Earth and Planetary Science Letters 452 (2016) 69–78

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Manganese oxide shuttling in pre-GOE oceans – evidence from molybdenum and iron isotopes

Florian Kurzweil[a,b,*], Martin Wille[a], Niklas Gantert[a], Nicolas J. Beukes[c], Ronny Schoenberg[a]

[a] Eberhard Karls University of Tuebingen, Department of Geosciences, Wilhelmstraße 56, 72074 Tuebingen, Germany
[b] University of Cologne, Department of Geosciences, Greinstraße 4-6, 50939 Cologne, Germany
[c] CIMERA and PPM, Department of Geology, University of Johannesburg, P.O. Box 524, Auckland Park 2006, South Africa

ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form 7 July 2016
Accepted 8 July 2016
Available online 8 August 2016
Editor: D. Vance

Keywords:
Great Oxidation Event
Mo isotopes
Fe isotopes
oxygen oases
redox stratification
Koegas Subgroup

ABSTRACT

The local occurrence of oxygen-rich shallow marine water environments has been suggested to significantly predate atmospheric oxygenation, which occurred during the Great Oxidation Event (GOE) ca. 2.4 billion years ago. However, the potential influence of such ‘oxygen oases’ on the mobility, distribution and isotopic composition of redox sensitive elements remains poorly understood. Here, we provide new molybdenum and iron isotopic data from shallow marine carbonate and silicate iron formations of the Koegas Subgroup, South Africa, that confirm local ocean redox stratification prior to the GOE.

Mn concentrations correlate negatively with both δ^{98}Mo and δ^{56}Fe values, which highlights the substantial role of particulate manganese for the cycling of Mo and Fe in the Paleoproterozoic oceans. Based on these trends we propose that pore water molybdate was recharged (1) by the diffusional transport of seawater molybdate with high δ^{98}Mo and (2) by the re-liberation of adsorbed molybdate with low δ^{98}Mo during Mn oxide dissolution within the sediment. The relative contribution of isotopically light Mo is highest close to a Mn chemocline, where the flux of Mn oxides is largest, causing the negative correlation of Mn concentrations and δ^{98}Mo values in the Koegas sediments. The negative correlation between δ^{56}Fe values and Mn concentrations is likely related to Fe isotope fractionation during Fe(II) oxidation by Mn oxides, resulting in lower δ^{56}Fe values in the uppermost water column close to a Mn chemocline. We argue that the preservation of these signals within Paleoproterozoic sediments implies the existence of vertically extended chemoclines with a smoother gradient, probably as a result of low atmospheric oxygen concentrations. Furthermore, we suggest that abiotic oxidation of Fe(II) by a Mn oxide particle shuttle might have promoted the deposition of the Koegas iron formations.

1. Introduction

The GOE, between 2.45 and 2.32 billion years (Ga) ago, represents one of the major environmental changes in Earth history (Holland, 2006). During this time period the amount of atmospheric oxygen rose from below 10^{-5} up to 10^{-2} of its present level (Farquhar et al., 2000; Holland, 2006; Pavlov and Kasting, 2002). This leap in atmospheric oxygen concentration most likely reflects a combination of increased primary production by oxygenic photosynthesis and organic carbon burial, a decrease in the O_2 buffer capacity of the Earth’s crust, hydrosphere and atmosphere or a combination of both (Catling et al., 2001; Holland, 2006; Kump and Barley, 2007).

There are several lines of evidence, which suggest that the onset of oxygen production occurred several hundred million years before the GOE and was most likely of biogenic origin (Kendall et al., 2010; Kurzweil et al., 2013; Planavsky et al., 2014). However, the reducing power of the upper continental crust, the atmosphere and the deep ocean outbalanced oxygen production and prevented the earlier accumulation of free oxygen (Lyons et al., 2014). Separated from anoxic deep waters, only some shallow marine habitats became oxygenated (Olson et al., 2013), which caused the development of a locally stratified ocean margin (Kendall et al., 2010). The existence of such oxygen oases is indicated by various geochemical parameters such as transition metal abundances (Kendall et al., 2010), Mo–Fe isotope constraints (Czaja et al., 2012; Planavsky et al., 2014), and the coupling of S and C isotopes

---

[*] Corresponding author. Present address: University of Cologne, Institute for Geology and Mineralogy, Zülpicher Straße 49b, 50674 Cologne, Germany. Fax: +49 707129571.
E-mail address: flokurzweil@hotmail.de (F. Kurzweil).

http://dx.doi.org/10.1016/j.epsl.2016.07.013
0012-821X/© 2016 Elsevier B.V. All rights reserved.

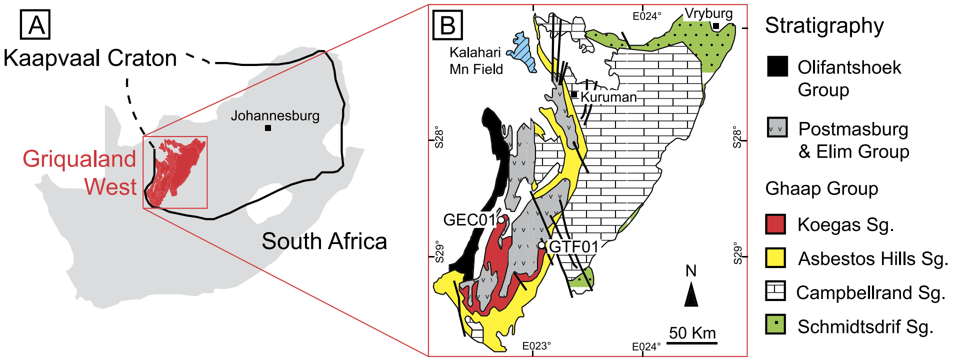

Fig. 1. A: Location of the Griqualand West Basin on the Kaapvaal Craton, South Africa (modified from Schröder et al., 2011). B: Geological map of the Griqualand West Basin and the location of drill cores of GEC01 and GTF01 (modified from Schröder et al., 2011).

(Kaufman et al., 2007). However, the temporal and spatial extension of oxygen oases and the implications for the local and global isotopic composition of different redox sensitive elements remain poorly understood.

Iron isotopes can potentially be used to reconstruct the ancient marine redox-state (Rouxel et al., 2005) because the redox dependent speciation of iron is accompanied by fractionation processes. Dissolved $\mathrm{Fe(II)_{aq}}$ and poorly soluble $\mathrm{Fe(III)_{aq}}$ isotopically equilibrate within minutes, with a large isotopic difference of $\Delta^{56}\mathrm{Fe_{FeII-FeIII}} = \delta^{56}\mathrm{Fe_{FeII}} - \delta^{56}\mathrm{Fe_{FeIII}} = -3‰$ (Welch et al., 2003), which is largely independent of the exact oxidation pathway (e.g. abiotic oxidation with O_2 or biological oxidation by anoxygenic photoferrotrophs (Croal et al., 2004)). The subsequent precipitation of $\mathrm{Fe(III)_{aq}}$ as Fe-oxyhydroxide minerals causes a kinetic isotope fractionation in the opposite direction, the magnitude being mainly dependent on the mineral species, temperature and reaction kinetics (Beard and Johnson, 2004). For zero age ferrihydrite the isotopic difference is $\Delta^{56}\mathrm{Fe_{FeIII-FeOOH}} = \delta^{56}\mathrm{Fe_{FeIII}} - \delta^{56}\mathrm{Fe_{FeOOH}} = +2‰$ (Beard and Johnson, 2004; Johnson et al., 2008b). Altogether the oxidation and precipitation of Fe(III) minerals cause the relative depletion of heavy Fe isotopes in the remaining $\mathrm{Fe(II)_{aq}}$ reservoir. The separation of anoxic $\mathrm{Fe(II)_{aq}}$-rich deep waters with a homogeneous isotopic composition and an oxic surface layer, where $\mathrm{Fe(II)_{aq}}$ is oxidized, therefore causes large isotopic gradients along the chemocline (Busigny et al., 2014). The Fe isotopic composition of sediments deposited along such chemoclines, thus, potentially records redox gradients at ancient local oxygen oases.

In contrast to Fe, Mo is poorly reactive in oxic, and probably also in anoxic-ferruginous, waters (Kurzweil et al., 2015). In the modern predominantly oxic ocean dissolved molybdate ($\mathrm{MoO_4^{2-}}$) has a residence time of around 440 ka (Miller et al., 2011) and is, therefore, homogeneously distributed in concentration as well as in its isotopic composition (Nakagawa et al., 2012; Siebert et al., 2003). In the absence of dissolved H_2S, the adsorption of Mo onto Mn-oxides probably represents the most important Mo sink in oxic deep marine settings (Bertine and Turekian, 1973; Scott and Lyons, 2012). This adsorption is associated with a change from tetrahedral ($\mathrm{MoO_4^{2-}}$) to octahedral coordination (adsorbed Mo), which causes large equilibrium Mo isotopic fractionation, thereby preferentially adsorbing light Mo isotopes (Barling and Anbar, 2004; Kashiwabara et al., 2011; Siebert et al., 2003).

The oxidation of Mn(II) and the formation of Mn oxides requires higher redox potentials than the oxidation of Fe(II) as well as the catalyzing effect of Mn oxidizing bacteria (Tebo et al., 2005). Reaction kinetics are accelerated in the presence of superoxide (O_2^-), which can be produced during biological processes or photochemical reactions, such as the photo-oxidation of dissolved organic matter (Learman et al., 2013). In an overall reducing ocean, shallow ocean environments with high primary productivity, therefore, represent the most likely setting, where the required availability of O_2 and/or O_2^- enables the formation of particulate Mn oxides. In these most proximal, shallow ocean areas the preferential scavenging of isotopically light Mo by Mn oxide particles is expected at Archean/Paleoproterozoic times (Planavsky et al., 2014). The combination of Fe and Mo isotopes from shallow marine, Superior type iron formations of the 2.48 Ga old Koegas Subgroup, South Africa, therefore offer great potential for the detailed reconstruction of the local environmental redox state of the Griqualand West Basin. We compare our results with isotopic data for modern anoxic lakes, which have been claimed as Archean ocean analogues (Busigny et al., 2014), as well as isotopic data for sediments from other oxygen oases (Planavsky et al., 2014). Furthermore, the combination of Mo and Fe isotopes in our study not only provides important insights into the local marine environment, with profound implications for the regional/global ocean redox state, but also constraints on the behavior of redox sensitive elements like Mo and Fe in such settings in general.

2. Geological setting and sample material

The Ghaap Group (Traansvaal Supergroup, South Africa) represents a continuous sedimentary succession, deposited in the Griqualand West Basin immediately before the GOE (Beukes and Gutzmer, 2008). The Koegas Subgroup is the uppermost unit of the Ghaap Group and represents the final stage of a long-term regressive period (Schröder et al., 2011). SHRIMP U–Pb zircon data of the subjacent Asbestheuwels Subgroup (Kuruman Formation) indicate a maximum depositional age of 2460 ± 5 Ma (Pickard, 2003). In contrast, Re–Os dating of shales from the Koegas Subgroup (Nelani Formation, Klipputs Member; GEC01 174–176) provide a depositional age of 2479 ± 22 Ma (Kendall et al., 2013), which might suggest a true depositional age at the lower end of this error range.

Shorter term sea level fluctuations are superimposed on the long-term regressive period, leading to periodical alternations of siliciclastic units during regressions (Pannetjie-, Naragas-, Heynskop Formation) and iron formations during transgressions (Doradale-, Rooinekke-, Nelani Formation) along a prograding delta or submarine fan system (Schröder et al., 2011). The terrigenous input was generally higher in the eastern parts of the basin, which argues for lateral basinal deepening from E to W (Schröder et al., 2011). The drillcore GTF01 situated in the eastern part of the basin therefore represents a more proximal depositional setting (Fig. 1). GTF01 samples of this study are from the Doradale Formation, which is associated with maximal sea level and the deposition of fine-grained and laminated iron formations. The western GEC01 drillcore comprises sediments from the deeper settings of the Rooinekke and Nelani formations. Beukes (1983) suggested a flooding surface at the base of the Nelani Formation during deposition