# Proposed Work

## Guiding Questions

I will investigate two high priority knowledge gaps regarding the marine Ni budget as important steps toward resolving the apparent Ni isotope imbalance. 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?
3. How do porphyrins, found in mature organic rich sediments, influence the Ni isotopic composition of organic matter? Does post-depositional incorporation of Ni alter the isotopic composition of the sediment?

The above questions will inform the first and second chapters of the dissertation, described below. 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 at this stage.

## Hypotheses and Project Summary

### Carbonates

Carbonates are a common 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 the range likely underestimated the flux. Ciscato et al. (2018) calculated the Ni flux into carbonates by exclusively considering the organic matter associated with carbonates. Their sample set (n=8) consisted of carbonate rich (34-75%), lagoon sediments, and they separated the organic-pyrite fraction from an HF-HCl digestible fraction (which contained the inorganic carbonate phase in addition to other HF-HCl digestible phases). To calculate the flux of Ni into carbonates, they multiplied the Ni/TOC from the organic-pyrite fraction and the organic carbon burial associated with carbonates (6x1012 g Corg/yr ± 50%; Berner, 1990, 1982)), and omit the output associated with inorganic C. Experiments have shown Ni s(Alvarez et al., 2021; Demina et al., 2016; Lakshtanov and Stipp, 2007; Munsel et al., 2010; Smith et al., 2020)

The higher end of the carbonate flux did consider the inorganic carbonate flux of Ni, but with lacking modern data, were estimated the average Ni concentration using samples that may not be representative of the modern sink. Alvarez et al. (2021) calculated the carbonate Ni output by multiplying the burial flux of carbonates (3.2x1013 to 14.7x1013 mol CaCO3/yr; Alvarez et al. (2021) and references therein) by the average Ni concentration in a set of Carboniferous marine limestone (Zhao and Zheng, 2014). It is unclear if the Ni concentrations used are representative of modern carbonate Ni concentrations. Assuming the Ni concentration in carbonates is related to the concentration of Ni in seawater, we must know the Ni concentration of Carboniferous seawater to determine how comparable the Ni concentration of Carboniferous carbonates are to modern ones. While seawater Ni concentrations appear to have been roughly constant for the past two billion years (Liu et al., 2021), there has been fluctuation, for example, just prior to the end Permian mass extinction (Li et al., 2021; Rampino et al., 2017; Rothman et al., 2014). In addition, the limestone samples used have undergone lithification and potentially also diagenetic alteration, both processes that have not been assessed in the context of Ni mobilization, to the best of our knowledge. Nickel concentration measurements of modern samples would surely improve the Alvarez et al. (2021) estimate and determine its applicability to the modern marine Ni budget.

[insert information about the isotopic composition of carbonates, maybe discuss bond length stuff here?]

I propose to perform the first Ni isotope measurements of modern marine carbonates to obtain a δ60Ni for carbonates and help assess its importance to the budget. Ideally, we would learn about the δ60Ni for carbonates from multiple settings and origins (*e.g.,* pelagic, shallow-water, biotic, abiotic), but there are of course time and sample availability limitations. carbonate mass flux However, there are challenges to attain pelagic samples especially those with accompanied diagenetic histories. Fortunately, we do have access to well characterized, primary to diagenetically altered shallow water carbonates which provide a reasonable and efficient path toward significantly advancing our knowledge of the carbonate sink.

By virtue of our sample selection, we are well positioned to evaluate shallow carbonates as a record of the δ60Ni of seawater. Shallow water carbonates may have the highest potential to serve as a record. They are more likely to be preserved compared to more distal carbonates because slope and deep-basin carbonates are more often subducted and removed or extremely deformed, as noted by Schrag et al. (2013) for δ13C records. In addition, 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). If diagenetic processes either preserve or systematically alter the δ60Ni of the primary carbonate value, shallow-water carbonates may be a robust record of δ60Ni from the contemporary seawater.

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). With these samples, we will obtain the first δ60Ni values for modern marine carbonates and assess the fidelity of shallow water carbonates as a robust record of the δ60Ni of 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 precipitated (Gall et al., 2013; Gueguen et al., 2020, 2016; Gueguen and Rouxel, 2021; Little et al., 2020; Vance et al., 2016). What could be causing the variability within this sediment type? Without better knowledge of the most important marine Ni sink, correctly modeling the marine Ni cycle is likely impossible.Past experimental data provide insight into which avenues of investigation are most promising. We will experimentally investigate two of the most promising explanations for the variability in Mn oxide sediments, described below. The primary mineral of focus will be birnessite, the dominant Mn phase in naturfraal marine Fe-Mn precipitates (*e.g.,* Burns and Burns, 1977; Yoshikawa, 1991).

A set of Ni-birnessite experiments point to two possible explanations for the variability in Fe-Mn deposits. [explain experimental stuff first? Then get into hypotheses and approaches. If I present the Ryan stuff about bigdNi getting smaller overtime. We can explain this in two ways. (1) there could be initial kinetic effects that are overwritten by equilibrium or 2 Ni migrates slowly into the lattice and the dif in fractionation between outside and inside ]

Past Ni-birnessite sorption experiments indicate two possible explanations for the isotope variations observed in natural sediments: differences in kinetic and equilibrium fractionation coupled to a slow equilibration time and differences in isotopic fractionation between multiple Ni coordination states. Wasylenki et al. (in preparation) performed Ni-birnessite sorption experiments in a simulated seawater solution with durations of 67 hr and 27 days. They found an extreme Δ60Nisolution-birnessite in their 67hr experiment (~4.0‰) which diminished significantly by their 27-day experiment, suggesting ephemeral kinetic trends were being overwritten by equilibrium fractionation with time. In addition, the data fit Rayleigh fractionation trends which indicates the data exhibit either irreversible equilibrium or kinetic fractionation. Manganese-rich sediments have a wide range of accumulation rates and, depending on the rate, may potentially capture different isotope fractionations (kinetic, equilibrium or a mix thereof). 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.

Based on these observations, I hypothesize that kinetic fractionation leads to isotopically lighter Ni sorbed to Mn oxides than equilibrium fractionation. 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 and rate of exchange, 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).

The variation could be due to differences in Ni coordination environment. Nickel can be structurally incorporated into Mn vacancy sites 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 Δ60Nisolution-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). Another study of found that, with increased percent sorbed Ni, there was a decrease in Δ60Nisolution-birnessite which the authors propose may be due to two complexes with distinct Δ60Nisolution-birnessite (Wasylenki et al., in preparation). Experimental results suggest Ni migrates very slowly into the vacancy sites (30% incorporation after 408 h) (Peacock, 2009). Extended X-ray absorption fine-structure spectroscopy spectra from high and low ionic strength Ni-birnessite sorption experiments supported the presence of significant Ni incorporation in the high ionic strength solutions compared to low ionic strength solutions (Wasylenki et al., n.d.). In natural Fe-Mn crusts, the majority of Ni is structurally incorporated (Peacock and Sherman, 2007), but the degree of structural incorporation within dispersed sediments is unknown. If surface-sorbed and incorporated Ni have different Δ60/58Nisolution-birnessite,differences in the proportions of sorbed to incorporated Ni would impact the δ60/58Ni of Mn-rich sediments.

Assessing the difference between total sorbed and incorporated Ni is a necessary first step in evaluating the importance of coordination on the variation of δ60Ni in Mn-rich sediments. We hypothesize that surface sorbed Ni is isotopically lighter than incorporated Ni within birnessite. To test this hypothesis, 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, this set of experiments can begin to address how coordination may impact the δ60Ni in Mn-rich sediments.

## Organic Matter – Porphyrin paragraph

## Risks

[Risk paragraph]

Maybe experimental birnessite not representative – maybe Mn oxide coatings on carboantes? Difference in isotopic composition between pelagic and shallow water carbs, biogenic carbs?

# Progress To Date

In the following section, I will describe the carbonate sample collection and the progress to date on the carbonate section of the proposal. The progress to date includes development of the purification protocol, analytical methods, preliminary results, and discussion with questions for future work.

## Methods from Draft 3

### Sample Collection and Site Description

The short cores in hand are <20cm bank-top cores from modern sediments in the Great Bahama Bank, specifically near the Little Darby and Lee Stocking Islands (labeled C1, C3, C4, and C5). 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 the mud pit datum (mbpm), respectively (Eberli et al., 1997; Swart and Melim, 2000). To correct mbmp to meters below seafloor (mbsf), remove 11.8 m and 14.9 m from the mbmp for Unda and Clino. 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 <50 mbmp and between 100 mbmp and 350 mbmp) and more minor contributions of dolomite starting below 150 mbmp (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 100 mbmp and 150 mbmp) and significant amounts of dolomite (nearly 100% between 275 mbmp and 350 mbmp).

The top ~100 mbmp 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 200 mbmp, there are large sections of coral with secondary amounts of skeletal sediments. Between ca. 200 mbmp and 370 mbmp, 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, Fig XXX.).

The top of the Unda core is quite 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 50 mbmp or so (Manfrino and Ginsburg, 2001). From approximately 110 mbmp to the bottom of the core, most sediments are peloidal and skeletal mixtures except for a brief hiatus between 290 mbmp and 360 mbmp 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 108 mbmp and 135 mbmp 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 200 mbsf for the Clino core (Swart and Oehlert, 2018). The C and O isotopes covary and become more positive between 60 mbsf and 110 mbsf in Unda and 90 mbsf and 180 mbsf 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).

### Purification development

Previously published methods for Ni purification do not work for carbonates because of the need to separate very large amounts of Ca from traces of Ni. 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 on 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 (4000 RPM for 10 min) and decanting the solution. The samples were stored in 15-30 mL Teflon vials and covered with Parafilm until aliquots were drawn for analysis.

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 Ce++/Ce+ and CeO/Ce, respectively which were always kept below 3%. 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?). The optimal sample-to-spike ratio for minimal uncertainty is 36:64, determined using the double-spike toolbox code of Rudge et al. (2009). Samples were then fluxed overnight at 120℃ to ensure equilibration of sample and spike. 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[[1]](#footnote-1), 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).

The δ18O, δ13C, mineralogy, and major and trace element concentration data are from published datasets, but a brief description of the methods are given here (Hardisty et al., 2017; Liu et al., 2019). Mineralogy data were calculated from the X-ray diffraction peak area ratios collected from a Panalytical X-Pert Pro at the University of Miami and have ±2 wt% uncertainties (Hardisty et al., 2017; Melim et al., 1995). Both the δ18O and δ13C are relative to Vienna Pee Dee Belemnite and are reported in delta notation in per mil units. The δ18O and δ13C for the Clino and Unda core were measured via continuous flow with a Delta V Thermo Advantage Isotope Ratio Mass spectrometer at the University of California, Riverside (Hardisty et al., 2017). For the short cores, δ18O and δ13C were measured with a GV IsoPrime mass spectrometer in dual inlet mode at The Center for Stable Isotope Biogeochemistry at UC, Berkeley (Hardisty et al., 2017). Standard deviations for δ18O and δ13C on replicate analyses were around 0.10‰. Major and trace element data were analyzed using two Agilent 7900 ICP-MSs at the University of North Carolina at Chapel Hill and at the University of California, Riverside (Liu et al., 2019). Repeated analysis of an in-house carbonate standard produced uncertainties of around 5% for the major elements and 10% for the trace elements.

## Preliminary Results from Draft 1

### Results

The short cores, which represent primary carbonate deposition, were generally isotopically similar to deep seawater and exhibited correlations with mineralogy and [Ni]. We selected 15 samples to analyze from three different cores, 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 ppm 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. There is no clear correlation between δ60Ni and δ18O or δ13C (Fig. x).

The Unda and Clino cores, which represent varying diagenetic processes, had wider ranges of δ60Ni compared to the short cores and exhibited more mild correlations with mineralogy. The samples were selected to target the different diagenetic regimes (*e.g.,* 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 (n=16) 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 effects 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 samples analyzed (n=10) 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 waters (depths <200 m) may or may not exhibit 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 can alter the initial deposition 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 and help identify the location of transition between low and high δ60Ni.

*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 200 mbsf to 350 mbsf that hover around the δ60Ni value of deep seawater (~1.3‰-1.4‰) and another set between 150 mbsf to 200 mbsf and >350 mbsf 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 we happen to have in hand 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. Because the samples were analyzed in bulk and the Clino samples analyzed all contain <10% dolomite, it is challenging to determine from these 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).

Given these initial results, we can make some tentative observations about the role of carbonates in the marine Ni budget. The primary carbonate δ60Ni measured here (1.31±0.28‰) is similar to the deep ocean’s δ60Ni (1.3‰-1.4‰). As mentioned, the deep ocean’s δ60Ni may be isotopically lighter than the isotopic composition of Bahamian seawater considering surface waters can be enriched in the heavier Ni isotopes. However, even if the heaviest observed surface waters (~1.8‰) are representative of Bahamian seawater, the primary carbonate δ60Ni would be 0.5‰ lighter than solution.

Focusing prarimly on the primary carboanes, slightly lighter than deep seawater and several permil lower than surface

# References

1. 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 analytically indistinguishable δ60Ni values. [↑](#footnote-ref-1)