# Abstract

# Introduction

The changes in trace metal marine chemistry over time reflects changes in the dynamics of atmosphere, solid earth, life, and oceans, but before we can attempt to interpret these shifts in the rock record, we need foundational knowledge of what controls their concentrations in the modern day. Several studies have suggested an intimate relationship between changes in marine trace metal concentrations and 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 and seawater concentration of these metals were likely key regulators on which organisms were favored for future diversification. The marine concentration of a particular metal is a function of inputs and outputs which are ultimately dictated by solid earth, marine and atmospheric processes. Shifts in trace metal concentrations, and therefore these processes, are recorded in the rock record. But before these shifts can have any meaning to us, we need to know what regulates these trace metals in the modern day. .

Nickel is a bio-essential element for modern and ancient, 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. Several studies hypothesize that shifts in trace metal marine chemistry had a profound impact on the evolution of early life; Ni is perhaps a prime example (*e.g.,* Glass and Dupont, 2017; Konhauser et al., 2009; Robbins et al., 2016; Zerkle et al., 2005). A dramatic decrease in Ni seawater concentrations, interpreted from the BIF rock record, just prior to the GOE is hypothesized to have starved Ni-dependent methanogens, inhibited the production of methane, and facilitated the GOE (Konhauser et al., 2015, 2009). In addition to drastically changing the redox state of the atmosphere, a shift towards a lower marine Ni concentration would favor cyanobacteria, which grow optimally in the Ni concentration range predicted for the Paleoproterozoic (Glass and Dupont, 2017). Before we can investigate the importance of and interpret shifts in Ni marine chemistry from the rock record, , we need knowledge of the processes which make up the marine Ni in the modern day at the very least. 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 use by modern 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). The N cycle is intimately associated with Ni availability because of N related Ni enzymes urease and Ni-Fe hydrogenase. Urease catalyzes the hydrolysis of urea into ammonia which can then act as source of N for marine organisms (Morel et al., 2003). Nickel-Iron hydrogenase catalyzes the reversible reduction of protons to hydrogen gas; because protons and hydrogen gas are substrates and products of nitrogen fixation, respectively, Ni-Fe hydrogenase can convert the byproduct hydrogen gas back to the usable proton form for continued fixation (Tamagnini et al., 2002). The Ni-enzyme Ni-super oxide dismutase (Ni-SOD) is related to the O cycle as it converts reactive oxygen species to hydrogen peroxide and oxygen gas. Finally, Ni is perhaps most associated with C cycle. The Ni enzymes methyl coenzyme M reductase (MCR) and CO dehydrogenase are Ni enzymes which produce and consume CO2 and CH4. In fact, MCR 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).

These enzymes don’t exist in a vacuum; they are produced and used by a variety of modern and ancient organisms. Nickel is found in association with both the internal biomass and inorganic (frustule) components of diatoms in roughly equal proportions (Twining et al., 2012). Foraminifera also have a Ni requirement because of their use of urease which may act as a pH regulator during shell formation (Bachmeier et al., 2002; Munsel et al., 2010; Smith and Goldstein, 2019). Perhaps because of this close association between urease and shell formation, foraminifera incorporate Ni into their tests (Munsel et al., 2010; Smith et al., 2020; Smith and Goldstein, 2019). Methanogens have been shown to have significant Ni requirements (Neubeck et al., 2016; Schonheit et al., 1979). This is not surprising consider Ni enzyme CO dehydrogenase assists in the assimilation of CO as a carbon source for methanogenesis and MCR catalyzes the last step of methanogenesis (Fuchs and Stupperich, 1986; Ragsdale, 2009).

As one might expect, the marine concentration of Ni, as an essential component of the aforementioned enzymes and a potential toxin has significant implications for the relative abundances of these organisms (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 (modern ocean concentrations 1-12 nM) and a steep drop off in abundance and general increase in shell deformities past this Ni concentration. In experiments which exposed natural phytoplankton assemblages from Peru and California to additional Ni and urea, there were clear associated increases in growth with increases in Ni and urea suggesting co-limitation in some of the species tested (Dupont et al., 2010). Clearly, these organisms are highly sensitive to fluctuations in [Ni], and shifts in [Ni] over time would impact the diversity and abundance of organisms.

## Ni abundances and cycling in Modern Oceans

Unsurprisingly, Ni has a nutrient like depth profile meaning it is depleted in the surface waters (~2nM) and encirhed in the deep-water (9-12nM). (Fig with water column Ni conc). Nickel regeneration is associated with P regeneration in upper waters ( associated with internal biomass) 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). This unavailable fraction of Ni could be organically complexed. 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 ) (Turner and Martino, 2006).

Despite Ni’s biogeochemical importance, we have a poor understanding of its marine cycling, even in the modern oceans. This is best evidenced by our best attempts at modelling the Ni marine budget.In 1976, Krishnaswami first identified a massive imbalance between the main input and its outputs; his calculations suggested that outputs were three times greater than the inputs. 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 this discovery, 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). What is missing from our understanding of the Ni marine cycle?

To investigate the imbalance, let us first consider the components that are generally agreed upon

**Inputs**

**Dust**To estimate the Ni contribution to the oceans from dust, we must know the yearly deposition of dust, the average concentration of Ni in dust, and the percent of that Ni which ultimately dissolves in the ocean. An estimated 450 Tg of dust is deposited in the ocean every year (Jickells et al., 2005 and references therein). Although there are significant anthropogenic Ni contributions to modern aerosols (Desboeufs et al., 2005; Galloway et al., 1982; Nriagu, 1989), because Ni has a residence time on the order of 10,000 years, the natural contributions are likely most relevant to the modern marine budget. Assuming the upper continental crust is compositionally similar to dust, the [Ni]upper continental crust, and therefore [Ni]dust, is 47 ppm (Rudnick and Gao, 2014). To approximate the fraction of Ni that will dissolve, represented here as the amount of Ni dissolved divided by the total Ni in bulk aerosol, several studies have performed leaching experiments with loess (Desboeufs et al., 2005) or particles filtered from air at coastal or island stations (Fishwick et al., 2017; Mackey et al., 2015) using leachates such as ultra-high purity water or filtered seawater. The percent of dissolved Ni ranges from 1 to 86% and appears to be primarily dependent on material provenance rather than leachate, oxygen content, pH, or temperature (Desboeufs et al., 2005; Fishwick et al., 2017; Mackey et al., 2015). The wide range in solubility may be due to variable anthropogenic contributions. One study which seasonally sampled aerosol samples found that increases in anthropogenic input, conventionally identified by an enrichment factor relative to continental crust greater than 10 (Jickells et al., 2016), correlated with increases in solubility (Hsu et al., 2005). To avoid potential anthropogenic contributions, I conservatively opt to use the dissolution value of 2% from Desboeufs et al. (2005), which used Loess from Cape Verde as the leached material, rather than studies which used modern aerosols and may be influenced by anthropogenic particles. The total yearly Ni input to the oceans from dust is then 7.2x106 mol/yr.

**Rivers [dissolved]**

Similarly, to calculate the riverine input of Ni, we need to know the annual riverine discharge and the Ni content of these rivers, with a focus on the dissolved load (which will be defined as the remaining Ni in solution after being passed through a 0.2 micron filter). The estimated annual total discharge for rivers is 3.6–3.8 × 1016 kg (references within berner and berener, Dai) based on available streamflow data of the world’s largest rivers. The average riverine dissolved Ni concentration can be estimated by taking the abundance weighted average dissolved Ni of the world’s largest, and ideally most representative, rivers. An early estimate from Martin and Whitfield 1983 and references therein suggested the average riverine Ni concentration was 8.5 nM. Gaillderat (2003) aggregated concentration and discharge data for >30 rivers and calculated 13.6 nM as the average riverine dissolved Ni concentration (although it is unclear if this is an abundance weighted value). Cameron and Vance 2014 calculated the abundance weighted average concentration of dissolved Ni from 8 rivers, which constitute 20% of the total riverine discharge, to be 9.6 nM. Given the general similarity of these estimates and the transparency with how Cameron and Vance calculated their average value, we use a total riverine annual discharge of 3.7x1016kg/yr and dissolved Ni concentration of 9.6 nM to calculate a Ni riverine input of 3.6x108 Ni mol/year.

**Outputs**

Fe-Mn deposits?

Ferro-manganese (Fe-Mn) deposits are potentially the most important output of Ni from the modern ocean, but estimating the size of this sink has remained challenging. The wide range of Ni output into this sink (from 3.08x108 to 1.5x109 Ni mol/yr) may be a consequence of the different approaches to quantifying the flux (Cameron and Vance, 2014; Gall et al., 2013; Little et al., 2020). Vance and Cameron (2009) estimated the flux of Ni into Fe-Mn deposits by coupling the Ni marine budget with the better constrained Momarine budget. By multiplying the Mo flux into Fe-Mn deposits by by the average Ni/Mo in Fe-Mn crusts and nodules , they calculated an output flux of 1.5x109 Ni mol/yr. Alternatively, Gall et al. 2013 estimated the flux of Ni into Fe-Mn deposits by multiplying the accumulation rate of 5 Fe-Mn crust and nodules by the average Fe-Mn crust [Ni] (unclear what this data is based on) and a predetermined and unexplained seafloor (based on back calculating their estimates, they assume Fe-Mn crust covers ~85% of the seafloor which is counter to survey studies (e.g., Dutkiewicz et al. 2015, Rothwell 2005 and references therein – I think I can use this here) and calculated a total flux of 5.1x108 Ni mol/yr. [Finally, Little et al 2020 estimated the Ni output into the oxic sink, which they describe as purely clays, by multiplying the seafloor coverage of clays by the Mn accumulation rate and Ni/Mn ratio of Fe-Mn sediments from the USGS.] Without better information, we adhere to the accepted and commonly used value in recent literature of 5.1x108 Ni mol/yr (Ciscato et al., 2018; Gall et al., 2013; Gueguen and Rouxel, 2021).

Organic Matter from productive upwelling zones

Nickel is a bioactive element associated with cellular uptake and can be buried with organic matter (OM) in high OM preservation areas such as productive upwelling zones (Böning et al., 2015). To consider the size of this output, we must consider the flux of organic matter out of the ocean which which originates from seawater (rather than rivers). A 1995 estimate of organic matter preservation used seafloor area, total sediment burial flux and average %TOC to calculate OM fluxes from high productivity zones and pelagic zones of 1013 g Corg/yr and 5x1012 g Corg/yr, respectively, with a 50% uncertainty (Hedges and Keil, 1995). A more recent estimate using 230Th normalized fluxes classified all deep-sea TOC burial (that which is buried at >1000m) of 20x1012 g Corg/yr. Considering the large uncertainty on the earlier estimate, these values are incredibly similar. The flux of Ni out with these sediments can be calculated from the [Ni]/TOC of the authigenic fraction. In productive regions across the world, Ni is often associated linearly with TOC, and the slope of this relationship can be applied to the flux calculation. However, if the intercept of the linear regression does not have a y-intercept of 0, there may be non-authigenic phases (e.g., detrital) contributing Ni. To avoid Ni/TOC relationships impacted by non authigenic phases, the Ni/TOC derived from the peru upwelling region, which have an Ni/TOC intercept of 0, will be applied here to calculate the fraction of Ni that is buried with organic matter at similar sites (9 Ni ppm/TOC wt%). Because this Ni/TOC relationship comes from a productive upwelling region and we lack similar investigations of Ni in pelagic OM, I only estimate the flux output of OM from upwelling regions and acknowledge that we may be omitting a nontrivial output of Ni in pelagic OM sediments. Using the flux of high productivivty zones from Hedges and Kiel 1995 (1013 g C­org/yr) and the Peru Ni/TOC, the flux of Ni out into organic matter is ca. 1.5x108 mol Ni/yr.

Euxinic Sediments

[write this Eva!]

The Imbalance

The sum of the sources equates to 3.6x108 Ni mol/yr and the sum of the sinks equates to 6.6x108 Ni mol/yr, nearly double the sum of the sources. If this were true, the ocean would be rapidly depleted in Ni, but there is no evidence for such deviation from steady state. In fact, the geologic record suggests Ni has been roughly constant for the past 500 mya (Konhauser et al., 2015, 2009). What is missing from our understanding of the Ni marine cycle?

**Resolving the imbalance**

There are two potential causes of the imbalance: missing fluxes or inaccurate flux estimates. Clearly, even with the best efforts, the flux estimates described above are tenuously estimated or themselves hold significant uncertainties. Of course, 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). This approach has previously been successfully applied to other elemental cycles (*e.g.,* Mo, I think), and is currently in use to better constrain similarly elusive metals (e.g., Cu, Zn I think). To apply this approach, we must know the isotopic compositions of major fluxes. ,

Applying the Isotope Constraint

Unsurprisingly, in addition to the mass imbalance Before discussing which fluxes are most important to isotopically characterize to resolve the isotope mass imbalance, I will review what is known about the isotopic composition of the aforementioned Ni fluxes.

**Oceans**

The oceans are often the point of reference when assessing the light or heaviness of a flux and will be described first. The deep ocean is globally homogenous, with an isotopic composition between1.3 to 1.4‰ (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 nutrient like surface [Ni] depletion, shows no 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 speciesbetween 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.

**Inputs**

The isotope imbalance is immediately apparent when comparing the isotopic comp known sources to the oceans; the majority of sources have an isotopically lighter composition than oceans . The isotopic composition of continental crust, which we assume to represent that of dust, s, has a limited isotopic composition, from -0.1 to +0.2‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013; Wu et al., 2019 and references therein). Basalts rock standards (e.g., BHVO-2, BCR-2) analyed across multiple studies have a δNi range 0.01 to 0.21‰, and loess standards have a δNi range of 0.03 to 0.21‰ (Wu et al., 2019). Rivers, the largest known source, appear to be isotopically variable, from +0.18 to +1.38‰ , with an average isotopic composition of +0.9‰ based on the tributaries of 9 different rivers (Cameron and Vance, 2014; Revels et al., 2021). The difference in isotopic composition between rivers and continental crust is not surprising; Iron oxides produced from weathering of ultra mafic t mafic rocks, which host the majority of the crust’s Ni, have been shown experimentally and in natural settings to 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)). Therefore, the solution (i.e., rivers) is expected to be isotopically heavier than the solid (i.e., bedrock, continents). In summary, sources’ Ni isotopic compositions are restricted to a range below 1.40 and has an abundance weighted isotopic composition of 0.88 which is lighter than seawater (ca. 1.3 to 1.7‰).

**Outputs**

The isotopic composition of the outputs further exacerbates the isotope imbalance. Generally, the major known sinks (e.g., organic matter, Fe-Mn crusts and nodules) appear to be isotopically similar to or heavier than seawater. Hydrogenetic Fe-Mn crusts have a wide range of δNi, 0.9 to 2.5‰, but generally cluster around 1.7‰ (average +/- 2SD 1.78+/-0.57; n=74).

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)

To address the imbalance, we will look at proposed solutions and dissect which ones are most promising.

## 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 mass 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