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Aerobic iron and manganese cycling in a redox-stratified Mesoarchean epicontinental sea

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ABSTRACT

Redox conditions in the marine realm prior to the Great Oxidation Event (GOE; ~2.46–2.32 Ga ago), during which the atmospheric oxygen level rose dramatically for the first time, are still debated. Here, we present C, O, Fe, and Mo stable isotope systematics of Fe-, Mn-, and carbonate-rich shales, deposited at different water depths in association with iron formations (IFs) of the Mesoarchean Mozaan Group, Pongola Supergroup, South Africa. $\delta^{13}C$ values between −22.3 and −13.5‰ VPDB, and $\delta^{18}O$ values between −21.1 and −8.6‰ VPDB for Fe–Mn-rich carbonate minerals indicate their precipitation out of equilibrium with seawater. Instead, early diagenetic reduction of Fe–Mn-oxyhydroxide precursor minerals, along with microbially induced oxidation of organic matter (OM), formed these carbonates. $\delta^{56}Fe_{IRMM\text{-}014}$ values between −1.27 and 0.14‰ and $\delta^{98}Mo_{NIST\ 3134+0.25}$ values between −0.46 and 0.56‰ co-vary with Mn concentrations and inferred water depth of deposition. This suggests that, despite the diagenetic origin of the Fe–Mn carbonates, the primary light Fe and Mo isotopic signature of Fe–Mn-oxyhydroxides that originally precipitated from seawater is still preserved. While isotopically light Mo implies that Mn(II) was oxidized to Mn(IV) due to the availability of free, photosynthetically produced O_2, Mn enrichment suggests that the water column was redox stratified with a Mn-redoxcline situated at a depth below the storm wave base. A trend to highly negative $\delta^{56}Fe$ values with increasing Mn/Fe ratios and decreasing depositional depth suggests progressive oxidation of Fe(II) as deep-waters upwelled across a redoxcline towards shallow, locally oxygenated waters where Mn(IV) oxyhydroxides precipitated. Combined $\delta^{56}Fe$ and $\delta^{98}Mo$ data indicate pervasive oxygenation of seawater with the O_2 content in the photic zone likely reaching levels higher than the maximum value of 10 µM proposed for Archean oxygen oases. Since abiotic Mn(II) oxidation is kinetically very slow in marine environments, it is likely that Mn-oxidizing microorganisms catalyzed Mn-oxidation in the oxygenated Pongola surface waters during deposition of IFs. This implies that aerobic metabolism had evolved before the GOE in shallow, aquatic habitats, where it exerted a first-order control on the deposition of shallow-marine, Mn-rich iron formations.

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1. Introduction

Mass-independent fractionation of sulfur isotopes in Archean sedimentary pyrites is the most compelling evidence for an anoxic Archean atmosphere (e.g., Farquhar et al., 2000; Pavlov and Kasting, 2002; Bekker et al., 2004). However, several studies suggest that free atmospheric oxygen began to rise well before the Great Oxidation Event (GOE) (Anbar et al., 2007; Wille et al., 2007; Lyons et al., 2014 and references therein), a time when atmospheric oxygen levels rose from $<10^{-5}$ of the present atmospheric level (PAL) to ~1–5% of PAL between 2.46 to 2.32 Ga (e.g., Farquhar et al., 2000; Bekker et al., 2004).

Iron-rich sediments (>15 wt.% Fe_2O_3) are widespread during the Precambrian Era, with most iron formations (IFs) deposited between 2.8 and 1.8 Ga (Bekker et al., 2014; Konhauser et al., 2017). The deposition of Fe-oxyhydroxides in IFs requires redox

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changes, identifying redox-sensitive elements in IFs as powerful paleoceanographic proxies for the reconstruction of past conditions of the atmosphere–hydrosphere system (e.g., Siebert et al., 2003; Rouxel et al., 2005; Beukes and Gutzmer, 2008; Konhauser et al., 2017). The main source for Fe enrichments in Archean sedimentary rocks is considered to be aqueous Fe(II) derived from submarine hydrothermal vents, which was oxidized and precipitated in the shallow parts of oceans to form IFs (e.g., Klein and Beukes, 1989; Beukes and Gutzmer, 2008). Stable isotope compositions of redox-sensitive metals (e.g., Fe and Mo) within Archean IFs have been interpreted to reflect locally oxygenated shallow-marine environments, leading to the deposition of Fe(III)-bearing minerals (Planavsky et al., 2014; Satkoski et al., 2015; Kurzweil et al., 2016). Wherever locally oxygenated surface waters were present in coastal marine environments, the water column must have been vertically stratified and laterally variable with respect to Fe concentrations (e.g., Klein and Beukes, 1989; Beukes and Gutzmer, 2008). The processes that led to the oxidation of dissolved Fe(II) to insoluble Fe(III) and precipitation of ferric oxyhydroxides in the Archean oceans remain highly debated. Two oxidation pathways are generally considered: (1) direct oxidation by anoxygenic photoferrotrophs in the photic zone (e.g., Kappler et al., 2005; Konhauser et al., 2017); and (2) Fe(II) oxidation by free, photosynthetically produced O_2 (Planavsky et al., 2014; Satkoski et al., 2015). A Fe(II) photo-oxidation pathway involving solar UV is regarded as too insignificant to account for deposition of IFs (Konhauser et al., 2017). An ultimate biological control for deposition of the bulk of IFs is thus inferred.

Oxidation of Mn(II) to Mn(IV) requires a higher redox potential compared to Fe(II) and takes place in the presence of free O_2, with participation of an aerobic microbial catalyst (Tebo et al., 2004). Furthermore, besides O_2, Mn(IV)-oxyhydroxides are themselves strong natural oxidants that can oxidize and influence the biogeochemical cycles of other transition metals and certain non-metals, such as C and S (Tebo et al., 2004). A pre-GOE example is the IF of the ca. 2.45 Ga Koegas Subgroup (Transvaal Supergroup, South Africa) which contain appreciable Mn enrichments (Beukes and Gutzmer, 2008; Kurzweil et al., 2016). Iron formation of the Koegas Subgroup is described as being deposited under an oxygenated seawater column where Mn-oxides and -oxyhydroxides have been regarded as important for aqueous Fe(II) oxidation as well as Mo shuttling (Kurzweil et al., 2016). Mn(II) oxidation by anoxygenic photosynthesizers has been proposed as an alternative process leading to Mn precipitation before the GOE (Johnson et al., 2013). Mn redox cycling and transition metal shuttling was proposed to already have operated in Mesoarchean shallow seawaters, ∼500 Ma before the GOE, based on a Mo isotope study of IF of the Sinqeni Formation (Mozaan Group, Pongola Supergroup) that were deposited on a shallow, outer shelf during a period of maximum transgression (Planavsky et al., 2014).

The present study is built on this initial work (Planavsky et al., 2014), but we present additional isotope data (C, O, Fe and Mo) from shales that were deposited above and below storm wave base at the Pongola Basin scale. This allows more refined insight into the redox state of the water-column, reaching from deeper- (below the photic zone) to shallow-marine environments (photic zone), in the Pongola sea. The same applies to the mechanisms leading to the Fe and Mn enrichments in the Mozaan Group. We place particular emphasis on identifying the role of water-column Mn mineral phases in metal cycling and biomass production.

2. Geological setting and samples

We investigated shales from two drill cores intersecting the Mozaan Group in the White Mfolozi Inlier and the Nongoma area (Fig. 1). The Pongola Supergroup is a Mesoarchean volcano-sedimentary sequence deposited ca. 2.98–2.85 Ga on the south-eastern margin of the Kaapvaal Craton, South Africa (Wilson and Zeh, 2018). It crops out in northern KwaZulu-Natal, Mpumalanga and Swaziland (Fig. 1) and is partially correlative with the Witwatersrand Supergroup (Beukes and Cairncross, 1991). The lithostratigraphic column includes two major stratigraphic units: (1) the volcano-sedimentary Nsuze Group, and (2) the predominantly siliciclastic Mozaan Group (Beukes and Cairncross, 1991; Hicks and Hofmann, 2012). Due to Phanerozoic erosion, the Mozaan Group in the White Mfolozi Inlier only consists of the Sinqeni and Ntombe formations (Fig. 1). In contrast, the stratigraphy in the Nongoma area is more complete, starting with the lowermost Sinqeni Formation to the uppermost Gabela Formation (Beukes and Cairncross, 1991; Nhleko, 2003). The Nongoma area also represents an overall more basinal and deeper depositional setting with thicker strata. Our samples are from the Sinqeni, Ntombe, and Thalu formations of these two areas (Fig. 1).

The Sinqeni Formation is characterized by predominantly shallow-marine sandstones with minor middle to outer shelf siltstones, shales and IFs (Beukes and Cairncross, 1991; Nhleko, 2003). In the White Mfolozi Inlier, drill core TSB07-26 intersects the entire 108 m thick Sinqeni Formation (Fig. 1), which consists of two sandstone units separated by a succession of ferruginous shale and IF. The lower sandstone includes (1) the laterally discontinuous Denny Dalton Member of braided alluvial plain conglomerates and pebbly sandstones, and (2) the shallow-marine, trough cross-bedded quartz arenites of the Dipka Member (Hicks and Hofmann, 2012; Ossa Ossa et al., 2016). The upper part of this unit sits on a transgressive ravinement surface, overlain by a 6 m thick succession of lower shales, a 3 m thick IF, and upper 1 m thick shales of the Vlakhoek Member, recording sub-storm wave base deposition on a clastic sediment-starved shelf (Hicks and Hofmann, 2012; Ossa Ossa et al., 2016). The upper sandstone unit, referred to as the Kwaaiman Member, overlies shale along an erosional contact related to sea-level fall (Hicks and Hofmann, 2012; Ossa Ossa et al., 2016). The sandstones show symmetrical and interference ripple marks, mud drapes with mud cracks, and flaser lamination (Hicks and Hofmann, 2012). A decrease in the abundance of sedimentary structures, indicative of periodic exposure upwards in the stratigraphy suggests deposition in an intertidal environment gradually deepening to a shallow subtidal environment over the interval intersected in the core from the upper Sinqeni Formation to the middle Ntombe Formation (Hicks and Hofmann, 2012; Ossa Ossa et al., 2016). The upper Ntombe Formation in the drill core is characterized by interbedded dark- to medium-grey shales, with wavy and lenticular bedding, load casts, and fluid-escape structures. It is overlain by very fine-grained grey to light-grey sandstones displaying normal grading to shale and having sharp contacts with the underlying shale layers. This facies succession is consistent with tempestite or storm-induced turbidite deposition. The overall trend suggests a deepening of the depositional environment to depths just above storm wave-base. Most samples taken from the White Mfolozi Inlier were deposited above the fair-weather wave base, and consist of carbonate-bearing shales with elevated concentrations of Fe and Mn (Ossa Ossa et al., 2016). Carbonates form concretions, thin layers, and disseminations in the shale matrix are the main mineral hosts of Fe and Mn (Ossa Ossa et al., 2016).

In the Nongoma area, 450 m of the upper Sinqeni Formation were intersected by drill core PNG2 (Fig. 1). It is characterized by intercalations of fine- to coarse-grained argillaceous sandstones showing hummocky cross-stratification (HCS) and planar-laminated dark-grey shales (Nhleko, 2003). The sequence is interpreted to have been deposited in a storm-influenced subtidal to offshore setting. In this area, drill core PNG2 intersects the entire 1600 m thick Ntombe Formation, which is characterized by

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