1 Introduction

The global Meridional Overturning Circulation (MOC) is considered of primary importance in defining the ocean's physical, chemical and biological properties and a crucial part of the climate system. This includes aspects of the oceans that have direct impacts on human activity, environmental stability and natural resources such as oceanic and atmospheric temperatures [*Crowley*, 1992], the atmospheric hydrological cycle [*Frierson et al.*, 2013], oxygen and carbon dioxide content [*Schmittner et al.*, 2007], and ecosystems [*Schmittner*, 2005; *Parsons et al.*, 2014]. As such, better understanding of factors impacting the MOC and its sensitivity to perturbations is not only intellectually rewarding but also has the potential to improve projections of future changes from both natural and anthropogenic causes.

Despite its importance, large gaps remain in our knowledge of past changes and drivers of the MOC [*Lynch-Stieglitz*, 2017]. This problem is partly caused by the difficulty in making direct MOC measurements, given the inaccessibility of the deep ocean, and the long time and massive spatial scales involved. Compounding these issues is a lack of understanding into the range of naturally possible MOC changes, a problem that paleoceanographers seek to overcome through the use of indirect MOC measures (proxies) using pre-historical records preserved in ocean sediments. Perhaps the best understood examples of these proxies are carbon isotopes $\delta^{13}C$ and $\Delta^{14}C$ (radiocarbon) preserved in fossil foraminifera. While powerful tools, these proxies are also influenced by processes other than circulation, which complicates their interpretations. $\delta^{13}C$, for example, is impacted by respiration of (isotopically light) organic matter and thus displays a nutrient-like distribution in the ocean, similar to nutrients with shallow remineralization profiles such as phosphate or nitrate. Moreover, both $\delta^{13}C$ and $\Delta^{14}C$ are modulated by air-sea gas exchange [*Broecker and Maier-Reimer*, 1992]. As such, while the proxies are essential to studies of circulation, they do not provide unambiguous circulation rate information [*Legrand and Wunsch*, 1995]. For example, a measured change in $\delta^{13}C$ can result from changes in circulation or biologic productivity. Similarly, a reconstructed change in benthic radiocarbon age could have been caused by a change in circulation or sea ice cover, which affects its preformed signature by modulating air-sea exchange [*Zhao et al.*, 2018; *Galbraith and de Lavergne*, 2019; *Khatiwala et al.*, 2019].

One proposed solution to this predicament is the use of multiple complementary proxies such as $\delta^{13}C$ and nitrogen isotopes ($\delta^{15}N$). $\delta^{15}N$ provide independent constraints of biological processes such as iron fertilization [*Schmittner and Somes*, 2016]. Thus, using both $\delta^{15}N$ and $\delta^{13}C$ and by combining sediment data with a three-dimensional model it may be possible to infer circulation rate and geometry. This approach, using $\delta^{13}C$, $\delta^{15}N$ and $\Delta^{14}C$, has recently been applied for the first time to reconstructing the MOC of the Last Glacial Maximum (LGM, ~21 ka BP). Initial results indicate that a weak and shallow upper MOC cell in the Atlantic (AMOC) provides a good fit to the sediment data [*Muglia et al.*, 2018]. However, because AMOC strength and depth were correlated in their tested model solutions, it remains unclear how well constrained the AMOC *rate* and other aspects of the MOC are using this method. In fact, new unpublished results with the same model, exploring additional circulation states such as a strong and shallow AMOC, indicate weak constraints from these isotopes on circulation *rates* (not shown).

Another solution is the use of abiotic tracers such as neodymium (Nd) isotopes [*Frank*, 2002; *Piotrowski et al.*, 2004; *Böhm et al.*, 2015; *Basak et al.*, 2018]. This method has only relatively recently been developed. As such, there have only been few attempts to incorporate Nd isotopes into three-dimensional global general circulation models, and those that have been attempted have been met with only limited success in reproducing observed modern distributions [*Jones et al.*, 2008; *Siddall et al.*, 2008; *Arsouze et al.*, 2009; *Rempfer et al.*, 2011; *Friedrich et al.*, 2014; *Gu et al.*, 2019]. A key outcome of one particular model was that there is a missing source of Nd to the oceans, on the order of 90% of the total input [*Arsouze et al.*, 2009], consistent with results from previous box modeling [*Tachikawa et al.*, 2003]. Recently, our group has argued that this missing source term can be reconciled, with surprising accuracy, to observations of a benthic flux from sediments to the oceans [*Haley et al.*, 2017]. That is, we have suggested that the predominant source function of Nd to the oceans is via pore fluid fluxes from marine sediments – not, as more traditionally held, via riverine and dust inputs at the surface.

There are a number of important outcomes to the adoption of a "bottom-up" control of marine Nd, versus a "top-down" (e.g., reverse scavenging) control. One such consequence is that we predict Nd isotopes should provide rate constraints on the *deep* ocean MOC, and thus will act in a very distinct manner to "top-down" proxies such as $\delta^{13}C$, which are more sensitive to *upper* ocean MOC changes (Fig. 1). ***This complementary behavior adds great strength to using Nd- and C-isotopes as paired tracers. Model solutions that satisfy both proxies will be more completely constrained.***

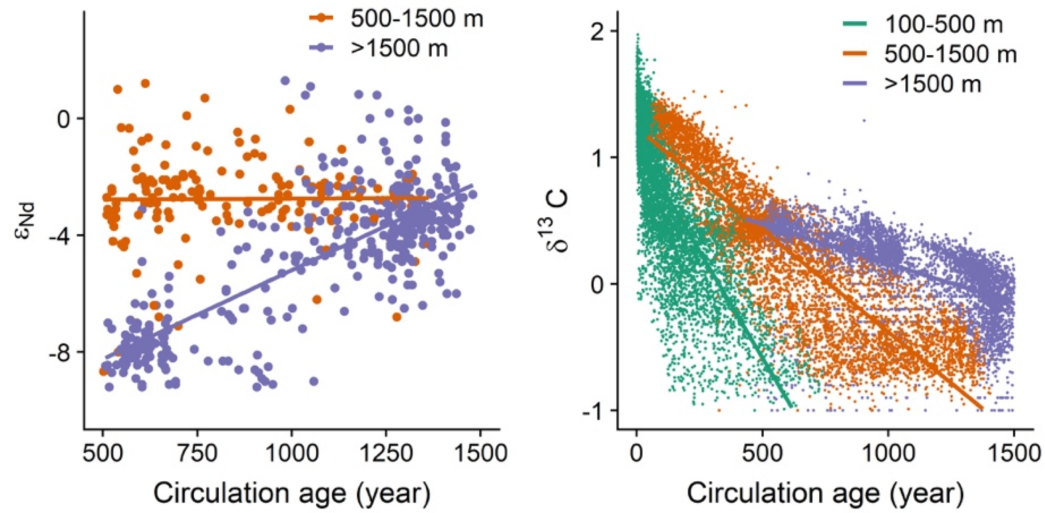

Figure 1: Comparison of circulation proxies ε_{Nd} versus $\delta^{13}C$. Left panel shows that ε_{Nd} in deep (>1500m) Pacific waters is correlated to circulation age with a relatively high sensitivity as indicated by the steep slope; a critical prediction of our "bottom up" hypothesis. In contrast, $\delta^{13}C$ is less sensitive to deep water (>1500m) circulation age changes (right panel). This is because $\delta^{13}C$ is mainly controlled by "top down" processes (shallow remineralization) that are largely spent in deep waters. While acknowledging the over-simplification of these data (e.g., preformed signals), they illustrate the contrast in proxy mechanism between ε_{Nd} and other bio-reactive elements and isotopes: a contrast that we propose to exploit to reconstruct both upper and deep aspects of the circulation by using both proxies. Circulation age data from Gebbie and Huybers [2012], $\delta^{13}C$ data from Olsen et al. [2016], ε_{Nd} data from Tachikawa et al. [2017], Lacan et al. [2012] and van de Flierdt et al. [2016]. Figures by J. Du.

Here, we propose to develop a global three-dimensional model that will, in addition to $\delta^{13}C$ and $\Delta^{14}C$, incorporate Nd isotopes and concentrations under our novel theoretical framework of a "bottom-up" mechanism. We plan to test the model and our parameterizations against the large, and growing, GEOTRACES database of Nd elemental and isotope distributions in the modern oceans. Subsequently, the model will be applied to reconstructing the LGM MOC.

2 Background

2.1 Primer on Nd and Nd Isotopes

Neodymium (Nd) is one of 14 rare earth (lanthanide) elements that occur at trace levels (pico molar) in the oceans. Neodymium has several isotopes, one of which (^{143}Nd) is the radiogenic daughter of samarium-147 decay ($t_{1/2}$ of 1.1×10^{11} y). Due to its long half-life, Nd can be considered a stable isotope system in modern and Pleistocene studies. Differences in Nd isotopes (notated as $\varepsilon_{Nd} = (R/R_{CHUR} - 1)\times10^4$ equal to deviations of the ratio $R={}^{143}Nd/{}^{144}Nd$ from a Chondritic Uniform Reservoir (CHUR)) arise in environmental samples based on the type and age of parent rocks weathered. Thus, old cratonic rocks, found in the Canadian Shield for example, have highly non-radiogenic (negative) ε_{Nd}: young arc volcanics, found around the Pacific rim for example, have highly radiogenic (positive) ε_{Nd}. The weathering of these rocks/minerals delivers Nd of differing isotopic ratios to the oceans. Traditionally, this delivery was thought to occur mostly through riverine and aeolian input at the surface and, more recently, through exchange with shallow continental margin sediments [*Tachikawa et al.*, 2003; *Jeandel et al.*, 2007; *Johannesson and Burdige*, 2007].

In the oceans, Nd and Nd isotopes appear to behave differently (Fig. 2): dissolved elemental Nd (Nd_d) increases with depth, appearing to be "nutrient-like" (e.g., Si with a deep remineralization profile) or "scavenged" in profile [*Elderfield et al.*, 1988], while dissolved isotopic Nd appears to be conservative within a water mass [e.g. *Frank*, 2002]. This disparity has been coined the "Nd paradox" and is often described in terms of irreconcilable differences in calculated residence times of elemental and isotopic Nd [*Bertram and Elderfield*, 1993; *Goldstein and Hemming*, 2003]. Consideration of only river and dust sources leads to a residence time much longer than the ocean mixing time, which would preclude significant isotopic differences between the ocean basins. This discrepancy led *Tachikawa et al.* [2003] to suggest an additional source, which they assumed to be concentrated along continental margins. Subsequent studies confirm the need for additional sources [van de *Flierdt et al.*, 2004] and suggest water-sediment interactions along the continental margins as one of several processes for isotopic exchange; those processes have collectively been termed "boundary exchange" and are assumed to be restricted to the upper ocean (< 3km) [*Lacan and Jeandel*, 2005; *Arsouze et al.*, 2007; *Jeandel*, 2016].

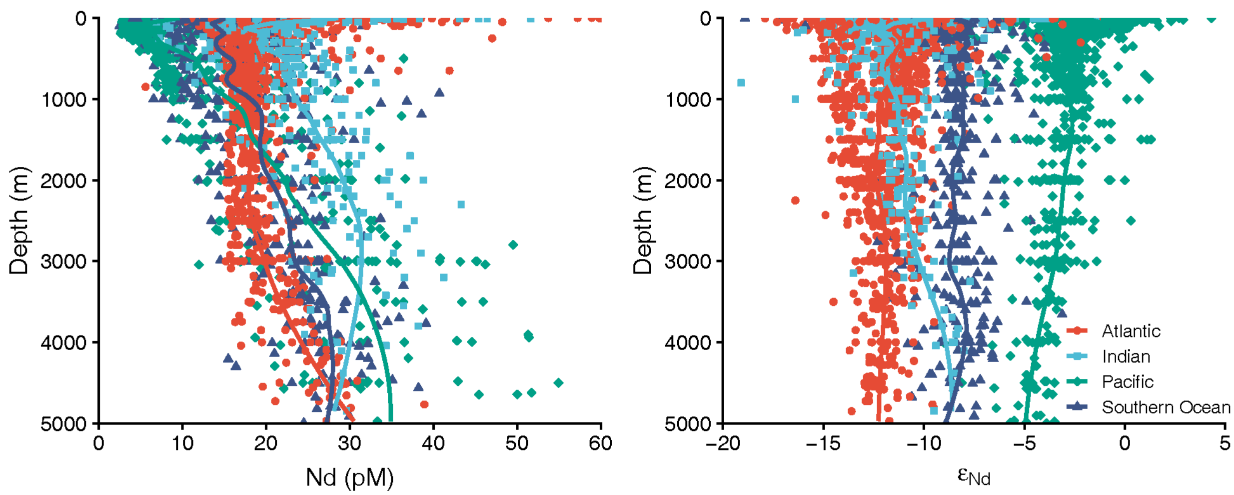

Figure 2: Observed vertical distributions of water column Nd and ε_{Nd} in the different ocean basins. Whereas dissolved [Nd_d] concentrations (left) increase with depth similar to profiles of silicate, ε_{Nd} (right) shows large inter-basin differences with low values in the Atlantic and more radiogenic (positive) values in the Pacific. Nd isotope data sources as in Fig. 1. Southern Ocean means south of 30°S. Figure by J. Du.

The prevalent solution to the Nd paradox invokes "reversible scavenging" of Nd [*Elderfield et al.*, 1988; *Byrne and Kim*, 1990; *Sholkovitz et al.*, 1994; *Byrne and Sholkovitz*, 1996; *Siddall et al.*, 2008]. Reversible scavenging summarizes the effects of adsorption onto and desorption from sinking particles, which leads to a downward transport of Nd within the water column and could explain observations of increasing concentrations of Nd_d with depth, similar to thorium (^{230}Th) isotopes [*Bacon and Anderson*, 1982]. While global three-dimensional general circulation models have attempted to implement this mechanism [*Siddall et al.*, 2008; *Arsouze et al.*, 2009; *Rempfer et al.*, 2012; *Gu et al.*, 2019], their results do not match observed Nd_d and ε_{Nd} distributions well [e.g. Fig. 4 in *Gu et al.*, 2019]. Typical systematic biases of these models are surface values of Nd_d that are too low and values in the deep Pacific that are too high. Another issue with these models is indicated by the fact that different parameter combinations result from fitting to isotope (ε_{Nd}) data versus concentration (Nd_d) data [Fig. 2 in *Rempfer et al.*, 2011]. Models that treat ε_{Nd} as a conservative tracer also have large biases [e.g. Fig. 3 in *Friedrich et al.*, 2014], suggesting fundamental issues with the underlaying geochemical assumptions.

Recently, our group has offered a differing mechanistic framework for Nd and Nd isotopes that is based on a dominant benthic flux to the oceans [*Abbott et al.*, 2015a; *Du et al.*, 2016; *Haley et al.*, 2017]. The idea is simply that early diagenesis releases Nd to pore water from solid and amorphous sedimentary phases, which in turn drives a diffusive flux of Nd into bottom water. Such a flux is consistent with observations of an order of magnitude larger Nd_d concentrations in pore-water than in the overlaying water column [Fig. 7 in *Abbott et al.*, 2015b]. We consider these fluxes to be widespread in the deep sea [*Haley et al., 2017*], which could account for the "missing" Nd source [*Haley and Klinkhammer*, 2003; *Abbott et al.*, 2016]. Our hypothesis holds many observational consistencies with previous suggestions of boundary exchange, but we do not consider the bottom to be a concentration-neutral exchange site and we do not consider the benthic influence to be limited to the upper 3 km and continental margins [*Lacan and Jeandel*, 2005; *Arsouze et al.*, 2009]. Rather, **our hypothesis is that a benthic flux exists to some extent everywhere at the sea floor**, consistent with the few existing pore-water-based observations of fluxes [*Sholkovitz*, 1989; *Haley et al.*, 2004; *Abbott et al.*, 2015a; Supplementary Fig. 1 in *Du et al.*, 2018; *Abbott*, 2019]. When extrapolated to the whole ocean these fluxes, which appear to be on the order of 10s of pmol cm^{-2} yr^{-1}, account for the missing source of 10^7-10^8 mol Nd yr^{-1} [*Abbott et al.*, 2015b]. Our benthic flux hypothesis implies most Nd enters below 3 km depth simply due to the hypsometry of the oceans [*Du et al.*, 2018], which does contrast previous interpretations of the boundary exchange hypothesis [*Tachikawa et al.*, 2003; *Siddall et al.*, 2008; *Arsouze et al.*, 2009; *Rempfer et al.*, 2011].

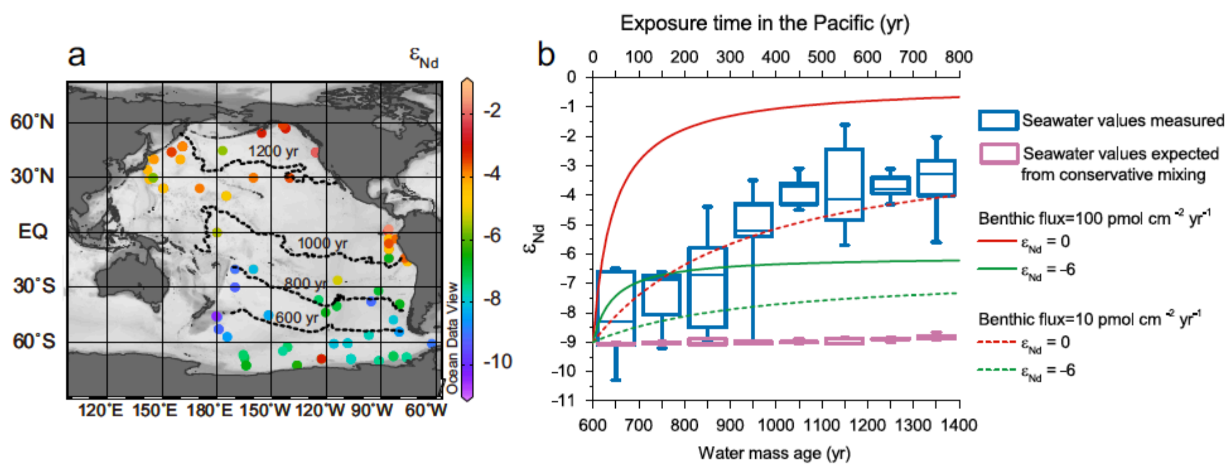

Figure 3: The relation between deep water ε_{Nd} and water mass age in the Pacific. Results from a simple box model with different (spatially constant) benthic fluxes and ε_{Nd} values of those fluxes are shown as different lines in the right panel. The model does not use reversible scavenging. Note that the data are inconsistent with the assumption of conservative mixing [Jones et al., 2008]. From Du et al. [2016].

Under our mechanistic hypothesis, the impact of the benthic flux in the ocean basins is a function of "exposure time" of bottom water to these benthic fluxes and the geometry of the basin (e.g., intermediate waters will have a lower exposed-surface-area to volume ratio compared to abyssal water masses). Critically, the notion of "exposure time," or time that a bottom water is exposed to a benthic flux, is a direct function of ventilation rate (Fig. 3). Moreover, our framework offers a relatively straightforward explanation for the distribution of elemental Nd_d in the oceans, wherein the concentration of Nd_d will increase with depth as this is approaching the dominant source. There are, of course, many nuances to this argument (e.g., variation in preformed Nd, or mixing of Nd) that will be explored in this proposal; the critical idea is that **we expect that implementation of our "bottom up" framework into a general circulation model will approximate the observed distribution of isotopic *and* elemental Nd better than previous models.** Preliminary box-modeling efforts of the "bottom up" hypothesis illustrate the potential (Fig. 3) [*Du et al.*, 2016; *Du et al.*, 2018], but are limited in their geographical and physical representation of the ocean. Here we want to take this research a substantial step forward by using a well-tested, three-dimensional, global model with realistic physics and geography.

2.2 Estimating the LGM MOC

In the paleo world, the LGM is a data-rich period. Recent global syntheses from LGM sediments include 480 $\delta^{13}C$ data [*Peterson et al.*, 2014], 256 radiocarbon measurements at 131 locations [*Skinner et al.*, 2017] and 105 nitrogen isotope data [*Galbraith et al.*, 2013; *Muglia et al.*, 2018]. However, modeling studies using these, and other sediment data come to different conclusions. Whereas *Kurahashi-Nakamura et al.* [2017], using an inverse model constrained with Atlantic $\delta^{13}C$ and $\delta^{18}O$ data, infer a shallow and strong AMOC in line with interpretations of protactinium thorium ratios ($^{231}Pa/^{230}Th$)[e.g. *Böhm et al.*, 2015], the forward-modeling studies by *Menviel et al.* [2017] and *Muglia et al.* [2018] find that a shallow and weak AMOC fits global $\delta^{13}C$ and radiocarbon data best. Thus, while these and other studies [e.g. *Gebbie*, 2014] agree on a shoaling of the AMOC, its strength and other aspects of the LGM MOC remain disputed. One of those disputed aspects is the flow rate of Antarctic Bottom Water (AABW), which has been suggested as weaker [*Menviel et al.,* 2017] and stronger [*Muglia et al.,* 2018] than present.

More recent simulations indicate that increased tidal mixing due to sea level lowering may have caused faster abyssal flow rates during the LGM [*Wilmes et al.*, 2019]. However, examining the carbon isotope distributions from those simulations indicates weak constraints from those data on abyssal flow rates [*Wilmes et al.*, in prep.]. Moreover, the rate of Circumpolar Deep Water (CPDW) flow into the Pacific and Indian oceans remains poorly constrained and questions remain about the existence of a shallow MOC in the North Pacific [*Menviel et al.*, 2017]. Here we suggest that neodymium isotopes provide additional and complementary constraints to carbon isotopes to reconstruct currently poorly known features of the LGM circulation, particularly its abyssal components that are especially important for carbon storage.

3 Goals & Hypotheses

We propose to implement elemental and isotopic Nd cycling in a global, three-dimensional ocean general circulation model that will specifically include a benthic source function. With this model we will seek to test the following hypotheses:

H1: The observed modern distribution of isotopic and elemental Nd can be reproduced to a first order through imposition of a simple global uniform benthic flux combined with scavenging.
H2: Deep ocean Nd isotope distributions are controlled by the exposure time of a water mass to sediments and thus by deep and abyssal MOC flow rates.
H3: Nd and carbon isotopes provide complementary constraints on the LGM MOC.

The over-arching goal of this proposal is two-fold: First, we hope to test our theoretical "bottom-up" idea in an integrated global manner, and second, we hope to generate model solutions for the MOC in the modern and glacial ocean that are consistent with different available observations (including temperature, salinity, radiocarbon, nutrients, oxygen, $\delta^{13}C$, elemental and isotopic Nd). There is clearly a significantly iterative nature to this project that will require us to proceed cautiously with a well-defined path, outlined below. However, we believe that this proposal is timely for three reasons: (1) the mechanistic "bottom up" framework is being recognized as important in observational studies and in its ability to reconcile downcore data sets; (2) there is a critical accumulation of global Nd elemental and isotopic observations made available in the GEOTRACES program from each ocean basin that can be used as model test; (3) an accurate model can offer invaluable insight into the integrated effects of the benthic flux – an insight that offers vital contrast to site-specific studies of the geochemistry that are underway (see section 6) and that may transform our understanding of Nd cycling in the ocean. Moreover, application to the LGM will quantify the additional constraints, if any, with respect to carbon isotopes, provided by Nd isotopes on the depth and rate of the MOC, not only in the Atlantic, but also in the Indian and Pacific oceans, which are especially important for carbon storage but which have been the Achilles heel of previous Nd models. Thus, this project has the potential to improve our understanding of the glacial ocean including its carbon cycle, which remains a major challenge.

4 Methods

We will use a combination of numerical model experiments and observations to test our hypotheses.

4.1 Model Description

The Model of Ocean Biogeochemistry and Isotopes (MOBI), developed by Schmittner and collaborators, features in its current version 2.0 prognostic equations for 30 tracers. Those include three phytoplankton functional groups (diazotrophs, coccolithophores, other phytoplankton), nitrate (NO_3), phosphate (PO_4) and dissolved iron (dFe) as inorganic, growth-limiting nutrients, zooplankton, dissolved organic matter (DOM), particulate organic matter (POM), calcium carbonate ($CaCO_3$), particulate iron (pFe), ^{15}N and ^{13}C in all nitrogen and carbon compartments, respectively, radiocarbon, dissolved inorganic carbon (DIC), alkalinity (ALK) and chlorofluorocarbons (CFCs). More detailed descriptions including equations, validation to modern observations and applications to past and future scenarios are available elsewhere [*Schmittner et al.*, 2005; *Schmittner et al.*, 2008; *Somes et al.*, 2010a; *Somes et al.*, 2010b; *Schmittner et al.*, 2013; *Somes et al.*, 2013; *Nickelsen et al.*, 2014; *Kvale et al.*, 2015; *Schmittner and Lund*, 2015; *Somes and Oschlies*, 2015; *Schmittner and Somes*, 2016; *Muglia et al.*, 2017; *Somes et al.*, 2017; *Khatiwala et al.*, 2019].

MOBI is available as an interactive component of the University of Victoria (UVic) climate model [*Weaver et al.*, 2001] and coupled to the Transport Matrix Method (TMM). The TMM is a numerical technique for fast, offline simulation of ocean biogeochemical tracers. Its computational efficiency and parallel performance allow a large number of long integration in a short period of time with a fixed (seasonally varying) circulation [*Khatiwala*, 2007]. It works by extracting transport matrices from an online model. Tests with matrices extracted from the UVic model show that the TMM results closely match the online model [*Kvale et al.*, 2017]. No extraction of transport matrices will be required for this project. We will use existing matrices and matrices that will be extracted as part of NSF funded project 1924215 (see section 6 and letter from Dr. Khatiwala). Most sensitivity tests and simulations required for parameter estimation and performed as part of this project will use the TMM. However, we will also use the UVic model for some transient simulations.

The UVic model includes a global, three-dimensional ocean circulation model at coarse resolution (1.8×3.6°, 19 levels), a dynamic-thermodynamic sea ice model, a 1-layer energy-moisture-balance model of the atmosphere, as well as biogeochemical components in the ocean and on land. It is computationally efficient and well tested both for modern and paleo simulations (see references above). Our LGM set-up follows the Paleoclimate Modeling Intercomparison Project (PMIP) protocol and includes prescribed orbital configuration, CO_2 and other greenhouse gas concentrations, and ice sheets, wind anomalies, effects of sea level lowering on salinity, benthic denitrification, iron fluxes and tides [*Muglia et al.*, 2017; *Muglia et al.*, 2018; *Wilmes et al.*, 2019]. Recent, yet unpublished developments include a parameterization of mesoscale eddies using temporally- and spatially-variable isopycnal thickness and along-isopycnal tracer diffusivities based on *Stanley and Saenko* [2014]. This allows calculation of variable mesoscale eddy kinetic energy, which has been suggested to impact benthic nepheloid layers [*Gardner et al.*, 2018]. This may permit prognostic calculation of nepheloid layers, which may affect deep ocean scavenging of elements such as Pa and Th [*Hayes et al.*, 2015; *Lerner et al.*, 2020]. NSF project 1924215 (see section 6) includes ^{231}Pa and ^{230}Th cycling in MOBI, which will provide additional constraints on the MOC, particularly the rate of its upper (North Atlantic Deep Water) cell [*McManus et al.*, 2004].

4.2 Modern Observations and GEOTRACES Data

A primary goal of the GEOTRACES international program is to provide a database that is conducive to ocean modeling [*GEOTRACES Planning Group, 2006*]; e.g., with comprehensive and consistent measurements between sections. With over one hundred cruises completed, there is now sufficient data to train and test the model, as proposed here. Moreover, there are a number of pending and planned cruises and we hope that we can use our model to make predictions on the distributions of elemental and isotopic Nd in these sections. Available but more limited data on particulate Nd will also be used. Co-PI Haley has been involved in the collection of many of the US-led efforts for the GEOTRACES program.

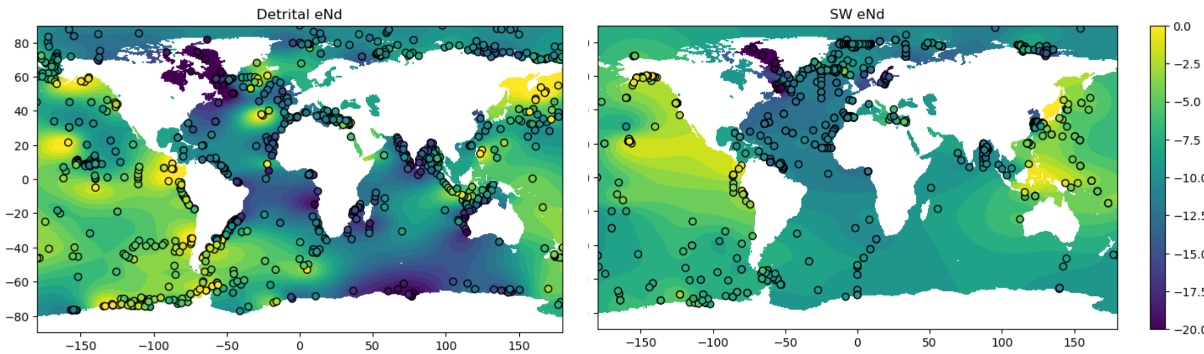

Figure 4: Detrital (left) [Du, 2019] and bottom water (within 500 m of seafloor, right) ε_{Nd} (data sources as in Fig. 1). Haley plans to increase the data density, where lacking, in the detrital map, and continuing GEOTRACES data will improve seawater ε_{Nd} data.

As will be discussed in detail below, the model will systematically test parameterizations of the benthic flux. An important aspect of this plan is that we will base the isotopic composition of the benthic flux on the observed detrital ε_{Nd}. To do this, we will use core top measurements of total digests of these sediments, for which there is a significant extant database available (Fig. 4). However, there are clear data deficiencies in parts of the global oceans; e.g., the Indian and Southern Oceans. As part of this proposal, Haley will use existing core repository samples to make further total digest analyses of sediments where there is a paucity.

4.3 LGM Data

We have already started a global compilation of LGM ε_{Nd} data based on a recently published Atlantic compilation [*Howe et al.*, 2016] to which data from other ocean basins have been added (Fig. 5c). The existing data show a similar pattern and interbasin difference to today, indicating a similar MOC, but overall higher (more radiogenic) values. *Howe et al.* [2016] assumed a conservative-mixing-based interpretation of the Atlantic data and suggested continued production of North Atlantic Deep Water during the LGM, in contrast to studies based on carbon isotopes that suggest a shoaling of the AMOC [e.g. *Gebbie*, 2014]. We re-iterate that conclusions based on our benthic flux hypothesis may differ significantly from those based on conservative mixing. Preliminary box modeling including benthic fluxes indicates that much of the LGM data can be readily explained by differences in pre-formed ε_{Nd} in the North Atlantic due to shifts in convection sites and/or shoaling of the AMOC [*Du*, 2019]. This seems to contrast with results from carbon isotope modeling, which indicate a reduced AMOC strength [e.g. *Menviel et al.*, 2018]. However, a consistent three-dimensional ocean model that includes carbon *and* Nd isotopes has never been used to address these questions. Here we will test whether such a model, trained in the modern ocean, can provide a solution to the LGM MOC that will satisfy both carbon-based and Nd isotopic data.

5 Work Plan

Initial Model Construction. ^{143}Nd and ^{144}Nd will be implemented as four additional prognostic tracers (two per isotope) in each grid box of the model. For each isotope dissolved and particulate Nd will be modeled separately according to $\partial^{143,144}Nd_{d,p}/\partial t = T + S$, where the rate of change is affected by transport T and both internal and external sources and sinks S. Physical transport will be considered by modeled advection with the resolved flow and diffusion of parameterized subgrid-scale processes such as mesoscale eddies and tidal mixing due to breaking internal waves. Modeling sources and sinks will involve specifying several aspects of the geochemistry of these isotopes. External input fluxes will include: (1) a riverine point-source based on *Goldstein and Jacobsen* [1987] and *Jeandel et al*. [2007]; (2) a surface ocean term that reflects dust sources [*Tachikawa et al.*, 2003], which will scale with the dust and iron fluxes that are already in the model [*Muglia et al.*, 2017]; (3) a novel benthic-flux term, which will be the basis of sensitivity tests described below.

The benthic input flux will consider sub-grid scale bathymetry based on a high-resolution, 2-minute gridded global relief map. MOBI already uses sub-grid bathymetry for the calculation of sedimentary iron and nitrogen fluxes [*Muglia et al.*, 2017]. Here, this scheme will be extended to Nd fluxes. This approach has the advantage that exchanges between the water column and the sediment occur at a realistic depth despite the highly smoothed resolved bathymetry of the coarse resolution model. Initially, the flux magnitude will be set as a constant 20 pmol cm^{-2} yr^{-1}, following observations and estimates that have been successful in box models [*Du et al.*, 2016]. The benthic input term will initially be prescribed isotopically as reflecting the bulk sediment and will mirror the detrital map (Fig. 4), with additions provided through this proposal effort (described later).

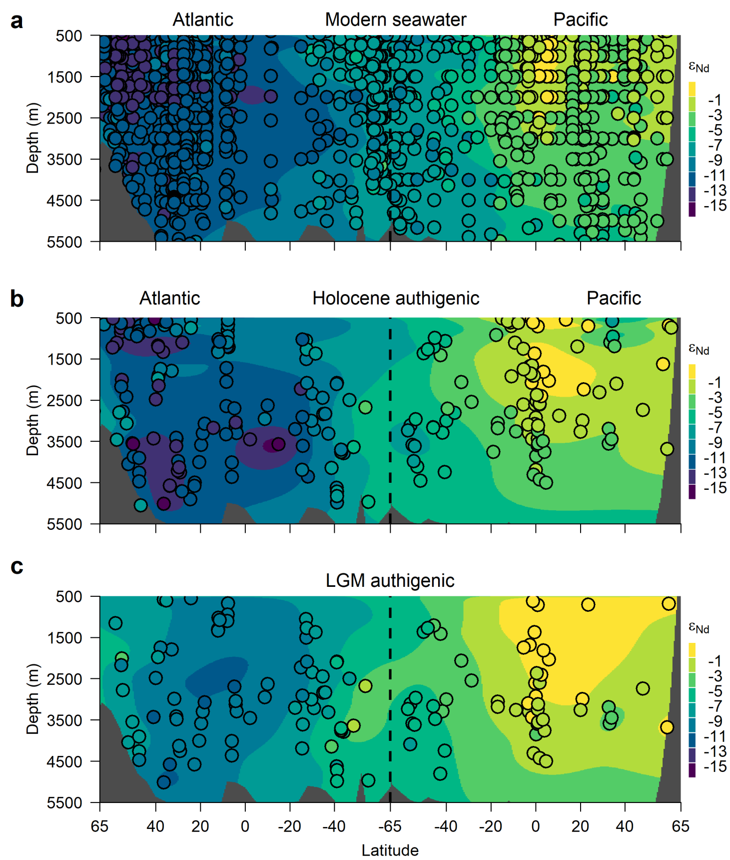

Figure 5: Latitude-depth sections through the Atlantic (left) and Pacific (right) of modern sea water ε_{Nd} (top; data sources as in Fig. 1), Holocene authigenic ε_{Nd} (center) and LGM authigenic (bottom) [Du, 2019].

Internal sources and sinks will represent complexation of free dissolved Nd_f and scavenging of Nd_f onto particles. Complexation of dissolved Nd is predominantly with carbonate ions CO_3^{2-} [*Stanley and Byrne*, 1990; *Millero*, 1992; *Byrne and Sholkovitz*, 1996; *Luo and Byrne*, 2001; 2004; *Schijf et al.*, 2015] $Nd_f + CO_3 \Leftrightarrow NdCO_3$ and $Nd_f + 2CO_3 \Leftrightarrow Nd(CO_3)_2$, which reduces the amount of Nd_f susceptible to scavenging, and will be included in the model. Total dissolved Nd will be modeled as the sum of free Nd and Nd complexed with CO_3: $[Nd_d] = [Nd_f] + [NdCO_3] + [Nd(CO_3)_2]$. The concentration of carbonate ion $[CO_3] = [ALK] - [DIC]$ will be calculated as the difference between the model-predicted concentrations of alkalinity and DIC. Stability constants $\beta_1 = [NdCO_3]/[Nd_f][CO_3] = 10^{5.9}$ M^{-1} and $\beta_2 = [Nd(CO_3)_2]/[Nd_f][CO_3]^2 = 10^{10.53}$ M^{-2} from *Schijf et al.* [2015; their Tab. 2] will be used. Thus, the ratio between total dissolved and free Nd will be a function of the carbonate ion concentration: $r_{df} := [Nd_d]/[Nd_f] = (1 + \beta_1[CO_3] + \beta_2 [CO_3]^2)$. For a pH of 8.2 $\log(r_{df}) = 1.99$ and it decreases with decreasing pH as $[CO_3]$ decreases [*Schijf et al.*, 2015]. Since $[CO_3]$ values range from about 350 µM in low-latitude surface waters to 100 µM in deep waters of the Atlantic and less than 10 µM in Pacific deep waters, the ratio r_{df} will vary by more than 2 orders of magnitude from about 4×10^3 in low-latitude surface waters to 4×10^2 and less than 10^1 in deep waters of the Atlantic and Pacific, respectively. To our knowledge, previous Nd modeling studies have not considered this effect, which we expect to increase Nd_f and thus increase the potential for scavenging of Nd_f in the deep ocean, particularly in the Pacific. Conversely, in low-latitude near-surface waters Nd_f will be relatively smaller – a higher percent of Nd will be complexed - and thus scavenging will be reduced there. Considering carbonate complexation thus may reduce the biases of previous models such as the too low surface and too high Nd concentrations in the deep Pacific noted by *Gu et al.* [2019] and implies a stronger benthic flux.

Two models of scavenging will be considered. In addition to the common model of reversible scavenging (**RS**) we will construct a model of irreversible scavenging (**IS**). Previous Nd modeling studies with only surface or upper ocean sources have used RS presumably because it leads to increasing dissolved concentrations with depth [*Bacon and Anderson*, 1982]. However, since the benthic flux mechanism provides a source at the bottom it can possibly explain increasing Nd_d with depth without the need for desorption. **IS** ($[Nd_f] + [P] \Rightarrow [NdP]$) will be modeled by including a sink for Nd_d and a source for Nd_p that are proportional to the particle concentration [P] and the concentration of free dissolved Nd: $S(Nd_p) = -S(Nd_d) = \Sigma_P \kappa_P [P][Nd_f]$, where the sum includes all particle types P and κ_P is the adsorption rate per particle concentration. Vertical transport of particles is governed in MOBI by sinking with different sinking speeds w_P. Thus, particulate Nd will have additional source and sink terms associated with particle sinking. Particles entering from the layer above are a source and particles sinking into the layer below are a sink. Particulate Nd will be released back into the dissolved pool through remineralization of particulate organic matter or dissolution of $CaCO_3$ for both IS and RS models. Particulate Nd that sinks out of the bottom layer will be lost to the sediments.

RS will be modeled as an equilibrium between free dissolved Nd and Nd adsorbed onto different particles P: $[Nd_f] + [P] \Leftrightarrow [NdP]$ with coefficients $k_P = [NdP]/[Nd_f][P]$. Note that this definition is different from the one used in previous modeling studies such as *Rempfer et al.* [2011], who model scavenging of total dissolved Nd_d and specify $K_P = [NdP]/[Nd_d][P]$, although they can be converted ($K_P = k_P/r_{df}$). Also note that our definition of k_P corresponds to constants K_S in *Schijf et al.*'s [2015] eq. 7b. Currently, little is known about the type of particles Nd attaches to and estimates for the scavenging coefficients based on ocean-based measurements are rare. Given the sparsity of empirical data we will initially implement scavenging in a simplified manner considering five particle types ($P \in$ [POC, PFe, opal, dust, $CaCO_3$]) including Particulate Organic Carbon (POC), Particulate iron (PFe) and calcium carbonate ($CaCO_3$). Initial values for the IS coefficients will be $\kappa_P = 10^{-3}$ yr^{-1} $[P]^{-1}$, based on generic loss rates used in box models [Du, 2019] and global mean particle concentrations [P] from MOBI. For RS, initial values will reflect the most recent observational estimates [*Schijf et al.*, 2015 and J. Schijf personal communication] and be constrained by existing and emerging GEOTRACES observations of Nd_p [*Tachikawa et al.*, 1999] and Nd_d, and model [P]. Total particulate Nd will thus be $[Nd_p] = \Sigma_P k_P [Nd_f][P] = r_{df}[Nd_d]\Sigma_P k_P[P]$ and total Nd will be $[Nd] = [Nd_p] + [Nd_d] = (1 + r_{df}\Sigma_P k_P[P])[Nd_d]$. Due to this relationship between Nd_p and Nd_d no separate prognostic equation for Nd_p is required for RS.

Scavenging will represent the only external loss term, as Nd that is scavenged onto particles and sinking out of the bottom grid box will be buried in sediments. Therefore, we expect that the value for the scavenging constant(s) will affect absolute Nd concentrations in the water column. The more efficient the scavenging (the larger κ_P or k_P) the smaller Nd concentrations will be. As in previous modeling studies isotopic fractionation during adsorption and desorption will be neglected due to the small mass difference between the isotopes [*Rempfer et al.*, 2011]. This work will be performed mainly by AS and GS in year 1 of the project.

Model Description Paper: In year 1 AS, with the help of other MOBI developers, will write a paper that provides a comprehensive description of MOBI. Recent code developments from different groups will be merged into one consistent version. These developments include a complete code restructuring that merged many C++ pre-processor options and improved readability. This will facilitate adding new prognostic tracers such as Nd isotopes. Before this restructuring the code had become very difficult to work with due to many different people who added various bits and pieces. Another purpose of the code restructuring was to enable the user to easily create different configurations, starting from a very simple NPZD model with only 4 prognostic tracers to the full model with all isotopes, which currently amount to 30 prognostic tracers. Even though much of the restructuring has already been completed, a number of components still need to be added such as diatoms, silicon and nitrous oxide cycling, which are currently being developed by Drs. Kvale and Somes in Kiel, and Pa/Th, which will be implemented as part of NSF project 1924215 (see section 6 below). Moreover, a comprehensive description of the full model and the different possible configurations is currently not available in one place. Different components have been described in separate papers, which makes it difficult for a new user to understand the model and code. Therefore, we will write a comprehensive model description paper, e.g. for the Journal of Advances in Modeling Earth Systems or a similar journal. Code and a user manual will also be produced, made available through a code-sharing website (gitlab), and linked to the paper. We believe that such a paper and user manual will be a helpful resource for scientists who consider using MOBI, with enhanced approachability for the GEOTRACES geochemical community. In years 2 and 3 we will organize a series of webinars explaining the model with the possibility of hands-on practice including a Hackathon practicing collaborative code development with git and gitlab. These webinars will be advertised to the GEOTRACES community.

New Measurements: Haley will canvas core repository samples for core top sediment samples where there is a paucity of ε_{Nd} data. Sediment samples will be preferentially selected based on (1) location (2) preservation quality (3) available ancillary data, such as $\delta^{18}O$ or $\delta^{13}C$ data associated with the sediment. These samples will be freeze-dried and split into two fractions. The first will be leached according to the protocols used by Du et al. [2016] as reflecting an "authigenic fraction". The second fraction will be digested using microwave or hot plate total digestion techniques [*Muratli et al.*, 2012]. These leachate and bulk digest samples will then be run through ion chromatographic separations [*Abbott et al.*, 2015a] to isolate first the REEs (collecting a strontium cut in the process) and then Nd. The Nd fractions will be run on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). We plan on making 100 measurements on sediment samples. The leach data will be added to a compilation of modern sediment leach data (Fig. 6) to investigate further the apparent 1-ε_{Nd} unit offset of leach data from bottom water observations. We will test the hypothesis that this offset is caused (at least partly) by ocean circulation. The offset will be analyzed in models with different circulations. If the offset is larger in models with a faster circulation the hypotheses is validated, if not it is falsified. This work will be performed by BH.

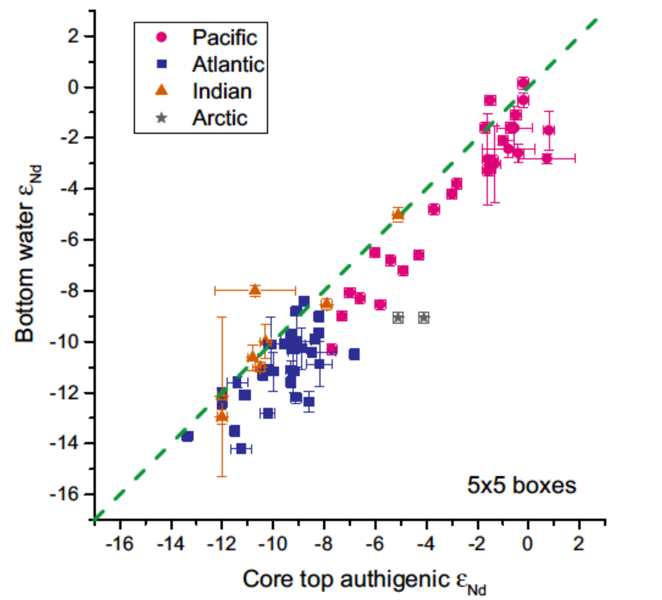

Figure 6: Comparison of core-top authigenic phases and bottom water. From Haley et al. (2017).

Model Tuning. The main uncertainties in the model construction are the magnitude of the benthic flux, the nature of the sink (IS vs RS) and the scavenging coefficients. These structural and parametric uncertainties will be systematically investigated. Structural uncertainties will be investigated by creating three structurally different models. Model **ISBF** will use **I**rreversible **S**cavenging and a **B**enthic **F**lux. Model **RSBF** will use **R**eversible **S**cavenging in combination with a **B**enthic **F**lux. Model **RSBE** will use **R**eversible **S**cavenging in combination with **B**oundary **E**xchange restricted to the upper ocean (< 3 km) and thus be similar to previous studies [*Arsouze et al.*, 2009; *Rempfer et al.*, 2011; *Gu et al.*, 2019]. We will not attempt to create a model with irreversible scavenging and boundary exchange because it will not be able to reproduce observations of increasing Nd_d with depth.

Parametric uncertainty will be investigated by creating a two-dimensional matrix of models with different parameter combinations. In this matrix the rows represent 14 different benthic flux F_b values (0, 1, 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 70, 100) ranging from 0 to 10^2 pmol cm^{-2} yr^{-1}, with increments of 5 units in the central part and unequal spacing in the lower and upper part of the range. The columns represent different generic scavenging coefficients κ or k. Such a matrix will be produced for each of the three structurally different models described above. For models RSBF and RSBE k will be ranging over more than two orders of magnitude with 13 constant log(k) increments [*Schijf et al.*, 2015]. For simplicity, coefficients will be estimated such that all particles contribute similarly to scavenging. The resulting matrix has 14×13 = 182 models spanning "Zero Benthic Flux" through "Maximum Benthic Flux" and "Negligible Scavenging" to "Extremely Efficient Scavenging" and all possible combinations in between. We choose exponential spacing for the scavenging coefficients and approximately exponential spacing in the lower and upper ranges for the benthic flux because this allows an efficient but coarse scan of the large parameter range. Depending on the results, additional experiments will be performed with a zoomed-in parameter range and finer increments.

The resulting simulated distributions of Nd concentrations *and* isotope ratios will be compared with existing and emerging observations, including GEOTRACES data. For this comparison the model will be sampled at the locations of the observations. We expect the global mean Nd concentration to be determined by the difference between the global mean source, i.e. the benthic flux, and the global mean sink, i.e. scavenging. Therefore, we expect that the observed global mean Nd concentration will provide a first basic limit on the combination of possible parameters. For a given benthic flux only a narrow range of scavenging coefficients will lead to a similar global sink consistent with the observed global mean Nd concentration. The larger the input flux the larger the required scavenging coefficient will need to be to match the observed global mean Nd concentration. Therefore, we expect that global mean Nd will be satisfied by a range of different fluxes and scavenging coefficients that occupy a diagonal region in the parameter matrix similar to the dashed contour lines in Fig. 2 of *Rempfer et al*. (2011).

For the model-data comparison we will also examine the spatial distribution of Nd concentrations and isotopic ratios. We expect that the larger the bottom fluxes the steeper the vertical gradients of Nd concentrations will be, even if scavenging is also more efficient to satisfy the global Nd constraint. For low and moderate benthic fluxes, we expect the upper ocean Nd concentrations to be dominated by riverine and aeolian surface input and loss through scavenging. However, deep and abyssal ocean Nd concentrations (and isotope ratios) will likely be dominated by the benthic flux. Due to strong tidal mixing in many parts of the abyssal ocean, which is captured by the model [*Schmittner and Egbert*, 2014], some of the Nd added at the bottom will diffuse upward, whereas some will be scavenged back to the sediments and some will be removed and supplied by lateral advection. Thus, we expect stronger bottom fluxes will increase bottom water Nd concentrations and vertical gradients. Stronger bottom fluxes will also increase the influence of local/regional input compared to the homogenizing effect of circulation and mixing. Therefore, we would expect stronger benthic fluxes to lead to larger horizontal differences in ε_{Nd} and generally to larger spatial variance. Thus, we surmise that horizontal gradients and spatial variance in observed ε_{Nd} will provide constraints on the magnitude of the benthic flux. Detailed comparisons of individual profiles and sections across ocean basins will also be produced.

Different global metrics of model-data comparison will be computed such as spatial variances, correlation coefficients and Root-Mean-Squared-Errors (RMSEs). In a first step the model-data misfit will be calculated as the dimensional $RMSE_d = (\Sigma_i(M_i - O_i)^2/N)^{0.5}$, where the sum goes over all N (i = 1, 2, …, N) pairs of differences (residuals) between the model (M) and the observations (O). In a second step, we will define the standard error σ as the *RMSE* of the best fitting model and normalize all residuals to calculate the normalized, non-dimensional $RMSE_n = (\Sigma((M - O)/\sigma)^2/N)^{0.5}$. Normalization allows us to combine errors of different variables such as Nd and ε_{Nd} in one metric. However, we will also consider them separately. The values of σ will also be used in the LGM comparison as estimates of model error.

For each of the three structurally different models we will select the parameter combination of benthic fluxes and scavenging coefficients that fits the combined Nd and ε_{Nd} data best. These three models will also be run in the online (UVic/MOBI) version of the model to check for robustness of the results. We expect model RSBE to result in similar parameter values to previous similar models such as that of *Rempfer et al.*

[2011]. In contrast, we expect the estimated scavenging coefficients of model RSBF to be much smaller and perhaps more consistent with observational estimates [*Schijf et al.*, 2015]. Because boundary exchange models will have the input of Nd at shallower depths compared with the benthic flux model, they presumably require larger scavenging coefficients to reproduce observed high Nd concentrations at depth. Comparing the best-fitting ISBF and RSBF models will indicate whether irreversible or reversible scavenging are more appropriate models for Nd cycling. Comparing the best-fitting benthic flux model with model RSBE will test our hypothesis H1. **If the benthic flux model is in considerably better agreement with the observations than the boundary exchange model, this would transform our understanding of Nd cycling in the ocean.** This work will be performed in year 2 mainly by the graduate student (GS) with guidance from Andreas Schmittner (AS) and Brian Haley (BH).

Sensitivity Experiments. Additional sensitivity experiments will be performed to explore finer details of uncertainties such as the specific roles of individual particles in scavenging and reasons for differences with previous studies. Since previous studies did not consider complexation with carbonate ion we will do an experiment with our best fitting model without [CO_3^{2-}] complexation. Similarly, in order to reproduce the results of *Rempfer et al.* (2011) we will create a boundary exchange model without [CO_3^{2-}] complexation, and with their exact scavenging coefficients. Experiments with different scavenging coefficients for different particles will be performed. A simple nepheloid layer parameterization will be tested in which the a particle source at the bottom will be included, which is proportional to the model-predicted eddy kinetic energy [*Gardner et al.*, 2018]. Additional experiments will explore different distributions and mechanisms for the benthic flux. One experiment will use a depth dependent flux according to Abbott et al. [2016]. Another experiment will use sediment composition to determine the benthic flux magnitude – but not the isotopic composition. Thus, we will set lower flux values in siliceous ooze sediment versus higher fluxes in lithogenic sediments. As with other aspects of this project, we will be informed significantly in these sensitivity tests from other ongoing projects (see section 6). For example, Abbott (2019) recently made observations that the flux from carbonate-rich sediment is 12 to 25 pmol cm^2 yr^{-1}; a range that we can adopt globally in these sensitivity tests. We will make the benthic flux magnitude dependent on sedimentation rate, as given in the model by the particulate flux to the sea floor. There is some idea that sediment "freshness" exerts a first-order control over the benthic flux [*Du et al.,* 2016], and this test will reflect a simple means to explore this hypothesis. We will also test the idea that the benthic flux depends on oxygen, similar to the iron flux from sediments [*Dale et al.*, 2015], by scaling the Nd flux to Fe flux that is already in the model.

Another sensitivity experiment will explore origins and uncertainties in the isotopic composition of the benthic flux. In a simplified view, sedimentary Nd originates either from scavenged (authigenic) particles or from lithogenic (dust, river) particles, or some combination of the two. We will do tests to explore the sensitivity of the model to each of these isotopic signatures, which can be quite distinct. That is, a model in which the ε_{Nd} of the benthic flux is set to the ε_{Nd} of scavenged particles will test the hypothesis that sedimentary Nd originates mainly from authigenic particles. This implies strong recycling and a small offset between detrital and bottom water ε_{Nd}. A model in which the ε_{Nd} of the benthic flux is set to the ε_{Nd} of the lithogenic input (dust and rivers) will test the hypothesis that most sedimentary Nd is lithogenic. In this case we expect a larger offset between detrital and bottom water column ε_{Nd}. We stress that our objective with this work is not to provide a mechanism for the benthic flux term – here we are trying to capture the ocean's response to an imposed benthic flux. The best-fit boundary condition information will, however, be very useful to help inform on-going mechanistic studies; for example, if the model is best-fit using a constant-offset ε_{Nd} benthic flux term, this information would be very useful for our geochemical understanding.

To test hypothesis H2, equilibrium simulations with different MOC strengths and geometries will be performed, following Muglia et al. (2018; their Fig. 1). Comparing cross plots of ε_{Nd} vs radiocarbon age with observations (left panel in Fig. 1) will be helpful in evaluating this hypothesis. Finally, we will execute a series of transient experiments in which the AMOC will be changed by application of positive or negative freshwater flux anomalies in the North Atlantic. This will explore the model's time-varying ε_{Nd} response to AMOC changes. This work will be performed in year 3 by the GS, who will also write a paper describing the results of model construction, tuning and sensitivity experiments. AS, BH and collaborator Dr. Jianghui Du (JD; currently postdoctoral researcher at ETH Zürich; see letter of collaboration) will assist in drafting the manuscript. Acceptance and publication in a journal will provide a *measure of success*.

LGM Experiments. To test hypothesis H3 we plan to generate a range of different LGM MOC states by exploring uncertainties in surface (buoyancy and momentum) forcing and interior mixing. This will be accomplished by extending the approach by *Muglia et al.* [2018] and *Wilmes et al.* [2019], who modified southern hemisphere buoyancy forcing and tidal mixing to produce a preliminary set of states in which AMOC depth and strength were strongly correlated. Thus, this set did not include the scenario of a strong and shallow AMOC proposed by *Kurahashi-Nakamura et al.* [2017]. However, recent (yet unpublished) experiments with additional buoyancy forcing in the north Atlantic result in decoupling of AMOC strength and depth, and produce a much larger variety of MOC states including the strong and shallow AMOC case. This strategy will be further explored as part of project 1924215 (see section 6) e.g. by using wind stress fields from different PMIP models. We expect to test about 20 circulation states, with different AMOC strength, depth and other MOC indices such as AABW and CPDW inflow into the Indian and Pacific oceans. All simulations will be run to equilibrium, which for carbon and nitrogen isotopes can take 5,000 years. The model-data comparison will be similar to that for the pre-industrial ocean. However, one difference will be that for the LGM comparison errors in proxy data will be considered. These errors can be estimated from the plot of sea water vs authigenic ε_{Nd} (Fig. 6). We expect to produce figures with two MOC indices (e.g. AMOC depth and strength) as horizontal and vertical axes and contour lines of RMSE for carbon isotopes and ε_{Nd} to illustrate the power of these different proxies to constrain different aspects of the MOC. If the benthic flux hypothesis is valid, we expect ε_{Nd} to provide particularly strong constraints on the abyssal flow such as AABW in the Atlantic and CPDW flow in the Pacific and Indian oceans. Contour plots of normalized RMSEs as a function of AABW and CPDW flows may illustrate crucial constraints provided from ε_{Nd} on abyssal parts of the LGM MOC that carbon isotopes do not constrain well. This work will be performed by the GS in year 3. We expect another paper from this part of the project, which will provide a *measure of success*. Subsequent studies may analyze the effects of the best-fitting model on the carbon cycle and atmospheric CO_2.

We will hold weekly meetings with the graduate student and monthly meetings with the whole team in which Du will participate remotely via skype.

6 Relationship with Other Projects

NSF 1850765: Haley has been and continues to be involved with the GEOTRACES program for measuring global distributions of elemental and isotopic Nd: data that will be used here to inform and test the model. Haley also has a funded project (with McManus at Bigelow and Johannesson at Tulane) to attempt detailed mechanistic studies of the early diagenetic processes that derive Nd fluxes into bottom water. This project will focus on measuring the geochemistry at 4 specific sites of differing sedimentary environment in the Pacific, and there is no overlap of work with this proposal. The two projects are intimately interconnected, however, in that they will inform each other based on their findings. For example, the detailed site-specific pore water study could isolate a particular aspect of the sediment (e.g., grain size or bulk mineralogy) that exerts a first-order influence on the flux magnitude or its isotopic composition. This information could then parlay into the model, where we can "fine-tune" prescribed fluxes. Alternatively, while optimizing boundary conditions in the model, if we find that organic carbon fluxes mirror the benthic fluxes of Nd on a regional scale, we could look at this closer in the sediment geochemistry. We will take all opportunities to integrate and coordinate the findings of these projects, a goal that we plan to facilitate through specified meetings between Schmittner, his student, Du, Haley, McManus and Johannesson (see Budget).

NSF 1924215: Schmittner and Khatiwala's project "NSFGEO-NERC: Quantifying the Modern and Glacial Ocean's Carbon Cycle Including Isotopes", provides synergies with the project proposed here, but there is no overlap of work. Transport matrices will be extracted from the UVic model for different modern and LGM MOCs including configurations featuring strong and shallow LGM AMOCs. These transport matrices will also be used for the project proposed here. Pa/Th will be implemented, which will benefit this project because both of these tracers are particle reactive and subject to scavenging, similar to Nd. Moreover, Pa/Th will provide additional constraints on the LGM MOC. Thus, both projects could provide the first reconstruction of the LGM MOC constrained by 5 complementary proxies ($\delta^{13}C$, $\Delta^{14}C$, $\delta^{15}N$, ε_{Nd} and Pa/Th. See also the letter of collaboration from Dr. Khatiwala.

7 Intellectual Merit

This project will improve understanding of Nd cycling in the ocean. It will test new ideas about its geochemistry such as that of a ubiquitous benthic flux in the deep ocean, the role of carbonate ion complexation, irreversible vs reversible scavenging, relations with iron cycling both for the benthic flux and scavenging on iron oxides, and the impact of nepheloid layers. Constraints of ε_{Nd} on the deep MOC will be evaluated and hypotheses about the LGM MOC will be tested. Thus, this project has the potential to transform our understanding of the geochemistry of Nd cycling in the ocean and our knowledge of the LGM MOC.

8 Broader Impacts

This project serves two distinct oceanographic communities. Firstly, the model will help marine geochemists to better understand trace element and isotopic tracers of processes in the ocean beyond just Nd. A benthic source may affect other rare earths, trace elements and isotopes [*Haley et al.*, 2017]. Fundamentally, the sediments at the sea floor have only very rudimentarily been investigated for trace metals and their isotopes. This work may be the proverbial "tip of the iceberg" for the impact of the sea floor on marine geochemistry. Second, the model can help oceanographers to construct quantitative models of ocean circulation at global scales. This topic also draws interest from scientists outside of oceanography, and from policy makers and other social and economic institutions. UVic/MOBI has a large user community and it is used for many scientific applications including future projections [e.g. *Matthews et al.*, 2009; *Jones et al.*, 2019]. Paleoclimate simulations provide critical model tests, which will be facilitated by implementing a widely used paleoceanographic proxy. A dedicated model description paper, user manual and webinars will make the model more accessible to the broader community including GEOTRACES.

If successful, the model will likely be used in other paleoclimate projects, such as simulations of the last deglaciation [e.g. *Basak et al.*, 2018] or deep-time studies [e.g. *Martin et al.*, 2012]. Our coarse-resolution model study may also enable future research with finer-resolution models using a similar approach. We plan to transfer our Nd code to the new ocean component (MOM6) of the Community Earth System Model (CESM) to facilitate simulations with this popular tool. For this purpose, Schmittner will participate in a CESM meeting in year 3. More generally, this work goes beyond offering a specific model solution, in that adding a reactive sea floor opens a new dimension to model studies.

This project will lead to a new interdisciplinary collaboration between an analytical geochemist (Haley) and a climate modeler (Schmittner). An early-career scientist (Du) and a graduate student will be supported, and undergraduate students will be involved as part of OSU's Research Experiences for Undergraduates program in marine sciences. Involvement of early-career scientists and students in a project that crosses traditional discipline boundaries will provide the next generation of scientists with more diverse skills and understandings. The graduate student will participate in science communication fellowship training organized by the Oregon Museum of Science and Industry (see letter of collaboration). As part of that training the student will develop a hands-on outreach activity related to the project and will present the activity to the public multiple times in the museum. International collaboration will be fostered by building new ties between OSU and ETH and by supporting two large international programs: GEOTRACES and PAGES (Past Global Changes). We will participate in meetings of both programs and write separate workshop proposals to organize a joint GEOTRACES-PAGES workshop in year 3, following up on the successful meeting in 2018 in Aix-Marseille, France. Such a meeting would benefit many early-career scientists and foster diversity by supporting researchers from developing countries and underrepresented groups. Our outreach plan includes to disseminate this work broadly through publications, national and international meetings, by working with the OSU press officer, and through local public events such as regular lab visits offered by Haley. Further dissemination of the ideas and progress of this work will be accomplished through a project website, webinars and interactive on-line activities, including uploading science short videos to YouTube and streaming video interactive visits of the lab.

9 Results from Prior NSF Support

Haley Award: NSF 1357529 "Gulf of Alaska deep and intermediate watermass changes and paleoventilation" 03/01/2014 - 02/28/2017 ($395,359).

Intellectual Merit: This project developed new robust methods for measurement of authigenic ε_{Nd} in sediments of the North Pacific and proposed a reconstruction for the deglacial history of ventilation in the Pacific Ocean. We found that the archived authigenic signal reflects a mix of bottom water and pore water (Du et al., 2016). We then applied our new understanding to core samples from the Gulf of Alaska and generated two high-resolution (century scale) records of authigenic ε_{Nd} spanning the last deglaciation. We compared these records to those of equally high resolution $\Delta^{14}C$ and formulated a 6-box model of the Pacific as an interpretive framework (Du et al., 2018). From these data and model, we inferred acceleration of deep Pacific circulation, from LGM overturning of ~8 Sv, to episodes of fast deglacial overturning reaching ~25 Sv, followed by Holocene relaxation to the modern value of ~14 Sv. The two episodes of acceleration align with times of rapid deglacial CO_2 rise, leading us to infer that accelerated overturning was a primary mechanism for release of CO_2 from the deep Pacific to the atmosphere via the Southern Ocean. Our interpretation posits deglacial acceleration of deep Pacific overturning as a mechanism to release CO_2. This work thus represents a significant contribution to our understanding of using ε_{Nd} as a proxy of circulation, and how changes in circulation may have affected past climate change.

Broader Impacts: This project supported the Ph.D. student Du and technicians Jesse Muratli and June Padman, representing an investment in both young scientists and science infrastructure, as well as including an external collaboration with Dr. Maureen Walczak. Both PIs were be engaged in public outreach activities. For example, Haley consistently participates in the National Ocean Sciences Bowl and hosts undergraduate experiential learning groups in the lab (e.g., REU, GeoBridge), and Mix volunteered as President of The Oceanography Society and as a lead author for IPCC AR6 assessment (WG1, chapter 9: Oceans, Cryosphere, and Sea Level). Both Haley and Mix folded research findings into lesson plans. Data are available at NOAA Paleoclimate and the PANGAEA databases.

Schmittner Award: NSF 1634719; Period: 09/01/2016 to 08/31/2019 (NCE to 08/31/2020); Amount: $497,913; Title: "The Biological Pump During the Last Glacial Maximum and Early Deglaciation"

Intellectual Merit: A new core-top compilation of benthic foraminiferal $\delta^{13}C$ measurements and their calibration to reconstruct $\delta^{13}C_{DIC}$ quantified carbonate ion effects [*Schmittner et al.*, 2017]. Through modeling and paleoceanographic data compilation we have improved understanding of the LGM ocean. We have shown that nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$, $\Delta^{14}C$) isotopes provide complementary constraints on glacial ocean circulation, carbon and nitrogen cycling [*Schmittner and Somes*, 2016; *Somes et al.*, 2017]. We have provided new estimates of the LGM's AMOC and iron fertilization [*Muglia et al.*, 2017; *Muglia et al.*, 2018]. A new, precise and complete method to quantify the ocean's carbon cycle has been developed and applied to the LGM with surprising new results such as a much larger role for temperature changes than previously thought [*Khatiwala et al.*, 2019].

Broader Impacts: The new core-top calibration will be useful for the broader paleocanographic community. International collaboration has been fostered through the PAGES working group OC3. OC3 has held 3 successful meetings: one in Corvallis, Oregon in 2017, one in Cambridge, UK in 2018, and one in San Francisco in 2019, produced compilations of core-top $\delta^{13}C$ data and two publications [*Schmittner et al.*, 2017; *Sikes et al.*, 2017] and is currently generating a new innovative and comprehensive database of down-core $\delta^{13}C$ data. Those meetings supported many early career- and developing country scientists. The project supported the PhD and postdoctoral work of Juan Muglia and two undergraduate students. Data and code are available on NOAA Paleoclimate and on github, respectively.