# Abstract

Not yet written

# Literature Review

Early life was likely profoundly impacted by the evolution of the trace metal composition of seawater. Common biological processes such as photosynthesis, methanogenesis and nitrogen fixation all require trace metals (e.g., Fe, Ni, Mn) (see Morel et al., 2003 for a review). Several studies have suggested an intimate relationship between the availability of trace metals and the evolution of early life (*e.g.,* Konhauser et al., 2009; Robbins et al., 2016; Zerkle et al., 2005). The trace metal composition of seawater is ultimately dictated by the dynamics of atmosphere, solid earth, ocean, and life and, with global changes, the availability of trace metals would change in response (*e.g.,* Liu et al., 2021; Saito et al., 2003; S. J. Wang et al., 2019). Efforts to reconstruct the evolution of the trace metal composition of seawater will surely inform the coevolution of Earth and life.

Life provides a link between the cycling of trace metals and the cycling of major elements. Reconstructing the marine cycles of major elements in the past and present will require knowledge of the controls on marine trace metals cycling. Many biological processes require trace metals to function. For example, the last step in every known methanogenesis pathway requires the Ni-enzyme methyl-coenzyme M reductase to proceed (Diekert et al., 1981; Ragsdale, 2009, 1998). Initiatives such as GEOTRACES were created from recognition of the influence and importance of trace metal cycling to marine life and major element cycling. A mechanistic, global view of the cycling of major elements must be accompanied by a similarly thorough picture of the cycling of trace metals. .

Here, we focus on Ni, an element whose marine cycling we know little about, but also one that is bio-essential for modern and ancient organisms. Nickel is a prime example of how shifts in trace metal marine concentrations due to changes in solid the Earth system can impact marine life. Aggregated Ni concentration data of volcanic rocks and marine sediments from the past 3.5 Ga suggest that the concentration of Ni in seawater dropped dramatically from 3.5 Ga to the Great Oxidation Event (GOE) and then remained roughly constant (Konhauser et al., 2009; Liu et al., 2021; S. J. Wang et al., 2019). Konhauser et al. (2009) hypothesized that the dramatic decrease in Ni seawater concentrations starved Ni-dependent methanogens, inhibited the production of methane, and facilitated the GOE (Konhauser et al., 2015, 2009; Liu et al., 2021). However, rather than Earth slipping into a permeant icehouse scenario, Ni isotope data from glacial diamictite composites suggest oxidative weathering of sulfides provided a new, crucial source of Ni which sustained methanogenesis, (S. J. Wang et al., 2019).

In more recent history, fluctuations in seawater Ni concentrations may have exacerbated or prolonged recovery from the end-Permian mass extinction (EPME), the largest mass extinction known to date. An increase in marine Ni input to the oceans from the eruption of the Siberian Traps may have caused non-limiting Ni conditions for methanogens, promoting marine anoxia (Rothman et al., 2014). In addition, Ni isotope variations of sedimentary rocks provide evidence for the eruptions of the Siberian Traps being the driving kill mechanism of the EPME (Li et al., 2021). Nickel also plays an important role in modern oceans, as a component of several enzymes used by a variety of organisms (*e.g.,* Bachmeier et al., 2002; Schonheit et al., 1979; Smith and Goldstein, 2019; Twining et al., 2012).

To investigate Ni and its marine evolution overtime, we must know the processes which govern the marine Ni cycle 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.*

## Nickel and Biology

In the modern ocean, Ni is an essential component of seven enzymes that regulate the global C, N, and O cycles (Ragsdale, 2009, 1998). For example, Ni-enzymes, urease and Ni-Fe hydrogenase are involved in the N cycle. 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 known for its association with the C cycle. The Ni-enzymes methyl coenzyme M reductase (MCR) and CO dehydrogenase 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).

Several modern and ancient organisms produce Ni-enzymes and rely on Ni. For instance, diatoms make urease and Ni-superoxide dismutase and contain Ni in association with both the internal biomass and inorganic (frustule) components of diatoms in roughly equal proportions (Benoiston et al., 2017; Twining et al., 2012). Foraminifera use urease as well, which may act as a pH regulator during shell formation, and contain Ni within their tests (Bachmeier et al., 2002; Munsel et al., 2010; Smith et al., 2020; Smith and Goldstein, 2019). Methanogens have been shown to have significant Ni requirements likely due to their use of MCR and CO dehydrogenase (Fuchs and Stupperich, 1986; Neubeck et al., 2016; Ragsdale, 2009; Schonheit et al., 1979).

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). 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 off the coast of 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 tested, ~0 nM, 85 nM, 1000 nM) (Schonheit et al., 1979). Clearly, marine life is highly sensitive to fluctuations in Ni concentration, and shifts in Ni concentration over time would impact the diversity and abundance of organisms.

## The Modern Marine Ni Budget and an Apparent Imbalance

Despite Ni’s biogeochemical importance, we have an incomplete picture of its marine cycling, even in the modern oceans. This perhaps is best evidenced by attempts to construct a modern Ni marine budget. Krishnaswami, (1976) first identified a massive apparent imbalance; their calculations indicated that a single output had a flux three times greater than the inputs. If this were true, the ocean would be rapidly depleted in Ni. Yet, there is no evidence for such extreme deviation from steady state. However, in the several decades that have followed this finding, 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 causing the apparent imbalance: large uncertainties, methods of estimation, missing fluxes, or a mix thereof?

In the following section, I will describe what we think is known about the distribution and cycling of Ni in the oceans by examining the methods used to estimate the fluxes in published Ni marine budgets (Ciscato et al., 2018; Gall et al., 2013; Gueguen and Rouxel, 2021; Little et al., 2020, 2015). They vary in terms of approach and confidence level. Through this exercise, I hope to highlight the greatest barriers to resolving the apparent Ni marine imbalance.

### Oceans

Nickel has a nutrient like depth profile, meaning it is depleted in the surface waters (~2nM) and enriched in the deep water (9-12nM) (*e.g.,* Archer et al., 2020; Cameron and Vance, 2014; Sclater et al., 1976; Yang et al., 2020), and has a residence time between 10 kyr and 30 kyr (Cameron and Vance, 2014; Little et al., 2020; Sclater et al., 1976). 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 (*e.g.,* Archer et al., 2020; 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). The distribution of Ni in ocean basins can primarily be described by mixing and biological processes (Middag et al., 2020; Yang et al., 2021). Nickel regeneration is associated with P regeneration in surface waters (*i.e.,* 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).

## Inputs

#### Dust

Dust can be a significant input for other metals to specific regions (*e.g.,* Fe; Ussher et al. (2013)), but, when assessed as a source of Ni, the flux appears quite small. Authors have estimated the flux of Ni from dust primarily 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]dust is 47 ppm, although past estimates show a range between 19 to 60 ppm (Rudnick and Gao, 2014 and references therein). To approximate the fraction of Ni that will dissolve, 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). Likely to avoid anthropogenic contributions, authors of marine Ni budgets typically include the dissolution value of 2% from Desboeufs et al. (2005), which leached loess from Cape Verde, rather than other studies which used modern aerosols and may be influenced by anthropogenic particles. From these values, the total yearly Ni input to the oceans from dust is 7.2x106 mol/yr.

#### Rivers: Dissolved and Suspended Particulate Loads

The trace metal composition of rivers is a product of its sources (*e.g.,* source rock and atmospheric deposition), weathering regime, and particulate load (Gaillardet et al., 2014, 2003). For nickel, trends in its riverine concentration is perhaps best explained by the weathering environment (Cameron and Vance, 2014; Revels et al., 2021). Rivers can contain metals within the dissolved phase or in the suspended particulate load (SPL) (*e.g.,* clays, carbonates, Fe and Mn oxyhydroxides, organic complexes). Because of Ni’s relatively immobile character, it is expected that a significant portion of Ni is hosted in the SPL relative to the dissolved load (Gaillardet et al., 2014, 2003; Gibbs, 1973; Viers et al., 2009). Both the dissolved and SPL may be important inputs of Ni to the oceans and so both are described below.

The dissolved load of rivers is a significant source of metals to the ocean and are estimated to be the greatest known source for Ni. To calculate the riverine input of Ni, others have primarily multiplied the annual riverine discharge and the dissolved Ni content of these rivers (which was defined by these papers as the remaining Ni in solution after being passed through a at least through a <0.45 μm filter[[1]](#footnote-1)). The estimated annual total discharge for rivers is 3.6–3.8×1016 kg based on available streamflow data of the world’s largest rivers (Berner and Berner, 1996; Dai and Trenberth, 2002). Estimates of the abundance weighted average Ni concentration of rivers have a fairly limited range. Martin and Whitfield, (1983) and references therein recorded an initial estimate for the global average riverine Ni concentration of 8.5 nM. Gaillardet et al. (2003) aggregated concentration and discharge data for >30 rivers and calculated 13.6 nM as the abundance weighted average riverine dissolved Ni concentration. Cameron and Vance (2014) collected Ni concentration data from 8 rivers, which constitute 20% of the total discharge, and calculated 9.6 nM as the abundance weighted average riverine dissolved Ni concentration. The most recent Ni marine budgets use an abundance weighted Ni concentration of 9.6 nM and an average riverine annual discharge of 3.7x1016kg/yr to calculate a Ni riverine input of 3.6x108 Ni mol/year.

Some have argued that the SPL is a significant source of Ni, but recent data suggest it plays a more minor role. A handful of studies have calculated the SPL/dissolved Ni in rivers and determined a wide range of values (0.4 to 40), with a large portion hosted by Fe and Mn oxyhydroxide phases (Dupré et al., 1996; Gibbs, 1977, 1973; Revels et al., 2021; Seyler and Boaventura, 2003; Viers et al., 2009).. A recent and incredibly detailed study of the SPL and dissolved Ni load in the Amazon and its tributaries found that the SPL contained only 0.25 to 0.7 times the dissolved load of Ni, which is a much smaller fraction than suggested by previous studies (Revels et al., 2021). Beyond the uncertainty of its Ni content, it is unclear how much of the SPL pool is actually mobilized. 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 or removal with flocculation products in estuaries (Boyle et al., 1982; Edmond et al., 1985; Sholkovitz, 1978). On the other hand, Ni may be leached from SPL deposited on continental shelves and margins over long time periods. However, this source of metals may be dampened by secondary mineral precipitation removing metal from solution (Jeandel and Oelkers, 2015; Jones et al., 2012; Oelkers et al., 2012). Because we still have much to learn about the size and mobilization of the SPL, and it has yet to be included in a published marine Ni budget, we do not propose a flux for it here and recognize it may be an important omitted component in the budget.

#### Hydrothermal Fluid

Hydrothermal fluid has been suggested as a possible Ni source, but no data yet suggest that hydrothermal activity is of the appropriate magnitude or isotopic composition to account for the isotope mass imbalance. To robustly calculate this flux, each hydrothermal regime must be considered individually, as they have different fluid fluxes and may have different Ni contents. For fluids from high temperature on axis systems, Ciscato et al. (2018) highlighted that, assuming an axial flux of 3x1013 kg/yr (Elderfield and Schultz, 1996), even if all of the hydrothermal fluid was as enriched in Ni as the highest recorded value (~3 μM from the Rainbow vent field on the Mid-Atlantic Ridge; Douville et al. (2002)), 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). The [Ni] from the Rainbow vent field is surely an overestimate, given vent fluids collected from six Mid-Atlantic Ridge hydrothermal systems all had Ni concentrations less than 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) (Ciscato et al., 2018; Schiltzer, 2017). Low temperature, ridge flank systems, which have much larger fluxes of water than the high temperature systems, also do not appear to be a source of Ni. Two studies explored Wheat et al., (2002) and (2003) fluxes out of or into ~65℃ and 25℃ ridge flank systems and found a very small source (1.5% of the riverine flux) or a very small sink (-1.8% of the riverine flux, corrected for modern estimate of river flux) of Ni, respectively. Ridge flanks of these temperatures (≥25℃) account for only 25% of the total convective heat loss from ridge flank type hydrothermal systems. 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 create fluids with different Ni concentrations and could either be a source or sink of Ni (Wheat et al., 2003).

### Benthic flux from Mn Oxide cycling

A recent hypothesis suggests that the redox cycling of Mn oxides in suboxic sediment columns acts as a benthic flux of Ni into the ocean (Little et al., 2020).. In pelagic sediments, the oxidation of organic matter down the sediment column results in a cascade of redox reactions, as each oxidant is exhausted (*e.g.,* Froelich et al., 1979; Klinkhammer et al., 1982; Klinkhammer, 1980; Shaw et al., 1990). Down this sequence, Mn oxides are reduced and Mn, along with its associated metals such as Ni, are released to porewater (*e.g.,* Heggie et al., 1986; Klinkhammer et al., 1982; Shaw et al., 1990; Versteegh et al., 2021). As Mn diffuses upward, it is reoxidized and precipitates as Mn oxides, creating a Mn oxide “cap” which sorbs the released Ni. However, in areas with low oxygen, the porewater Ni may not get efficiently trapped and diffuses up into the bottom water (see San Nicolas Basin in Shaw et al. (1990)).

Little et al. (2020) hypothesize this process provides a significant amount of Ni to the ocean (0.6 to 2.3x108 Ni mol/yr or 0.2 to 0.6 times the riverine flux) (Little et al., 2020), but it is unclear whether or not the described mechanism can feasibly provide a flux of this size. The flux is proposed to occur in suboxic sediments (those at >1000m depth with sediment O2 penetration <1cm; Morford and Emerson, (1999)), as oxic sediments efficiently trap Ni in the Mn oxide cap and exhibit small to nonexistent gradients between bottom water and surface porewater Ni concentrations (*e.g.,* Klinkhammer, 1980; Shaw et al., 1990; Versteegh et al., 2021). To calculate the flux of Ni out of suboxic sediments, Little et al. (2020) assumed Ni fluxes are coupled to Mn and multiplied the Ni/Mn ratio from porewater in oxic sediments (MANOP sites H and M; Klinkhammer, (1980)) by the suboxic Mn benthic flux. Given the expected seafloor coverage of suboxic sediments (4%; Morford and Emerson, (1999)), the benthic flux of Ni would be 400 to 1600 nmol Ni/cm2 kyr which is equal to or many times the delivery flux of Ni based on sediment trap data from the Atlantic (Kuss and Kremling, 1999; Spencer et al., 1978). Because the size of the proposed benthic flux is unclear, we tentatively omit it from the marine Ni budget described here, while acknowledging this hypothesis warrants further exploration.

## 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 proven challenging (Cameron and Vance, 2014; Gall et al., 2013; Little et al., 2020). Ferromanganese deposits exist as crusts, nodules and dispersed minerals, with Fe-Mn crusts receiving significant attention in marine Ni budgets until recently. Nickel is enriched in Fe-Mn crusts relative to seawater by ca. 106 (e.g., Li and Schoonmaker, 2003)and is primarily associated with Mn phases, such as birnessite, rather than Fe (*e.g.,* Hens et al., 2019; Koschinsky and Hein, 2003; Peacock and Sherman, 2007a). Peacock and Sherman, (2007b) developed a surface complexation model for the sorption of Ni onto hexagonal birnessite, an analog for natural phyllomanganates. Using their model with some assumptions, they predicted the dissolved Ni seawater concentration in equilibrium with birnessite, and, while an approximation, their results (7.2 nM) are surprisingly similar to concentrations found in modern seawater (2-12nM) (*e.g.,* Archer et al., 2020; Bruland, 1980; Cameron and Vance, 2014; Yang et al., 2020).

Previous estimates of the Ni flux into Fe-Mn deposits 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; Little et al., 2020). Past studies have typically either assumed Fe-Mn crust or dispersed Fe-Mn sediments are representative of the entire sink. We propose that these are not mutually exclusive and represent two distinct sinks, as suggested by previous authors (Gueguen and Rouxel, 2021). Gall et al. (2013) estimated the flux of Ni into Fe-Mn deposits by multiplying the accumulation rate of Fe-Mn crust and nodules (n=5) by the average Fe-Mn crust concentration and an unexplained estimated seafloor coverage and calculated a total flux of 5.1x108 Ni mol/yr. Cameron and Vance (2014) estimated the flux of Ni into Fe-Mn deposits by coupling the Ni fluxwith 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 (n>700), they calculated an output flux of 1.5x109 Ni mol/yr. Both estimates assume that Fe-Mn crusts and nodules are representative of all Fe-Mn deposits. Instead, Little et al. (2020) slightly decoupled their estimates from Fe-Mn crusts by instead calculating the flux of Ni into a pelagic clay/oxic sink which are functionally described as dispersed Fe-Mn oxides here. They assume that all Ni incorporated into pelagic clay is coupled to Mn and calculate a Ni flux of 1.5 to 5.9×108 Ni mol/yr by multiplying the seafloor coverage of clays, Mn accumulation rate in pelagic clays and Ni/Mn ratio of Fe-Mn crusts. The estimates for the Fe-Mn deposit flux(s) vary considerably. For Ni marine budgets, the most often used value is 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 associated and buried with organic matter (OM). Nickel in sinking particles is believed to be primarily hosted by organic biogenic phases. (Böning et al., 2004; Takano et al., 2020; Yang et al., 2021). Nickel exhibits a strong linear relationship with TOC in organic rich sediment from upwelling regions (r2 = 0.75 to 0.95) (Böning et al., 2015, 2012, 2004; Inthorn et al., 2006; Paulmier et al., 2006). The Ni ppm/TOC wt% ratio progressively increases with depth, perhaps due to preferential remineralization of C over Ni (Böning et al., 2015). As organic matter decays, Ni may be trapped in sediment by sulfides rather than being lost to solution (Ciscato et al., 2018; Tribovillard et al., 2006). During post depositional processes, porphyrins, the degradation product of organic molecules such as chlorophyl and heme found in mature organic rich materials, can incorporate significant levels of Ni (Callot et al., 1990; Grosjean et al., 2004; Lewan, 1984; Lewan and Maynard, 1982; Tribovillard et al., 2006).

Potentially due to the lack of data, only a flux for Ni into modern organic rich sediments in upwelling regions has been published (Ciscato et al., 2018). To calculate this flux, Ciscato et al. (2018) multiplied the total flux of the sediment (OM burial/year) by the associated Ni content (Ni/TOC) in samples from modern upwelling regions. 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 1x1013 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 calculated a total TOC burial for deep-sea sediments deposited >1000m of 20x1012 g Corg/yr (Hayes et al., 2021). To estimate the Ni/TOC, Ciscato et al. (2018) applied the Ni/TOC derived from the Peru upwelling region (9 Ni ppm/TOC wt%), which has a Ni ppm/TOC wt% linear regression intercept of 0 and therefore has a negligible non-authigenic Ni contribution. The only published OM Ni output flux used the flux of high productivity zones from Hedges and Kiel (1995) (1013 g C­org/yr) and the Peru margin Ni/TOC to calculate an Ni flux into upwelling regions organic rich sediments of 1.5x108 mol Ni/yr (Ciscato et al., 2018)s.

#### Euxinic Sediments

The euxinic 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 all euxinic sediments. Little et al. (2015) applied 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. Ciscato et al. (2018) instead calculated the euxinic sink similar to the productive region OM output. 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 ppm/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 quite different. However, both estimates are very small relative to the other outputs and, therefore, unless they are off by an order of magnitude, the euxinic output is mostly unimportant in modern oceans.

### Carbonates

Every year, a massive amount of carbonate is deposited (*e.g.,* Hayes et al., 2021; Milliman and Droxler, 1995) which makes them 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 organic matter associated with the carbonate flux (Ciscato et al., 2018). They used the organic carbon flux into shallow water carbonates (6x1012 g 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 0.31x107 to 4.4x107 Ni mol/yr (Ciscato et al., 2018)However, this calculation omits any Ni that might be incorporated within 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 a Ni flux into carbonates of 1.5 to 6.7x108 Ni mol/yr using the annual flux of CaCO­3 (3.2x1013 to 14.7x1013 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)). It is unclear how applicable the Ni concentration in carboniferous marine limestones would be to the modern carbonate flux, especially without information on the impact of diagenesis on the carbonate Ni concentration. Depending on the chosen estimate, the carbonate flux is either as important as the OM or Fe-Mn deposits fluxes or as inconsequential to the modern budget as the euxinic flux. Therefore, we omit it from the budget here.

## Identifying the Problem and Resolving the Apparent Imbalance through Isotope Mass Balance

What is missing from our understanding of the Ni marine cycle, and how can we remedy it? Taken together, the sum of the inputs and outputs equates to 3.6x108 Ni mol/yr and 6.8x108 Ni mol/yr, respectively. This implies the outputs are nearly double the inputs, but, again, no evidence suggests such drastic deviation from steady state. There are two potential causes of the apparent imbalance: missing fluxes or inaccurate flux estimates. Clearly, even with the best efforts, the flux estimates described above are tenuous, and hold significant uncertainties; some fluxes are even occasionally omitted when lacking. As discussed, refining the estimates directly is very difficult, and thus many in the community have applied a new constraint to the puzzle, Ni isotopic composition (δ60Ni, eq. X) (*e.g.,* 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 elemental fluxes and flux weighted isotopic compositions of the Ni inputs and outputs should balance (eq. 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 δ60Ni). This approach has been successfully applied to support the balance of inputs and outputs for other elemental cycles (*e.g.,* Mo, summaryized in Kendall et al. (2017)), and is currently in use to better constrain other apparent marine metal budget imbalances (*e.g.,* Cu, Zn; Little et al. (2014)).

To apply this approach, we must know the isotopic compositions of major fluxes. Initial investigations found that all known major sinks were isotopically heavier than sources, suggesting a missing light sink or heavy source or largely misunderstood isotopic compositions (Cameron et al., 2009; Cameron and Vance, 2014; Gall et al., 2013). Subsequent studies have highlighted exciting areas for further studies but have yet to conclusively identify the missing light sink or heavy source. Most either corroborated the findings of early studies, that outputs are isotopically heavier than inputs, or highlighted areas which require further exploration (Alvarez et al., 2021; Ciscato et al., 2018; Gueguen et al., 2020, 2016; Gueguen and Rouxel, 2021; Little et al., 2020; Sorensen et al., 2020; Vance et al., 2016). While the isotopic compositions of known sources are reasonably well characterized, the sinks are difficult to ascertain. To identify which fluxes are in most need of additional examination, we first look at what is known about the isotopic composition of components within the previously modeled marine Ni budgets

## Oceans

The distribution of Ni isotopes in the oceans can be explained by fractionation due to biological activity and endmember mixing (Yang et al., 2021). The deep ocean is globally homogenous, with an isotopic composition between 1.3‰ to 1.4‰ while the surface ocean varies (Archer et al., 2020; Cameron and Vance, 2014; Takano et al., 2017; Yang et al., 2020). 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 exhibit a nutrient like surface [Ni] depletion although less pronounced, shows no enrichment in the heavier Ni isotopes in surface waters (R. M. 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.

## Inputs

### Dust

The isotopic composition of continental crust, which we assume to represent that of dust, has a tight range between -0.1‰ and +0.2‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013; Wu et al., 2019 and references therein). Basalts rock standards analyzed across multiple studies have a δ60Ni range from 0.01 to 0.21‰, and loess standards have a δ60Ni range of 0.03 to 0.21‰ (Wu et al., 2019 and references therein).

### Rivers: Dissolved and Suspended Particulate Load

There have been three studies of the Ni isotopic composition of the dissolved load of rivers, and while there is a large range, the flux weighted average is clearly below the Ni isotopic composition of the oceans. Cameron and Vance (2014) performed a broad survey of the Ni isotopic composition of the dissolved load of several of the world’s largest rivers. They found a broad range of compositions (0.29‰ to 1.34‰) and a flux weighted average composition of 0.80‰. Isotopic compositions generally correlated with [Ni] and suggested a role of partitioning between solid phase and solution either during weathering or transport. A later study of the Amazon and its tributaries largely supported this interpretation (see below for further discussion). Their slightly widened the range of and increased the flux weighted average Ni isotopic composition of the dissolved load of rivers (0.18‰ to 1.38‰, flux weighted average = 0.90‰) (Revels et al., 2021). Finally, Takano et al. (2021) analyzed Ni isotopes in a variety of freshwater samples, including the Uji and Tawara rivers in Japan, observed a similar range of δ60Ni(0.72‰ to 1.24‰)

In the search for an isotopically heavy source of Ni, Revels et al. (2021) performed an incredibly detailed study of the suspended load of the Amazon river and its tributaries and found that all SPL phases (*i.e.,* carbonates, oxides, organic, and residual) were isotopically lighter than solution (all <0.35‰ compared to ~0.90‰ in the riverine dissolved load) (Revels et al., 2021). Nickel was generally mostly hosted by oxides and residual phases. They concluded that the main control on the isotopic composition of the dissolved load is Ni removal with secondary minerals, such as Fe oxides, during weathering or transport. Experimental and natural data demonstrate that Fe oxides, produced from weathering of ultra-mafic to mafic rocks, sorb isotopically light Ni (Δ60Nidissolved-ferrihydrite = +0.35 ± 0.20‰ 2sd and Δ60Nidissolved-goethite = +0.77 ± 0.23‰ 2sd, where Δ60Nix-y = δ60Nix - δ60Niy) (Gueguen et al., 2018; Spivak-Birndorf et al., 2018; Wasylenki et al., 2015). Even if the Amazon river has a SPL not representative of the global SPL, 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 SPL input would be anything, but isotopically light relative to seawater.

### Hydrothermal Fluids

Most of what is known about the isotopic composition of hydrothermal fluids is indirect, but almost all data point to hydrothermal fluids being isotopically light relative to seawater. The first authors to estimate of hydrothermal fluid δ60Ni are also the only ones to suggest that they are isotopically similar to seawater (~1.5‰), based on analyses of Fe-Mn crusts near mid-ocean ridges (Gall et al., 2013). However, they found no correlation between δ60Ni and distance from mid-ocean ridges. Other estimates focused on the narrow range of δ60Ni for ultramafic and mafic rock (~0.1‰), from which hydrothermal fluids would likely 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 of seawater interacting with lava from the 2018 eruption of Kīlauea. They observed a mixing relationship with two end-members isotopically similar to seawater (1.3‰ to 1.4‰) and basalt (0.1‰) (Hawco et al., 2020). Finally, 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.

### Benthic Flux

Little et al. (2020) hypothesize a mechanism that results in an isotopically heavy benthic flux, however no available data strongly supports this interpretation. In this mechanism, Ni arrives to the sediment associated with Mn oxides with an isotopic composition similar to Fe-Mn crusts (~1.6‰) which uptake isotopically *heavy* Ni relative to solution (1.3 to 1.4) (Gall et al., 2013; Gueguen et al., 2020, 2016; Little et al., 2020). As the sediment is buried and organic matter is oxidized, Mn oxides are reduced, and Ni is released. Assuming quantitative release and the amount of Ni in pore fluid before Mn oxide reduction is much less than that which is released from Mn oxides, the porewater has a Ni isotopic composition of 1.6 ‰. Next, Mn is re-oxidized as it diffuses upwards, and some Ni resorbs to the Mn oxides. An experimental Ni-birnessite sorption study recorded extreme isotope fractionations between surface sorbed Ni and Ni in solution, (Δ60NiMn oxides-solution­ = −2.76‰ to −3.35‰) (Sorensen et al., 2020). Given this fractionation, Little et al (2020) inferred isotopically *light* Ni would sorb to the precipitated Mn oxides and the leftover benthic flux Ni would therefore be extremely isotopically heavy (~3‰), resulting in an isotopically heavy benthic flux.

With little information, Little et al. (2020) were forced to make assumptions about the benthic flux mechanism. The proposed mechanism requires that Mn oxides sorb isotopically heavy Ni when Ni is delivered to the sediment as Ni associated with Mn oxide phases, but then sorbs isotopically light Ni when Ni resorbs to the Mn oxide cap. In addition, perhaps most problematic for this hypothesis, one would expect the sediments to reflect drastic isotopic changes in the Mn reduction zone and Mn oxide cap, but this is not reflected in the sediment data. In fact, the Ni isotopic compositions of sediments are generally flat across the reduction and oxidation zones (Fleischmann et al., 2021; Little et al., 2020) For example, at MANOP site M, the sediment Ni concentration plummets by over 50% across the Mn reduction zone (from ~880ppm to 380 ppm), and pore water Ni concentrations increase from 10nM to 200nM, but the Ni isotopic composition of the sediment varies by only 0.1‰ (Klinkhammer, 1980; Little et al., 2020). Nickel isotope analysis of porewaters and additional experiments of Ni sorption onto Mn oxides will add great value to this discussion, but, for the reasons above, the proposed hypothesis currently appears improbable

## Outputs

#### Fe-Mn deposits

The δ60Ni of hydrogenetic Fe-Mn crust is fairly consistent, but, given the homogeneity of the deep ocean from which they ultimately precipitate, covers a unexpectedly large range. Gall et al. (2013) measured 24 surface scrapings of Fe-Mn crusts across the globe and found a variable isotopic range from 0.9 to 2.5‰ with an average of 1.67±0.8‰. A subsequent study of four North and South Pacific Fe-M crust ~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) (Gueguen et al., 2016). 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 deposits generally incorporate isotopically heavy Ni relative to solution.

In stark contrast to pure hydrogenetic Fe-Mn crusts, mixed hydrothermal-hydrogenetic and hydrothermal Fe-Mn crusts are 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). The handful of Fe-Mn nodules analyzed also exhibit isotopically lighter and variable δ60Ni values (0.23±0.90‰ 2sd, n=6) (Little et al., 2020; Wu et al., 2019 and references therein). From this set of data, it appears 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, after correcting for detrital Ni contributions, calculated an authigenic δ60Ni range of 1.19‰ to 1.20‰, although their best estimate is oddly 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). To the best of our knowledge, there are no Ni isotope data for the pelagic OM sink.

The only available δ60Ni data for euxinic sediments comes from a single location, but, because this is a small output, and its isotopic composition is not expected to have a major impact on the global marine isotope mass balance. 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 Sea seawater have Ni isotopic compositions of 0.3‰ to 0.6‰ and ~1.35‰, respectively. While euxinic sediments are isotopically lighter than seawater, the sink is not of sufficient size to significantly alter the budget.

### Carbonates

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 within carbonates. Carbonate rich coastal lagoon samples were leached to isolate the organic-rich pyrite fraction and found a δ60Ni range of 1.10–1.64‰ (Ciscato et al., 2018). Again, this omits Ni associated with the inorganic fraction. A single dolomite standard Another study measured a δ60Ni of 0.82 ± 0.1‰ 2sd in a Permian dolomite from central Japan, JDO-1 (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 rates in the presence of Ni and measuring the δ60Nifluid and δ60Nicalcite once the solution composition appeared constant. Based on the relationship they found between Δ60Nicalcite-fluid and precipitation rate, they asserted that the equilibrium isotope fractionation between fluid and solidmust be lower than the fractionation of the experiment with the slowest precipitation rate (Δ60Nicalcite-fluid < -1‰). No additional justification or reasoning for this constraint on equilibrium fractionation was 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. From these spare observations, it is unclear how important carbonates are to the modern marine Ni budget. As a potentially large and isotopically light sink, it seems that carbonates may help balance the overwhelmingly isotopically light sources and are an important sediment to investigate further.

1. Some authors use a <0.2 μm definition for dissolved. [↑](#footnote-ref-1)