An isotopically light nitrogen reservoir in the ocean: evidence from ferromanganese crusts

E.E. Stüeken¹*, M. Bau²

Abstract

Ferromanganese (FeMn) oxide crusts and nodules in the deep ocean have been studied extensively in the context of critical metals and metal isotope mass balances; however, their role in the marine nitrogen cycle has been unexplored. Here we investigated a suite of hydrogenetic and diagenetic marine FeMn crusts and nodules from the Pacific to determine their isotopic signature and contribution as another N sink from the modern ocean. Our results reveal unusually low δ¹⁵N values down to −12 ‰ in some hydrogenetic crusts, paired with low δ¹³C values in carbonate associated with these crusts and nodules. This pattern is most parsimoniously explained by partial oxidation of ammonium (nitrification) derived from benthic biomass. Nitrification generates isotopically light nitrite, which may adhere to FeMn oxides by adsorption. In contrast, the diagenetic and hydrogenetic nodules are enriched in ¹⁵N/¹⁴N to up to +12 ‰, likely due to retention of ammonium in phyllosilicate minerals. Overall, we conclude that FeMn oxide crusts and nodules are a novel archive of microbial activity that may be preserved in the sedimentary record on Earth and possibly Mars.

Introduction

Ferromanganese (FeMn) oxide deposits in the deep ocean have received increasing attention over the past two decades as they have become recognised as reservoirs of critical metals with potentially economic value (Hein et al., 2000; Lusty et al., 2018). There are three “end member types” of marine FeMn oxide deposits: hydrogenic crusts and nodules that form very slowly (at a rate of only a few mm/Myr) on exposed rock surfaces at the sediment-water interface; diagenetic nodules that form from pore waters within marine sediments around a nucleus such as a rock fragment; and hydrothermal precipitates that may form as plume fallout or within the sediment (e.g., Koschinsky and Hein, 2017, and references therein). Rare earths and yttrium (REY) concentrations and REY patterns can be used to discriminate between these three genetic pathways, which further attests to their distinct fluid sources, growth rates, and formation mechanisms (Bau et al., 2014). One potentially important factor in the formation of these deposits may be microbial activity, but its role is still unclear. Manganese oxidisers have been detected with genomic techniques (Shiraishi et al., 2016). To our knowledge, FeMn oxides have not previously been studied as geological N repositories. To fill this gap, we selected a suite of hydrogenetic and diagenetic FeMn crusts and nodules from the northern, eastern and southern Central Pacific and three hydrogenetic and mixed type hydrogenetic-diagenetic FeMn nodule certified reference materials from the Atlantic and Pacific (see Supplementary Information for a detailed description of the methods employed). Classification as hydrogenetic versus diagenetic is based on the REY concentration and distribution, following the approach outlined in detail by Bau et al. (2014). For further discussion of some of these samples see also Bau et al. (1996), Schier et al. (2021) and Ernst et al. (2022).

Results

We find that FeMn oxide nodules, both diagenetic and hydrogenetic, tend to be enriched in total nitrogen (TN) content by a factor of 2.3 on average and display heavier bulk δ¹⁵N values (+3 ‰ to +12 ‰) compared to the hydrogenetic crusts (−12 ‰ to +3 ‰) (Table S-1, Fig. 1a). In contrast, the hydrogenetic crusts are enriched in total inorganic carbon (TIC) by a mean factor of 2.6 (Fig. 1b). Total organic carbon (TOC) does not vary systematically between crusts and nodules (Fig. 1c), but the hydrogenetic crusts express relatively lower organic carbon isotope values (δ¹³Corg = −27.8 ± 0.6 ‰ versus −22.6 ± 2.0 ‰) (Fig. 2a). Carbonate carbon isotope values (δ¹³Ccarb) do not vary systematically, but all samples fall below −8 ‰ and are thus depleted relative to open marine carbonate which falls near 0 ‰ (Fig. 2b). Our results for the certified reference materials NOD-P1, NOD-A1 and JMn-1 fall within the respective range observed for the other samples (Fig. 1a).

Received 25 October 2022 | Accepted 14 February 2023 | Published 15 March 2023

1. School of Earth and Environmental Sciences, University of St Andrews, Bute Building, Queen’s Terrace, St Andrews, Fife, KY16 9TS, United Kingdom
2. CritMET – Critical Metals for Enabling Technologies, School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany
* Corresponding author (email: ees4@st-andrews.ac.uk)
The nitrogen isotopic composition of some of the hydrogenetic crusts is unusually depleted in $^{15}$N. For comparison, average marine mud from the modern ocean clusters around a mean of $–6\%$ (Tesdal et al., 2013), which reflects the isotopic composition of seawater nitrate – the major nitrogen source for algae that is captured in sediments via biomass burial. However, values in the negative range are rare throughout the siliciclastic rock record (Adet et al., 2016). There are four possible mechanisms that could explain such low $^{15}$N values:

1. Biological nitrogen fixation by alternative nitrogenases. When dissolved N becomes biologically limiting, some microbes are able to convert N$_2$ into ammonium, a process known as nitrogen fixation that is catalysed by the enzyme nitrogenase. Most nitrogenases contain Mo at a catalytic centre, and these so called alternative nitrogenases impart larger fractionations of up to $8\%$ (Zhang et al., 2014). However, it is unlikely that this metabolism caused the low $^{15}$N values in our samples, because the deep ocean is enriched in both nitrate and Mo, meaning that nitrogen fixation is not required, and, if necessary, the more efficient Mo-based nitrogenase would likely be preferred.

2. Dissimilatory nitrate reduction to ammonium (DNRA). Given the high abundance of nitrate in the deep ocean with an isotopic composition of around $+5\%$ to $+6\%$, it is conceivable that the low $^{15}$N values reflect ammonium generated by DNRA, which imparts a fractionation of up to $30\%$ (McCready et al., 1983).

However, this metabolism is unlikely to take place within an environment where Mn(IV) oxides are thermodynamically stable, because Mn has a high redox potential that is not compatible with nitrate reduction (Brookins, 1988).

3. Partial assimilation of either ammonium or nitrate into biomass. It has been suggested that FeMn crusts are populated by microorganisms (e.g., Kato et al., 2019), and these could be fractionating $^{15}$N/$^{14}$N ratios as they uptake nitrate ($\varepsilon = 5–10\%$) or ammonium ($\varepsilon = 14–27\%$) into their biomass (Casciotti, 2009). Nitrate is readily available in seawater (30 μM on average; e.g., Webb, 2021), and ammonium could potentially be supplied by decaying biomass underneath or within the FeMn crust. Both would likely have a starting composition of $+5\%$ to $+6\%$, as observed for marine nitrate and average marine sediments (Tesdal et al., 2013). Hence this mechanism offers a plausible explanation for the $^{15}$N data; however, it does not account for the light $^{15}$N values in the same samples.

4. Partial oxidation of ammonium (nitrification) to nitrite and nitrate. In the oxidising environment of the FeMn crusts, ammonium would likely undergo oxidation. This microbially catalysed reaction produces isotopically light nitrite and later nitrate in a second step, while the residual ammonium becomes enriched in $^{15}$N (Fig. 3). If the oxidation process does not go to completion, perhaps due to diffusion limited O$_2$ migration into the crusts as described in sediments elsewhere (Morales et al., 2014), isotopically light nitrite/nitrate may accumulate and become incorporated into the crust, either by uptake into fresh biomass or by adsorption to the mineral surface (as documented for nitrate by Takematsu et al., 1990). This could plausibly explain the $^{15}$N values of the hydrogenetic crusts. Indeed, nitrifying
organisms of the phylum *Thaumarchaea* have been documented by molecular techniques from several deep marine FeMn oxides (e.g., Kato et al., 2019; Bergo et al., 2021).

It has been suggested that these nitrifying organisms are feeding on trace levels of ammonium dissolved in the deep ocean (Wuchter et al., 2006; Kato et al., 2019). While this appears possible, it would, however, leave the light δ15N values unexplained. Such light δ15N values most likely reflect in situ oxidation of organic matter to dissolved inorganic carbon (DIC) within pore waters. This diagenetic DIC pool would inherit the isotopic composition of local biomass (<−20 ‰, Fig. 2a), such that variable mixing with seawater (δ15N° = 0 ‰) can explain the observed δ15N values between −28 ‰ and −8 ‰ (Fig. 2b). The carbon isotope data are thus evidence for degradation of older biomass from within the FeMn oxides. This biomass is the most likely source of ammonium for nitrification, because the Redfield ratio of average marine organisms dictates that 1 mole of N is released for every 7–10 mole of organic C (Godfrey and Glass, 2011). We note that δ15N of bulk and δ13C values are not directly correlated, but as the isotopically light N and C are likely associated with different minerals and undergo variable mixing with isotopically heavier phases, a correlation cannot necessarily be expected.

Overall, the most plausible scenario for the N-C isotope systematics observed in the hydrogenic FeMn crusts is, therefore, the presence of a benthic biosphere, where older biomass underwent oxidation and nitrification, catalysed by active organisms. Some of the products (including isotopically light nitrite/nitrate) were re-assimilated into fresh biomass and/or adsorbed to mineral surfaces, while the oxidised organic carbon was partly redeposited as carbonate. This interpretation is consistent with biomolecular evidence of nitrifiers from FeMn crusts worldwide (see above). However, it leaves open the question as to what happened to the residual isotopically heavy ammonium. We speculate that in the case of the isotopically lightest hydrogenic FeMn crusts this ammonium was diffusively lost to the water column. This may indicate that the preferential retention of nitrite/nitrate within the FeMn crust was driven by adsorption rather than biological uptake, because the latter would typically prefer ammonium. Nitrite adsorption on FeMn oxides has to our knowledge not been studied systematically, but we note that empirical data from one study suggest concentrations of around 50 μg g⁻¹ of nitrate at equilibrium with seawater (Takematsu et al., 1990), which is consistent with our data.

In the case of the diagenetic and hydrogenic nodules, we also see low δ13C and δ15N values indicative of biomass oxidation; however, δ15N shows no evidence of light nitrite/nitrate retention. Instead, δ15N values of up to 12 ‰ and comparatively high TN abundances may indicate that isotopically heavy ammonium (i.e. the residuum after partial nitrification) was preferentially retained (Fig. 3), possibly due to a higher clay or active biomass content within these samples. Ammonium (NH₄⁺) has a similar ionic radius to K⁺, which allows it to substitute into potassic phyllosilicates during diagenesis (Müller, 1977). Retention of isotopically heavy ammonium in the clay matrix would probably have overwhelmed the proportion of adsorbed isotopically light nitrite/nitrate, such that the bulk average δ15N value of the nodular samples is positive. Further work is needed to test this hypothesis. We also note the systematically higher δ13C values within nodules compared to crusts (Fig. 3a), which likely point towards an ecosystem with different carbon fixation pathways. This interpretation is broadly consistent with a distinct microenvironment with differing nutrient inventories.

**Conclusions**

In summary, our data reveal novel insights into biological processes that take place within FeMn oxide deposits in the deep sea, including biological oxidation of biomass in situ, which led to the formation of isotopically light DIC and nitrite/nitrate (Figs. 3, 4). The latter may be trapped by adsorption to oxide minerals. Our results thus uncover a mechanism for generating a previously unknown repository of isotopically light nitrogen in marine sediments. However, it is unlikely that this repository contributes significantly to the global mass balance of N burial from the ocean. For example, assuming a global average mass accumulation rate of 24.8×10⁹ g for FeMn oxides in the deep ocean (e.g., Ernst et al., 2022) with an average concentration of TN of 57 ± 12 μg g⁻¹ (Table S-1) would lead to a N burial flux of 1.4-1.0⁹ g yr⁻¹. For comparison, the amount of N buried in siliciclastic marine sediments globally with a mean concentration of 560 ± 230 μg g⁻¹ (Johnson and Goldblatt, 2015) at a sedimentation rate of 10¹⁶ g yr⁻¹ (Gregor, 1985) yields an N burial flux of 5.6×10¹⁸ g yr⁻¹ and thus dominates as the major sink. However, our study uncovers a novel archive of microbial activity that may be preserved in the rock record and contribute reconstructions of biological
evolution over Earth history, or serve as a biosignature in Martian settings.

Acknowledgements

EES acknowledges funding from a NERC Frontiers grant (NE/V010824/1). MB acknowledges funding from Deutsche Forschungsgemeinschaft (DFG SPP1833 grant BA-2289/8-1). We thank Claudine Stirling for editorial handling and two anonymous reviewers for constructive feedback that improved the manuscript.

Editor: Claudine Stirling

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2308.

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Figure 4  Environmental sketch. Dead biomass (dotted brown lines) releases ammonium during degradation, which is partially oxidised to nitrite. Some of this nitrite is trapped in FeMn oxides by adsorption and possibly by assimilation into fresh biomass (dotted pale green lines). (a) In hydrogenetic crusts, the residual 15N-enriched ammonium is lost to the water column by diffusion. (b) In diagenetic and hydrogenetic nodules, some of the ammonium is retained in clay minerals, leading to higher bulk δ15N values and TN abundances.

References


