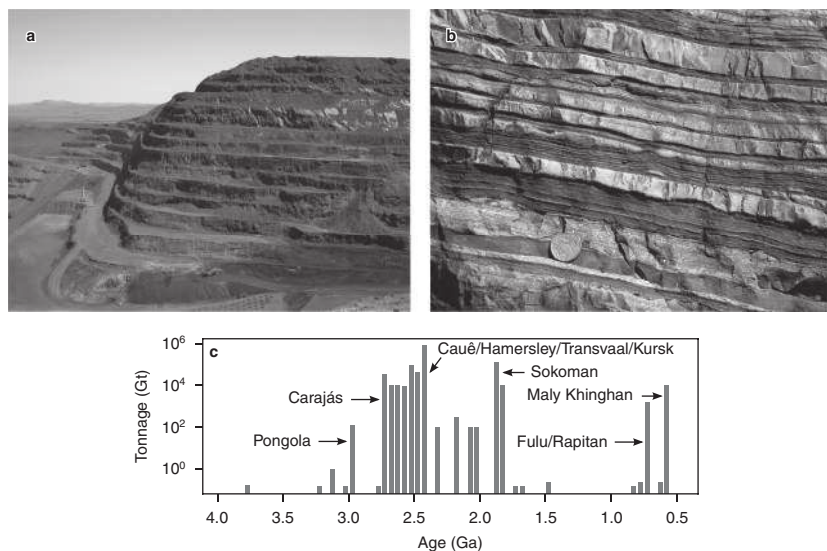


## 1 Introduction

Iron formations (IF) are iron-rich (15–40 wt.% Fe) and siliceous (40–60 wt.% SiO<sub>2</sub>) chemical sedimentary rocks (Figure 1) that precipitated from hydrothermally influenced seawater throughout the Precambrian aeons but with the majority of the preserved IF having been deposited between 2.80 and 1.85 billion years ago (Ga) in the Neoarchaeon and Palaeoproterozoic eras (see Bekker et al. 2014; Konhauser et al. 2017 for reviews). IF formed in an array of environmental settings and, hence, display diverse textures and mineral compositions (Bekker & Kovalick 2021). Based on the geometry and tectonic setting of individual IF deposits, they are broadly divided into Algoma type and Superior type (Gross 1980), which in reality form the endmembers of a continuum (Bekker et al. 2012; Konhauser et al. 2017). The former are commonly described as smaller in extent, deposited in deeper-water conditions, and associated with local hydrothermal or volcanic activity. This hydrothermal or volcanic influence would have provided the dissolved Fe necessary for their formation. On the other hand, Superior-type IF formed more distally from Fe sources, are associated with diverse continental shelf sediments, and are more voluminous. In some instances Superior-type IF can be traced over distances of thousands of kilometres – they highlight the influence of reduced Fe(II)-bearing hydrothermal waters on Archaean and Palaeoproterozoic ocean chemistry (Konhauser et al. 2017).

Texturally, IF can be divided into those composed predominantly of granules (granular IF) and those consisting predominantly of fine-grained chemically precipitated muds (micritic IF) (e.g., Beukes & Gutzmer 2008). Micritic IF are composed of iron-rich muds and microcrystalline quartz (i.e., chert, composed of SiO<sub>2</sub>). They often occur as distinctive, repetitive iron and chert layers, commonly termed ‘banded IF’. The layering may be of variable thickness, from macrobands (metre thick) to mesobands (centimetre thick) to microbands (millimetre and submillimetre layers), the latter believed to represent an annual deposition process (Trendall & Blockey 1970; for a different view, see Bekker et al. 2012). Granular IF, instead, are characterised by granules of various sizes, composed of microcrystalline quartz, iron oxides, iron carbonates, and/or iron silicates that are cemented by chert, carbonate, or hematite. Most commonly, the granules were derived from local sedimentary reworking of earlier IF (Beukes & Gutzmer 2008). These different textures are indicative of specific sedimentary environments in which the IF formed. For instance, Beukes and Gutzmer (2008) divided the voluminous Superior-type Neoarchaeon to Palaeoproterozoic IF in the Transvaal Supergroup, South Africa, into three main lithological facies. (1) Microlaminated chert-banded IF commonly formed in neutral-pH deepwater environments (hundreds of metres

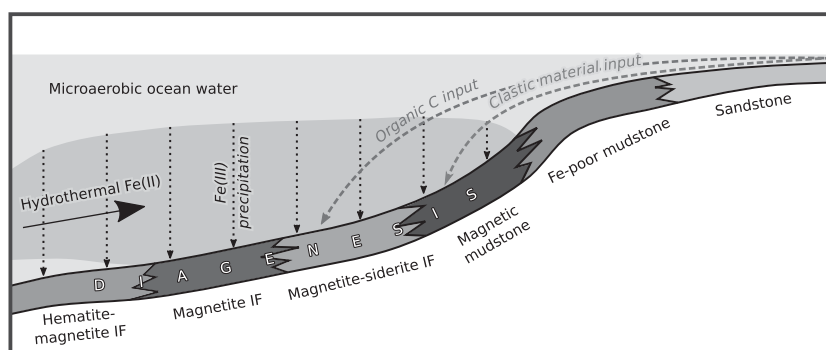


**Figure 1** (a) The 2.46-billion-year-old Brockman iron formation, Western Australia (Southern Ridge at Mount Tom Price mine). This is considered to rank among the largest known banded iron formations (IF) in the world. (b) Characteristic banding of the Dales Gorge Member of the Brockman iron formation. Photographs courtesy of Mark Barley. (c) Relative tonnage of IF in the preserved Precambrian rock record. Labels point out major contributions from individual iron formation deposits. Data from Bekker et al. (2014)

of water depth) where wave action had no effect; similar facies in Western Australia have been interpreted as having formed through submarine gravity flows carrying IF muds deposited in shallower settings (Krapež et al. 2003). (2) Chert-poor microlaminated IF with iron-silicate layers in South Africa were associated with somewhat shallower settings as they contain a component of fine-grained, storm wave-transported sediments. These must also have been precipitated in more alkaline, anaerobic water masses where iron-silicates were stable. (3) Micritic IF and granular IF lacking clear banding and sometimes rich in siderite were associated with shallower settings dominated by wave activity (Beukes & Gutzmer 2008).

Aside from textural classifications, IF may also be divided into sedimentary facies based on their mineralogy. In addition to chert, the best-preserved IF successions are composed of Fe oxides (e.g., magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ )), iron-rich silicate minerals (e.g., greenalite ( $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$ )), or carbonate minerals (e.g., siderite ( $\text{FeCO}_3$ )), with locally sparse sulphides (e.g., pyrite ( $\text{FeS}_2$ )). The first three of these define the oxide, silicate, and carbonate

facies of IF, respectively (James 1954). A sulphide facies postulated by James (1954) is now recognised to be more reflective of a shale facies and is not considered to be genetically related to IF (Bekker et al. 2010). It is generally agreed that none of the minerals in IF are primary in origin, in the sense that the original seafloor precipitate mineralogy was not preserved. Instead, the observed minerals reflect multiple post-depositional alteration events that occurred under both diagenetic (at low temperatures during progressive burial in sedimentary basins) and metamorphic (high-temperature transformations induced by tectonic and magmatic events) conditions. Nevertheless, it has been shown that preserved mineral assemblages change across a transect from deeper-water settings close to hydrothermal Fe(II) sources to shallower environments further away. For example, in the Mesoarchaeon Witwatersrand IF in South Africa, this is expressed as a transition from hematite-dominated facies furthest from the shore to magnetite, and finally to siderite closest to the shore, reflecting increasing input of organic matter that enabled diagenetic Fe(III) reduction (Figure 2) (Smith et al. 2013). The specific form that this mineralogical succession takes depends on both global and local seawater, as well as sediment chemistry, and is in turn affected by basin geometry and biological factors (e.g., compare with Raye et al. 2015). It should also be pointed out that not all IF follow this mineralogical succession from deep to shallow. For instance, Wang et al. (2015) showed that in the 2.38–2.22 Ga Yuanjiaocun IF,



**Figure 2** Mineralogical facies succession in the Mesoarchaeon micritic Witwatersrand IF in South Africa (based on Smith et al. 2013). The IF are interpreted to have formed in relatively deepwater settings under a plume of hydrothermal Fe(II)-rich water, which was oxidised by chemolithoautotrophic bacteria to produce Fe(III) precipitates. During sediment diagenesis, Fe(III) was reduced to Fe(II), forming either magnetite or siderite, depending on the amount of available organic carbon as electron donor.

located in the North China Craton, in deeper waters more proximal to the hydrothermal vents, nutrients were abundant, and high biomass productivity was coupled to increased carbon burial, leading to the deposition of iron-rich carbonates. By contrast, hematite was deposited in shallow, well-oxygenated waters.

Traditionally, iron oxides in IF were interpreted to have formed from an initial ferric oxyhydroxide phase (e.g., ferrihydrite ( $\text{Fe}(\text{OH})_3$ )), which precipitated in the photic zone from seawater via the oxidation of dissolved ferrous iron,  $\text{Fe}(\text{II})$ , at concentrations that may have ranged from 0.03 to 0.5 mM (e.g., Holland 1973). More recent work suggests that, in the presence of dissolved silica at concentrations estimated to have been as high as ~1 to 2 mM in the Archaean, the initial water column precipitate may instead have been a ferric oxyhydroxide-Si gel (e.g., Percak-Dennett et al. 2011). During IF mineralisation, the sinking of ferric oxyhydroxide-silica particles to the seafloor was followed by the formation of (1) magnetite or iron carbonates when the remineralisation of buried organic matter was coupled to  $\text{Fe}(\text{III})$  reduction, either during diagenesis or metamorphism; (2) hematite, through dewatering and silica release, when organic carbon was insufficient for  $\text{Fe}(\text{III})$  reduction; (3) iron silicates, such as greenalite, when silica sorbed onto or incorporated in ferric oxyhydroxides reacted with other cationic species within sediment pore waters (e.g., Morris 1993; Fischer & Knoll 2009); and (4) quartz, through dehydration of opaline silica and/or  $\text{Fe}(\text{III})$ -Si gels. Ferrous iron sorption to these particles may also have given rise to ‘green rust’-type deposits that eventually transformed into magnetite or iron silicates (Halevy et al. 2017). Critically, however, Archaean IF contain a large range of iron isotope ratios which are inconsistent with small iron isotopic effects induced by direct seawater precipitation of iron silicates (e.g., greenalite) (Rasmussen et al. 2017). Furthermore, the conversion of green rust to ferric oxides requires extensive reworking of sediments by percolating oxidising fluids, whereas recent hydrological modelling suggests that such ‘supergene’ processes could not have been pervasive throughout the IF (Robbins et al. 2019a). In short, there is compelling evidence that iron-silicates were not the quantitatively important water-column precipitates in IF mass balance, despite this idea being proposed multiple times recently (see Johnson et al. 2020 and references therein).

The generation of ferric iron minerals in IF depositional settings is generally ascribed to the metabolic activity of planktonic bacteria in ancient oceanic photic zones. The classic model invokes a redox-stratified ocean, with ferric iron precipitation occurring at the interface between oxygenated shallow waters and reduced upwelling ferrous iron-rich waters, the oxygen being sourced from cyanobacteria or their predecessors (Cloud 1973). These

photoautotrophs would have flourished when nutrients were available and passively induced the precipitation of Fe(III) oxyhydroxide through their metabolic activity. Alternatively, anoxygenic photoautotrophic Fe(II)-oxidising bacteria (known as photoferrotrophs) could have directly oxidised Fe(II) and coupled this to the fixation of carbon-utilising light energy without any need for O<sub>2</sub> availability (Hartman 1984); this process may have accounted for most, if not all, Fe(III) deposited in IF (Konhauser et al. 2002). Furthermore, Kappler et al. (2005) calculated that the photoferrotrophs could have oxidised all hydrothermally derived Fe(II) before it reached surface waters, even if cyanobacteria were present in the oxic layer above – though iron isotope ratios of IF suggest that partial iron oxidation prevailed in Archaean and, to a lesser degree, Palaeoproterozoic oceans (Konhauser et al. 2017). Many aspects of the biology of cyanobacteria and photoferrotrophs seem to agree with an enhanced role of the latter – photoferrotrophs would have had a competitive advantage over early cyanobacteria since the former were better poised to benefit from upwelling phosphorous-rich deepwaters, given their adaptation to low-light conditions, especially since cyanobacteria have higher phosphate requirements (Jones et al. 2015). Furthermore, the ferruginous conditions associated with IF deposition may have been toxic to cyanobacteria (Swanner et al. 2015). Quantifying the relative contributions and extent of photoferrotrophs and cyanobacteria to IF deposition remains an area of ongoing research (Konhauser et al. 2018).

It should, however, be acknowledged that the story on IF deposition can be more complicated. For instance, IF deposition has also been attributed to mixing of discrete hydrothermally derived Fe(II) and Si-rich water plumes with seawater possibly containing photosynthetic oxygen diffusing or downwelling from the photic zone. In cases where Fe(III) or Mn phases are preserved in sediments, deposition may also have occurred on the lower margins of the hydrothermal plume in contact with microaerobic water in a complex mixing configuration (Smith et al. 2013; Beukes et al. 2016). Those authors favoured this model because of the difficulty in explaining the retention of these oxidised phases as they settled through Fe(II)-rich bottom seawater. If true, this means that the depth and nature of Fe(III) precipitation, as well as the relative influence of hydrothermal water versus ambient seawater, were likely to have been highly variable in space and time, depending on the strength of both of these fluxes (Beukes & Gutzmer 2008). Moreover, Thompson et al. (2019) recently demonstrated with certain photoferrotrophic cultures that the ferric iron precipitates (ferrihydrite) did not attach to the cell surfaces such that ferrihydrite and biomass were not deposited together. This is important because this could lead to large-scale sedimentation of IF lean in organic matter, with excess

biomass being deposited in coastal sediments elsewhere (i.e., forming organic-rich shales).

## 2 Iron Formations as Geochemical Proxies

IF are ubiquitous throughout the Archaean record and through the early part of the Palaeoproterozoic, beginning with the oldest known (metamorphosed) sedimentary succession in the world, the >3.77 Ga Nuvvuagittuq Supracrustal Belt, Canada (Mloszewska et al. 2012) (Figure 1c). Micritic IF remained abundant until around 1.85 Ga after which they declined in number due to a variety of environmental, tectonic, and magmatic factors. In contrast, granular IF first appeared in the rock record at ca. 2.90 Ga (Smith et al. 2017), reached their acme at ca. 1.88 Ga, and were then succeeded by smaller-scale IF, often lacking a chert component, in the Neoproterozoic and Phanerozoic record (after ca. 700 Ma) (Bekker et al. 2014). The other peak in the deposition of IF occurred in association with the Neoproterozoic glaciations – the so-called Snowball Earth events – when a dissolved iron reservoir was built in the oceans under ice cover either via hydrothermal supply or anoxic dissolution of reactive iron from sediments (see Bekker et al. 2014).

With a 2-billion-year record, IF have helped constrain both the redox conditions and transitions in the atmosphere-ocean system, as well as the composition of palaeo-seawater and its relationship to the evolution of the marine biosphere (see Robbins et al. 2016; Konhauser et al. 2017 for reviews). The utility of IF is based on a number of assumptions and conditions. First, ferrihydrite, the likely precursor phase for hematite and magnetite in IF, can faithfully preserve in the mineral the rare earth element (REE) distribution patterns of the mixture of seawater and hydrothermal water from which the IF precipitated (Bau & Dulski 1996) and, more broadly, other elemental and isotopic compositions of water, as has been demonstrated through ferrihydrite adsorption and diagenesis experiments (e.g., Døssing et al. 2011; Robbins et al. 2015; however, see also Halevy et al. 2017 for a different view). Second, this signal is commonly uncontaminated by continentally derived detrital materials, given that IF contain very low levels of detrital tracer elements such as aluminium and titanium. This means that IF geochemical data often provide a purely ‘authigenic’ record of marine chemistry. Finally, the generally low permeability and element mobility in IF mean that these geochemical signals have the potential to survive even high levels of metamorphism and are unlikely to have experienced widespread alteration by secondary fluids, the exception being later-stage ore formation (Frost et al. 2006; Robbins et al. 2015).

Yet a number of pitfalls complicate the straightforward interpretation of IF proxies, the foremost among them being the recent suggestion that the ferric iron-containing minerals now preserved in IF formed through post-depositional oxidation of primary Fe(II)-silicate minerals (e.g., Rasmussen et al. 2017; Muhling & Rasmussen 2020). In these models, the geochemical signals stored within IF would closely track basinal oxidising fluids rather than seawater (see aforementioned objections). Second, the straightforward back-calculation of isotope ratios and element concentrations in seawater based on IF data is often overly simplistic – for example, elemental adsorption coefficients and isotope fractionations involved in the precipitation of ferrihydrite are often known only through empirical observations (Konhauser et al. 2007) and may not fully capture the complex interplay among different components in solution, such as competing ions and dissolved organic compounds (see Robbins et al. 2016). This difficulty is compounded by a lack of direct modern analogues to IF that would allow us to study such mechanisms in the natural environment – a challenge not faced by the carbonate or shale records. Hydrothermal exhalative deposits, ironstones, and marine iron-manganese-oxide crusts may help to bridge this gap (e.g., Goto et al. 2020) even though these lithologies are genetically different from IF. Third, inefficient adsorption of some elements leading to low authigenic concentrations means that even minor addition of volcanic ash or detritus may overprint seawater chemical signals in IF (Haugaard et al. 2016; Thibon et al. 2019). In these cases, it is imperative that the mineral host of the studied chemical component be established and mixing relationships with detritus investigated. Finally, caution must be taken before interpreting IF chemical signals as that of open seawater since IF deposition may have taken place not in a homogeneously stratified ocean but in a mixture of hydrothermally derived plume water and seawater, as evidenced by the mineralogical complexity of preserved IF (e.g., Smith et al. 2013) and widespread Eu anomalies indicating hydrothermal influence (e.g., Planavsky et al. 2010a). Even more, the deposition of many IF – especially, but not exclusively, Algoma type – was likely to have occurred in partially enclosed basins where water chemistry may have differed from that of the open ocean (Hoffman 1987; Beukes & Gutzmer 2008; Bekker et al. 2010). Hence it becomes very important for the interpretation of geochemical data to first gain an understanding of basin-wide facies architecture and to develop depositional models.

Despite these complexities, both the concentrations and isotope ratios of numerous elements in IF have been utilised to track a variety of palaeoenvironmental characteristics including first-order trends in trace-element availability through time (Robbins et al. 2016). In the subsequent sections we

provide examples of the type of palaeoenvironmental data that IF have offered insights on.

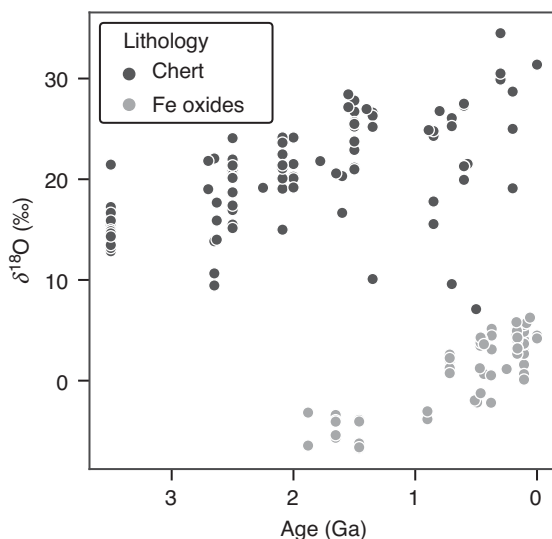
### 3 Palaeotemperature

Minor but predictable differences in the partitioning of isotopes of the same element among different phases (i.e., isotope fractionation) in nature underlie the utility of stable isotope geochemistry. Since isotope fractionations are dependent on temperature, knowing the difference between an element's isotope ratios in an aqueous (e.g., seawater) and solid (e.g., chert) phase allows for the back-calculation of temperature coincident to formation. However, other factors affecting isotopic composition may overwhelm this signal, not least among them the possibility that IF deposited from heterogeneous mixtures of hydrothermal fluids and seawater. For example, an increasing trend in the ratio of the two main silicon isotopes ( $^{30}\text{Si}/^{28}\text{Si}$ , normalised to a reference standard and reported as  $\delta^{30}\text{Si}$ ) of Archaean and Proterozoic IF was initially attributed to decreasing palaeotemperature (Robert & Chaussidon 2006) but was later reinterpreted to reflect a changing mixture of different Si sources and sinks bearing different  $\delta^{30}\text{Si}$  values (Trower & Fischer 2019).

The most utilised palaeothermometer in chemical sediments is the oxygen isotope system ( $^{18}\text{O}/^{16}\text{O}$  or  $\delta^{18}\text{O}$ ) (Urey 1947). However, sedimentary  $\delta^{18}\text{O}$  values are also dependent on the composition of seawater, leading to a long-standing debate on whether secular change in sedimentary  $\delta^{18}\text{O}$  values is driven by variations in seawater composition or temperature (Knauth 2005; Bindeman et al. 2016). The study of  $\delta^{18}\text{O}$  values in the chert layers of IF extended this debate into the Archaean, producing a trend of increasing  $\delta^{18}\text{O}$  values from the Archaean to the Phanerozoic (Figure 3) (Perry 1967; Knauth 2005). Recent work has identified a similar  $\delta^{18}\text{O}$  trend in ferric oxyhydroxides (Figure 3), where fractionation is known to be less dependent on temperature, thereby supporting secular change in seawater composition as the cause (Galili et al. 2019). However, measurements of the minor isotope  $^{17}\text{O}$  have recently become more accessible (Bindeman et al. 2018; Bao 2019) and suggest that a more complex interplay among seawater composition, temperature, diagenesis, metamorphic exchange, and emergence of landmasses has shaped the preserved  $\delta^{18}\text{O}$  trend (e.g., Liljestrand et al. 2020).

### 4 Nutrient Availability

Among the most straightforward palaeoenvironmental information stored in IF is a first-order reflection of the concentration of different elements in seawater. Simply by measuring elemental concentrations in IF formed at different times,



**Figure 3** The oxygen isotope composition of chert and iron oxides through Earth history, which indicates either changing seawater composition or temperature. Chert (Robert & Chaussidon 2006) and iron oxide (Galili et al. 2019) data include iron formation samples; the offset in  $\delta^{18}\text{O}$  values of these two phases is due to differing fractionation factors from seawater

temporal trends in the relative availability of nutrients or toxicity have been identified, although back-calculation to seawater concentrations can be complicated (see the previous section). For example, the IF record has been used to infer consistent and relatively high bottom water marine phosphorous (Planavsky et al. 2010b) and zinc (Robbins et al. 2013) concentrations in the Archaean and Palaeoproterozoic, but highly dynamic cobalt (Swanner et al. 2014) and nickel (Konhauser et al. 2009) trends with implications for ecosystems that utilise these nutrients. On the other hand, toxic elements like chromium (Konhauser et al. 2011) and arsenic (Chi Fru et al. 2019) show an increase in the early Palaeoproterozoic, suggesting that early organisms had to adapt to these new forms of toxicity.

A more nuanced tracer of nutrient cycling is the nitrogen isotope system ( $\delta^{15}\text{N}$ ) – different N isotope ratios are indicative of different biological fixation and redox cycling pathways of this critical macronutrient (Stüeken et al. 2016). Nitrogen isotope data from highly metamorphosed IF of the earliest Archaean tentatively suggest the biological utilisation of hydrothermal nitrogen (Pinti et al. 2001), but Neoarchaeal IF instead record the likely partial oxidation of ammonia to nitrate, indicating the onset of an oxic N cycle (Garvin et al. 2009; Busigny et al. 2013).

The composition of IF may also be useful for assessing the chemical composition of the marine phytoplankton community during Fe(II) oxidation and IF deposition. In this regard, spurred by the similarities among the trace-element ratios in the 2.48 Ga Dales Gorge Member in Western Australia IF and anoxygenic phytoplankton biomass, Konhauser et al. (2018) suggested that much of the trace-element inventory preserved in the IF was at some point biologically assimilated in the water column, released from degrading photoferrotrophic biomass at the seafloor and in the sediment pile, and ultimately fixed in the iron-rich sediment in approximately stoichiometric proportions by near-quantitative adsorption to ferrihydrite. Crucially, their observations suggest that, as today, phytoplankton and the recycling of their biomass exerted control over the trace-element composition of ancient seawater and sediment.

## 5 Palaeoredox

Redox-sensitive elements – that is, elements that occur in different valence states with contrasting chemical behaviour in natural environments – are a valuable tool for tracking the abundance of oxygen in Earth's atmosphere and oceans and, by extension, the emergence and prevalence of oxygenic photosynthesis (e.g., Farquhar et al. 2014). For instance, the IF record can be used to identify concentration trends of an element like uranium, which is significantly more soluble in oxygen-rich water, so that higher U concentrations in the IF record point to higher oxygen availability at that time in Earth's history (Partin et al. 2013). REEs constitute another widely applied redox proxy – this otherwise similarly acting set of lanthanide elements displays differing adsorption affinities to manganese oxides (e.g., Bau & Dulski 1996). Since manganese oxides only form in oxic conditions (see, e.g., Johnson et al. 2013; Daye et al. 2019 for alternate interpretations), specific anomalies in REE concentration patterns, namely negative cerium anomalies, attest to the presence of oxygen and redox-stratified water masses; the lack of such anomalies in Archaean IF signifies a predominantly anoxic world (Planavsky et al. 2010a).

The most recent palaeoredox work, instead, utilises redox-sensitive isotope systems. Perhaps the best example is the iron isotope system ( $\delta^{56}\text{Fe}$ ) (see Dauphas et al. 2017; Johnson et al. 2020). The isotope fractionation in ferric oxyhydroxides is always expected to be positive; that is, the precipitating phase is enriched in heavy Fe isotopes compared to seawater, regardless of the mechanism of Fe(II) oxidation to Fe(III) (see references in Dauphas et al. 2017). This fractionation, however, is only expressed if Fe(II) oxidation is partial, not quantitative (Rouxel et al. 2005). As such, predominantly positive  $\delta^{56}\text{Fe}$  values in Archaean and Palaeoproterozoic IF indicate that ferric