



Geochemical stratigraphy, sedimentology, and Mo isotope systematics of the ca. 2.58–2.50 Ga-old Transvaal Supergroup carbonate platform, South Africa



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ABSTRACT

The Neoproterozoic–Paleoproterozoic Transvaal Supergroup in South Africa contains the well-preserved stromatolitic Campbellrand–Malmani carbonate platform, which was deposited in shallow seawater shortly before the 2.40–2.32 Ga Great Oxidation Event (GOE). This platform is composed of alternating stromatolitic carbonates and mudstones and is a prominent candidate for (isotope-) geochemical mapping to investigate the appearance of very small amounts of free oxygen that accumulated in shallow waters preceding the GOE. Mo isotopes in sedimentary archives are widely used as a proxy for redox-changes in modern and ancient environments and recent evidence suggests that oxy-molybdate (MoO_4^{2-}) is directly transferred from ocean water to inorganic carbonates with negligible fractionation, thus reflecting oceanic Mo isotope signatures.

In this study we analyzed major and trace element compositions as well as Mo isotopic compositions of carbonate and mudstone samples from the KMF-5 drill core. Geochemical indicators, such as Fe and Mn concentrations and Fe-to-Mn abundance ratios reveal the preservation of some geochemical indicators despite the widespread silicification and dolomitization of the platform. Heavy $\delta^{30}\text{Si}$ values of silicified carbonates between 0.53 and 2.35‰ point to Si precipitation from surface water during early diagenesis rather than to a later hydrothermal overprint. This assessment is supported by the frequent observation of rip-up structures of silica (chert) layers within the entire sedimentary succession. The $\delta^{98}\text{Mo}$ values of whole rock samples throughout the Malmani–Campbellrand platform range between -0.82 and $+1.40$ ‰, similar to values reported for deeper slope carbonates from the Griqualand West area, but variations are independent from lithology or depositional water depth. These large variations in $\delta^{98}\text{Mo}$ values indicate molybdenum redox cycling and thus the presence of free oxygen in the atmosphere–ocean system at that time, in agreement with earlier Mo isotopic studies on Campbellrand carbonates and shales. A similar range in $\delta^{98}\text{Mo}$ values for carbonates between $+0.40$ and $+0.87$ ‰, however, was also found on the hand specimen scale, indicating the danger of a sample bias on the Mo isotopic stratigraphy of this carbonate platform. Results of previously unpublished adsorption experiments of Mo on CaCO_3 clearly indicate that the Mo inventory of Malmani–Campbellrand carbonates was not only influenced by primary adsorption from seawater, but to a much larger degree by secondary processes during early diagenesis, which also affected the Mo isotopic composition of the samples on a local scale. Our results indicate that Mo concentrations and isotopic compositions in ancient stromatolitic carbonates were subject to redox changes within microbial mats and within the soft sediment during early diagenesis and later lithification, and as such cannot be used to quantitatively reconstruct the amount of free atmospheric oxygen or its fluctuations through Earth's history. Nevertheless, we interpret our heavy Mo isotopic signatures from carbonates as a minimum value for Neoproterozoic seawater and reinforce the assumption that free atmospheric oxygen built up a heavy oceanic Mo reservoir at that time.

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1. Introduction

Deciphering the conditions of the atmosphere–hydrosphere system before the Great Oxidation Event (GOE) at ~ 2.45 Ga (Canfield, 2005; Farquhar et al., 2000) is a challenging issue, as the exact mode and timing for a transition from a reduced to an oxygenated Earth somewhere around Neoproterozoic to Paleoproterozoic times (Holland, 1962) are still highly debated in the scientific community (Bekker et al., 2004; Canfield, 1998; Hoashi et al., 2009; Holland, 2006; Kasting, 2001; Lyons et al., 2014; Ohmoto et al., 2006; Posth et al., 2013; Wille et al., 2013). Geological indicators for a shift to more oxidizing conditions at that time are the appearance of red beds and oxidized paleosols, the disappearance of uraninite, siderite, and pyrite placers, and the occurrence of large marine manganese deposits (Beukes, 1987; Beukes et al., 2002; Rasmussen et al., 1999; Roy, 1992). The most prominent geochemical evidence for a clearly oxygenated atmosphere ($>10^{-5}$ present atmospheric level (PAL)) is the disappearance of mass independent isotopic fractionation of sulfur in sediments deposited around 2.40–2.32 Ga (Bekker et al., 2004; Farquhar et al., 2000; Hannah et al., 2004; Pavlov and Kasting, 2002).

With the beginning of the Neoproterozoic the first extensive carbonate platforms developed, resulting from the evolution of large continents and epicontinental seas, which provided the accommodation space and required shallow marine conditions for carbonate growth (Hoffman, 1988; Hoffman and Grotzinger, 1988). These platforms could have been the site of early O_2 production on our planet, as Archean carbonates mostly consist of stromatolites. These are the laminated, organosedimentary, non-skeletal products of microbial communities, which may have included cyanobacteria, the first photosynthetic organisms to produce oxygen (Burne and Moore, 1987). Although the appearance of cyanobacteria and therefore the onset of oxygenic photosynthesis is proposed to have happened by about 2.8 Ga (Farquhar et al., 2011), the final trigger for a significant accumulation of atmospheric O_2 at ca. 2.45 Ga and thus the GOE is still debated. One theory is that the formation of stable cratons enabled enhanced burial of organic carbon, which prevented consumption of oxygen via decay of these organics (Falkowski and Isozaki, 2008), leading to a net production of oxygen. Hydrogen escape to space prior to reaction with oxygen by ultraviolet photolysis of abundant methane has also been proposed as a mechanism for irreversible atmospheric oxidation (Catling et al., 2001). The third major theory is that the stabilization of large continents at Archean/Proterozoic times and a shift from submarine to subaerial volcanism led to a change in the redox state of volcanic gases from reduced to more oxidized, which ultimately oxidized the atmosphere (Gaillard et al., 2011; Kump and Barley, 2007).

In addition to the mineralogical and isotopic proxies cited above, more recent studies have exploited variations in the concentration and the isotopic composition of selected trace elements for their potential as tracers of free atmospheric oxygen, as these elements may be even more sensitive to redox-changes of the ambient environment than sulfur isotopes (Anbar et al., 2007; Crowe et al., 2013; Dahl et al., 2010, 2011; Frei et al., 2009; Planavsky et al., 2011, 2014; Siebert et al., 2005; Wille et al., 2007).

Molybdenum, for instance, shows variations of its isotopic composition and concentration in chemical sediments depending on the redox potential of the ambient ocean and pore fluids (e.g. Barling et al., 2001; Emerson and Huested, 1991; Shimmield and Price, 1986; Siebert et al., 2003). In the modern oxygen-rich environment Mo is normally oxidized during oxidative continental weathering from its tetravalent oxidation state in rocks and soils to hexavalent Mo, forming soluble oxy-molybdate MoO_4^{2-} , which then enters the ocean (Barling et al., 2001; Morford and Emerson, 1999). Molybdate with a crustal $\delta^{98}Mo_{input}$ value of ca. -0.2 to

$+0.6\%$ (relative to NIST3134 standard solution, set to $+0.25\%$ (Nägler et al., 2014)) is transported by rivers and groundwater to the oceans, where it behaves conservatively with a long residence time of 440,000–800,000 years (Collier, 1985; Emerson and Huested, 1991; Miller et al., 2011; Morford and Emerson, 1999). Light Mo-isotopes are preferentially adsorbed onto oxic sediments, predominantly pelagic Fe-Mn crusts and nodules, due to sorption of molybdate to the reactive surfaces of Mn- and Fe-oxide minerals. This process results in an isotopic difference for $\Delta^{98}Mo_{seawater-FeMn\ crust}$ of $+2.7$ to $+3.2\%$ (Barling and Anbar, 2004; Goldberg et al., 2009; Nägler et al., 2014; McManus et al., 2006; Siebert et al., 2001, 2003; Tossell, 2005). Under slightly euxinic conditions, where H_2S is present in the water column or in pore water at concentrations below $11\ \mu M$, molybdate is incompletely transformed to (oxy)thio-molybdates $Mo^{(VI)}O_{4-x}S_x^{2-}$, which readily adsorb on positively charged particle surfaces, like organic matter or Fe sulfide phases of sediments (Helz et al., 1996; McManus et al., 2002; Nägler et al., 2011; Tribouillard et al., 2006). However, transformation favors the lighter Mo to be incorporated within the thiomolybdate. Therefore, the preferential incorporation of isotopically light Mo in oxic to slightly euxinic sediments results in a heavy open ocean water $\delta^{98}Mo$ of $+2.3\%$, which is homogenous due to the long mean ocean residence time of Mo. Above a threshold value of $11\ \mu M\ H_2S$ the transition from molybdate to thiomolybdate is very effective and Mo is nearly quantitatively scavenged into reduced sediments, such as black shales, whereby this authigenic Mo mirrors the isotopic composition of the coeval seawater (Arnold et al., 2004; Barling et al., 2001; Erickson and Helz, 2000; Helz et al., 1996; Siebert et al., 2003). Between these two “end-members” of sedimentary redox conditions (oxic and euxinic), authigenic Mo enrichments in sediments show a broad range in their isotopic composition and are mainly controlled by redox gradients in the sediment pore fluids, induced by early diagenesis (Brucker et al., 2009; Dahl et al., 2010; Nägler et al., 2011; Romaniello, 2012; Scott and Lyons, 2012).

Assuming that redox changes of the atmosphere–hydrosphere system over geological times should perturb the marine Mo isotopic cycle by introducing heterogeneities in the sedimentary redox regimes described above, this should result in an evolution of the seawater $\delta^{98}Mo$ value, which can be mirrored in black shales precipitated within an euxinic setting. Several studies suggest the build-up of small amounts of free oxygen before the GOE, based on fluctuations of Mo concentrations and isotopic compositions of Archean chemical sediments (e.g. Anbar et al., 2007; Duan et al., 2010; Planavsky et al., 2014; Voegelin et al., 2010; Wille et al., 2007).

Recently, it has been suggested that non-skeletal marine carbonates also might mirror the Mo isotopic composition of the ambient seawater and thus provide another viable rock archive to reconstruct the redox-evolution of the hydrosphere–atmosphere system over Earth’s history through variations in seawater $\delta^{98}Mo$ values (Voegelin et al., 2009, 2010). Particularly, Voegelin et al. (2010) found shifts toward heavy $\delta^{98}Mo$ values in carbonates from drill core samples of the 2.6–2.5 Ga old Ghaap Group of the Griqualand West Basin (South Africa), which were suggested to result from changes in redox-conditions of the ambient environment, such as fluctuations in free atmospheric oxygen at that time. Contemporaneous black shales from the same drill cores follow an overall increasing trend in $\delta^{98}Mo$ up-section, corroborating the interpretation of gradually rising atmospheric oxygen during this time (Wille et al., 2007).

There are several advantages to exploring the carbonate record of Mo, if these sediments are indeed high-fidelity records of the seawater Mo reservoir. Carbonates are deposited over a much wider range of sedimentary environments than black shales, which are deposited under specifically reducing conditions. Carbonates are also well preserved in sedimentary successions as far back as the

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