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A RECONSTRUCTION OF $\delta^{15}\text{N}$ OF DEEP OCEAN NITRATE IN THE
PAST USING PORE FLUID

BY

ANNE M. HARTWELL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

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IN

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MASTER OF SCIENCE THESIS

OF

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2013

Abstract

Dissolved nitrogen in the water column is an essential nutrient and its distribution is linked to the cycling of carbon, phosphorus, and oxygen. The mean isotopic composition of nitrate ($\delta^{15}\text{N}_{\text{global}}$) is nearly uniform in the homogeneous deep ocean and appears to reflect the dominant nitrate removal processes. As a result, it is directly related to the absolute inventory of available nitrogen (Sigman et al., 1999; Brandes and Devol 2002). Constraining whether the isotopic composition of deep water nitrate has varied in time will allow examination of variations in the relative magnitude of removal processes and how climate may control them. A limitation to understanding these changes is the lack of direct or proxy measurements of $\delta^{15}\text{N}$ of deep ocean nitrate in the past. This thesis represents an attempted reconstruction of the mean nitrogen isotopic composition of the deep ocean using nitrogen (N) and oxygen (O) isotope values measured on dissolved nitrate in sedimentary porefluid from two sites in the North Pacific Gyre. The measured pore fluid profiles were corrected for *in situ* nitrate production. A $>1.5\text{‰}$ decrease in $\delta^{15}\text{N}$ values and a $>2\text{‰}$ shift in $\delta^{18}\text{O}$ values were observed. These are lower limit estimates because of the dampening effects of diffusion. The reconstructed profiles are compared with predicted diffusive profiles of a measured sedimentary $\delta^{15}\text{N}$ record and a modeled estimate of $\delta^{15}\text{N}_{\text{global}}$, output from a 1-D time dependent diffusion analysis. The comparison suggests that local processes are most likely responsible for such a large shift in $\delta^{15}\text{N}$. The porefluid profiles record changes in deep ocean nitrate in the deep North Pacific Ocean since the LGM. A possible driving mechanism for this change is the occurrence of water

column denitrification in the deep waters of the North Pacific. Additional explanations include an enhanced transfer of surface/IW N isotopic signal via organic matter export since the LGM, or an elevated $\delta^{15}\text{N}$ of preformed nitrate transferred from the surface ocean to the Pacific interior, although neither mechanism satisfactorily describes the concurrent $\delta^{18}\text{O}$ shift. Understanding the changes observed in these porefluid records could lead to a deepened understanding of the relationship between large scale climate change (glacial/interglacial transitions) and the nitrogen cycle, as well as the role they play in carbon storage in the deep ocean and sequestration at the surface. Improvements would come from a more tightly constrained, higher resolution data record, particularly in terms of the oxygen isotopes of relict nitrate. As well as from increased knowledge of isotopic changes in organic poor, deep, slow sedimentation rate sediments, and comparison with samples from similar sites.

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Introduction

Nitrogen is an essential nutrient and its distribution in the water column is linked to the cycling of carbon, phosphorus, and oxygen. The lack of available nitrate, the most abundant form of fixed nitrogen, in the euphotic zone limits primary production in many regions of the ocean (Redfield, 1963; Altabet and Curry, 1989; Tyrell, 1999). The primary source of dissolved nitrogen to the ocean is biological N-fixation (140 Tg N per year) and minor sources are riverine input and atmospheric deposition. Dissolved nitrogen exists as inorganic ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-), as well as dissolved organic substances such as urea and amino acids. Nitrogen is assimilated into organic matter (OM) in the surface ocean and is either remineralized back to inorganic species in the water column or buried in the sediment (Figure 1) (Altabet and Francois, 1994). Nitrate, utilized as an electron acceptor (denitrification), returns N to the atmosphere as either $\text{N}_2(\text{g})$ or $\text{N}_2\text{O}(\text{g})$ (Cline and Kaplan, 1975). The conversion of nitrogen between species and phases is reflected in the nitrogen isotopic composition ($\delta^{15}\text{N}$) of the various N species.

The utilization and cycling of nitrogen between chemical species and phases causes the nitrogen isotopic ratio ($R = ^{15}\text{N}/^{14}\text{N}$) to change as the result of isotopic fractionations that discriminate against the heavy isotopes during enzymatically mediated reactions. The magnitude of fractionation between two species (A and B) is represented by an isotope fractionation factor ($\alpha_{\text{A-B}} = R_{\text{A}}/R_{\text{B}}$), more commonly represented in permil notation as an isotope effect ($\epsilon = (\alpha_{\text{A-B}} - 1) * 1000$). The isotopic ratio of a single species is expressed as a delta value ($\delta^{15}\text{N} = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$) with respect to a reference standard (R_{standard}), atmospheric N_2 for nitrogen, and an

ocean water standard VSMOW (Vienna Standard Mean Ocean Water) for oxygen.

The delta value of a product species is a function of the isotopic composition of the source chemical species and the fractionation associated with the reaction (Lui and Kaplan, 1989).

Figure 1: Schematic diagram of nitrogen cycling between the atmosphere and within the ocean. The figure illustrates cycling processes that occur in oxic environment (assimilation, remineralization, and nitrification) and in anoxic environments (denitrification); Nitrogen fixation occurs in the surface ocean where nitrogen supply is low and nitrogen fixing cyanobacteria are present. The arrows indicate the direction of reaction and typical cycling path of different species. Isotopic effects (ϵ) are shown for N-fixation, nitrification, water column denitrification, and sedimentary denitrification.

Statement of problem

From a global perspective, the $\delta^{15}\text{N}$ of nitrate in the deep ocean is relatively uniform (Lui and Kaplan, 1989; Sigman *et al.*, 1999). The mean steady state isotopic composition of deep ocean nitrate ($\delta^{15}\text{N}_{\text{global}}$) is controlled by a balance between inventory altering processes, biological N-fixation and denitrification, and has the potential to be a useful paleoceanographic tracer of changes in the global nitrogen cycle (Altabet and Curry, 1989; Altabet and Francois, 1994; Brandes and Devol, 2002).

Biological N-fixation in the surface of the tropical oceans accounts for the majority of the nitrogen input; it introduces newly fixed nitrogen with $\delta^{15}\text{N}$ values between 0 and -3‰, with only a small fractionation ($\epsilon = 1.7\text{‰}$) from the large atmospheric N_2 reservoir with a $\delta^{15}\text{N}$ of 0‰ (Hoering and Ford, 1960; Bauersachs *et al.*, 2009). Considering N-fixation as the primary source of nitrogen to the open ocean simplifies $\delta^{15}\text{N}_{\text{global}}$ to being a function of the ratio between water column (pelagic) and sedimentary (benthic) denitrification (Brandes and Devol, 2002; Deutsch *et al.*, 2004).

Denitrification in oxygen minimum zones in the Eastern Tropical Pacific and the Arabian Sea (OMZ; $[\text{O}_2] < 5\mu\text{M}$), and in shallow, anoxic sediment is the major pathway of nitrogen loss (Cline and Kaplan, 1975; Christensen *et al.*, 1987). Water column denitrification ($\epsilon = 20\text{‰}$ to 30‰) leaves residual nitrate enriched in ^{15}N (Cline and Kaplan, 1975; Altabet and Francois, 1994; Brandes and Devol, 1998; Bardford *et al.*, 1999). The effect of isotopic fractionation during sedimentary denitrification is less clearly understood. Within sediment, the fractionation due to denitrification is of

the same magnitude as when it occurs in the water column (Sigman *et al.*, 2001; Lehmann *et al.*, 2007). However, diffusive limitation and near complete consumption of sedimentary nitrate hampers exchange of residual nitrate with overlying water (Brandes and Devol, 1997; Lehmann *et al.*, 2004), resulting in an apparent net isotope effect of sedimentary denitrification between 1‰ and 3.5‰ (Brandes and Devol, 2002; Lehmann *et al.*, 2004; Granger *et al.*, 2011). The influence of the nitrate flux out of the sediment on $\delta^{15}\text{N}_{\text{global}}$ is small relative to the observed isotopic shift *in-situ* (Brandes and Devol, 2002; Lehmann *et al.*, 2004; Deutsch *et al.*, 2004). The relative contribution of water column and sedimentary denitrification to total denitrification is not easily directly measurable; however it may be calculated from measured $\delta^{15}\text{N}_{\text{global}}$ and the isotopic balance.

$$\delta^{15}\text{N}_{\text{global}} = \epsilon_{\text{N-fixation}} + (f * \epsilon_{\text{water column denitrification}} + (1-f) * \epsilon_{\text{sedimentary denitrification}});$$

$$f = (\delta^{15}\text{N}_{\text{global}} - \epsilon_{\text{N-fixation}} - \epsilon_{\text{sedimentary denitrification}}) / (\epsilon_{\text{water column denitrification}} - \epsilon_{\text{sedimentary denitrification}})$$

Using the present day $\delta^{15}\text{N}_{\text{global}}$ value of $5.0 \pm 0.5\text{‰}$ (Cline and Kaplan, 1975) the contributions of nitrogen loss by water column and sedimentary denitrification in the modern marine system are around 20% and 80%, respectively assuming $\epsilon_{\text{N-fixation}}$ is 0.0‰, $\epsilon_{\text{sedimentary denitrification}}$ is 0.0‰ and $\epsilon_{\text{water column denitrification}}$ is 25.0‰, in accordance with a steady state box model published by Sigman *et al.*, (2009). One way to assess changes in this balance is to monitor changes in the mean value with time (Brandes and Devol, 2002).

Sediment profiles of particulate organic matter (POM) N isotopic composition ($\delta^{15}\text{N}_{\text{sediment}}$) provide evidence of regional variability of denitrification (Figure 2)

(Altabet *et al.*, 1995; Altabet *et al.*, 2002; Gruber and Galloway 2008; Galbraith *et al.*, 2008; Sigman *et al.*, 2009). $\delta^{15}\text{N}_{\text{sediment}}$ values record changes in OMZ denitrification because nitrate impacted by denitrification spreads via diffusion and advection to the surrounding ocean interior. When the impacted nitrate is upwelled, the signal is transferred to the surface and becomes assimilated into OM export. The greater the degree of denitrification occurring, the higher the delta value expected. Sedimentary records from within and near OMZs record isotopically light $\delta^{15}\text{N}$ values during glacial periods compared to isotopically heavy $\delta^{15}\text{N}$ during the last glacial termination (Altabet *et al.*, 2002, Ganeshram *et al.*, 2000, De Pol-Holz *et al.*, 2010). These records imply strong, climate driven controls on the extent of low oxygen zones globally with a reduction in denitrification, and likely in the intensity of the OMZs globally (Christensen *et al.*, 1987; Brandes and Devol, 1998; Sigman *et al.* 2009). The signal is relatively widespread and coherent globally; mixing and advection has a tendency to spread regional signals $\delta^{15}\text{N}_{\text{nitrate}}$ of active water column denitrification (Jaccard and Galbraith, 2011), with the potential to impact the deep ocean through the biological pump.

Sedimentary denitrification is assumed to have varied with climate as well. This is due to sea level and oceanic export production changes (Christensen *et al.*, 1987). The rise and fall of sea level with the formation and succession of land ice directly changes the volume of anoxic sediments available for sedimentary denitrification to take place. During the LGM, when land ice was at a maximum, sedimentary denitrification was restricted to the reduced shelf area.

Galbraith *et al.*, (2013) present a mean ocean approximation of nitrate $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_{\text{Gal-global}}$) by using flux weighted $\delta^{15}\text{N}_{\text{export}}$ values from their defined provinces. In an ocean that is perfectly mixed in terms of N isotopes, it is expected that $\delta^{15}\text{N}_{\text{export}}$ is equal to $\delta^{15}\text{N}_{\text{mean}}$; however, the heterogeneous distribution of N isotopes in the modern ocean causes $\delta^{15}\text{N}_{\text{export}}$ to deviate from $\delta^{15}\text{N}_{\text{Gal-global}}$. Province-based estimates of $\delta^{15}\text{N}_{\text{seafloor}}$ were weighted with satellite-derived estimates of export production within each province to estimate $\delta^{15}\text{N}_{\text{export}}$. A Monte Carlo estimate of $\delta^{15}\text{N}_{\text{export}}$ from a two-box model with a range of N-fixation, denitrification, terrigenous N-supply, and utilization, were compared with simulations of ocean-biogeochemistry models. The result is a $\delta^{15}\text{N}_{\text{Gal-global}}$ (Figure 3) curve. The modeled record reveals minimal variability of nitrate $\delta^{15}\text{N}_{\text{Gal-global}}$ from the LGM to the Holocene, with the exception of a small but significant peak during the mid-deglaciation. This suggests that there was a nearly constant ratio of pelagic to benthic denitrification in the global ocean and argues against large changes in the concentration of dissolved nitrate through time.

Figure 2: Downcore sedimentary $\delta^{15}\text{N}$ records from the major OMZs over the last 70 kya. Green- Arabian Sea: RC27-23 depth 829m (Altabet *et al.*, 2002); Red- ETNP: CD38-02 depth 2525m (Ganeshram *et al.*, 2000); Black- ETSP, GeoB 7139-2 depth 3267m (De Pol-Holz *et al.*, 2010).

Figure 3: Galbraith *et al.*, (2013) 30-kyr-model estimate of mean ocean nitrate isotopic composition ($\delta^{15}\text{N}_{\text{Gal-global}}$). The model reveals little variability in the $\delta^{15}\text{N}_{\text{Gal-global}}$ value with only a small but significant peak observed during the mid-deglaciation.

Additional evidence for changes in marine denitrification during glacial/interglacial transitions comes from fluctuations in atmospheric N₂O from ice core records (Flückiger *et al.*, 2002). Large increases (~50 ppb) of N₂O during interglacial periods are correlated with variation in temperature, atmospheric CO₂, and $\delta^{15}\text{N}_{\text{sediment}}$ (Gruber and Galloway, 2008).

Currently there is no directly measured record of the $\delta^{15}\text{N}_{\text{global}}$ value before present day. Here, I measure a record of past $\delta^{15}\text{N}_{\text{global}}$ using N and O isotopes in nitrate from a unique set of sediment pore fluid samples. The residence time of nitrogen in the ocean, 2- 3 kyr, is short, such that significant changes imposed in the nitrogen cycle since the LGM can cause changes in $\delta^{15}\text{N}_{\text{global}}$ (Deutsch *et al.*, 2004; Gruber and Galloway, 2008). If the $\delta^{15}\text{N}$ value of bottom water nitrate has changed since the LGM, these changes should be reflected in $\delta^{15}\text{N}$ record of relict nitrate in pore fluid. Measurements corrected for *in situ* nitrification, nitrogen produced by respiration of organic nitrogen, are compared to the predicted profiles of $\delta^{15}\text{N}$ time series from sediment to investigate possible controls of the observations. The predicted profiles are calculated using a time-dependent diffusion model from Lado-Insua *et al.*, (*submitted*).

Oceanographic setting

Pore fluid samples were extracted from sediment cores recovered on R/V Knorr cruise 195, during January-February of 2009 at two sites in the North Pacific Gyre (Figure 4). The two sites, EQP 10, located at 20°41' N, 143°21' W, in 5410 m water depth and EQP 11, located at 30°21' N, 157°52' W, in 5819 m water were selected because they contained measureable oxygen throughout the sediment column.

Bottom water in the Pacific is ventilated by lower circumpolar deep water (LCDW), a well-mixed source of NADW (North Atlantic Deep Water) and AABW (Antarctic Bottom Water) (Talley *et al.*, 2011). The Pacific represents roughly half of the global oceans and has a ^{14}C age near 1,000 years (Stuiver, *et al.*, 1983). The temperature and salinity are relatively homogenous, however the transition between the glacial and interglacial climate state are correlated with changes in the average values. Since the LGM the bottom water mean salinity has shifted from ~ 35.9 mg/kg to 34.7mg/kg and mean potential temperature has increased by 3°C to modern day temperature of 1.6°C (Adkins *et al.*, 2002; Antonov, 2010). Modern deep Pacific nitrate concentration is $35\mu\text{M}$: $22\mu\text{M}$ is preformed (fraction of unutilized nitrate that are subducted into the interior of the ocean when thermocline and deep waters are newly formed) and the remainder is regenerated (fraction of nitrate added during transport from remineralization by respiration) (Ito and Follows, 2005). Available evidence suggests no change in the concentration of preformed nitrate since the LGM (Spivack *et al.*, *in review*).

Biological production in the upper water column of the oligotrophic gyre location is $5\text{-}10\text{ gC/m}^2\text{yr}^{-1}$, and as a result there is relatively little organic matter sedimentation in this environment where sedimentation accumulation is $\sim 0.2\text{ cm/kyr}$ (Fischer *et al.*, 2009). Pore fluids contain a record of bottom water concentrations dispersed by diffusion (McDuff, 1984; Adkins and Schrag, 2003; Spivack *et al.*, *in review*). Diffusion length varies with the square root of time, thus deeper fluids reflect the composition of older bottom water.

Figure 4: A bathymetric map of the study area with the two sites, EQP 10 (20°41' N, 143°21' W, depth: 5410 m) and EQP 11 (30°21' N, 157°52' W, depth: 5819 m), marked with triangles.

Methods

Shipboard Methods

Samples from multiple core types collected at each site were used. At EQP 10 the profiles were developed from gravity core and long core samples (WHOI: Long Core, 2007). At EQP 11, gravity core, long core, and multi-core samples were obtained. Pore fluids were extracted using Rhizon[™] samplers and stored in 4 mL plastic vials in -80 °C. Dissolved nitrate concentrations were measured shipboard by UV absorbance detection by ion-chromatography. Dissolved oxygen concentrations were determined with needle-shaped optical O₂ sensors (PreSens Precision Sensing GmbH, Regensburg, Germany) (Røy *et al.*, 2012). A pertinent feature of the dissolved down core oxygen data is that the concentrations remained above the suboxic limit of 5µM [O₂] at both Sites 10 and 11.

Pore fluid is not coeval with sediment age. Chlorinity is used here as a proxy for the magnitude of the LGM signal represented in the samples. Chlorinity increases with depth as expected, reflecting the diffusion of low salinity interglacial water into higher salinity relict water at depth. An increase in chloride concentration with depth to >99% of the LGM value expected (Adkins and Schrag, 2003) is observed at 26.6 and 27.7 mbsf for EQP 10 and EQP 11, respectively (Lado-Insua *et al.*, (submitted) (Figure 5).

Figure 5: Modeled chlorinity (mM/L) with depth Lado-Insua *et al.*, (*submitted*) is a proxy for the percent of LGM signal captured in the deepest samples at EQP 10 and EQP 11. The LGM is at 46 mbsf where chlorinity is at its peak (561.811 mM/L). The deepest sample depths and the corresponding chlorinity at site EQP 10 and EQP 11 are 26.57mbsf and 651.085 mM/L, and 27.65 mbsf and 561.172 mM/L, respectively. At EQP 10 and EQP 11 99.87% and 99.89% of the LGM signal is captured, respectively.

Analytical Methods

Pore water nitrate was converted to N_2O (g) and analyzed by Gas Chromatography- Isotope Ratio Mass Spectrometry (GC-IRMS) using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). Denitrifying bacteria that lack the enzyme nitrous oxide reductase, convert nitrate to N_2O . Bacterium *Pseudomonas aureofaciens* (*P. aur*) was used for analysis of oxygen isotopes and *Pseudomonas chlororaphis* (*P. chlor*) was used for analysis of nitrogen isotopes in nitrate. Concentrated bacteria in a solution of media and 35‰ sodium chloride (2:1) and ~1mM ammonium sulfate, which provides nitrogen for assimilation, were distributed into acid and combustion cleaned glass vials, crimp sealed with butyl rubber stoppers, and purged with helium gas for 5-6 hours. Samples of nitrate were injected into the purged vials with a target of 10nmol for *P. chlor* and *P. aur*, and left upside down for 8-12 hours before being killed with 10M sodium hydroxide. Samples were measured by GC-IRMS with an automated purge and trap system in the Robinson Lab at the University of Rhode Island, Graduate School of Oceanography. Samples were standardized to KNO_3^- reference materials with known $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, IAEA-N3 ($\delta^{15}\text{N}=+4.7\text{‰}$, $\delta^{18}\text{O}=+25.6\text{‰}$), USGS 32 ($\delta^{15}\text{N}=+180.0\text{‰}$, $\delta^{18}\text{O}=+25.7\text{‰}$), and USGS 34 ($\delta^{15}\text{N}=-1.8\text{‰}$, $\delta^{18}\text{O}=-27.9\text{‰}$). Instrumental analytical precision was determined based on replicate analyses of IAEA-N3 standards, and an in-house seawater mixture of EQP bottom water. Standard deviations were $\pm 0.3\text{‰}$ and 0.5‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. The reproducibility of samples, based on standard deviations of sample replicates was on average 0.5‰ for $\delta^{15}\text{N}$ and 0.6‰ for $\delta^{18}\text{O}$; both values were greater than the analytical error. The origin of the precision loss is

likely related to sample handling, perhaps sample degradation during storage (samples were measured over span of 2 years) or insufficient mixing after thawing. Downcore sediment N isotopic compositions ($\delta^{15}\text{N}_{\text{sed}}$) were also available; bulk measurements were made by EA-IRMS (Elemental Analysis Isotope Ratio Mass Spectrometry) in the Robinson Lab at URI.

Results

Profiles of N and O isotopic compositions of dissolved nitrate in pore fluid ($\delta^{15}\text{N}_{\text{measured}}$, $\delta^{18}\text{O}_{\text{measured}}$) are similar at the two sites (Figure 6). Both N and O isotopic compositions at EQP 10 and EQP 11 increase with sample depth. Contrary to the expected smoothed profile from diffusion all measured profiles have a noticeable degree of scatter, the majority of it occurring in the top and bottom meters.

Significant outliers are removed from the data profile if they differ ($\pm$) by two or more standard deviations from the mean of all measured values; outliers are removed from data figures herein. The cause of the scatter is unclear, as it is not associated with core section breaks or analysis dates, for example, at EQP 11 $\delta^{15}\text{N}_{\text{measured}}$ appears to be systematically jumping from values around 6.2‰ to values of 6.9‰ episodically below five meters. Therefore it is likely a sampling handling artifact or contamination.

The smoothed trends from the LOWESS function (locally weighted scatter plot smoothing; solid lines), and measured data (solid circles) are illustrated in figure 5 in red and blue for EQP 10 and EQP 11, respectively. At both sites the greatest ranges of measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are in the top meter: 5.2‰ to 6.5‰ at EQP 10 and 4.3‰ to 6.2‰ at EQP 11 for $\delta^{15}\text{N}$; 1.0‰ to 3.0‰ at EQP 10 and 1.8‰ to 3.3‰ at EQP 11 for $\delta^{18}\text{O}$. Values in the top 0.7 meters, and bottom 2.5 meters of each profile were averaged. EQP 10 $\delta^{15}\text{N}_{\text{measured}}$ ranges from an average of 5.2‰ in the top 0.7 m depth to an average of 7.7‰ in the bottom 2.5 m, an approximate change of 2.5‰ down core. EQP 11 $\delta^{15}\text{N}_{\text{measured}}$ ranges from an average of 5.9‰ in the top 0.7 m to an average of 7.0 ‰ in the bottom 2.5 m, an approximate increase of 1.1‰ down core. EQP 10 the average value in the top 0.7 m is 1.9‰ compared to average of 4.5‰ in

the bottom 2.5 meters for a total shift of 2.6‰. EQP 11 $\delta^{18}\text{O}_{\text{measured}}$ has a 2.4‰ increase from 2.6‰ in the top 0.7 m to 4.0‰ in the bottom 2.5 m. Both $\delta^{15}\text{N}_{\text{measured}}$ and $\delta^{18}\text{O}_{\text{measured}}$ at EQP 10 and EQP 11 increase with depth.

Figure 6: Measured N and O isotopic compositions ($\delta^{15}\text{N}_{\text{measured}}$, $\delta^{18}\text{O}_{\text{measured}}$) down core for EQP 10 (red) and EQP 11 (blue). Left: Overlain profiles of $\delta^{15}\text{N}_{\text{measured}}$ (closed circles) from EQP 10 and EQP 11. Right: Overlain profiles of $\delta^{18}\text{O}_{\text{measured}}$ from EQP 10 and EQP 11. Solid lines are smoothed trends from the LOWESS function. Outliers (open squares) are identified as $\geq 2\sigma$ away from the mean of all measured data, are retired from further analysis.

Discussion:

Correction for in-situ nitrate production

Several observations from available down core data at EQP 10 and EQP 11 suggest that the pore fluid nitrate concentrations, $\delta^{18}\text{O}_{\text{measured}}$, and $\delta^{15}\text{N}_{\text{measured}}$ are a mixture of two sources: relict nitrate and a sediment regenerated nitrate, where relict nitrate is the total nitrate in the bottom water before diffusion.

$$[\text{NO}_3^-]_{\text{measured}} = [\text{NO}_3^-]_{\text{produced}} + [\text{NO}_3^-]_{\text{relict}}$$

The presence of a curved oxygen concentration profile along with the linear correlation between nitrate and oxygen are evidence for *in-situ* nitrate production (sediment regenerated nitrate). In addition, nitrate throughout the sediment column, coupled with the absence of ammonium and nitrite indicates that any ammonium released during organic matter respiration was completely oxidized to nitrate. In addition, the natural log of the nitrate concentration plotted against $\delta^{15}\text{N}_{\text{measured}}$ is not linear (Figure 7), indicating a system with more than two end members (Mariotti *et al.*, 1988; Kendall, 1998), possibly an affect from *in-situ* nitrate production.

In order to determine the extent to which *in-situ* reactions alter nitrate concentration in the pore fluid, the amount of regenerated nitrate must be determined. The correction is based on the assumption that the release of nutrients during organic matter respiration is in constant proportion to oxygen consumption. The concentration of regenerated nitrate produced is calculated using the concentration of oxygen consumed and a modified version of the Redfield ratio (atomic ratio of carbon, nitrogen, and phosphorus found in phytoplankton and through out the deep oceans),

^{16}N : -170 O_2 (Anderson and Sarmiento, 1994). Dissolved oxygen concentrations are interpolated from measured $[\text{O}_2]$ to account for the lack of measurements of dissolved oxygen and nitrate concentrations at corresponding depths.

$$[\text{NO}_3^-]_{\text{produced}} = ([\text{O}_2]_x - [\text{O}_2]_0) * (16/-170)$$

Concentrations of relict nitrate are calculated by subtracting the concentration of nitrate produced in the sediment from the measured nitrate concentration (Figures 8 and 9):

$$[\text{NO}_3^-]_{\text{relict}} = [\text{NO}_3^-]_{\text{measured}} - [\text{NO}_3^-]_{\text{produced}}$$

Similar to the measured nitrate concentrations, $\delta^{15}\text{N}_{\text{measured}}$ and $\delta^{18}\text{O}_{\text{measured}}$ are also mixture of the isotopic compositions of sediment-regenerated nitrate ($\delta^{15}\text{N}_{\text{produced}}$, $\delta^{18}\text{O}_{\text{produced}}$) and those of relict nitrate ($\delta^{15}\text{N}_{\text{relict}}$, $\delta^{18}\text{O}_{\text{relict}}$). Mass balance constraints can be used to correct for the effect of sediment-regenerated nitrate on the pore fluid the N and O isotopic compositions. The relative isotopic composition a pool contributes to the measured value is a function of the weighted nitrate concentration (x) and isotopic composition specific to that pool.

$$\delta^{15}\text{N}_{\text{measured}} = \delta^{15}\text{N}_{\text{produced}} * f + \delta^{15}\text{N}_{\text{relict}} * (1-x)$$

$$\delta^{18}\text{O}_{\text{measured}} = \delta^{18}\text{O}_{\text{BW}} * \epsilon_{\text{nitrification}} * f + \delta^{18}\text{O}_{\text{relict}} * (1-x)$$

$$x = [\text{NO}_3^-]_{\text{produced}} / [\text{NO}_3^-]_{\text{measured}}$$

The equation can be rearranged to isolate $\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$:

$$\delta^{15}\text{N}_{\text{relict}} = (\delta^{15}\text{N}_{\text{measured}} - \delta^{15}\text{N}_{\text{produced}} * x) / (1-x)$$

$$\delta^{18}\text{O}_{\text{relict}} = (\delta^{18}\text{O}_{\text{measured}} - \delta^{18}\text{O}_{\text{BW}} * \epsilon_{\text{nitrification}} * x) / (1-x)$$

Values of $\delta^{15}\text{N}_{\text{produced}}$ are assumed to be the same as bulk sedimentary $\delta^{15}\text{N}$ values ($\delta^{15}\text{N}_{\text{sed}}$) measured in each core (Mariotti *et al.*, 1981). It is also assumed that

organic matter remineralization is the sole source of ammonium, and that oxidation of that ammonium to nitrate comprises the entirety of the produced nitrate. The effect of fractionation during nitrification on produced nitrate is negligible because nitrification is complete and occurs prior to significant diffusion transport. A potential complication to the assumed relationship between $\delta^{15}\text{N}_{\text{produced}}$ and $\delta^{15}\text{N}_{\text{sed}}$ is that there is evidence of alteration of $\delta^{15}\text{N}_{\text{sed}}$ near the sediment water interface in areas of low organic matter flux with enrichment of ^{15}N as high as 6‰ (Brandes and Devol, 2002; Robinson *et al.*, 2012). If this alteration has occurred in the sediment used for this study than the relationship between $\delta^{15}\text{N}_{\text{produced}}$ and $\delta^{15}\text{N}_{\text{sed}}$ deeper in the core will differ from that of the nitrate and sediment N near the top of the core. In addition to diagenesis, nitrate produced deeper in the core may have a different $\delta^{15}\text{N}_{\text{produced}}$ than when produced towards the core top if $\delta^{15}\text{N}_{\text{sed}}$ varied in the past. This can be accounted for using downcore $\delta^{15}\text{N}_{\text{sed}}$ if local alteration is temporally constant. To test the sensitivity of a $\delta^{15}\text{N}_{\text{relict}}$ to the values used for $\delta^{15}\text{N}_{\text{produced}}$, three corrections were compared, each assigning a unique value for $\delta^{15}\text{N}_{\text{sed}}$. In case 1 $\delta^{15}\text{N}_{\text{sed}}$ is constant and assigned the value of the measured $\delta^{15}\text{N}_{\text{sed}}$ at the sediment water interface (0 mbsf) (EQP 10: $\delta^{15}\text{N}_{\text{sed}} = 7.8\text{‰}$; EQP 11: $\delta^{15}\text{N}_{\text{sed}} = 5.6\text{‰}$). Case 1 assumes that all nitrate produced in the pore fluid is at the very top of the core. In case 2 $\delta^{15}\text{N}_{\text{sed}}$ is a constant value representing the average measured $\delta^{15}\text{N}_{\text{sed}}$ in the top 10 meters of the core (EQP10: $\delta^{15}\text{N}_{\text{sed}} = 7.8\text{‰}$; EQP11: $\delta^{15}\text{N}_{\text{sed}} = 5.5\text{‰}$). Case 2 assumes that nitrate production is limited to the top 10 meters of the core. In case 3 $\delta^{15}\text{N}_{\text{sed}}$ is not constant. Downcore $\delta^{15}\text{N}_{\text{sed}}$ is interpolated from a linear regression of all measured $\delta^{15}\text{N}_{\text{sed}}$ data (Table A.7-A.10). Case 3 assumes that nitrate is produced throughout the

core such that newly produced nitrate will acquire $\delta^{15}\text{N}_{\text{sed}}$ of a specific depth interval. The $\delta^{15}\text{N}_{\text{produced}}$ used for the correction of $\delta^{15}\text{N}_{\text{measured}}$ at depth is determined by weighting the contribution of produced nitrate at all depth intervals above a given depth:

$$1 * \delta^{15}\text{N}_{\text{produced from 0 to } x} = \delta^{15}\text{N}_{\text{produced 0 to } x-1} * (w) + \delta^{15}\text{N}_{\text{produced } x-1 \text{ to } x} * (1-w)$$

$$w = [\text{NO}_3^-]_{\text{produced 0 to } x-1} / [\text{NO}_3^-]_{\text{produced 0 to } x}$$

The controls on the nitrate O isotopic composition are more complicated than N isotopic composition: first, $\delta^{18}\text{O}_{\text{produced}}$ reflects the source of oxygen for nitrification, which is either ambient seawater or dissolved oxygen, although it is usually sea water; second, $\delta^{18}\text{O}_{\text{ambient}}$ varies with sea level and temperature; third, assigning an age to porefluid is essentially not-possible so there is no way to determine the appropriate $\delta^{18}\text{O}_{\text{ambient}}$ value to use for a given sample depth in case 3. The oxygen reacted with ammonium to yield nitrate in the process of nitrification is either sourced from dissolved O_2 or H_2O , which have differing $\delta^{18}\text{O}$ values. Dissolved oxygen typically has a $\delta^{18}\text{O}_{\text{oxygen}} > 20\text{‰}$; the value varies as a result of fractionation during respiration in the oceans interior. For ambient sea water the $\delta^{18}\text{O}$ is usually low (0-2‰); variability in $\delta^{18}\text{O}_{\text{ambient}}$ is observed over glacial-interglacial cycling with the expansion and contraction of sea ice with a lower $\delta^{18}\text{O}$ (Sigman *et al.*, 2009 and references within). The incorporation of more O atoms from O_2 rather than from H_2O will drive $\delta^{18}\text{O}_{\text{nitrate}}$ to higher values.

Assuming that $\delta^{18}\text{O}_{\text{BW}}$ represents $\delta^{18}\text{O}_{\text{ambient}}$, the sensitivity of $\delta^{18}\text{O}_{\text{relict}}$ to $\delta^{18}\text{O}_{\text{BW}}$ was tested with a similar approach as case 1, 2, and 3. For case 1 and 2 the value used to represent $\delta^{18}\text{O}_{\text{ambient}}$ is -0.7‰, (interpolated from Lea *et al.*, 2002). Case

3, although poorly constrained and with uncertainty, was accomplished by assuming the time passed for a sample to diffuse to depth was approximately how long ago it was at the sediment-water interface; the $\delta^{18}\text{O}_{\text{ambient}}$ at my best estimate of corresponding age, interpolated from Lea *et al.*, (2002), was assigned as $\delta^{18}\text{O}_{\text{BW}}$ for that sample.

$$1 * \delta^{18}\text{O}_{\text{produced from 0 to } x} = \delta^{18}\text{O}_{\text{produced 0 to } x-1} * (w) + \delta^{18}\text{O}_{\text{produced } x-1 \text{ to } x} * (1-w)$$

Evidence that the eliminated the additional end member (sediment regenerated nitrate) is that the log of the relict concentration plotted against the $\delta^{15}\text{N}_{\text{relict}}$ values is linear (Figure 10). The difference between the results of the correction cases for EQP 10 and 11 for both N and O isotopes (Figures 11-14) was less than the precision of measurements. For case 1 and case 2 the value of $\delta^{15}\text{N}_{\text{sed}}$ at 0 mbsf is the same of the average value in the top 10 mbsf. None of the cases imposed any significant alteration to shape of the measured profiles. The magnitude of correction is a function of the fraction of produced nitrate above a given depth; the corrections are greater when the fraction of nitrate produced (f) increases. The direction of change, to a higher or lower value is a function of the magnitude of the value assigned as $\delta^{15}\text{N}_{\text{sed}}$ relative to $\delta^{15}\text{N}_{\text{measured}}$. At EQP 10 measured values are less than $\delta^{15}\text{N}_{\text{sed}}$ and therefore corrected to lower values. At EQP 11 the value assigned for $\delta^{15}\text{N}_{\text{sed}}$ are less/equal to the measured values only in the top few meters; most of the relict values are calculated as being higher than $\delta^{15}\text{N}_{\text{measured}}$. For further analysis a single case, case 2, was chosen (Figure 15). Case 2 was chosen because it averages the top 10 mbsf of the core, which is where the greatest change of oxygen and nitrate occur, indicating the site of most reactivity.

Figure 7: Natural log of measured nitrate concentration against $\delta^{15}\text{N}_{\text{measured}}$ at EQP 10 (left, solid circles) and EQP 11 (right, open circles). Both plots show significant curvature indicating a system with more than two end members.

Figure 8: Downcore profiles of $[O_2]$ and $[NO_3^-]$ with calculated concentration of nitrate produced down core during nitrification and estimated relict concentrations of nitrate at EQP 10. The $[O_2]$ profile is the interpolated dissolved oxygen concentrations derived from measured concentrations (Røy *et al.*, 2012). Measured $[NO_3^-]$ are from Spivack *et al.*, (*in review*).

Figure 9: Downcore profiles of $[O_2]$ and $[NO_3^-]$ with calculated concentration of nitrate produced down core during nitrification and estimated relict concentrations of nitrate at EQP 11. The $[O_2]$ profile is the interpolated dissolved oxygen concentrations derived from measured concentrations (Røy *et al.*, 2012). Measured $[NO_3^-]$ are from Spivack *et al.*, (*in review*).

Figure 10: Natural log of relict concentration against $\delta^{15}\text{N}_{\text{relict}}$ at EQP 10 (left, solid circles) and EQP 11 (right, open circles). The linear trend of the plot suggests that the system has two members: LGM and modern day.

Figure 11: Measured and relict pore fluid nitrate $\delta^{15}\text{N}$ profiles for the three cases presented at EQP 10; $\delta^{15}\text{N}_{\text{relict}}$ (open circles) for case 1 (red), case 2 (blue), and case 3 (green) are overlain on $\delta^{15}\text{N}_{\text{measured}}$ (solid circles) and plotted with depth. $\delta^{15}\text{N}_{\text{sed}}$ assigned in case 1 is 7.8‰, in case 2 is 7.8‰, and is interpolated for case 3.

Figure 12: Measured and relict pore fluid nitrate $\delta^{15}\text{N}$ profiles for the three cases presented at EQP 11; $\delta^{15}\text{N}_{\text{relict}}$ (open circles) for case 1 (red), case 2 (blue), and case 3 (green) are overlain on $\delta^{15}\text{N}_{\text{measured}}$ (solid circles) and plotted with depth. $\delta^{15}\text{N}_{\text{sed}}$ assigned in case 1 is 5.6‰, in case 2 is 5.5‰, and is interpolated for case 3.

Figure 13: Measured and relict pore fluid nitrate $\delta^{18}\text{O}$ profiles for the three cases presented at EQP 10; $\delta^{18}\text{O}_{\text{relict}}$ (open circles) for case 1 (red), case 2 (blue), and case 3 (green) are overlain on $\delta^{18}\text{O}_{\text{measured}}$ (solid circles) and plotted with depth.

Figure 14: Measured and relict pore fluid nitrate $\delta^{18}\text{O}$ profiles for the three cases presented at EQP 11; $\delta^{18}\text{O}_{\text{relict}}$ (open circles) for case 1 (red), case 2 (blue), and case 3 (green) are overlain on $\delta^{18}\text{O}_{\text{measured}}$ (solid circles) and plotted with depth.

Figure 15: Case 2 values of $\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$ from sites EQP 10 (red) and 11 (blue). The left plot is $\delta^{15}\text{N}_{\text{relict}}$ at EQP 10 and $\delta^{15}\text{N}_{\text{relict}}$ at EQP 11. The right plot is $\delta^{18}\text{O}_{\text{relict}}$ at EQP 10 and $\delta^{18}\text{O}_{\text{relict}}$ at EQP 11. Solid lines are smoothed trends from the LOWESS function. Case 2 best represents a sediment column where the greatest amount of nitrate production occurs in the top 10 mbsf.

$\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$: mechanisms for change

At EQP 10 and EQP 11 values of $\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$ exhibit a shift from high to low between the deepest and the shallowest samples (Figure 15). At EQP 10, $\delta^{15}\text{N}_{\text{relict}}$ shifts between $\sim 7.6\text{‰}$ and $\sim 5.0\text{‰}$, a total change of 2.6‰ , and $\delta^{18}\text{O}_{\text{relict}}$ shifts from 6.2‰ and 2.0‰ , an overall change of 4.2‰ . At EQP 11, $\delta^{15}\text{N}_{\text{relict}}$ changes from 7.6‰ and $\sim 6.0\text{‰}$, an overall change of 1.4‰ , and $\delta^{18}\text{O}_{\text{relict}}$ shifts from 5.5‰ to 2.2‰ , a total of 3.3‰ . The 2.5‰ shift in EQP 10 $\delta^{15}\text{N}_{\text{relict}}$ is 66% greater than the observed range in the modern deep ocean ($\sim 4.5\text{--}6\text{‰}$) (Sigman *et al.*, 2009). How can such a substantial shift in values be explained?

Processes controlling gradients in the isotopic compositions of nitrate can be understood with dual isotope plots (Figure 16), where X the Y axes are $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, respectively (Kendall, 1998; Lehmann *et al.*, 2004; Sigman *et al.*, 2005; Wankel *et al.*, 2009; Sigman *et al.*, 2009). The slope of a dual isotope plot represents the change imparted on $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ by nitrogen cycling. Processes that have an equivalent isotope effect on $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ such as denitrification and assimilation result in a slope of 1 ($^{18}\epsilon = ^{15}\epsilon$) (Granger *et al.*, 2004; Sigman *et al.*, 2009). Processes that decouple the isotope effect on $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$, like regeneration and assimilation, pull the slope away from 1. Regeneration and assimilation decouple N and O fractionation because regeneration of OM releases NH_4^+ , which has no associated oxygen. When NH_4^+ is oxidized through nitrification, the nitrate that results has a $\delta^{15}\text{N}$ that reflects the OM plus the associated isotope effects (when only partial cycling occurs), and a $\delta^{18}\text{O}$ that reflects the $\delta^{18}\text{O}$ of the oxygen source plus the isotope effect of nitrification.

Sigman *et al.*, (2009) used dual isotopes to better understand spatial gradients in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values between different water masses in the global ocean (Figure 17). Four of the water masses they investigated were relevant to this study: Pacific Antarctic deep water (PADW), Subtropical North Pacific intermediate water (STNPIW), subtropical North Pacific deep water (NPDW) and Eastern Tropical North Pacific (ETNPIW) (Figure 18). PADW is in the interior of the Southern Ocean. It has low $\delta^{15}\text{N}$ (4.7‰) and a $\delta^{18}\text{O}$ (1.9‰) values as a result of the regeneration of OM with a low a $\delta^{15}\text{N}$ signal from OM export and $\delta^{18}\text{O}$ from nitrification. Between the Southern Ocean and low latitude deep ocean partial regeneration/nitrification of OM export adds regenerated nitrate (nitrate that is remineralized in water mass after subduction) with an elevated $\delta^{15}\text{N}$ (5.3‰) and a $\delta^{18}\text{O}$ (~1.9‰) from nitrification. Also occurring is the transport of preformed nitrate (nitrate that exists in the water mass when it is subducted from the surface) with a high $\delta^{15}\text{N}$ ($\geq 5\text{‰}$) and $\delta^{18}\text{O}$ (~2.5‰) from partial nitrate consumption in the surface of the Southern Ocean. The combined affects result in a stronger $\delta^{15}\text{N}$ gradient than $\delta^{18}\text{O}$ gradient between the PADW and STNPDW. At intermediate depths in the North Pacific (STNPIW) the continued influence of partial regeneration/nitrification coupled with the diffusion of nitrate with high $\delta^{15}\text{N}$ (6.4‰) and $\delta^{18}\text{O}$ (2.9‰) from denitrification in the nearby OMZs (ETNPIW: $\delta^{15}\text{N}=8.9\text{‰}$ and $\delta^{18}\text{O} = 6.1\text{‰}$) further enhances the gradient between the Southern Ocean and low latitudes.

Values of $\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$ at EQP 10 and EQP 11 were plotted on dual isotopes plots (shaded by sample depth) (Figures 19 and 20). The slopes are 1.5 and 0.78 for EQP 10 and EQP 11, respectively, suggesting that the cycling of N and O

isotopes are decoupled. Slopes <1 , like for EQP 11, can be explained by partial regeneration and nitrification. Slopes >1 , like at EQP 10, indicate a greater shift in $\delta^{18}\text{O}$ than $\delta^{15}\text{N}$. It may be caused by a greater relative contribution of oxygen molecules from dissolved O_2 than from H_2O during nitrification. Alternatively, and more likely, the >1 slope is an artifact of the correction for $\delta^{15}\text{N}_{\text{produced}}$ and $\delta^{18}\text{O}_{\text{produced}}$ on $\delta^{15}\text{N}_{\text{measured}}$ and $\delta^{18}\text{O}_{\text{measured}}$, respectively. At EQP 10 there is a decrease of $\sim 140\mu\text{M} [\text{O}_2]$ between the deepest and shallowest sample (increase of $\sim 13\mu\text{M} [\text{NO}_3^-]$) and $\delta^{15}\text{N}_{\text{sed}}$ is $\sim 7.8\text{‰}$, resulting in a $\delta^{15}\text{N}_{\text{relict}}$ that is less than $\delta^{15}\text{N}_{\text{measured}}$ for all samples. The correction to $\delta^{18}\text{O}_{\text{relict}}$ from $\delta^{18}\text{O}_{\text{measured}}$ has the opposite effect; all relict values are greater than measure values. The result of the corrections on EQP 10 samples may cause a greater *apparent* shift in $\delta^{18}\text{O}$ than $\delta^{15}\text{N}$ that is not representative of what is actually occurring. A better constraint on the isotopic composition of nitrate produced *in situ* is needed to resolve this issue. This is particularly important for the oxygen reconstruction.

Relict values are compared with modern water masses discussed above to reveal an interesting parallel between the spatial gradient in the modern ocean DW and IW and the temporal shift in the pore fluid samples. At EQP 10 the deepest samples plot between the ETNPIW and STNPIW modern values and the shallower samples plot near STNPDW and PADW. For EQP 11, samples span smaller range than samples from EQP 10, but, similar to EQP 10, the deepest sample lies between ETNPIW and STNPIW. The youngest sample at EQP 11 plots near STNPDW; however, the majority of the young samples are clustered midway between STNPIW and STNPDW. At both sites there is a shift in points from similar to the modern day

IW to values more like modern day DW in the shallowest pore fluid. Three mechanisms can be proposed that would cause this shift between LGM and present day. First, preformed nitrate transported from the surface of the Southern Ocean could have had elevated $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values relative to modern day due to increased partial nitrate assimilation; second, there could have been enhanced transfer of an elevated IW/surface $\delta^{15}\text{N}$ signal to the deep by remineralization; and lastly, there could have been denitrification occurring in the deep waters of the Pacific Ocean.

The N and O isotopic compositions of preformed nitrate, $\delta^{15}\text{N}_{\text{preformed}}$ and $\delta^{18}\text{O}_{\text{preformed}}$, are influenced by partial nitrate assimilation in the surface, which drives equivalent change to $\delta^{15}\text{N}_{\text{preformed}}$ and $\delta^{18}\text{O}_{\text{preformed}}$. Measurements of sedimentary $\delta^{15}\text{N}$ suggest that nitrate consumption in the Antarctic Zone (AZ) surface was higher during the LGM and decreased toward modern day (Robinson *et al.*, 2008). This would increase $\delta^{15}\text{N}_{\text{preformed}}$ entering the deep Pacific via AABW formation during the LGM (Figure 21). Although this mechanism provides an explanation for the gradients in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, evidence for changes in preformed concentrations are not apparent at these sites (Spivack *et al.*, *in review*), and the weight of the preformed nitrate pool's isotope effect on the deep ocean is dampened as concentration decreases.

Alternatively, the shift may be the result of a proportional increase in the contribution of regenerated nutrients resulting from OM export from the low latitude interior since the LGM (Figure 22). This would introduce elevated $\delta^{15}\text{N}$ nitrate into the deep ocean. However nitrification of this OM would result in a lowering of the $\delta^{18}\text{O}$ nitrate to values more like ambient seawater, which is in disagreement with what is observed. This mechanism does not account for the observed shift in both $\delta^{15}\text{N}$ and

$\delta^{18}\text{O}$, and is only plausible if regeneration increased following the LGM because it requires the regeneration of organic matter with an elevated isotopic composition, which does not become evident across the low latitudes until after the LGM (Figure 2) (Galbraith *et al.*, 2013).

The final mechanism proposed to drive the change is denitrification in the deep ocean, which would account for the observed increase in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ during the LGM (Figure 23). The concentration of the oxygen in the ocean is a function of the solubility, which is controlled by temperature and salinity, the amount of consumption/respiration that occurs, and the movement and distribution via circulation. A decrease in dissolved oxygen concentration in the deep ocean interior during the LGM can be explained by the weakening/northward shift in Circumpolar Deep Water (CDW) upwelling related to changes in the eastward winds or salinity-stratification caused by sea ice. Such a reduction in upwelling during the LGM would have restricted ventilation of the deep ocean. When reduced ventilation is coupled with the remineralization of OM, the combined effects could create an oxygen-limited environment in the deep ocean. If the depletion was intense enough, it could have hosted water column denitrification (Sigman and Boyle, 2000). Following the LGM, the reinvigoration of upwelling explains the observed increase in dissolved oxygen from the LGM to the early Holocene (EH) (Jaccard and Galbraith, 2011). Multiple lines of evidence including the concentration of redox metals (Ca/Cd ratios, Uranium), benthic foraminifera assemblages, and sedimentary laminations suggest that from the LGM to the EH the concentration of dissolved oxygen in the deep Pacific (>2000 m) increased, despite the expected decrease in solubility with increasing ocean

temperature (Jaccard, 2009; Jaccard and Galbraith, 2011; Jaccard and Galbraith, 2013). It should be noted that there is no evidence for oxygenation changes at the extremely deep depths of these sites or beneath the gyres at all; this inference is extrapolated from shallower and more marginal locations. This extrapolation is supported by porefluid chloride data that imply a relatively homogeneous, although colder and saltier, deep Pacific during the LGM (Lado-Insua *et al.*, *submitted*; Adkins and Schrag, 2003). The occurrence of water column denitrification in bottom waters is expected to leave some evidence of change in the dissolved oxygen or nitrate concentrations in the pore fluid. These sites preserve no such evidence, however, if deep water denitrification was a transient event than it is possible that any abrupt concentration changes would be smeared out by diffusion.

The best mechanism for explaining the shift from deep samples like modern day IW to shallow samples like modern day DW is an increase in deep water denitrification during the LGM. This mechanism is in agreement with observations that the oxygen concentration of the deep ocean had increased since the LGM, and provides an explanation for the observed shifts in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. An important point to keep in mind is that if the mechanism is deep water denitrification than the effects may be localized, and the signal observed may be recording the influence on denitrification on North Pacific bottom water, instead of the global ocean. It is also possible that the water mass distribution during the LGM was different than today, such that bottom water at these sites during the LGM was not a well mixed representation of the deep ocean, but was instead a dense water mass with different

properties than the surrounding water masses. This is unlikely based on porefluid chloride data and profiles of nitrate and oxygen.

One-Dimension diffusion analysis

To evaluate the extent to which $\delta^{15}\text{N}_{\text{global}}$ values resemble Galbraith *et al.*, (2013) model, and the extent of how $\delta^{15}\text{N}_{\text{global}}$ may have been forced by regional changes in water column denitrification, $\delta^{15}\text{N}_{\text{relict}}$ profiles were compared with sedimentary records of water column denitrification output of a one-dimensional diffusion analysis modified from Adkins *et al.*, (2002) and Lado-Insua *et al.*, (submitted). A predicted depth distribution of a time variant $\delta^{15}\text{N}$ signal, such as a downcore denitrification record is created using a time dependent diffusion equation. It has been demonstrated that comparing downcore data of dissolved conservative constituents in pore fluids is an effective method for evaluating if observations can be explained as a signal expected from diffusion, or if there are other processes occurring to cause change in the signal (Schrag *et al.*, 1993; Adkins *et al.*, 2002). For example, Schrag *et al.*, (1993) matched oxygen isotope data from McDuff (1984) to a diffusive transport model with the goal of explaining the controls on the distribution of $\delta^{18}\text{O}$ in sedimentary pore fluids. Similarly, Adkins *et al.*, (2002) used dissolved chloride concentrations in pore fluids as a paleoceanographic archive to reconstruct deep water salinity.

The comparison is applicable for sediment where porosity is great enough so there is free diffusion of bottom water into sediment pore space and where there is sufficient evidence that there has been no *in-situ* diagenesis or alteration during biologically mediated reactions, such that relict bottom water is preserved as pore fluid

(Bender *et al.*, 1977; McDuff *et al.*, 1984; Adkins and Schrag, 2003). A simple method for modeling diffusion in a sediment column is to assume that it is analogous to diffusion in a pipe (Adkins *et al.*, 2002). Using a pipe analogy simplifies the system to one dimension and only requires two boundary conditions, a bottom boundary and a side boundary, and an initial condition of a time variation in bottom water composition.

The analytical code used was adopted from Lado-Insua *et al.*, (*submitted*) and Adkins and Schrag (2003). The approach used here has been simplified from a system with reactive and advective terms and diffusive transport to a system that only has diffusive transport. The *in-situ* reactive term is zero; the effect of nitrification was expunged by corrections for *in-situ* nitrate production on the measured data. It is assumed that there is no addition of nitrate in either the horizontal or vertical direction, and that there is no apparent isotopic fractionation of nitrate with diffusion (Brandes and Devol, 1997). The model is bounded by the mean value of the initial conditions and the value at the LGM, and it is assumed that there is no flux from the basement. The diffusion of isotopic composition in pore fluid is a function of the change in flux with depth ($\text{mol}^1\text{m}^{-2}\text{s}^{-1}$), porosity (ϕ), and the diffusion coefficient ($D \text{ (m}^1\text{s}^{-2}\text{)}$), which is a function of temperature, porosity, and formation factor.

$$\phi(dC/dt) = (d/dz)*(\phi*D*dC/dz)$$

Relict profiles corrected from measured data were compared to the modeled diffusive profiles of $\delta^{15}\text{N}$ values that record the signal of IW pelagic denitrification in Eastern Tropical North Pacific (Ganeshram *et al.*, 2000) (Figures 24) and to the $\delta^{15}\text{N}_{\text{Gal-global}}$ record (Galbraith *et al.*, 2013) (Figures 25). It was hypothesized that the

down core records at EQP 10 and EQP 11 represent a diffused profile of global mean nitrate $\delta^{15}\text{N}$ values, however, the relict profile does not compare well with the predicted profile of Galbraith *et al.*, (2013). Rather, the trends are more similar to regional records directly affected by enhanced water column denitrification (i.e. Figure 2). It is possible that the Galbraith *et al.*, (2013) model underestimates the sensitivity of the global value to regional changes, or that these sites in the North Pacific Gyre are particularly sensitive to regional changes and are not representing a global mean of nitrate isotopic composition.

What if ' $\delta^{15}\text{N}_{\text{global}}$ ' is not really a Global?

The possibility that the samples measured are not representing $\delta^{15}\text{N}_{\text{global}}$ must be addressed. The dampening effect from diffusion causes the shift observed in relict values to be an underestimate of the actual change. Example's of the dampening effect with time is illustrated in time-depth diffusion profiles for the initial conditions (Figures A.D.1 and A.D.2) in which the evolution of diffusion is captured. If dampening reduced the diffused value by a third (see example in ETNP initial conditions, Figure A.D.2) it would mean the shift observed is 33% greater, and that $\delta^{15}\text{N}_{\text{global}}$ could have been as high as 10 or 11‰ during the LGM. If this is the case the deepest sample for $\delta^{15}\text{N}_{\text{relict}}$ may be viewed as a lower bound of $\delta^{15}\text{N}_{\text{global}}$ during the LGM. A shift as large as 4‰ between the LGM and the present day at these sites is substantial and may be more reasonably explained as a regional record of an increase in deep water denitrification rather than as a global shift.

Shift in $\delta^{15}\text{N}$: implications for pelagic: benthic denitrification

Whether it is a global or regional shift, the reconstructed change in $\delta^{15}\text{N}$ values can be used to estimate the relative role of pelagic denitrification to total denitrification. Assuming the isotope effect of sedimentary denitrification, water column denitrification, and nitrogen fixation have remained not changed the relative importance of water column denitrification on total N-loss appears to have been at least 50% greater than what it is today (assuming a shift of 2.5‰) during the LGM (see appendix B). In the case that the signal was dampened by diffusion, and the LGM $\delta^{15}\text{N}$ value is nearer to 11‰, than the relative contribution of pelagic denitrification was more than double what it is today. Large increases such as these may be explained deep water denitrification, in which case the samples are capturing local change. If the signal is global, the shift could be explained by sea level that was ~100-120 m lower during the LGM, making available shelf space for OM sedimentation and sedimentary denitrification reduced and shunting OM sedimentation to the slopes, allowing for the increased potential of WC denitrification in the IW. However, an increase in IW denitrification during the LGM is not supported by any evidence, further support that the signals observed regional and the result of deep water denitrification in the North Pacific.

Additional Factors to consider

Lack of available knowledge of sedimentary nitrogen cycling is a limitation to this research. For example, there were many assumptions made about the pore fluids and the effect of *in situ* nitrification that likely have introduced uncertainty to the discussion. Possible erroneous assumptions may be related to the Redfield ratio, no

loss to diffusion and the absence of alteration. If the Redfield ratio is not applicable to the nitrification occurring *in-situ* at these sites the estimated concentration of produced nitrate maybe incorrect. If a greater concentration of nitrate was produced than estimated it makes the current correction for $\delta^{15}\text{N}_{\text{relict}}$ less than it should be, and vice versa if a lesser concentration was produced. If the system were to have a loss of ammonium out of the sediment via diffusion than it is possible that too large of a correction was made and that there was some N isotopic fractionation associated with the transformation from OM to nitrate. It was also assumed that all O consumed can be accounted for by N produced, but if N is escaping as ammonium than the estimation for what has been added to the relict nitrate will be too much, and an over correction is made. Similarly unconstrained is the impact that isotopic alteration has on $\delta^{15}\text{N}_{\text{measured}}$ and $\delta^{18}\text{O}_{\text{measured}}$. Lastly, in addition to the limited understanding to the correction for $\delta^{18}\text{O}_{\text{produced}}$ on $\delta^{18}\text{O}_{\text{measured}}$, it is unclear how much of the shift in $\delta^{18}\text{O}_{\text{relict}}$ is from variation in $\delta^{18}\text{O}_{\text{ambient}}$ since the LGM and how much is from changes in N-cycling. If 1.0-2.0‰ of the shift observed in $\delta^{18}\text{O}_{\text{relict}}$ is from variation in $\delta^{18}\text{O}_{\text{ambient}}$ (Schrag and Depaolo 1993; Adkins and Schrag, 2003) than the remaining change is from N-cycling. How to address this issue is uncertain.

Relationship to climate

If these data are significant, they have implications for nitrogen, oxygen, and carbon cycling through their interaction in the biological pump. If water column denitrification is the primary driver of the observed change than it has direct consequences for oxygen availability at bottom depths and sedimentary redox processes during the LGM, including the role of oxygen during remineralization,

potentially resulting in an increase in carbon storage at depth. On the other hand, if change is driven by the isotopic composition of preformed nitrate transported to the deep ocean, it supports previous suggestions that the greater degree of assimilation in the surface reflects an increase in carbon sequestration in the deep (e.g. Ito and Follows, 2005; Robinson and Sigman, 2008).

Dual Isotope Plot

Figure 16: Dual isotope plot of $\delta^{15}\text{N}$ versus $\delta^{18}\text{O}$ with 1:1 lines dashed in for reference. Shift along a 1:1 line is evidence of denitrification and assimilation. Shifts with slopes not equal to 1 are evidence of N-cycling that decouples the isotope effects on O and N, like regeneration and nitrification.

Figure 17: Sigman *et al.*, (2009) used dual isotope plots to determine mechanisms for spatial gradients in modern $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$. Four of the water masses relevant to this work are the Pacific Antarctic deep water (depth 1500m to bottom- PADW), Subtropical North Pacific intermediate water (300-1500m: STNPIW), Subtropical North Pacific deep water (1500m-bottom: STNPDW), and Eastern Tropical North Pacific intermediate water (300-1500m: ETNP).

Figure 18: Mechanisms controlling spatial distribution of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in modern water masses. PADW in the Southern Ocean interior has low $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ as a result of remineralized nitrate with low $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. As water is transported to lower latitudes regeneration and nitrification causes an increase in $\delta^{15}\text{N}$ and keeps $\delta^{18}\text{O}$ low. The addition of preformed nitrate from the surface of the Southern Ocean causes additional shift towards high $\delta^{15}\text{N}$ and is the reason for an increase $\delta^{18}\text{O}$. In the intermediate water of the STNP $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ continues to elevate from the input of regenerated nitrate and the diffusion of nitrate with high $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ from OMZs, like in the ETNP intermediate water.

Figure 19: $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of nitrate at EQP 10. The grey dotted lines represents a $^{18}\epsilon:^{15}\epsilon=1$. The dashed line is the linear trend of the plotted data ($m=1.5$). The solid squares represent $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of various water masses in the PADW (turquoise), STNPIW (blue), STNPDW (red), and ETNPIW (green).

Figure 20: $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of nitrate at EQP 11. The grey dotted lines represents a $^{18}\epsilon:^{15}\epsilon=1$. The dashed line is the linear trends of plotted data ($m=0.78$). The solid squares represent $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of various water masses in the PADW (turquoise), STNPIW (blue), STNPDW (red), and ETNPIW (green).

1) Higher $\delta^{15}\text{N}_{\text{preformed}}$ transferred to the low latitude deep water during the LGM

Figure 21: Schematic diagram of higher $\delta^{15}\text{N}_{\text{preformed}}$ transferred to the low latitude interior during the LGM to explain shifts from DW-like values to IW-like values in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate between the deepest and shallowest samples. This would explain the observed shifts in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$; however, the impact of an elevated preformed isotopic ratio would be shunted with the expected decrease in concentration.

2) Enhanced transfer of IW/surface $\delta^{15}\text{N}$ signal to depth by remineralization since the LGM

Figure 22: Schematic diagram of enhanced nitrate regeneration since the LGM to explain shifts from DW-like values to IW-like values in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate between the deepest and shallowest samples. This possibility accounts for an increase in $\delta^{15}\text{N}$ just after the LGM, but does not explain the observed shift in $\delta^{18}\text{O}$.

3) Denitrification in the deep ocean during the LGM

Figure 23: Schematic diagram of an increase in deep ocean denitrification to explain shifts from DW-like values to IW-like values in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate between the deepest and shallowest samples. This would explain a shift in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

Figure 24: $\delta^{15}\text{N}$ record from the ETNP (Ganeshram *et al.*, 2000) (red line) compared to EQP 10 relict values (left, solid circles) (left) and EQP 11 relict values (right, open circles) (right).

Figure 25: $\delta^{15}\text{N}$ record from Galbraith *et al.*, (2013) (red line) compared to EQP 10 relict values (left, solid circles) (left) and EQP 11 relict values (right, open circles).

Conclusion

In conclusion, the pore fluid from EQP 10 and EQP 11 show a large change in $\delta^{15}\text{N}_{\text{relict}}$ and $\delta^{18}\text{O}_{\text{relict}}$ values in the upper 25 mbsf that may be useful for interpreting changes imparted on nitrate O and N isotopes in the deep North Pacific through time. Measured values were not directly interpretable; they needed to first be corrected for *in-situ* nitrate production. This correction resulted in a linear relationship between nitrate concentration and $\delta^{15}\text{N}/\delta^{18}\text{O}$ values that reflects conservative mixing between two end members. At both sites in the North Pacific corrected nitrate N isotopic composition shifts by greater than 2‰ permil since the LGM, concurrent with a shift from like modern day IW waters to like modern day DW. The decrease in $\delta^{15}\text{N}$ and associated decrease in $\delta^{18}\text{O}$ can be explained most convincingly by enhanced denitrification in the deep Pacific. Additional explanations are related to the transfer surface/IW signal to the ocean interior through enhanced regeneration since the LGM or a change in the isotopic compositions of preformed nutrients transported to the low latitude interior ocean during the LGM, though neither mechanism can fully explain the changes observed. Uncertainty as to whether the signal is global or regional is a topic for future discussion. Comparison of the samples to diffusion models of $\delta^{15}\text{N}$ in sediment and the model by Galbraith *et al.*, (2013) supports that the changes observed are more similar to regional changes than global change. In addition, correcting for the effects of dampening by diffusion on the observed shifts, suggest a significantly greater $\delta^{15}\text{N}$ value during the LGM that may only be practically explained as a regional change.

Future Work

Future work could include expanding the pore fluid record to capture the 100% of the LGM signal, and comparing samples to pore fluid from a like environment, such as the South Pacific Gyre to help discern if the observations are regional or a more wide spread view. Also, better constraints on $\delta^{18}\text{O}$ measurements and corrections should be determined for reasons discussed throughout. Additional investigation could include reviewing the results in unison with work on preformed nitrate concentration reconstruction by Spivack *et al.*, (*in review*) to help discern the plausibility of the performed nitrate mechanism as a driver for the shifts in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ observed since the LGM.

Appendix: *Not included are other authors published data i.e. Siddall *et al.*, (2003)

A. Tables of data used in research

Table A.1: Measure corrected $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ for EQP 10. *Italicized* numbers are outliers, identified as values ≥ 2 standard deviations from the mean of all measured data ($\sigma=1.63\text{‰}$ and mean= 2.61‰ for $\delta^{18}\text{O}_{\text{measured}}$; $\sigma=1.16\text{‰}$ and mean= 6.50‰ for $\delta^{15}\text{N}_{\text{measured}}$)

sample ID	$\delta^{18}\text{O}_{\text{measured}}$ (‰ vs. VSMOW)	$\delta^{15}\text{N}_{\text{measured}}$ (‰ vs. N_2 in air)	depth (mbsf)
BW	1.27	4.29	0.00
EQP10_G2_S1_0_5	1.78	4.88	0.03
EQP10_G1_S1_5_10	1.17	4.56	0.08
EQP10_G2_S1_5_10	2.21		0.08
EQP10_G2_S1_10_15	2.40	5.32	0.13
EQP10_G2_S1_15_20	1.95		0.18
EQP10_G2_S1_20_25	2.13	5.43	0.23
EQP10_G1_S1_25_30	1.23		0.28
EQP10_G2_S1_25_30	2.78	6.22	0.28
EQP10_G2_S1_30_35	1.35	5.86	0.33
EQP10_G2_S1_35_40	1.24		0.38
EQP10_G2_S1_40_45	1.76	5.62	0.43
EQP10_L1_S1_40_45	1.61	4.69	0.43
EQP10_G1_S1_45_50	3.04		0.48
EQP10_G2_S1_45_50	2.36	4.87	0.48
EQP10_G1_S1_65_70	1.78	5.40	0.68
EQP10_G1_S1_100_105	1.19		1.03
EQP10_L1_S1_115_120	1.59		1.18
EQP10_G1_S1_120_125	1.09		1.23

EQP10_G1_S1_135_140	1.27	5.92	1.38
EQP10_G1_S2_10_15	1.40	6.87	1.63
EQP10_G1_S2_30_35	2.39		1.83
EQP10_L1_S2_50_55	0.95		1.88
EQP10_G1_S2_50_55	0.81	5.76	2.03
EQP10_G1_S2_70_75	1.43		2.23
EQP10_G1_S2_105_110	2.16	5.78	2.58
EQP10_L1_S2_125_130	1.48	6.40	2.63
EQP10_G1_S2_125_130	1.92		2.78
EQP10_G1_S2_145_150	2.18		2.98
EQP10_G1_S2_165_170	0.51	4.64	3.18
EQP10_L1_S3_50_55	2.70		3.44
EQP10_L1_S3_125_130	0.91	5.48	4.19
EQP10_L1_S4_55_60	5.63		4.99
EQP10_L1_S4_130_135	1.70	6.32	5.74
EQP10_L1_S5_55_60	1.93	6.72	6.55
EQP10_L1_S5_130_135	1.45	6.62	7.30
EQP10_L1_S6_60_65	1.71	6.72	8.10
EQP10_L1_S6_135_140		6.39	8.85
EQP10_L1_S7_60_65	2.88	6.88	9.66
EQP10_L1_S7_135_140	2.88		10.41
EQP10_L1_S8_55_60	2.74	7.10	11.12
EQP10_S1_S8_130_135	3.18	6.37	11.87
EQP10_L1_S9_50_55		6.94	12.62
EQP10_L1_S9_125_130		7.27	13.37
EQP10_L1_S10_55_60	2.40	6.88	14.17
EQP10_L1_S10_130_135	3.73	7.30	14.92

EQP10_L1_S11_55_60	3.76	7.07	15.73
EQP10_L1_S11_130_135	4.44	8.10	16.48
EQP10_L1_S12_55_60	2.74	6.97	17.26
EQP10_L1_S12_130_135	3.96	7.56	18.01
EQP10_L1_S13_55-60	6.85	6.80	18.80
EQP10_L1_S14_130_135	4.73	7.47	21.10
EQP10_L1_S15_55_60	8.34	9.69	21.88
EQP10_L1_S15_121_125	3.49	8.01	22.53
EQP10_L1_S16_55_60	4.20	7.56	23.41
EQP10_L1_S16_130-135	6.18	8.70	24.16
EQP10_L1_S17_55_60	6.05	6.97	24.94
EQP10_L1_S18_30_35	3.57	7.72	26.22
EQP10_L1_S18_65_70	3.82	7.40	26.57

Table A.2: Sample ID, Measured $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, and sample depths for EQP 11.
Italicized numbers are outliers, identified as values ≥ 2 or more standard deviations from the mean of all measured data ($\sigma=0.98\text{‰}$ and mean= 2.78‰ for $\delta^{18}\text{O}_{\text{measured}}$; $\sigma=0.58\text{‰}$ and mean= 6.32‰ for $\delta^{15}\text{N}_{\text{measured}}$)

sample ID	$\delta^{18}\text{O}_{\text{measured}}$ (‰ vs. VSMOW)	$\delta^{15}\text{N}_{\text{measured}}$ (‰ vs. N_2 in air)	depth (mbsf)
EQP11_MC4_BW	1.03		0.00
EQP11_MC4_0_5	1.40		0.03
EQP11_MC4_5_10	5.15	6.47	0.08
EQP11_MC4_10_15	4.67	6.14	0.13
EQP11_G1_S1_10_15			0.13
EQP11_MC_15_20	2.46	5.28	0.18
EQP11_MC4_20_25	2.17	5.70	0.23
EQP11_MC_25_30	2.60	5.79	0.28

EQP11_G1_S1_25_30	2.15	5.90	0.28
EQP11_L1_S1_25-30	2.66	6.05	0.28
EQP11_MC4_30_35			0.33
EQP11_MC4_35_40	1.91	5.75	0.38
EQP11_MC4_40_43	3.31		0.42
EQP11_G1_S1_45_50		5.52	0.48
EQP11_G1_S1_65_70	2.05	6.02	0.68
EQP11_L1_S1_65-70		6.12	0.68
EQP11_G1_S1_100_105	1.82	5.25	1.03
EQP11_G1_S1_125_130		5.54	1.28
EQP11_G1_S1_140_145	1.80	5.24	1.43
EQP11_L1_S2_55_60	2.32	6.18	1.44
EQP11_G1_S2_15_20	2.72	5.86	1.68
EQP11_G1_S2_50_55		6.50	2.03
EQP11_L1_S2_130-135	3.49		2.19
EQP11_G1_S2_70_75		5.11	2.23
EQP11_G1_S2_95_100	1.77	5.93	2.48
EQP11_G1_S2_130_135	3.14	6.11	2.83
EQP11_L1_S3_55_60	1.66	6.19	2.97
EQP11_G1_S3_7_12	3.05	5.90	3.10
EQP11_G1_S3_25_30	2.80	6.29	3.28
EQP11_G1_S3_40_45	1.89	6.85	3.43
EQP11_L1_S3_130_135	2.70	6.41	3.72
EQP11_G1_S3_80_85	2.76	6.36	3.83
EQP11_G1_S3_100_105	1.77	6.23	4.03
EQP11_G1_S3_120_125		6.96	4.23
EQP11_L1_S4_55_60	1.98	6.51	4.50

EQP11_L1_S4_130-135	3.29	5.95	5.25
EQP11_L1_S5_55_60	1.93	6.04	6.03
EQP11_L1_S5_130_135	3.70	6.95	6.78
EQP11_L1_S6_55_60	2.34	6.22	7.52
EQP11_L1_S6_130_135	2.97	6.98	8.27
EQP11_L1_S7_55_60	2.48	6.01	9.08
EQP11_L1_S7_130_135	2.56	6.34	9.83
EQP11_L1_S8_55_60	2.90	5.34	10.58
EQP11_L1_S8_130_135	2.29	6.86	11.33
EQP11_L1_S9_55_60	2.91	6.86	12.14
EQP11_L1_S9_130_135	3.44	6.29	12.89
EQP11_L1_S10_55_60	4.29	6.21	13.64
EQP11_L1_S10_130_135	2.62		14.39
EQP11_L1_S11_55_60	2.98	6.77	15.19
EQP11_L1_S11_130_135	1.65	6.20	15.94
EQP11_L1_S12_55_60	2.78	6.79	16.72
EQP11_L1_S12_130_135			17.47
EQP11_L1_S13_55_60		6.21	18.25
EQP11_L1_S13_130_135	3.64	7.25	19.00
EQP11_L1_S14_55_60		7.40	19.78
EQP11_L1_S14_130_135	4.73	7.55	20.53
EQP11_L1_S15_55_60	3.42	6.44	21.31
EQP11_L1_S15_130_135	1.31	6.72	22.06
EQP11_L1_S16_55_60	4.42	6.63	22.84
EQP11_L1_S16_90_95	2.45	6.76	23.19
EQP11_L1_S17_55_60		7.56	24.93

EQP11_L1_S17_130_135	1.81	6.83	24.99
EQP11_L1_S18_55_60	4.87		25.74
EQP11_L1_S18_130_135	4.75	7.07	26.49
EQP11_L1_S19_45_50	3.73	6.83	27.20
EQP11_L1_S19_90_95	2.70	6.98	27.65

Table A.3: Measured dissolved oxygen concentration at site EQP 10. These values were interpolated for dissolved oxygen at sites for which $[\text{NO}_3^-]$ was measured.

Depth (mbsf)	O ₂ (μM)
0.00	175.00
0.20	145.41
0.35	138.91
0.50	138.67
0.65	127.65
0.80	121.50
0.95	112.33
1.10	109.89
1.25	102.89
1.43	98.98
1.73	95.98
1.88	92.43
2.03	92.13
2.18	89.73
2.33	87.92
2.48	86.86
2.63	84.58
2.78	82.89

3.28	77.81
3.85	72.15
4.25	69.19
4.45	66.53
4.75	64.06
5.10	61.16
5.40	58.45
5.80	55.49
6.09	49.36
6.83	48.09
7.05	46.29
7.55	44.77
7.85	42.79
8.25	39.28
8.44	36.42
8.83	36.15
9.37	33.42
9.86	31.37
10.75	28.66
11.20	27.18
11.45	26.47
11.55	26.05
12.75	23.45
13.71	21.97
14.45	20.76
15.75	19.11
17.45	17.08

18.43	15.61
18.94	15.73
20.25	14.69
20.83	12.48
21.42	14.63
21.42	11.53
22.00	11.65
25.95	13.18
26.30	12.21

Table A.4: Measured dissolved oxygen concentration at site EQP 11. These values were interpolated for dissolved oxygen at sites for which $[\text{NO}_3^-]$ was measured.

Depth (mbsf)	$[\text{O}_2]$ (μM)
0.00	146.75
0.05	134.87
0.08	130.86
0.10	125.55
0.13	122.65
0.15	120.91
0.18	119.48
0.2	118.50
0.23	117.59
0.25	116.48
0.28	115.26
0.3	114.57
0.33	113.51
0.37	112.32

0.42	111.25
0.47	109.80
0.52	108.71
0.57	107.37
0.58	101.06
1.1	90.11
1.185	87.59
1.28	85.54
1.35	84.97
1.48	82.14
1.58	80.82
1.64	78.69
1.74	76.92
1.84	75.37
1.94	74.44
2.04	73.35
2.14	72.36
2.3	70.52
2.39	72.03
2.4	69.76
2.49	70.05
2.61	68.97
2.76	68.18
2.93	65.65
2.94	67.00
3.05	64.82
3.14	64.66

3.19	63.80
3.34	64.36
3.35	62.44
3.48	61.82
3.52	67.92
3.54	64.36
3.72	61.24
3.89	58.09
3.92	60.69
3.96	57.37
4.12	59.89
4.13	56.60
4.29	55.71
4.32	58.90
4.52	58.40
4.72	57.24
4.92	56.06
5.07	55.57
5.12	55.90
5.55	54.39
5.8	53.74
6.05	54.13
6.3	52.51
6.56	51.29
6.81	51.03
7.06	50.32
7.31	49.77

7.55	49.62
7.82	48.83
8.07	48.49
8.57	47.42
8.87	47.07
9.23	46.85
9.58	45.60
9.98	45.47
10.38	44.61
10.78	44.61
11.18	44.13
11.63	43.87
12.13	43.27
12.64	41.18
13.14	42.41
13.64	39.81
14.2	41.49
14.75	40.83
15.25	40.23
15.85	39.85
16.5	39.07
17.15	38.95
17.85	39.01
18.63	38.40
19.38	38.13
20.16	37.89
20.91	37.68

21.69	37.43
22.44	37.22
23.22	37.00
24.02	36.82
24.77	36.28
25.52	35.73
26.27	36.45
27.02	36.57
27.83	36.25
28.58	36.32

Table A.5: Interpolated dissolved oxygen, measured nitrate concentration, calculated nitrate produced *in-situ* and relict nitrate concentration at EQP 10.

sample ID	[O ₂] interpolated (μM)	[NO ₃] measured (μM)	[NO ₃] produced (μM)	[NO ₃] relict (μM)	[NO ₃] produced in intervals (μM)
BW	165.42	35.00	0.00	35.00	0.00
EQP10_G2_S1_0_5	163.98	37.93	0.14	37.79	0.14
EQP10_G1_S1_5_10	161.10	39.07	0.41	38.66	0.27
EQP10_G2_S1_5_10	159.67	38.50	0.54	37.96	0.14
EQP10_G2_S1_10_15	158.23	39.38	0.68	38.71	0.14
EQP10_G2_S1_15_20	155.35	39.07	0.95	38.12	0.27
EQP10_G2_S1_20_25	152.47	40.23	1.22	39.01	0.27
EQP10_G1_S1_25_30	151.04	39.40	1.35	38.04	0.14
EQP10_G2_S1_25_30	149.60	39.74	1.49	38.25	0.14
EQP10_G2_S1_30_35	146.72	40.09	1.76	38.33	0.27
EQP10_G2_S1_35_40	143.84	40.48	2.03	38.45	0.27

EQP10_G2_S1_40_45	142.41	40.49	2.17	38.32	0.14
EQP10_L1_S1_40_45	140.97	38.91	2.30	36.61	0.14
EQP10_G1_S1_45_50	139.53	39.57	2.44	37.13	0.14
EQP10_G2_S1_45-50	138.09	41.40	2.57	38.82	0.14
EQP10_G1_S1_65_70	126.58	39.98	3.66	36.33	1.08
EQP10_G1_S1_100_1 05	116.34	40.94	4.62	36.32	0.96
EQP10_L1_S1_115_1 20	111.37	41.64	5.09	36.55	0.47
EQP10_G1_S1_120_1 25	109.85	41.96	5.23	36.73	0.14
EQP10_G1_S1_135_1 40	105.65	42.50	5.63	36.87	0.40
EQP10_G1_S2_10_15	99.57	42.93	6.20	36.73	0.57
EQP10_G1_S2_30_35	95.35	43.51	6.59	36.92	0.40
EQP10_L1_S2_50_55	94.36	43.40	6.69	36.72	0.09
EQP10_G1_S2_50_55	91.56	43.87	6.95	36.91	0.26
EQP10_G1_S2_70_75	88.14	43.86	7.27	36.59	0.32
EQP10_G1_S2_105_1 10	82.82	44.12	7.77	36.35	0.50
EQP10_L1_S2_125_1 30	82.12	46.09	7.84	38.25	0.07
EQP10_G1_S2_125_1 30	80.10	44.42	8.03	36.39	0.19
EQP10_G1_S2_145_1 50	77.57	44.69	8.27	36.42	0.24
EQP10_G1_S2_165_1 70	75.20	45.01	8.49	36.52	0.22
EQP10_L1_S3_50_55	72.33	45.53	8.76	36.77	0.27
EQP10_L1_S3_125_1 30	65.15	45.97	9.44	36.53	0.68
EQP10_L1_S4_55_60	58.78	48.12	10.04	38.09	0.60
EQP10_L1_S4_130_1 35	53.68	47.48	10.52	36.96	0.48
EQP10_L1_S5_55_60	48.87	48.81	10.97	37.84	0.45
EQP10_L1_S5_130_1 35	44.93	49.15	11.34	37.81	0.37

EQP10_L1_S6_60_65	41.14	50.96	11.70	39.26	0.36
EQP10_L1_S6_135_1 40	37.92	51.41	12.00	39.41	0.30
EQP10_L1_S7_60_65	34.73	50.65	12.30	38.35	0.30
EQP10_L1_S7_135_1 40	32.00	51.83	12.56	39.27	0.26
EQP10_L1_S8_55_60	29.60	50.89	12.78	38.11	0.23
EQP10_S1_S8_130_13 5	27.23	51.55	13.01	38.54	0.22
EQP10_L1_S9_50_55	25.00	51.84	13.22	38.62	0.21
EQP10_L1_S9_125_1 30	22.89	52.17	13.41	38.76	0.20
EQP10_L1_S10_55_6 0	20.78	52.13	13.61	38.51	0.20
EQP10_L1_S10_130_ 135	18.90	52.50	13.79	38.71	0.18
EQP10_L1_S11_55_6 0	17.33	52.72	13.94	38.79	0.15
EQP10_L1_S11_130_ 135	16.89	52.72	13.98	38.74	0.04
EQP10_L1_S12_55_6 0	16.43	52.67	14.02	38.65	0.04
EQP10_L1_S12_130_ 135	15.99	53.00	14.06	38.93	0.04
EQP10_L1_S13_55-60	15.53	53.23	14.11	39.12	0.04
EQP10_L1_S14_130_ 135	14.18	52.83	14.23	38.60	0.13
EQP10_L1_S15_55_6 0	13.72	53.96	14.28	39.68	0.04
EQP10_L1_S15_121_ 125	13.34	55.03	14.31	40.72	0.04
EQP10_L1_S16_55_6 0	12.82	53.66	14.36	39.30	0.05
EQP10_L1_S16_130- 135	12.39	53.13	14.40	38.73	0.04
EQP10_L1_S17_55_6 0	11.93	52.77	14.45	38.32	0.04
EQP10_L1_S18_30_3 5	11.18	53.12	14.52	38.60	0.07
EQP10_L1_S18_65_7 0	10.97	52.68	14.54	38.15	0.02

Table A.6: Interpolated dissolved oxygen, measured nitrate concentration, calculated nitrate produced *in-situ* and relict nitrate concentration at EQP 11.

sample ID	[O ₂] interpolated (μM)	[NO ₃ ⁻] measured (μM)	[NO ₃ ⁻] produced (μM)	[NO ₃ ⁻] relict (μM)	[NO ₃ ⁻] produced in intervals (μM)
EQP11_MC4_BW	146.75	36.51	0.00	36.51	0.00
EQP11_MC4_0_5	144.86	39.94	0.18	39.77	0.18
EQP11_MC4_5_10	141.09	38.29	0.53	37.75	0.36
EQP11_MC4_10_15	137.31	40.63	0.89	39.74	0.36
EQP11_G1_S1_10_15	135.42	40.48	1.07	39.41	0.18
EQP11_MC_15_20	133.54	40.98	1.24	39.73	0.18
EQP11_MC4_20_25	129.76	43.38	1.60	41.78	0.36
EQP11_MC_25_30	125.99	41.00	1.95	39.05	0.36
EQP11_G1_S1_25_30	124.10	42.52	2.13	40.39	0.18
EQP11_L1_S1_25-30	123.15	37.93	2.22	35.71	0.09
EQP11_MC4_30_35	122.21	42.40	2.31	40.09	0.09
EQP11_MC4_35_40	118.43	40.35	2.67	37.68	0.36
EQP11_MC4_40_43	115.41	42.27	2.95	39.33	0.28
EQP11_G1_S1_45_50	110.88	41.05	3.38	37.67	0.43
EQP11_G1_S1_65_70	95.78	41.68	4.80	36.88	1.42
EQP11_L1_S1_65-70	91.31	41.01	5.22	35.79	0.42
EQP11_G1_S1_100_105	86.83	43.04	5.64	37.40	0.42
EQP11_G1_S1_125_130	82.77	42.94	6.02	36.92	0.38
EQP11_G1_S1_140_145	80.70	44.16	6.22	37.94	0.19
EQP11_L1_S2_55_60	80.57	44.60	6.23	38.37	0.01
EQP11_G1_S2_15_20	77.69	43.81	6.50	37.31	0.27
EQP11_G1_S2_50_55	74.17	46.90	6.83	40.07	0.33

EQP11_L1_S2_130-135	72.75	44.46	6.96	37.50	0.13
EQP11_G1_S2_70_75	72.41	44.81	7.00	37.81	0.03
EQP11_G1_S2_95_100	70.43	46.23	7.18	39.05	0.19
EQP11_G1_S2_130_135	67.97	47.34	7.41	39.93	0.23
EQP11_L1_S3_55_60	67.07	45.79	7.50	38.29	0.08
EQP11_G1_S3_7_12	66.27	45.08	7.57	37.51	0.08
EQP11_G1_S3_25_30	65.22	45.16	7.67	37.49	0.10
EQP11_G1_S3_40_45	64.39	46.04	7.75	38.29	0.08
EQP11_L1_S3_130_135	62.88	46.11	7.89	38.21	0.14
EQP11_G1_S3_80_85	62.34	45.63	7.94	37.69	0.05
EQP11_G1_S3_100_105	61.39	46.03	8.03	38.00	0.09
EQP11_G1_S3_120_125	60.49	46.61	8.12	38.50	0.08
EQP11_L1_S4_55_60	59.33	46.54	8.23	38.31	0.11
EQP11_L1_S4_130-135	56.46	45.84	8.50	37.35	0.27
EQP11_L1_S5_55_60	53.88	46.77	8.74	38.03	0.24
EQP11_L1_S5_130_135	51.70	47.19	8.95	38.25	0.21
EQP11_L1_S6_55_60	49.77	47.30	9.13	38.17	0.18
EQP11_L1_S6_130_135	48.01	46.27	9.29	36.97	0.17
EQP11_L1_S7_55_60	46.27	46.46	9.46	37.00	0.16
EQP11_L1_S7_130_135	44.79	46.53	9.60	36.93	0.14
EQP11_L1_S8_55_60	43.03	47.33	9.76	37.57	0.17
EQP11_L1_S8_130_135	42.69	47.12	9.79	37.32	0.03
EQP11_L1_S9_55_60	42.31	46.78	9.83	36.95	0.04
EQP11_L1_S9_130_135	41.97	46.74	9.86	36.88	0.03
EQP11_L1_S10_55_60	41.62	46.88	9.89	36.99	0.03
EQP11_L1_S10_130_13	41.28	47.17	9.93	37.25	0.03
5					

EQP11_L1_S11_55_60	40.91	47.76	9.96	37.80	0.03
EQP11_L1_S11_130_13 5	40.56	47.36	9.99	37.37	0.03
EQP11_L1_S12_55_60	40.20	47.12	10.03	37.09	0.03
EQP11_L1_S12_130_13 5	39.86	47.38	10.06	37.32	0.03
EQP11_L1_S13_55_60	39.50	46.84	10.09	36.74	0.03
EQP11_L1_S13_130_13 5	39.15	47.29	10.13	37.16	0.03
EQP11_L1_S14_55_60	38.79	47.35	10.16	37.19	0.03
EQP11_L1_S14_130_13 5	38.44	47.35	10.19	37.16	0.03
EQP11_L1_S15_55_60	38.09	47.45	10.23	37.22	0.03
EQP11_L1_S15_130_13 5	37.74	47.26	10.26	37.00	0.03
EQP11_L1_S16_55_60	37.38	47.04	10.29	36.75	0.03
EQP11_L1_S16_90_95	37.22	47.29	10.31	36.99	0.02
EQP11_L1_S17_55_60	36.42	47.20	10.38	36.81	0.08
EQP11_L1_S17_130_13 5	36.39	47.10	10.39	36.71	0.00
EQP11_L1_S18_55_60	36.04	47.03	10.42	36.61	0.03
EQP11_L1_S18_130_13 5	35.70	47.35	10.45	36.90	0.03
EQP11_L1_S19_45_50	35.37	46.78	10.48	36.29	0.03
EQP11_L1_S19_90_95	35.16	46.62	10.50	36.11	0.02

Table A.7: Measured N isotopic composition of bulk sediment at EQP 10. Case 1 d15N sed is the top most measured value and case 2 is the average d15Nmeasured value in the top 1000m; both are *italicized*.

sample ID	depth (mbsf)	$\delta^{15}\text{N}$ sediment (‰) measured
EQP10_G2_S1_0_5	0.025	7.88
EQP10_L1_S2_125_130	2.625	7.81
EQP10_L1_S12_55_60	17.255	4.90

EQP10_L1_S14_130_135	21.095	4.73
EQP10_L1_S15_55_60	21.875	4.63
EQP10_L1_S18_30_35	26.215	2.72
Average 0-1000m		7.85

Table A.8: Interpolated $\delta^{15}\text{N}_{\text{sediment}}$ for case 3 of site EQP 10.

sample ID	$\delta^{15}\text{N}$ sediment (‰) interpolated
BW	7.88
EQP10_G2_S1_0_5	7.88
EQP10_G1_S1_5_10	7.87
EQP10_G2_S1_5_10	7.87
EQP10_G2_S1_10_15	7.86
EQP10_G2_S1_15_20	7.85
EQP10_G2_S1_20_25	7.84
EQP10_G1_S1_25_30	7.83
EQP10_G2_S1_25_30	7.83
EQP10_G2_S1_30_35	7.82
EQP10_G2_S1_35_40	7.82
EQP10_G2_S1_40_45	7.81
EQP10_L1_S1_40_45	7.81
EQP10_G1_S1_45_50	7.80
EQP10_G2_S1_45-50	7.80
EQP10_G1_S1_65_70	7.77
EQP10_G1_S1_100_105	7.71
EQP10_L1_S1_115_120	7.68
EQP10_G1_S1_120_125	7.67
EQP10_G1_S1_135_140	7.65

EQP10_G1_S2_10_15	7.60
EQP10_G1_S2_30_35	7.57
EQP10_L1_S2_50_55	7.56
EQP10_G1_S2_50_55	7.54
EQP10_G1_S2_70_75	7.50
EQP10_G1_S2_105_110	7.44
EQP10_L1_S2_125_130	7.44
EQP10_G1_S2_125_130	7.41
EQP10_G1_S2_145_150	7.38
EQP10_G1_S2_165_170	7.34
EQP10_L1_S3_50_55	7.30
EQP10_L1_S3_125_130	7.17
EQP10_L1_S4_55_60	7.04
EQP10_L1_S4_130_135	6.91
EQP10_L1_S5_55_60	6.77
EQP10_L1_S5_130_135	6.64
EQP10_L1_S6_60_65	6.51
EQP10_L1_S6_135_140	6.38
EQP10_L1_S7_60_65	6.25
EQP10_L1_S7_135_140	6.12
EQP10_L1_S8_55_60	6.00
EQP10_S1_S8_130_135	5.87
EQP10_L1_S9_50_55	5.74
EQP10_L1_S9_125_130	5.62
EQP10_L1_S10_55_60	5.48
EQP10_L1_S10_130_135	5.35
EQP10_L1_S11_55_60	5.22
EQP10_L1_S11_130_135	5.09

EQP10_L1_S12_55_60	4.96
EQP10_L1_S12_130_135	4.83
EQP10_L1_S13_55-60	4.70
EQP10_L1_S14_130_135	4.31
EQP10_L1_S15_55_60	4.18
EQP10_L1_S15_121_125	4.07
EQP10_L1_S16_55_60	3.92
EQP10_L1_S16_130-135	3.79
EQP10_L1_S17_55_60	3.66
EQP10_L1_S18_30_35	3.44
EQP10_L1_S18_65_70	3.38

Table A.9: Measured N isotopic composition of bulk sediment at EQP 11. Case 1 d15N sed is the top most measured value and case 2 is the average d15N_{measured} value in the top 1000m; both are *italicized*.

sample ID	depth (mbsf)	$\delta^{15}\text{N}$ sediment (‰) measured
EQP11_MC4_BW	0	<i>5.67</i>
EQP11_MC4_0_5	0.025	<i>5.79</i>
EQP11_G1_S1_25_30	0.275	<i>6.21</i>
EQP11_G1_S1_45_50	0.475	<i>6.08</i>
EQP11_G1_S1_100_105	1.025	<i>5.97</i>
EQP11_G1_S1_125_130	1.275	<i>5.38</i>
EQP11_L1_S2_55_60	1.435	<i>5.29</i>
EQP11_G1_S2_70_75	2.225	<i>5.37</i>
EQP11_G1_S3_7_12	3.095	<i>5.70</i>
EQP11_L1_S3_130_135	3.715	<i>5.20</i>
EQP11_L1_S7_55_60	9.075	<i>4.32</i>

Average 0-1000m	5.54
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Table A.10: Interpolated $\delta^{15}\text{N}_{\text{sediment}}$ for case 3 of site EQP 11.

sample ID	$\delta^{15}\text{N}$ sediment (‰) interpolated
EQP11_MC4_BW	5.66
EQP11_MC4_0_5	5.66
EQP11_MC4_5_10	5.65
EQP11_MC4_10_15	5.64
EQP11_G1_S1_10_15	5.64
EQP11_MC_15_20	5.64
EQP11_MC4_20_25	5.63
EQP11_MC_25_30	5.63
EQP11_G1_S1_25_30	5.63
EQP11_L1_S1_25-30	5.63
EQP11_MC4_30_35	5.62
EQP11_MC4_35_40	5.61
EQP11_MC4_40_43	5.61
EQP11_G1_S1_45_50	5.60
EQP11_G1_S1_65_70	5.58
EQP11_L1_S1_65-70	5.58
EQP11_G1_S1_100_105	5.53
EQP11_G1_S1_125_130	5.50
EQP11_G1_S1_140_145	5.48
EQP11_L1_S2_55_60	5.48
EQP11_G1_S2_15_20	5.45
EQP11_G1_S2_50_55	5.41

EQP11_L1_S2_130-135	5.39
EQP11_G1_S2_70_75	5.38
EQP11_G1_S2_95_100	5.35
EQP11_G1_S2_130_135	5.30
EQP11_L1_S3_55_60	5.29
EQP11_G1_S3_7_12	5.27
EQP11_G1_S3_25_30	5.25
EQP11_G1_S3_40_45	5.23
EQP11_L1_S3_130_135	5.19
EQP11_G1_S3_80_85	5.18
EQP11_G1_S3_100_105	5.15
EQP11_G1_S3_120_125	5.13
EQP11_L1_S4_55_60	5.09
EQP11_L1_S4_130-135	5.00
EQP11_L1_S5_55_60	4.90
EQP11_L1_S5_130_135	4.81
EQP11_L1_S6_55_60	4.71
EQP11_L1_S6_130_135	4.62
EQP11_L1_S7_55_60	4.52
EQP11_L1_S7_130_135	4.42
EQP11_L1_S8_55_60	4.33
EQP11_L1_S8_130_135	4.24
EQP11_L1_S9_55_60	4.13
EQP11_L1_S9_130_135	4.04
EQP11_L1_S10_55_60	3.94
EQP11_L1_S10_130_135	3.85
EQP11_L1_S11_55_60	3.75

EQP11_L1_S11_130_135	3.66
EQP11_L1_S12_55_60	3.56
EQP11_L1_S12_130_135	3.46
EQP11_L1_S13_55_60	3.36
EQP11_L1_S13_130_135	3.27
EQP11_L1_S14_55_60	3.17
EQP11_L1_S14_130_135	3.08
EQP11_L1_S15_55_60	2.98
EQP11_L1_S15_130_135	2.89
EQP11_L1_S16_55_60	2.79
EQP11_L1_S16_90_95	2.74
EQP11_L1_S17_55_60	2.52
EQP11_L1_S17_130_135	2.52
EQP11_L1_S18_55_60	2.42
EQP11_L1_S18_130_135	2.33
EQP11_L1_S19_45_50	2.24
EQP11_L1_S19_90_95	2.18

Table A.11: Calculated $\delta^{15}\text{N}_{\text{relict}}$ in Case 1, Case 2, and Case 3 for site EQP 10. Outliers removed. *Case 2 was chosen for interpretation.*

sample ID	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 1	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 2	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 3
BW	4.29	4.29	4.29
EQP10_G2_S1_0_5	4.87	4.87	4.87
EQP10_G1_S1_5_10	4.53	4.53	4.53
EQP10_G2_S1_5_10			
EQP10_G2_S1_10_15	5.27	5.27	5.27

EQP10_G2_S1_15_20			
EQP10_G2_S1_20_25	5.35	5.35	5.35
EQP10_G1_S1_25_30			
EQP10_G2_S1_25_30	6.15	6.15	6.15
EQP10_G2_S1_30_35	5.77	5.77	5.77
EQP10_G2_S1_35_40			
EQP10_G2_S1_40_45	5.49	5.49	5.49
EQP10_L1_S1_40_45	4.49	4.49	4.49
EQP10_G1_S1_45_50			
EQP10_G2_S1_45_50	4.67	4.67	4.68
EQP10_G1_S1_65_70	5.15	5.15	5.16
EQP10_G1_S1_100_105			
EQP10_L1_S1_115_120			
EQP10_G1_S1_120_125			
EQP10_G1_S1_135_140	5.63	5.63	5.64
EQP10_G1_S2_10_15	6.70	6.70	6.72
EQP10_G1_S2_30_35			
EQP10_L1_S2_50_55			
EQP10_G1_S2_50_55	5.36	5.36	5.38
EQP10_G1_S2_70_75			
EQP10_G1_S2_105_110	5.33	5.33	5.36
EQP10_L1_S2_125_130	6.10	6.10	6.13
EQP10_G1_S2_125_130			
EQP10_G1_S2_145_150			
EQP10_G1_S2_165_170	3.89	3.89	3.93
EQP10_L1_S3_50_55			
EQP10_L1_S3_125_130	4.86	4.87	4.92
EQP10_L1_S4_55_60			
EQP10_L1_S4_130_135	5.88	5.88	5.97
EQP10_L1_S5_55_60	6.38	6.39	6.48

EQP10_L1_S5_130_135	6.24	6.25	6.35
EQP10_L1_S6_60_65	6.37	6.38	6.50
EQP10_L1_S6_135_140	5.94	5.95	6.07
EQP10_L1_S7_60_65	6.56	6.57	6.71
EQP10_L1_S7_135_140			
EQP10_L1_S8_55_60	6.83	6.84	7.01
EQP10_S1_S8_130_135	5.86	5.87	6.04
EQP10_L1_S9_50_55	6.62	6.63	6.81
EQP10_L1_S9_125_130	7.06	7.07	7.26
EQP10_L1_S10_55_60	6.53	6.54	6.75
EQP10_L1_S10_130_135	7.10	7.11	7.32
EQP10_L1_S11_55_60	6.78	6.79	7.01
EQP10_L1_S11_130_135	8.18	8.19	8.42
EQP10_L1_S12_55_60	6.64	6.65	6.89
EQP10_L1_S12_130_135	7.44	7.45	7.69
EQP10_L1_S13_55-60	6.41	6.42	6.66
EQP10_L1_S14_130_135	7.33	7.34	7.59
EQP10_L1_S15_55_60			
EQP10_L1_S15_121_125	8.05	8.06	8.31
EQP10_L1_S16_55_60	7.44	7.45	7.71
EQP10_L1_S16_130-135	9.00	9.01	9.28
EQP10_L1_S17_55_60	6.63	6.64	6.92
EQP10_L1_S18_30_35	7.66	7.68	7.96
EQP10_L1_S18_65_70	7.22	7.23	7.51

Table A.12: Calculated $\delta^{18}\text{O}_{\text{relict}}$ in Case 1, Case 2, and Case 3 for site EQP 10. Outliers removed. *Case 2 was chosen for interpretation.*

sample ID	$\delta^{18}\text{O}_{\text{relict}}$ (‰ vs.VSMOW) case 1	$\delta^{18}\text{O}_{\text{relict}}$ (‰ vs.VSMOW) case 2	$\delta^{18}\text{O}_{\text{relict}}$ (‰ vs.VSMOW) case 3
BW	1.27	1.27	1.27

EQP10_G2_S1_0_5	1.79	<i>1.79</i>	1.79
EQP10_G1_S1_5_10	1.19	<i>1.19</i>	1.19
EQP10_G2_S1_5_10	2.24	<i>2.24</i>	2.24
EQP10_G2_S1_10_15	2.44	<i>2.44</i>	2.44
EQP10_G2_S1_15_20	2.00	<i>2.00</i>	2.00
EQP10_G2_S1_20_25	2.20	<i>2.20</i>	2.20
EQP10_G1_S1_25_30	1.27	<i>1.27</i>	1.27
EQP10_G2_S1_25_30	2.89	<i>2.89</i>	2.89
EQP10_G2_S1_30_35	1.41	<i>1.41</i>	1.41
EQP10_G2_S1_35_40	1.30	<i>1.30</i>	1.30
EQP10_G2_S1_40_45	1.87	<i>1.87</i>	1.86
EQP10_L1_S1_40_45	1.72	<i>1.72</i>	1.71
EQP10_G1_S1_45_50	3.24	<i>3.24</i>	3.23
EQP10_G2_S1_45_50	2.52	<i>2.52</i>	2.51
EQP10_G1_S1_65_70	1.97	<i>1.97</i>	1.96
EQP10_G1_S1_100_105	1.35	<i>1.35</i>	1.35
EQP10_L1_S1_115_120	1.82	<i>1.82</i>	1.81
EQP10_G1_S1_120_125	1.26	<i>1.26</i>	1.25
EQP10_G1_S1_135_140	1.47	<i>1.47</i>	1.46
EQP10_G1_S2_10_15	1.65	<i>1.65</i>	1.64
EQP10_G1_S2_30_35	2.83	<i>2.83</i>	2.82
EQP10_L1_S2_50_55	1.14	<i>1.14</i>	1.13
EQP10_G1_S2_50_55	0.97	<i>0.97</i>	0.96
EQP10_G1_S2_70_75	1.72	<i>1.72</i>	1.71
EQP10_G1_S2_105_110	2.63	<i>2.63</i>	2.62
EQP10_L1_S2_125_130	1.80	<i>1.80</i>	1.79
EQP10_G1_S2_125_130	2.36	<i>2.36</i>	2.34
EQP10_G1_S2_145_150	2.69	<i>2.69</i>	2.68
EQP10_G1_S2_165_170	0.64	<i>0.64</i>	0.63
EQP10_L1_S3_50_55	3.36	<i>3.36</i>	3.35
EQP10_L1_S3_125_130	1.16	<i>1.16</i>	1.14

EQP10_L1_S4_55_60	7.13	7.13	7.11
EQP10_L1_S4_130_135	2.20	2.20	2.18
EQP10_L1_S5_55_60	2.52	2.52	2.50
EQP10_L1_S5_130_135	1.91	1.91	1.89
EQP10_L1_S6_60_65	2.24	2.24	2.22
EQP10_L1_S6_135_140			
EQP10_L1_S7_60_65	3.83	3.83	3.81
EQP10_L1_S7_135_140	3.83	3.83	3.81
EQP10_L1_S8_55_60	3.69	3.69	3.66
EQP10_L1_S8_130_135	4.28	4.28	4.26
EQP10_L1_S9_50_55			
EQP10_L1_S9_125_130			
EQP10_L1_S10_55_60	3.28	3.27	3.25
EQP10_L1_S10_130_135	5.08	5.08	5.06
EQP10_L1_S11_55_60	5.13	5.13	5.11
EQP10_L1_S11_130_135	6.07	6.07	6.04
EQP10_L1_S12_55_60	3.77	3.76	3.74
EQP10_L1_S12_130_135	5.42	5.42	5.39
EQP10_L1_S13_55-60			
EQP10_L1_S14_130_135	6.50	6.49	6.47
EQP10_L1_S15_55_60			
EQP10_L1_S15_121_125	4.75	4.75	4.72
EQP10_L1_S16_55_60	5.76	5.76	5.74
EQP10_L1_S16_130-135			
EQP10_L1_S17_55_60			
EQP10_L1_S18_30_35	4.94	4.94	4.92
EQP10_L1_S18_65_70	5.30	5.30	5.28

Table A.13: Calculated $\delta^{15}\text{N}_{\text{relict}}$ in Case 1, Case 2, and Case 3 for site EQP 11. Outliers removed. *Case 2 was chosen for interpretation.*

sample ID	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 1	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 2	$\delta^{15}\text{N}_{\text{relict}}$ (‰ vs. N_2 in air) case 3
EQP11_MC4_BW			
EQP11_MC4_0_5			
EQP11_MC4_5_10	6.48	6.48	6.48
EQP11_MC4_10_15	6.15	6.15	6.15
EQP11_G1_S1_10_15			
EQP11_MC_15_20	5.27	5.27	5.27
EQP11_MC4_20_25	5.70	5.71	5.71
EQP11_MC_25_30	5.80	5.80	5.80
EQP11_G1_S1_25_30	5.91	5.92	5.91
EQP11_L1_S1_25-30	6.08	6.08	6.08
EQP11_MC4_30_35			
EQP11_MC4_35_40	5.76	5.77	5.76
EQP11_MC4_40_43			
EQP11_G1_S1_45_50	5.51	5.52	5.51
EQP11_G1_S1_65_70	6.07	6.08	6.07
EQP11_L1_S1_65-70	6.19	6.21	6.20
EQP11_G1_S1_100_105	5.18	5.20	5.19
EQP11_G1_S1_125_130	5.53	5.55	5.54
EQP11_G1_S1_140_145	5.17	5.19	5.18
EQP11_L1_S2_55_60	6.27	6.29	6.28
EQP11_G1_S2_15_20	5.89	5.91	5.91
EQP11_G1_S2_50_55	6.64	6.66	6.65
EQP11_L1_S2_130-135			
EQP11_G1_S2_70_75			
EQP11_G1_S2_95_100	5.98	6.00	5.99
EQP11_G1_S2_130_135	6.19	6.21	6.21
EQP11_L1_S3_55_60	6.29	6.32	6.31
EQP11_G1_S3_7_12	5.95	5.98	5.97

EQP11_G1_S3_25_30	6.41	<i>6.44</i>	6.43
EQP11_G1_S3_40_45	7.09	<i>7.11</i>	7.11
EQP11_L1_S3_130_135	6.57	<i>6.59</i>	6.59
EQP11_G1_S3_80_85	6.51	<i>6.53</i>	6.53
EQP11_G1_S3_100_105	6.35	<i>6.38</i>	6.38
EQP11_G1_S3_120_125	7.23	<i>7.25</i>	7.26
EQP11_L1_S4_55_60	6.69	<i>6.71</i>	6.72
EQP11_L1_S4_130-135	6.02	<i>6.05</i>	6.05
EQP11_L1_S5_55_60	6.12	<i>6.15</i>	6.16
EQP11_L1_S5_130_135	7.25	<i>7.27</i>	7.29
EQP11_L1_S6_55_60	6.35	<i>6.38</i>	6.40
EQP11_L1_S6_130_135	7.31	<i>7.34</i>	7.37
EQP11_L1_S7_55_60	6.10	<i>6.13</i>	6.16
EQP11_L1_S7_130_135	6.51	<i>6.54</i>	6.58
EQP11_L1_S8_55_60	5.26	<i>5.29</i>	5.33
EQP11_L1_S8_130_135	7.17	<i>7.20</i>	7.24
EQP11_L1_S9_55_60	7.18	<i>7.21</i>	7.25
EQP11_L1_S9_130_135	6.46	<i>6.50</i>	6.54
EQP11_L1_S10_55_60	6.36	<i>6.39</i>	6.43
EQP11_L1_S10_130_135			
EQP11_L1_S11_55_60	7.06	<i>7.10</i>	7.14
EQP11_L1_S11_130_135	6.34	<i>6.37</i>	6.42
EQP11_L1_S12_55_60	7.09	<i>7.12</i>	7.17
EQP11_L1_S12_130_135			
EQP11_L1_S13_55_60	6.36	<i>6.39</i>	6.44
EQP11_L1_S13_130_135	7.68	<i>7.72</i>	7.77
EQP11_L1_S14_55_60	7.87	<i>7.91</i>	7.96
EQP11_L1_S14_130_135			
EQP11_L1_S15_55_60	6.66	<i>6.69</i>	6.75
EQP11_L1_S15_130_135	7.02	<i>7.05</i>	7.11

EQP11_L1_S16_55_60	6.90	6.94	7.00
EQP11_L1_S16_90_95	7.06	7.10	7.16
EQP11_L1_S17_55_60			
EQP11_L1_S17_130_135	7.16	7.20	7.27
EQP11_L1_S18_55_60			
EQP11_L1_S18_130_135	7.47	7.51	7.58
EQP11_L1_S19_45_50	7.17	7.20	7.28
EQP11_L1_S19_90_95	7.37	7.40	7.49

Table A.14: Calculated $\delta^{18}\text{O}_{\text{relict}}$ in Case 1, Case 2, and Case 3 for site EQP 11. Outliers removed. *Case 2 was chosen for interpretation.*

sample ID	(‰ vs.VSMOW) case 1	(‰ vs.VSMOW) case 2	(‰ vs.VSMOW) case 3
EQP11_MC4_BW	1.03	1.03	1.03
EQP11_MC4_0_5	1.41	1.41	1.41
EQP11_MC4_5_10			
EQP11_MC4_10_15	4.77	4.77	4.77
EQP11_G1_S1_10_15			
EQP11_MC_15_20	2.54	2.54	2.54
EQP11_MC4_20_25	2.26	2.26	2.26
EQP11_MC_25_30	2.73	2.73	2.73
EQP11_G1_S1_25_30	2.27	2.27	2.27
EQP11_L1_S1_25-30	2.83	2.83	2.83
EQP11_MC4_30_35			
EQP11_MC4_35_40	2.05	2.05	2.05
EQP11_MC4_40_43	3.57	3.56	3.56
EQP11_G1_S1_45_50			
EQP11_G1_S1_65_70	2.32	2.32	2.31

EQP11_L1_S1_65-70			
EQP11_G1_S1_100_105	2.10	<i>2.10</i>	2.09
EQP11_G1_S1_125_130			
EQP11_G1_S1_140_145	2.11	<i>2.11</i>	2.10
EQP11_L1_S2_55_60	2.71	<i>2.71</i>	2.70
EQP11_G1_S2_15_20	3.20	<i>3.20</i>	3.19
EQP11_G1_S2_50_55			
EQP11_L1_S2_130-135	4.15	<i>4.15</i>	4.13
EQP11_G1_S2_70_75			
EQP11_G1_S2_95_100	2.10	<i>2.10</i>	2.09
EQP11_G1_S2_130_135	3.73	<i>3.73</i>	3.72
EQP11_L1_S3_55_60	1.99	<i>1.99</i>	1.98
EQP11_G1_S3_7_12	3.68	<i>3.68</i>	3.67
EQP11_G1_S3_25_30	3.38	<i>3.38</i>	3.37
EQP11_G1_S3_40_45	2.28	<i>2.28</i>	2.27
EQP11_L1_S3_130_135	3.27	<i>3.27</i>	3.26
EQP11_G1_S3_80_85	3.35	<i>3.35</i>	3.34
EQP11_G1_S3_100_105	2.16	<i>2.16</i>	2.15
EQP11_G1_S3_120_125			
EQP11_L1_S4_55_60	2.42	<i>2.42</i>	2.41
EQP11_L1_S4_130-135	4.05	<i>4.05</i>	4.04
EQP11_L1_S5_55_60	2.38	<i>2.38</i>	2.37
EQP11_L1_S5_130_135	4.58	<i>4.58</i>	4.57
EQP11_L1_S6_55_60	2.92	<i>2.92</i>	2.91
EQP11_L1_S6_130_135	3.73	<i>3.73</i>	3.72
EQP11_L1_S7_55_60	3.14	<i>3.14</i>	3.12
EQP11_L1_S7_130_135	3.24	<i>3.24</i>	3.23
EQP11_L1_S8_55_60	3.68	<i>3.67</i>	3.66
EQP11_L1_S8_130_135	2.90	<i>2.90</i>	2.89
EQP11_L1_S9_55_60	3.70	<i>3.70</i>	3.69

EQP11_L1_S9_130_135	4.38	<i>4.38</i>	4.37
EQP11_L1_S10_55_60	5.46	<i>5.46</i>	5.45
EQP11_L1_S10_130_135	3.34	<i>3.34</i>	3.32
EQP11_L1_S11_55_60	3.79	<i>3.79</i>	3.77
EQP11_L1_S11_130_135	2.11	<i>2.11</i>	2.09
EQP11_L1_S12_55_60	3.54	<i>3.54</i>	3.53
EQP11_L1_S12_130_135			
EQP11_L1_S13_55_60			
EQP11_L1_S13_130_135	4.65	<i>4.65</i>	4.63
EQP11_L1_S14_55_60			
EQP11_L1_S14_130_135			
EQP11_L1_S15_55_60	4.38	<i>4.38</i>	4.36
EQP11_L1_S15_130_135	1.70	<i>1.70</i>	1.68
EQP11_L1_S16_55_60	5.67	<i>5.67</i>	5.65
EQP11_L1_S16_90_95	3.15	<i>3.15</i>	3.13
EQP11_L1_S17_55_60			
EQP11_L1_S17_130_135	2.34	<i>2.34</i>	2.32
EQP11_L1_S18_55_60			
EQP11_L1_S18_130_135			
EQP11_L1_S19_45_50	4.82	<i>4.82</i>	4.80

B. Estimation of How much f would need to change in order to observe a mean global $\delta^{15}\text{N}_{\text{nitrate}}$ of 7.5‰

$$\delta^{15}\text{N}_{\text{global}} = 1 * (\epsilon_{\text{fixation}}) + (f * (\epsilon_{\text{Seddenit}}) + (1-f) * (\epsilon_{\text{wcdenit}}))$$

Present: $\delta^{15}\text{N}_{\text{global}} = 5.0 \pm .5\text{‰}$

$$\epsilon_{\text{fixation}} = 0.0\text{‰}$$

$$\epsilon_{\text{Seddenit}} = 0.0\text{‰}$$

$$\epsilon_{\text{wcdenit}} = 25\text{‰}$$

$$f = .8$$

Oldest sample, when $\delta^{15}\text{N}_{\text{global}} = 7.5\text{‰}$

$$\epsilon_{\text{fixation}} = 0.0\text{‰}$$

$$\epsilon_{\text{Seddenit}} = 0.0\text{‰}$$

$$\epsilon_{\text{wcdenit}} = 25\text{‰}$$

$$f = .7$$

C. MATLAB codes

C.1 MATLAB code for Diffusion Model:

```
% FINAL VERSION OF THE DIFUSSION MODEL FOR THE PACIFIC OCEAN

% Anne Hartwell: 1D diffusion model for Nitrate in deep clays (EQP 10
and
% EQP 11)-- modified from:
% Tania Lado Insua 1D diffusion model for chlorinity in deep clays

% Measured FF and porosity
% Programmed for nitrate
% code units: m and yr

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%Works with EQP10, EQP11
%sites where basement is not reached need to have an extra point to
final
%depth for the model with the same value as the last measurement
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

clear all;close all;clc;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%FILES (exchange EQP10 by EQP11 in these lines for the other site)
load ten_alldepths.txt
load eleven_alldepths.txt
ten_depths=ten_alldepths;
eleven_depths=eleven_alldepths;

load d15N_EQP10.txt; %case 2 relict d15N EQP 10
load d15N_EQP11.txt; %case 2 relict d15N EQP 11...code is written to
analysis one site at a time.
EQP10_data=d15N_EQP10;
EQP11_data=d15N_EQP11;

load d18O_EQP10.txt; %case 2 relict d18O EQP 10
load d18O_EQP11.txt; %case 2 relict d18O EQP 11
EQP10_O_data=d18O_EQP10;
EQP11_O_data=d18O_EQP11;

%%EQP 10%%
%Measrued data is call Nit.
% Nit=d15N_EQP10;
% %Diffusitiy coefficient
% load Chl_EQP10.txt %chlorinity
% File_Ch1=Chl_EQP10;
% load EQP10_FF.txt; %formation factor
% coreFF=EQP10_FF;
% load EQP10_Por.txt;%porosity
% corepor=EQP10_Por;

% %%EQP 11%%
```



```

%%Measrued data is call Nit.
Nit=d15N_EQP11;
%Diffusitiy coefficient
load Chl_EQP11.txt %chlorinity
File_Ch1=Chl_EQP11;
load EQP11_FF.txt; %formation factor
coreFF=EQP11_FF;
load EQP11_Por.txt;%porosity
corepor=EQP11_Por;
% % %
%
%

%%LOAD INITIAL CONDITION --- NB if kyr or yr....adjust data set as
appropriate--code is written for kyr. IF YOU MUST CHANGE CODE REMOVE
THE
%%*1000 AT LINE 146.
% time 0 if missing = to most recent data point in record.
load TBC.txt; %d15N galbraith (Montecarlo d15N)5-30
load TBC2.txt; %d15N Arabian Sea (Altabet) *age in kyr .13-63
load TBC3.txt; %d15N_DePolHolz_Chili 30S **age in kyr** .8-66
load TBC4.txt; %d15N Ganeshram et al., 2000 ETNP **age in kyr 1.6-265
load TBC5.txt; %d15N Orca .49-23
load TBC6.txt; %d15N SBB (Emmer) .03-48 kyr
load TBC7.txt; %d18O Ganeshram et al., 2000 ETNP 1.6-265
load TBC8.txt; %d18O Lisecki and Raymo 2009, benthing d18O pacific 0-
800kyr
load TBC9.txt; %d15N .8-40kyr De Pol-Holz et al. 2007 GeoB 7139-2
Nitrogen Data ETSP

sl=TBC; %Input of sl is any of the loaded inital conditions.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%TO INVESTIGATE HOW ALPHA EFFECTS TEH MODEL CHANGE 'PERC' AT LINE 81

%an extra point was added at the bottom of the site for porosity and
%Formation factor, since the measurements go only to 28.05mbsf for
EQP11
%and to 26.77mbsf for EQP10

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%IDENTIFICATION VARIABLES
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%Formation Factor measurements
nzz=coreFF(:,1); %nodes for depth (adimensional)
zz=coreFF(:,2); %depths (m)

%Chlorinity measurements
Cl_IAPSO=19.2787; %g/kg according to IFM-GEOMAR mM/L
IAP=559.55; %(g/kg) IAPSO chlorinity
m_Ch1=File_Ch1(:,2); %chlorinity measurements

```

```

m_z=File_Ch1(:,1); %depth for chlorinity
datainCh1=[m_z m_Ch1]; %Data in the Chlorinity file

>Loading the porosity data
nzz_p=corepor(:,1); %nodes for depth for porosity(adimensional)
zz_p=corepor(:,2); %depths for porosity (m)
P=corepor(:,3); %Porosity (adimensional)
numzz_p=nzz_p(end); %number of measurements/nodes in depth of
porosity
zzmax_p=zz_p(end); %maximum depth for porosity

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%PARAMETERS
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%

n_sml=0.4; %for fastsmooth of the curve to correct FF
perCh12=0.3; %for lowess of the Chloride data curve
perFF=0.2; %for lowess of the curve to interpolate and smooth FF
perPor=0.2; %for lowess of the curve to interpolate and smooth Por
qua=0.95; %quantil error outliers %set to 1 if no outliers
perc=1.5; %percentaje for the sea level
%YOU NEED TO MODIFY perc IN ORDER TO ADDAPT THE MODEL FOR THE BEST
FIT
%AN ERROR WILL BE OUTPUT FOR YOU TO COMPARE AS YOU OPTIMIZE THIS
VARIABLE
d=0.5; %distance between nodes of depth
%INCREASE TO MAKE IT WORK!
%WHEN VISCOSITY DECREASES OR D INCREASES
T0=1.3; %Temperature at 0m for that site. Change value according to:
%Site EQP11 and EQP10 =1.3 (same value for both)
GradT=0.03;%gradient of temperature in C/m. Change value according
to:
%EQP10 and EQP11 =0.030 (same value for both)

%Steps
dt=5e7; %per year6e12; %time step 1e8s=3.1710 yr %REDUCE TO MAKE IT
WORK!
pres_time=1700; %present time value
change=365*24*60*60; %change from yrs to seconds
zmax_mod=zzmax_p; %maximum depth of model

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%CHLORINITY MEASUREMENTS OUTLIERS
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%

%Remove outliers Ch1
fs_Ch1=lowess(datainCh1,n_sml,0); %smooth formation factor

%Substact curve value from measured value
dif_Ch1=m_Ch1-fs_Ch1(:,3);

```

```

%quantile of the difference
qu_Ch1=quantile(dif_Ch1,qua);
ind_Ch1=find(abs(dif_Ch1)>qu_Ch1); %finds outliers positive,
%outputs location

% remove outliers for Chlorinity
subset_data=[m_z m_Ch1];
subset_data(ind_Ch1,:)=[];

%Designate two arrays per file without outliers
m_z2=subset_data(:,1); %depth data (m)
m_Ch12=subset_data(:,2); %Cl without outliers

%smoothing Ch1 without outliers for FF nodes
m_z3=[0;m_z2(1:end);zmax_mod];
m_Ch13=[m_Ch12(1);m_Ch12(1:end);m_Ch12(end)];

datainCh12=[m_z3 m_Ch13];

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%FORMATION FACTOR CORRECTION BASED ON MEASURED CHLORINITY
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
Ch13=interp1(m_z3,m_Ch13,zz); %FF interpolated
corr=(Ch13/IAP);
FFF=(coreFF(:,3));
F=ones(length(nzz),1);
for i=1:length(nzz);
    F(i)=FFF(i)*corr(i); %ff (adimensional)
end
numzz=nzz(end); %number of measurements/nodes in depth
zzmax=zz(end); %maximum depth

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%
%MODEL BOUNDARY CONDITIONS
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%

%Salinity values for boundary condition over time
yy=s1(:,1)*change*1000; %Initially, time yr now changed into seconds
xx=s1(:,2);%.*28.708; %Sealevel values for chlorinity %28.726
yr_max=yy(end);%Max time value
yr_min=yy(1);
y=[yr_min:dt:yr_max]; %Time vector for Cl boundary condition
chl=interp1(yy,xx,y); %Cl boundary condition for top

%values of Chlorinity for the BC
%last=m_Ch12((end-5):end)
BC=mean(chl); %Mean value as average of the last 115ky of the record
%for sealevel TBC

%time nodes

```

```

nt=length(ch1);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%CHANGE IN TOP BOUNDARY CONDITION: SEA LEVEL INCREASE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

ch0=ch1(end);
delta=ch1-ch0;
ch12=ch0+perc.*delta;
BC2=mean(ch12); %Mean value as average of the last 115ky of the
record
%for new sealevel TBC after multiplying by the variable perc which is
the
%optimized increase value

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
% SMOOTHING AND INTERPOLATION OF THE POROSITY AND FORMATION FACTOR
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%

%Smoothing the data with LOWESS
F1=[zz F];
P1=[zz_p P];
sFF2=lowess(F1,perFF,0); %smooth formation factor
sFF=sFF2(:,3);
zz_lowFF=sFF2(:,1);
sP2=lowess(P1,perPor,0); %smooth porosity
sP=sP2(:,3);
zz_plow=sP2(:,1);

%Interpolation of the data formation factor
z=[0:d:zzmax]; %array of depth for sampling each d separation
FF=interp1(zz_lowFF,sFF,z); %FF interpolated
FF(1:2)=FF(3);
nz=[1:1:length(z)]; %vector of depth nodes for the FF
numz=numz(end); %number of nodes in depth
zmax=z(end); %maximum depth

%time nodes
nt=length(ch1); %number of time steps

%Interpolation of the data porosity
phi=interp1(zz_plow,sP,z); %Porosity interpolated
phi(1:2)=phi(3);

IF=1./FF; %inverse of the formation factors (adimensional)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%DIFFUSION COEFFICIENT WITH DEPTH
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Interpolation of the data temperature
T=T0+GradT*z; %temperature gradient with depth
Tr=20; %reference temperature

```

```

etar=1.0039; %reference viscosity (g/(cm*s))
Dr=0.00000000172; %reference diffusion coefficient for Tr
for Tx=[1:length(z)] %loop made only for T<20C
    a(Tx)=((20-T(Tx))/(T(Tx)+96))*(1.2364-0.00137*(20-T(Tx))+...
        0.0000057*(20-T(Tx))^2);
    b(Tx)=10^(a(Tx));
    eta(Tx)=1.002*b(Tx);
    D(Tx)=((T(Tx)+273.15)*etar*Dr)/(eta(Tx)*(Tr+273.15));
end

%%Age appriximation: age=depth^2 (cm^2)/2*diffusion coefficient
(cm^2/sec)
x=length(ten_depths);
for i=1:x;
    age10(i)=(ten_depths(i)^2)/(2*(D(i)));
end
ageinyears10=age10/(change);

y=length(eleven_depths);
for i=1:y;
    age11(i)=(eleven_depths(i)^2)/(2*(D(i)));
end
ageinyears11=age11/(change);

% figure(1);subplot(1,2,1);plot(ageinyears10,ten_depths);
% set(gca,'ydir','reverse');xlabel('age (years)');ylabel('depth (m)');
% title('EQP 10: maximum age is 11,652 years');
% subplot(1,2,2);plot(ageinyears11,eleven_depths);
% set(gca,'ydir','reverse');xlabel('age (years)');ylabel('depth (m)');
% title('EQP 11: maximum age is 12,507 years ');
%
% a10=ageinyears10';
% agemodel10=[a10 ten_depths];
% a11=ageinyears11';
% helly=EQP11_data(:,2);
% agemodel11=[a11
eleven_depths];%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% DIFFUSION MODEL WITH OUR DATA
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%

%Chloride matrix
Chl=BC*ones(numz,nt); %matrix of zeros (nodes in z, time nodes)

% %Initial conditions
Chl(:,1)=(BC); %Initial values for clorinity for time step one

%Loop to calculate the clorinity at different time steps
%lambda=(D*dt); %lambda=1000;

rp=3:numz;
rc=2:numz-1;
rm=1:numz-2;
B=zeros(numz,1)';
oldB=zeros(numz,1)';

```

```

for t=1:nt-1; %loop over time

% time derivative
B(rc)=( (dt*D(rc) ./ (phi(rc) .*FF(rc)*d^2)) ).*(Chl(rp,t) '-...
2*Chl(rc,t) '+Chl(rm,t) ')+...
(dt*D(rc) ./ (phi(rc) .*d^2)) .*(Chl(rp,t) '-...
Chl(rm,t) ')/2.*(IF(rp)-IF(rm))/2+...
(dt ./ (phi(rc) .*FF(rc)*d^2)) .*(Chl(rp,t) '-...
Chl(rm,t) ')/2.*(D(rp)-D(rm))/2;

% time integration
if (t==1)
    Chl(rc,t+1) = Chl(rc,t) + B(rc)';
else
    Chl(rc,t+1)=Chl(rc,t)+1.5*B(rc) '-0.5*oldB(rc)';
end
oldB=B;
% boundary conditions
Chl(1,t+1)=chl(t+1); %Top boundary condition
%Chl(end,t+1)=BC; %BBC=concentration
Chl(end,t+1)=Chl(end-1,t+1); %No-flux bottom BC
%You shouldn't need it, but just in case!
end

%Line graph chlorinity changes over time
% figure(2)
% for tt=[1:500:nt-2]
%     plot(Chl(:,tt),z)
%     set(gca,'ydir','reverse')
%     hold on
% end
% ylabel('Depth (m)')
% xlabel ('\delta^1^5N')
% title('Predicted 1-D diffusion through time')

%Color graph with depth and time
% figure(3)
% time_axis=[-yr_max:dt:yr_min]./(change*1000);%[-y(end):dt:y(1)]%
% imagesc(time_axis,z,Chl);
% colorbar
% title('\delta^1^5N diffusion with time and depth')
% ylabel('Depth (m)')
% xlabel('Time (kyr)')

%Line graph last chlorinity value
% figure(4)
% res=Chl(1:end,end);
% plot(res,z)
% set(gca,'ydir','reverse')
% hold on
% plot(Nit(:,2),Nit(:,1),'*r')
% ylabel('Depth (m)')
% xlabel ('\delta^1^5N')

```

```
% title('\delta^1^5N Arabian Sea (Altabet) (x1.5) and EQP 10 relict
values')
```

```
%Interpolation result to calculate best model
ch5int=Chl(1:end,end);
int_Ch1=interp1(z,Chl(1:end,end),Nit(:,1));
mean_error_AS=mean((Nit(:,2)-int_Ch1).^2);
sd_error_AS=std((Nit(:,2)-int_Ch1).^2);
error_AS=[mean_error_AS]
```

C.2 MATLAB code lowess

```
%% LOWESS- Locally Weighted Scatterplot Smoothing
%% Modifications:
%
% This regression will work on linear and non-linear relationships
between
% X and Y.
%
% 12/19/2008 - added upper and lower LOWESS smooths. These
additional
% smooths show how the distribution of Y varies with X. These
smooths
% are simply LOWESS applied to the positive and negative residuals
% separately, then added to the original lowess of the data. The
same
% smoothing factor is applied to both the upper and lower limits.
%
% 2/21/2009 - added sorting to the function, data no longer need
to be
% sorted. Also added a routine such that if a user also supplies
a
% second dataset, linear interpolations are done one the lowess
and used
% to predict y-values for the supplied x-values.
%
% 10/22/2009 - modified the second user provided X-data for
obtaining
% predictions. Matlab function unique sorts by default. It
really was
% not needed in the section of code to perform linear
interpolations of
% the x-data using the y-predicted LOWESS results. If the user
does not
% supply a second x-data set, it will assume to use the supplied
x-y
% data set. Thus there is an output (xy) that maintains the
original
% sequence of the input. Additionally, the user can now include a
% sequence index as the first column of input data. This can be a
% datenum or some other ordering index. The output will be
sequenced
% using that index. If a sequence index is provided a second
subplot
```

```

% will be created show the predicted Y-values in the order of the
% included sequence index. I suspect this sequence index most
often will
% be a DateTime (i.e. datenum). Just to the function generic
enough,
% the X-axis labels are not converted to a nice date format, but
the
% user could easily change that with a datetic attribute in the
subplot.
%
% An example dataset (sklla.mat) is also included in the ZIP file
for
% convenience.
%
%% Description
%
% Using a robust regression like LOWESS allows one the ability to
detect a
% trend in data that may otherwise have too much variance resulting
in
% non-significance p-values.
%
% Yhat (prediction) is computed from a weghted least squares
regression
% whose weights are both a function of distance from X and magnitude
% from of the residual from the previous regression.
%
% The conceptual of these functions and subfunctions follow the USGS
% Kendall.exe routines. Because matlab is 8-byte precision, there are
% some very small differences between FORTRAN compiled and matlab.
% Maybe 64-bit OS's has 16-byte precision in matlab?
%
% There is a very simple subfunction to create a plot of the data and
% regression if the user so choses with a flag in the call to the
lowess
% function. BTW-- the png file looks much better than what the figure
looks
% like on screen.
%
% There are loops in these routines to keep the memory requirements
to a
% minimum, since it is foreseeable that one may have very large
datasets to
% work with.
%
% f = a smoothing factor between 0 and 1. The closer to one, the
more
% smoothing done.
%
% Syntax:
%
% [dataout lowerLimit upperLimit xy] =
lowess(datain,f,wantplot,imagefile,xdata)
%
% datain = n x 2 (or 3 if sequend index is included) matrix
% dataout = n x 3 matrix
% wantplot = scaler (optional)

```



```

%         if ~= 0 then create plot
%     imagefile = full path and file name where to output the figure to
an
%         png file type at 600 dpi. If imagefile not provided, a
figure will
%         be displayed but not exported to a graphics file.
%         e.g. imagefile = 'd:\temp\lowess.png';
%     xdata = n x 1 vector. The user can supply a second dataset of x-
values
%         that will be used to predict y-values using the lowess
regression
%         results.
%     xy = x-values supplied by the user in xdata (or taken from the
input
%         data), and y-predictions using the lowess regression
results. If
%         a sequence index is given this will be included as well and
%         inserted as the first column.
%
% where:
%
% * datain(:,1) = x
% * datain(:,2) = y
% * f = scaler (0 < f < 1)
% * wantplot = scaler
% * imagefile = string
%
% * dataout(:,1) = x
% * dataout(:,2) = y
% * dataout(:,3) = y-prediction (aka yhat)
% * lowerLimit(:,1) = x with negative residuals
% * lowerLimit(:,2) = y-prediction of residuals + original y-
prediction
% * upperLimit(:,1) = x with positive residuals
% * upperLimit(:,2) = y-prediction of residuals + original y-
prediction
%
% Requirements:  none
%
% Written by
%
% Jeff Burkey
% King County Department of Natural Resources and Parks
% email: jeff.burkey@kingcounty.gov
% 12/16/2008
%
% Example syntax:
% [dataout lowerLimit upperLimit xy] =
lowess(sk11a,.25,1,'c:\temp\test.png',xdata)

%% Primary Function: lowess
% The main engine for this function.
function [dataout lowerLimit upperLimit xy] =
lowess(datain,f,wantplot,imagefile,xdata)

```

```

% start timer
start = tic;

load lowessd18011.txt;
datain=lowessd18011;
rowcol = size(datain);
f=1

if rowcol(2) == 3
    % assume time index for first column
    dte = datain(:,1);
    x_data = datain(:,2);
    y_data = datain(:,3);
else % assign empty set
    dte = [];
    x_data = datain(:,1);
    y_data = datain(:,2);
end

if exist('xdata','var') == 0
    % User didn't provide any x-values for generating a dataset
use
    % supplied set prior to sorting.
    xdata = x_data;
end

datain = sortrows([x_data y_data]);

if exist('wantplot','var') == 0 || wantplot == 0
    % user didn't provide assume zero (i.e. no plot)
    fprintf('\nNo plot will be created.\n');
    wantplot = 0;
    imagefile = '';
    limits = 1;
    upperLimit = nan;
    lowerLimit = nan;
else
    limits = 3;
end
if exist('imagefile','var') == 0
    % User didn't provide do not export to graphics file
    fprintf('\nNo plot will be exported.\n');
    imagefile = '';
end

dataout = [];

for nplots=1:limits
    % if limits is turned on, then plot the upper and lower
limits of
    % the lowess- set to plot residuals lowess
    row = find(datain(:,1));
    x = datain(row,1);
    y = datain(row,2);

```

```

switch nplots
case 2
    row = lwsResiduals > 0;
    x = dataout(row,1);
    y = lwsResiduals(row);
case 3
    row = lwsResiduals < 0;
    x = dataout(row,1);
    y = lwsResiduals(row);
end

n = length(x);

if (f <= 0.0)
    f=0.25; % set to default
end

m=fix(n*f+0.5);
window = zeros(n,1);
yhat = zeros(n,1);

for j=1:n
    % This could be done in a matrix, but need to keep memory
    footprint
    % small, thus the loop.
    d = abs(x- x(j));
    r1 = ones(n,1);
    d = sort(d);

    window(j)=d(m);
    yhat(j)= rwlreg(x,y,n,window(j),r1,x(j));
end

for it=1:2
    e = abs(y-yhat);

    n = length(e);
    s=median(e);

    r = e/(6*s);
    r = 1-r.^2;
    r = max(0,d0,r);
    r = r.^2;

    for j=1:n
        yhat(j)= rwlreg(x,y,n,window(j),r,x(j));
    end
end

switch nplots
case 1
    % calculate residuals otherwise skip
    lwsResiduals = y - yhat;

```

```

        dataout = [x y yhat];
    case 2
        ul = [x y yhat];
        [~, ia, ib] = intersect(dataout(:,1),ul(:,1));
        upperLimit = [ul(ib,1) ul(ib,3) + dataout(ia,3)];
        clear ul c ia ib
    case 3
        ll = [x y yhat];
        [~, ia, ib] = intersect(dataout(:,1),ll(:,1));
        lowerLimit = [ll(ib,1) ll(ib,3) + dataout(ia,3)];
        clear ul c ia ib
    end
end

fprintf('\nCompute time %6.4f seconds.\n',toc(start));

%% Generate predicted XY data
% Using linear interpolation to estimate y from the lowess
regression
% Any x-values beyond the range given to generate the lowess will
be
% ignored. Matlab unique function sorts the data, thus a
modified
% unique function (usunique) was developed to return an unsorted
vector.
if xdata
    xyd = [dataout(:,1) dataout(:,3)];
    xyd = unique(xyd,'rows');
    xd = xdata(xdata >= min(xyd(:,1)));
    xd = xd(xd <= max(xyd(:,1)));
    if ~isnan(xyd)
        % if f value was too small, it's possible that multiple

        % Note: it may be possible to have a few nan's in the
data set
        % while the results would still be valid. I haven't come
        % across a case of this but is possible. If so, then the
user
        % may need to incorporate a threshold of just how many
nan's
        % would be acceptable before dumping the whole
regression. But
        % to be conservative, if there are any nan's throw out
the
        % whole result dataset.
        yinterp = interp1(xyd(:,1),xyd(:,2),xd);

        xy = [dte xd yinterp];

        if length(xd) ~= length(xdata)
            fprintf('\nOne or more x-values were beyond the range
supplied to lowess.\nOr there were duplicate values.\nThey will be
ignored.\n');
        end
    else

```

```

        fprintf('\nThere were NaNs in the lowess results. No plot
will be created.\n');
        wantplot = 0;
        xy = nan;
    end
end

    if wantplot ~= 0
        customplot(dataout,upperLimit,lowerLimit,f,[dte x_data
y_data],xy,imagefile);
    end

end

%% Modification of check for 10 or more non-zero weights
% by Hirsch June 1987
%
% Robust weighted least squares regression, bisquare weights by
% distance on X-axis.
% x = is the estimation point
% yy = is the estimate value of y at x
% dd = is half the width of the window
% r = is the robustness weight, a bisquare weight of residuals.
function [yy] = rwlreg(x,y,n,d,r,xx)
    dd=d;
    ddmax = abs(x(n) - x(1));
    if dd == 0.0
        error('Regression:lowess','LOWESS window size = 0. Increase
f. ');
    else
        while dd <= ddmax
            c = 0;
            total = 0.0;
            f = (abs(x-xx)/dd);
            f = 1.0-f.^3;
            w = ((max(0,d0,f)).^3).*r;
            total = sum(w);
            c = sum(w>0);
            if c > 3
                break % out of while loop
            else
                dd=1.28*dd;
                fprintf('\nrobust size of window = %5.0f.\nLowess
window size increased to %3.2f\n', c, dd);
            end
        end
        end
        w = w/total;
        [a b] = wlsq(x,y,w);
        yy=a+b*xx;
    end

%% Weighted least squares
% This subfunction does not require any toolboxes in matlab to
execute.
function[a b] = wlsq(x,y,w)

```

```

sumw = abs(1-sum(w));
if sumw > 1e-10
    % The weights, w, must sum to one. Precision assuming type
double,
    % The user may want to adjust this value.
    error('Regression:wlsq','\nThere is an error in the
weights.\nWeights do not equal zero (%10.9f).\n',sumw);
end
wxx = sum(w.*x.^2);
wx = sum(w.*x);
wxy = sum(w.*x.*y);
wy = sum(w.*y);
b = (wxy-wy*wx)/(wxx-wx^2);
a = wy-b*wx;
end

%% Plotting of data and lowess regression line
% If a sequence vector is included in the data, the figure will
contain two
% subplots. The first one is the LOWESS regression of the data, the
second
% plots the time in the original sequence using the first column of
input
% data. Example a datenum for when the data were observed would be
common.
% The second plot will plot the observed Y-data and the predicted Y-
data.
function customplot(lws,uplmt,lwrlmt,f,oldxy,newxy,imgfile)
    figure1 = figure;

    try
        rowcol = size(newxy);
        if rowcol(2) == 3 % Users provided a sequence index e.g.
Datenum
            % The second subplot id defined first as a matter of
            % readability in the code. This Conditional segment will
not
            % be executed if no sequence index is provided (e.g.
datetime).
            subplot(2,2,3:4,'Parent',figure1,...
                'YScale','linear','YMinorTick','off',...
                'XScale','linear','XMinorTick','on',...
                'YMinorGrid','off',...
                'XMinorTick','on',...
                'XMinorGrid','on');
            box('on');
            grid('on');
            hold('all');

            line(oldxy(:,1),oldxy(:,3),'LineStyle','none', ...
                'Marker','o','MarkerSize',7,...
                'MarkerEdgeColor','k',...
                'MarkerFaceColor','b',...
                'DisplayName','Observed');

            line(newxy(:,1),newxy(:,3),'LineStyle','-',' ...

```

```

        'LineWidth',2,'Color','r',...
        'DisplayName','Simulated');

ylabel('y-Values');
xlabel('Sequence Index (e.g. datenum)');
title('Simulated y-Values using LOWESS Regression');
hold('off');

% This is the primary plot that will be generate either
from % this conditional statement or in the ELSEIF below. They
are % exact same except for defining Subplot space as either
two % plots or one.
subplot(2,2,[1 2],'Parent',figure1,...
        'YScale','linear','YMinorTick','off',...
        'XScale','linear','XMinorTick','on',...
        'YMinorGrid','off',...
        'XMinorTick','on',...
        'XMinorGrid','on');

elseif rowcol(2) == 2
    % No sequence index is given, second plot would be
identical to % first plot. Define plot to occupy space of both
subplots. % This could be revised and not even call it a subplot,
but for % consistency it is.
subplot(2,1,[1 2],'Parent',figure1,...
        'YScale','linear','YMinorTick','off',...
        'XScale','linear','XMinorTick','on',...
        'YMinorGrid','off',...
        'XMinorTick','on',...
        'XMinorGrid','on');
end

box('on');
grid('on');
hold('all');

x = lws(:,1);
y = lws(:,2);
yh = lws(:,3);

% Point plot of points of the observed data on the LOWESS
plot line(x,y,'LineStyle','none', ...
        'Marker','o','MarkerSize',7,...
        'MarkerEdgeColor','k',...
        'MarkerFaceColor','b',...
        'DisplayName','Data');

% Line plot of the LOWESS regression

```

```

line(x,yh, 'Color','r', 'LineWidth',2, 'LineStyle','-')

x = uplmt(:,1);
yh = uplmt(:,2);

% Line plot of the upper limit LOWESS regression
line(x,yh, 'Color', 'r', 'LineWidth',2,'LineStyle',':')

x = lwrlmt(:,1);
yh = lwrlmt(:,2);

% Line plot of the lower limit LOWESS regression
line(x,yh, 'Color', 'r', 'LineWidth',2,'LineStyle',':')

grid on
xlabel('x-Values')
ylabel('y-Values')
ts = strcat('LOWESS Regression plot f=',num2str(f));
title(ts)
hold('off');

if ~isempty(imgfile)
    % If a filename is give for the plot, create a PNG file.
    fprintf('\nCreating plot. Give a few tics.\n');
    print('-dpng','-r600', imgfile);
    fprintf('\nFinished...\n');
end
close(figure1)
catch ME1
    disp(ME1)
end
end
end

```


D. Figures

Figure A.D.1: Diffusion with time and depth for ETNP (Ganeshram *et al.*, 2000) initial conditions

Figure A.D.2: Diffusion with time and depth for Galbraith *et al.*, (2013) initial conditions

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