

**Supplementary material for:**

## **Post-depositional REE mobility in a Paleoproterozoic banded iron formation revealed by La-Ce geochronology: A cautionary tale for signals of ancient oxygenation**

P. Bonnand<sup>1</sup>, S.V. Lalonde<sup>2</sup>, M. Boyet<sup>1</sup>, C. Heubeck<sup>3</sup>, M. Homann<sup>2,4</sup>, P. Nonnotte<sup>2</sup>, I. Foster<sup>2</sup>, K.O. Konhauser<sup>5</sup>, I. Köhler<sup>3,6</sup>

### **1. Stratigraphic context, field localities, and sampling of Moodies Group BIF**

Samples were collected from two banded iron formation (BIF) units from three locations in three tectonic blocks of the Moodies Group: unit MdI2 at the Devil's Staircase Road locality (Moodies Hills Block) and at the Clutha Creek Section (Eureka Syncline), and unit MdI1 at the Belvue Section (Stolzberg Syncline). This section summarizes briefly the stratigraphic context of the two sampled units at these locations.

MdI1 is a BIF-jaspilite unit composed of multiple thin (1-30 cm thick) beds that occur dispersed within a 20-to-40-m-thick interval within the 400-to-1000-m-thick MdS1 unit, overlying the ca. 80-m-thick basal Moodies conglomerate (MdbC) and the 300 to 1100 m thick, poorly to moderately sorted, quartzofeldspathic and lithic sandstones of MdQ1. While MdbC is a fluvial deposit, most of MdQ1 represents tidal and estuarine settings; MdS1 includes one or several deltaic sandstone complexes (e.g. Stutenbecker et al., 2019), and the BIF-jaspilite unit MdI1 occurs within a below-wavebase prodelta slope setting.

MdI2 contains thick-bedded jaspilite and thinly bedded BIF along with magnetic shale. It is interbedded with siltstones and very-fine-grained sandstones, and reaches up to 18 m thick in the Moodies Hills Block and a comparable thickness in the Eureka Syncline. MdI2 occurs approximately 1000 m stratigraphically above MdI1 and overlies the Moodies basaltic lava MdL2, which has been interpreted as a coastal subaerial basaltic flow complex. MdI2 is overlain by gravelly, cross-bedded, braided-fluvial-facies sandstone with mud-cracked shale coatings, minor tuffaceous siltstone, and conglomerate, comprising the ~300 m thick unit MdS2. Significant variability in lithologies and thicknesses render correlation of units above MdI2 difficult, suggesting that the Moodies basin may have become tectonically segmented after the eruption of the Moodies lavas, resulting in a laterally heterogeneous environment responding to local tectonic controls on unit thickness and composition. See Lowe and Heubeck (1994) and Heubeck (2019) for reviews of Moodies Group sedimentation and stratigraphy.

## ***Location Descriptions***

### ***Samples from Devil's Staircase Road section, Moodies Hills Block***

BIF of Mdl2 were sampled at the roadcut exposure of Devil's Staircase Road, also known as Ameide Road (25°49'55.82"S, 31°0'50.49"E) (Fig. S3). This section, located in steep grassland, is located on the topographic north flank of the central BGB and exposes Mdl2 in a slightly overturned sequence within the ca. 2500-m-thick section of the Moodies Hills Block, presumably the fault-truncated southern limb of a major syncline. Bontognali et al. (2013) provide a partial, Rabethge (2015) a more detailed measured section. At Devil's Staircase Road, Mdl2 reaches approximately 18 m thick and is comprised of jaspilite, BIF, shale-siltstone couplets and rare very-fine-grained thin sandstone beds. A total of 21 BIF samples were collected from outcrop using hammer and chisel of which 19 were analyzed for this study (Fig. S4). Samples with fractures, white quartz veins, friable material, or other overt signs of surficial weathering were avoided. Samples are composed largely of red hematite and dark magnetite laminae interbedded with red jaspilite. Representative hand samples are shown in Fig. S5.

### ***Samples from the Clutha Creek Section, Eureka Syncline***

BIF of Mdl2 were sampled in the Clutha Creek drainage of the Eureka Syncline at 25°41'52.81"S, 31°5'10.89"E. Exposure in the narrow, partially bushy, mostly dry streambed is intermittent and consists of stream-polished outcrops which show no overt signs of significant surface weathering. At this locality, up to 15-cm-thick BIF and jaspilite bands associated with magnetic shale occur within a >200m-thick section of dark grey siltstone and shale (MdS2) with common signs of soft-sediment deformation, including slumping and fluid-escape structures. MdS2, interpreted as a prodelta slope, forms the uppermost part of a continuous, >900m-thick, subvertically dipping, overall fining- and deepening-upward section of Moodies strata along the western limb of the Eureka Syncline (Anhaeusser, 1976; Heubeck, unpublished). A total of 17 samples were collected from Mdl2. They are composed primarily of hematite, magnetite, and chert. Representative hand samples are shown in Fig. S5.

### ***Samples from the Belvue Section, Stolzberg Syncline***

BIF of Mdl1, within unit MdS1, were sampled at 25°54'8.04"S, 30°50'44.90"E in open grassland in the eastern Stolzberg Syncline on Farm Belvue 711 JT (Luber, 2015; Nabhan et al., 2016). There, Mdl1 reaches about 25 m thick. Within this section, several clusters of 1- to 20-cm-thick beds of BIF and jaspilite occur; they are interbedded with ferruginous shales, siltstones and fine-grained sandstones comprising unit MdS1. All beds, including the weathering-resistant BIFs, are commonly contorted, disrupted and slumped. As elsewhere in the BGB, MdS1 at this location represents prodelta deposition. The unit overlies conformably (and is part of) a continuous sequence of (base to top) coastal floodplain, sandy shoreline, incised estuarine channel and delta-mouth-bar sediments, totaling about 600 m thick. Twelve samples were collected with hammer and chisel from outcrop, avoiding friable or fractured samples and rocks with other recognizable signs of surficial weathering.

## 2. Methods

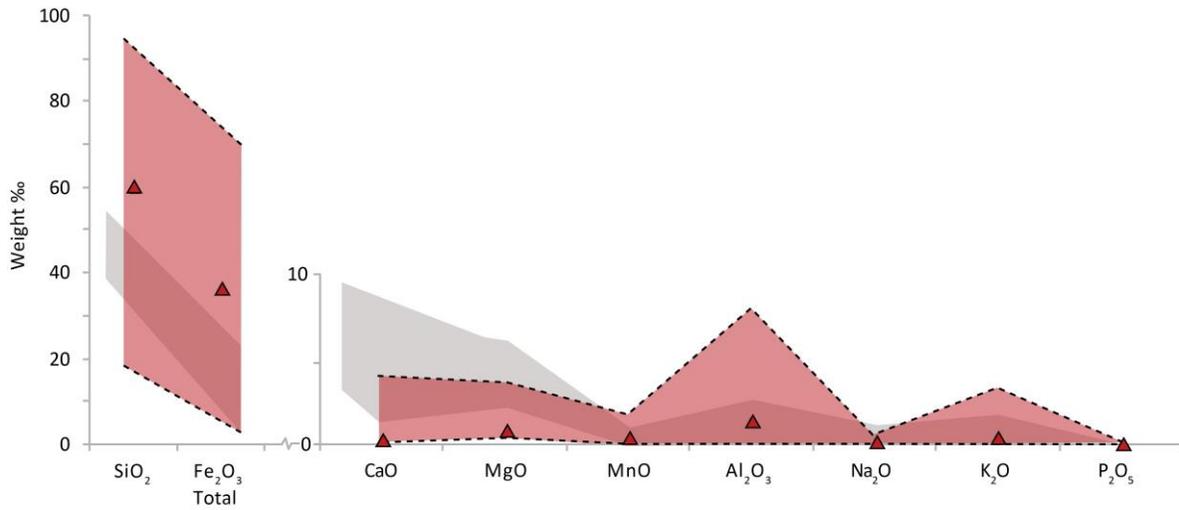
All samples were prepared using trace-element clean methods (crushing and powdering in pure tungsten carbide and agate, respectively) and all digestions and column separations were performed in clean laboratories at the European Institute for Marine Studies in Brest and at the Laboratoire Magmas et Volcans in Clermont-Ferrand, France. For analysis of major elements, samples were digested at 90° C in PFA vials using concentrated HNO<sub>3</sub> and HF, followed by immediate neutralization with 20 g L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> to retain Si, as per Cotten et al. (1995). After dilution by a factor of 400, samples were analyzed using an Yvon Horiba Ultima 2 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) calibrated against a standard curve comprised of the CRPG reference materials Mica-Fe, UB-N, MORB-E, GB2, IF-G, AC-E, and WS-E digested in the same batch, using the working values of Govindaraju (1995), and with replicates of IF-G and AC-E treated as unknowns to monitor accuracy. Precision based on 5 replicate analyses was better than 4.5% (2 relative standard deviations, RSD) for all major elements except for Mg, Ca, and Na, which showed lower precision (14 to 21%) between replicates due to their low concentrations in iron formation. For analysis of trace elements and Nd isotopes, between 80 and 120 mg of powder was digested sequentially in PFA vials at 90° C using concentrated HF-HNO<sub>3</sub>, aqua regia, and 6M HCl. For trace element analysis, aliquots were re-suspended in 2% HNO<sub>3</sub> with indium as an internal standard and analyzed using a Thermo Scientific Element2 High-Resolution Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Pôle Spectrométrie Océan in Brest, France. The instrument was tuned to minimize oxide production, and mixed mono-elemental Pr-Nd, Ba-Ce, and Sm-Tb solutions were analyzed to quantify potential oxide interferences prior to the session, which were negligible. Calibration was performed against gravimetrically prepared multi-element solutions, and geostandards IF-G and AC-E were analysed in the same session as unknowns to monitor accuracy, which was better than 5% for REE and 10% for most other trace elements (2 RSD). For major and trace method analyses, detection limits were determined using blanks prepared alongside samples and are reported in Table S2 as either the detected blank concentration (normalized to the typical amount of rock powder analyzed) or the method detection limit determined by three relative standard deviations of the end-of-rinse intensities that were systematically measured prior to each sample. Sm-Nd and La-Ce parent/daughter ratios were calculated from HR-ICP-MS data of non-spiked samples using  $^{147}\text{Sm}/^{144}\text{Nd} = 0.6045 \times \text{Sm}/\text{Nd}$  and  $^{138}\text{La}/^{142}\text{Ce} = 0.0080 \times \text{La}/\text{Ce}$ . Propagated relative standard errors on these ratios were constrained to less than 1% by periodic measurements (n=8) of a multi-element solution throughout the session, and to less than 10% for all trace element concentrations, and less than 2–3% for most REE, based on the same repeat analyses.

To assure complete digestion and confirm the REE data acquired after HF-HNO<sub>3</sub>-Aqua Regia digestion in PFA beakers, a selected set of sample powders were re-analyzed by HR-ICP-MS after Na<sub>2</sub>O<sub>2</sub>-NaOH alkaline fusion in glassy carbon crucibles at 650°C in the presence of a Tm spike, following the protocol and data reduction procedure of Bayon et al. (2009).

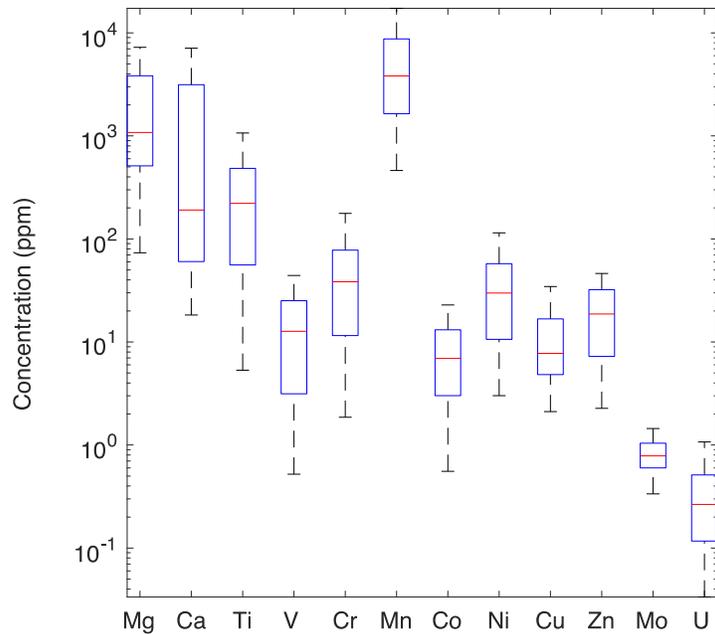
For Nd isotopes, aliquots were evaporated and re-dissolved in 2.5M HCl for chemical separation of REE using cationic BioRad® AG50X8 200-400 mesh columns, followed by further purification on LnSpec Eichrom resin. Nd isotopic measurements were performed during two

analytical sessions at the Pôle de Spectrométrie Océan in Brest using a Thermo Scientific Neptune multi-collector ICP-MS and a Thermo Scientific Triton Thermal Ionisation Mass Spectrometer (TIMS, Triton). A  $^{146/144}\text{Nd}$  ratio of 0.7219 was used for mass bias correction. Recovered Nd fractions contained between 1266 and 16  $\mu\text{g}$  of Nd (mean 134  $\mu\text{g}$ ) while blanks prepared alongside samples contained less than 140 pg of Nd. For TIMS measurements, analyses were made in static mode using 10 blocks of 10 cycles each, with 1 s integration times and baselines measured for 30 s between each block. For MC-ICP-MS measurements, one block of 30 cycles with integration times of 4.196 s was employed, preceded by a 30 s baseline measurement. Results obtained on the international standard JNdi-1 are reported in Table S1. JNdi-1  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios measured during the TIMS session are slightly lower ( $0.512086 \pm 0.000017$ , 2 s.d.,  $n=5$ ) than the accepted value obtained using a dynamic routine over a period of 1.5 years on 3 different Triton mass spectrometers ( $0.512099 \pm 0.000005$ , 2 s.d.,  $n=61$ , Garçon et al., 2018). Thus, the measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios have been normalized. Aside from correction for instrumental drift using sample-standard bracketing with JNdi-1, no further correction is applied to the Nd isotope ratios during the MC-ICP-MS session since the JNdi-1 results are in agreement with the accepted value ( $0.512095 \pm 0.000005$ , 2 s.d.,  $n=17$ ).

For Ce isotopes, 100-150 mg of rock powder was digested using a HF-HNO<sub>3</sub> dissolution technique. The chemical separation used to separate the Ce fraction involved four steps of column chemistry. The first step, aimed at removing the Fe fraction, was performed on anionic AG1-X8 resin (100-200 mesh). The sample was loaded onto the resin in strong HCl and Ce was not retained by the resin. The second step was used to separate the REE from other main cations of the matrix. To this end, the samples were loaded in 2.5N HCl onto AG50-X8 resin (200-400 mesh). REE were retained by the resin while major cations were eluted in 2.5N HCl, and REE were then eluted in 6M HCl. The third column procedure was designed to separate Ce<sup>4+</sup> from other REE and was performed using Ln spec resin (Eichrom). The samples were loaded in 10M HNO<sub>3</sub> + NaBrO<sub>3</sub>, and Ce<sup>4+</sup> was retained on the column while other REE were not. The Ce<sup>4+</sup> fraction was eluted in 6M HCl + H<sub>2</sub>O<sub>2</sub>. Finally, the samples were processed through the second step to make sure the Ce fraction was cleaned of any remaining matrix cations. The total procedural blanks prepared alongside samples contained less than 0.5 ng of Ce. Isotopic measurements were performed on a Thermo Scientific Thermal Ionisation Mass Spectrometer (TIMS) at the Laboratoire Magmas et Volcans as previously described by Bonnard et al. (2019). Together with the samples, Ce<sub>AMES</sub> and Ce<sub>LMV</sub> reference materials were analysed and gave  $^{138}\text{Ce}/^{142}\text{Ce}$  values of  $0.0225743 \pm 0.0000007$  (2 s.d.;  $n=26$ ) and  $0.0225705 \pm 0.0000006$  (2 s.d.;  $n=48$ ), respectively. The values are comparable to previously published values (e.g. Willbold, 2007).



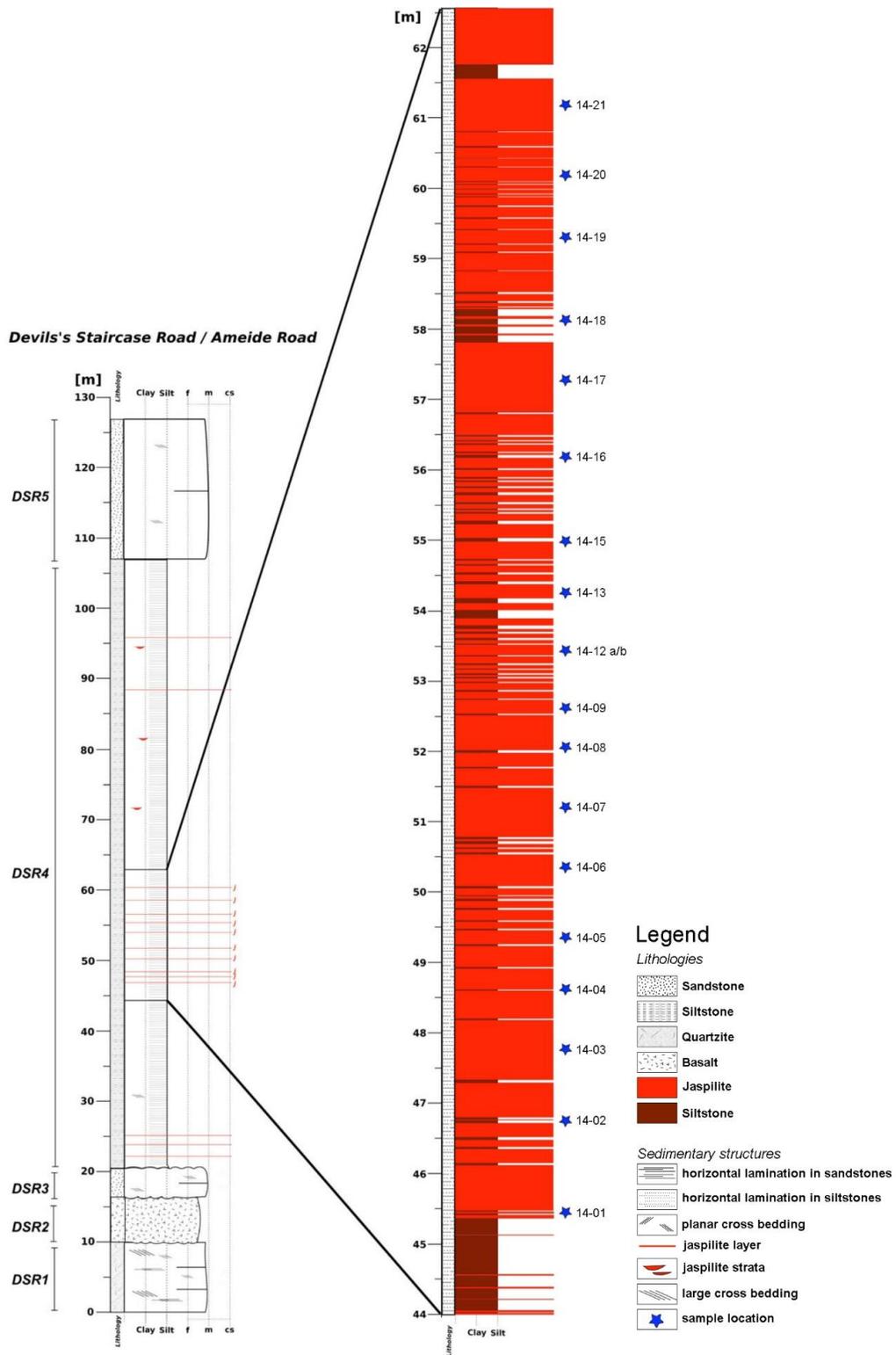
**Figure S1.** Mean (triangles) as well as maximum and minimum concentrations (red shaded area) of major elements in Moodies Group BIF (n=48). The gray shaded area is the range of values provided by Klein (2005) for a large compilation of Archean and Paleoproterozoic BIF (n=90).



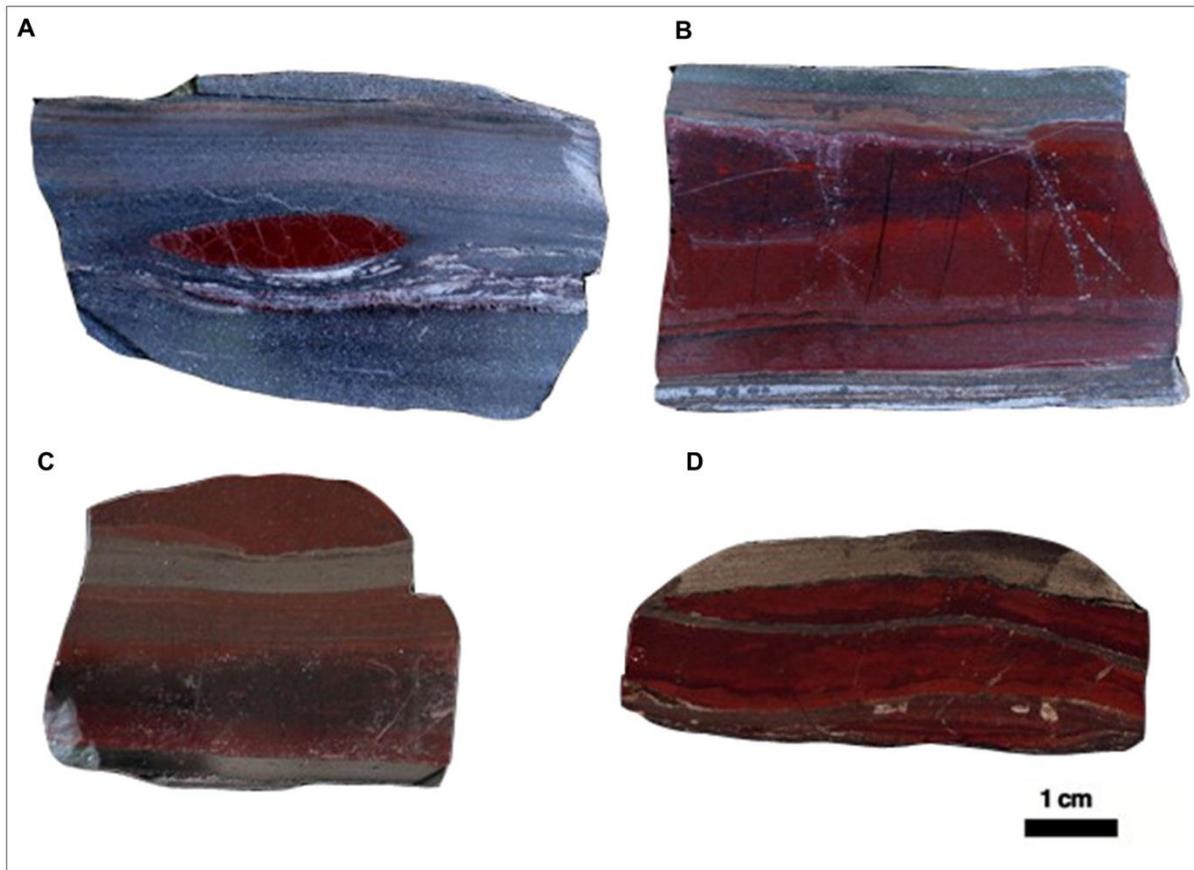
**Figure S2.** Box-and-whisker plot of selected major elements and transition metals in Moodies Group BIF (n=51). Red lines represent mean values, box limits denote 75<sup>th</sup> and 25<sup>th</sup> percentiles, and whiskers show the full range of values.



**Figure S3.** Outcrop-scale photographs at the Devil's Staircase Road locality in the Moodies Hills Block (A/B), the Clutha Creek locality in the Eureka Syncline (C/D), and the Belvue section in the Stolzberg Syncline locality (E/F).



**Figure S4.** Stratigraphic column of Mdi2 at the Devil's Staircase Road locality (Rabethge, 2015) with an expanded view of the principal BIF-bearing section, showing sample locations.



**Figure S5.** Representative Fe- (A) and Si-rich (B) polished hand samples from the DSR locality showing dark hematite- and magnetite-rich layers and red chert. A chert nodule (red) and quartz vein (white) are visible in (A). Representative polished hand samples from the Clutha Creek locality (C, D).

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