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Also, please tell me the document is not going to be so long that it really needs a TOC?

Abstract

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Literature Review

The trajectory of early life was likely profoundly impacted by evolution the of the trace metal composition of seawater. Ubiquitous 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. Therefore, with global changes, we would anticipate the availability of trace metals would change in response (e.g., Konhauser et al., 2009; Saito et al., 2003). Efforts to reconstruct the evolution of the trace metal composition of seawater will surely inform how early life and Earth evolved as well.

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Understanding the modern cycling of trace metals is also of interest to better determine their relationship with 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.

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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 can potentially impact marine life. Aggregated data of global source rocks and marine sediments from the past 3.5Ga suggest that the concentration of Ni in seawater dropped dramatically across 3.5Ga to 2.2Ga and then remained roughly constant (Konhauser et al., 2009; Liu et al., 2021; Wasylenki et al., 2015). Konhauser et al. (2009) hypothesized that the dramatic decrease in Ni seawater concentrations, just prior to the GOE, starved Ni-dependent methanogens, inhibited the production of methane, and facilitated the GOE (Konhauser et al., 2015, 2009; Liu et al., 2021). However, after the decline in Ni, Ni isotope data from glacial diamictite composites suggest oxidative weathering of sulfides provided a new sustaining source of Ni for methanogens, which may have prevented a snowball earth scenario post-GOE (S. J. Wang et al., 2019).

In more recent history, fluctuations in seawater Ni concentrations may have increased 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 approximately 500ky prior to the EPME 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 require knowledge of the processes which govern 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.*

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-superoxide 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 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).

Several modern and ancient organisms rely on Ni because they use these enzymes. Diatoms use urease and Ni-superoxide dismutase (Benoitson 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 use urease as well 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). 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 tested, ~0 nM, 85 nM, 1000 nM) (Schonheit et al., 1979). Clearly, these organisms are highly sensitive to fluctuations in Ni concentration and shifts in Ni concentration over time would impact the diversity and abundance of organisms.

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The Modern Marine Ni Budget and an Apparent Imbalance

Unsurprisingly, Ni 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). Nickel has a residence time between 10 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., 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).

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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 imbalance; their calculations suggested 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. There is no evidence for such extreme deviation from steady state. However, in the several decades that have followed this conclusion, 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). Is this discrepancy due to large uncertainties, different methods of estimation, missing fluxes, or a mix thereof?

In the following section, I will describe the methods used to estimate the inputs and outputs listed 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.

Inputs

Dust

Dust can be a significant source of other metals to specific regions (*e.g.*, Fe; Ussher et al. (2013)), but, when assessed as a source of Ni, the flux has been found to be quite small. Others 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 $[\text{Ni}]_{\text{dust}}$ 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 dissolve¹, 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 to 30 times the mixing time of the ocean (Cameron and Vance, 2014; Little et al., 2020; Sclater et al., 1976), the natural contributions are likely still most relevant to the modern marine budget. 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 7.2×10^6 mol/yr.

¹ The fraction of soluble Ni is typically represented as the amount of Ni dissolved divided by the total Ni in bulk aerosol.

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Rivers: Dissolved and Suspended Particulate Loads

[Chunk about how Ni gets into rivers] 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). Nickel is considered an intermediate mobile element and a (Gaillardet et al., 2003) because of its relatively immobile character, it is expected that a significant portion of Ni is hosted in the suspended particulate load (SPL) relative to the dissolved load. Both the dissolved and SPL may be important inputs of Ni to the oceans and so both are described below.

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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. Similarly, 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 0.2 μm filter). The estimated annual total discharge for rivers is $3.6\text{--}3.8 \times 10^{16}$ 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) 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 average riverine dissolved Ni concentration. 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 most recent Ni marine budgets use the abundance weighted Ni concentration from Cameron and Vance (2014) and an average riverine annual discharge of 3.7×10^{16} kg/yr to calculate a Ni riverine input of 3.6×10^8 Ni mol/year.

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The SPL of rivers has yet to be included in a published marine Ni budget because of a lack of information, but recent data suggests it may not be as important as previously proposed.. 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; Viers et al., 2009). A handful of studies have calculated the SPL/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 (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 Ni, which is a much smaller fraction than suggested by previous studies (Revels et al., 2021). Beyond the uncertainty of its size, 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 humic acid-hydrous iron oxide flocculation products in estuaries (Boyle et al., 1982; Edmond et al., 1985; Sholkovitz, 1978). However, it is also possible for SPL deposited on continental shelves and margins to leach metals over long time periods, but this source of metals may be dampened by secondary mineral precipitation (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 important to 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 may have different Ni fluxes. For fluids from high temperature on axis systems, to the best of our knowledge, the highest observed [Ni] is $\sim 3 \mu\text{M}$ from the Rainbow vent field on the Mid-Atlantic Ridge (Douville et al., 2002). Ciscato et al. (2018) highlighted that even if all of the hydrothermal fluid was so enriched in Ni, assuming an axial flux of $3 \times 10^{13} \text{ kg/yr}$ (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 $9 \times 10^7 \text{ Ni mol/yr}$ here). Vent fluids collected from six Mid-Atlantic Ridge hydrothermal systems all had Ni concentrations less than $2 \mu\text{M}$ (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 than the high temperature than the high temperature systems, also do not appear to be a source of Ni. (Wheat et al., 2003, 2002) conducted two studies exploring $\sim 65^\circ\text{C}$ and 25°C 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. However, ridge flanks of these temperatures ($\geq 25^\circ\text{C}$) 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 ($\leq 25^\circ\text{C}$) which may create fluids with different Ni concentrations and could either be a source or sink of Ni (Wheat et al., 2003). [include estimates of flux here]

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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 (Little et al., 2020). However, while Mn oxide redox cycling has an obvious impact on the distribution of Ni, the available data do not support such a process. In pelagic sediments, the oxidation of organic matter results in a cascade of redox reactions down the sediment column, 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 reaches a zone with available oxygen and precipitates as Mn oxides, creating a Mn oxide “cap” which resorbs 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)).

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Little et al. (2020) hypothesize this process occurs in suboxic sediments and provides a significant amount of Ni to the ocean (0.6 to $2.3 \times 10^8 \text{ Ni mol/yr}$ or 0.2 to 0.6 times the riverine flux) (Little et al., 2020), but it is unclear if such a mechanism can feasibly provide a flux of this

size. Sub-oxic sediments are defined as those at >1000m water depth with sediment O₂ penetration <1cm and are estimated to have a Mn benthic flux of 0.7–1.3×10¹⁰ Mn mol/yr (Morford and Emerson, 1999). 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. (can calculate representative flux from Shaw maybe? To say whether or not the oxic values used were a good guess?).

Given suboxic sediments cover approximately 4% of the seafloor (Morford and Emerson, 1999) and area of the seafloor is ~354×10⁶ km² (Costello et al., 2010), 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 in the Atlantic (Klinkhammer, 1980; Kuss and Kremling, 1999). Therefore, all initially buried Ni must be mobilized to provide the described benthic flux, but Ni does get buried with sediment (Little et al., 2020; Shaw et al., 1990; Versteegh et al., 2021). Such a high benthic flux would not be necessary if it occurred in oxic settings as well, but this appears unlikely. Sediments from more common, pelagic oxic settings efficiently trap Ni in the Mn oxide cap and exhibit small to nonexistent gradients between bottom water and surface porewater Ni concentrations (Klinkhammer, 1980; Shaw et al., 1990; Versteegh et al., 2021). While there may be a benthic flux of Ni from suboxic sediments, it currently seems infeasible for the described mechanism to contribute such a significant Ni flux.

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. Ferromanganese deposits exist as crusts, nodules and dispersed minerals, with Fe-Mn crusts receiving significant attention in marine Ni budgets. 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, 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 phyllosulfates. 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 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 either assumed Fe-Mn crust or Mn-rich pelagic 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 (based on of five samples) by the average Fe-Mn crust concentration and an unexplained estimated seafloor coverage and calculated a total flux of 5.1×10⁸ Ni mol/yr. Cameron and Vance (2014) estimated the flux of Ni into Fe-Mn deposits by coupling the Ni marine budget

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Commented [EJB16]: Maybe need to expand on peacock thing... it's sort of awkward.

Commented [EJB17]: I write "as suggested by previous authors" because Gueguen 2021 does have these two sinks as separate parts of their mass balance, which implies they are two different sinks.

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 1.5×10^9 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 decoupled 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 dispersed Fe-Mn deposits could be defined, we consider this an estimate of the Fe-Mn deposit sink. They assume that all Ni incorporated into pelagic clay is coupled to Mn and calculate the Ni flux 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 Fe-Mn deposit sink, 1.5 to 5.9×10^8 Ni mol/yr. The estimates for this flux vary considerably and cover greatly differing sediment types. For Ni marine budgets, the most often used value is 5.1×10^8 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 exhibits a strong linear relationship with TOC in organic rich sediment from upwelling regions in the Gulf of California, Chile, Peru, and Namibia ($r^2 = 0.75$ 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; Tribouillard et al., 2006). During post depositional processes, porphyrins, the degradation product of chlorophyll and heme, found in mature organic rich materials can incorporate significant levels of Ni from potentially a combination of Ni sourced from the water column (acting as an additional output) and Ni redistribution in the sediment (Callot et al., 1990; Grosjean et al., 2004; Lewan, 1984; Lewan and Maynard, 1982; Tribouillard et al., 2006).

The approach taken in the literature to quantify this sink multiplies 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 1×10^{13} g C_{org} /yr and 5×10^{12} g C_{org} /yr, respectively, with a 50% uncertainty (Hedges and Keil, 1995). A more recent estimate using ^{230}Th normalized fluxes calculated a total TOC burial for deep-sea sediments deposited ($>1000\text{m}$) of 20×10^{12} g C_{org} /yr (Hayes et al., 2021). To estimate the Ni/TOC, past studies have primarily focused on productive regions. Ciscato et al. (2018) applied the Ni/TOC derived from the Peru upwelling region (9 Ni ppm/TOC wt%), which has a Ni/TOC intercept of 0 and therefore has a negligible non-authigenic Ni contribution, to calculate the fraction of Ni that is buried with organic matter at productive upwelling regions. To the best of our knowledge, there is no estimate of the Ni/TOC for OM buried in pelagic zones, and therefore pelagic OM may be an omitted nontrivial output of Ni. The only published OM Ni output flux comes from Ciscato et al. (2018). They used the flux of high productivity zones from Hedges and Kiel (1995) (10^{13} g C_{org} /yr) and the Peru Ni/TOC to calculate an OM Ni flux of 1.5×10^8 mol Ni/yr.

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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 euxinic sediments. Little et al. (2015) 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 0.4×10^8 Ni mol/yr. 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 (1×10^{12} g C/year with an uncertainty of 50%; Berner, (1982)) and the Ni/TOC ratios from Black Sea euxinic sediments ($0.54\text{--}1.49 \times 10^{-3}$ Ni ppm/TOC wt% (Little et al., 2015; Vance et al., 2016) to calculate a total flux of 0.15×10^8 Ni mol/yr (Ciscato et al., 2018; Vance et al., 2016). The estimates are quite 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.

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Taken together, the sum of the sources equates to 3.6×10^8 Ni mol/yr and the sum of the sinks equates to 6.8×10^8 Ni mol/yr, nearly double the sum of the sources. What is missing from our understanding of the Ni marine cycle?

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, if not omitted altogether. 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 ($\delta^{60}\text{Ni}$, 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 fluxweighted isotopic compositions of the Ni sources and sinks 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 $\delta^{60}\text{Ni}$). This approach has been successfully applied to support the balance of inputs and outputs for other elemental cycles (e.g., Mo, summarized 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)).

$$\delta^{60}\text{Ni}_{\text{sample}} = \left(\frac{\left(\frac{{}^x\text{Ni}}{{}^{58}\text{Ni}} \right)_{\text{sample}}}{\left(\frac{{}^x\text{Ni}}{{}^{58}\text{Ni}} \right)_{\text{SRM 986}}} - 1 \right) \times 1000\text{‰} \text{ where SRM 986 is a Ni isotope standard}$$

$$\sum_{i=\text{input}} \text{Flux}_i \times \delta^{60}\text{Ni}_i = \sum_{j=\text{output}} \text{Flux}_j \times \delta^{60}\text{Ni}_j$$

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

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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 yet to conclusively identify the missing light sink or heavy source, and mostly either corroborated the findings of early studies 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. But which fluxes are the most in need of additional examination and which fluxes may be significant, but are missing from the previous budgets? To address these questions, we first look at what is known about the isotopic composition of components within the previously modeled marine Ni budgets

Commented [EJB20]: I don't think this tense is correct.

Oceans

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 displays a nutrient like surface [Ni] depletion although less pronounced, shows no enrichment in the heavier 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.

Commented [EJB21]: I should add something about the new shun-chung yang paper

Inputs

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 $\delta^{60}\text{Ni}$ range from 0.01 to 0.21‰, and loess standards have a $\delta^{60}\text{Ni}$ range of 0.03 to 0.21‰ (Wu et al., 2019).

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There have been two 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 some 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, detailed study of the Amazon and its tributaries largely supported this interpretation (see below for further discussion) and 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).

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 $<0.35\text{‰}$ compared to $\sim 0.90\text{‰}$ of rivers) (Revels et al., 2021). Nickel was generally mostly hosted by oxides and residual particles. 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 which host the majority of the crust's Ni exposed to weathering, sorb isotopically light Ni ($\Delta^{60/58}\text{Ni}_{\text{dissolved-ferrihydrite}} = +0.35 \pm 0.20\text{‰}$ 2sd and $\Delta^{60/58}\text{Ni}_{\text{dissolved-goethite}} = +0.77 \pm 0.23\text{‰}$ 2sd) (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.

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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 estimate of hydrothermal fluid $\delta^{60}\text{Ni}$ was also the only one to suggest that they were isotopically similar to seawater ($\sim 1.5\text{‰}$), based on analyses of Fe-Mn crusts near the mid-ocean ridge (Gall et al., 2013). However, there was no correlation with $\delta^{60}\text{Ni}$ and distance from a mid-ocean ridge. Other estimates focused on the narrow range of $\delta^{60}\text{Ni}$ for ultramafic and mafic rock ($\sim 0.1\text{‰}$, 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 $\delta^{60}\text{Ni}$ 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 Kilauea and found for the $\delta^{60}\text{Ni}$ data followed mixing between two end-members isotopically similar to seawater and basalt (0.1 to 0.3‰) (Hawco et al., 2020). Pašava et al., (2019) measured a $\delta^{60}\text{Ni}$ 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.

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Outputs

Fe-Mn deposits

The isotopic compositions of the outputs further exacerbate, or at the very least complicate, the isotope imbalance. The Fe-Mn deposit sink may be the largest sink (see above section), but also the most difficult to determine what is representative, perhaps because of the many sediment types this sink is expected to represent. In marine Ni budgets, Fe-Mn deposits are often isotopically represented by hydrogenetic Fe-Mn crusts. 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 $1.67 \pm 0.8\text{‰}$. They did not observe any strong correlation between $\delta^{60}\text{Ni}$ and ocean basin, oxygen saturation or Ni concentration (Fig xx), but there was a mild correlation between $\delta^{60}\text{Ni}$ and distance to continental shelf, likely reflecting the contribution of isotopically lighter detrital sediments. A subsequent study of four North and South Pacific Fe-M crust ~ 20 mm cores found similar values to Gall et al. (2013) ($1.79 \pm 0.21\text{‰}$ 2sd, $n = 31$ for North Pacific and $1.73 \pm 0.21\text{‰}$ 2sd, $n = 21$ for South Pacific) (Gueguen et al., 2016). One core from the South Pacific had a systematic and dramatic drop in $\delta^{60}\text{Ni}$ downcore (from 1.89‰ to 0.25‰) associated with lower Mn/Ni, which may be a result of

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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 $\delta^{60}\text{Ni}$ 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.

However, if we consider virtually any other Fe-Mn sediment type, there is no clear consensus regarding whether Fe-Mn deposits have an insignificant or extreme fractionation (and if extreme, in which direction?). In contrast to pure hydrogenetic crusts, mixed hydrothermal-hydrogenetic and hydrothermal Fe-Mn crusts are isotopically lighter than seawater with $\delta^{60}\text{Ni}$ 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 $\delta^{60}\text{Ni}$ values (0.23 ± 0.90 ‰ 2sd, $n=6$) (Little et al., 2020; Wu et al., 2019 and references therein). This range in $\delta^{60}\text{Ni}$ has been attributed to differences in mineralogy (phyllosulfates or todorokite), 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, and release of its associated Ni, in the water column of the Black Sea corresponds to a significant decrease in $\delta^{60/58}\text{Ni}_{\text{solution}}$, with a calculated $\Delta^{60/58}\text{Ni}_{\text{solution-solid}} \sim 4.0$ ‰ (Vance et al., 2016). 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 $\delta^{60}\text{Ni}$ 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 $\delta^{60}\text{Ni}$ 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 ($\delta^{60}\text{Ni} = -0.84$ ‰ 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.

Again, a single paper has investigated the $\delta^{60}\text{Ni}$ of euxinic sediments, but this is a small sink, 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. In published marine Ni budgets, euxinic sediments are assigned a Ni isotopic composition of +0.45‰ (Ciscato et al., 2018; Gueguen and Rouxel, 2021; 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 major 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 and there is no readily available measurements of $\delta^{60}\text{Ni}$ in pelagic OM. Work to better understand $\delta^{60}\text{Ni}$ variability in Fe-Mn sediments and adding to the small OM sample set will surely be useful.

Commented [LEW26]: Wait, there is a consensus about the deposits—the data are what they are. What EXACTLY has no consensus?

Commented [LEW27]: Never yet mentioned....

Commented [LEW28]: It's worse than that—they have the phyllosulfates versus todorokite phases WRONG in some samples.

Commented [LEW29]: I doubt any of your committee members will be able to understand this sentence. Gotta give them what they need. And they will be confused about why this is in the “outputs” section.

I would not use solid-solution, but MnOx particle-water.

Commented [LEW30]: Papers can't investigate. No brains.

Commented [LEW31]: What is this doing under the OM/Euxinic heading?

Missing Components

Riverine Suspended Particulate Load

There may be direct Ni isotope measurements of the benthic flux in the not too distant future (Little et al., 2020), but, in the meantime, authors have attempted to estimate the flux's isotopic composition given the available, yet conflicting, information about Ni fraction with Mn oxides. 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 ($\sim 1.6\text{‰}$) which uptake isotopically *heavy* Ni relative to solution (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 reduction, the porewater has a Ni isotopic composition of 1.6‰ ². 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, ($\Delta^{60}\text{Ni}_{\text{Mn oxides-solution}} = -2.76\text{‰}$ 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 ($\sim 3\text{‰}$).

Commented [EJB32]: Need to move this to the isotope settings

² Nickel released from Mn oxide reduction will mix with the ambient Ni in pore fluids. However, I believe the isotopic composition of the mixture will be indistinguishable from the isotopic composition of the released Ni because of the significant Ni concentration difference between pore fluid above and below the zone of Mn reduction. Pore fluid Ni concentrations above the Mn oxide cap is typically similar to seawater ($\sim 10\text{ nM}$) and in the Mn reduction zone are typically an order of magnitude greater than seawater (100–400 nM) (Klinkhammer et al., 1982; Klinkhammer, 1980; Shaw et al., 1990). Therefore, the ambient pore fluid would have to be extremely isotopically different from the Ni released from Mn reduction to have an impact on the isotopic composition of the mixture.

With little information, Little et al. (2020) were forced to make assumptions about the benthic flux mechanism. Unfortunately, these assumptions are not internally consistent or supported by sediment data. The proposed mechanism requires that Mn oxides sorb isotopically heavy Ni when Ni is delivered to the sediment, 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 further 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. 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 the Ni associated with organic matter associated derived from the carbonate flux (Ciscato et al., 2018). They used the organic carbon flux into shallow water carbonates (6×10^{12} g $C_{org}/yr \pm 50\%$; Berner, 1990, 1982) and the Ni/TOC ratio ($0.3\text{--}4.3 \times 10^{-4}$ 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 0.31×10^7 to 4.4×10^7 Ni mol/yr (Ciscato et al., 2018), an order of magnitude smaller than the organic matter or Fe-Mn deposit fluxes. 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 6.7×10^8 Ni mol/yr using the annual flux of $CaCO_3$ (3.2×10^{13} to 14.7×10^{13} mol $CaCO_3/yr$; 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 buried, 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.

No study yet has measured $\delta^{60}Ni$ 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 $\delta^{60}Ni$ of carbonates focused on the organic associated Ni. Carbonate rich coastal lagoon samples were leached to isolate the organic-rich pyrite fraction and found a $\delta^{60}Ni$ range of 1.10–1.64‰ (Ciscato et al., 2018). Again, this omits Ni associated with the inorganic fraction. Another study measured a $\delta^{60}Ni$ of $0.82 \pm 0.1\%$ 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 rates in the presence of Ni and measuring the $\delta^{60}\text{Ni}_{\text{fluid}}$ and $\delta^{60}\text{Ni}_{\text{calcite}}$ once the solution composition appeared constant. Based on the relationship they found between $\Delta^{60}\text{Ni}_{\text{calcite-fluid}}$ and precipitation rate, they asserted that the equilibrium isotope fractionation between fluid and solid must be lower than the fractionation of the experiment with the slowest precipitation rate ($\Delta^{60}\text{Ni}_{\text{calcite-fluid}} < -1\text{‰}$). 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 $\delta^{60}\text{Ni}_{\text{carbonate}}$ and the effective isotopic composition of the carbonate flux. From these sparse 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.

Commented [EJB33]: I'm having a hard time talking about this and don't even mention the Ni adsorption experiments they did

Commented [EJB34]: Maybe add a sentence about the bond length differences between Ni-O in aquo complex and the estimated Ni-O in carbonate

Commented [EJB35]: Can I find an example of this as being important for another system?