# Abstract

Not yet written

# Literature Review

The trajectory of early life was likely profoundly impacted by 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 trace metal marine chemistry will surely inform how early life and Earth evolved as well.

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.

Here, we focus on Ni, an element whose marine cycling we know little about, but also one that is a bio-essential element for modern and ancient organisms. 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 and prolonged recovery from the end-Permian extinction, the largest mass extinction known to date. An increase in marine Ni input to the oceans from the eruption of the Siberian Traps may have caused non-limiting Ni conditions for methanogens, promoting marine anoxia (Rothman et al., 2014). In addition, the variations in Ni isotope ratios just before this period have been used to identify that the Siberian Traps [inset Li et al 2019 info about P-T] In the modern ocean, Ni is an essential component of seven enzymes that regulate the global C, N, and O cycles (Ragsdale, 2009, 1998). To investigate Ni and its marine evolution overtime, we require knowledge of the processes which 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

Nickel-enzymes have roles in the C, O, and N cycles. 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 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 (Benoiston et al., 2017; Twining et al., 2012). Nickel is found in association with both the internal biomass and inorganic (frustule) components of diatoms in roughly equal proportions (Twining et al., 2012). Foraminifera 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 concenration and shifts in Ni concentration over time would impact the diversity and abundance of organisms.

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 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). Nickel has a residence time between 10 to 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 Apparent Modern Marine Ni Mass Imbalance

Despite Ni’s biogeochemical importance, we have a poor understanding 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). To investigate what might be causing the perceived imbalance, we can examine the methods used to calculate the fluxes and their associated uncertainties.

## Inputs

#### Dust

Dust can be a significant source in specific regions for other metals (e.g., Fe; Ussher et al. (2013)), but, when assessed as a source of Ni, 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 [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[[1]](#footnote-1), several studies have performed leaching experiments with loess (Desboeufs et al., 2005) or particles filtered from air at coastal or island stations (Fishwick et al., 2017; Mackey et al., 2015) using leachates such as ultra-high purity water or filtered seawater. The percent of dissolved Ni ranges from 1% to 86% and appears to be primarily dependent on material provenance rather than leachate, oxygen content, pH, or temperature (Desboeufs et al., 2005; Fishwick et al., 2017; Mackey et al., 2015). The wide range in solubility may be due to variable anthropogenic contributions. One study which seasonally sampled aerosol samples found that increases in anthropogenic input, conventionally identified by an enrichment factor relative to continental crust greater than 10 (Jickells et al., 2016), correlated with increases in solubility (Hsu et al., 2005). Although there are significant anthropogenic Ni contributions to modern aerosols (Desboeufs et al., 2005; Galloway et al., 1982; Nriagu, 1989), because Ni has a residence time 10 times the mixing time of the ocean, the natural contributions are likely still most relevant to the modern marine budget. 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.

#### Dissolved Riverine Load

Rivers are also a significant source of metals to the ocean and are estimated to be the greatest known source for Ni. 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 micron filter). 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) 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 3.7x1016kg/yr to calculate a Ni riverine input of 3.6x108 Ni mol/year.

## Outputs

#### Fe-Mn deposits

Ferromanganese (Fe-Mn) deposits are potentially the most important output of Ni from the modern ocean, but estimating the size of this sink has remained challenging. Previous estimates vary by an order of magnitude, which may be a consequence of the different approaches to quantifying the flux (Cameron and Vance, 2014; Gall et al., 2013; Little et al., 2020). Cameron and Vance (2014) estimated the flux of Ni into Fe-Mn deposits by coupling the Ni marine budget with the better constrained Mo marine budget. By multiplying the Mo flux into Fe-Mn deposits by the average Ni/Mo in Fe-Mn crusts and nodules, they calculated an output flux of 1.5x109 Ni mol/yr. Gall et al. (2013) independently estimated the flux of Ni into Fe-Mn deposits by multiplying the accumulation rate of Fe-Mn crust and nodules (based off of five samples) by the average Fe-Mn crust concentration and an unexplained estimated seafloor coverage and calculated a total flux of 5.1x108 Ni mol/yr. Both estimates assume that Fe-Mn crusts and nodules are representative of all Fe-Mn deposits. In contrast, Little et al. (2020) slightly 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 Fe-Mn deposits could be defined (*i.e.,* deposits with Fe and Mn oxides), we consider this an estimate of the Fe-Mn deposit sink. They assume that all Ni incorporated into pelagic clay is coupled to Mn[[2]](#footnote-2) 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 5.9×108 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 5.1x108 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 potentially buried with organic matter (OM). 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). 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, past studies have primarily focused on productive regions. Nickel is often associated linearly with TOC, and the slope of this relationship can be applied to the flux calculation. The Ni/TOC derived from the Peru upwelling region, which have an Ni/TOC intercept of 0 and therefore has a negligible non-authigenic Ni contribution, has been used to calculate the fraction of Ni that is buried with organic matter at productive upwelling regions (9 Ni ppm/TOC wt%). 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 generally cited calculation from Ciscato et al. (2018) uses the flux of high productivity zones from Hedges and Kiel (1995) (1013 g C­org/yr) and the Peru Ni/TOC to calculate a flux of Ni out into organic matter 1.5x108 mol Ni/yr.

#### 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 0.4x108 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 (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, 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. The most often used value in Ni marine budgets is 0.15x108 Ni mol/yr (Ciscato et al., 2018; Gueguen and Rouxel, 2021; Little et al., 2020).

Taking these values together, the sum of the sources equates to 3.6x108 Ni mol/yr and the sum of the sinks equates to 6.8x108 Ni mol/yr, nearly double the sum of the sources. What is missing from our understanding of the Ni marine cycle?

## Resolving the imbalance

There are two potential causes of the apparent imbalance: missing fluxes or inaccurate flux estimates. Clearly, even with the best efforts, the flux estimates described above are often tenuously estimated or omitted and hold significant uncertainties. As shown, refining those directly is very difficult, and thus many in the community aim to apply a new constraint to the puzzle (*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 fluxes and the abundance weighted isotopic compositions of the Ni sources and sinks should balance (eq. X and X). Therefore, one can use isotope mass balance to constrain the fluxes and Ni marine budget in three dimensions (*i.e.,* mass flux, Ni concentration, and δ60/58Ni). 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 similarly elusive metals (*e.g.,* Cu, Zn; Little et al. (2014)). To apply this approach, we must know the isotopic compositions of major fluxes. While the isotopic compositions of known sources are reasonably well characterized, the sinks are difficult to ascertain. Once the major isotope parameters have been identified, we can apply the isotope mass balance constraint, evaluate the flux estimates, and hopefully resolve the mass imbalance.

Maybe unsurprisingly, there is an isotope mass imbalance. The known sources are isotopically lighter than the oceans and the known sinks are seemingly incredibly variable or have isotopic compositions greater than or equal to the ocean. The combination of these imbalances points to a significant missing component (or components) or largely misunderstood isotopic compositions. But which fluxes are the most in need of 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.

## Oceans

The oceans are often the point of reference for the isotopically light or heavy character of a flux and will be described first. The deep ocean is globally homogenous, with an isotopic composition between 1.3‰ to 1.4‰ (Archer et al., 2020; Takano et al., 2017; Yang et al., 2020) while the surface ocean varies. The South Pacific (Takano et al., 2017), North Pacific (Yang et al., 2020), and South Atlantic (Archer et al., 2020) all show significant trends towards isotopically heavy values in the surface waters, up to 1.78‰, which are coupled with surface [Ni] depletions down to ca. 2 nM. In contrast, the Indian sector of the Southern Ocean, which 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.

## Inputs

All known sources are isotopically lighter than oceans. The isotopic composition of continental crust, which we assume to represent that of dust, has a limited isotopic composition, from -0.1 to +0.2‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013; Wu et al., 2019 and references therein). Basalts rock standards 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). Rivers, the largest known source, appear to be isotopically variable, from +0.18 to +1.38‰ , but cluster distinctly below typical ocean δ60Ni values, with an average isotopic composition of +0.9‰ (Cameron and Vance, 2014; Revels et al., 2021). The difference in isotopic composition between rivers and continental crust can be explained by weathering; Fe oxides produced from weathering of ultra-mafic to mafic rocks, which host the majority of the crust’s Ni exposed to weathering, have been shown experimentally and in natural settings to sorb isotopically light Ni (Δ60/58Nidissolved-ferrihydrite = +0.35 ± 0.20‰ 2sd and Δ60/58Nidissolved-goethite = +0.77 ± 0.23‰ 2sd) (Gueguen et al., 2018; Spivak-Birndorf et al., 2018; Wasylenki et al., 2015). Therefore, the rivers are expected to be isotopically heavier than the continents. In summary, the Ni isotopic composition of sources seem relatively well known, are restricted to a range below 1.40‰, and have an abundance weighted isotopic composition of 0.88‰ which is significantly isotopically lighter than seawater (ca. 1.3‰ to 1.8‰).

## Outputs

#### Fe-Mn deposits

The isotopic compositions of the outputs further exacerbate, or at the very least complicate, the isotope imbalance. The Fe-Mn deposit sink may be the most important, 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±0.8‰. They did not observe any strong correlation between δ60Ni and ocean basin, oxygen saturation or Ni concentration (Fig xx), but there was a mild correlation between δ60Ni and distance to continental shelf, likely reflecting the contribution of isotopically lighter detrital 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 ± 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.

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 δ60Ni of 0.3‰ to 0.4‰ and -1.5‰ to 1.1‰, respectively (Gueguen et al., 2020). It is currently hypothesized that, rather than significant differences in source Ni (*i.e.,* hydrothermal fluid or seawater), these differences may be due to differences in the phase Ni is primarily associated with (*e.g.,* Fe oxides or Mn oxides), depositional environment and/or rate of formation (Gueguen et al., 2020; Little et al., 2020). Ferromanganese nodules also typically have isotopically lighter and variable δ60Ni values (0.23±0.90‰ 2sd, n=6) (Little et al., 2020; Wu et al., 2019 and references therein). This range in δ60Ni has been attributed to differences in mineralogy (phyllomanganates or 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 δ60/58Nisolution, with a calculated Δ60/58Nisolution-solid ~ 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 δ60Ni in modern organic rich sediments thus far. Ciscato et al. (2018) obtained organic rich sediments from a productive upwelling region off the coast of Peru and performed a detrital Ni correction to obtain an authigenic δ60Ni range of 1.19‰ to 1.20‰, although their best estimate is 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.

Again, a single paper has investigated the δ60Ni 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 δ60Ni in pelagic OM. Work to better understand δ60Ni variability in Fe-Mn sediments and adding to the small OM sample set will surely be useful. But, what about the fluxes that have been often omitted from previous marine Ni budgets?

## Missing Components

#### Hydrothermal Fluid

Hydrothermal fluid has been suggested as a possible Ni source, but no data yet suggests that hydrothermal activity is of the appropriate magnitude or isotopic composition to account for the isotope mass imbalance. To robustly investigate 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 ~3 μM 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 3x1013 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 9x107 Ni mol/yr here). 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) (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 ~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. However, ridge flanks of these temperatures (≥25℃) account for only 25% of the total convective heat loss from ridge flank type hydrothermal systems (and 17% of the total oceanic convective heat loss). The remaining 75% of the convective heat loss, and a significant portion of the fluid flux, comes from cooler ridge flank systems (≤25℃) which may create fluids with different Ni concentrations and could either be a source or sink of Ni (Wheat et al., 2003).

If the hydrothermal flux was of the appropriate size, would it be the appropriate isotopic composition to balance the equation? Most of what 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 estimates of hydrothermal fluid δ60Ni was also the only one to suggest that they were isotopically similar to seawater (~1.5‰), based on analyses of Fe-Mn crusts near the mid-ocean ridge (Gall et al., 2013). However, there was no correlation with δ60Ni and distance from a mid-ocean ridge. Other estimates focused on the narrow range of δ60Ni for ultramafic and mafic rock (~0.1‰, Cameron et al., 2009; Elliott and Steele, 2017; Gall et al., 2013; Gueguen et al., 2013; Wu et al., 2019), from which hydrothermal fluids derive their composition, and assumed a similar δ60Ni for the hydrothermal fluid (Ciscato et al., 2018; Gueguen and Rouxel, 2021). One study documented a form of hydrothermal interaction by measuring the change in isotopic composition as seawater interacted with lava from the 2018 eruption of Kīlauea and found for the δ60Ni data followed mixing between two end-members isotopically similar to seawater and basalt (0.1 to 0.3‰) (Hawco et al., 2020). Perhaps most representative, Pašava et al., (2019) measured a δ60Ni value of -0.24‰ from a pyrite-marcasite crust within the Logatchev hydrothermal field, Mid-Atlantic Ridge. Besides the estimate of Gall et al. (2013), all available data indicate hydrothermal fluids are isotopically light relative to seawater and would exacerbate the isotope mass imbalance.

#### Riverine Suspended Particulate Load

The suspended particulate load (SPL) of rivers has been suggested as potential resolution to the mass and isotope imbalance, but, again, there are two problems: the debated size of this flux and the generally isotopically light composition of the known components relative to seawater and their source fluid. The SPL consists of a variety of particles (*e.g.,* clays, carbonates, Fe and Mn oxyhydroxides, organic complexes) which can contain a significant fraction of the total riverine load for a given metal (Gaillardet et al., 2003; Gibbs, 1973). A handful of studies have calculated the SPL Ni/dissolved Ni in a variety of rivers and determined a wide range of values (0.4 to 40), with a large portion hosted by Fe and Mn oxyhydroxide phases (Gibbs, 1977, 1973; Revels et al., 2021; Seyler and Boaventura, 2003; Viers et al., 2009). Depending on the study, either a very small portion or the entirety (including the silicate fraction) of the Ni in the SPL would have to be mobilized to resolve the mass imbalance. The sparse data documenting estuarine processes, where labile Ni associated with the riverine SPL would likely desorb and enter the dissolved pool, suggest conservative behavior in estuaries (Boyle et al., 1982; Edmond et al., 1985).

While this source pushes the marine Ni budget in the right mass direction, what does this mean for the isotope mass balance (which also must be satisfied)? A recent study diligently explored the Ni isotopic composition in a variety of SPL particles of the Amazon river’s major tributaries and found that all SPL phases (*i.e.,* carbonates, oxides, organic, and residual) were isotopically lighter than solution (all <0.35‰ compared to ~0.9‰ of rivers) (Revels et al., 2021). Therefore, even if the entire particulate load were mobilized and dissolved in the oceans, it would provide isotopically light Ni and worsen the isotope imbalance. Even if the Amazon river has a SPL phase composition 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 source would be anything, but isotopically light relative to seawater.

#### Carbonates

Carbonate’s ubiquity in marine settings makes it an attractive candidate as a missing light sink, but greatly variable estimates of the flux size and isotopic composition (and the unknown impact of diagenesis) make it challenging to determine their importance to the budget. An initial estimate of the Ni flux into carbonate exclusively focused on the Ni associated with organic matter associated derived from 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), 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 6.7x108 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 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 δ60Ni in modern marine carbonates, but the sparse available data suggest they are isotopically light relative to or similar to seawater. The first attempt to estimate the δ60Ni of carbonates focused on the organic associated Ni. Carbonate rich coastal lagoon samples were leached to isolate the organic-rich pyrite fraction and found a δ60Ni range of 1.10–1.64‰ (Ciscato et al., 2018). Again, this omits Ni associated with the inorganic fraction. Another study measured a δ60Ni of 0.82 ± 0.1‰ 2sd in a single dolomite standard, JDo-1 which is a Permian dolomite from central Japan (Wu et al., 2019). Alvarez et al. (2021) experimentally investigated the relationship between Ni isotope fractionation and calcite precipitation rate by precipitating calcite at varying rates in the presence of Ni and measuring the δ60Nifluid and δ60Nicalcite once the solution composition appeared constant. Based off 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.

# Proposed Work

## Guiding Questions

While the apparent marine Ni isotope imbalance is quite complicated and will take several studies to resolve, we can begin to investigate the cause by tackling two high priority knowledge gaps. The aim of this dissertation is to investigate the following questions:

1. Are marine carbonates an isotopically light sink of Ni? Does carbonate early diagenesis lead to release or uptake of additional Ni and how does this impact the effective Ni isotopic composition and Ni mass flux of carbonates? Finally, can carbonates be used as a faithful geologic record of Ni isotopic composition?
2. What governs the isotopic composition of Fe-Mn deposits? Can the observed variation in δ60Ni of Fe-Mn deposits be explained by differences in mineralogy or accumulation rate?

The above questions will inform the first and second chapter of the dissertation. The third and final chapter of the dissertation will be guided by the challenges and knowledge gaps described in the literature review, but will not be described in detail here.

## Hypotheses and Project Summary

### Carbonates

Carbonates are a ubiquitous sediment across time and space and may be a nontrivial and perhaps isotopically light sink of Ni. There is clear disagreement within the community about its importance to the modern marine Ni budget, with estimates for its output ranging from 3 to 180% of the riverine input (Alvarez et al., 2021; Ciscato et al., 2018). The estimate at the lower end of that range likely underestimated the flux because it only considers Ni associated with TOC in carbonates and omits any Ni which might incorporate into the inorganic component. Nickel has been experimentally found to partition moderately into abiotic and biotic calcite, suggesting the inorganic component may be important to consider as a host of Ni (Alvarez et al., 2021; Lakshtanov and Stipp, 2007; Munsel et al., 2010; Smith et al., 2020). The estimate at the higher end of the range likely overestimated the flux because of the odd sample set selection to represent the average Ni concentration of primary carbonates (*i.e.,* carboniferous limestones from a single region with elevated Ni concentrations relative to other carbonates) (Alvarez et al., 2021; Zhao and Zheng, 2014). We anticipate that the true estimation lies somewhere between these values. Considering the available indirect evidence suggests carbonates are an isotopically light sink, they may be the missing component to resolve the isotope imbalance. Until the isotopic composition of modern carbonates are investigated, we cannot confidently model the modern marine Ni budget.

I propose to perform the first Ni isotope measurements of modern marine carbonates to obtain a representative δ60Ni for carbonates and help assess its importance to the budget. For this study, we have selected a set of well-characterized, primary to diagenetically altered shallow-water carbonates from the Great Bahama Bank. Our set includes samples from short cores (representing initial deposition of primary carbonates) and the Clino (representing forms of meteoric diagenesis and marine burial diagenesis) and Unda cores (representing massive dolomitization).

However, by virtue of selecting shallow-water carbonates, we are not capturing the Ni isotopic composition of pelagic carbonates which will not necessarily be equivalent to shallow-water carbonates. Based on the mass distribution in modern CaCO3 accumulation budgets, pelagic carbonates appear to dominate the budget (*e.g.,* Iglesias-Rodriguez et al., 2002; Milliman, 1993; Opdyke and Wilkinson, 1988; Smith and Mackenzie, 2016; Wilkinson and Walker, 1989). However, we believe the chosen samples are an appropriate first look at δ60Ni in carbonates for several reasons. First and foremost, we have immediate access to the samples and experts. These samples, in particular the Unda and Clino cores, have a wealth of associated information detailing their mineralogy and depositional and diagenetic histories (*e.g.,* Eberli et al., 1997; Hardisty et al., 2017; Higgins et al., 2018; Kenter et al., 2001; Liu et al., 2019; Manfrino and Ginsburg, 2001; Melim et al., 2002; Swart and Melim, 2000; Swart and Oehlert, 2018; Wang et al., 2020). The extensive history and access to primary carbonates allows us to assess the influence of early marine diagenesis which may have an impact on the retained Ni in the carbonate sink. Because of the many attractive features listed for this sample set, they have been used for a number of other elements, and these studies interpretations can be used to inform our own (*e.g.,* Dellinger et al., 2020; Hardisty et al., 2017; Romaniello et al., 2013; Zhang et al., 2017).

Interestingly, our chosen sample set provides an opportunity to assess the fidelity of shallow-water carbonates as a record of the Ni isotopic composition of seawater. While shallow-water carbonates do not make up significant portion of the modern carbonate flux, they are believed to have been more abundant in the past. The proportion of pelagic to shallow water carbonate burial has likely been steadily increasing to present values, with the dominance of pelagic carbonates perhaps being a characteristic of only the past 10-30 Ma (Nakamori, 2001; Opdyke and Wilkinson, 1988; van der Ploeg et al., 2019). In addition to the difference in relative abundance, shallow water carbonates are a more available geologic record because slope and deep-basin carbonates are more often subducted and removed or extremely deformed relative to shallow water carbonates, as noted by Schrag et al. (2013) for δ13C records. If diagenetic processes either preserve or systematically alter the δ60Ni of the primary carbonate value, which we will be able to evaluate with the data from the proposed sample set, shallow-water carbonates may be a robust record of δ60Ni from the contemporary seawater.

### Mn oxides

As discussed above, several studies aimed to determine δ60Ni for Mn-rich sediments, perhaps the largest sink of Ni, but the results so far are extremely puzzling. Nickel is enriched in Fe-Mn deposits relative to seawater (ca. 106 (Ni mol/g Fe-Mn deposits)/ (Ni mol/g seawater)) (e.g., Li and Schoonmaker, 2003) and primarily associated with Mn phases, rather than Fe (*e.g.,* Hens et al., 2019; Koschinsky and Hein, 2003; Peacock and Sherman, 2007). The δ60Ni of Mn-rich deposits span the entire known natural range of Ni isotopic compositions (ca. -1.8 to 2.5‰) and, inexplicably, appear to be sometimes isotopically heavier and sometimes isotopically lighter than the solution from which they precipitate (Gall et al., 2013; Gueguen et al., 2020, 2016; Gueguen and Rouxel, 2021; Little et al., 2020; Vance et al., 2016). Without better knowledge of the main marine Ni sink, correctly modeling the marine Ni cycle is likely impossible.

We will experimentally investigate two of the most promising explanations for the variability in Mn oxide sediments. The primary mineral of focus will be birnessite, the dominant Mn phase in natural marine Fe-Mn precipitates (*e.g.,* Burns and Burns, 1977; Yoshikawa, 1991).

We hypothesize thatsurface sorbed Ni is isotopically lighter than incorporated Ni within birnessite. Nickel can be structurally incorporated into Mn vacancy sites in birnessite or sorbed on {001} surface sites (triple corner sharing) or edge sites (double corner sharing) (Simanova et al., 2015) (Fig. XX). A Ni-birnessite sorption study indicated Δ60/58Nisolution-birnessite positively correlates with the ratio of surface-sorbed to incorporated Ni, suggesting that sorbed Ni is isotopically lighter than incorporated Ni (Sorensen et al., 2020). Experimental results suggest Ni migrates very slowly into the vacancy sites (30% incorporation after 408 h) (Peacock, 2009). In natural Fe-Mn crusts, the majority of Ni is structurally incorporated (Peacock and Sherman, 2007), but the degree of structural incorporation within sediments like the relatively ephemeral Mn oxide particles in the Black Sea is unknown. If surface-sorbed and incorporated Ni have different Δ60Nisolution-birnessite,differences in the proportions of sorbed to incorporated Ni would impact the δ60Ni of Mn-rich sediments.

To test this hypotheses, I will differentiate between the fractionations of surface-sorbed Ni versus structurally incorporated Ni within birnessite by performing Ni sorption experiments with synthetic, triclinic birnessite (*i.e.,* no or very few available vacancy sites for incorporation and therefore only or mostly surface-sorbed Ni) and highly crystalline, hexagonal birnessite (*i.e.,* many available vacancy sites for Ni incorporation and therefore a combination of sorbed and incorporated Ni). While my experimental design cannot differentiate between the potentially different isotopic behaviors of triple and double corner sharing Ni, the difference between total sorbed and incorporated Ni is a necessary first step in assessing the importance of coordination on the variation of δ60Ni in Mn-rich sediments.

We hypothesis that kinetic fractionation leads to isotopically lighter Ni sorbed to Mn oxides than equilibrium fractionation. Mn-rich sediments have a wide range of accumulation rates and, depending on the rate, may capture different isotope fractionations (kinetic, equilibrium or a mix thereof). Experiments varying in duration from 67 hours to 27 days found that Δ60/58Nisolution-birnessite decreased progressively over time, which suggests equilibrium had not yet been reached, and short-term experiments may be recording an initial kinetic effect (Sorensen et al., 2020; Wasylenki et al., 2019). If kinetic and equilibrium fractionations are distinct, the δ60/58Ni of fast-accumulating versus slow-accumulating Mn-rich sediments may record different Ni isotope offsets from dissolved Ni in the water column

To address this hypothesis and robustly calculate the equilibrium and kinetic fractionations, I propose to perform three-isotope (62Ni-60Ni-58Ni) experiments. Currently, the three-isotope experiment is considered to be a rigorous approach to determining equilibrium isotope fractionation (Chanda et al., 2020; Frierdich et al., 2014; Lazar et al., 2012; Matsuhisa et al., 1978)(Frierdich et al., 2014). In this method, a typical sorption experiment is performed, but the solution is doped with a small amount of significantly enriched 62Ni solution with a slightly different δ60/58Ni (Fig. XX). The extreme exchange of 62Ni between solid and solution tracks the percent of isotope mixing, while the subtle change in δ60/58Ni­tracks isotope fractionation. At 100% mixing, the system is assumed to be at equilibrium, and the difference between δ60Ni­solution andδ60Ni­solid equals Δ60Nisolution-solid. If we cannot attain 100% mixing in a reasonable time, the δ60Ni­solid and δ60Ni­solution data can be extrapolated to 100% mixing (Fig XX). If kinetic and equilibrium fractionations differ, we will observe two trends (like in Fig. XX) and can discriminate between the first (kinetic) and second (equilibrium) trends’ fractionation values. Time permitting, I will perform multi-directional three-isotope experiments, with varied starting δ60Ni to ensure robust identification of equilibrium fractionation (Frierdich et al., 2014).

# Progress Thus Far

## Methods from Draft 3

### Sample Collection and Site Description

The short cores in possession, labeled C1, C3, C4, and C5, are <20cm bank-top cores from modern sediments in the Great Bahama Bank, specifically near the Little Darby and Lee Stocking Islands. Samples from this region are often used to represent initial deposition of primary shallow water carbonates (Hardisty et al., 2017; Pogge von Strandmann et al., 2019; Romaniello et al., 2013; Zhang et al., 2017). Detailed information of their collection and sample locations can be found in Hardisty et al. (2017), but a brief description will be given here. Modern carbonates from the Great Bahama Bank are primarily composed of inorganic components such as ooids, grapestones, and peloids. The sediments are composed of primarily aragonite with significant, but secondary amounts of high magnesium calcite (HMC) (Hardisty et al., 2017). Samples were collected by hammering polyethylene tubing into sediment, removing and slicing the sediment into the appropriate intervals, drying the sediment in a muffle furnace at 60°C, and finally powdering them using a mortar and pestle. The C1 core is the only core that comes from an intertidal area (water depth <1m). Cores C3, C4, and C5 all come from subtidal areas. The C4 and C5 cores come from active or former ooid shoals. There were *Thalassia testudinum* beds (seagrass) where cores C3 and C5 were collected.

A number of papers have covered the mineralogy, sedimentology, and diagenesis of the Clino and Unda cores in detail (Eberli et al., 1997; Higgins et al., 2018; Kenter et al., 2001; Manfrino and Ginsburg, 2001; Melim et al., 2002, 1995; Murray et al., 2021; Swart et al., 2012; Swart and Melim, 2000; Swart and Oehlert, 2018). A summary of the relevant components will be provided here. The Clino and Unda cores were retrieved 5 km and 13.5 km away from the edge of the Great Bahama Bank (GBB), respectively, in 1990 as part of the Bahamas Drilling Project (Swart and Melim, 2000). They were collected along the Western seismic line from the platform top of the GBB and extend back to the late Miocene. The Unda and Clino cores penetrate 454 and 677 meters below mudpit datum and are covered currently by approximately 10 m of water (Eberli et al., 1997). The Clino core contains overlying platform sediments, similar to those of the modern GBB, and slope deposits (Eberli et al., 1997). The Unda core contains primarily platform margin deposits.

The Clino core contains significant LMC throughout the core, with secondary contributions of aragonite (especially <50m and between 100m and 350m) and more minor contributions of dolomite starting below 150m (Melim et al., 2001; Swart and Melim, 2000). The Unda core also contains significant amounts of LMC throughout but has lower amounts of aragonite (between 100m and 150m) and significant amounts of dolomite (nearly 100% between 275m and 350m).

The top ~100m of Clino are dubbed the layered cap and alternate primarily between sections of peloidal and skeletal lithologies with varying grain size and contains minor sections composed of coral floatstone (Manfrino and Ginsburg, 2001). Below the layered cap to about 200m, there are large sections of coral with secondary amounts of skeletal sediments. Between ca. 200m and 370m, the dominant sediment is nonskeletal, peloidal sediments. Below 370m, the sediments are primarily peloidal and skeletal mixtures (Kenter et al., 2001) (Include figure 3 in Kenter 2001 for a nice representation of this).

The top of the Unda core is quiet similar to Clino. The layered cap, approximately the top 70m, consists of alternating sections of skeletal and peloidal sediment and overlays the coral bearing section, the next 50m or so (Manfrino and Ginsburg, 2001). From approximately 110m to the bottom of the core, most sediments are peloidal and skeletal mixtures except for a brief hiatus between 290m and 360m where reefal deposits dominate (Kenter et al., 2001).

The Clino core contains well documented aragonite to LMC neomorphism in meteoric and marine burial scenarios, while the Unda core captures the process of dolomitization. Both cores contain several subaerial exposure surfaces (Manfrino and Ginsburg, 2001; Swart and Oehlert, 2018). During repeated sea-level changes during the Pleistocene, meteoric fluids infiltrated into the upper portions of the cores (Melim et al., 1995; Swart and Oehlert, 2018). As a consequence of the repeated exposure to meteoric water, oxygen and carbon isotopes are isotopically depleted in the upper 108m and 135m of the Unda and Clino cores, respectively (Eberli et al., 1997; Melim et al., 1995). However, the freshwater phreatic zone may have penetrated deeper into the sediments, estimated to be 200m for the Clino core (Swart and Oehlert, 2018). The C and O isotopes covary and become more positive between 60m and 110m in Unda and 90m and 180m in Clino. The covariance is believed to be a result of higher rates of recrystallization and neomorphism due to oxidizing organic matter at the interface of the phreatic and vadose zone (Swart and Oehlert, 2018). After these zones, early and late marine burial diagenesis are the dominant diagenesis regimes (*e.g.,* marine hardgrounds, neomorphism, compaction), with periods of extensive dolomitization in Unda (discussed in section XX) (Eberli et al., 1997; Higgins et al., 2018; Melim et al., 2001).

### Chemistry development

Separating Ni from the carbonate matrix has proved to be a technical challenge . The available techniques to purify Ni from difficult matrices often require >3 columns and/or the use of Ni Dimethylglyoxime (DMG) which readily complexes with Ni, but is difficult to break down and can lead to low recoveries (*e.g.,* Cameron et al., 2009; Chernonozhkin et al., 2015; Gueguen et al., 2013; Little et al., 2020; Wu et al., 2019). With no previous examples yet published for the separation of Ni and carbonate to the best of our knowledge, we developed a methodology that could adequately isolate Ni.

To remove Ca and other common carbonate elements (*e.g.,* Mg), we tested three different methods. The methods were tested by first doping an aliquot of dissolved calcite with Ni (starting Ca/Ni ~105), passing the aliquot through the protocol while collecting fractions of eluate throughout, and analyzing the fractions on an Agilent 7900 ICP-MS to determine yield and Ca/Ni of the final fraction. First, we tested a method by Strelow et al. (1972) which used AG1-X8 anion resin and mixtures of oxalic acid and hydrochloric acid to separate Ni from Ca (Ni is retained on the resin in low concentrations of HCl and oxalic acid, while Ca, Sr, Na, and Mg are not retained in any mixture). While this method did remove some Ca, the amount of Ca was still quiet high relative to Ni (Ca/Ni~8000), and the Ni recovery was low (<50%).

The second method tested was based off methods from Gall et al. (2012) and Strelow, (1990) and used AG50W-X8 cation resin with an ammonium hydroxide-ammonium citrate loading solution. The differences in affinity for citrate (which elutes) or ammonia (which is retained on the resin) between elements cause Ni to be retained on the resin, while Ca, Mg, and a number of transition metals elute. This method achieved an 85% Ni recovery and a final Ca/Ni purification of 0.5 which were adequate for our analysis routine. However, because of the large amount of material required, very large quantities of loading solution (60mL) were required to prevent precipitation of a white substance. Such large loading quantities would result in higher Ni contamination, the need for expensive >60 mL Teflon containers for sample preparation, and very long elution times.

The third method tested used the first step of a protocol developed by Yang et al. (2020) to purify Ni from seawater and used NOBIAS-PA1 resin with an ammonium acetate solution (pH 6±0.2). This method effectively removed (99%) of the Ca, Na, Mg, and S in their samples and had a Ni recovery of >99%. Our tests had similar findings, with a Ca/Ni of ~0.4 and Ni recovery of >98%. Only 10 mL of loading solution was required, so significant Ni contamination from reagents and the need for large sample preparation vessels were no longer of concerns. This method appears the most appropriate to perform a bulk separation of Ni from Ca and is the first step in the purification procedure developed here.

The next challenge was to remove interfering transition metals such as Zn, Ti, Mn, and Fe. For these tests, a trace metal solution containing the anticipated trace metal composition of the Bahama carbonate samples and the post-Ca cleanup Ca concentration was passed through the test method. The method described above and developed by Gall et al. (2012) and Strelow, (1990) effectively removed Ti, V, Fe, and leftover Ca and the Ni recovery was 95%. With most of the Ca removed at this step, no precipitates were observed in a 3 mL loading solution. For these reasons, this method is used as the transition metal removal step in the purification procedure developed here.

Finally, we performed a finishing cleanup step which removed Zn, Cu and residual Fe. We used a common column for Ni-Fe separation which uses AG1-X8 anion resin and (>6M) hydrochloric acid (Gall et al., 2012; Wasylenki et al., 2015). Iron, Cu and Zn form negatively charged chloride complexes which sorb to the resin, while Ni elutes (Kraus and Moore, 1953). This effectively removes Fe, Zn, and Cu from Ni. Because of the simplicity of the column and its short duration (<15min to elute), it can be easily repeated if needed. The combination of these three columns effectively purifies Ni from a carbonate matrix and individual columns can be easily repeated if necessary to achieve adequate purification (see table XXX for full method).

### Sample preparation and analysis

Approximately 0.1 to 1g of each sample was dissolved in ca. 40 mL of 1M HNO3 and allowed to react at room temperature, uncapped overnight (similar to Chen et al. (2018)). Additional acid was adding to ensure the complete reaction of carbonate. Samples were dried down and brought back up in 0.2 M HNO3. Residual undissolved material was then removed by centrifugation (X RPM for Y min) and decanting the solution. The samples were stored in 15-30 mL Teflon vials and parafilmed until sample aliquoting.

To obtain concentration data for appropriate spiking, samples were diluted to obtain a Ca concentration of 100-200 ppm for concentration analysis using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer (ICP-MS). Nickel isotopes 60 and 58 were measured using He-mode to reduce isobaric interferences (*e.g.,* CaO, others, check out interference printout in office). At least three calibrating standards were used for each run. A multi-element internal standard was used to account for beam intensity fluctuations during measurement. Doubly charged ions and oxide formation were monitored using X and Ce/CeO, respectively which were always kept below 2.5%. Beam suppression was monitored by checking the percent recovery for the internal standard elements and was always within a range of 80-120% of the original blank solution measurement.

Approximately 75 to 360 ng of Ni from each sample was aliquoted and spiked with a Ni 61-62 double spike prepared by the SESAME Lab at Indiana University (cite papers who have used this spike before and maybe add a table of the spike composition?) in a 36:64 sample-to-spike ratio, to the best of our ability. The optimal sample-spike ratio was determined using the double-spike toolbox (Rudge et al., 2009) given the double spike. Samples were then fluxed overnight at 120℃. Subsequently, they were then put through the ion chromatography protocol developed here, described above and in table X. After the chemical separation, samples were analyzed for Ca, Mg, Fe, Mn, and Zn to ensure proper purification and repurified through columns as needed. Nickel recoveries ranged from 70 to 105%, except for a few outliers. The values exceeding 100% may be due to uncertainty in the ICP-MS measurement (RSD ~3-5%).

Nickel isotope analysis was performed on a ThermoScientific Neptune Plus MC-ICP-MS in combination with an apex omega coupled to an ESI introduction system (Sc-μ DX) at Lawrence Livermore National Laboratory (LLNL). We measured voltages for Fe, Ni, and Cu on masses 57, 58, 60, 61, 62, and 63. Voltages were measured on the lower end of the mass range to avoid Ca and Ar oxides interreferences on 57Fe (*e.g.,* 40Ar16OH, 40Ar17O), 58Ni (e.g., 40Ca18O, 42Ca16O, 40Ar18O, 40Ar17O1H) and 60Ni (*e.g.,* 44Ca16O, 43Ca16O1H). In addition, tuning was performed specifically to minimize oxide formation which was monitored using Ce/CeO and always kept below 1%.

All samples and bracketing standards were run at a Ni concentration of 250 ppb with an uptake rate of 50 μL/min using a jet sampler cone and X-skimmer cone in high resolution mode which resulted in a 58Ni beam of ~2V. Each sample analysis was bracketed by a blank acid measurement, for later background subtraction, and a bracketing standard spiked with same double spike and in the same proportion as the samples. Instrumental mass bias correction was performed using the double-spike correction as described in Rudge et al. (2009) and Siebert et al. (2001) which resulted in analytically indistinguishable results. Samples were measured at least twice across multiple days and runs.

We took several different approaches to monitor the quality of the data. Based on repeated measurements of double spiked NIST SRM 986 over the course of the entire analysis, the long term reproducibility of our analysis is δ60Ni=0.00±0.06‰, n=283. We also passed NIST SRM986 through the purification procedure and analyzed it along with samples. This yielded an average δ60Ni of 0.03±0.03‰, n=8. A secondary standard, Ni AAS[[3]](#footnote-3), was also measured along with samples to monitor the day to day reproducibility and efficacy of the chemical purification procedure. Double spiked aliquots of Ni AAS, one which had gone through the purification protocol and one which had not, had analytically indistinguishable δ60Ni, -0.43±0.08‰, n=64 and -0.44±0.06‰, n=9, respectively. In addition, an aliquot of Ni AAS was doped with Ca, Mg, Fe, Mn, and Zn, passed through the purification protocol and measured along with samples, and, again, had an isotopic composition indistinguishable from the previously described aliquots (δ60Ni=-0.42±0.07‰, n=16). Finally, crosses of NIST SRM 986 and Ni AAS (3:1, 1:1, 1:3) were passed through chemistry and analyzed for Ni isotopic composition. The linear regression of the expected versus the measured δ60Ni for the crosses has a slope of 1.06 and an R2 of 0.89 (presented in graph Y and table X).

[mention the external data used here, dO, dC, mineralogy, TE concentrations, how it was collected and who collected it super briefly]

## Preliminary Results from Draft 1

### Results

A subset of the carbonates in possession were selected for analysis to direct more pointed future analysis. For the short cores, we selected 15 samples to analyze from three different, C1, C4 and C5. The cores are generally homogenous within a site and exhibit no obvious trends downcore with regard to δ60Ni or [Ni]. The δ60Ni and [Ni] values range from 1.11‰ to 1.61‰ and 0.3 to 1.36 ppm, and the average δ60Ni and [Ni] values are 1.31‰ and 0.72 ppm, respectively. The core C5 has the lowest average [Ni] and δ60Ni values (0.32 ppm and 1.14‰), and C4 has the highest average [Ni] and δ60Ni values (1.29 ppm and 1.40‰). There appears to be a correlation between δ60Ni and [Ni], although two data points clearly fall off trend (Fig. X). Nickel concentrations and δ60Ni generally decrease with increasing aragonite content (R2=0.49 for δ60Ni vs. aragonite wt. % and R2=0.61 for [Ni] vs. aragonite wt. %). Nickel concentrations and δ60Ni generally increase with increasing HMC content (R62). There is no clear correlation between δ60Ni and δ18O or δ13C (Fig. x).

A set of 16 and 10 samples were selected for the first round of analysis of the Clino and Unda cores, respectively. The samples were selected to target the different diagenetic regimes (*i.e.,* zones of meteoric vadose and phreatic diagenesis, marine burial diagenesis, and massive dolomitization). The Clino core has both meteoric diagenetic and marine burial diagenesis zones. The overall ranges for [Ni] and δ60Ni in Clino are 0.24 ppm to 3.99 ppm and 0.86‰ to 1.67‰, respectively, and clearly exhibit a larger spread than the primary carbonates. The isotopically lightest and lowest [Ni] values come from the zones of meteoric diagenesis. Unlike the primary carbonates, there is no apparent correlation between [Ni] and δ60Ni, although this may be due to sample size and the differing affects of diagenetic regimes. The primary mineralogy of Clino is LMC and aragonite with minor components of dolomite. Comparing δ60Ni and aragonite plus HMC content produces a profile which looks similar to some sort of three-end member mixing, although again this is complicated by diagenesis and the small sample size. There is no clear correlation between δ60Ni and δ18O or δ13C.

For Unda, the 10 samples analyzed clustered around the transition between meteoric and marine burial diagenesis zones and the zone of massive dolomitization. The Unda core had the isotopically lightest and highest [Ni] samples of the entire set analyzed here. The ranges for [Ni] and δ60Ni are 0.30 ppm to 5.36 ppm and 0.48‰ to 1.52‰, respectively. This is an even greater spread than in the Clino or short core samples. The highest [Ni] and lowest δ60Ni values came from the zone of massive dolomitization. The primary mineralogy of the Unda core is dolomite and LMC with minor contributions from aragonite. Higher [Ni] and lower δ60Ni are generally correlated with increased dolomite content and, increases in δ60Ni and decreases in [Ni] are generally correlated with increased LMC content. As seen for the Clino and short cores, there is no clear correlation between δ60Ni and δ18O or δ13C.

## Discussion and Questions to Pursue

At first glance, carbonates do not appear to be an isotopically light enough sink to fully resolve the imbalance, but they do lessen the demand for an incredibly isotopically heavy source. However, the present data teases at several questions. Addressing these questions will further explore the role of carbonates as an isotopically light sink of Ni and the potential for shallow-water carbonates as a record of δ60Ni.

The short cores have a relatively tight bulk range of δ60Ni (1.31±0.28‰ 2sd) that is quite similar to deep seawater (~1.3-1.4‰). However, it is unclear if the isotopic composition of deep seawater is an appropriate analog for the solution from which the short cores ultimately precipitated. Surface water (depths <200 m) has been observed to both have and not have enrichment in the heavier Ni isotopes relative to deep seawater (Archer et al., 2020; Cameron and Vance, 2014; Takano et al., 2017; Yang et al., 2020). Considering the samples here were collected from locations <10 m water depth, the overlying waters may have δ60Ni greater than that observed for the deep ocean (up to 1.8‰). If this were the case, the primary carbonates would be isotopically light relative to the solution from which they precipitate, as suggested by the indirect data discussed in section X. *What is the δ60Ni of modern Bahama seawater?* To address this question, we will ideally obtain and analyze seawater samples from this area. If this is not possible, we will use a hypothesis developed by Archer et al. (2020), which proposes that the ambient biology determines whether there is a surface enrichment in heavy Ni isotopes, to infer whether the δ60Ni is expected to be greater than the δ60Ni of deep seawater.

*Is there difference in isotopic composition between meteoric and marine burial diagenesis zones, and, if so, what causes this?* The Clino and Unda cores both have larger ranges in δ60Ni compared to the short cores and show correlations with diagenetic zones. In Clino, the δ60Ni of meteoric (vadose) diagenesis samples cluster around 1.1‰, which is similar to the value of primary aragonite extrapolated from the short core mineralogy relationships. The measured δ60Ni of the meteoric samples may be recording the preserved primary aragonitic δ60Ni. On the other hand, the lighter values may be a result of exchange with isotopically lighter meteoric fluids. Rivers typically have δ60Ni values lighter than seawater (~0.9‰) and the few available δ60Ni values for snow and rain are all below 1.0‰ (although these samples had clear anthropogenic influences) (Cameron and Vance, 2014; Revels et al., 2021; Takano et al., 2021). The marine burial diagenesis samples cluster around 1.4‰, which is similar to the bulk values of the primary short cores. The sediments in this region experienced aragonite to LMC neomorphism in exchange with reducing marine pore which alters the initial signature for some systems and not others (Hardisty et al., 2017; Melim et al., 1995; Swart and Melim, 2000; Wang et al., 2020). There is a clear difference in isotopic composition between samples from the meteoric and marine burial diagenesis zones, however we only have a handful of samples from these areas, concentrated to certain locations*. If there is a difference between these two regimes, where in the column does the transition in δ60Ni occur?* Additional analysis of meteoric and marine burial diagenesis samples from areas of varied mineralogy will indicate if these trends are persistent throughout the core.

*What may be causing the variations in the marine burial diagenesis zone of Clino?* In the Clino core, there are a set of samples between 200m to 350m that hover around the δ60Ni value of deep seawater (~1.3‰-1.4‰) and another set between 150m to 200m and >350m that hovers around 1.6‰. While this difference is not too dissimilar to the variability observed in the primary carbonates (1.31±0.28‰ 2sd), the variations coincide with changes in lithology and warrant further investigation. The regions with isotopically lighter values are dominated by peloids whereas the regions with isotopically heavier values contain mixtures of peloids and skeletal components. *Are biogenic carbonates isotopically heavier than abiotic carbonates?* To address these questions, we plan to target areas with significant coral and skeletal components (as described by Kenter et al., 2001 and Manfrino and Ginsburg, 2001) in future sample analysis. In addition, we will also analyze a sample containing forams and microfossils from the Santa Barbara Formation.

*Does the process of dolomitization cause the δ60Ni value of the primary carbonate to become lighter?*. There are three categorizations of dolomite in the Unda and Clino cores: hardground dolomite which form near nondepositional surfaces, background dolomite which form in the void space of sediments from the recrystallization of precursor minerals or direct precipitation, and finally massive dolomite, from the Unda core, which may have formed near the sediment water interface, where advective exchange can occur between seawater and pore fluid (Swart and Melim, 2000; Wang et al., 2020). The massive dolomite samples analyzed in this data set have both the highest [Ni] and the lowest isotopic compositions. There is a general trend between higher dolomite content and higher [Ni] and lower δ60Ni values. Because the samples were analyzed in bulk and the Clino samples analyzed all contain <10% dolomite, it is challenging to determine from this data whether or not similar trends would be present in the Clino dolomite, which likely formed under very different conditions with different diagenetic fluids (Hardisty et al., 2017; Swart and Melim, 2000; Wang et al., 2020). In addition, the trace metal composition of the massive dolomites may be influenced by the contemporary reduction of Mn oxides as suggested for Cr (Wang et al., 2020). The reduction of Mn oxides may have acted a source of Ni to the system. Similar to Cr, the [Ni] and δ60Ni values of the massive dolomite correlate with Mn contents, which range from 9.7 ppm to 15.7 ppm (Liu et al., 2019). To further investigate the isotope fractionation and incorporation of Ni into dolomite and the potential influence of Mn oxide reduction, and the influence of differing diagenetic fluids, we hope to analyze dolomite separates or at the very least additional samples with significant dolomite contents from Unda and Clino (e.g., 365 mbsf–380 mbsf, 550 mbsf–600 mbsf).

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1. The fraction of soluble Ni is typically represented as the amount of Ni dissolved divided by the total Ni in bulk aerosol. [↑](#footnote-ref-1)
2. In Fe-Mn deposits, Ni is primarily associated with Mn oxides rather than Fe oxides (Peacock and Sherman, 2007). [↑](#footnote-ref-2)
3. While Ni AAS is not a Ni isotope standard, we feel confident in, at the very least, interpreting the relative differences between the different fractions of Ni AAS. Furthermore, Ni AAS has been analyzed at LLNL with a Neptune MC-ICP-MS and at Northern Arizona University with a Nu III MC-ICP-MS (-0.44±0.06, n=20), and both instruments yielded the analytically indistinguishable δ60Ni values. [↑](#footnote-ref-3)