# Abstract

# Introduction

The evolution of trace metal marine chemistry across Earth’s history reflects changes in atmosphere, solid earth and ocean dynamics and perhaps profoundly influenced the evolution of early life (*e.g.,* Glass and Dupont, 2017; Konhauser et al., 2009; Robbins et al., 2016; Zerkle et al., 2005). Ubiquitous biological processes such as photosynthesis, methanogenesis and nitrogen fixation all require trace metals [citations]. Thus, the bioavailability of these metals, and how their concentrations may have changed over time, were likely key regulators on which organisms were favored for future diversification. Marine compositions change as a function of changing inputs and outputs and redox conditions, which are ultimately dictated by solid earth processes and atmospheric chemistry. Efforts to reconstruct trace metal marine concentrations from the rock record will surely shed light on the co-evolution of earth and life. However, before we can begin to interpret trace metal signatures in the rock record, we need foundational understanding of their modern cycles.

Nickel is a bio-essential element for a variety of modern organisms and may have played a surprisingly important role in Earth’s oxygenation, but we have a poor understanding of its marine cycling, even in the modern day. [Sentence about how Ni might have gone from >400 nM optimal for methanogens, to ~200 nM post GOE, which would have not favored methanogens and favored cyanobacteria] [To investigate the importance of this proposed event, we need a good understanding of how Ni cycles in the modern day] The goal of the proposed work is to improve our knowledge of the modern Ni marine cycle and our ability to interpret changes in Ni marine chemistry from the rock record.

## Ni and modern and ancient marine biology

In the modern ocean, Ni is an essential component of seven enzymes that regulate the global C, N, and O cycles (Ragsdale, 2009)(Table of Ni enzyme fig). Diatoms, silica-shelled phytoplankton that produce around 45% of the Earth’s oxygen and comprise ~1% of Earth’s biomass, rely on Ni because they use the Ni-enzymes urease and Ni-superoxide dismutase (Benoiston et al., 2017; Twining et al., 2012). Foraminifera also exhibit a Ni reliance, potentially because of their use of urease as a pH regulator during shell formation (Bachmeier et al., 2002; Munsel et al., 2010; Smith and Goldstein, 2019). Nickel is perhaps most well known as a bioessential metal for methanogens; the Ni-containing enzyme methyl-coenzyme M reductase, catalyzes the final step in every known methanogenesis pathway (Boer et al., 2012; Ragsdale, 2009; Schonheit et al., 1979). This Ni-enzyme also catalyzes the first step in anaerobic oxidation of methane (Scheller et al., 2010).

As one might expect, the marine concentration of Ni has significant implications for the abundance of these organisms, as an essential component of the aforementioned enzymes and a potential toxin. Foraminifera, diatoms, and cyanobacteria all exhibit optimal, Ni limiting, and toxic Ni concentrations (Dupont et al., 2010; Glass and Dupont, 2017; Munsel et al., 2010; Panneerselvam et al., 2018; Schonheit et al., 1979; Smith and Goldstein, 2019; Twining et al., 2012) (Fig XX). For example, Smith and Goldstein (2019) exposed juvenile benthic foraminifera from Little Duck Key, Florida and Sapelo Island, Georgia to varying Ni concentration and observed total foraminifera abundance peaked around 125 nM (although lower [Ni] were not tested for Little Duck Key samples) and a steep drop off in abundance and general increase in shell deformities past this Ni concentration. Clearly, these organisms are highly sensitive to fluctuations in [Ni]. Fluctuations Ni bioavailability would have severe impacts on their abundances.

## Ni abundances and cycling in Modern Oceans

So, what do we know about marine Ni chemistry and its cycling? In the modern ocean, Ni has a nutrient like depth profile with surface depletions around 2 nM and deep-water enrichments around 9-12 nM. (Fig with water column Ni conc). The vertical distribution of Ni may be mediated by diatoms; Ni regeneration is associated with P regeneration in upper waters (*i.e.,* associated with the organic soft parts) and then associated with Si regeneration in deep waters (*i.e.,* association with the biological hard parts) (Archer et al., 2020; Bruland, 1980; Sclater et al., 1976; Twining et al., 2012). Because Ni is not fully depleted in surface waters, it was believed that seawater Ni concentrations were biologically nonlimiting, but recent studies suggest that the remaining surface water Ni is simply not bioavailable (Dupont et al., 2010). Past equilibrium speciation calculations have focused on inorganic ligands and suggest, in seawater at pH 8.2, Ni primarily exists as a free ion (47%) with most of the remaining fraction complexed with Cl or CO3 (34 and 14%, respectively) (Turner et al., 1981). However, the degree of complexation with organic ligands, varies depending on the model used (1 to 90% of the total Ni could be complexed )Depending (Turner and Martino, 2006).

Despite Ni’s biogeochemical importance, we have a poor understanding of its marine cycling, even in the modern oceans. In 1976, Krishnaswami (Krishnaswami, 1976), identified an apparent, substantial marine Ni mass imbalance. If this were true, the ocean would be rapidly depleted in Ni, but there is no evidence for such deviation from steady. However, in the several decades that have followed, we have yet to resolve the apparent imbalance. Currently, our best estimates indicate that Ni sink fluxes from the ocean are twice the size of source fluxes (Ciscato et al., 2018; Gall et al., 2013; Sclater et al., 1976). If we can reconcile the modern marine Ni budget, we can identify the key modern controls of marine Ni cycling. Knowledge of the modern marine cycle will enable robust modelling of the marine Ni cycle over time.

To investigate the imbalance, let us first consider the known components. There are a number of Ni marine budgets now revolving around in the community; I will highlight the sources and sinks that are generally agreed upon. The main source of Ni is [the dissolved load of] rivers which contribute an estimated X to x. Dust is a minor secondary source, with an estimated source flux of XXX to XXX. Only considering these two sources, the total source flux is X to X. Sink fluxes are a little less clear. Fe-Mn deposits are a major sink (X to X). Organic matter constitutes the next largest sink flux (x to X). Euxinic sediments make up a minor component. The total sink flux is then X to X and Yx the source flux.

**Resolving the imbalance**

There are two potential causes of the imbalance: (1) missing fluxes or (2) inaccurate flux estimates, or both. Some of the flux estimates are likely incorrect, but refining those directly is very difficult, and thus we aim here to apply a new constraint to the puzzle. Assuming the ocean is at or near steady state with respect to Ni, the fluxes and the abundance weighted isotopic compositions of the Ni sources and sinks should balance. Therefore, we can use isotope mass balance to constrain the fluxes and Ni marine budget in three dimensions (*i.e.,* mass flux, Ni concentration, and δ60/58Ni, where δ60/58Nisample = (60/58Nisample/60/58Nistandard -1) x 1000‰) (mass balance example fig, colors). To apply this approach, we must know the isotopic compositions of major fluxes. Similar to marine mass budget, there is an isotope mass imbalance as well. The known sinks are isotopically heavier than the sources. The combination of these imbalances points to a significant missing component (or components) or wildly incorrect estimations for the source and sink isotopic compositions. While the isotopic compositions of known sources are reasonably well characterized, the sinks, which are dependent on the isotopic composition of seawater and the sink’s isotope fractionation (Δ60/58Nisolution-output = δ60/58Nisolution - δ60/58Nisink), are difficult to ascertain. Once the major isotope parameters have been identified, we can apply the isotope mass balance constraint, evaluate the flux estimates, and hopefully resolve the mass imbalance.

**Inputs**

The majority of sources have an isotopically lighter composition than oceans (1.44). Dust, which we assume to share the isotopic composition of the continental crust, has a limited isotopic composition, from -0.1 to +0.2‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013). The dissolved load of rivers is isotopically varied, from +0.29 to +1.38‰, with an abundance weighted isotopic composition of +0.9‰ (Cameron and Vance, 2014; Revels et al., 2021). The riverine particulate load is similar to continental curst and isotopically light compared to the dissolved (Revels et al., 2021). The difference in isotopic composition of rivers and continental crust (*i.e.,* the ultimate source of Ni to rivers can be explained by the formation of Fe-oxyhydroxides, a secondary weathering product of ultra mafic to mafic rocks which host the majority of the crust’s Ni (Spivak-Birndorf et al., 2018). Experiments and natural observations indicate that iron oxides sorb isotopically light Ni (Δ60/58Nidissolved-ferrihydrite = +0.35 ± 0.20‰ 2sd (Wasylenki et al., 2015) and Δ60/58Nidissolved-goethite = +0.77 ± 0.23‰ 2sd (Gueguen et al., 2018)) which agrees well with the offset between rivers and continents. As mentioned, a single study proposed that Mn redox cycling provides a significant input of Ni, and is hypothesized to have an isotopic composition of +3‰ (calculated from a monte carlo simulation of the Ni marine budget and qualitatively from sediments they presumed to have undergone the redox cycling process) (Little et al., 2020). In summary, the majority of sources’ Ni isotopic compositions are restricted to a range of -0.1 to 1.38‰ which are generally lighter than seawater (ca. 1.3 to 1.7‰).

**Oceans**

The deep ocean is globally homogenous, with an isotopic composition around 1.3‰ (Archer et al., 2020; Takano et al., 2017; Yang et al., 2020) while the surface ocean varies. The South Pacific (Takano et al., 2017), North Pacific (Yang et al., 2020), and South Atlantic (Archer et al., 2020) all show significant trends towards isotopically heavy values in the surface waters, up to 1.78‰, which are coupled with surface [Ni] depletions down to ca. 2 nM. On the other hand, the Indian sector of the Southern Ocean, which also displays a less pronounced, but similarly systematic surface [Ni] depletion, shows no isotopic enrichment in the heavier isotopes in surface waters (Wang et al., 2019). This discrepancy may be due to regional biology; Archer et al. (2020), hypothesize that the differing dominating species, cyanobacteria or diatoms, between south (diatom dominated) and north (cyanobacteria dominated) of the polar front results in the differing surface water isotopic compositions (Archer et al., 2020). Additional studies in other diatom dominated waters or through culture experiments could further explore this hypothesis.

**Outputs**

Generally, the major sinks appear to be isotopically heavier than seawater. However, the isotopic compositions of Fe-Mn deposits have an incredibly broad range (-1.8 to +2.5‰), which may be due to diagenetic processes (Gall et al., 2013; Gueguen et al., 2016; Little et al., 2020) (for additional discussion, see section XXX). Experimental results consistently suggest that Fe-Mn deposits should be isotopically light compared to seawater (Δ60/58Niaqueous-Fe oxyhydrides = −0.35 to −0.77‰; Δ60/58NiMn oxides-aqueous −2.76 to −4‰) (Gueguen et al., 2018; Sorensen et al., 2020; Wasylenki et al., 2019, 2015). Generally, studies assign a primary Ni isotopic composition ca. +1.6‰ to Fe-Mn deposits (based on the isotopic composition of Fe-Mn crusts analyzed by Gall et al., 2013 and Gueguen et al., 2016) which is isotopically heavier than deep seawater. Organic rich matter is assumed to have a seawater like isotopic composition (+1.3 ± 0.4) based on the organic rich-pyrite fraction of samples from the upwelling sediments in the Peru Margin (Ciscato et al., 2018); however, there is significant variation within shales (δ60Ni = −0.84 to +2.50‰) which may be due to degrees of sulfidization/removal of Ni into sulfides and variable source Ni (Pašava et al., 2019; Porter et al., 2014). The primary isotopic composition of organic rich sediments is generally assigned a value of 1.2 in mass balance calculations (reflecting the Peru Margin sediments from Ciscato et al., 2018) (Ciscato et al., 2018; Little et al., 2020). Euxinic sulfide-rich sediments from the Black Sea have an isotopic range of +0.3 to +0.6‰ (Vance et al., 2016) and sulfidization in organic matter appears to produce isotopically lighter sediment in shales (Pašava et al., 2019). Generally euxinic sediments are assigned a Ni isotopic composition of +0.45‰ in isotope mass balance calculations (Ciscato et al., 2018; Little et al., 2020).

What do we need to resolve the mass and isotope imbalance. Based on the data presented above, we require an increase of the source flux (or decrease of the sink flux) of X. To resolve the isotope imbalance, the isotope composition of this source would need to be X OR, a sink of Y. (I can make a little graph of the sink flux vs isotopic composition)

## Proposed Solutions

**Hydrothermal paragraph**

Hydrothermal activity has been suggested as a possible Ni source, but no data yet suggests that hydrothermal activity is of the appropriate magnitude or isotopic composition to account for the isotope imbalance. The hydrothermal input of Ni appears to be negligible compared to other sources (i.e., rivers), and therefore the related isotope fractionation would have to be extreme for the hydrothermal flux to resolve the isotope imbalance. There is no observed increase in [Ni] across the Mid-Atlantic Ridge from the GEOTRACES transect GP16 (Fig XXX) (cite ciscato or geotraces?), suggesting high temperature hydrothermal systems are not a significant input of Ni. Low temperature ridge flank systems, which have much larger fluxes of water, also do not appear to be a source of Ni. (Wheat et al., 2003, 2002) conducted two studies exploring ~65℃ and 25℃ ridge flank systems and found a very small source (1.5% of the riverine flux, correct for modern estimate of river flux) or a very small sink (-1.8% of the riverine flux, corrected for modern estimate of river flux), respectively. However, ridge flanks of these temperatures (≥25℃) account for only 25% of the total convective heat loss from ridge flank type hydrothermal systems (and 17% of the total oceanic convective heat loss). The remaining 75% of the convective heat loss, and a significant portion of the fluid flux, comes from cooler ridge flank systems (≤25℃) which may have different [Ni] and could either be a source or sink of Ni (Wheat et al., 2003).

If the hydrothermal flux was of the appropriate size, would it be the appropriate isotopic composition to balance the equation? [Pasava black smoker sample, Gall Fe-Mn crust vs distance from ridge axes, hawco paper]

**Riverine Particulate Load Paragraph**

The suspended particulate load (SPL) of rivers has been suggested as potential resolution to the mass and isotope imbalance, but there are two problems (1) the debated size this flux and (2) the generally isotopically light composition of the known components. The SPL consists of a variety of particles (*e.g.,* clays, carbonates, Fe and Mn oxyhydroxides, organic complexes) which can contain a significant fraction of the total riverine load for a given metal (Gaillardet et al., 2003; Gibbs, 1973). A handful of studies have calculated the SPL Ni/dissolved Ni in a variety of rivers and determined a wide range of values (0.4x to 40x), with a large portion hosted by Fe and Mn oxyhydroxide phases (Gibbs, 1977, 1973; Revels et al., 2021; Seyler and Boaventura, 2003; Viers et al., 2009). Depending on the study, either only a very small portion or the entirety (including the silicate fraction) of the SPL would have to be mobilized to resolve the mass imbalance. [maybe add a sentence about the uncertainty of SPL lability and estuary processes?]

While this source pushes us in the right mass direction, what does this mean for the isotope mass balance? A recent study explored the Ni isotopic composition in a variety of SPL particles of the Amazon river and its major tributaries and found that all of SPL phases (i.e., carbonates, oxides, organic, and residual) were isotopically lighter than solution (all <0.35‰ compared to ~0.9‰ of rivers) (Revels et al., 2021) (Fig xxx). Therefore, even if the entire particulate load were mobilized and reactive in the oceans, it would provide isotopically light Ni and worsen the isotope imbalance. However, this study focused exclusively on Amazon and its major tributaries. Further studies of other major rivers, estuaries and continental shelves could reveal that the particulate load is an important Ni source; although, it appears unlikely that the source would be anything but isotopically light relative to solution based on the trends observed by Revels et al. 2021 and the isotopic fractionation of Fe oxides (Gueguen et al., 2018; Wasylenki et al., 2015).

**Light sinks**

**Carbonate Sink**

Carbonate’s ubiquity in marine settings makes it an attractive candidate as the missing light sink but greatly variable estimates of the flux size and isotopic composition (and the unknown impact of diagenesis) make it difficult to infer their importance to the budget. Nickel partition coefficients for calcite precipitated either abiotically or biotically (via shallow water benthic foraminifer *Ammonia tepida*) are approximately 1 with a very weak negative relationship with precipitation rate (Lakshtanov and Stipp, 2007; Munsel et al., 2010). Concerning the size of the sink, while (Ciscato et al., 2018) estimates carbonates only account for 1.4 x 107 mol Ni/yr (an order of magnitude smaller than rivers) based on Ni/TOC value of carbonate rich sediments from Lagoa Salgada and the total global carbonate carbon burial flux in deep sea sediments, Alvarez et al. 2021 estimates carbonates account of 1.5 to 6.7 x 108 mol Ni/year based on [Ni] data in carbonates from (Zhao and Zheng 2014) and the carbonate carbon burial flux from deltaic, continental shelf and deep sea sediments.

Previous studies have attempted to estimate δ60/58Ni for the carbonate Ni sink, but these estimates might only be partially applicable to marine carbonate precipitation. Ciscato et al., 2018 estimated a carbonate δ60/58Ni range of 1.10–1.64‰. However, they based their estimate on a small sample set (n<8) of carbonate rich (34-75%), organic sediments, rather than pure carbonate samples, without diagenetic histories. [Brandi Revels carbonate data?]. Alvarez 2020 and 2021 have tackled carbonates experimentally (although not equilibrium probably) and found isotopically light Ni sorbs and coprecipitates with carbonates (give estimates of values). [mention short comings of these experiments]. None of these studies have explored the effect of diagenesis which could be another source/sink of Ni (and indicate carbonate’s usefulness as a record of Ni isotopic comp). Considering this may be a significant sink of Ni, getting better estimates of the Ni isotope fractionation of carbonates will be an important step towards resolving the imbalance (at least narrowing down the possibilities).

Organic matter

Porter paper, Pasava paper and ciscato (initial organic matter seawaterish, and then porter, pasava have super wide range of values. Is their a release of heavy Ni?)

**Light sink/Heavy source?**

**Mn oxides**

Several studies aimed to determine δ60/58Ni for Mn-rich sediments, perhaps largest sink of Ni, but the results so far are extremely puzzling. Nickel is enriched in Fe-Mn deposits relative to seawater (ca. 106 Ni mol/g Fe-Mn deposits/ Ni mol/g seawater) (e.g., Li and Schoonmaker, 2003) and primarily associated with Mn phases, rather than Fe (e.g., Peacock and Sherman, 2007). The δ60/58Ni of Mn-rich deposits span the entire known natural range of Ni isotopic compositions (ca. -1.8 to 2.5‰) and, inexplicably, appear to be sometimes isotopically heavier and sometimes isotopically lighter than the solution from which they precipitate (Gall et al., 2013; Gueguen et al., 2020, 2016; Gueguen and Rouxel, 2021; Little et al., 2020; Vance et al., 2016). For instance, given the homogeneity of the deep ocean (~1.4 ‰), hydrogenetic ferromanganese crusts have a surprisingly variable isotopic range from 0.25 to 2.47‰, with an average of 1.70 ± 0.63‰ (Gall et al., 2013; Gueguen et al., 2020, 2016). This generally suggests Mn oxides incorporate isotopically heavy Ni relative to solution. [should I add a mention of hydrothermal crusts here?] In stark contrast, the dissolution of Mn oxides in the water column of the Black Sea corresponds to a decrease in δ60/58Nisolution, suggesting isotopically light Ni is associated with Mn oxides (calculated Δ60/58Nisolution-solid ~ 4.0‰) (Vance et al., 2016). More recent studies of hydrothermal Fe-Mn deposits and Mn rich pelagic clays have found a similarly wide range of values, -0.85 ± 0.67‰ (excluding 2 anomalously high values) and 0.07 ± 0.75 ‰, respectively (Gueguen et al., 2020; Gueguen and Rouxel, 2021; Little et al., 2020). Without better knowledge of the main marine Ni sink, correctly modeling the marine Ni cycle is likely impossible.

There are two explanations for the observed 60/58Ni variation in Mn-rich sediments: (1) the initial δ60/58Ni could be roughly the same across sediments, but diagenesis (Mn redox cycling and/or transformation to todorokite) perhaps redistributes Ni isotopes and (2) natural variations could be a consequence of variable initial δ60/58Ni. The first explanation has an added “conceptual” benefit in that this process could provide an input of Ni to the ocean and address the mass balance issue. Suboxic diagenesis of Mn oxides appears to release Ni into porewater, however, corresponding isotope data does not conclusively suggest this Ni is isotopically heavy relative to solid or has any isotope effect at all (Fig XX) (Gueguen and Rouxel, 2021; Little et al., 2020)[insert sentences about (1) the isotope data does not seem to necessarily agree with this, although the conc data might]. Experimental transformation from birnessite to todorokite showed a 50% release of the Ni originally associated with birnessite (~1 wt%), and natural data roughly corroborates this trend (Atkins et al., 2016). However, the rate and extent of this transformation is largely unknown, as well as the Ni isotopic fractionation it may impart. Thus far, only three todorokite rich nodules have been measured for Ni isotopic composition (δ60/58Ni~ -0.22 to 0.01); they tentatively appear to be isotopically lighter than measured phyllomanganate rich nodules (0.28 to 1.06, n =3) and suggest isotopically heavy Ni may be released, although further investigation is clearly warranted. [Does not explain difference between hydrogenetic Fe-Mn crust and black sea sediments]

If the natural variations is due to variable initial δ60/58Ni, what mechanisms might control the variation? Based on natural and experimental observations, there are two readily apparent working hypotheses. First, the variation could be due to differences in Ni coordination environment. Nickel can be structurally incorporated into Mn vacancy sites in birnessite, the dominant Mn phase in natural marine Fe-Mn precipitates (Peacock, 2009), or sorbed on {001} surface sites (triple corner sharing) or edge sites (double corner sharing) (Simanova et al., 2015). A Ni-birnessite sorption study indicated Δ60/58Nisolution-birnessite positively correlates with the ratio of surface-sorbed to incorporated Ni, suggesting that sorbed Ni is isotopically lighter than incorporated Ni (Sorensen et al., 2020). Experimental results suggest Ni migrates very slowly into the vacancy sites (30% incorporation after 408 h) (Peacock, 2009). In natural Fe-Mn crusts, the majority of Ni is structurally incorporated (Peacock and Sherman, 2007), but the degree of structural incorporation within sediments like the Black Sea particles is unknown. If surface-sorbed and incorporated Ni have different Δ60/58Nisolution-birnessite,differences in the proportions of sorbed to incorporated Ni would impact the δ60/58Ni of Mn-rich sediments. Second, Mn-rich sediments have a wide range of accumulation rates and, depending on the rate, may capture different isotope fractionations (kinetic, equilibrium or a mix thereof). Experiments varying in duration from 24 hours to 27 days found that Δ60/58Nisolution-birnessite decreased progressively over time, which suggests equilibrium had not yet been reached, and short-term experiments may be recording an initial kinetic effect (Fig. 1)(Sorensen et al., 2020; Wasylenki et al., 2019). If kinetic and equilibrium fractionations are distinct, the δ60/58Ni of fast-accumulating versus slow-accumulating Mn-rich sediments may record different Ni isotope offsets from dissolved Ni in the water column.

Organic Matter paragraph?

Parapgrah about hypothesis and driving questions

# Progress Thus Far