



Pervasive aerobic nitrogen cycling in the surface ocean across the Paleoproterozoic Era

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ABSTRACT

Nitrogen isotope ratios in marine sedimentary rocks have become a widely used biogeochemical proxy that records information about nutrient cycling and redox conditions in Earth's distant past. While the past two decades have seen considerable progress in our understanding of the Precambrian sedimentary nitrogen isotope record, it is still compromised by substantial temporal gaps. Furthermore, quantitative links between nitrogen isotope data, marine redox conditions, and nutrient availability are largely lacking in a Precambrian context. Here we present new nitrogen isotope data from a suite of marine sedimentary rocks with ca. 2.4 to 1.8 Ga ages, spanning the Great Oxidation Event in the Paleoproterozoic, to better constrain the response of the nitrogen cycle to the first major redox transition in Earth's history. We further construct a simple box model to describe the major pathways that influenced the nitrogen isotope mass balance of the Precambrian ocean and use this as a platform to evaluate the Precambrian nitrogen isotope record. Within this framework, we find that consistently positive nitrogen isotope values, ranging from +1.1 to +7.7‰, across the early Paleoproterozoic are strong evidence for an expansion of oxygenated surface waters. Since the isotopic signature of aerobic nitrogen cycling is recorded in the biomass of nitrate-assimilating organisms, this implicates widespread nitrate bioavailability in this time interval. The decline in offshore nitrogen isotope ratios in the Mesoproterozoic is consistent with the contraction of oxic waters, which could have inhibited the expansion of nitrate-fueled ecosystems to pelagic waters until the widespread oxygenation of the ocean in the latest Neoproterozoic to early Phanerozoic.

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1. Introduction

At the beginning of the Paleoproterozoic Era, Earth's atmosphere underwent a permanent shift from a reducing to an oxidizing state. This transition – termed the “Great Oxidation Event” (GOE) – began by ca. 2.43 Ga (Gumsley et al., 2017) and was characterized by oxygen-rich marine and terrestrial settings lasting until ca. 2.06 Ga (Bekker and Holland, 2012). In the aftermath of the GOE, atmospheric oxygen fell to an intermediate level that was substantially higher than in the Archean, but lower than Phanerozoic concentrations (Lyons et al., 2014). While the exact timing and mechanism of the GOE remain debated, the magnitude of its impli-

cations is clear: the biogeochemical pathways operating at Earth's surface were dramatically and permanently altered (Lyons et al., 2014), and the stage was set for the emergence of aerobically-respiring organisms, including the first eukaryotes (Javaux and Lepot, 2018).

Several paleo-redox proxies have been used to characterize the transition toward oxygenated surface environments in the Paleoproterozoic. Early evidence from oxidized paleosols documented the influence of atmospheric oxygen in weathering environments by ca. 2.2 Ga (e.g. Beukes et al., 2002), and the recognition of a large perturbation in the global carbon cycle through carbon isotope systematics of carbonates has long been used to support a notion of extreme oxygen production during the GOE (e.g. Karhu and Holland, 1996). More recently, the disappearance of mass-independent fractionation of sulfur isotopes (MIF-S) has been used to pinpoint the crossing of a threshold of 10^{-5} times the present

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atmospheric level of oxygen (PAL) between 2.46 and 2.32 Ga (Farquhar et al., 2000; Gumsley et al., 2017; Luo et al., 2016; Bekker et al., 2004), which has come to define the onset of the GOE proper.

The redox states of the atmosphere and ocean are coupled on geologic timescales, and so the rise of atmospheric oxygen, the “oxygen overshoot,” and the subsequent deoxygenation should have considerably affected marine redox chemistry. Indeed, enrichments of redox-sensitive trace elements in organic-rich shales implicate an expansion of oxygenated seawater during the GOE (Scott et al., 2008; Partin et al., 2013; Kipp et al., 2017), as do sulfur isotope ratios in marine sedimentary rocks, which suggest a waxing and waning seawater sulfate reservoir (Planavsky et al., 2012; Scott et al., 2014). Beyond these converging lines of evidence for widespread ocean oxygenation during the GOE, recent work has begun to decipher even regional redox gradients. Highly positive selenium isotope ratios in offshore marine sediments during the GOE imply oxygenated surface oceans, with anoxia prevailing at depth (Kipp et al., 2017). This finding is corroborated by the record of iodine enrichment in shallow-marine carbonates deposited at the same time, which requires at least mildly oxygenated surface waters (Hardisty et al., 2017).

Nitrogen isotope geochemistry can bring additional perspective to bear on the question of basinal redox structure, as nitrogen has a high redox potential – similar to that of selenium and iodine – and is sensitive to redox conditions in the photic zone, where primary productivity is highest. The nitrogen isotope composition of organic matter in offshore marine sediments can thus speak to redox chemistry in the photic zone overlying the outer shelf and open ocean. Furthermore, as nitrogen is an essential macronutrient, nitrogen isotopes in marine sediments also record the balance between nitrogen-fixing organisms (strictly prokaryotic) and nitrogen-assimilating organisms (which can be either prokaryotic or eukaryotic). Since nitrate (NO_3^-) is the preferred nitrogenous substrate for eukaryotes in the modern ocean (e.g. Karl et al., 2001), tracing the prevalence of aerobic nitrogen cycling during the Paleoproterozoic can both constrain redox conditions and speak directly to the bioavailability of NO_3^- for eukaryotic organisms.

Notably, despite the wealth of evidence from a variety of well-established paleo-redox proxies, the immediate response of the nitrogen cycle to the GOE has only been investigated in a few studies that focused specifically on the onset, culmination, or aftermath of the GOE (Kump et al., 2011; Luo et al., 2018; Papineau et al., 2009; Zerkle et al., 2017). While those studies have provided important evidence for the presence of aerobic nitrogen cycling during the GOE, the sparse record through the Paleoproterozoic hinders reconstructions of global temporal and spatial patterns across the proposed “oxygen overshoot.”

Here we present nitrogen isotope data from a suite of Paleoproterozoic marine sedimentary rocks that span the GOE in order to better characterize the response of the biogeochemical nitrogen cycle to the first permanent increase in atmospheric and marine oxygen levels. Taking this a step further, we then construct a simple steady-state isotope box model and use it as a platform for evaluating secular trends in the Precambrian nitrogen isotope record. To date, nitrogen isotopes in ancient marine sediments have been used at best as a semi-quantitative redox proxy. We find that even with this simple view of the nitrogen cycle, a robust correlation can be drawn between nitrogen isotope ratios in marine sediments and the extent of oxic surface waters. This new, quantitative framework for interpreting the nitrogen isotope record enables a direct comparison with results from other proxies, thereby refining our view of ocean oxygenation during and after the GOE.

2. Materials

We collected nitrogen and organic carbon isotopic data from a large sample set ($n = 144$) of marine, siliciclastic sedimentary rocks with ages spanning ca. 2.4 to 1.8 Ga. We targeted shales deposited in offshore depositional environments (below wave base) in basins that were open with respect to exchange with the global ocean. When viewed together, these lithologies capture a representative view of secular trends in global nitrogen cycling. None of the units studied here have experienced metamorphism beyond lower greenschist facies. Detailed descriptions of individual units can be found in the Supplementary Materials.

3. Methods

3.1. Sample preparation for bulk rock analyses

Sample preparation followed published methods (Stüeken, 2013; Koehler et al., 2017). Samples were crushed into centimeter-sized chips, and equipment was cleaned between samples with methanol and 18 M Ω DI-H₂O. Rock chips were sequentially cleaned with ethanol, 2 N HCl, and DI-H₂O to remove modern contaminants, then dried in an oven at 60 °C. Clean chips were pulverized using an aluminum oxide puck mill that was cleaned between samples using methanol, DI-H₂O, and pre-combusted (500 °C) silica sand. Prior to analysis, powders were decarbonated using 6 N HCl, then rinsed with DI-H₂O and dried in an oven at 60 °C.

3.2. Kerogen extraction

Kerogen was extracted from bulk rock powders following published protocols (Stüeken et al., 2015). Rock powders were weighed out into teflon bottles and treated with a 50:50 mixture of DI-H₂O and concentrated (29 N) hydrofluoric acid (HF) in a shaking water bath at 55 °C. Digests were then centrifuged and the supernatant was decanted. A BF₃ solution (62.5 g H₃BO₃, 100 mL DI-H₂O, 100 mL 29 N HF) was then added, and the samples were placed in a shaking water bath at 55 °C to dissolve remaining fluoride minerals. Samples were then centrifuged, the supernatant was decanted, and the samples were washed with three iterations of DI-H₂O. The isolated kerogen was transferred to a combusted pyrex vial in DI-H₂O and freeze-dried to remove all moisture prior to analysis.

3.3. Isotopic analyses

The isotopic composition ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$) of decarbonated powders and kerogen isolates was measured on a Costech™ ECS 4010 Elemental Analyzer coupled to a Thermo Finnigan™ MAT253 continuous flow isotope-ratio mass spectrometer housed in IsoLab at the Department of Earth & Space Sciences, University of Washington. Combustion was carried out with 20 ml O₂ at 1000 °C. A magnesium perchlorate trap was used to remove water from the gas stream. Isotopic measurements were standardized against three in-house standards (two glutamic acids “GA1” and “GA2”, and dried salmon “SA”), which are calibrated to international reference materials USGS40 and USGS41. An aliquot of the Neoproterozoic Mt. McRae Shale was analyzed as an in-house standard to test long-term precision. Isotopic data are reported in delta notation relative to air for nitrogen and Vienna PeeDee Belemnite (V-PDB) for carbon.

Analytical blanks resulting from combustion were monitored and subtracted from nitrogen data; blanks were negligible for carbon measurements. Average analytical accuracy of $\delta^{15}\text{N}$ among individual runs, based on in-house standard “GA1” was $-0.03 \pm 0.19\text{‰}$ (1σ). Accuracy of $\delta^{13}\text{C}_{\text{org}}$ measurements based on in-house standard “SA” was $-0.05 \pm 0.07\text{‰}$ (1σ). The average analytical

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