# Abstract

# Introduction

Understanding the marine cycles of bioactive trace metals will not only inform the controls on cycling of major elements they are coupled to, but also help us decipher how the marine cycling of these trace metals evolved across history and why. Changes in trace metal marine chemistry over time reflects changes in the dynamics of atmosphere, solid earth, oceans, and life. Ubiquitous biological processes such as photosynthesis, methanogenesis and nitrogen fixation all require trace metals (e.g., Fe, Ni, Mn). Several studies have suggested an intimate relationship between changes in marine trace metal chemistry and the evolution of early life (*e.g.,* Konhauser et al., 2009; Robbins et al., 2016; Zerkle et al., 2005). Efforts to reconstruct the evolution of trace metal marine chemistry will surely inform how early life and Earth evolved as well.

The modern cycling of trace metals is also of interest to better understand the cycling of major elements in the modern ocean. The cycling of C, O, N, and other major elements are intertwined with biological processes. Because many biological processes also require trace metals to function, there is an intrinsic link between the modern cycles of the major elements with the modern cycles of the trace metals. Therefore, investigations of trace metal marine cycles will contribute to our knowledge of greater biogeochemical cycles.

Here, we focus on Ni, an element whose marine cycling we know little about, but also one that is a bio-essential element for modern and ancient organisms which may have played a surprisingly important role in Earth’s oxygenation. Nickel is a prime example of how shifts in trace metal marine concentrations can potentially impact marine life. 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) and also may have changed [Ni] from toxic to optimal for cyanobacteria (Glass and Dupont, 2017). In more recent history, Ni may have exacerbated the end-Permian extinction, the largest mass extinction known to date. An increase in marine Ni input to the oceans from the eruption of the Siberian flood basalts may have increased caused non-limiting Ni conditions for methanogens (Rothman et al., 2014). In the modern ocean, Ni is an essential component of seven enzymes that regulate the global C, N, and O cycles (Ragsdale, 2009, 1998). To investigate Ni and its marine evolution overtime, we require 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

As mentioned, Ni-enzymes have roles in the C, O, and N cycles. The N cycle is 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-Fe hydrogenase catalyzes the reversible reduction of protons to hydrogen gas; because protons and hydrogen gas are substrates and products of nitrogen fixation, 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. Nickel is perhaps most associated with the 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. Diatoms use urease and Ni-superoxide dismutase and have Ni demands (Benoiston et al., 2017; Twining et al., 2012). 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 concentrations and observed total foraminifera abundance peaked around 125 nM (modern ocean concentrations 1-12 nM). Past 125 nM, there was a steep drop off in abundance and general increase in shell deformities. In experiments which added Ni and urea to natural phytoplankton assemblages from Peru and California, there were increases in growth with increases in Ni and urea, suggesting co-limitation in some of the species tested (Dupont et al., 2010). Early experiments with methanogen species *Methanobacterium thermoautotrophicum* found that the abundance of cells was proportional to the amount of Ni added to the medium (concentrations test, ~0 nM, 85 nM, 1000 nM) (Schonheit et al., 1979). 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 is poorly constrained between 1-90% (Horner et al., 2021 and references therein; 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 constructing a modern Ni marine budget. In 1976, Krishnaswami first identified a massive imbalance; their calculations suggested that a single output had a flux three times greater than the main input. If this were true, the ocean would be rapidly depleted in Ni, considering the residence time of Ni is between 10 to 30 kyr (Cameron and Vance, 2014; Little et al., 2020; Sclater et al., 1976). There is no evidence for such extreme deviation from steady state. 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 estimations and measurements lead to this imbalance, and what are the uncertainties on these values? What sinks and sources appear to be most influential? To investigate what might be causing the perceived imbalance, let us first consider how the estimations were made and what may be the best path forward for resolution.

## Inputs

#### Dust

Dust is a significant source for other metals (e.g., Fe) and has been assessed as a source of Ni and found to be quite small. To determine the importance of dust to the budget, we need an estimate of the contribution of Ni to oceans from dust. The primary method others have estimated the Ni contribution to the oceans from dust has been by multiplying the yearly deposition of dust, the average concentration of Ni in dust, and the percent of 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). 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). 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 10 times the mixing time of the ocean, the natural contributions are likely still most relevant to the modern marine budget. 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.

#### Dissolved Riverine Load

Rivers are also a significant source of metals to the ocean and are estimated to be the greatest known source for Ni as well. 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 was defined by these papers 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 recorded an initial estimate for the average riverine Ni concentration of 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 of 9.6 nM from 8 rivers, which constitute 20% of the total riverine discharge. The often cited riverine flux comes uses the abundance weighted [Ni] derived by Cameron and Vance (2014) and total riverine annual discharge of 3.7x1016kg/yr to calculate a Ni riverine input of 3.6x108 Ni mol/year.

## Outputs

#### Fe-Mn deposits

Ferromanganese (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. Previous estimates vary by an order of magnitude which may be a consequence of the different approaches to quantifying the flux (Cameron and Vance, 2014; Gall et al., 2013). Cameron and Vance (2009) estimated the flux of Ni into Fe-Mn deposits by coupling the Ni marine budget with the better constrained Mo marine budget. By multiplying the Mo flux into Fe-Mn deposits 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) and calculated a total flux of 5.1x108 Ni mol/yr. Both estimates assume that Fe-Mn crusts and nodules are representative of all Fe-Mn deposits. [In contrast, Little et al 2020 slightly decouples their estimates from Fe-Mn crusts by instead calculating the flux of Ni into a pelagic clay/oxic sink. Because their method of calculation functionally overlaps with how Fe-Mn deposits could be defined (*i.e.,* deposits with Fe and Mn (oxyhydr)oxides), I consider this an estimate of the Fe-Mn deposit sink. They assume that all Ni incorporated into pelagic clay is coupled to Mn[[1]](#footnote-1) and calculate the sink’s flux of Ni by multiplying the seafloor coverage of clays, Mn accumulation rate in pelagic clays and Ni/Mn ratio of Fe-Mn crusts. They calculate the lowest range for the Fe-Mn deposit sink, 1.5 to 5.9×108 Ni mol/yr]. 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

Because Ni is a bioactive element associated with cellular uptake, it can be buried with organic matter (OM), but a previous estimation of this sink exclusively focused on burial in high OM preservation areas such as productive upwelling zones, rather than OM burial in pelagic regions (Ciscato et al., 2018). Again, the main approach to quantifying this sink focused on multiplying the total flux of the sediment (OM burial/year) by the associated Ni content (Ni/TOC). An early 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, a tracer with a known particle flux, 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, has been applied 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, there is only a published estimate of the Ni flux into OM for upwelling regions, to the best of our knowledge. Pelagic OM may be a nontrivial output of Ni that is being omitted. The generally accepted calculation from Ciscato et al. (2018) uses the flux of high productivity zones from Hedges and Kiel (1995) (1013 g C­org/yr) and the Peru Ni/TOC to calculate a flux of Ni out into organic matter pf 1.5x108 mol Ni/yr.

#### Euxinic Sediments

This flux is one of the smallest estimated thus far (Ciscato et al., 2018; Little et al., 2015). There have been two approaches to calculating the euxinic flux: one using a Ni-TOC relationship and one using Ni-Mo relationship. Both calculations used sediments from the Black Sea as representative of euxinic sediments. Little et al. (2015) again used the better constrained Mo mass balance along with the authigenic Ni/Mo values from Black Sea sediments to calculate the euxinic sink of Ni of 0.4x108 Ni mol/yr (Little et al., 2015). Ciscato et al. (2018) instead calculated the euxinic sink similar to the productive region OM sink. They used an estimation of the organic carbon flux into anoxic basins (1x1012 g C/year with an uncertainty of 50%, Berner 1982) and the Ni/TOC ratios from Black Sea euxinic sediments (0.54-1.49x10-3 Ni/TOC wt% (Little et al., 2015; Vance et al., 2016) to calculate a total flux of 0.15x108 Ni mol/yr (Ciscato et al., 2018; Vance et al., 2016). The estimates are quiet different, however, they are both very small relative to the other sinks and, therefore, unless the estimates are off by an order of magnitude, the euxinic sink is mostly unimportant in modern oceans. We adhere to the value most often used in Ni marine budgets of 0.15x108 Ni mol/yr (Ciscato et al., 2018; Gueguen and Rouxel, 2021; Little et al., 2020).

The sum of the sources equates to 3.6x108 Ni mol/yr and the sum of the sinks equates to 6.8x108 Ni mol/yr, nearly double the sum of the sources. 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 omitted and themselves hold significant uncertainties. As shown, refining those directly is very difficult, and thus many in the community aim to apply a new constraint to the puzzle (Cameron and Vance, 2014; Ciscato et al., 2018; Little et al., 2020; Vance et al., 2016). 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 (eq. X and X). Therefore, one 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 (mass balance example fig, colors). This approach has 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. While the isotopic compositions of known sources (*e.g.,* rivers and dust) are reasonably well characterized, the sinks 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.

## Barriers to Applying the Isotope Constraint

Maybe unsurprisingly, there is an isotope mass imbalance in addition to the mass imbalance. The known sources are isotopically lighter than the oceans and the known sinks are seemingly increadibly variable or have isotopic compositions greater than or equal to the ocean. The combination of these imbalances points to a significant missing component (or components) or largely misunderstood isotopic compositions. But which fluxes are the most in need of a more thorough examination and which fluxes may be significant, but are missing from the budget? To address these questions, we first look at what is known about the isotopic composition of components within the previously modeled marine Ni budgets.

## Oceans

The oceans are often the point of reference when assessing how isotopically light or heavy a flux is and will be described first. The deep ocean is globally homogenous, with an isotopic composition between 1.3‰ 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. In contrast, the Indian sector of the Southern Ocean, which also displays a less pronounced, 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 species 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.

## Inputs

The isotope imbalance is immediately apparent when comparing the isotopic composition of the oceans to known sources; 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, 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) analyzed across multiple studies have a δNi range from 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; Fe oxides produced from weathering of ultra-mafic to 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, the Ni isotopic composition of sources seem relatively well known, are restricted to a range below 1.40‰, and have an abundance weighted isotopic composition of 0.88‰ which is significantly isotopically lighter than seawater (ca. 1.3‰ to 1.8‰).

## Outputs

#### Fe-Mn deposits

The isotopic composition of the outputs further exacerbates, or at the very least complicates, the isotope imbalance. The Fe-Mn deposit sink may be the most important, but also the most difficult to determine what is representative. This sink is often clumped together and isotopically represented by hydrogenetic Fe-Mn crusts, which may be a faulty assumption. Gall et al. (2013) measured 24 surface scrapings of Fe-Mn crusts across the globe and, given the homogeneity of the deep ocean (1.3 to 1.4 ‰), found a surprisingly variable isotopic range from 0.9 to 2.5‰ with an average of 1.67±0.8‰. They did not observe any strong correlation between δ60Ni and ocean basin, oxygen saturation or Ni concentration (Fig xx), but there was a mild correlation between δ60Ni and distance to continental shelf, likely reflecting the contribution of isotopically lighter detrital, continental sediments. A subsequent study of four North and South Pacific Fe-M crust ca. 20 mm cores found similar values to Gall et al. (2013) (1.79 ± 0.21‰ 2sd, n = 31 for North Pacific and 1.73 ± 0.21‰ 2sd, n = 21 for South Pacific). One core from the South Pacific had a systematic and dramatic drop in δ60Ni downcore (from 1.89‰ to 0.25‰) associated with lower Mn/Ni, which may be a result of hydrothermal influence or post depositional processes (see section XX for further discussion). Most recently, a study of hydrogenetic Fe-Mn crusts from the Atlantic and Pacific Oceans again found δ60Ni isotopically similar to previous results (0.7‰ to 2.6‰) (Gueguen et al., 2020). These results suggest Fe-Mn incorporate isotopically heavy Ni relative to solution.

However, if we consider virtually any other Fe-Mn sediment type, there is no clear consensus whether Fe-Mn deposits have an extreme or insignificant fractionation (and if extreme, in which direction?). In contrast to pure hydrogenetic crusts, mixed hydrothermal-hydrogenetic and hydrothermal Fe-Mn crusts have exclusively been found to be isotopically lighter than seawater with δ60Ni of 0.3‰ to 0.4‰ and -1.5‰ to 1.1‰, respectively (Gueguen et al., 2020). It is currently hypothesized that, rather than significant differences in source Ni (*i.e.,* hydrothermal fluid or seawater), these differences may be due to differences in the phase Ni is primarily associated with (*e.g.,* Fe oxides or Mn oxides), depositional environment and/or rate of formation (Gueguen et al., 2020; Little et al., 2020). Ferromanganese nodules also have typically isotopically lighter and variable δ60Ni values (0.23±0.90‰ 2sd, n=6) (Little et al., 2020; Wu et al., 2019 and references therein). This range in δ60Ni has been attributed to differences in mineralogy (phyllomanganates or todorkite), but with such a small sample size with limited mineralogy data, this is a tentative explanation (Little et al., 2020). Finally, and maybe most extreme, the dissolution of Mn oxides in the water column of the Black Sea corresponds to a decrease in δ60/58Nisolution, with a calculated Δ60/58Nisolution-solid ~ 4.0‰ (Vance et al., 2016). From this set of data, Fe-Mn deposits incorporate isotopically light Ni relative to solution, a direct contradiction to the conclusion based on hydrogenetic Fe-Mn crusts.

#### Organic Matter and Euxinic sediments

Only one paper has measured δ60Ni in modern organic rich sediments thus far. Ciscato et al. (2018) obtained organic rich sediments from a productive upwelling region off the coast of Peru and performed a detrital Ni correction to obtain an authigenic δ60Ni range of 1.19‰ to 1.20‰, although their best estimate is 1.22‰. In contrast to the narrow range of modern sediments, there is significant variation within shales (δ60Ni = −0.84 to +2.50‰), which may be due to degrees of removal of Ni into sulfides and variable source Ni (Pašava et al., 2019; Porter et al., 2014). As far as we are aware, there are no Ni isotope data for the pelagic OM sink.

Again, a single paper has investigated the δ60Ni of euxinic sediments, but this is a small sink. To obtain a representation of the euxinic sink in the open ocean, Vance et al., (2016) measured euxinic sulfide-rich sediments from the Black Sea and found sediments and Black seawater have Ni isotopic compositions of 0.3‰ to 0.6‰ and ~1.35‰, respectively. 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). While euxinic sediments are isotopically lighter than seawater, the sink is not of sufficient size to significantly alter the budget.

The isotopic compositions of the sinks are clearly less known than the sources. The Ni isotopic composition of the largest known sink, Fe-Mn sediments, encompasses the entire known natural range of Ni isotopic composition. There are only a handful of samples to represent the upwelling region OM sink. Work to better understand δ60Ni variability in Fe-Mn sediments and adding to the small OM sample set will surely be useful. But, what about missing fluxes?

## Missing Components

#### Hydrothermal Fluid

Hydrothermal fluid 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 different hydrothermal regimes may have unique Ni fluxes, and so they must be considered individually. For fluids from high temperature on axis systems, to the best of our knowledge, the highest observed [Ni] is ~3 μM from the Rainbow vent field on the Mid-Atlantic Ridge (Douville et al., 2002). Ciscato et al. (2018) pointed out that even if all of the hydrothermal fluid was so enriched in Ni, assuming an axial flux of 3x1013kg/yr (Elderfield and Schultz, 1996), the total flux from these types of hydrothermal systems would be less than 25% of the riverine Ni flux (calculated as 9x107 Ni mol/yr here). Vent fluids collected from six Mid-Atlantic Ridge hydrothermal systems were all < 2 μM (Douville et al., 2002 and references therein). In addition, there is no observed increase in [Ni] across the Mid-Atlantic Ridge from the GEOTRACES transect GP16, suggesting these types of hydrothermal systems are not a significant input of Ni (Fig XXX) (cite ciscato and geotraces?). 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? Most of what we know about the isotopic composition of hydrothermal fluids is indirect, but almost all data point to them being an isotopically light source. One of the first estimates of hydrothermal fluid δ60Ni was also the only one to suggest that they were isotopically similar to seawater (~1.5‰) based on analyses of Fe-Mn crusts near the mid-ocean ridge, although there was no correlation with δ60Ni and distance from a mid-ocean ridge (Gall et al., 2013). Other estimates focused on the narrow range of δ60Ni for ultramafic and mafic rock (~0.1‰, Cameron et al., 2009; Elliott and Steele, 2017; Gall et al., 2013; Gueguen et al., 2013; Wu et al., 2019), from which hydrothermal fluids derive their composition, and assumed a similar δ60Ni for the hydrothermal fluid (Ciscato et al., 2018; Gueguen and Rouxel, 2021). One study documented a form of hydrothermal interaction by measuring the change in isotopic composition as seawater interacted with lava from the 2018 eruption of Kīlauea and found for δ60Ni the data followed mixing between two end-members isotopically similar to seawater and basalt (0.1 to 0.3‰) (Hawco et al., 2020). Perhaps most representative, Pašava et al., (2019) measured a δ60Ni value of -0.24‰ from a pyrite-marcasite crust within the Logatchev hydrothermal field, Mid-Atlantic Ridge. Besides the estimate of Gall et al. (2013), all available data indicate hydrothermal fluids are isotopically light relative to seawater and would exacerbate the isotope mass imbalance.

#### Riverine Suspended Particulate Load

The suspended particulate load (SPL) of rivers has been suggested as potential resolution to the mass and isotope imbalance, but, again, there are two problems: the debated size of this flux and 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 (0.4 to 40), 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. The sparse data documenting estuarine processes, where labile Ni associated with the riverine SPL would likely desorb and enter the dissolved pool, suggest conservative behavior in estuaries (Boyle et al., 1982; Edmond et al., 1985).

While this source pushes the mass budget in the right mass direction, what does this mean for the isotope mass balance (which also has to be satisfied)? A recent study explored the Ni isotopic composition in a variety of SPL particles of the Amazon river’s major tributaries and found that all 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. It could be that the Amazon is not representative of the global Ni SPL and the SPL is a significant source of Ni, but, given the trends observed by Revels et al. (2021) and experimentally derived isotope fractionations (Gueguen et al., 2018; Wasylenki et al., 2015), it seems unlikely that the source would be anything, but isotopically light relative to solution.

#### Carbonates

Carbonate’s ubiquity in marine settings makes it an attractive candidate as a missing light sink, but greatly variable estimates of the flux size and isotopic composition (and the unknown impact of diagenesis) make it challenging to determine their importance to the budget. An initial estimate of the Ni flux into carbonate exclusively focused on the Ni sink associated with organic matter associated with the carbonate flux (Ciscato et al., 2018). They used the organic carbon flux into shallow water carbonates (6x1012 mol Corg/yr +/- 50% ; Berner, 1990, 1982) and the Ni/TOC ratio (0.3-4.3x10-4 Ni ppm/TOC wt%) from a set of carbonate rich (34-75%) samples from a coastal lagoon to calculate a Ni flux into carbonates of 0.31 to 4.4x107 Ni mol/yr (Ciscato et al., 2018), an order of magnitude smaller than the organic matter or Fe-Mn deposit flux. However, this calculation omits any Ni that might be removed into the inorganic components of carbonates, which makes up a significant portion of the mass flux (Hayes et al., 2021; Milliman and Droxler, 1995). Alternatively, Alvarez et al. (2021) estimated the Ni flux into carbonates using the annual flux of CaCO­3 (3.2 and 14.7 x 1013 mol CaCO3/yr; Alvarez et al. (2021) and references therein) and an average concentration of Ni in carbonates derived from a Carboniferous marine limestone section in South China (2.7 ppm Ni; Zhao and Zheng, (2014)) and calculated a value of 1.5 to 6.7x108 Ni mol/yr. It is unclear how applicable the Ni concentration in buried, carboniferous marine limestones would be to the modern carbonate flux, especially without information on the impact of diagenesis on [Ni] of carbonates. Depending on the chosen estimate, the carbonate flux is either as important as the OM flux or Fe-Mn deposits or as inconsequential to the modern budget as the euxinic flux.

No study yet has measured δ60Ni in modern marine carbonates, but the sparse available data suggest they are isotopically light relative to or similar to seawater. The first attempt to estimate the δ60Ni of carbonates focused on the organic associated Ni. Carbonate rich coastal lagoon samples were leached to isolate the organic-rich pyrite fraction and (Ciscato et al., 2018) found a δ60Ni range of 1.10–1.64‰. Again, this omits Ni associated with the inorganic fraction. Another study measured δ60Ni 0.82 ± 0.1‰ 2sd in a single dolomite standard, JDo-1 which is a Permian dolomite from central Japan (Wu et al., 2019). Alvarez et al. (2021) experimentally investigated the relationship between Ni isotope fractionation and calcite precipitation rate by precipitating calcite at varying precipitations rates in the presence of Ni and measuring the δ60Nifluid and δ60Nicalcite once the solution composition remained constant. Based off the linear, direct relationship they found between Δ60Nicalcite-fluid and precipitation rate, they asserted that the equilibrium Δ60Nicalcite-fluid must be lower than the Δ60Nicalcite-fluid of the experiment with the slowest precipitation rate (Δ60Nicalcite-fluid < -1‰). No additional justification or reasoning for this constraint on equilibrium Δ60Nicalcite-fluidwas given. In addition, to the best of our knowledge, no studies have explored how diagenesis may impact δ60Nicarbonate and the effective isotopic composition of the carbonate flux. Evidently, it is unclear how important carbonates are to the modern marine Ni budget, as a potentially large, and isotopically light sink relative to seawater, but it seems that they may help balance the overwhelmingly isotopically light sources.

# Proposed Work

While the apparent marine Ni isotope imbalance seems quite complicated and will take several studies to resolve, we can begin to investigate the cause by tackling three high priority knowledge gaps. Based on the literature, a handful seem most pressing to investigate. The aim of this dissertation is

## Guiding Questions

1. Are marine carbonates an isotopically light sink of Ni? Does carbonate diagenesis lead to release or uptake of additional Ni and how does this impact the effective Ni isotopic composition and Ni mass flux of carbonates?
2. What governs the isotopic composition of Fe-Mn deposits? Can the observed variation in δ60Ni of Fe-Mn deposits be explained by differences in mineralogy or accumulation rate?
3. What is the Ni concentration and isotopic composition of pelagic OM and is the only dataset available for Ni isotopic composition in productive region OM representative?

## Project Summary

**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

1. In Fe-Mn deposits, Ni is primarily associated with Mn oxides rather than Fe oxides (Peacock and Sherman, 2007). [↑](#footnote-ref-1)