastos da Silva Fanta A, Bromiley G, Dunin-Borkowski RE, Feinberg JM, Russell S, Harrison RJ (2011) Mineral magnetism of dusty olivine: a credible recorder of pre-accretionary remanence. Geochem. Geophys. Geosys. doi:10.1029/2011GC003811.

microstructures of representative slices through the region of interest. Fig. 3 illustrates how electron holography can be used to reveal the presence of both uniformly magnetised and non-uniformly magnetised particles within the dusty olivine sample shown in Fig. 2.<sup>4</sup> Experiments will be performed at elevated temperatures in order to determine how the magnetic domain states and microcoercivities vary during slow cooling, thereby reproducing the conditions under which the sample acquired its original remanence.

#### Work Package 4: Nanoscale imaging of magnetisation reversal dynamics

WP4 will apply a combination of established and emerging synchrotron X-ray magnetic imaging techniques to geological materials for the first time, with the aim of understanding the hysteresis and dynamic properties of the magnetic structures observed in WP3. State-of-the-art X-ray magnetic imaging offers high lateral resolution (down to 15 nm), sub-nanosecond time resolution, elemental specificity, a large field of view (typical tens of microns) and short exposure times (typically seconds per image). Sample requirements for X-ray imaging are similar to those for TEM, meaning that the same samples investigated using electron holography in WP3 can also be studied in WP4. Although the spatial resolution is not as good as that offered by electron holography, X-ray techniques offer several advantages that promise to overcome other limitations of electron holography. Domain states can be imaged rapidly in a constantly varying applied magnetic field, enabling hysteresis and magnetic switching behaviour to be studied in geological materials

for the first time at this spatial resolution. By utilising the pulsed nature of the synchrotron beam and operating in stroboscopic mode, magnetic images can be obtained with sub-nanosecond time resolution, opening up the possibility of imaging dynamic reversal mechanisms. The feasibility of this approach is well established within the solid state physics community. WP4 would represent the first attempt to perform such measurements on geological materials.

#### Work Package 5: Modeling and theory

WP5 builds on the P.I.s track record in the area of computer simulations that relate nanoscale processes to macroscopic behaviour. The primary aim of WP5 is to develop a 'Generalised Remanence Simulator' (GRS) that allows the magnetic behaviour of the region of interest to be explored 'in silico'. The GRS will simulate a range of laboratory experiments, including hysteresis, FORC diagrams, alternating-field demagnetisation, scanning magnetic microscopy and electron/X-ray holography. The GRS will also replicate the physical processes that lead to the acquisition of remanence within the region of interest, and explore the variation in remanence as a function magnetic field, temperature and time. WP5 represents an ambitious goal that will require a number of theoretical and computational challenges to be overcome. To reduce the risk, I will adopt a modular approach to the development of the GRS. This modular approach enables the code to evolve and improve over time as new theories



Figure. 4. (a) Preisach distribution determined from FORC diagram. (b) Simulation of remanence versus applied field. (c) Comparison of observed (circles) and simulated (red curve) alternating-field demagnetisation spectra. (d) Comparison of paleofield calculated from simulation (circles) with known paleofield at locality (dashed line). Muxworthy, **Harrison**, unpublished analysis.

and modeling approaches are developed, rather than requiring all aspects to be completed at once. This will enable significant progress to be made on major parts of the GRS while the more challenging theoretical aspects are developed. Proof-of-concept work on historical basaltic lavas from the 1913 eruption of Hekla, Iceland has demonstrated the great potential of the proposed approach (Fig. 4). Here the acquisition of remanence is accurately reproduced in-silico using a thermal relaxation method based on an empirical Preisach distribution of microcoercivities extracted from the FORC diagram.<sup>5</sup>

<sup>&</sup>lt;sup>5</sup>Muxworthy AR, Heslop D (2011) A Preisach method for estimating absolute paleofield intensity under the constraint of using only isothermal measurements: 1. Theoretical framework. JGR, 116, B04102.