Chemical Geology 362 (2013) 115–130

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Nitrogen cycle in the Late Archean ferruginous ocean

Vincent Busigny [a,*], Oanez Lebeau [a], Magali Ader [a], Bryan Krapež [b], Andrey Bekker [c]

[a] Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154 CNRS, 1 rue Jussieu, 75238 Paris, France
[b] The Institute for Geoscience Research, Department of Applied Geology, Curtin University, GPO Box U1987, Perth WA 6845, Australia
[c] Department of Geological Sciences, University of Manitoba, 125 Dysart Road (Wallace Building), Winnipeg, Manitoba, R3T 2N2, Canada

ARTICLE INFO

Article history:
Accepted 24 June 2013
Available online 2 July 2013

Keywords:
Nitrogen
Carbon
Isotopes
Archean ocean
Banded iron formation

ABSTRACT

The Hamersley Group comprises a Late Archean sedimentary succession, which is thought to record the prelude to the atmospheric oxygenation in the Paleoproterozoic, the so-called Great Oxidation Event (GOE), at ~2.4 Ga. We studied drill-core samples of sedimentary rocks from the upper Mount McRae Shale and Brockman Iron Formation deposited before the GOE at ~2.5 Ga in order to characterize the environments and ecosystems prevailing during their deposition. The rocks from the Mount McRae Shale and Brockman Iron Formation represent, respectively, proximal euxinic conditions and distal ferruginous depositional environments, thus providing an opportunity to examine lateral variability in the open-marine basin. We analyzed the concentration and isotopic composition of carbon in carbonate and organic matter, bulk nitrogen content and its isotopic composition as well as major element concentrations. The $\delta^{13}C_{carb}$ values and carbonate content range from −3.2 to −10.7‰ and 0.1 to 58 wt.%, respectively. Organic carbon content also varies over a large range from 0.05 to 4.6 wt.% with a near constant $\delta^{13}C_{org}$ value of −28.7 ± 0.8‰. Negative $\delta^{13}C_{org}$ excursions (down to −31‰) are generally correlated with high organic matter content. Bulk nitrogen shows highly variable concentration, between 1.3 and 785 ppm, and $\delta^{15}N$ values between 0.4 and 13.4‰.

The $\delta^{13}C_{carb}$ values reflect a diagenetic carbonate origin, with negative values typical for Fe-rich carbonates formed by organic matter mineralization with ferric oxyhydroxides. In contrast, $\delta^{13}C_{org}$ and $\delta^{15}N$ values record primary isotope signatures derived from ancient living organisms. The relatively constant $\delta^{13}C_{org}$ values at around −28.7‰ are interpreted as reflecting photoautotrophs utilizing a large pool of dissolved inorganic carbon. Inverse stratigraphic co-variation between $\delta^{15}N$ and $\delta^{13}C_{carb}$ values was observed for the Brockman Iron Formation. We propose that N and C biogeochemical cycles were coupled by Fe redox cycling in the water column and in sediments of the Late Archean ocean. Several models for biogeochemical N cycling linked to the redox structure of the water column are considered. Under fully anoxic conditions, the dominant N species available for assimilation by micro-organisms in the photic zone could be ammonium (NH_4^+). Highly positive $\delta^{15}N$ values would reflect the assimilation of NH_4^+ enriched in ^{15}N by partial oxidation to nitrite, followed by quantitative removal of the produced nitrite by denitrification or anamox processes. Ammonium oxidation could have been driven by (i) O_2 produced locally via oxygenic photosynthesis, or (ii) microbial oxidation utilizing Fe(III)-oxyhydroxides formed in the water column. Under redox-stratified conditions, N assimilated by primary producers could have been in the form of NO_3^-, based on modern and Phanerozoic analogs. The positive $\delta^{15}N$ values would have resulted in this case from partial denitrification of NO_3^- coupled to anaerobic microbial oxidation of Fe(II) to Fe(III). We conclude that similar positive $\delta^{15}N$ signatures may record very different N biogeochemical cycles under anoxic, stratified and fully oxic conditions in the ocean. Interpretation of the N isotopes in terms of N biogeochemical cycle thus requires independent constraints on the redox structure of the ocean.

1. Introduction

One of the most important changes in Earth's surface history is the oxygenation of the atmosphere–ocean system (Holland, 1984, 2009). The oxygenation imparted major modifications to the geochemical cycles of many redox-sensitive elements, such as C, O, N, S, and base metals, with dramatic implications for the development and evolution of life (Anbar and Knoll, 2002). It is now well established that the first irreversible oxygenation of the atmosphere, the so called Great Oxidation Event (GOE), occurred between 2.4 and 2.3 Ga (Holland, 2002; Bekker et al., 2004; Guo et al., 2009), although transient oxygenation could have occurred earlier. Recent studies of the Mount McRae Shale, Western Australia suggested that atmospheric oxygenation started at 2.5 Ga, based on Mo and Re concentrations and isotopic compositions (Anbar et al., 2007), and C and S isotope

---

* Corresponding author.
E-mail address: busigny@ipgp.fr (V. Busigny).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.06.023

values of whole-rock shale samples (Kaufman et al., 2007). Nitrogen isotope (Garvin et al., 2009) and Fe speciation (Reinhard et al., 2009; Raiswell et al., 2011) studies of the same sample set also argued for surface ocean oxygenation at that time. Earlier oxygenation of the surface ocean at ~2.67 Ga was proposed based on N isotope composition of shales from the Campbellrand-Malmani carbonate platform, South Africa (Godfrey and Falkowski, 2009). Besides the question of timing, the secular trend of O_2 accumulation in the atmosphere–ocean system is also highly debated. Two secular trends have been proposed: (1) gradual O_2 increase and accumulation (e.g., Holland, 2006; Murakami et al., 2011), and (2) oscillatory variations in O_2 level in association with the early Paleoproterozoic glacial events and the Lomagundi carbon isotope excursion (Bekker and Kaufman, 2007; Bekker and Holland, 2012). The Late Archean may also have been characterized by transient and local low-levels of oxygen, so-called “whiffs” of oxygen (Anbar et al., 2007).

Nitrogen isotopes represent a unique tool for exploring the secular evolution of oxygen because (i) N biogeochemistry is mainly controlled by redox reactions and (ii) N is present in all sedimentary rocks, providing a continuous record in different geological settings. In contrast to the Archean, the modern N cycle in the ocean is relatively well understood (see reviews in Brandes et al., 2007; Sigman et al., 2009). The main reservoir of N at the Earth's surface is the atmosphere with a present $\delta^{15}N$ value of 0‰ (N isotope composition is expressed as $\delta^{15}N = [(^{15}N / ^{14}N)_{sample} / (^{15}N / ^{14}N)_{standard} - 1] \times 1000$, where the standard is atmospheric N_2). Nitrogen enters the oceanic cycle through atmospheric N_2 fixation by aerobic and anaerobic autotrophs with minor N isotope fractionation (<3‰; e.g., Wada et al., 1975; Minagawa and Wada, 1986). After the death of these autotrophic organisms, organic matter mineralization releases N as ammonium (NH_4^+), with very little isotopic fractionation (Prokopenko et al., 2006; Möbius, 2013). In the presence of free O_2, NH_4^+ is oxidized into nitrate (NO_3^-) during a two-step biological process called nitrification, which is associated with significant N isotope fractionation ~16‰ (Sigman et al., 2009). This fractionation is rarely fully expressed in modern marine environments since the transformation of NH_4^+ to NO_3^- is generally complete. In O_2-depleted environments such as oxygen-minimum zones or anoxic sediments, nitrates are partially reduced by denitrification or anammox (i.e., anaerobic ammonium oxidation) into gaseous N_2 or N_2O. During denitrification, ^{14}N is preferentially released relative to ^{15}N, leaving residual marine NO_3^- enriched in the heavy isotope (average marine $\delta^{15}N_{NO_3^-} = +5‰$; e.g., Altabet and Francois, 1994). The heavy isotope signature of NO_3^- is transferred by assimilation to organisms living in the water column or in the diagenetic realm and then recorded in sedimentary organic matter. Accordingly, assuming a steady-state system, the N isotope composition of organic matter in modern marine environment reflects mainly the relative proportion of N denitrification (in the water column and in sediments) and N fixation. In O_2-free environments such as the Early Archean oceans, the nitrification and thus subsequent denitrification are unlikely, and dissolved N species may have been dominated by NH_4^+ (Holland, 1984, 2002; Beaumont and Robert, 1999; Papineau et al., 2005). Accordingly, N cycle and isotope composition of Archean ocean and sediments may have been significantly different from those of the modern world (Canfield et al., 2010).

Most of the N in the Earth exosphere is contained as N_2 in the atmosphere (presently ~3.98×10^{21} g). Based on data from fluid inclusion in cherts (Sano and Pillinger, 1990) and geochemical modeling (Tolstikhin and Marty, 1998), the N isotope composition of the atmosphere is believed to have remained largely constant during the last 3 Ga with $\delta^{15}N$ values of about 0‰. The use of N isotope compositions of Precambrian sedimentary rocks as a tracer of NO_3^-, and thus O_2, content was proposed in the pioneering work of Beaumont and Robert (1999). In their study, the authors analyzed cherts of various ages and suggested a dramatic change in the N biogeochemical cycle between 3 and 2 Ga. Negative $\delta^{15}N$ values were observed in cherts older than ~2.4 Ga and interpreted as reflecting N_2 fixation or NH_4^+ assimilation (Beaumont and Robert, 1999; Papineau et al., 2005), a result compatible with low NO_3^- concentrations (if any) under anoxic conditions in the early Earth oceans. However, this interpretation was questioned since some of these cherts were deposited in hydrothermal settings and may have recorded N isotope signatures of chemoautotrophic organisms specific to these environments (Pinti and Hashizume, 2001; Pinti et al., 2001, 2009). If this was the case, their N isotope signature would not reflect phototrophic organisms living in the photic zone of the upper ocean and the N isotope composition of seawater nitrogen compounds. Two recent N-isotope studies of Archean sedimentary sequences from Western Australia and South Africa suggested earlier oxygenation of the Earth's surface ocean starting at 2.5 Ga (Garvin et al., 2009) and 2.67 Ga (Godfrey and Falkowski, 2009), respectively. Both studies identified $\delta^{15}N$ shifts from near 0‰ to positive values, up to 7.5‰, and interpreted these trends as evidence for coupled nitrification–denitrification, pathways typical of a surface ocean containing free O_2. According to their interpretations, denitrification had to be partial so that N isotope fractionation can be expressed. Bulk rock N isotope analyses of ~2.72 Ga carbonates from the Tumbiana Formation, Western Australia revealed extreme $\delta^{15}N$ values up to +50.4‰, possibly recording the onset of nitrification coupled to consumption of its products (nitrite and nitrate) via biological denitrification (Thomazo et al., 2011). Such extreme N isotope compositions could only be expressed under oxygen-limited conditions so that partial nitrification would be associated with complete denitrification (Thomazo et al., 2011). High $\delta^{15}N$ values, up to +20‰, were also observed in ~2.7 Ga carbonaceous shales from the Western Abitibi Greenstone Belt (Canada) and Penhalonga Formation (Botswana). These values were explained by an Archean ^{15}N-enriched atmosphere resulted from secondary accretion of C1 chondrite-like material (Jia and Kerrich, 2004a, 2004b). However, discrete N isotope excursions in time seem more likely than a long-term evolution in composition of the atmosphere since other datasets illustrate very small, if any, N isotope variations in the atmosphere through time (e.g., Sano and Pillinger, 1990; Tolstikhin and Marty, 1998; Marty et al., 2012).

Previous studies of N isotopes in Precambrian rocks either (1) focused on samples of different lithologies and ages from different areas (e.g., Beaumont and Robert, 1999; Pinti et al., 2001, 2009; Jia and Kerrich, 2004b; Papineau et al., 2005, 2009), or (2) analyzed stratigraphic sequences of organic-rich shales (i.e., Garvin et al., 2009; Godfrey and Falkowski, 2009) or carbonates (Thomazo et al., 2011). However, no study has presented so far a stratigraphic dataset for a drill-core section of banded iron formation, which is one of the common Archean sedimentary rocks. In this work, we analyzed the N isotope composition of drill core samples of organic carbon-poor and Fe-rich sediments from the Brockman Iron Formation, Western Australia, one of the best preserved banded iron formations in the world (Trendall and Blockley, 1970). The unit contains the products of redox reactions, including Fe oxidation in the water column either by oxygenic or anoxygenic photosynthesis (e.g., Cloud, 1973; Konhauser et al., 2002; Kappler et al., 2005; see also review in Bekker et al., 2010). Systematic N isotope study of banded iron formations has never been performed before since they contain only small amounts of N, requiring high-sensitivity techniques based on static mass-spectrometry. The Brockman Iron Formation was deposited immediately above the Mount McRae Shale, which was extensively studied previously to constrain the redox state of the atmosphere–ocean system (Anbar et al., 2007; Kaufman et al., 2007; Garvin et al., 2009; Reinhard et al., 2009; Raiswell et al., 2011). Accordingly, we build on these previous studies and continue to explore the Hamersley Group in order to constrain environmental changes for the time period between ~2.5 and 2.46 Ga. In addition, samples from the Brockman Iron Formation were also selected because they