Introduction

The availability of transition metals has likely directed the course of evolution for a variety of life forms. Key, life supporting enzymes incorporate metals such as Mg in photosynthesis, Ni in methanogenesis and Fe in hemoglobin. As massive shifts in Earth’s atmosphere, ocean circulation and redox conditions occurred, the concentration of trace metals likely varied in the oceans and required biological adaptations. Determining how and when these shifts occurred will inform how life co-evolved with Earth.

Nickel is a bio-essential element for a variety of modern and ancient life and there were likely large fluctuations in its concentration in the oceans. [Insert sentence about residence time]. In the modern ocean, Ni has a nutrient like depth profile, meaning it is depleted in the surface and enriched through remineralization in the deeper waters. [associated with Si and P]. Nickel is essential to seven enzymes that regulate the global C, N, and O cycles. Because of Ni’s incorporation into these enzymes, marine Ni-dependent organisms, such as phytoplankton and foraminifera, are severely affected by fluctuations in ocean Ni concentrations (Schonheit et al., 1979; Dupont et al., 2010; Munsel et al., 2010; Twining et al., 2012; Smith and Goldstein, 2019). [ include a table listing important enzymes, their functions, and examples of life that have them, see table below to adapt]. [include Ni reliance graphs]

In the modern ocean, Ni is used by X, Y, Z. Diatoms, silica-shelled phytoplankton that produce around 45% of the Earth’s O and comprise ~1% of Earth’s biomass, rely on Ni because they use Ni-enzymes, urease and Ni-superoxide dismutase (Twining et al., 2012; Benoiston et al., 2017). [Insert study about Ni reliance] Foraminifera also exhibit a Ni reliance, potentially because of their use of urease as a pH regulator during shell formation (Munsel et al., 2010; Smith and Goldstein, 2019). In addition to Ni requirements, some of these organisms have been shown to have Ni toxicity limits. A study performed on a diverse group of foraminifera species showed that while the toxicity limits ranged, the general behavior was a slight increase in [Ni]SW (insert X nM) caused an increase in most foraminifera abundance whereas a significant increase (insert X nM) caused most foraminifera cell death (I need to find this study). The sources and sinks that regulate ocean Ni concentrations therefore also regulate the diversity and abundances of these organisms.

During the Archean, Ni was likely an incredibly important ingredient for early life. Methanogens likely dominated in the predominately anoxic ocean. One of the most notable biochemical uses of Ni is its incorporation into the cofactor f340 which is used by a crucial enzyme for methanogens, methyl-coenzyme M reductase. (Ragsdale, 1998; Cameron et al., 2009). [insert study about Ni reliance study]. Methyl coenzyme M reductase catalyzes the final step in methanogenic, and first step in methanotrophic pathways. [include sentence about the methane haze that likely kept the earth warm and how methane suppressed the rise of O] Clearly, there is and has been a biological need for Ni since the very beginnings of life. How ocean Ni concentrations have fluctuated would have large implications for the evolution of marine life’s diversity and abundance.

The shifts in ocean Ni concentrations appear to be quite drastic across Earth’s history. Using Ni/Fe data from banded iron formations (BIFs), Konhauser et al., detected a massive shift in the Ni concentration of Precambrian oceans from 400 nM to 200 nM approximately 2.5 Ga. [insert sentence about how this isn’t entirely conclusive because it’s one data set and has a large uncertainty]. Today, ocean Ni concentrations hover around 8 nM. As these shifts occurred, Ni-dependent life would have been greatly affected and either become more limited in abundance or evolved to exist with a lower Ni dependence. Again, determining the causes and timing of these shifts would help define pivotal moments when Ni-dependent life was challenged. However, before the past marine Ni cycle can be reconstructed, a fundamental modern marine Ni cycle needs to be established.

**Ni Marine Cycle**

Despite Ni’s biological importance, the marine Ni cycle appears to be lacking key components as evidenced by the imbalanced marine budget (Ciscato et al., 2018; Gall et al., 2013; Sclater et al., 1976). The budget is imbalanced in terms of mass and isotopic composition. In 1976, Krishnaswami (Krishnaswami, 1976), identified a massive mass imbalance which was confirmed in future studies (Ciscato et al., 2018; Gall et al., 2013); the sum of the sinks is estimated to be twice the sum of the sources. The identification of the mass balance spurred the use of isotopic mass balance to constrain the flux estimates. However, attempting this application revealed that there was also an isotope imbalance as well; the sinks are isotopically heavier than the sources. The combination of these imbalances points to a significant missing component (or components) rather than simply incorrect flux and isotopic estimations and measurements. A recent study may have found the solution (Little et al., 2020), but further work is clearly necessary. Once the modern marine Ni budget is balanced, we will have identified the key modern controls of marine Ni cycling and this will enable robust modelling of the marine Ni cycle, and the subsequent affects, over time.

The identified primary sources of Ni to the ocean are dust, rivers, and, potentially, a benthic flux from either the recycling of Mn oxide particles and/or their diagenetic transformation to todorokite. The estimated total Ni transported to the ocean varies from 3.68 x 108 to 1.63 x 109 mol/yr (Ciscato et al., 2018; Gall et al., 2013; Little et al., 2020). Dust, which we assume to share the isotopic composition of the continental crust, has a limited isotopic predominately range from -0.1 to +0.2‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013) and is estimated to contribute 2% to 28% of the total marine Ni flux. Rivers are the main contributor of Ni to the oceans and make up an estimated 32% to 97% of the total marine Ni flux. The dissolved load of rivers is isotopically varied, from +0.29 to +1.38‰, with an abundance weighted isotopic composition of +0.9‰ (Cameron and Vance, 2014; Revels et al., 2021). The difference in isotopic composition of rivers and continental crust, the ultimate source of Ni to rivers, can be explained by the formation of iron oxides, a secondary weathering product of ultra mafic to mafic rocks which host the majority of the crust’s Ni. Experiments and natural observations indicate that iron oxides sorb isotopically light Ni (e.g., ferrihydrite has a fractionation of Δ60/58Nidissolved-sorbed = +0.35 ± 0.10‰) (Spivak-Birndorf et al., 2018; Wasylenki et al., 2015). The riverine particulate load may be an additional source of Ni to the ocean to help resolve the imbalance. How much Ni is retained in the particulate load versus the dissolved load and how much the particulate load could be mobilized remains unclear. What data we do have suggests that the particulate load is isotopically light compared to the dissolved load and is isotopically similar to continental crust (Revels et al., 2021). A recent effort to resolve the imbalance suggests a significant benthic source from Mn oxide redox cycling and/or diagenetic processes is of the appropriate size and isotopic composition (3.17 ± 1.08‰) to resolve the imbalance (Little et al., 2020). Thus far, the estimated input and isotopic contribution is approximately 0.6 to 2.3 x 108 mol/yr and 3.17 ± 1.08‰, respectively. However, the size of this flux and the exact mechanisms at play remain unclear and require further exploration (see section XXX for further discussion). In summary, the majority of the sources’ Ni isotopic compositions are restricted to -0.1 to 1.38‰ which are all lighter than seawater (ca. 1.3 to 1.7‰).

The deep ocean is globally homogenous, with an isotopic composition around 1.3‰ (Archer et al., 2020; Takano et al., 2017; Yang et al., 2020) while the surface ocean varies. The South Pacific (Takano et al., 2017), North Pacific (Yang et al., 2020), and South Atlantic (Archer et al., 2020) all show significant trends towards isotopically heavy values in the surface waters, up to 1.78‰, which are coupled with surface [Ni] depletions down to ca. 2 nM. On the other hand, the Indian sector of the Southern Ocean, which also displays a less pronounced, but similarly systematic surface [Ni] depletion, shows no isotopic enrichment in the heavier isotopes in surface waters (Wang et al., 2019). This discrepancy may be due to regional biology; Archer et al., hypothesize that the differing dominating species, cyanobacteria or diatoms, between south (diatom dominated) and north (cyanobacteria dominated) of the polar front results in the differing surface water isotopic compositions (Archer et al., 2020). Additional studies in other diatom dominated waters or through culture experiments could further explore this hypothesis.

Once Ni enters the ocean, its fate is a little less clear, partially because of the large isotopic variability in the dominant sinks. Previous studies have focused on Fe-Mn deposits, organic rich matter, and euxinic sediments. [I need to talk about organic rich matter and sulfides before getting into Fe-Mn isotope stuff and I need to do the percent sink thing]. Fe-Mn deposits are typically believed to represent the most significant sink; they compromise between 16% to 73% of the total estimated Ni sink (Ciscato et al., 2018; Gall et al., 2013; Little et al., 2020). However, the isotopic compositions of Fe-Mn deposits have an incredibly broad range (-1.5 to +1.8‰), which may be due to diagenetic processes (Gall et al., 2013; Gueguen et al., 2016; Little et al., 2020) (for additional discussion, see section XXX). Experimental results consistently suggest that Fe-Mn deposits should be isotopically light compared to seawater (Δ60/58NiFe oxides-aqueous = −0.35 to −0.77‰; Δ60/58NiMn oxides-aqueous −2.76 to −4‰) (Gueguen et al., 2018; Sorensen et al., 2020; Wasylenki et al., 2019, 2015). Generally, studies assign a primary Ni isotopic composition ca. 1.6‰ to Fe-Mn deposits (based on the isotopic composition of Fe-Mn crusts analyzed by Gall et al., 2013 and Gueguen et al., 2016) which is isotopically heavier than deep seawater. Organic rich matter is estimated to be the next most significant sink and make up 23 to 34% of the total estimated Ni sink (Ciscato et al., 2018; Little et al., 2020). The organic rich-pyrite fraction of samples from the upwelling sediments in the Peru Margin were found to have seawater like isotopic compositions (+1.3 ± 0.4) (Ciscato et al., 2018); however, there is significant variation within shales (δ60Ni = −0.84 to +2.50‰) which may be due to degrees of sulfidization/removal of Ni into sulfides and variable source Ni (Pašava et al., 2019; Porter et al., 2014). The primary isotopic composition of organic rich sediments is generally assigned a value of 1.2 in mass balance calculations (reflecting the Peru Margin sediments from Ciscato et al., 2018) (Ciscato et al., 2018; Little et al., 2020). Euxinic sediments appear to be a much smaller constituent of the total Ni sink, around 2.5% (Ciscato et al., 2018; Little et al., 2020), although the significance of sulfidizaiton in organic matter has not been assessed. Euxinic, sulfide rich sediments from the Black Sea have an isotopic range of +0.3 to +0.6‰ (Vance et al., 2016) and sulfidization in organic matter appears to produce isotopically lighter sediment in shales (Pašava et al., 2019).

From this data, there are two paths forward that need to be met before the Ni mass balance is resolved and before we can interpret Ni isotopic composition in the rock record. First, we must identify the primary isotopic fractionations and diagenetic mechanisms which cause the large variability observed in the two main Ni sinks, Fe-Mn deposits and organic rich sediments. Second, to reconstruct the Ni marine cycle of ancient oceans, we must find a reliable, consistent Ni record. To this end, my dissertation will pursue each of these paths. For my first project, I plan to measure the Ni isotopic compositions of primary to diagenetically altered carbonates, to determine the impact of diagenesis on the retained Ni isotopic signature of carbonates and determine the usefulness as a record of Ni. In my second project, I will experimentally determine the equilibrium fractionation of birnessite in seawater as well as todorkite, a diagenetic product of birnessite which may release Ni to the ocean during transformation. The combination of natural and experimental samples along with characterization of primary and diagenetic signatures will isolate the isotopic contributions of primary and diagenetic mechanisms. With this information, we can produce a more informed model marine Ni cycle and better predict how the marine Ni cycle may have looked different in the past.

**Birnessite to Todorokite Project**

Manganese (hydro-)oxides, specifically hexagonal birnessite which is thought to be representative of the poorly crystalline phyllomangates found in the deep ocean, have received significant attention because of their, potentially dominating, control on Ni ocean concentrations (Peacock and Sherman, 2007a). Nickel sorbs as a surface complex and can become structurally incorporated into vacancy sites. Using their sorption complexation model of Ni-bearing hexagonal birnessite, Peacock et al., 2007 calculated the concentration of dissolved Ni in seawater in equilibrium with birnessite to be approximately 7.2 nM at pH 8.2 (Peacock and Sherman, 2007b). This is in good agreement with observed concentrations of Ni in seawater(ca. 3-12 nM) (e.g., Cameron and Vance, 2014; Sclater et al., 1976) and suggests that birnessite, or a similar Mn oxide phase, may be the dominate buffer of seawater Ni concentrations. Our knowledge of Ni’s retention or remobilization, and these processes’ isotopic fractionations, within Mn oxides is becoming increasingly complicated.

Gall et al., 2013 measured 24 surface scrapings of Fe-Mn crusts across the globe and found a variable isotopic range from 0.9 to 2.5‰ with an average of 1.67±0.8‰ (Gall et al., 2013). They did not observe any strong correlation between δ60Ni and ocean basin, oxygen saturation or Ni concentration (Fig xx), but there was a correlation between δ60Ni and distance to continental shelf, likely reflecting the contribution of isotopically lighter continental sediments. This presented the isotopic imbalance and suggested there was no isotopic fractionation associated with Ni sorption on Mn oxides. Gueguen et al., 2016 observed generally similar trends; of the four North and South Pacific Fe-Mn crusts they analyzed, they all generally overlapped with the values found in 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). In addition, they measured every 1 to 2 mm into the crust for ca. 20 mm and, for three of the cores, there was little isotopic variation down core. 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, suggesting that post-depositional processes associated with Mn-oxide phases may lead to alteration of the primary δ60Ni signature. Overall, Fe-Mn crust, and therefore Ni associated with Mn-oxides, appeared to isotopically reflect seawater.

In contrast, Vance et al., 2016 observed light Ni isotopic compositions associated with Mn oxides in water columns sampled within the Black Sea (Vance et al., 2016). Across the oxygen minimum, (i.e., where Mn oxide particles dissolve) the Ni isotopic composition of the water decreased significantly from ca. 1.2 to 0.8‰ while the [Ni] increased which they calculate is associated with an isotopic fractionation of ca. -4‰. They attribute this to Ni sorbed on Mn oxide being released back into the water column upon oxide dissolution at the oxygen minimum. This clearly contradicts the findings of Gueguen et al., 2016 and Gall et al., 2013. A subsequent study found both isotopically heavy and light Ni within Fe-Mn sediments; Gueguen et al., 2020 found a measured a mix of hydrogenetic Fe-Mn crusts and hydrothermal Fe-Mn deposits (Gueguen et al., 2020). Like Gall et al., 2013 and Gueguen et al., 2016, the hydrogenetic Fe-Mn crusts were isotopically similar to seawater (0.8 to 1.8‰), but, like Vance et al., 2016, hydrothermal deposits have a generally wider, isotopically lighter range (-1.5 to 1.1‰). Finally, Little et al., 2020 analyzed the Ni isotopic composition of Mn rich crusts in the Eastern Pacific, where measured Fe-Mn crust samples in that region were +1.6‰, and predominately found isotopically light sediments (−0.8 to −0.2‰) (Little et al., 2020).

Experiments exploring Ni sorption and/or incorporation into Fe oxides and Mn oxides have indicated that the solid will sorb and/or incorporate isotopically light Ni relative to solution (Gueguen et al., 2018; Sorensen et al., 2020; Wasylenki et al., 2019, 2015). Sorption onto Fe oxides such as ferrihydrite and goethite have moderate fractionations of Δ60/58Nimineral-aqueous = -0.35 ± 0.08‰ (2sd) and Δ60/58Nimineral-aqueous = -0.77 ± 0.23‰ (2sd), respectively (Gueguen et al., 2018). Nickel sorption onto Mn oxides, specifically have surprisingly large fractionation factors, considering there is no change in coordination environment or valence, of Δ60/58Nimineral-aqueous −2.76‰ to −3.35‰ depending on pH in low ionic strength solutions (Sorensen et al., 2020) and up to Δ60/58Nimineral-aqueous = -4.0‰ in high ionic strength solutions (Wasylenki et al., 2019), which exactly matches the calculated fractionation of Mn oxide dissolution in the Black Sea water column (Vance et al., 2016). However, Wasylenki et al., 2019 observed decreasing fractionation in longer duration (ca. 1 month) experiments that indicate equilibrium has not yet been reached.

A number of mechanisms have been evoked to explain these variations. Vance et al., 2016

experimental work exactly supports the Black Sea data. Sorenson et al.,

**Carbonate Project**

**Introduction**

**Methodology**

General Data Quality:

Our long term reproducibility of double spike corrected, sample standard bracketed NIST SRM 986 is δ60Ni = 0.000±0.052‰ (n=321).

Challenges

Measuring a sample on a multi-collector inductively coupled plasma mass spectrometer requires that the sample be free of impurities (i.e., any other elements or complexes besides the element of interest). Without purification, there may be isobaric interferences or matrix effects which complicate data interpretation and reliability. We determined the maximum acceptable Element/Ni for Ca, Fe, Zn and Ti by doping SRM 986 Ni standard with the interfering elements at Element/Ni between 0.01 and 1. The threshold value is designated as the greatest Element/Ni that results in a δ60Ni value within the long term 2 SD of δ60NiSRM986. For Ca, Fe, Zn, and Ti, the acceptable Element/Ni were 1, 0.1, 1, and 1 respectively. These data provided clear, quantitative goals for developing our chemical separation plan.

Separating Ni from the carbonate matrix has proved to be a technical challenge (alvarez paper?). The first obstacle is removing the abundance of Ca; the Ca/Ni of the Bahama carbonate samples were approximately 4x105. Next, residual interfering transition metals such as Fe, Zn, and Ti, which may be in equivalent or greater abundance than Ni, must be removed. Finally, if Fe is not yet adequately purified (as determined by the sensitivity tests), an additional purification step should be performed.

To remove Ca and other common seawater constituents (*e.g.,* Mg, Na), we dissolved a generic sample of calcite, aliquoted the amount we would need for isotopic analysis based on the estimated Ni content in the Bahama samples and spiked it with Ni for column tests. We first tested a method from Strelow et al., 1972 which used oxalic acid-hydrochloric acid mixtures and AG1-X8 anion resin in chloride form (Strelow et al., 1972). Elements like Ca do not sorb on the resin in any oxalic-hydrochloric mixture while Ni sorbs at very low hydrochloric acid molarities (ca. 0.1 M) and 0.05 M oxalic acid. However, the insolubility of certain oxalate complexes, such as Ca oxalates, resulted in white precipitates forming which interfered with the column’s efficiency. Ultimately, the final Ni fraction had a Ca/Ni of approximately 7900 and a Ni recovery of <50% which indicates the sample will not be rid of matrix effects or have enough Ni for the double spike technique.

Next, we attempted an augmented version of the methods within Gall et al., 2012 and Strelow, 1990 (Gall et al., 2012; Strelow, 1990) to remove Ca. By combing excess ammonia with ammonium citrate on cation AG50W-X8 resin, Ni binds to ammonia and sorbs to the resin while Ca elutes as a citrate complex. Then, Ni can be easily eluted with 3 M hydrochloric acid. Again, white precipitates, which may have been Ca citrate precipitates, formed when less than 60 mL of loading solution was added to the sample. With this method, we achieved a 85% Ni recovery and final Ca/Ni of ~0.5. This method also removed some transition metals such as Ti, Fe and, V. Unfortunately, the large initial loading requirement would pose two issues. First, using such a large amount of solution increases the amount of Ni contamination. Second, the costly >60 mL Teflon containers needed to handle the samples would slow throughput because purchasing the appropriate number of containers is financially challenging.

We looked to a third method which would ideally remove the issues mentioned above, but still achieve the >70% Ni recovery and Ca/Ni <1. Yang et al., 2020 published a novel method to purify Ni from seawater using a lesser-known resin, NOBIAS-PA1 resin, and ammonium acetate (Yang et al., 2020). They were able to effectively remove >99% of Ca, Na, Mg, and S and had a Ni recovery of >99%. Using this method, we were able to effectively remove Ca to a Ca/Ni of ~0.4 and had a Ni recovery of >98% with only 10 mL of starting solution. We decided to use this column chromatography for the bulk Ca removal step.

The next challenge was to remove the residual interfering transition metals such as Zn, Ti, and Fe. For these tests, we created a trace metal solution which resemble the anticipated trace metal composition of the Bahama carbonate samples using ICP solutions and the Ca concentration after the NOBIAS column. The method described by Gall et al., 2012 and Strelow, 1990 was able to reduce the Ti/Ni, V/Ni and Fe/Ni from 3, 2.5, and 15 to 1, 0.02, and 0.4, respectively. The Ni recovery was >95%. The method did not remove any Zn, which effectively behaved exactly as Ni on the column. We found that, after the bulk Ca removal, there were no white precipitates in 3 mL of loading solution. We decided to use this method to remove most transition metals.

Finally, we needed to remove Zn and residual Fe. To do this, 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 and Zn form negatively charged chloride complexes which sorb to the resin, while Ni elutes(Kraus and Moore, 1953). Our tests showed this method was able to reduce Fe/Ni and Zn/Ni from 4.5 and 2.5 to 0.01 and 0.3, respectively. The combination of these three columns appears to be adequate to effectively purify Ni from a carbonate matrix (see table XXX for full method).

Ni AAS standard processed through the entire method has a δ60Ni = -0.43±0.05‰ (n=21) which is analytically indistinguishable from the unprocessed Ni AAS standard δ60Ni = -0.44±0.07‰ (n=16).









