As a key nutrient, nitrogen can limit primary productivity and carbon cycle dynamics, but also evolutionary progress. Given strong redox-dependency of its molecular speciation, environmental conditions can control nitrogen localization and bioavailability. This particularly applies to periods in Earth history with strong and frequent redox fluctuations, such as the Neoproterozoic. We here report on chlorophyll-derived porphyrins and maleimides in Ediacaran sediments from Oman. Exceptionally light δ^{15}N values (< −10‰) in maleimides derived from anoxygenic phototrophs point towards ammonium assimilation at the chemocline, whereas the isotopic offset between kerogens and chlorophyll-derivatives indicates a variable regime of cyanobacterial and eukaryotic primary production in surface waters. Biomarker and maleimide mass balance considerations imply shallow euxinia during the terminal Ediacaran and a stronger contribution of anoxygenic phototrophs to primary productivity, possibly as a consequence of nutrient 'lockup' in a large anoxic ammonium reservoir. Synchronous δ^{13}C and δ^{15}N anomalies at the Ediacaran–Cambrian boundary may reflect one in a series of overturn events, mixing ammonium and isotopically-light DIC into oxic surface waters. By modulating access to nitrogen, environmental redox conditions may have periodically affected Ediacaran primary productivity, carbon cycle perturbations, and possibly played a role in the timing of the metazoan radiation across the terminal Ediacaran and early Cambrian.

Keywords: ediacaran, ammonium, porphyrin, nutrient, nitrogen, animal evolution

INTRODUCTION

An increase in algal diversity during the Ediacaran (Knoll et al., 2006) and the advent of metazoan organismic complexity (Love et al., 2009) have traditionally been attributed to enhanced oxygen availability (e.g., Catling et al., 2005) or the demise of widespread marine sulfidic conditions (e.g. Cohen et al., 2009) toxic to complex eukaryotes. But the realisation that basal metazoan metabolism can proceed under exceedingly low oxygen partial pressures (Mills et al., 2014), a limited spatial extent of pervasive euxinia (Reinhard et al., 2013) and a slow oxygenation that continued into the early Paleozoic (Sperling, 2015) warrant revisiting these hypotheses. Only recently have researchers begun to examine the role of marine redox conditions in controlling the abundance of essential
nutrients that could have retarded or stimulated evolutionary processes. While an increase in bioavailable phosphorus likely fueled the rise of eukaryotic algae to ecological significance during the Cryogenian (Brocks et al., 2017), P/Fe ratios in iron formations (Planavsky et al., 2010), P in fine-grained sediments (Reinhard et al., 2017) and an abundance of late Neoproterozoic peritidal phosphate deposits (Brasier, 1999) suggest that phosphorus was likely widely bioavailable in the Ediacaran ocean. In terms of understanding the role that bioavailable nitrogen has played during the later Neoproterozoic, most studies have focused on measuring bulk δ15N values (e.g., Ader et al., 2014; Zhang et al., 2017; Wang et al., 2017; Wang et al., 2018a,b; Chen et al., 2019) yet there are limits to the amount of information that can be gained from bulk δ15N signals. Here we aim to address this limitation by studying compound-specific δ15N signals.

Repeated imbalance of the Neoproterozoic marine carbon cycle is evident from frequent and extreme stable carbon isotope fluctuations recorded in Ediacaran carbonates and kerogens (e.g., Halverson and Shields-Zhou, 2011), yet relatively little is known about Neoproterozoic nitrogen cycling (Ader et al., 2014) or its availability as a potentially limiting nutrient. In modern oceans, the carbon and nitrogen cycles are tightly coupled through biological dependence on the fixed inorganic nitrogen species nitrate (NO₃⁻) and ammonium (NH₄⁺), which frequently limit primary productivity (Falkowski and Godfrey, 2008). The primary source of these nutrients is the cyanobacterial fixation of dissolved N₂, but the subsequent fate and transformation of nitrogen species is strongly dependent on environmental redox conditions (Canfield et al., 2010), thereby implying a tight connection between ecosystem diversity, environmental conditions and biogeochemical cycling. In particular the Neoproterozoic Era witnessed strong water column redox gradients and temporal fluctuations thereof (Li et al., 2010; Sperling et al., 2013). This has been recorded by a notable instability in the secular stable carbon isotope curve (e.g., Halverson and Shields-Zhou, 2011), with many anomalies and excursions that may reflect chemocline instability (e.g., Ji et al., 2008) on shorter time scales or oxidative events (Rothman et al., 2003). One of these, the largest recorded negative carbon isotope anomaly, can be traced globally (Grotzinger et al., 2011) and occurred during deposition of the Shuram Formation in the South Oman Salt Basin (Fike et al., 2006). During such redox-driven perturbations, the speciation of fixed nitrogen and the nitrogen cycle would have been vulnerable to environmental factors. Ediacaran redox variability could thus have indirectly exerted a significant control on nitrogen nutrient availability and the marine carbon cycle, as well as on ecosystem structure and evolution.

The stable nitrogen isotopic composition of sedimentary organic matter can be used to constrain the nitrogen source as well as isotopic fractionation during assimilation of the precursor biomass (Ohkouchi and Takano, 2014). However, the δ15N value of bulk organic matter represents an amalgamated signal of primary producing bacteria and algae, as well as heterotrophs—all of which fractionate nitrogen isotopes differently during assimilation (Higgins et al., 2008). Nitrogen in sedimentary porphyrins that represent the diageneric product of chlorophylls is not only covalently bound and resistant to diageneric overprinting, but also highly source-specific (Sachs et al., 1999). Yet the sensitivity of porphyrins to geothermal heating precludes their survival in most Precambrian rocks that have experienced deep burial (Baker et al., 1987). The South Oman Salt Basin (SOSB; Figure 1) hosts one of the most complete and thermally best preserved Ediacaran sedimentary sequences (Figure 2; Fike et al., 2006; Amthor et al., 2003; Grosjean et al., 2009) that was initially deposited under open marine conditions (Nafun Group) and subsequently in a restricted but marine sed epicratonic basin (Ara Group), witnessing periodic transgressive cycles that led to the deposition of six (A0–A5) shallow water carbonate-evaporite couplets (Amthor et al., 2003; Mattes and Conway-Morris, 1990). These are well developed on the southern carbonate platform (Figure 1), with carbonate ‘strings’ sandwiched between sulphate and halite evaporites, but form a more continuous carbonate platform on the eastern flank. For more details of the geology of the SOSB the reader is referred to (Gorin et al., 1982) or (Loosveld and Terken, 1996). An ash bed in the A4 unit of the Ara Group was U-Pb dated at 541 ± 0.13 Ma (Bowring et al., 2007) and contains a δ13C_carbonate excursion that marks the Precambrian-Cambrian boundary. Rifting around 543 Ma opened up a deeper sub-basin (Athel Basin) that hosts organic rich fine siliciclastics of the U Shale and Thuleiat Fm, as well as the somewhat enigmatic Athel Silicilite, which all were deposited synchronously with the platform A4 carbonate-evaporite unit (Figures 1, 2) and thus also record the Ediacaran–Cambrian boundary. The Athel Fm (or, Al Shomou silicilyte) is a thick, finely laminated and organic rich quartz deposit deposited in deep waters, which stands in marked contrast to other Neoproterozoic silica sinks that are largely restricted to peritidal settings (Stolper et al., 2017). However the carbonates of its laterally equivalent shallow water facies appear to lack authigenic chert (e.g., Schröder et al., 2005; Stolper et al., 2017). To date, the origin and uniqueness of this formation remain debated (Ramsay et al., 2013; Al Rajaibi et al., 2015; Stolper et al., 2017). We here report on porphyrins and maleimides recovered from basinal Ediacaran sediments of the South Oman Salt Basin and discuss their stable nitrogen isotope values in the context of biological assimilation pathways and different nitrogen reservoirs in the Ediacaran ocean.

**METHODS**

Cutting aliquots weighing between ca. 3 and 20 g (Supplementary Table S1) were powdered in a stainless steel puck mill and solvent extracted with dichloromethane/methanol (DCM/MeOH, 9:1) in a Dionex Accelerated Solvent Extractor (ASE) device. Asphaltenes were precipitated from the resulting bitumen extracts using n-pentane. Asphaltene-free fractions were treated with activated copper in order to remove elemental sulfur and separated into saturated hydrocarbons, aromatic hydrocarbons and a polar fraction by open column liquid chromatography over silica gel, eluting sequentially with
n-hexane, n-hexane/DCM (1:1) and DCM/MeOH (1:1). The aromatic and polar fractions were further fractionated on a silica gel column to afford subfractions enriched in nickel and vanadyl porphyrins, respectively, by elution with DCM (Grice et al., 1996). Quantification of porphyrins was carried out on these enriched fractions using a UV-visible spectrophotometer as described in more detail elsewhere (Grosjean et al., 2004). While nickel porphyrins were not detected, vanadyl porphyrin concentrations were measured from visible spectra using an extinction coefficient of 31.6 L mmol^{-1} cm^{-1} at 574 nm (Buchler et al., 1971; Mackenzie et al., 1981).

The porphyrin-enriched fractions were dissolved in DCM/MeOH (1:4 vol.) and analyzed on a Thermo Finnigan LCQ system fitted with a Hypersil BDS C18 column (4.6 × 150 mm) coupled to a UV photospectrometer and operated in full scan mode: m/z 400–1,500. During liquid chromatography samples were eluted at 0.8 ml/min with a concentration gradient from 100% MeOH (containing 0.1% formic acid) at t = 0–90% MeOH (containing 0.1% formic acid), 10% DCM at t = 15 min. Subsequently pure MeOH (containing 0.1% formic acid) was eluted for 10 further minutes.

A detailed procedure of the nitrogen isotope analysis of maleimides was described in (Chikaraishi et al., 2008) and is briefly described below. Porphyrin fractions were oxidized to maleimides using a 1:1 (v/v) mixture of 10% aqueous chromic acid and 15% aqueous H2SO4 at 0°C for 1 h and then at room temperature for 1 h (Nomoto et al., 2001). It was shown that this procedure involves no isotopic fractionation (Chikaraishi et al., 2008). Maleimides were extracted with benzene (5 x) from the solution. The extracts were then methyl-esterified and analyzed by GC-MS for screening. The nitrogen isotopic composition of maleimides was determined by GC-C-IRMS using an Agilent 6890N GC fitted with an Ultra-2 capillary column (25 m, 0.32 mm i.d., 0.52 µm film thickness) coupled to a Thermo Finnigan Delta Plus XP IRMS. The analytical error of repeated measurements was consistently better than 0.5‰. This number represents the average of analytical errors (1 sigma) of various in-house synthesized maleimide injections (also see Chikaraishi et al., 2008). The δ15N values of these maleimides were independently determined at JAMSTEC on an EA/IRMS (described in Isaji et al., 2020) that was calibrated with IAEA authentic standards. Methyl-isobutyl-maleimides were below the limit of reliable analysis.

Bulk nitrogen isotope values shown in Figure 2 (δ15Norg) and discussed in the context of the synchronicity of the δ13C and δ15N signals across the Ediacaran/Cambrian boundary derive from Chapter 4 in (Fike, 2007) and were determined at MIT on organic extracts (bitumens) in order to avoid falsification of the bulk organic δ15N signal by nitrogen adsorbed on clay particles. Although likely to be offset from bulk δ15N values, for samples of a similar range of moderate thermal maturity like the ones studied here, such offsets are likely small (Stueeken et al., 2017) and should not impact ensuing interpretations, especially if solely used to indicate stratigraphic trends (Figure 2). Bitumens were recovered by solvent extraction (dichloromethane/methanol 9:1 in a Dionex Accelerated Solvent Extractor), as described in (Fike, 2008), and the indigeneity of the bitumen was tested and asserted using biomarkers and stable isotope patterns. Bitumens were weighed into tin cups and flash combusted at 1,060°C in a Carlo Erba NA1500 Elemental Analyser fitted with an AS200 autosampler. The resulting gas, reduced to N2, was analyzed in continuous flow mode using a Delta Plus XP Isotope Ratio Mass Spectrometer. Nitrogen isotope values are reported in units of per mil relative to Air after calibration using international standards and in-house references interspersed with the analysed samples (NBS-22, Acetanilide and Penn State kerogen).

Bulk δ15N values shown in Figure 5 and used for the calculation of ε values were determined at the Max-Planck-Institute for Biogeochemistry on kerogen isolates that were obtained after digestion of carbonates and silicates using aqueous HCl and HF, respectively. Despite an expected slight offset to whole-rock bulk δ15N values, for the here studied unmetamorphosed rocks, both δ15Nkerogen as well as δ15Nbulk should be good approximations of δ15Nbiomass (Stueeken et al., 2017). Homogenized kerogen powders, weighed into tin cups, were flash combusted in an NA 1110 elemental analyser (CE Instruments) coupled to a Delta-Plus XL IRMS (Thermo Finnigan) via a ConFlow III. Nitrogen isotope values (averages of duplicate measurements) are reported in units of per mil relative to Air after calibration using in-house reference standards acetanilide (δ15N = −1.51 ± 0.1 permil and caffeine (δ15N = −15.46 ± 0.1 per mil). For further details of this method see (Werner and Brand, 2001).
RESULTS AND DISCUSSION

Intact Preserved Neoproterozoic Porphyrins

LC-UVvis and LC-MS revealed the presence of intact porphyrin molecules in 18 of the 27 studied samples, with only vanadyl-complexed species and both DPEP (deoxophylloerythroetioporphyrins) and Etio (etio porphyrins) structures being present (Figure 3), which are characterised by a closed or opened pentacyclic ring, respectively. Given the conversion of DPEP to Etio during thermal maturation (Baker et al., 1987), we conclude that the observed VO-porphyrin dominance throughout the Ediacaran SOSB sedimentary sequence (Table 1) is not due to thermal destruction of the generally more labile Ni-porphyrins (Baker et al., 1987) but rather points to environmental conditions: sulphilic by nucleation on elevated levels of dissolved organic matter as a consequence of strongly enhanced heterotrophy (Ferris et al., 1988).

The detection of a wide range of VO-porphyrins, including structures > C135, in all of the other stratigraphic units indicates an original input of both chlorophyll-a (Chl-a) and bacteriochlorophylls (BChl), including such structures adapted to light intensities at greater water depths and typically biosynthesized by anoxygenic phototrophs inhabiting chemoclines. To allow for their stable isotopic analyses, whole porphyrin fractions were oxidized to GC-amenable maleimides in the laboratory (Figure 2). This process involves no isotopic fractionation (Chikaraishi et al., 2008) and the retention of characteristic alkylation patterns allows for the recognition of precursor-product relationships. Structural and isotopic studies have previously shown that maleimides with a methyl-ethyl substitution pattern (MEM) are principally derived from Chl-a and thus largely representative of carbon and nitrogen fixation in surface waters, whereas both methyl-n-propyl (MPM) and methyl-isobutyl maleimides (MBM) largely derive from the same (Naeher et al., 2013) Chlorobi-derived BChl-c, BChl-d or BChl-e molecular precursors (Grice et al., 1996) that are indicative of processes occurring in anoxic waters below a chemocline.

Nitrogen Isotopes and Nutrient Assimilation in Surface Waters: Cyanobacteria and Algae

By knowing the stable nitrogen isotopic fractionation that occurs during porphyrin biosynthesis, the original composition of precursor biomass ($\delta^{15}N_{\text{biomass}}$) can be reconstructed from $\delta^{15}N_{\text{porphyrin}}$. By now several studies have focused on this biosynthetic fractionation ($\epsilon_{\text{por}} = \delta^{15}N_{\text{biomass}} - \delta^{15}N_{\text{porphyrin}}$) and found that eukaryotic algae typically fractionate by 5–7‰ (Kennicutt et al., 1992; Sachs, 1997; Sachs et al., 1999; Sachs and Repeta, 1999; Sigman et al., 2009; Higgins et al., 2011) meaning that the pigments are depleted in 15N relative to biomass. Negative epsilon values of freshwater cyanobacteria
(Higgins et al., 2011; i.e. porphyrins heavier than biomass by \(\sim 10\%\)) are irrelevant to this study given that a marine depositional environment is well constrained for the studied deposits, whereas marine cyanobacteria tend to be characterized by exceedingly low \(\varepsilon_{\text{por}}\) values around 0\% (Higgins et al., 2011). The variability of \(\varepsilon_{\text{por}}\) values appears to be independent of phylogeny (Higgins et al., 2011) and, because \(\varepsilon_{\text{por}}\) reflects intracellular partitioning of N isotopes downstream of glutamate, it is also independent of N substrate (Higgins et al., 2011, 2012). In the marine realm Chl-a, which is the principal molecular precursor to MEM, is predominantly biosynthesized by eukaryotic algae and cyanobacteria. Hence, when reconstructing \(\delta^{15}N_{\text{biomass}}\) from \(\delta^{15}N_{\text{porphyrin}}\) values we must consider both end-member options.
In the studied SOSB samples, surface water derived MEM that principally reflect Chl-a exhibit δ¹⁵N values ranging between –5.2‰ and +7.2‰ (Air) (Figure 5). If these melaninides were derived 100% from cyanobacteria, an identical range of values could be reconstructed for the bulk precursor biomass. Given an average δ¹⁵N value of +0.7‰ for dissolved marine N₂ and the fact that the nitrogenase enzyme typically fractionates by 0–2‰ (εassimilation, Higgins et al., 2011; Bauersachs et al., 2009), the biomass of diazotrophic marine cyanobacteria should carry average values around –1.3‰ (Higgins et al., 2011) and should not be lighter than ~2‰ (Higgins et al., 2012). This implies that the lighter range of observed MEM values (i.e., those between ~5.2‰ and ca. ~2‰) cannot be attributed to nitrogen fixing cyanobacteria utilising the common and widespread Mo-based nitrogenase enzyme. These ¹⁵N-depleted values may reflect the cyanobacterial use of a different substrate, a (partial) eukaryotic source of MEM or the activity of ‘alternative’ (i.e., Fe- or V-based) nitrogenases. The latter may have been more active under Mo-scarce conditions, as possibly induced by strong euxinia, and fractionate more strongly during nitrogen fixation, leading to lower δ¹⁵N values (Zhang et al., 2014). Under the assumed environmental conditions, which will be discussed in more detail further below, such alternative nitrogenases could indeed have been relevant. However the role that such alternative nitrogenases have generally played in the geological past is unknown and debated, and it remains unresolved when they evolved (Boyd et al., 2011; García et al., 2020). As will also be discussed in more detail further below, we consider the cyanobacterial use of different substrates—nitrate or, more likely, ammonium—as the most plausible source of the observed light isotopic values. Despite typically higher positive environmental δ¹⁵Nnitrate values that are a consequence of microbial water-column denitrification (Sigman et al., 2009), a stronger fractionation during assimilation can generate cyanobacterial δ¹⁵Nbiomass values as light as ~5.3‰ (corresponding to εassimilation of 10.2‰, Higgins et al., 2012). Alternatively, cyanobacterial assimilation of ammonium may be considered, which can explain δ¹⁵Nbiomass < 2.0 and lead to values as low as ~5.0‰ (εassimilation of 13.9‰) in Anabaena (Macko et al., 1987). In principle, the full range of δ¹⁵NMEM can plausibly be explained by a sole cyanobacterial source of primary produced organic matter in surface waters of the SOSB. Nevertheless, the studied deposits are not low in eukaryotic steranes, indicating that algae did provide a contribution to fossilized biomass.

Assuming a 100% contribution of eukaryotic algae to MEM, on the other hand, the precursor biomass can be reconstructed to δ¹⁵N values between ~0.2 and 12.2‰ (εpor = ~5 ± 2‰, Sachs et al., 1999; Higgins et al., 2011). The heavier range of these values would be typical for nitrate-assimilating eukaryotic algae and zooplankton (e.g., Minagawa and Wada, 1984; Sigman et al., 2009) but these processes are incompatible with observed values around 0‰. Here again, the lighter range of values can be achieved when algae assimilate ammonium (εassimilation of ~6.7‰ to +7.2‰; average ~0.92 ± 3.88‰; data from Table 1 in Higgins et al., 2011). Taking into account that we need to find an explanation for δ¹⁵NMEM between ~5.2‰ and ca. ~2.0‰ that likely cannot be attributed to diazotrophic cyanobacteria or to nitrate-assimilating algae, it appears likely that ammonium may have played a relevant role as a nitrogen substrate for Ediacaran primary producers, as will be discussed in more detail below.

Apart from allowing for the tentative reconstruction of the main nitrogen substrates used during assimilation, the wide range of observed values likely suggests that surface waters were inhabited by a mixed population of diazotrophic cyanobacteria, nitrate- or ammonium-assimilating cyanobacteria and eukaryotic algae. This is corroborated by εpor values (kerogen-MEM)—i.e. Δδ¹⁵Nkerogen–MEM that can yield further insight to the source of biomass under the assumption that δ¹⁵Nbiomass ≈ δ¹⁵Nkerogen. In organic-rich sediments, such as the here-studied SOSB rocks (with total organic carbon [TOC] values between 1.6 and 10.4%: Table 1), δ¹⁵Nkerogen is considered to faithfully reflect δ¹⁵Nbiomass (Robinson et al., 2012). The SOSB rocks (early-middle oil window) have never seen the advanced stages of thermal maturation during which δ¹⁵Nkerogen values are significantly altered (Boudou et al., 2008). With the previously discussed knowledge—and under exclusion of freshwater cyanobacteria—the εpor values can be used to tentatively differentiate between marine cyanobacterial and marine algal primary production (Higgins et al., 2011, 2012). The Δδ¹⁵Nkerogen–MEM values obtained on SOSB samples range from ~3.82 to +8.79 (Figure 5; Table 2), where the higher values are most likely characteristic of eukaryote-dominated primary productivity in surface waters (Higgins et al., 2011). This is not surprising, since a rise of mostly green algae (Hoshino et al., 2017) to ecological dominance was recorded at the onset of
the Ediacaran (Brocks et al., 2017; van Maldegem et al., 2019) and C27–C29 steranes are prominently present in all studied SOSB samples (Grosjean et al., 2009). The negative εpor values observed in some samples, however imply primary productivity that is strongly shifted towards marine cyanobacteria (Higgins et al., 2011). While overall algae dominated marine productivity during the Ediacaran, the range of Δδ15Nkerogen–MEM values observed here suggests that fluctuations in the composition of the primary producing community occurred during the course of the Ediacaran with periodic return to (cyano)bacterial dominance. In broad terms, this is in agreement with a strikingly large variation of bacterial hopanes over eukaryotic steranes observed throughout the Ediacaran (Brocks et al., 2017; Pehr et al., 2018; van Maldegem et al., 2019), which led to the suggestion that on regional scales primary productivity was likely modulated by local determinants such as nutrient supply (Pehr et al., 2018). It is also consistent with distributions of carotenoid pigments (Cui et al., 2020).

**Nitrogen Isotopes and Nutrients at the Chemocline: Ammonium Assimilation**

In contrast to MEM, deriving from cyanobacterial or algal Chl-a in surface waters, MPM is thought to largely derive from anoxygenic phototrophs thriving at a deeper chemocline. In contrast to MBM, which can only derive from anoxygenic phototrophs, but whose abundances were too low to allow for the reliable determination of δ15N values in the here studied samples, MPM can theoretically represent a mixture of anoxygenic phototroph-derived MPM and an additional MPM-component deriving from Chl-a by phytol ester hydrolysis and reduction of the resulting C-3 acid (Baker et al., 1987; Verne-Mismer et al., 1986). In principle, the relative contribution of anoxygenic phototrophs engaging in the rTCA cycle for carbon fixation to the pool of fossil MPM can be recognized on the basis of 'heavy' δ13C values. Yet this was not achieved in the present study due to chromatographic co-elution: although we managed to purify the samples sufficiently to allow for the chromatographic baseline separation of individual maleimides from other nitrogen-bearing compounds, we could not achieve a baseline separation from other carbon-containing molecules. Nevertheless, in practical terms MPM and MBM seem to largely derive from the same biological precursors, which has been confirmed in multiple individual instances where MBM and MPM concentrations are linearly correlated with R² values of 0.95–0.99 (Naheer et al., 2013, 2015), confirming that these compounds either share the same origin or that populations of source bacteria thrive under the same, highly specific conditions.
environmental conditions (Naeher et al., 2013). In samples of the Permian Kupferschiefer, (Grice et al., 1997), found MPM to be isotopically similar to MBM: with a simple mixing model of two samples characterized by $\delta^{13}$CMBM of $-15.4$‰ and $-14.7$‰, $\delta^{13}$CMPM of $-17.0$‰ and $-17.3$‰ and $\delta^{13}$CMEM of $-26.2$‰ and $-25.9$‰ (data from Table 3 and from Figure 8 in Grice et al., 1997) we can reconstruct that not more than $14.8$–$23.2$% of all MPM in the Kupferschiefer samples (Grice et al., 1997) derives from a different biological source, implying that MPM sufficiently faithfully represents anoxygenic phototrophs.

Characterized by $\delta^{15}$N values of $-5.1$‰ to $-13.0$‰, MPM in the here studied SOSB samples, largely reflecting nitrogen assimilation at the chemocline, carry some of the lightest biological stable nitrogen isotope values ever reported (Figure 5). These numbers systematically exclude either diazotrophy, which is rare in anoxygenic phototrophs (Madigan, 1995), or the assimilation of nitrate. Some cyanobacteria assimilating ammonium are known to fractionate strongly ($\varepsilon_{\text{assimilation}}$ of $13.9$‰, Macko et al., 1987) but cyanobacteria tend to produce significantly more MEM than MPM and rarely generate $\delta^{15}$Nbiomass $< -5$‰ (nota bene that alternative nitrogenases may generate $\delta^{15}$Nbiomass as low as $-7$ or $-8$‰; Zhang et al., 2014), and hence even lighter porphyrins. Unfortunately, our knowledge of nitrogen isotope fractionation during assimilation and porphyrin biosynthesis by anoxygenic phototrophs is highly limited. As a best approximation, it has been shown that Rhodobacter capsulatus, a purple non-sulfur bacterium, fractionates by $0.8$–$1.8$‰ ($\varepsilon_{\text{assimilation}}$) during photoautotrophic and photoheterotrophic growth on N$_2$, whereas these values increase to $10.6$ and $12.4$‰ during photoheterotrophic growth with NH$_4^+$ (Beaumont et al., 2000). Porphyrins synthesized during growth on ammonium were depleted relative to biomass ($\varepsilon_{\text{por}}$) by another $8.6$–$10.9$‰, leading to BChl-a as light as $-21.0$‰ (Beaumont et al., 2000) despite much heavier biomass. Hence the presence of this process would never be visible in bulk $\delta^{15}$N values of fossil organic matter. We conclude that the most likely explanation for observed light $\delta^{15}$NMPM values in the SOSB lies in a scenario involving assimilation of ammonium (Higgins et al., 2011, 2012; Vo et al., 2013) that likely accumulated in deep anoxic waters,

Table 2 | Stable nitrogen isotopic composition of kerogen and maleimides in studied samples.

| Unit     | Sample     | Depth min (m) | Depth max (m) | $\delta^{15}$N (ker) | $\delta^{15}$N maleimides (%) | $\varepsilon_{\text{por}}$ (Ker–MEM) |
|----------|------------|---------------|---------------|---------------------|------------------------------|-----------------------------------|
| U Shale  | OMR006     | 1,527         | 1,650         | 2.7                 | 1.1                          | -8.8                              |
| U Shale  | OMR007     | 1773          | 1872          | 2.8                 | 1.5                          | -5.1                              |
| U Shale  | OMR014     | 2,420         | 2,460         | 3.4                 | 7.2                          | -10.5                             |
| Thuleiat | OMR021     | 1,417.5       | 1,483         | 3.2                 | 1.0                          | -9.3                              |
| U Shale  | OMR025     | 1,751         | 1,833         | 3.1                 | -5.2                         | -13.0                             |
| Shuram   | OMR026     | 1,905         | 1,940         | 5.20                | -3.6                         | n.a                               |

FIGURE 6 | Preservation of porphyrins and mass balance of autotrophy. (A) Porphyrin abundances are a function of preservation and thermal maturity (based on the hopanoids Ts and Tm; see main text). VO-porphyrins are systematically absent from the Athel Fm (red symbols) despite a suitable thermal maturity, pointing to strongly differing ecologies or environmental conditions. (B) Isotopic mass balance calculations ($^{13}$C for the Kupferschiefer after Grice et al., 1997: Supplementary Table S3, $^{15}$N for the SOSB: Table 2) on the basis of comparing the isotope value of summed MMM and EEM to those of MEM and MPM end members can hint towards the relative proportion of oxygenic vs anoxygenic phototropic biomass. SOSB primary productivity during deposition of the U-shale (n = 3) was shifted towards a markedly higher contribution of anoxygenic phototrophs. Negative values for some Kupferschiefer samples, i.e. $\delta^{13}$CMEM+EEM beyond the 0–100% spectrum spanned by $\delta^{13}$CMEM and $\delta^{13}$CQFPE, likely derive from analytical error.
similar to what is frequently observed in modern stratified meromictic lakes such as Lake Cadagno and Lake Kaiike (e.g., Ohkouchi et al., 2005, 2007; Halm et al., 2009). Although not providing a direct analog in terms of salinity and the presence of benthic phototrophic mats that were likely absent in deeper facies of the SOSB, stratified Lake Kaike contains relevant amounts of dissolved ammonium below a chemocline inhabited by green and purple sulfur bacteria, whose $BChl$ is characterized by similarly low $\delta^{15}N$ values to those found in the SOSB (Ohkouchi et al., 2005, 2007). At present, such a scenario provides the most plausible explanation for the anomalously light nitrogen isotopes encountered in MPM of the studied SOSB samples.

**Isotope Mass Balance Suggests Significant Anoxygenic Productivity**

Me, Me- and Et-maleimides (MMM, EEM) are considered as source-unspecific since they can potentially derive from both $Chl$-a and from $BChls$. In modern, predominantly aerobic marine ecosystems, the relative proportion of anoxygenic phototrophs dwindles in comparison to oxygenic primary producers (Raven, 2009), which is evident from the molecular sedimentary remnants of phototrophic organisms: bacteriochlorophyll-derived porphyrins and farnesane are much less common than $Chl$-a derived porphyrins and phytol hydrocarbons. Since independent of the nitrogen substrate used, MMM and EEM represent a mixture between a purely anoxygenic phototrophic source on one hand ($BChl$) and a mostly oxygenic phototrophic source ($Chl$-a) on the other, their stable isotopic composition—be it nitrogen or carbon—in comparison to those of MEM and MPM, can be used to establish a rough mass balance of phototrophic primary productivity.

Under modern aerobic conditions, the $\delta^{15}N$ value of MMM + EEM should lie close to that of MEM, given dominant oxygenic photosynthesis in surface waters, and such a constellation of values is even observed during episodes of mild euxinia (Figure 6), when reconstructing the predominant source of MMM and EEM using their $\delta^{13}C$ values in samples of the Permian Kupferschiefer (using data from Grice et al., 1997). Results from the SOSB that are based on $\delta^{15}N$ suggest that MMM and EEM are isotopically much more similar to MPM. Given the uncommon light $\delta^{15}N$ values of MPM that we attribute to chemocline-dwelling phototrophs, we posit that a significant portion of MMM and EEM is predominantly derived from $BChls$ biosynthesized at the chemocline, and hence from anoxygenic phototrophs (Figure 6B). This appears to contradict the relatively low abundance of VO-porphyrins > C$_{33}$ (Figure 3), but it must be kept in mind that the fate of $Chls$ after demetallation is highly complex and that many different, yet uncharacterized chelates can form that evade characterization (Gueneli et al., 2018). Even if MPM do not constitute a pure anoxygenic phototrophic end member but contain some non-$BChl$ sourced portion (e.g., up to ca. 25% as calculated for the Kupferschiefer), the SOSB ecosystem would still be remarkably different from modern oceans in that a sizable portion of productivity was performed by anoxygenic phototrophs in deeper waters. Considering the possibility of a preservational bias, a larger proportion of $Chl$-a produced in surface waters may indeed be oxidatively degraded than $BChl$ produced at the chemocline, thereby artificially shifting the balance of preserved porphyrins towards anoxygenic phototrophs. However, episodic euxinia with a shallow chemocline was corroborated for deep-water facies of the SOSB by the presence of the molecular markers okenane and chlorobactane (French et al., 2015; Roussel et al., 2020). In the deep-water depositional environments of the SOSB, the observed carotenoid pigments cannot derive from benthic mats but must represent planktonic purple sulfur bacteria and the green strains of green sulfur bacteria, respectively—microbes requiring access to reduced sulfur and with high light requirements. In the absence of isorenieratane that derives from brown strains of green sulfur bacteria, and irrespective of the generally lesser ecological relevance of green sulfur bacteria prior to the Phanerozoic (Cui et al., 2020), these data point to persistent stratification and a shallow chemocline (<25 m, Brocks and Schaeffer, 2008). Given the short transit through oxygenated surface waters, any preferential degradation of surface-derived $Chl$ may have been minimal. From this perspective the reconstructed mass balance would not require significant correction to account for preservational biases. On the other hand one could argue that remineralisation rates tend to be highest in the upper water column, where organic export fluxes are highest, whereas the maintenance of euxinic conditions requires a particularly high remineralisation rate in shallow waters in order to maintain anoxia. From this perspective a relevant preservation bias may be given. Nevertheless if such biases were large, they should have similarly affected the Kupferschiefer samples that are not shifted towards an anoxygenic phototrophic source of MMM and EEM despite only mild euxinia (Grice et al., 1997). Most recently, a study of fossil aromatic carotenoids in terminal Ediacaran SOSB sediments (Roussel et al., 2020) reported an elevated proportion of structures that were likely sourced by cyanobacteria rather than by anoxygenic phototrophs (Cui et al., 2020). However, the taphonomy of carotenoids is complicated by sulphidic preservation bias, we posit that during the terminal Ediacaran a relevant portion of photosynthetic primary production in the distal facies of the SOSB (Athel subbasin) could have been taking place at the chemocline and not in surface waters.

While such conditions do not exist in modern oceans, the best modern analogue environments are shallow stratified lakes, where anoxygenic phototrophs can indeed dominate primary production (van Gemenden and Mas, 1995), and which are known to develop an ammonium reservoir in deeper anoxic waters (Ohkouchi et al., 2005). In trying to understand the here presented data, we hypothesize on a model where under persistently stratified conditions, sinking biomass of marine primary producers continuously contributed nitrogen to a deep-water ammonium pool in the SOSB, whose diffusion back up into the mixed zone would have been minimal. This
large pool of reduced nitrogen remained inaccessible to aerobic primary producers inhabiting surface waters. With an exceedingly shallow chemocline, suggested by the biomarkers okene and chlorobactene, the biomass of diazotrophic cyanobacteria containing freshly fixed nitrogen would have rapidly exited the mixed layer, maintaining nitrogen scarcity in surface waters. This in turn would have led to a relative shift in overall primary productivity towards anoxygenic phototrophs inhabiting the chemocline and tapping into the deep pool of reduced nitrogen. In this scenario, the deep-water ammonium that is controlled by the redox structure of the water column represents a 'locked-up' nutrient reservoir capable of modulating primary productivity: under persistently stratified conditions, primary productivity will be throttled, whereas the overturn of such a setting will release abundant nutrients and stimulate surface water productivity.

**Periodic Ammonium Overturn and Nutrient Release**

The Ediacaran–Cambrian boundary in the SOSB not only records a characteristic and well-documented negative δ13C Carm anomaly (Halverson and Shields-Zhou, 2011; Fike et al., 2006; Amthor et al., 2003) but (Fike, 2007) also reported a positive δ15NORG excursion with an exactly synchronous onset, which jumps abruptly from values around 1–3‰ to values close to 10‰ before gradually returning to pre-excursion values (Figure 2). Apart from the perfect synchronicity of their onset, nitrogen and carbon isotopes are not directly correlated (Supplementary Table S2), thereby rather excluding an explanation by coupled ammonium oxidation and methanotrophy (Thomazo et al., 2011). Rather than intense denitrification and depletion of the nitrate reservoir, as seen in modern low-productivity ocean regions (Sigman et al., 2009), we suggest that these heavy nitrogen isotopes may be the result of intense nitrate assimilation, which discriminates against 15N with ~5‰, caused by enhanced productivity following basinal overturn and oxidation of a deep ammonium reservoir. Alternatively, direct cyanobacterial utilization of liberated ammonium—sourced from upwelling or overturn—could result in similar heavy values, as a consequence of Rayleigh fractionation of ammonium during anoxygenic photosynthetic assimilation. Such a situation was observed in meromictic Lake Kaiike (Ohkouchi et al., 2005) and may also provide an explanation for heavy MEM values (Figure 5). In the first scenario, availability of NO3− supplied by nitrification is eventu- ally dependent on oxidant and NH4+ availability. Given persistent oxic surface waters as testified by the δ15N of MEM and overall elevated εpor, we suggest that Ediacaran surface water productivity could have been episodically limited by deep-water nutrient capture during stratified sulfidic conditions, and stimulated by overturn—the observed anomalies at the Ediacaran–Cambrian boundary (Figure 1) representing one such overturn event. Strong environmental redox fluctuations (e.g., Sperling et al., 2013; Li et al., 2010) could have exerted principal control on nitrogen nutrient availability by controlling the N supply pathway, thereby modulating primary productivity on shorter time scales and providing an explanation for the repeated return to cyanobacterial-dominated (Pehr et al., 2018) and mixed ecosystems (Figure 3D) during the Ediacaran. Models have suggested that the Ediacaran transition towards an oxygen-rich ocean-atmosphere system was inhibited or delayed by a need for elevated abundances of fixed nitrogen (Reinhard et al., 2017). The here suggested mechanistic link to redox-driven nitrogen nutrient dynamics may not only solve the timing of the latter, but also provides an explanation for the aberrant Neoproterozoic carbon cycle, while the progressive overturn of 'locked-up' nitrogen around the Ediacaran-Cambrian boundary could have contributed towards the enhanced nutrient requirements of an increasingly complex biosphere.

**CONCLUSION**

Together with previously published accounts of fossil pigments (French et al., 2015; Roussel et al., 2020), the distribution and stable nitrogen isotope composition of vanadyl porphyrins and porphyrin-derived maleimides in sediments of the Ediacaran SOSB is indicative of shallow euxinia. The δ15N values of surface water (Chl-a) derived maleimides likely indicates the presence of both cyanobacteria as well as eukaryotic algae, as confirmed by steroid abundances in SOSB rocks (Grosjean et al., 2009), yet ranges into values that may point towards the use of ammonium as a nitrogen substrate. This notion is strengthened by δ15N of chemoline (BChl) derived maleimides, whose exceptionally light values are best explained by the assimilation of ammonium by anoxygenic phototrophs (Beaumont et al., 2000; Vo et al., 2013), in analogy to the situation in some stratified meromictic lakes (Ohkouchi et al., 2005, 2007). Notably, such information would remain masked by bulk δ15N analyses only. In such modern lake systems, a sizable portion of primary productivity can be shifted towards anoxygenic phototrophs. Using an isotope mass balance of maleimides we reconstruct a similar ecosystem structure for the SOSB and tentatively attribute this currently rare condition to the redox-controlled storage of ammonium-nitrogen in deep waters, which may have been periodically overturned. A coupled negative δ13C and positive δ15N excursion at the Ediacaran–Cambrian boundary (Fike, 2007) may reflect one such overturn event that released 13C-depleted DIC and ammonium into surface waters, where it would be rapidly oxidized to nitrate and subjected to denitrification and algal assimilation. Our data may be explained by redox-controlled nitrogen scarceness in surface waters, which would have restricted eukaryotic, and reduced cyanobacterial activity. Under such conditions access to fixed nitrogen would have exerted fundamental control on phytoplankton community structure and possibly primary productivity (Johnston et al., 2009). Although more investigation is needed, such redox-driven nitrogen limitation may have played a role in delaying the transition to a fully oxygenated atmosphere-ocean system (Reinhard et al., 2017) and possibly the timing for the rise of animals.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.
AUTHOR CONTRIBUTIONS
EG, NO, DF, NS, YK,YC, and RS performed research and analyzed data; CH analyzed and interpreted data and wrote the paper with input from all others.

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