THE EFFECTS OF VOLCANIC ASH ON DISSOLVED NEODYMIUM AS A WATER MASS TRACER

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by

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ABSTRACT

The Effects of Volcanic Ash on Dissolved Neodymium as a Water Mass Tracer

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Dissolved Neodymium (Nd) in the ocean is often used as a water mass tracer to reconstruct what the oceanic circulation in a certain area may have looked like in the past (van de Flierdt et al. 2012). The incorporated Nd in fish debris, specifically teeth, generally retains a sound record of deep seawater (Martin and Scher 2003). However, continental input may alter or add to the dissolved Nd, which further leads to Nd isotopic compositions that reflect sediment input and not ocean circulation (van de Flierdt et al. 2012). Additionally, dispersed volcanic ash in the ocean affects the isotopic composition of pore water and the pore water Nd is incorporated into fish debris (Abbott et al. 2015). By understanding how volcanic ash input affects the dissolved Nd isotopic signal we can further elucidate how to successfully determine oceanic circulation changes over time in the North Pacific. Understanding the paleo-ocean circulation, and the factors and processes that drive and affect it, is necessary to understand the current state of the ocean, as well as how it may change in the future. This requires a comprehensive understanding of the components may alter the dissolved isotopic Nd signal, such as volcanic ash. Here we compare the Nd isotopic composition of fish debris with the isotopic composition

across three leached sediment phases of the same site to establish an understanding of how volcanic ash input affects the Nd in fish debris, as well as the Nd isotopic composition in the North Pacific over time. It is necessary to understand and be able to account for the effect of volcanic ash input when using dissolved Nd as a water mass tracer in order to get an accurate representation of the paleo-ocean circulation in the North Pacific over time.

My research focuses on sediment dating back to the Cretaceous period (125-180 Ma) using samples collected from Ocean Drilling Program (ODP) Site 1149 in the North Pacific.

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NOMENCLATURE

Nd	Neodymium
ODP	Ocean Drilling Program
Ma	Million years ago
Fe-Mn	Ferromanganese
εNd	Nd isotopic composition of seawater

INTRODUCTION

The study of marine sediment has well been underway for hundreds of years. Scientists have successfully identified and quantified many components that make up marine sediment. However, many questions remain. Neodymium in the water column has been of great interest to the scientific community for many years. From the comparisons of the Nd isotopic composition of rocks on land, the first direct measurement of isotopic Nd in the ocean, along with indirect measurements of isotopic Nd in fish debris, ferromanganese (Fe-Mn) crusts and manganese nodules, it was apparent that the Nd isotopic ratio in the ocean is closely related to that of the surrounding continents. With these measurements we are able to determine how the ocean currents have changed over time. However, according to Van de Flierdt et al. 2012, there is a lack of knowledge on the sources, sinks, and internal cycling of Nd in the ocean. This has been mainly attributed to the poor number of observations of Nd in the ocean (Van de Flierdt et al. 2012). Furthermore, these observations are densely located in the North Atlantic and North Pacific oceans instead of spread out over the globe (Van de Flierdt et al. 2012). It is important to improve this situation to further expand our knowledge of the ocean, its trace metal composition and circulation.

Quantification of dispersed volcanic ash in marine sediment has long been a challenge for marine scientists. Dispersed ash is characterized as volcanic ash material of various grain sizes combined throughout bulk sediment (Scudder et al. 2016). Perhaps due to its dauntingly fine grain size, dispersed volcanic ash has largely been overlooked, or lumped together with detrital terrigenous clay (non-ash, derived from land). In this paper, I present new Nd isotope data from

fish debris for comparison to leached sediment from ODP Site 1149 to quantify the relationship between isotopic Nd and volcanic ash.

CHAPTER I

OVERVIEW OF ODP SITE 1149

ODP Site 1149 is located in the northwestern Pacific, east of the Izu-Bonin Arc (Figure 1). Four holes were drilled in this area with a total core recovery of 250 meters (m). The age of the core dates back to 125 to 180 Ma, representing the Cretaceous period. The water depth at this site is 5817.6 m. The sediment in this area is rich in volcanic ash and diatoms near the top and siliceous nanofossils near the bottom, with radiolarian chert throughout the core.

This site was drilled on ODP Leg 185 as a reference point for the Cretaceous crust. The main goal of this expedition was analyze the sediments that will be subducted into the Izu-Bonin-Mariana Arc (Plank et al. 2000; Scudder et al. 2016). Understanding the geochemical budgets requires an understanding the origin of the different sediment components that make up the sediment column. For this particular site, quantifying the terrigenous sediment and ash input via the subduction plate is essential to determining the amount of "recycled" input from the arc was present (Scudder et al. 2016). This particular project has led us to understand and become interested in the dispersed ash found in this core. It has been determined that 33 ± 9 wt.% of the sediment in this core is composed of dispersed ash (Scudder et al. 2016). Findings suggest that the dominant source of the high amounts of dispersed ash found in this core originates from Honshu Rhyolite, despite the distance (Scudder et al. 2016).

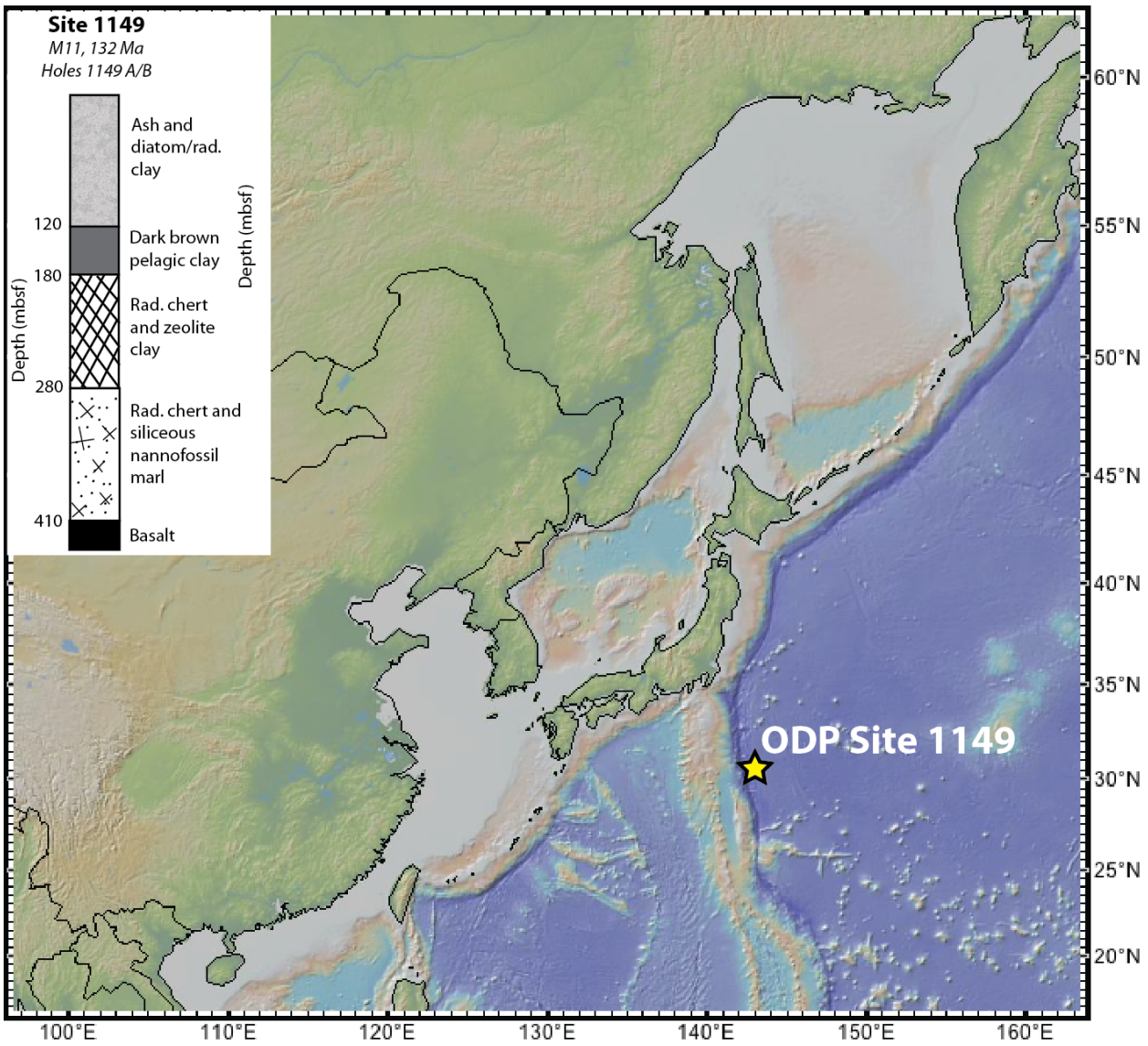

Figure 1. Location and stratigraphy of ODP Site 1149.

CHAPTER II

METHODS

Nd Isotopes used as a water mass tracer

Nd isotopic compositions in seawater can be used as a water mass tracer to determine paleo-ocean circulation. Nd has seven naturally occurring isotopes, but only two isotopes are interpreted in this study. The isotopes of interest are ^{143}Nd, a radiogenic isotope produced by the decay of ^{147}Sm, and ^{144}Nd, a stable (meaning no other isotopes decay to it, nor will it decay) isotope. The $^{143}Nd/^{144}Nd$ ratio acts as a fingerprint, for rocks, indicating age and lithology (van de Flierdt et al. 2016). The difference in ratios is generally expressed as deviations in parts per ten thousand from the chondritic uniform reservoir (CHUR) ($\varepsilon Nd = ([^{143}Nd/^{144}Nd]_0/[^{143}Nd/^{144}Nd]_{CHUR(t)}-1) \times 10^4$) (DePaolo and Wasserburg, 1976). According to this model, low $^{143}Nd/^{144}Nd$ values result in negative εNd values, which indicate origin from older, crustal rock. High $^{143}Nd/^{144}Nd$ values result in negative εNd values, which indicate origin from younger, mantle-derived rock (DePaolo and Wasserburg, 1976).

While it was previously thought that isotopic Nd in the ocean was primarily a result of atmospheric dust and riverine input, recently it has been established that sediment and seawater interactions along continental margins, or, simply put, 'boundary exchange' (van de Flierdt et al. 2016). Trace metal fluxes moving from pore water (Abbott et al., 2015) also control the isotopic Nd found in the ocean.

Sequential leaching

Sequential leaching was conducted prior to my contribution to this project. The purpose of this procedure is to separate the desired portion of the sediment in different phases. In this case, the sediment underwent three phases of leaching. The data used for comparison with the fish debris is from the first phase (L1) and the third, detrital phase (DET). Sediment samples from ODP Site 1149 were powdered and weighed in preparation for the leaching protocol. The samples were then leached in an acid-reductive solution of hydroxylamine hydrochloride for one hour in order to remove the authigenic Fe-Mn oxide coating from the sediment (Wilson, 2013). The liquid (supernaut) was centrifuged and collected to be dissolved for analysis. The sediment was then leached in the same acid-reductive solution of hydroxylamine hydrochloride for 12 hours in order to remove the rest of the components associated with oxide coatings. The remaining residue following the first two phases of leaching is considered the detrital component of the sediment (Wilson, 2013).

Column chemistry

Samples for this project were taken from ODP Site 1149, which is currently stored in the International Ocean Discovery's Gulf Coast Repository at Texas A&M University. Fish debris were handpicked from sediment samples that had been washed through a 63μm sieve to separate the fish debris and coarse sediment. The samples were then dried in preparation for picking fish debris. Three of these samples were rich in volcanic ash, which resulted in a lack of fish debris. Four samples did not provide enough fish debris in the first round of washing, but will potentially supply enough fish debris to be analyzed after washing and sieving more sediment. Three samples contained enough fish debris (about 10 – 12) for isotopic Nd analysis. Once

picked, the fish debris were dissolved in 2N acid in preparation for two separate column separation procedures.

In order to chemically separate the Nd in the samples, column chemistry was preformed in order to minimize any type of elemental interference during analysis (van de Flierdt et al. 2012). This was accomplished using two column separation processes: TRU Spec, followed by Ln Spec resins. These ion exchange resins use HNO_3 followed by HCl. The first column procedure employed TRU Spec columns to separate the bulk rare earth element concentration (REE) from the sample matrix (van de Flierdt et al. 2012). The second procedure employed Ln Spec columns to separate the Nd from the other REEs (van de Flierdt et al. 2012). Finally, the Thermo Triton Thermal Ionization Mass Spectrometer (TIMS) in the R. Ken Williams ’45 Radiogenic Isotope Geosciences Laboratory at Texas A&M University was used to measure the Nd isotopes.

CHAPTER III

RESULTS

The first set of data is comparing εNd(t) of leached sediment (L1 and DET) and fish debris with age. At this point, three fish debris samples have been run through column chemistry and TIMS. The results thus far show that εNd from fish debris and εNd from leached sediment compare well with each other, showing the same trends. Of the three fish debris analyzed, age 36.78 shows fish tooth value of -5.53, where age 39.01 shows an L1 value of -5.49, and a DET value of -5.49. Age 22.29 shows a fish tooth value of -3.59, where age 17.43 shows an L1 value of -3.93, and a DET value of -3.93. Finally, age 5.19 shoes a fish tooth value of -3.69, where age 4.33 shows an L1 value of -2.40, and a DET value of -2.40. The oldest data point indicates an εNd(t) value about -5 trending towards 0 until about 2 Ma. Around 2 Ma, the data points begin trending towards increasingly negative εNd(t) values until Age 0.

The second set of data is showing the average Nd concentration in parts per million (ppm) with time. The results suggest little variation in Nd concentration through time, ranging from about 8 to just above 20 ppm with one outlier at just above 55 ppm.

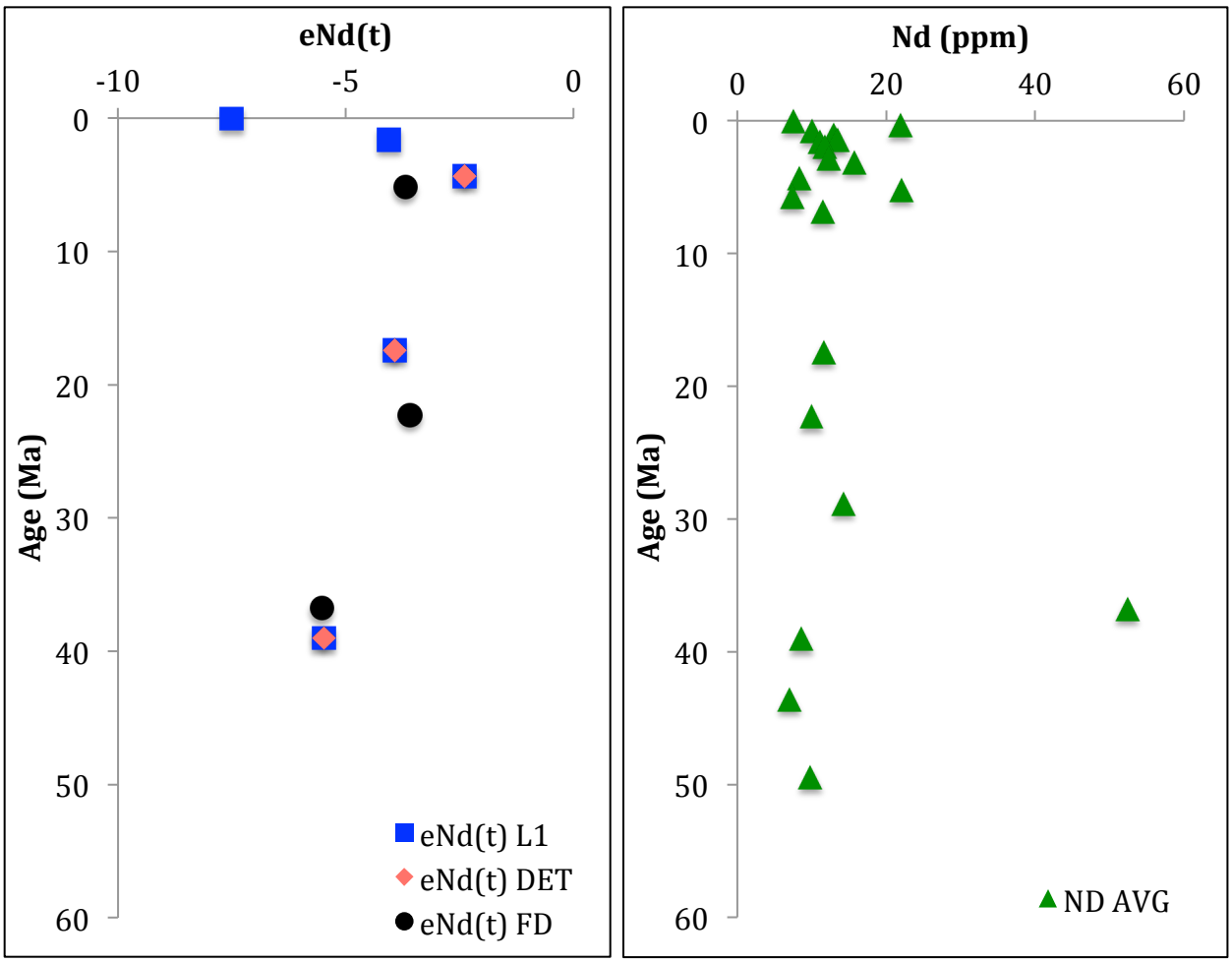

Figure 2. εNd(t) and Nd isotopic ratios with age.

CHAPTER IV

CONCLUSIONS

Comparison of Nd from leached sediment with Nd from fish debris

The results presented in Figure 2 indicate that εNd(t) L1 and εNd(t) DET show the same values. This may indicate that the volcanic ash highly reactive, dissolving with the Fe-Mn oxide coatings in the first leaching phase. Moreover, the since the εNd from fish debris also match up with the leached sediment it is also possible that the fish debris is reflecting volcanic ash input as well. Figure 2 also indicates that the average Nd concentration in sediment through time has only varied slightly through time, fluctuating around 10 to 20 ppm. However, there is one data point that indicates an average Nd concentration of about 50 ppm at 36.78 Ma. This point comes from a section of the core composed of dark brown pelagic clay, not on any boundary. This strikingly high value could potentially be due to a pocket composed of a material with high amounts of Nd, but more data and analysis is required to verify this hypothesis.

Paleoceanographic implications

The data presented here may suggest that the sequential chemical leaching is not successfully leaching the component of the sediment we wish to target. Ideally, the leaching procedure should separate the desired portion of the sediment from the rest through the three step separation phases. However, in this case, volcanic ash seems to have been dissolved along with the Fe-Mn oxide coating (as opposed to just the Fe-Mn oxide coating) in the first phase. This indicates a lack of separation, which leads to implications regarding future paleoceanographic interpretations made based on the leaching process. A lack of separation from the leaching

procedure could bias the results and further inhibit future reconstructions of water mass compositions.

CHAPTER IV

FUTURE WORK

The primary goal for future work regarding this project is to augment the preliminary data (leached sediment) and collect more isotopic Nd data from fish debris for further comparison to leached sediment for ODP Site 1149. This will lead to clearer results, and will potentially reinforce the conclusions made herein. Further, improving the resolution of seawater Nd isotope ratios will produce clearer results that will lead to an improved reconstruction of water mass composition through time. Finally, the data point that indicates an unusually high composition of Nd should be further analyzed to understand why the value is so much higher than the rest of the data points.

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