Uncovering the Origin of Magnetism in Early Proterozoic Rocks From Lake Superior

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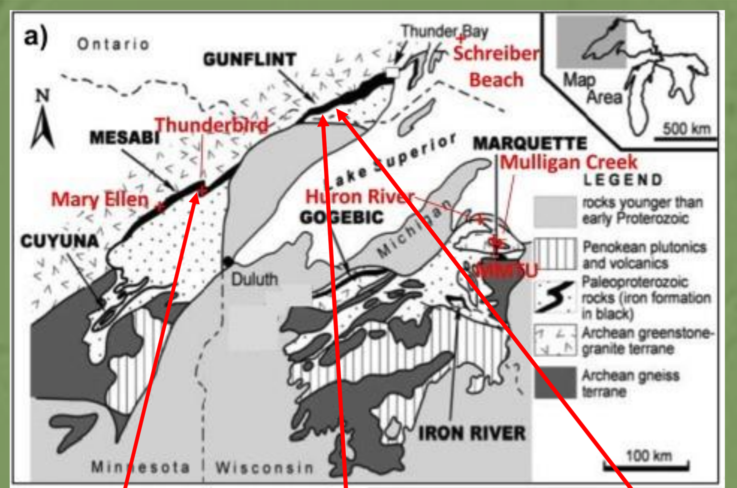
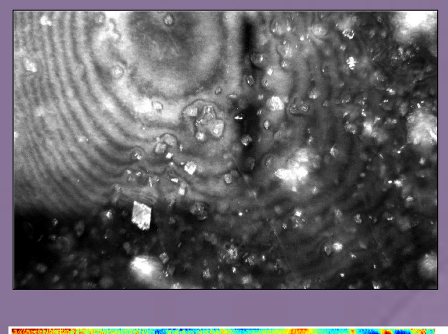
Introduction & Background

Magnetotactic bacteria biomineralize magnetic material today and are thought to have done so at least throughout the Phanerozoic. They synthesize minerals, such as magnetite, intracellularly, producing particles that are single domain magnets. They are arranged in chains, which are used as mini-compasses for navigating along the Earth's magnetic field lines, a phenomenon known as magnetotaxis. One question with implications for the origin of magnetotaxis and biomineralization in higher organisms is: When did magnetotactic bacteria appear? Precambrian evidence for magnetofossils is tentative, but there are indications that putative magnetofossils might exist in Early Proterozoic rocks from the Lake Superior region, such as the Gunflint and Biwabik iron formations from Minnesota and Ontario (Kopp and Kirschvink, 2008). During the accretion of the supercontinent Laurentia basins, where hydrothermal activity was accumulating copious amounts of Fe, were closed off. This material was preserved as Banded Iron Formations (BIFs) of the Gunflint and Mesabi (Biwabik) ranges (Papineau et al. 2017). Two samples from the Gunflint formation (Strom 14 and 15) and one sample from the Biwabik (Strom 16) were studied (all samples are from the NMNH collections).

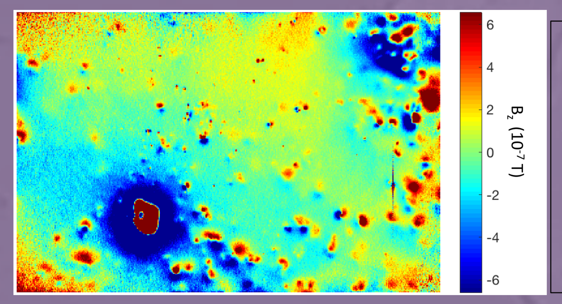


Map of Iron Formations in the Lake Superior region. *Papineau et al. 2017*

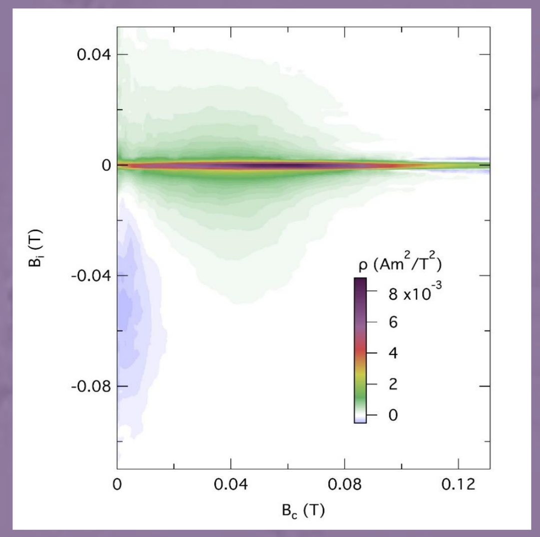
Gunflint Formation (Strom 14 - Chert)



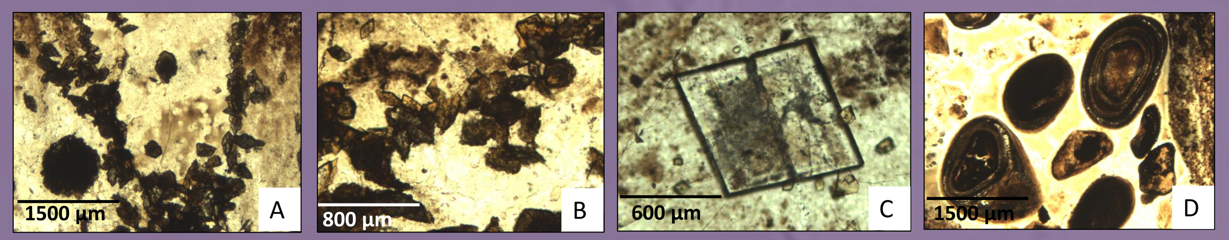
Optical Image of the chert with siderite crystals used to create the magnetic map below. The concentric lines indicate differences in sample surface topography (higher in the upper left). The vertical axis of the field of view is 1.4 mm.



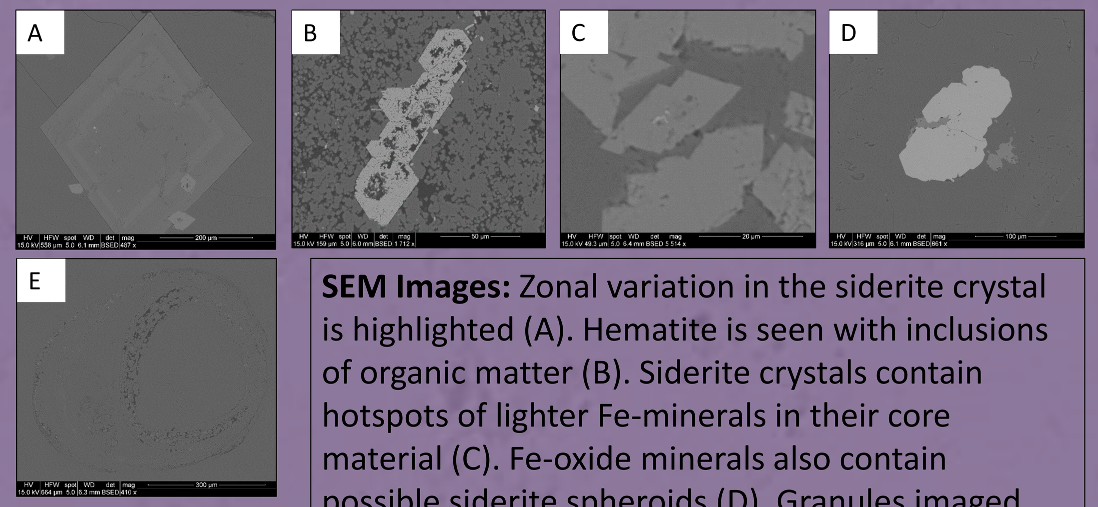
Magnetic Map showing the intensity of the sample magnetic field in the Z direction (perpendicular to the sample surface). High field values are associated with the siderite crystals.



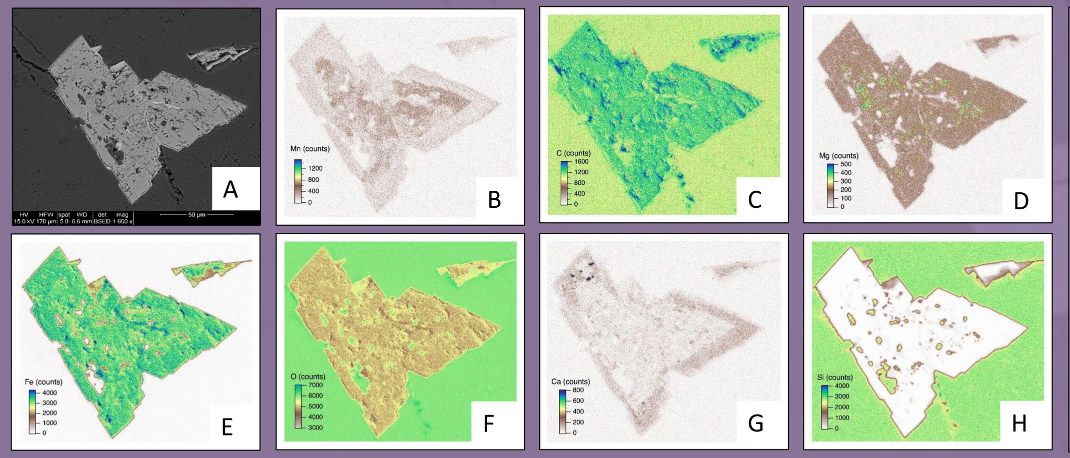
FORC Diagram: This diagram is a visual representation of the second derivative of the FORCs (ρ). Coercivity is represented on the X-axis and the interaction field is displayed on the Y-axis. The diagram shows a central ridge along the horizontal axis, which is a fingerprint of single domain magnetic particles that may be arranged in linear chains. The green circular background indicates that there are also interactions between some particles that clump together. This diagram suggests that this sample may contain magnetofossils.



Optical Microscope Images reveal fine grained (A-B) and coarse grained (C) siderite crystals that are sub-euhedral. The coarser grained crystals often are zoned, and have inclusions of smaller siderite crystals. The finer grained crystals are darker and often have centers that are void or occupied by other material such as organic matter or magnetite. Granules (D) are also ubiquitous within this sample. The granules are concentrically layered, containing quartz, organic matter, and possibly iron minerals. The main matrix of the sample is composed primarily of quartz.

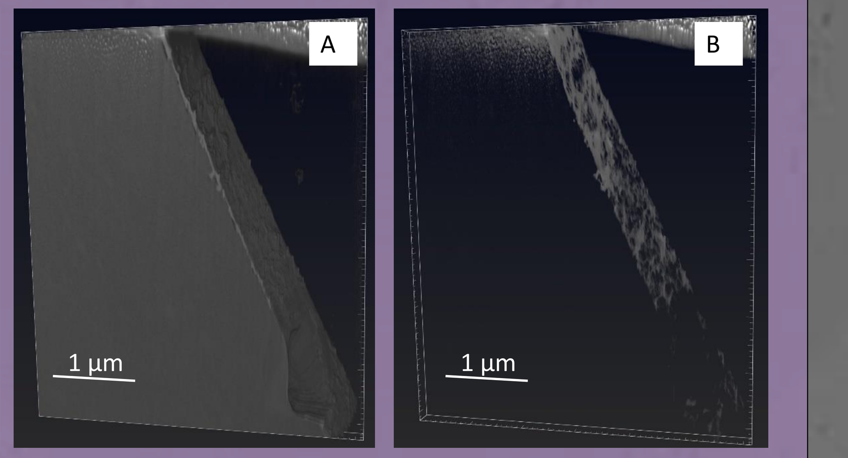


SEM Images: Zonal variation in the siderite crystal is highlighted (A). Hematite is seen with inclusions of organic matter (B). Siderite crystals contain hotspots of lighter Fe-minerals in their core material (C). Fe-oxide minerals also contain possible siderite spheroids (D). Granules imaged contain concentrically layered hematite and organic matter(E).



EDS Maps (Left): A zoned siderite crystal (A) was imaged and subjected to a chemical map scan, showing abundances of 7 elements (B-H)

FIB-SEM 3D Reconstruction (Right) depicts a siderite crystal edge showing its surface topography (A) and a highlight of the outmost lighter layer (<100 nm thick) of the crystal (B).

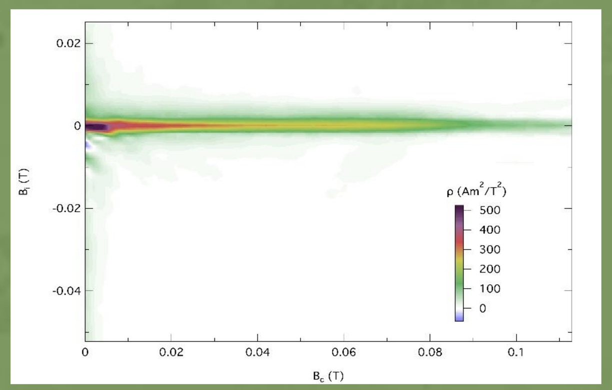


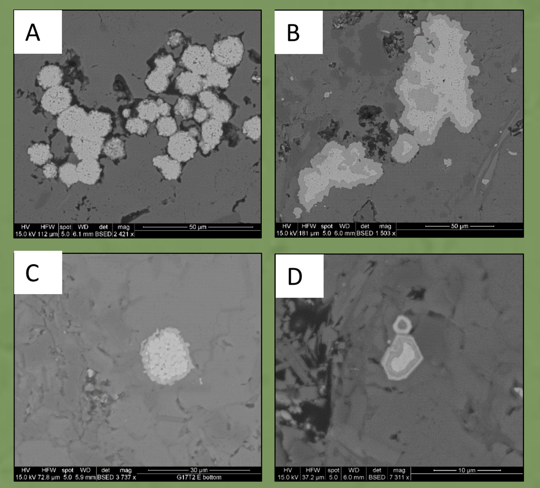
Methods

- **Mineral Magnetism:** First Order Reversal Curves (FORCs) were acquired using a vibrating sample magnetometer at the University of Minnesota Institute for Rock Magnetism. These curves help to characterize the magnetic components of a material. A magnetic map was acquired using a quantum diamond microscope at Harvard University.
- **Thin Section/Optical Microscopy:** Thin sections of each sample were made and a Nikon Optiphot 2-POL microscope was used to conduct transmitted and reflected light optical microscopy on the polished thin sections.
- **Scanning Electron Microscopy (SEM):** A FEI scanning electron microscope was used to take back-scattered electron images of each sample. Chemical composition was determined using energy-dispersive X-ray spectroscopy (EDS).
- **Focused Ion Beam (FIB) SEM:** FIB-SEM microscopy was conducted at George Washington University. Serial milling at 10 nm intervals using the FIB and subsequent imaging were conducted on sample Strom 14 at the contact between the chert matrix and a siderite crystal.
- **Raman Spectroscopy:** was performed using a 532 nm laser. Spot readings were taken for each sample and compared to known spectra.

Gunflint Formation (Strom 15 - Limestone)

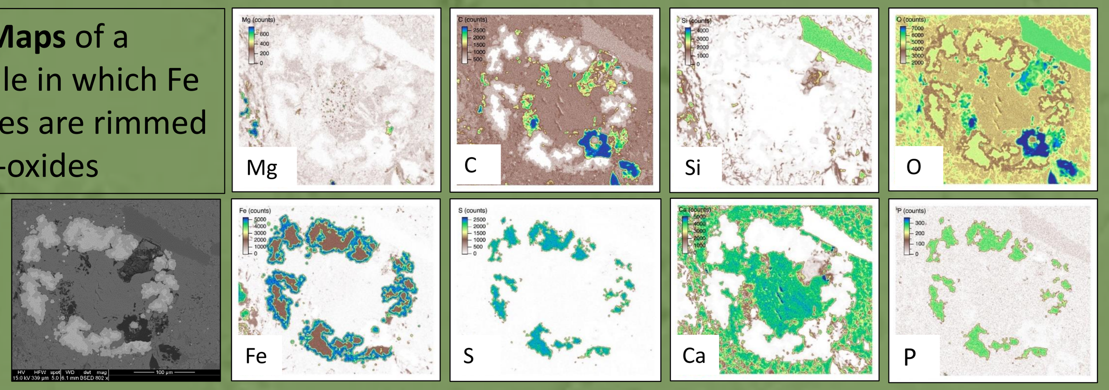
FORC Diagram showing a central ridge, indicative of non-interacting single domain magnetite. The coercivity profile peaks at low values (intensity maximum near origin), indicate the presence of ultrafine magnetite particles (<25 nm).

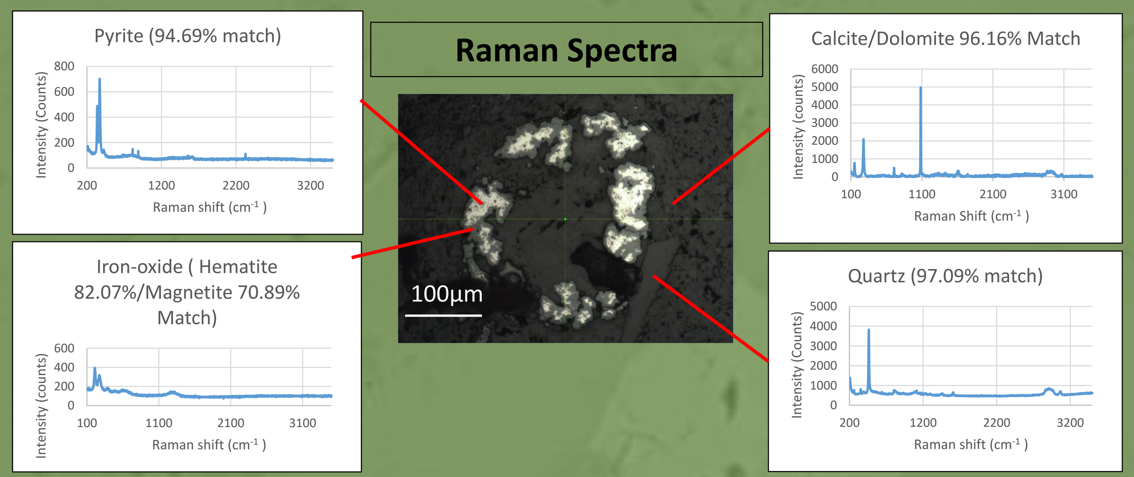




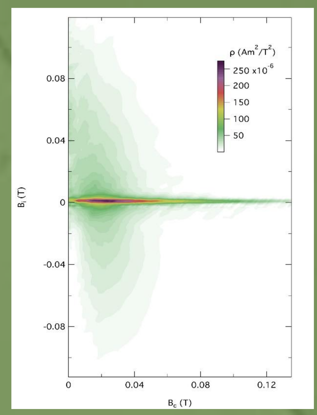
SEM Images demonstrate color zoning in crystals where an Fe-sulfide (light material) is rimmed by an Fe-oxide (light gray material) (A-D). Many of the crystals have a euhedral shape wherein they are clumped together into an even larger mass. The dark grey matrix is composed of calcite.

EDS Maps of a granule in which Fe sulfides are rimmed by Fe-oxides



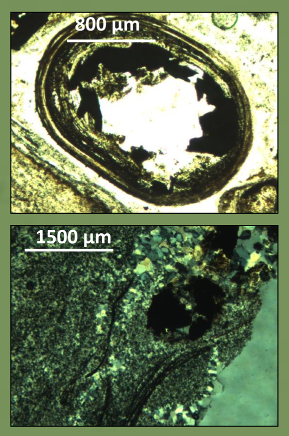


Biwabik Formation (Strom 16 - Jasper)

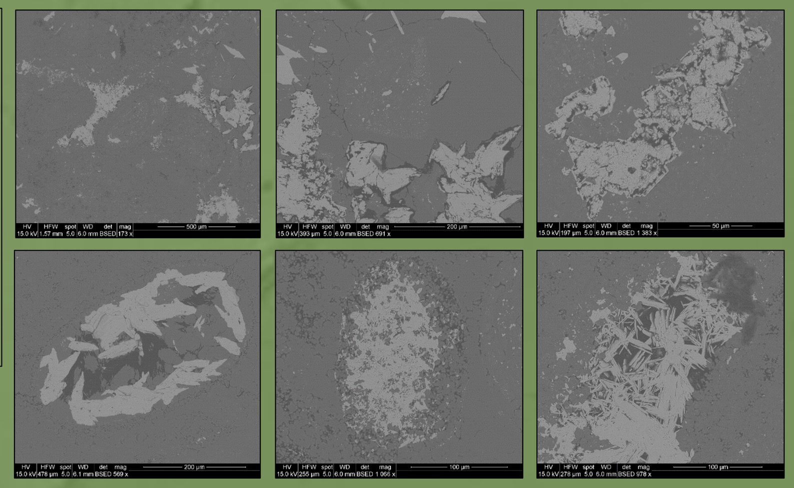


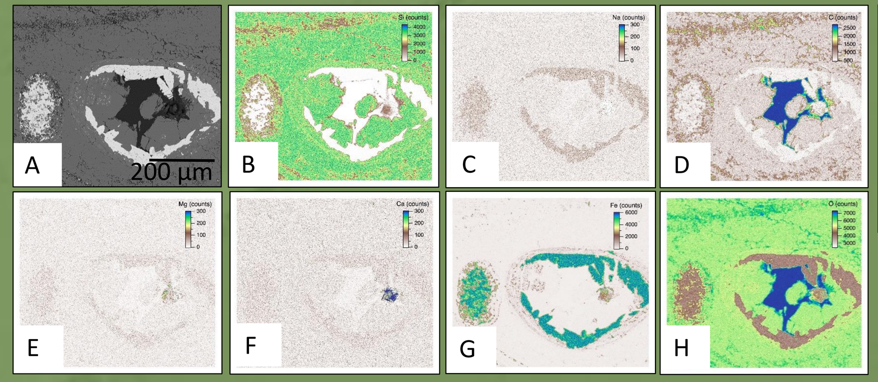
FORC Diagram showing a central ridge, indicative of non-interacting single domain particles. The low intensity background lobes indicate the presence of larger grains in the vortex state (0.1-1 µm)

Optical Microscope Images show that the sample is mainly composed of fine-grained quartz, with stromatolitic layers of Hematitic silica (jasper). Granules are a prominent characteristic of the sample, and contain coarse grained Fe-oxide minerals, fine grained quartz and layers of hematite. Most of the iron minerals in the sample are linked to these granules.



SEM Images corroborate optical microscopy images showing hematite (light grey material) and organic matter (black material) within/adjacent to granules. The main matrix of the sample is quartz.





EDS Maps of two granules showing abundance of Si (B), Na (C), C (D), Mg (E), Ca (F), Fe (G), O (H).

The iron mineralogy and source of magnetism in Lake Superior Rocks

In the Gunflint Chert, iron was primarily concentrated in siderite, hematite, and subordinately in magnetite. SEM images and chemical analysis showed zonal variations in the siderite crystals. Previous studies concluded that organic matter, in association with Fe(III) mineral precipitates, forms spherical siderite structures under diagenetic conditions *(Kohler et al. 2012)*. Rhombohedral siderite seen in the sample could have formed from a spheroidal siderite precursor, accounting for the spheroidal voids in some siderite cores. Zoning in the siderite could be due to differences in Fe oxidation and organic matter accumulation during crystal growth. The FIB-SEM 3D reconstruction revealed a thin layer coating the siderite. An increase in Fe in this layer, coupled with high magnetic field intensities around the siderite crystals suggest that this veneer is magnetite. The thickness of the layer (< 100 nm), together with its web-like morphology, with strands the size of single domain particles, indicate that this is the source of the magnetofossil-like signal in the FORC diagram. Further analyses are needed to unambiguously identify the mineralogy of this layer, but if confirmed as magnetite, it likely formed as product of diagenesis (*Rasmussen et al. 2018*). The next step is to fabricate a lamella (using the FIB) for high resolution imaging using transmission electron microscopy.

The Gunflint Limestone SEM images showed iron minerals that were zoned with Fe-oxide surrounding Fe-sulfide. Raman spectroscopy showed that the sulfide is pyrite and the oxide is hematite. Particles of Fe-sulfide rimmed by an Fe-oxide could have formed due to the deposition of sediment in a basin floor environment, where hydrous, silica- and iron-rich minerals were recrystallized in response to diagenesis, metamorphism, de-formation and oxidation (*Rasmussen et al.*). In the Biwabik Formation, optical microscopy showed that much of the iron minerals present in the samples were linked to the granules. These granules likely formed as a result of the diagenetic oxidation of organic matter during a chemically-oscillating reaction (*Papineau et al. 2017).* The magnetite nanoparticles identified magnetically in samples Strom 15 and 16 could not be imaged using traditional SEM, likely due to their very small sizes. The magnetofossil hunt continues!

Acknowledgements & References

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