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Supplementary Information

This supplementary text provides:

- i.) Additional discussion of the question of sample bias in $\delta^{56}\text{Fe}$ records.
- ii.) Lists of references used in compiling $\delta^{56}\text{Fe}$ and $\delta^{34}\text{S}$ records for the Archean–Paleoproterozoic.

The compiled datasets used in this study are published in the EarthChem library. URL: <https://doi.org/10.1594/IEDA/111446>

FIDELITY OF THE ANCIENT FE ISOTOPE RECORD

The Archean–Paleoproterozoic $\delta^{56}\text{Fe}$ record is notably sparse when compared to traditional stable isotope proxies, including the $\delta^{34}\text{S}$ data we have compiled. However, interpretations of the $\delta^{56}\text{Fe}$ record have in the past extrapolated the findings of relatively localized sampling in time and space, in order to develop models with broad implications for the marine Fe cycle and its relevance to the evolution of Earth surface redox conditions (*e.g.* Rouxel et al., 2005; Planavsky et al., 2012; Rolison et al., 2018; Czaja et al., 2018). Such interpretations all require that the existing $\delta^{56}\text{Fe}$ records of IF and pyrite provide a representative sampling of these sediment types. In our study, sample bias concerns are arguably greater because of how they might affect subtler trends in the $\delta^{56}\text{Fe}$ record. Therefore, we identify three main ways in which sample bias could affect our interpretations of $\delta^{56}\text{Fe}$ records, and suggest mitigating factors in each case.

Heterogeneous sampling in time and space

The first type of sampling bias we consider is that of inhomogeneous sampling of the IF and pyrite $\delta^{56}\text{Fe}$ records in time and space. The patchy nature of both records, often with long gaps containing little to no data throughout the 2000 Ma time span we consider, makes it clear that rocks of all ages have not been sampled equally. This is unavoidable because rocks of Archean age are preserved on few cratons, and in the case of IFs, because their geological occurrence is thought to be sporadic and linked to periods of high hydrothermal Fe^{2+} supply driven by the occurrence of oceanic large igneous provinces (Isley and Abbott, 1999; Bekker et al., 2010; Konhauser et al., 2017). Care must be taken not to over-extrapolate interpretations to include spans of Earth history where no data is available. In order to address this possible bias, we choose not to interpolate $\delta^{56}\text{Fe}$ records across unsampled time periods, and base our

interpretations of possible covariations between $\delta^{56}\text{Fe}_{\text{py}}$, $\delta^{56}\text{Fe}_{\text{IF}}$ and sulfur records by binning by age and only comparing time bins which contain data. In addition to time binning, we note that that $\delta^{56}\text{Fe}$ data for both IF and pyrites of a given age, in addition to more extensively sample S records, often include samples from the same sedimentary basins or successions. In particular, late Neoarchean and early Paleoproterozoic sedimentary records are very well sampled in the West Australian Hamersley and South African Transvaal Supergroups. This is where $\delta^{56}\text{Fe}$ records are the most complete, and therefore we are confident that the compilations we present capture the time period around the GOE as it affected marine Fe cycling in these locations. Whilst the possibility exists that the Hamersley and Transvaal sub-basins are not representative of late Neoarchean to early Paleoproterozoic geochemistry, such a concern is equally applicable to the numerous interpretations of global biogeochemical change that have been formulated principally making use of samples from these very well sampled regions.

Similarly, sampling is sparse in the Meso- and Paleo-Archean. $\delta^{56}\text{Fe}$ records, where they exist, are available for IF and pyrites from closely associated formations, and therefore the covariations we present may still be descriptive of the shared evolution of Fe, S, and O_2 cycling at these times and locations (Planavsky et al., 2014; Busigny et al., 2017; Eickmann et al., 2018; Ossa Ossa et al., 2018). For example, around 2950 Ma, elevated $\delta^{56}\text{Fe}_{\text{py}}$, negative $\delta^{56}\text{Fe}_{\text{IF}}$, and a large range in $\delta^{34}\text{S}$ are all consistent with a proposed Mesoarchean environment with increased S availability in addition to multiple lines of evidence for free O_2 , including Cr and Mo isotopic data (Crowe et al., 2013; Planavsky et al., 2014; Eickmann et al., 2018; Ossa Ossa et al., 2018). The fact that this record is restricted to the Pongola Supergroup of South Africa means we cannot make broader interpretations about the global ocean redox state or the entirety of the Mesoarchean. However, these highly localized data still provide meaningful information about the interaction of the Pre-GOE Fe, S, and O_2 cycles. We suggest that they can serve as a case study for how $\delta^{56}\text{Fe}$ records might be expected to change in the transition from an anoxic, low S environment to one more replete in O_2 and S, as is thought to have occurred on a global scale during the GOE. We cannot rule out that the Pongola Supergroup represents a biased sampling of Mesoarchean global biogeochemistry, capturing a localized environment in which oxidants and sulfur accumulated in quantities well in excess of the global average for the Mesoarchean. This should be testable in the future through extensive geochemical studies of other Mesoarchean sedimentary successions of similar age, including $\delta^{56}\text{Fe}$ studies.

Preservation bias in the rock record

The second form of sample bias we consider is whether the types of rocks preserved at Earth's surface may have changed over time, such that trends in $\delta^{56}\text{Fe}$ records could reflect changes in post-depositional alteration of rocks or preferential destruction of certain lithofacies. For example, could the general trend of decreasing $\delta^{56}\text{Fe}_{\text{IF}}$ from the Eoarchean through to the GOE, noted previously by Czaja et al. (2018), reflect geological processes that led to the preferential

loss of low $\delta^{56}\text{Fe}$ IF over time, such that only high $\delta^{56}\text{Fe}_{\text{IF}}$ values are preserved in the earliest portion of the rock record? This question is particularly pertinent for the IF record, because there is an observed change in the dominant style of IF deposited in through the earlier Archean versus the latest Neoproterozoic and Paleoproterozoic, with older, more volcanically-influenced and laterally restricted Algoma style IF giving way to basin-scale Superior style IF deposition that occurred on more stable passive continental margins (Bekker et al., 2010; Konhauser et al., 2017). Algoma style IFs typically display positive, and less variable, $\delta^{56}\text{Fe}$ values, whereas Superior style IF show more larger ranges of $\delta^{56}\text{Fe}$, with negative values being common (Dauphas et al., 2016; Czaja et al., 2018). Gradual removal of ferric oxyhydroxide precipitates with positive $\delta^{56}\text{Fe}$ from the ocean is thought to leave the residual dissolved Fe^{2+} with complementary negative $\delta^{56}\text{Fe}$ values (Rouxel et al., 2005; Planavsky et al., 2012). Therefore, the $\delta^{56}\text{Fe}$ range seen in Superior style IF could be explained by their deposition further from hydrothermal Fe sources than Algoma style IF, with the former precipitating from an Fe^{2+} reservoir that had greater opportunity to be depleted by partial oxidation during upwelling.

In light of this distinction in $\delta^{56}\text{Fe}$ systematics of different styles of IF, a preservation bias favoring one style of IF over another could theoretically lead to spurious trends in the observed $\delta^{56}\text{Fe}_{\text{IF}}$ record. The preservation bias required to reproduce our observed $\delta^{56}\text{Fe}_{\text{IF}}$ record must comprise of two factors: i.) Preferential destruction of younger Algoma style IF with almost entirely positive $\delta^{56}\text{Fe}$ in the late Neoproterozoic to early Paleoproterozoic, and ii.) Preferential destruction of low $\delta^{56}\text{Fe}$ Superior style IF in the Eoarchean through to the early Neoproterozoic. Such a preservation bias would imply that Superior style IF were deposited throughout the Archean but only preserved later in Earth history. We consider i.) to be plausible, because volcanically associated Algoma style IF were not deposited on stable craton margins and therefore their destruction by tectonic processes would appear to be likely relative to the that of Superior style IF. In addition, early high mantle potential temperatures may have enabled formation of hotter, more buoyant Eoarchean oceanic crust that was not so easily destroyed by subduction, aiding the survival of early Algoma style IF. However, we do not consider it geologically plausible that expansive Superior style IF could have been entirely eradicated from the first 1000 Ma of the geological record, in order to create the dearth of lower- $\delta^{56}\text{Fe}$ IF seen in the early Archean, because this would require preferential preservation of oceanic crustal material relative to stable passive margin sedimentary sequences, a phenomenon which is not known otherwise in the geological record.

Theoretically, we could contrive various scenarios that explain each trend in the $\delta^{56}\text{Fe}_{\text{IF}}$ and $\delta^{56}\text{Fe}_{\text{py}}$ records entirely via preservation biases in an unchanging ocean geochemical regime. However, we would argue that these scenarios generally require non-uniformitarian geological processes. By contrast, we consider the interpretations we can make for $\delta^{56}\text{Fe}$ records by taking them at face value do not present such internal inconsistencies. Our preferred interpretation of these data can and should be subject to debate and testing by greater sampling of gaps in the geological record. However, we believe that sampling biases are not so severe as to completely

disqualify meaningful interpretation of the $\delta^{56}\text{Fe}$ record as it relates to the interaction of the Fe, S and O_2 cycles.

Hydrothermal or metamorphic overprinting of $\delta^{56}\text{Fe}$ records

The third way in which sample biases could affect our interpretation of the $\delta^{56}\text{Fe}$ record is if it were dominated by hydrothermal or metamorphic overprinting as opposed to primary sedimentary signatures. For the sake of discussion, we consider early diagenetic processes such as microbial dissimilatory Fe^{3+} reduction (DIR) to be ‘primary’ processes inasmuch as they occur in unconsolidated sedimentary piles still in diffusive exchange with the marine water column, and are biogeochemical rather than metamorphic processes. A forgiving aspect of $\delta^{56}\text{Fe}$ systematics is that they are generally resistant to metamorphic overprinting, as Fe is quite immobile during metamorphism (Dauphas et al., 2016). This is epitomized by the preservation of chemical sedimentary $\delta^{56}\text{Fe}$ signatures in ~3800 Ma IF from the Isua and Nuvvuagittuq supracrustal belts, which have experienced metamorphism up to amphibolite facies (Dauphas et al., 2004, 2007a, 2007b; Czaja et al., 2013). Despite this, $\delta^{56}\text{Fe}$ in these rocks clearly distinguishes them from banded gneisses with igneous protoliths. The high Fe contents of IF mean that large quantities of Fe must be lost or gained in order to significantly alter their $\delta^{56}\text{Fe}$ values. Metamorphic recrystallization can redistribute Fe isotopes among constituent minerals, but high temperature equilibrium fractionations occurring in these reactions are small relative to the ‰-scale low temperature primary fractionations recorded in the bulk composition of these rocks (Dauphas et al., 2016). In addition, late-altering metamorphic fluids are expected to have formed in equilibrium with a more oxidizing atmosphere than the one under which ancient IF formed, such that metamorphic fluids are unlikely to reduce IF-hosted iron, which would be required for large scale Fe loss from IF because Fe^{3+} is fluid immobile.

Some ancient pyrites may also have been influenced by post-depositional hydrothermal and/or metamorphic processes. At first glance, pyrite has a high Fe content and is highly insoluble, which might suggest that metamorphic alteration to $\delta^{56}\text{Fe}_{\text{py}}$ is unlikely. However, we do not omit the possibility that pyrite can form as a secondary phase during hydrothermal and metamorphic processes. Textural studies suggests that some pyrites in the well-studied Mt McRae shale were dissolved and reprecipitated in coarse-grained nodules and laminae, with internally homogenized $\delta^{34}\text{S}$ (Takegawa et al., 1998). Furthermore, O isotope thermometry of pyrite-rimming quartz grains in this formation suggest homogenization at 100-240 °C, which supports a role for hydrothermal alteration in this pyrite reprecipitation (Haruna et al., 2003). However, this dissolution-reprecipitation of pyrite appears to have occurred in a closed system (Takegawa et al., 1998). In many cases, Archean-Paleoproterozoic pyrites have internal crystalline structure indicative of secondary grain growth, but the deformation of primary shale laminae around such pyrite grains argue for a primary sedimentary origin and subsequent closed system recrystallization (Rouxel et al., 2005). Again, in such cases a large quantity of new Fe, or

significant loss of primary Fe, would be required to significantly overprint primary sedimentary $\delta^{56}\text{Fe}_{\text{py}}$ signatures. While hydrothermally-influenced dissolution-reprecipitation played an important role in homogenization and textural evolution of these ancient pyrites, it is unlikely to have affected their bulk $\delta^{56}\text{Fe}$ composition, particularly given the high temperatures at which these reactions occurred. Crucially, to produce the trends through time seen in $\delta^{56}\text{Fe}_{\text{py}}$ records, hydrothermal/metamorphic alteration of pyrites would need to be both pervasive, and undergo a systematic change in its effect on $\delta^{56}\text{Fe}$ through time. Whilst this is a difficult proposition to entirely rule out, it appeals to non-uniformitarian processes and therefore we consider it unlikely as a driver of global $\delta^{56}\text{Fe}$ trends through time. More fundamentally, our data compilation relies on good analytical practice on the part of workers generating geochemical data, both for $\delta^{56}\text{Fe}$ and $\delta^{34}\text{S}$ records. Such good practice should include screening for hydrothermally or metamorphically altered samples on the basis of mineralogical and trace elemental systematics, as is demonstrated through Mn/Fe systematics by Busigny et al. (2017).

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