

Fe isotope composition of Archean sulfides do not record progressive oxygenation of the ocean

Johanna Marin Carbonne

Institut des sciences de la Terre, University of Lausanne, 1015 Lausanne, Switzerland

In the history of this continuously evolving planet, the Great Oxygenation Event (GOE), which occurred at ca. 2.3 Ga (Bekker et al., 2004; Holland, 2006) was a critical environmental change. This event was first recognized by the disappearance of detrital uraninite, pyrite, and siderite, from the siliciclastic record, as well as by shales that do not contain appreciable amounts of redox-sensitive elements and paleosols that are not oxidized before ca. 2.3 Ga (Holland, 2006). These observations are most consistent with a change from an anoxic to a moderately oxygenated atmosphere during the GOE. The discovery of mass independent fractionation (S-MIF) in sulfur isotopes brought new constraints on the emergence of oxygen and on the atmospheric composition (Farquhar et al., 2000). Indeed, Archean sulfate and sulfides from sediments older than 2.45 Ga display S-MIF up to 10‰ (see Ono, 2017, for a review), while sulfates and sulfides from younger sedimentary rocks have close to 0‰ S-MIF. The consensual mechanism for producing the S-MIF in sulfur isotopes is photochemical dissociation of volcanic SO₂ in an anoxic atmosphere (Farquhar et al., 2000; Thiemens et Lin, 2019) with O₂ levels below 10⁻⁵ × the present atmospheric level (PAL), though alternative views exist (see Oduro et al., 2011). In the past decades, numerous studies have documented in detail the timing of, extent of, and processes responsible for the GOE (Claire et al., 2006; Halevy, 2013; Zahnle et al. 2013; Lyons et al., 2014; Luo et al., 2016). Studies based on stable isotope compositions of redox elements (like S, Mo, Fe, Th, and Cr) have suggested the existence of oxygenated oases before 2.3 Ga (see Anbar et al., 2007; Partin et al., 2013; Izon et al., 2015; Eickmann et al., 2018; Ostrander et al., 2019; among others).

Complementary to the sulfur isotope record, the Fe stable isotope systematics was used to highlight a secular evolution both in iron oxides and sulfides. Pre-GOE pyrites display negative Fe isotope compositions down to -3.5‰, while post-GOE pyrites have more homogeneous δ⁵⁶Fe

values. This Fe isotope evolution has been interpreted as reflecting progressive oxidation of the ocean before the GOE, with partial removal of iron oxides decreasing the δ⁵⁶Fe values of Fe²⁺ by distillation (Rouxel et al., 2005), but also reflecting significant microbial dissimilatory Fe³⁺ reduction (DIR) metabolic activity (Severmann et al., 2008). Experimental studies have proposed that Fe isotope compositions in pyrite are controlled mostly by kinetic isotope effects (KIE; Guilbaud et al., 2011; Rolison et al., 2018; Mansor and Fantle, 2019) and thus that pyrite can record fractionation during limited pyritization. Therefore, the reliability of pyrite as a true proxy of the Fe(II) isotope composition of the parent fluid has been recently challenged (Busigny et al., 2014; Rolison et al., 2018; Frierdich et al., 2019). Consequently, the Fe secular isotope evolution through the Archean-Proterozoic transition needs to be investigated in detail.

In this issue of *Geology*, Heard and Dauphas (2020, p. 358) have gracefully reexamined what controlled Fe isotope composition in the oxic and sulfidic sinks of the ocean throughout the GOE. By compiling published bulk sedimentary Fe isotope records from both iron oxides and sulfides, they have tested two hypotheses: either (1) pyrite Fe isotope compositions reflect partial oxidation of the ocean, or (2) they are due to partial pyritization with a large KIE. The absence of positive correlations between δ⁵⁶Fe values of iron oxides and pyrites led the authors to rule out the first hypothesis. The presence of a positive correlation between δ⁵⁶Fe and δ³⁴S in pyrite is within the framework of the second hypothesis. In a low-sulfate ocean, characteristic of the Archean (Crowe et al., 2014), pyritization should have been limited, and thus a large KIE is anticipated. Therefore, based on the ambivalent correlation between δ⁵⁶Fe and δ³⁴S, and also based on the recognition of Rayleigh distillation distribution in Archean pyrites at bulk and at microscale, Heard and Dauphas thus argue that the Fe isotope compositions in pyrite are controlled by the sulfur availability, rather than

reflecting partial oxidation of the ocean. This conclusion is not entirely new and has already been suggested by several authors; however, this is the first study that takes advantage of the entire literature on Fe isotope compositions of Archean and Proterozoic sediments published to date.

This elegant study highlights the complexity of Fe isotope records in pyrite through time, that need to be further investigated. In fact, the influence of DIR on pyrite Fe isotope compositions is still not defined precisely and cannot be ruled out from this study. Future studies should also focus on post-GOE iron oxides and sulfides, as only one iron oxide formation has been thus far studied for Fe isotope systematics. Further experimental studies and microscale analyses of sedimentary pyrites will offer quantitative data that will help to decipher what exactly controls Fe isotope compositions during pyrite formation. Even if both Fe and S pyrite isotope records have many subtleties, Heard and Dauphas have made a useful reinterpretation of the Fe secular isotope evolution, and have provided a geochemical framework to better understand the sedimentary pyrite record.

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CITATION: Marin Carbonne, J., 2020, Fe isotope composition of Archean sulfides do not record progressive oxygenation of the ocean: *Geology*, v. 48, p. 415–416, <https://doi.org/10.1130/focus042020.1>.

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Printed in USA