Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue

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A B S T R A C T

The chemical response of the Precambrian oceans to rising atmospheric O_2 levels remains controversial. The iron isotope signature of sedimentary pyrite is widely used to trace the microbial and redox states of the ocean, yet the iron isotope fractionation accompanying pyrite formation in nature is difficult to constrain due to the complexity of the pyrite formation process, difficulties in translating the iron isotope systematics of experimental studies to natural settings, and insufficient iron isotope datasets for natural euxinic (i.e. anoxic and sulfidic) marine basins where pyrite formation occurs. Herein we demonstrate, that a large, permil-level shift in the isotope composition of dissolved iron occurs in the Black Sea euxinic water column during syngenetic pyrite formation. Specifically, iron removal to syngenetic pyrite gives rise to an iron isotope fractionation factor between Fe(II) and FeS_2 of 2.75 permil (‰), the largest yet reported for reactions under natural conditions that do not involve iron redox chemistry. These iron isotope systematics offer the potential to generate permil-level shifts in the sedimentary pyrite iron isotope record due to partial drawdown of the oceanic iron inventory. The implication is that the iron stable isotope signatures of sedimentary pyrites may record fundamental regime shifts between pyrite formation under sulfur-limited conditions and pyrite formation under iron-limited conditions. To this end, the iron isotope signatures of sedimentary pyrite may best represent the extent of euxinia in the past global ocean, rather than its oxygenation state. On this basis, the reinterpreted sedimentary pyrite Fe isotope record suggests a fundamental shift towards more sulfidic oceanic conditions coincident with the 'Great Oxidation Event' around 2.3 billion years ago. Importantly, this does not require the chemical state of the ocean to shift from mainly de-oxygenated to predominantly oxygenated in parallel with the permanent rise in atmospheric oxygen, contrary to other interpretations based on iron isotope systematics.

1. Introduction

Reliable reconstruction of the rise and fall of oxygen (O_2) in the past ocean–atmosphere system is crucial for understanding the evolution of life on Earth and the potential for life on inter- and extra-solar planets. Crucial to reconstruction efforts are the sedimentary signatures of redox-sensitive metals, such as iron (Fe). These have recently emerged as robust tracers of oxygena-tion and de-oxygenation due to pronounced changes in their spe-ciation, biogeochemical cycling, and stable isotope fractionation, when environmental conditions transition between oxic, anoxic (e.g. no oxygen with nitrogenous, manganous, and/or ferruginous conditions), and euxinic states (i.e. no oxygen with sulfidic con-ditions) (Lyons et al., 2009). The robust reconstruction of the rise in atmospheric O_2 to appreciable levels during the 'Great Oxida-tion Event' or GOE around 2.3 billion years ago (Ga) (Holland, 2002) and the response of the global ocean to increasing lev-els of O_2 is critical for evolutionary models. Before the GOE, the ocean and atmosphere were largely devoid of oxygen, although intermittent 'whiffs' of oxygen in the atmosphere and surface ocean may have occurred up to 0.5 billion years before the on-set of the GOE proper (Anbar et al., 2007; Crowe et al., 2013;

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Planavsky et al., 2014). Such large-scale oxygen depletion resulted in a biogeochemical Fe cycle that was much different than today's where oxygenated conditions prevail. Instead, a vast anoxic and ferruginous ocean, enriched in highly soluble, reduced Fe(II) dominated the Precambrian Earth with at least the possibility of localized environments of euxinia (Poulton and Canfield, 2011; Reinhard et al., 2009). Post-GOE, oxidation of sulfide minerals on the continents would have increased due to elevated atmospheric oxygen levels, thus providing an increased source of sulfate to the oceans and potentially increasing the extent of euxinia in marine environments with a sufficient supply of organic matter (Lyons et al., 2014; Planavsky et al., 2011). Via an intrinsic link with Earth's carbon and sulfur cycles, the GOE coincided with a dramatic change in Earth's oceanic Fe cycle marked by concomitant Fe stable isotope (^{56}Fe/^{54}Fe ratio; expressed as δ^{56}Fe) fractionation recorded in Precambrian sedimentary pyrite (FeS$_2$). In particular, the δ^{56}Fe of pyrites (δ^{56}Fe$_{py}$) formed before the GOE between ca. 2.8 to 2.3 Ga ago commonly show highly variable negative excursions of up to -3.5‰, while pyrites formed between ca. 2.3 Ga and 1.8 Ga display more positive δ^{56}Fe values with a limited range between $+1.2$ to -0.5‰ (Archer and Vance, 2006; Rouxel et al., 2005).

The exact response of the chemical state of the oceans to rising oxygenation during the GOE remains under-constrained, partly because the origin of the strongly negative δ^{56}Fe signatures of Archean pyrite is contentious. Proposed scenarios to explain the δ^{56}Fe$_{py}$ record often include the assumption that pyrite is a passive recorder of seawater δ^{56}Fe whereby essentially no Fe isotope fractionation occurs during its precipitation from oceanic waters (Rouxel et al., 2005). Scenarios of this type then require mechanisms to drive the vast dissolved Fe(II) reservoir of the oxygen-deficient pre-GOE ocean towards negative δ^{56}Fe signatures before pyrite formation occurs (Planavsky et al., 2012; Rouxel et al., 2005). As Fe(II)–Fe(III) redox reactions produce large Fe isotope fractionations that enrich the Fe(III) product in heavy iron isotopes (e.g. Johnson et al., 2008), it is theoretically possible to drive the dissolved Fe(II) reservoir to the negative δ^{56}Fe values observed in Archean pyrites if 50 to 90% of the oceanic Fe(II) reservoir is biologically or abiologically oxidized to Fe(III) and removed (Busigny et al., 2014; Planavsky et al., 2012; Rouxel et al., 2005). Archean iron formations with positive δ^{56}Fe values offer important evidence in support of this idea (Planavsky et al., 2012). Microbial Fe(III)–Fe(II) reduction (MIR) may have also contributed to generating a marine Fe(II) reservoir strongly depleted in heavy Fe isotopes (Beard et al., 1999; Johnson et al., 2008; Welch et al., 2003). Contrarily, other proposed scenarios call for significant iron fractionation during pyrite formation in combination with the other mechanisms listed above to explain the δ^{56}Fe signatures of Archean pyrite (e.g. Severmann et al., 2008). None of the above-described scenarios have been adequately tested in a natural euxinic environment.

The assumption that pyrite is a passive recorder of seawater δ^{56}Fe is speculative because the Fe isotope fractionation associated with pyrite formation in natural systems has proven difficult to constrain. This is, in large part, due to the complexity of the pyrite formation process. In particular, pyrite formation occurs via a two-step process, involving pyrite nucleation, which is a potentially slow and rate-limiting step, followed by relatively fast crystal growth (Rickard and Luther, 2007). Furthermore, pyrite formation occurs via either the H$_2$S or polysulfide pathways, each with different nanoparticulate precursor minerals (Rickard and Luther, 2007). For both pathways, the precursor minerals dissolve to form aqueous FeS cluster complexes as intermediates, which then react with H$_2$S or polysulfide to form pyrite (Rickard and Luther, 2007). The pyrite formation process can occur very rapidly in environments that are supersaturated with respect to pyrite and saturated with

respect to its precursor minerals, such as in the Black Sea euxinic water column, allowing spontaneous nucleation to occur (Rickard and Luther, 2007).

Each of the above described processes have the potential to fractionate Fe isotopes in a different manner, and there is inherent difficulty in translating experimental findings, which cannot capture all aspects of the pyrite formation process, to natural settings. For example, some experimental studies suggest that the precipitation of pyrite, via the dissolution of the precursor mineral mackinawite (FeS$_m$), is governed by a unidirectional kinetic process. This gives rise to the residual dissolved Fe(II) being ca. 3‰ heavier than the precipitated pyrite, described by an overall isotope fractionation factor $\varepsilon_{Fe(II)\text{-pyrite}}$ of $+3.1 \pm 1.0$‰ (Guilbaud et al., 2011). Experiments by Wu et al. (2012) suggest that equilibrium iron isotope fractionation during the reaction between Fe(II) and FeS$_m$, which is described by a significantly smaller isotope fractionation factor of ca. -0.5‰, may be important for determining the final Fe isotope composition of pyrite. Because experimental conditions can never perfectly match natural systems, there will always be uncertainty regarding the validity of applying experimental results to natural environments. Thus, it is vital to independently confirm laboratory results under natural conditions to increase the degree of confidence in interpretations. Clearly, the magnitude of Fe isotope fractionation between seawater and pyrite has important implications for reconstructions of ocean–atmosphere evolution during the early stages of Earth's history.

Here we report the first observations of Fe isotope fractionation in the Black Sea water column that provide important constraints on the Fe isotope systematics associated with pyrite formation in a natural setting. As the world's largest anoxic marine basin, with distinct oxic, anoxic and euxinic layers, the Black Sea serves as an excellent natural laboratory for investigating Fe isotope fractionation during pyrite formation in the Precambrian ocean where globally expansive ferruginous (i.e. anoxic and Fe-rich) and, at times, marginal sulfidic conditions prevailed (Lyons et al., 2014; Reinhard et al., 2009). Seawater samples were collected for dissolved Fe concentration (Fe$_d$), dissolved δ^{56}Fe, and supporting measurements of other oceanographic parameters (see Supplementary Material), from the western and eastern central basin of the Black Sea during the 2013 GEOTRACES expedition 64PE373 (Fig. 1). These observations for a natural euxinic basin provide new evidence in support of the initial framework described by Guilbaud et al. (2011) for the origin of the large, negative δ^{56}Fe$_{py}$ signatures in Precambrian sediments and shed new light on the chemical state of the Precambrian ocean.

2. Oceanographic setting

The Black Sea water column represents an ideal location to examine the behavior of trace metals across a gradient in redox conditions in a marine environment (Lewis and Landing, 1991). The unique hydrography and resulting redox structure of the Black Sea water column is are discussed in turn below.

2.1. Hydrography

The chemical and physical characteristics of the Black Sea water column are controlled by its hydrological balance (Caspers and Schmidt, 1957). European rivers, primarily the Danube, Dniester, Dnieper, Don, and Kuban Rivers, supply low salinity freshwater to the upper surface layer of the Black Sea. This freshwater input is coupled to a limited supply of saltwater from the Mediterranean Sea, which enters via flow along the bottom of the shallow Bosporus straight (sill depth ∼60 m), filling the deep central basin with salty, dense water. Consequentially, a strong vertical salinity gradient (pyncnocline) exists in the Black Sea water column