IMPROVED Nd COLUMN CHEMICAL METHODS AND IMPLICATIONS FOR

RECONSTRUCTION OF WATER MASS CIRCULATION OVER THE MID-

EOCENE CLIMATIC OPTIMUM (MECO)

A Thesis

by

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ABSTRACT

The mid to late Eocene (49—34 Ma) is characterized as a long-term cooling (7°C) transition from greenhouse to icehouse conditions. However, this long-term cooling period was interrupted by a rapid warming event: the Mid Eocene Climatic Optimum (MECO; 40.6 Ma). During this episode of transient warming, Southern Ocean temperatures gradually rose 4 to 6°C over ~500 ka, and then warmed ~1.5°C more over a brief period at the peak of the MECO (40.0 Ma). After the peak warming, rapid cooling occurred over ~200 ka returning the Southern Ocean waters to pre-MECO temperatures.

Such prominent and transient warming may have affected (or been influenced) by a change in deep-water formation and circulation. Seawater Neodymium (Nd) isotope ratios are commonly used as a proxy for ocean circulation, however, due to the multiple column chemistry steps in sample preparation, traces of Nd are frequently lost throughout the methods. Consequently, in some samples, where Nd is scarce, it is difficult to record an isotope signal.

Here we dissect our sample preparation procedures in order to best optimize Nd collection for isotope analysis. We test the yield of Nd through the columns and suggest and alternative in order for maximum collection. Additionally, we investigate the potential relationship between the meridional overturning circulation (MOC) and climate change during the MECO using a high-resolution record of water mass Nd isotopes at Ocean Drilling Project Site 464, in the North Pacific.

An approximately -1 ε_{Nd} shift concurrent with warming occurs over an ~500kyr period at about 42Ma could suggest stronger water mass intrusion from the south or an increase in weathering to the surface ventilated source water of the Pacific. Utilizing the methods adjustments compiled here along with generating a dataset over a North-South Pacific transect can provide a more clear answer to the type and magnitude of potential shifts in ocean circulation.

ACKNOWLEDGMENTS

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1. INTRODUCTION AND GOALS

In this study we had two goals: 1) to ensure that the data produced for this project is as robust as possible, 2) to understand the paleocirculation of the ocean during the Mid-Eocene Climatic Optimum (MECO). In order to accomplish the second goal we had to address the first. The first portion of this thesis, sections 2 to through 5, addresses our recent method testing and development, and the second portion, sections 6 through 9, presents preliminary data from the MECO.

2. IMPROVED Nd COLUMN CHEMICAL METHODS

2.1 Proxies for Ocean Circulation

One aspect of climate dynamics that may be particularly sensitive to future warming is the global overturning circulation (Broecker, 1997). It is known that changes in overturning circulation are strongly related to climate change, as the global overturning circulation is an important mechanism for heat transport in today's ocean and climate systems (Broecker, 1997). In order to investigate the relationship between climate change and overturning circulation in the past, we must compare proxies of environmental conditions (such as the temperature of seawater recorded by oxygen isotope values) with proxies of ocean circulation.

The isotopic composition of Neodymium (Nd) in seawater is a commonly used proxy for tracing water masses and weathering sources (Frank, 2002; Goldstein and Hemming, 2003) . Neodymium has a short residence time (~500-1000 years; Tachikawa et al., 2003; Bayon et al., 2004) relative to oceanic mixing (~1500 years; Broecker et al., 1960), resulting in inter-basinal compositional differences. The dominant source of dissolved Nd to the oceans is continental weathering via river runoff into the ocean basins (Goldstein and Jacobsen, 1988). In specific regions, especially near shore, pore water has recently been shown to contribute to Nd isotopic composition of bottom water (Abbott et al., 2015). While water in the region has a long time to accumulate a Nd signal from the pore water, we expect the pore water Nd flux out of pelagic sites to be minimal. Dissolved inputs of Nd via hydrothermal activity and dust dissolution have

been shown to be negligible (Halliday et al., 1992; Jones et al., 2000). Therefore at this time, we consider the primary source to bottom water to be water mass transport.

The Nd isotopic composition of seawater in a given region is primarily determined by the weathering and river drainage of the nearby landmasses. Different rocks have distinct Nd isotope ratios based on their age and composition. For example, Nd is less compatible than Sm, the parent element of ^{143}Nd, and thus more likely to partition into a melt than Sm. Therefore continents have lower Sm/Nd (and consequently evolve lower ^{143}Nd/^{144}Nd) values than the mantle. Additionally, features derived from melting of the depleted mantle, such as mid-ocean ridge basalts and ocean island basalts, have higher Sm and ^{143}Nd/^{144}Nd values than the continents (e.g., Jacobsen and Wasserburg, 1980). The ^{143}Nd/^{144}Nd values of samples are expressed as ε_{Nd} values, which normalize the ^{143}Nd/^{144}Nd recorded in a sample to that of the bulk Earth (as inferred from chondritic meteorites). The ε_{Nd} value is in units of parts per 10^4 deviations from bulk Earth and is determined by the following equation in order to express as a whole number:

$$\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd_{sample}/^{143}Nd/^{144}Nd_{CHUR})-1] \times 10^4$$

Where the present day Chondritic Uniform Reservoir (CHUR) ^{143}Nd/^{144}Nd$_{CHUR}$ = 0.512638 (DePaolo and Wasserburg, 1976).

A water mass acquires its isotopic fingerprint from the surface waters in which it sinks and the isotope signature is slowly modified through mixing with other water masses, boundary exchange, and the accumulation of dissolved Nd from sediment diagenesis and pore water fluxes (Peipgras and Wasserburg, 1987; Amakawa et al.,

2000; Lacan and Jeandel, 2005; Abbott et al., 2015;). The North Atlantic has the lowest ε_{Nd} values (ε_{Nd} = -13 to -14) and the Pacific has the highest ε_{Nd} values (ε_{Nd} = 0 to -5).

Formation of North Atlantic Deep Water (NADW) is influenced by water from Baffin Bay, the Denmark Straits and the Norwegian Sea. Due to the very old continental crust source with very low Nd isotope ratios, the ε_{Nd} values are much more negative in Baffin Bay (ε_{Nd} <-20) than in the Denmark Straits and Norwegian Sea (ε_{Nd} = -7 to -9). The mixing of these two water masses upon formation of North Atlantic Deep Water characterizes the Atlantic Nd signature at ε_{Nd} = -13 to -14 (Piepgras and Wasserburg, 1987; Goldstein and Hemming, 2003; 2014, and references therein).

The Pacific has significantly higher ε_{Nd} values (ε_{Nd} = 0 to -5), resulting from direct weathering and drainage of the relatively young ocean islands and volcanic arc terranes or the diagenesis of sediment derived from those materials. Both the pore water flux and drainage have significantly higher ε_{Nd} values than any of the other sources of Nd to the oceans (ε_{Nd} = +7 to +10; Jeandel et al., 1998; Amakawa et al., 2000). The considerably higher ε_{Nd} values of these volcanic sources sufficiently increase the overall Nd-isotopic signature of the Pacific to their ε_{Nd} range of 0 to -5 (Piepgras and Wasserburg, 1980; Piepgras and Jacobsen, 1988; Goldstein and Jacobsen, 1988).

The Indian Ocean and the Circum-Antarctic have ε_{Nd} values intermediate to the Atlantic and Pacific. The Circum-Antarctic shows a Nd signature that reflects a mixing of the waters of the Atlantic and Pacific oceans via Antarctic Circumpolar Current (ε_{Nd} = -8 to -9; Goldstein and Jacobsen, 1988). Additionally, the Indian Ocean is fed by northward advecting waters circulating from the Antarctic and has no other unique

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source, thus reflecting ε_{Nd} values intermediate to Atlantic and Pacific waters with $\varepsilon_{Nd} = -8$ to -9 (Piepgras and Wasserburg, 1980; Piepgras and Jacobsen, 1988; Goldstein and Jacobsen, 1988).

The Fe-Mn crusts, which precipitate directly from seawater, record the Nd isotopic composition of the seawater from which they grew (e.g., Abouchami et al., 1997; van de Flierdt et al., 2004). However the Fe-Mn crusts precipitate very slowly (a few mm per million years), and thus may not resolve abrupt and transient changes in thermohaline circulation (Frank, 2002). Extraction of disseminated authigenic Fe-Mn oxide minerals from marine sediments permits construction of higher temporal resolution proxy records (Gutjahar, 2007; Basak et al., 2011). However, recent studies suggest that it is difficult to isolate the pure authigenic phase without leaching other minerals, which may interfere with the assumed seawater Nd signature (Wilson et al., 2013; Molina-Kescher et al., 2014).

Fossil fish debris likely preserve the Nd isotopic composition dissolved in seawater at the sediment water interface. Rare earth elements are incorporated into fish debris via a postmortem diagenetic process (Staudigel et al., 1985; Reynard et al., 1999). Several lines of evidence establish fish debris as the phase that most reliably records bottom water Nd: 1) the concentration of Nd in fish teeth/debris does not increase systematically with fish teeth burial depth, 2) the lower the sediment accumulation rate, the longer fish debris stays at the sediment-water interface, incorporating a higher concentration in Nd, 3) fish debris in core tops have the same isotopic composition as

bottom water, and 4) Nd match contemporaneous ferromanganese crusts (Martin and Scher, 2004).

2.2 Challenges with Current Nd Isolation Methods

After washing the samples and picking fish debris, each sample is run through a series of column chemistry in order to isolate the Nd fraction for analysis on the thermal ionization mass spectrometer. In some samples where Nd concentrations are low, it is important that the methods are efficient and that there is minimal Nd loss through each step. Due to low Nd yield we had many Nd isotope sample analyses on the TIMS failed. In order to continue generating high quality geochemical data it was necessary to carefully assess and reevaluate our column chemistry methods. In this study we ran numerous internal standards through the different stages of column chemistry in order to determine the most efficient way to extract Nd from samples. We tested our established column chemistry methods by running a standard through each individual step of our column chemistry methods and checking the Nd yields. We also ran standards through an alternative progression of column chemistry that is commonly used in order to compare. The goal of these tests was to identify a more optimal way of isolating Nd and maximizing its yield through various types of column chemistry. This involved calibrating the columns and determining alternative types of column chemistry that were more effective in maximizing Nd yields. The methods for column calibrations are discussed in detail in Appendix C.

3. SAMPLES AND METHODS

3.1 Testing the Column Chemistry

Column chemistry tests were performed on 26 spiked JNdi-1 300ng standards eluted through different stages of column chemistry in order to determine how well the total Nd is extracted from each type of column. Tests were performed on the columns that have previously been used in our lab consisting of Re-Spec and Ln-Spec stages, in addition to testing an alternative column chemistry procedure consisting of a clean up column, Tru-Spec and Ln-Spec stages. After our initial tests, our Ln spec columns were calibrated in order to improve the yields of Nd eluted through them. Figure 1 shows the different steps to each of the column chemistry tests performed.

In order to test the yields of the different columns, we spiked and analyzed JNdi-1 standards to provide a baseline for comparison to spiked standards processed through columns. Unspiked JNdi-1 standards were also analyzed on the TIMS without previously going through column chemistry in order to ensure machine precision and to measure the $^{150}Nd/^{144}Nd$ ratio of the unspiked standard for calculation of the final yield. An additional Fe clean-up step that precedes the RE- or Tru-spec columns adapted from Harvey and Baxter, 2009 was tested. It is intended to clean out Fe (as well as Ca, Mn and Mg) in any samples that may be high in those cations that may interfere with the Nd collection. Referred to as the Fe clean-up column, this procedure consists of a sample drip through AG50w-X4 resin and followed by a 1.5N HCl rinse to remove the iron (Harvey and Baxter, 2009). The REE's are collected during an elution of 6N HCl and the sample is then moved along to Tru spec.

The first stage of the column chemistry procedures (RE spec) involves dripping a sample through resin in order to isolate the rare earth elements (REE) in a sample. Once the REE split is collected, the sample is then processed through the second stage (Ln spec chromatographic columns), which isolates the Nd from the REE with similar atomic masses (Pr and Sm). After the Nd fraction is collected, it is dried down and loaded onto a Re filament. The filaments, each with one separate standard or sample loaded onto them, are loaded into the TIMS on a turret. Isotope ratios are recorded and collected from the TIMS data acquisition method, which is programmable and set to the particular set of isotope ratios desired, in this case, those of the Nd isotopes.

In our methods tests, spiked standards were run through a series of three different column progressions. Additionally, the second stage of columns (Ln spec) was calibrated to optimize Nd collection and the tests were run before and after the calibrations. Initially, separate spiked standards were run through RE spec only and then through the progression of RE spec plus Ln spec. We ran separate and combined yield tests in order to check the yields both on the RE spec portion and to check how well the Ln spec columns were calibrated. The Ln spec columns were rebuilt with new resin and calibrated (procedure described in section 2.3). JNDi-1 standards were run through Re spec and the new Ln spec columns. Standards were also tested through the supplementary column procedure. A suite (2 to 4 total) of replicate, spiked standards were run through each of the following progressions of columns: i) Tru spec columns only, ii) Tru spec plus the newly calibrated Ln spec columns, iii) clean up columns alone, iv) Fe clean-up columns plus Tru spec columns, and, v. Fe clean-up columns plus

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Tru spec columns plus Ln spec columns. After all of the column chemistry was complete, each sample was spiked with 0.01g of concentrated ^{150}Nd spike and loaded onto a Re filament using ~1N HCl for analysis on the thermal ionization mass spectrometer (TIMS) in the R. Ken Williams '45 Radiogenic Isotope Geosciences Laboratory at Texas A&M University. The spike was added to each standard after chemistry in order to look at the ^{150}Nd/^{144}Nd and compare this ratio to that of each spiked standard that was not run through chemistry.

3.2 Ln Spec Column Calibrations

The resin in the Ln spec columns is reusable after a thorough acid cleaning following each use. Because this resin is reused, it is susceptible to degradation over time. Thus the columns may not consistently yield the most optimal separation between Pr, Nd and Sm. For the full column calibration procedure details see Appendix C. The Ln Spec columns were purged of all of the old resin and washed with ultrapure water. Nine centimeters (column height) of new and clean Ln Spec resin was then added to each column and rinsed with ultrapure water. The new columns were then pre-cleaned with 6N HCl and ultrapure water as they are for each normal sample run. The column procedure begins with a conditioning step with 0.18N HCl, and is the simulation of the sample-processing step of this procedure. Splits were taken every 1 ml for the first 8 ml of 0.18N HCl added and then every 0.5 ml for the next 10 ml. These splits were then analyzed on the ICP-MS in order to determine what volume of acid needs to wash through the resin before collection of the most efficient split for sample processing. The

goal of this calibration is to find the split in which the Nd concentration is high and increasing while the concentration of Pr is decreasing and before the concentration of Sm begins to increase (Figure 2). A potentially more challenging variable is the concentration of the acids that are used in the chromatographic column procedures. Slight variations in the concentration of the acid can greatly alter the calibration of the column. In general columns need to be rebuilt periodically and recalibrated every time a new batch of acid is started.

4. METHODS TEST RESULTS

We present the results from the yield tests performed, as well as the new dissolved fish debris Nd isotope data from the North Pacific (Figures 3 and 4).

4.1 Unspiked and Spiked Standards

Each of the three unspiked JNdi-1 standards that were analyzed without going through column chemistry had a $^{150}Nd/^{144}Nd$ ratio of 0.236. The three spiked JNdi-1 standards had an average $^{150}Nd/^{144}Nd$ ratio of 1.64. Because the standards did not go through columns and were loaded directly into the TIMS, it is assumed that they had a maximum Nd yield. Table 1 shows the $^{150}Nd/^{144}Nd$ ratios of both the unspiked and spiked standards.

4.2 Column Chemistry Tests: Pre-Calibration

Four spiked standards were run through Re Spec columns only. The $^{150}Nd/^{144}Nd$ ratios for these four spiked standards were 3.08, 2.72, 2.66 and 3.25 (Table 2), with an average $^{150}Nd/^{144}Nd$ ratio of 2.93 (Table 3).

Nine spiked standards were run through Re Spec columns and then dried down and prepared and run through Ln Spec columns. This combination of columns is the typical progression used in our lab procedures. The $^{150}Nd/^{144}Nd$ ratios for these nine spiked standards are shown in Table 2 with an average $^{150}Nd/^{144}Nd$ ratio of 9.14.

Three spiked standards were run through Tru Spec columns only. The $^{150}Nd/^{144}Nd$ ratio for these three spiked standards were 1.91, 1.76, and 1.96 (Table 2), with an average $^{150}Nd/^{144}Nd$ ratio of 1.88 (Table 3).

4.3 Column Chemistry Tests: Post Calibration

After the Ln Spec columns were rebuilt and calibrated, it was deemed necessary to collect the Nd split after 13 ml of 0.18N HCl has washed through the resin. Previously, 9 ml of acid was washed through the old Ln Spec columns.

Four spiked standards were run through Tru Spec columns and then dried down and prepared and run through Ln Spec columns (after the columns were rebuilt and calibrated). The ^{150}Nd/^{144}Nd ratios of these four spiked standards were 2.58, 5.90, 3.07 and 9.83 (Table 2), with an average ^{150}Nd/^{144}Nd ratio of 5.35 (Table 3).

4.4 Iron Clean-up Column Tests

The Fe clean-up column was tested at the beginning of the Tru Spec – Ln Spec progression and the standards were run through only the clean-up column, through the clean-up and Tru-spec columns only, and through all three steps (clean-up – Tru Spec – Ln Spec). Two spiked standards were tested through each of these three progressions (Table 2). The two spiked standards that were run through the clean up column only had ^{150}Nd/^{144}Nd ratios of 55.5 and 19.9. The two spiked standards that were run through the clean up and Tru Spec columns had ^{150}Nd/^{144}Nd ratios of 107 and 106. The two spiked standards that were run through all three column of the progression had ^{150}Nd/^{144}Nd ratios of 72.2 and 65.2.

5. DISCUSSION OF METHODS

As expected, the Nd yields on our column chemistry procedures improved after rebuilding and calibrating the Ln Spec columns. It was also found that the Re spec column procedure was not efficient, as almost half of the Nd was already lost through the first stage of columns. Additionally, the clean up column was not effectively tested and a more appropriate test should be applied to that procedure. The clean up column resulted in almost a complete loss of Nd, however, this step is just intended to rid a sample of any cations (Fe, Ca, Mn, Mg) that might interfere in Nd processing. Running a spiked Nd standard through this column did not provide any useful information.

Tables 2 and 3 show the individual and average yields, respectively, for each test. Using the Tru Spec column as opposed to the Re Spec column is far more efficient in processing Nd. About 86% of Nd was collected from the Tru Spec column, whereas only about 52% was collected from the Re Spec column. In the nine standards that were run through Re Spec before Ln Spec, only about 17% of the Nd that was collected from the Re Spec column got through the Ln Spec column as well. Figure 3 shows the steps that were run through each progression of columns, along with the percent of Nd that made it through each step. For example, of the 52.1% that was collected through Re spec, only 17.7% of that 52.1% of Nd from the original spiked standard made it through the Ln Spec columns. The percent yield of Nd through the Tru Spec columns was much greater and seems to be a more effective recipe for extracting the REE's from a sample. Although two of the Tru spec – Ln spec standards yielded a low percentage similar to those of the Re spec – Ln spec progression, the Tru spec columns had much higher

yields by themselves (83.5%, 91.8%, 81.1%, per Table 2). Additionally, the total yields of the Tru spec – Ln spec were also much higher than the RE spec – Ln spec (31.35% compared to 9.22% total yield, per Figure 4).

6. CONCLUSIONS FROM METHODS TESTS

It is necessary to test lab procedures more frequently and maintain efficient methods in order to confidently and successfully run samples for Nd. We reiterate that poor yields should not impact the isotopic data generated from column chemistry, however poor yields make it impossible to analyze samples with low concentrations of Nd. Running yield tests on column chemistry methods is therefore an important step to add to general lab procedures in order to determine when it may be necessary to rebuild or recalibrate columns. RE spec and Tru spec column chemistry stages are similar, however, Tru spec proves to be a more efficient means of isolating the REEs to process through Ln with the ultimate goal of collecting Nd splits. Running samples through Tru Spec and rebuilt and calibrated Ln spec columns provides the best chance for efficient and successful sample runs.

7. RECONSTRUCTION OF OCEAN CIRCULATION OVER THE MECO

7.1 The Mid-Eocene Climatic Optimum (MECO)

As the Earth's climate warms, concerns about how the Earth system will respond continued to increases. There have been significant, rapid climate change events in Earth's geologic history that provide an opportunity to study how the Earth can be affected by such events. One such rapid climate event ~40.6 Ma, the Mid-Eocene Climatic Optimum (MECO), is characterized by a ~4 to 6°C increase in surface and deepwater temperatures over the course of ~500 kyr. It was first recognized by a ~ -1‰ oxygen isotope excursion recorded in foraminifera in the southern ocean (Bohaty et al., 2003). The MECO is distinct from other upper Paleocene-lower Eocene hyperthermals by three main features: 1) the ~4-6°C warming that occurred at the MECO was gradual and short lived relative to the much more rapid cooling that followed, while other hyperthermals from the upper Paleocene-lower Eocene had more symmetrical warming and cooling periods. 2) There was no carbon isotope excursion at the MECO concurrent with warming, as seen in other hyperthermals. 3) The MECO took place during an eccentricity minimum, while the other hyperthermals occurred during eccentricity maxima. These differences between the MECO and the other hyperthermals suggest that the MECO has a unique causal mechanism. The early to middle Eocene (49—39 Ma) is recognized as an interval of general climate cooling after peak Eocene warmth ~50 Ma, however the MECO interrupted this cooling trend (Figure 5). After the MECO, the cooling trend continued through the E-O boundary, where the climate transitions from greenhouse to icehouse conditions (Lyle et al. 2008).

Here we investigate the potential role of oceanic overturning circulation during the MECO. In the modern ocean, meridional overturning circulation is responsible for transporting heat towards the poles and contributes to the global heat balance. Due to the ocean's role in the redistribution of heat, changes in drivers of ocean circulation are a potential mechanism for paleoceanographic events. The lack of a carbon isotope excursion makes investigating the ocean circulation around the MECO a pertinent next step in understanding the mechanism of the hyperthermal. As there is no obvious mechanism, we are investigating the possibility that an ocean circulation change is the driving force.

7.2 Paleoceanographic Reconstruction Across the MECO

The data presented was collected from analysis of fish debris picked from Site 464. Site 464 is located at 39°51.64'N, 173°53.33'E at a water depth of 4637m. Deep Sea Drilling Project Site 464 was drilled in the central North Pacific, recovering a sediment core from the northern part of the Hess Rise. This Site is composed primarily of clay minerals and is divided into four lithologic units: Clayey radiolarians, siliceous ooze and siliceous clay; Pelagic brown clay; Red-brown chert; and Basalt. The interval of interest for this study (~43 Ma to ~ 38 Ma) is in the pelagic brown clay lithology (DSDP Initial Reports Volume LXII, Ch. 3). This section, however, lacks biostratigraphic age control. Three age datums have previously been identified to constrain the ages on samples from this site: the basement age (75.00 Ma, 89.00 mbsf), an intermediate point based on the most precisely identified icthyolith age available (55.80 Ma, 50.00 mbsf), and the last occurrence (LO) of *S. pentas* (2.8 Ma, 32.0 mbsf)

(Hague et al., 2012). A constant sedimentation rate of 0.38 m/my is assumed between 9.05 Ma and 55.96 Ma, and 2.04 m/my between 55.96 Ma and 75.00 Ma based upon ichtyolith ages (Doyle and Riedel, 1981).

7.3 Analytical Methods

We sampled the sedimentary interval recovered at the Pacific Ocean drill core DSDP) Site 464 across the MECO (~43 Ma to ~38 Ma) from the International Ocean Discovery Program (IODP) Gulf Coast Core Repository located on the campus of Texas A&M University. We collected 5 cc bulk sediment samples every ~10 – 50 cm of Core 6-1 to Core 6-3 in order to capture the interval leading up to, and through the MECO.

We prepared each sample by separating the Nd fraction from the fish debris that was collected from the bulk sediment. To isolate fish debris from the bulk sediment, we disaggregated samples collected from IODP in distilled water with ~2% sodium metaphosphate water-calgon mixture in order to saturate, wash and break up the sediments. After disaggregation, samples were washed over a 63μm sieve to isolate the coarse fraction. The remaining fraction of sample includes fish debris, foraminifera and other fossilized planktonic fragments and was dried to pick fish debris. About 10 to 30 fragments of fish debris were handpicked from each sample and transferred to a 0.75ml micro-centrifuge tube. The fish debris was washed four times in ultrapure water, siphoning off the milli-Q and replacing it with clean milli-Q each time. After cleaning, we dissolved the fish debris in 2N HNO_3 in preparation for the two-stage column chemistry. The dissolved fish debris samples are then run through RE spec. We dried and then redissolved the REE split in 0.18N HCl to be run through Ln spec. The Nd split

from each sample was then loaded onto Rhenium filaments to be analyzed on the TIMS.

Figure 6 outlines the sample prep and progression from the bulk sediment stage to the

sample being analyzed in the TIMS.

8. RESULTS AND DISCUSSION OF PALEOCEANOGRAPHIC DATA ACROSS THE MECO

Site 464 seawater ^{143}Nd/^{144}Nd values decreased from -4.2 to -5.7 over the approximate interval ~42.4 to ~41.6 Ma (Figure 7). The values then increased back to -4.2 through the MECO and entered a period of oscillating values, decreasing from -4.4 at 41.1 Ma to -4.9 at ~40.1 Ma, then increasing to -3.4 at ~40.3 Ma, and finally decreasing again to -4.7 at ~40.1 Ma after the MECO. Given the uncertainty in the age model, it should be noted that the observed shift in Nd may not occur concurrently with the MECO.

At this stage in our analysis there appears to be a gradual, shift in ε_{Nd} towards a less radiogenic signal followed by an abrupt return to pre-event values over the MECO (Figure 6). Between ocean basins, a 2 ε_{Nd} shift seems to be the lowest magnitude change in ε_{Nd} that is interpreted as a change in ocean circulation (Scher and Martin, 2008, Thomas et al., 2014). The 1 ε_{Nd} shift observed in the data may not be globally significant, but we are interpreting the data in the context of a Pacific Ocean where water mass composition generally ranges from -6 to -2 ε_{Nd} values throughout our 70 million year record of the Pacific. Therefore the shift is likely significant. Our data is consistent with the observations regarding the length of onset and termination from previous studies (Bohaty et al., 2003). This negative shift in the ε_{Nd} values, which coincides with a rapid increase in temperature (-1‰ shift in δ^{18}O and aforementioned no change in δ^{13}C), could suggest a stronger water mass intrusion from the south, as this negative shift shows a water mass signature more similar to that of the Southern Ocean. The negative

shift could also indicate an increase in eolian and riverine weathering, or ash deposition to the surface ventilated source water to the Pacific (Goldstein and Hemming, 2003). These potential sources could come from either the Asian continent (ε_{Nd} values range from -9.6 to -12.6) or from the West Coast of the United States (ε_{Nd} values range from -5.5 to -6.5) (Jones, 1994). However, the error on the data point suggesting the shift is large (2.0×10^{-5} compared to $\sim 4.5 \times 10^{-6}$ on average) and a higher resolution suite of samples must be analyzed at this interval in order to draw stronger conclusions as to the cause and or source of the shift.

9. SUMMARY

The MECO marked a period of warming during an otherwise cooling climate and provides information for how ocean circulation may drive or respond to rapid changes in global temperature. Although the data generated thus far is not ideal, including an age model that is not robust, it is evident that either ocean circulation patterns shift or a change of weathering source occurs in association with an abrupt temperature change. Utilizing the more focused and accurate methods adjustments detailed here can provide a more clear answer to the exact type and magnitude of a temperature-driven shift in ocean circulation. The warming event causing a major change in the Pacific ocean circulation could have major implications for understanding how the modern Pacific will respond to increasing ocean temperatures.

With the improvements in our methods, we can begin investigating the MECO with a more robust dataset. We would like to combine a higher resolution set of samples to capture the ε_{Nd} signature in more detail. This would include 1) replicating our existing samples, most notably, samples through the excursion at ~41.5 Ma, 2) analyzing samples over the MECO at several sites in a North-South Pacific transect, and 3) analyzing samples at sites with more robust age models because the age model at Site 464 is not well constrained, so it is possible that the ε_{Nd} excursion observed in this study precedes the MECO.

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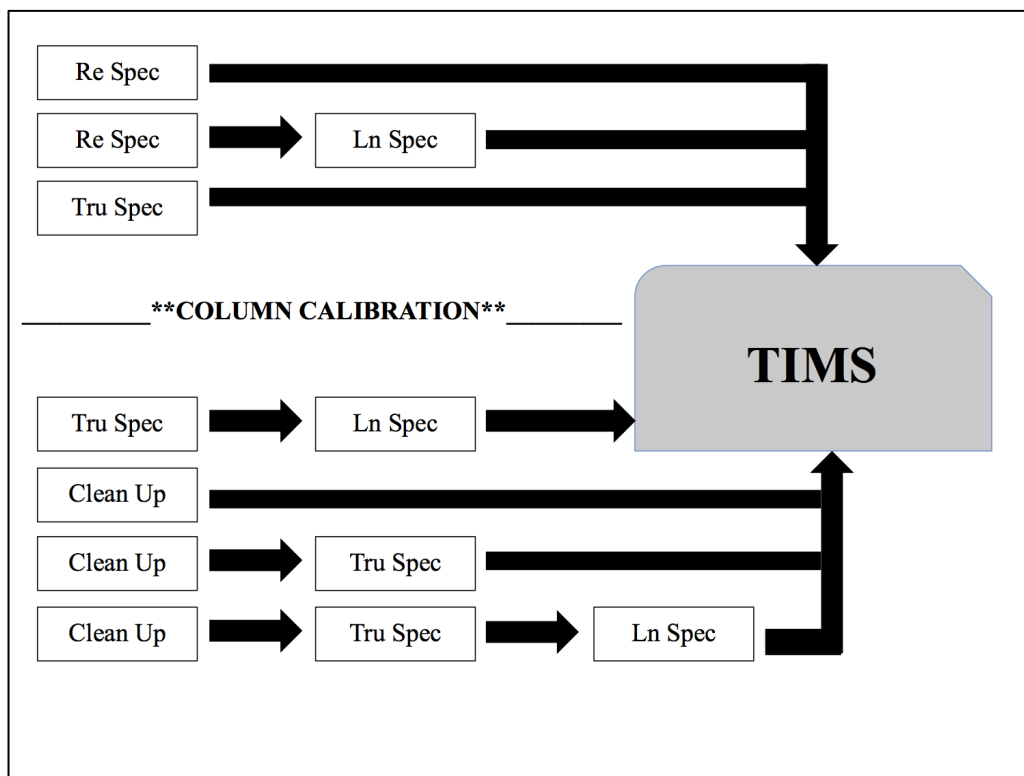
Figure 1. The progression of columns tests. The column calibration was done on the Ln spec columns and the second series of tests (bottom half of the diagram) were done after the column calibration.
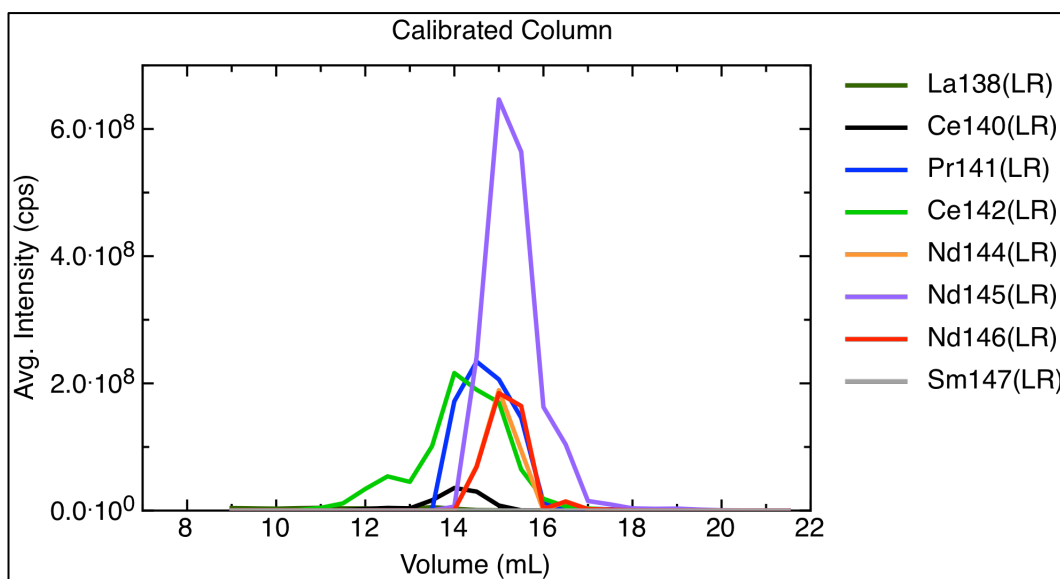
Figure 2. Calibration curve showing the separation of each isotope as more volume of acid dripped through the column. The collection for Nd is optimized as Nd counts are increasing while Pr are decreasing, all prior to Sm counts begin to increase.
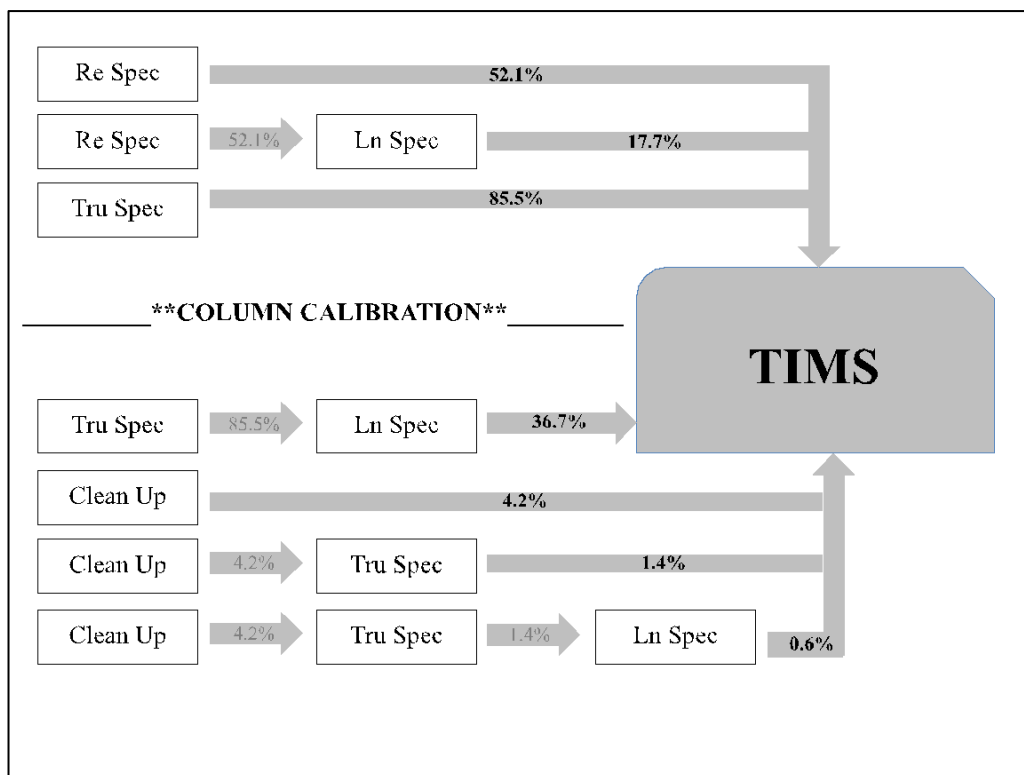
Figure 3. Shows the yields through each step of column chemistry. Note that the percent that is shown to the TIMS is the part of the percent that made it through the previous column. For example, in the case before the column calibrations, of the 52.1% of Nd that made it through Re Spec, 17.7% of that was the fraction analyzed on the TIMS.
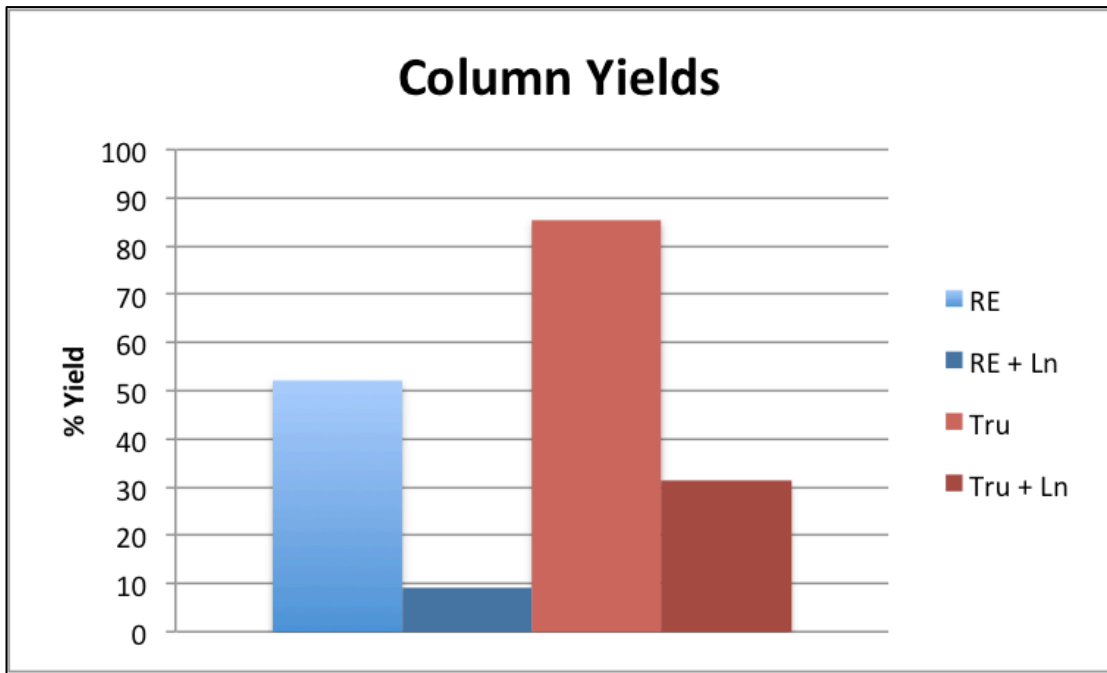
Figure 4. Shows the total yields of RE Spec, RE Spec + Ln Spec, Tru Spec, and Tru Spec + Ln Spec. The total yield through RE Spec + Ln Spec is 9.22% and the total yield through Tru Spec + Ln Spec is 31.35%.
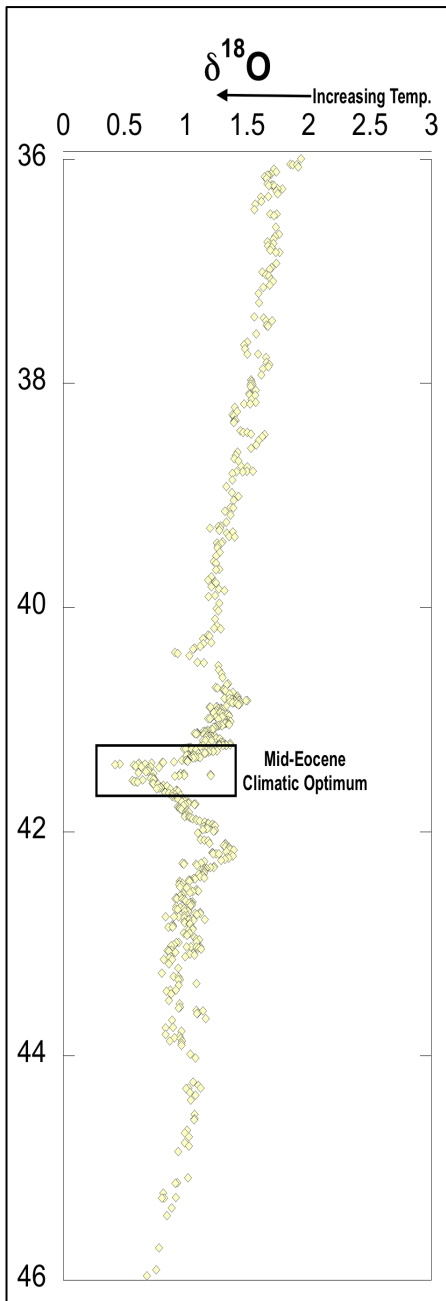
Figure 5. δ^{18}O isotope record from 46 Ma to 36 Ma plotted with data presented in Zachos, 2008. The box is highlighting the excursion at the Mid Eocene Climatic Optimum (MECO).

Figure 6. The step-by-step progression from bulk sediment through sample prep and chemistry to the TIMS. Bulk sediment is washed through a 63μm sieve and dried. Fish debris is picked from the coarse (>63μm) fraction and dissolved in 2N HNO_3 and run through the first round of chemistry (Re or Tru spec). It is dried down and redissolved in 0.18N HCl and run through the second round of chemistry (Ln Spec). It is dried down and loaded onto a Rhenium filament using 2N HCl as a mechanism for transferring the dry sample onto the filament. It is dried onto the filament once loaded. Filaments are loaded onto the turret from and run in the TIMS.

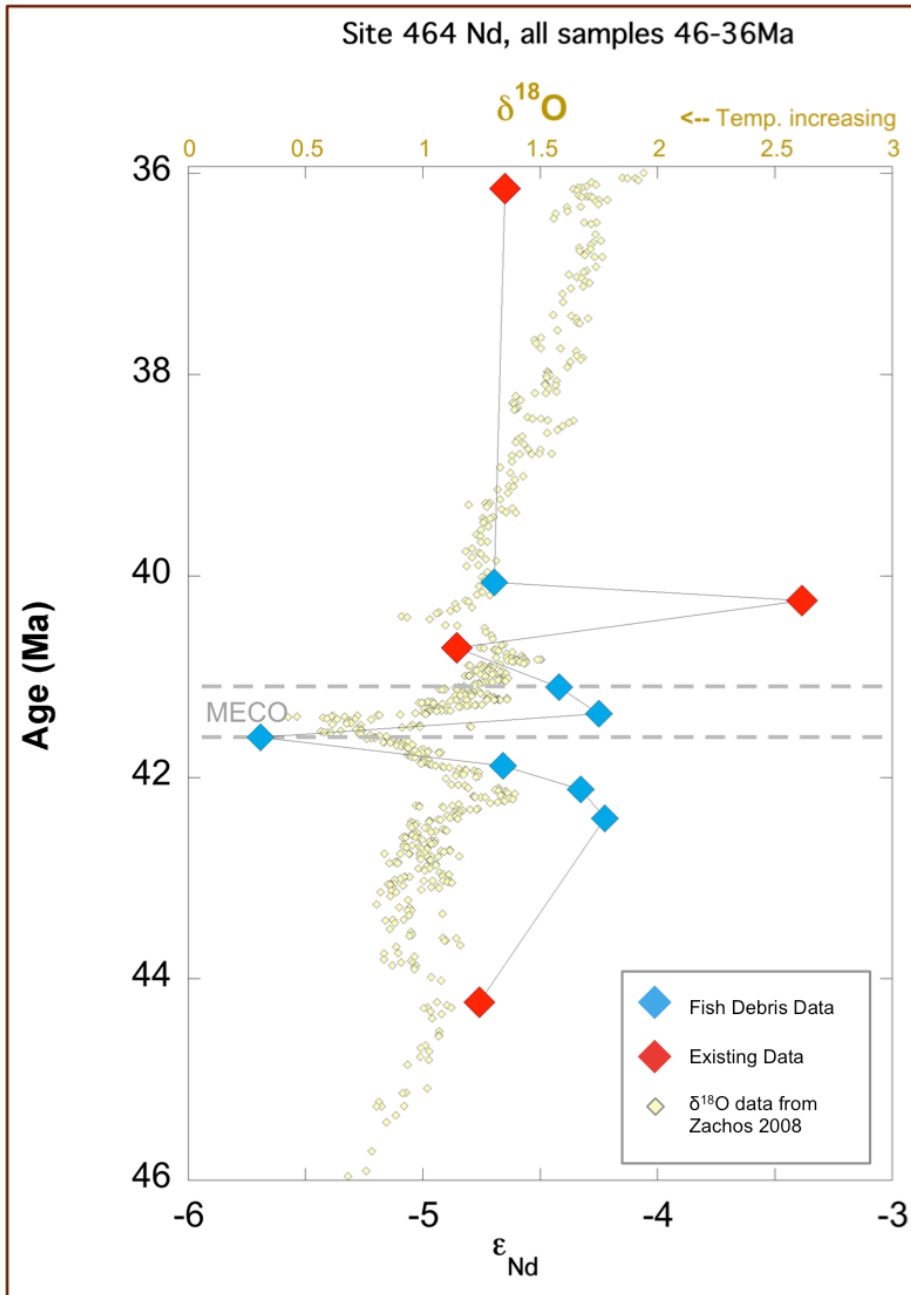**Figure 7.** Fish debris data recorded at Site 464, superimposed on Zachos 2008 $\delta^{18}O$ record across the MECO. Red points are previous ϵ_{Nd} data. Blue points are new fish debris data. The excursion at ~41.5 Ma falls just before the temperature spike shown in the $\delta^{18}O$ record.

APPENDIX B

TABLES

Standards	Number	$^{150}Nd/^{144}Nd$	
Unspiked	1	0.236452	
	2	0.236439	
	3	0.236446	
	Number	$^{150}Nd/^{144}Nd$	^{144}Nd micromols
Spiked	1	1.68	8.55E-04
	2	1.74	8.21E-04
	3	1.51	9.70E-04

Table 1. The $^{150}Nd/^{144}Nd$ ratios from both the unspiked and spiked standards used as a baseline in the methods tests. The ^{144}Nd micromoles were used to calculate the Nd yield through each column.

Chemistry Tests (Before Column Calibrations)	Number	^{150}Nd/^{144}Nd	% Yield
Re Spec Only	1	3.08	48.9%
	2	2.72	56.1%
	3	2.66	57.5%
	4	3.25	46.1%
	Number	**^{150}Nd/^{144}Nd**	**% Yield**
Re Spec + Ln Spec	1	9.99	13.7%
	2	19.00	6.8%
	3	6.55	21.6%
	4	4.60	31.6%
	5	9.04	15.3%
	6	10.30	13.3%
	7	8.60	16.1%
	8	8.17	17.1%
	9	6.04	23.6%
	Number	**^{150}Nd/^{144}Nd**	**% Yield**
Tru Spec Only	1	1.91	83.5%
	2	1.76	91.8%
	3	1.96	81.1%

COLUMN CALIBRATION

Chemistry Tests (After Column Calibrations)	Number	^{150}Nd/^{144}Nd	% Yield
Tru Spec + Ln Spec	1	2.58	59.4%
	2	5.9	24.2%
	3	3.07	49.0%
	4	9.83	14.0%
	Number	**^{150}Nd/^{144}Nd**	**% Yield**
Clean up Only	1	55.5	1.8%
	2	19.9	6.5%
	Number	**^{150}Nd/^{144}Nd**	**% Yield**
Clean up + Tru Spec	1	107	0.6%
	2	106	0.6%
	Number	**^{150}Nd/^{144}Nd**	**% Yield**
Clean up + Tru Spec + Ln Spec	1	72.2	1.3%
	2	65.2	1.5%

Table 2. The ratios and percent yields of each of the sample runs.

Standards	$^{150}Nd/^{144}Nd$	% Yield
Unspiked	0.236446	-
Spiked	1.64	100%

Chemistry Tests (Before Column Calibrations)	$^{150}Nd/^{144}Nd$	% Yield
Re Spec Only	2.93	52.1%
Re Spec + Ln Spec	9.14	17.7%
Tru Spec Only	1.88	85.5%

COLUMN CALIBRATION

Chemistry Tests (After Column Calibrations)	$^{150}Nd/^{144}Nd$	% Yield
Tru Spec + Ln Spec	5.345	36.7%
Clean up Only	37.7	4.2%
Clean up + Tru Spec	106.5	0.6%
Clean up + Tru Spec + Ln Spec	68.7	1.4%

Table 3. Average ratios and percent yields through each series of columns.

APPENDIX C

COLUMN CALIBRATION PROCEDURES

The purpose of this appendix is to document the procedures for Ln-Spec column creation and calibration.

When to calibrate and or re-build your columns:
The timing of re-building columns and re-calibrating is a balance between producing the best yields and the time it takes to do the calibration. We recommend doing yield tests and re-building every 40 uses. The number one most important variable impacting the amount of acid you need is the acid concentration. Thus, you must recalibrate between re-building the columns if you have to mix more acid. In general there are several reasons to calibrate your columns including:
> i. Every time you mix new acid that is used in the column procedure
> ii. When you re-build the columns.
> iii. If you are noticing yield issues in your runs (i.e., samples having consistently low beams, or not having a beam at all) first test the yield on your columns. Some yield issues could be due to low concentrations in the sample, or problems with loading, which is why you would only yield test and then re-calibrate if you have consistent low yield issues.

How to build Ln-Spec columns:
1. Fill reservoir of column half full of MQ water, let drain through check for resin leaks. If leaky replace the frit.
2. Wash out the resin that is currently in the column (be careful not to pop the frit out while doing this!).
3. Rinse column 1x with 6N HCl
4. Rinse 3x with MQ water
5. Measure the length of of the column from base of the reservoir place the frit at 9cm from the base of the reservoir and mark that location with a teflon pen.
6. Visually inspect the frit placement to make sure that it is level and completely filling the column. (If it is not well placed resin will leak out).
7. Attach a piece of tubing to the end of a 1mL pipette tip.
8. Do a final rinse of MQ and begin adding resin (Step 9) before all of the water drips out of the column.
9. Bring up a slurry of resin and MQ into the tubing.
10. Gently lower the tubing into the column to just above the frit (or previous resin level) and expel the resin/MQ mix into the column pulling the tube up (above the level of the resin) as you slowly press the pipette plunger. Hold column over clean beaker and be careful not to punch out the frit during this process.

11. Let the resin settle while you repeat this procedure with each column in turn.
12. Repeat steps 9 through 11 until each column has 9cm of resin in them (from the frit to the base of the reservoir).
13. Inspect for bubbles, carefully using your tubing to remove them as needed.
14. Run MQ water through the column to determine that they are running properly and have no resin leaks. Note: Settling will occur so you will need to top off the column until settling ceases and it is full.

How to re-suspend a column that has bubbles in it:
Bubbles, or a separation of the resin from the wall of the column appear in columns either because they have dried out, or if they sit for a long period of time. In order to fix this problem you must resuspend the resin and let it settle again.

1. Attach a piece of tubing to the end of a 1mL pipette tip.
2. Add 1-3mL of MQ to the column in order to make a slurry of resin and MQ.
3. Slowly bring up resin and MQ slurry into tube, pushing the tube progressively deeper into the column as you go. You may move the frit during this process, be careful not to punch out the frit and be mindful of maintaining the 9cm length.
4. Expel the resin slurry into the reservoir of the column.
5. Repeat steps 3 and 4 until all resin has been pulled out of the column neck.
6. Bring up a slurry of resin and MQ into the tubing.
7. Gently lower the tubing into the column to just above the frit and load the resin back in, resin from the reservoir will also settle during this process.
8. Let settle, topping off with resin as needed.
9. Inspect for bubbles, if any exist carefully remove them with your tubing.
10. Condition column as usual

How to perform a "yield test" on columns:
1. Using the JNdi-1, 300ng standard in place of your sample for each column that you are testing follow the TRU-Spec column procedure
2. Follow the Ln-Spec procedure including final dry down and resuspension for TIMS
3. Spike sample with 0.01g of concentrated ^{150}Nd (weigh beaker with sample before and after spiking, record weights).
4. Follow filament loading procedure
5. Run sample(s) on TIMS

6. Calculate yield using the following equation:

^{144}Ndsample (micromoles) = ((Rm*(Spk*Conc)/199.67)-(Spk*Conc))/(0.2364-Rm)

Where:

Rm = measured ^{150}Nd/^{144}Nd ratio

Conc = ^{150}Nd concentration in spike (micromoles /g) = 0.124491 in TAMU Conc ^{150}Nd spike

Spk = spike weight in grams

^{150}Nd/^{144}Ndspk = 199.67

^{150}Nd/^{144}Ndsamp = 0.2364

This will give you micromoles ^{144}Nd in the JNdi that came through columns. If you also calculate (or know) ^{144}Nd micromoles you put into the column, then the yield is just the percent that made it through.

How to calibrate your columns:

Day one:

1. Evaluate if the columns need to be rebuilt, or resuspended. If they have been used almost 40 times, consider replacing the Ln-Spec resin. If there are any visible bubbles re-suspend them and let them settle before proceeding.

Day two:

2. Condition your columns following the column conditioning procedure.

3. Mix or obtain a column calibration solution with known quantities of known isotopes of Pr, Nd, and Sm.

4. Pipette 0.1 mL calibration solution and 0.1 mL 0.18M HCl per column into a clean teflon beaker. For example if you are going to calibrate all 12 columns you would need 1.2mL of 0.18M HCl and 1.2mL of calibration solution in order to mix the 2.4mL you need. You may consider diluting an extra columns worth in case of accidents.

5. Set up a series of columns for calibration, the more you calibrate the better your calibration will be.

6. Follow the column procedure as it stands to the "load sample" step.

7. Load 0.2 mL of the dilute column calibration solution onto each column

8. Wash 3x with 0.1 mL 0.18M HCl as per the regular Ln-Spec column procedure.

9. Wash ~5* mL 0.18M HCl

10. Pipette and collect in disposable scintillation vials the next ~4* mL of 0.18M HCl "Wash" in 1mL increments.

11. Pipette and collect in disposable scintillation vials the next ~4* mL of 0.18M HCl "Wash" in 0.5mL increments.

12. Pipette and collect in disposable scintillation vials the next ~4* mL of 0.3M HCl "Wash" in 0.5mL increments.

13. Clean and put away the columns following the usual column procedure (Clean with 6N HCl, condition with 0.18M HCl)

*NOTE: The amounts of acids and increment splits listed above are a very general guidelines for the calibration procedure. At the time of writing (1/22/16) our calibration is employing 13mL of 0.18M HCl wash, and 4 mL of 0.3M HCl to collect. If you are calibrating columns simply because you have made a new batch of acid this may be sufficient. However, if you are troubleshooting a problem with yields you may wish to do some or all of the following:

    i. Decrease the amount of 0.18M HCl you wash without collecting in Step 10.
    ii. Decrease the number of 1mL 0.18M HCl steps you collect before transitioning to 0.5 mL increments in Step 12.
    iii. Do not transition from 0.18M HCl to 0.3M HCL in step 12. The intention behind using 0.3M is that it will make the collection process go more quickly. We selected the 13mL of 0.18M HCl wash based on doing a calibration with 0.18M HCl, only instead of doing 4 mL 0.3M HCl collect we used 8mL of 0.18M HCl.
    iv. Extend the calibration out past the total of 17mL that we outline above. You may not be capturing the transition between the Nd and Sm, so you could push the limit on the amount of acid you put through.

Day three (doesn't have to be consecutive to Days 1 and 2):
14. Make a set of 1mL "calibration curve" solutions with 0%, 25%, 50%, 75%, and 100% concentrations with the % indicating the amount of calibration solution in the solution (i.e., 0% = 0mL calibration solution, 1mL 0.18M HCl, 25% = 0.25mL calibration solution, 0.75 mL 0.18M HCl, etc…)
15. Run samples and "calibration curve solutions" on HR-ICP-MS
16. Make sure you are using the method created for column calibrations or are analyzing the isotopes of each element that is included in the calibration solution.
17. Compile all run files into one single file with all the data.
18. For each column plot all isotope data on a single diagram with step # (or mL value equivalent) on the x-axis and average intensity on the y-axis.
19. Determine where the majority of the Nd is coming out of your column, make a pick for wash length based on the the decrease in Pr and simultaneous increase in Nd.