# 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[[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).

[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. 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-1)