Preliminary 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

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. meteoric samples are in a zone of area with aragonite to LMC neomorphism, and the measured δ60Ni may be preserving the 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‰ (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 fluids (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 will indicate if these trends are persistent throughout the core and help support interpretations.

*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., 365–380mbsf, 550m-600m).

* Note that all of the dolomites in the massive dolomite region have isotopically light Ni and the most Ni
* Massive dolomites formed differently than the background dolomites one might find in Clino
* Diagenetic fluid of massive dolomites may be seawater like, as many have suggested, or not, as suggested by the Cr paper.

General Short Core trends

* 1. Describe sites
  2. No obvious trends downcore
     1. Can mention seagrass pumping O2 into core and fueling diagenesis not showing up in dNi
     2. Dalton suggested variations may be due to simple differences in the environment, time of precipitation, etc.
  3. Trends with dNi and [Ni]
  4. Trends with mineralogy
  5. Point out unclear if precipitated from deep water esque dNi or surface water phytoplankton like dominated dNi