EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

Experiment title: High resolution synchrotron Mössbauer spectroscopy of iron redox cycling within magnetite in Banded Iron Formations (BIFs)	Experiment number: ES-725

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Report:

Banded iron formations (BIFs) provide one of the most comprehensive archives of the history of life on Earth. The exact mechanism behind BIF genesis remains under debate, however microbial activity is considered to be one of the most important factors. We recently used ^{57}Fe Mössbauer spectroscopy to show that magnetite, a common constituent of BIFs, can undergo either microbial Fe(II) oxidation or Fe(III) reduction (*1*). We speculate that such processes could have taken place following the initial formation of primary BIF minerals, and thus contributed to the overall oxidation state and mineral content of magnetite in BIFs. Many Fe layers within BIFs have submillimeter thickness, which means conventional Mössbauer spectroscopy (typical beam diameter 1 cm) cannot distinguish between Fe minerals in different layers. However, synchrotron Mössbauer spectroscopy (SMS), has a spot size of 15 x 10 µm^2, making it ideal for such high-resolution spectroscopy. We used SMS to investigate evidence of microbial Fe cycling of magnetite within several BIF thin sections. We observed deviations in the magnetite Fe(II)/Fe(III) ratio from the stoichiometric value of 0.5 to either oxidized (0.2), or reduced (>0.5). Some of these differences appear to correlate to proximity to either siderite or hematite layers. This high-resolution data provides evidence of magnetite redox cycling, either during sedimentation or during diagenesis. These results have important implications for the interpretation of biosignatures within BIFs, especially with regard to understanding the (trans)formation processes involved in their genesis.

Materials and methods

- ### *Investigated BIF:*

Pre-GOE Banded Iron Formations were obtained from the Kuruman Iron Formation, Transvaal Group, South Africa during asbestos exploration drilling in the 1960s. The core was sampled by Nic Beukes and archived at the University of Johannesburg, South Africa. Drill cores were collected at depths between ca. 43 and 250 m, roughly corresponding to an age range of ca. 2.52 to 2.43 Ga. Several parts of the core were selected for high, intermediate and low magnetite (Fe_3O_4) content (Figure 1A).
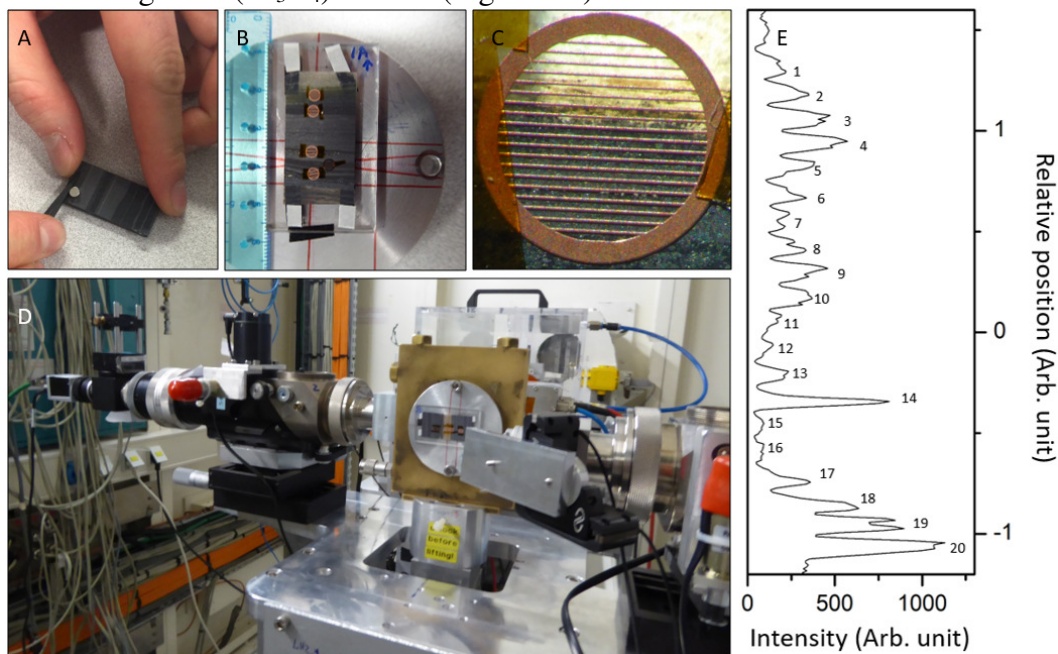
Figure 1 – Experimental setup. The location of magnetite rich bands was determined via the use of a small neodymium magnet (A). Thin sections were mounted onto a plate for easy transfer onto the beamline (B). TEM bar grids, diameter (3 mm) were used to provide alignment of the beam within segments of 90 µm thickness (C). The thin section and holder was easily mounted in the beamline and secured with two screws. Alignment was carried by comparison to the attenuation of the beam on the Cu grid.

Thin sections were prepared with a thickness of 150 µm without a glass substrate to enable a Plexiglas holder to be fixed to the back of the thin section in order to prevent attenuation of the synchrotron radiation. The thickness was chosen for optimal Fe content and counting time. Sections were not polished to avoid local heating effects which could potentially influence mineralogy and stoichiometry. Non coated TEM Cu grids with horizontal bars (90 µm spacing 'slits' between bars) were placed at various locations on each thin section, corresponding to areas which responded to a bar magnet, i.e. high magnetite content (Figure 1B and C).

- ### *Synchrotron* **Mössbauer** *spectroscopy (SMS)*

Alignment of each grid was performed suing a light microscope, with the parallel bars of each grid aligned along the orientation of the layers with each sample. The centre of the grid was aligned by scanning in the y-axis and identifying the regions where intensity was close to zero, i.e. where the beam was on the thicker edges of the grid. The distance was measured and if this extinction was close to 3 mm, we were confident we had found the middle of the grid. The centre point was then selected, and a full scan in the y-axis performed. When the beam passed over copper, the intensity of the beam decreased relative to when there was no copper present (Gigure 1E). Using this approach, we were able to count the slits within the grid. This was most effective in regions where the Fe content was sufficiently low to enable transmission of gamma radiation, as minerals with higher mass, such as magnetite attenuated the beam, resulting in a low intensity which could be misinterpreted as corresponding to a low Fe content. Each spectrum was collected for 40 minutes. This time was based on a reasonable signal to noise ratio, coupled with the ability to obtain large volume of data. SMS data were fitted using MossA (2), and the Lorentz Squared function was used for the source (Lor2 SrcFunc). The calibration full width half maximum (FWHM) was set to 0.215 mm/s. The FWHM of the source was determined from fitting of the single line absorber and in most samples varied from 0.45 to 0.49 mm/s.

Results

All samples showed clear microbanding, with alternating layers of silicates, magnetite, hematite and carbonate (Figure 2). Higher magnification light micrographs can be used to distinguish specific features in the samples. For example, section 14, grid 4 was characterized by a silver coloured band with thickness of ~0.5 mm. This was anticipated to be magnetite. In contrast, the dark grey region above and below the silver band was expected to consist of hematite, carbonate or silicate. Within some of the slits of this grid, three spectra were collected, corresponding to a step size of just 30 µm (Figure 2C & D).
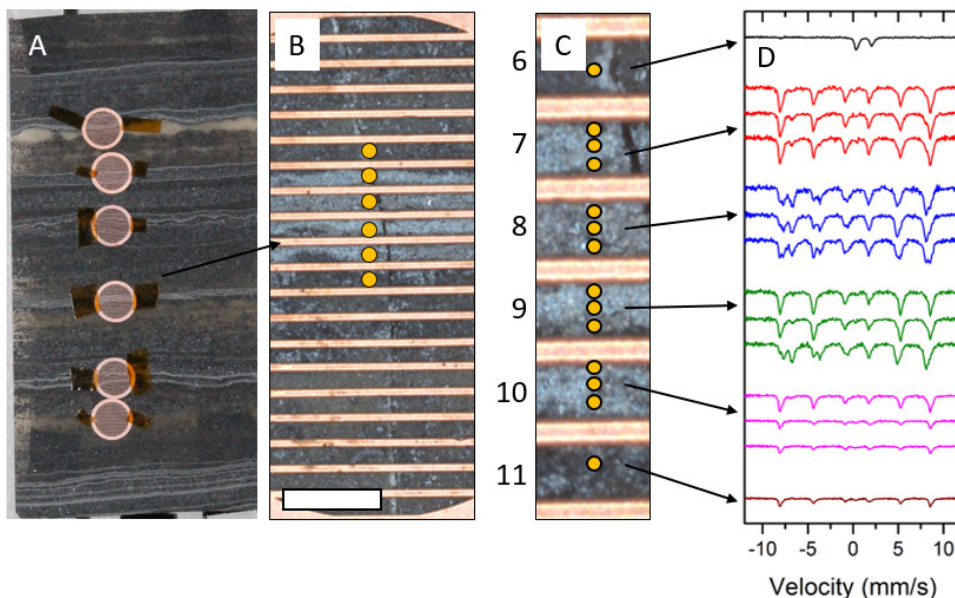
Figure 2 – High resolution SMS of section 14, grid 4. Grids were imaged using high resolution light microscopy (A & B). Within each grid, several spots were identified for SMS (C). Each spectrum was collected in just 40 minutes in order to obtain sufficient signal to noise ratio.

Fitting of the Mössbauer spectra revealed differences in the Fe minerals present in each BIF thin section. In each sample analysed, we were able to identify the presence of magnetite, hematite and siderite. An Fe(II) containing silicate phase was also identified in one section, though it was not assigned a specific mineral type. The stoichiometry (i.e. Fe(II)/Fe(III) ratio) of the magnetie was also determied according to Gorski et al. 2010 (*3*). Section 14, grid 4 showed highly oxidized magnetite near the top of the silver band in close association with an Fe(II) carbonate phase. The presence of siderite was confirmed using synchrotron XRD. The change in stoichiometry is not dependent on the abundance of magnetite. The middle of the silver band shows the highest stoichiometry which is at the theoretical value of 0.5 expected of magnetite. At the bottom of the band, the Fe mineral composition consists of a mixture of hematite and magnetite before tending towards pure hematite. Further analysis of all samples showed the consistent observation that the magnetite stoichimetry varied across the microbands, thus indicating a redox reaction must have occurred. The exact nature of the reaction is still unknown and it is also unclear whether the oxidation happened during or post deposition.

Conclusions

The results obtained by this project indicate the presence of oxidation state gradients in magnetite within BIF microbands. These samples, which were desposited before the GOE provide clear evidence that some type of oxidative mechanism was present before the advent of widespread molecular oxygen on the early Earth. The challenge however is to try and isolate and determine the potential causes of this oxidation. Additional work on these samples is currently being carried out, e.g. using petrography to elucidate the processes which may be responsible for the oxidative gradients observed. Ultimately, our experiment has demonstrated the power of using SMS to investigate the oxidation state of Fe minerals in rock samples such as BIFs in a way which could apply to many other rock types.

References

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