# Influence of the Amazon River on the Nd isotope composition of deep water in the western equatorial Atlantic during the Oligocene-**Miocene transition**

Joseph A. Stewart a,b\*, Marcus Gutjahr C, Rachael H. James A, Pallavi Anand D, Paul A. Wilson D

- <sup>a</sup> National Oceanography Centre Southampton, University of Southampton, European Way, Southampton, SO14
- <sup>b</sup> National Institute of Standards and Technology, Hollings Marine Laboratory, 331 Fort Johnson Rd, Charleston, SC, 29412, USA
- <sup>c</sup> GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstraße 1-3 D-24148 Kiel, Germany
- 5 6 7 8 9 10 11 12 13 <sup>d</sup> School of Environment, Earth and Ecosystem Science, Walton Hall, The Open University, Milton Keynes, MK7
  - \*Corresponding author. Tel: +1 843 725 4833, Email: Joseph.Stewart@noaa.gov

### Abstract:

1

2 3

4

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

Dissolved and particulate neodymium (Nd) are mainly supplied to the oceans via rivers, dust, and release from marine sediments along continental margins. This process, together with the short oceanic residence time of Nd, gives rise to pronounced spatial gradients in oceanic  $^{143}$ Nd/ $^{144}$ Nd ratios ( $\varepsilon_{Nd}$ ). However, we do not yet have a good understanding of the extent to which the influence of riverine pointsource Nd supply can be distinguished from changes in mixing between different water masses in the marine geological record. This gap in knowledge is important to fill because there is growing awareness that major global climate transitions may be associated not only with changes in large-scale ocean water mass mixing, but also with important changes in continental hydroclimate and weathering. Here we present  $\varepsilon_{Nd}$  data for fossilised fish teeth, planktonic foraminifera, and the Fe-Mn oxyhydroxide and detrital fractions of sediments recovered from Ocean Drilling Project (ODP) Site 926 on Ceara Rise, situated approximately 800 km from the mouth of the River Amazon. Our records span the Mi-1 glaciation event during the Oligocene-Miocene transition (OMT;  $\sim$ 23 Ma). We compare our  $\varepsilon_{Nd}$  records with data for ambient deep Atlantic northern and southern component waters to assess the influence of particulate input from the Amazon River on Nd in ancient deep waters at this site.  $\varepsilon_{Nd}$  values for all of our fish teeth, foraminifera, and Fe-Mn oxyhydroxide samples are extremely unradiogenic ( $\varepsilon_{Nd} \approx -15$ ); much lower than the  $\varepsilon_{Nd}$  for deep waters of modern or Oligocene-Miocene age from the North Atlantic ( $\varepsilon_{Nd} \approx -10$ ) and

35 South Atlantic ( $\varepsilon_{Nd} \approx -8$ ). This finding suggests that partial dissolution of detrital particulate material from the Amazon ( $\varepsilon_{Nd} \approx -18$ ) strongly influences the  $\varepsilon_{Nd}$  values 36 37 of deep waters at Ceara Rise across the OMT. We conclude that terrestrially derived 38 inputs of Nd can affect  $\varepsilon_{Nd}$  values of deep water many hundreds of kilometres from 39 source. Our results both underscore the need for care in reconstructing changes in 40 large-scale oceanic water-mass mixing using sites proximal to major rivers, and 41 highlight the potential of these marine archives for tracing changes in continental 42 hydroclimate and weathering.

Keywords: Neodymium isotopes, fish teeth, foraminifera, Amazon, Oligocene-Miocene, ODP Site 926

## 1 Introduction

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

The weathering and transport of continental rock substrate is a major source of dissolved neodymium to the oceans (Goldstein and Jacobsen, 1987). The neodymium isotopic composition ( $\epsilon_{Nd} = [(^{143}Nd_{sample})^{144}Nd_{sample}) / (^{143}Nd_{CHUR})^{144}Nd_{CHUR}) - 1] \times$ 10<sup>4</sup>; where CHUR is the chondritic uniform reservoir) of continental rocks varies according to both the Sm/Nd ratio and age of the rock, such that ancient continental crust exhibits very low (unradiogenic) ε<sub>Nd</sub> values (down to −40), whereas younger volcanic sequences generally have much higher (radiogenic) values (up to +12; Goldstein and Hemming, 2003). Because neodymium has a residence time on the order of the mixing time of the ocean (500 to 2000 yr; Piepgras and Wasserburg, 1987; Tachikawa et al., 2003), deep waters formed in the North Atlantic, which is surrounded by Proterozoic and Archean rocks, are characterised by low  $\varepsilon_{Nd}$  (-13.5; Piepgras and Wasserburg, 1987; Lacan and Jeandel, 2005a). On the other hand, deep water masses formed in the Southern Ocean have higher  $\varepsilon_{Nd}$  (between -7 and -9; Piepgras and Wasserburg, 1987; Jeandel, 1993; Stichel et al., 2012) due to the contribution of young mantle-derived material surrounding the Pacific Ocean that mixes with Atlantic waters in this region. Records of seawater  $\epsilon_{Nd}$  values recorded in marine sediments have therefore been widely used to identify the source of the overlying water masses (Scher and Martin, 2004; Piotrowski et al., 2005).

64

65

66

67

68

69

70

71

72

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

In addition to the influence of riverine solute inputs, the isotopic composition of dissolved Nd in seawater can be modified by exchange of Nd in river-born particulate material with seawater via "boundary exchange" on continental margins (Jeandel et al., 2007; Pearce et al., 2013) and also in certain deep sea settings (Lacan and Jeandel, 2005b; Carter et al., 2012; Wilson et al., 2012; Abbott et al., 2015b). Various modelling studies even suggest that release of Nd from continental margins is by far the dominant source of Nd to the oceans (contributing as much as 90%; Arsouze et al., 2009; Rempfer et al., 2011). Dissolved deep water  $\varepsilon_{Nd}$  at these continental margin locations is likely a function of three variables: (i) the magnitude of the Nd flux from sediment pore fluids, (ii) the difference between the  $\varepsilon_{Nd}$  value of the overlying water and the pore fluid, and (iii) the exposure time to this benthic flux of Nd (Abbott et al., 2015a).

The Amazon River is the world's largest river and each year carries  $5 \times 10^8$  tons of suspended sediment (Gibbs, 1967) that is relatively enriched in Nd (~40 ppm; McDaniel et al., 1997) compared to seawater (typically <10 ppb; Piepgras and Wasserburg, 1987). These Nd-rich Amazon sediments have been shown to influence the dissolved  $\varepsilon_{Nd}$  of near-shore seawater (e.g. the mid-salinity zone of the Amazon Estuary; Rousseau et al., 2015), and have also been suggested to affect deep water  $\varepsilon_{Nd}$ as far afield as the Caribbean Sea (Osborne et al., 2014). An improved understanding of the extent to which river-born particulate material can influence deep water  $\varepsilon_{Nd}$  is, therefore, critical to our understanding of Nd cycling in the oceans (Stichel et al., 2012; Kraft et al., 2013; Pearce et al., 2013). This is particularly true for major climate transitions when rock weathering and the flux of riverine particulate material may vary (West et al., 2005), centres of precipitation can shift altering river drainage patterns (Wang et al., 2004), and ocean circulation can change the exposure time of water masses to benthic sources of Nd (Abbott et al., 2015a). Records of past seawater and associated sediment  $\varepsilon_{Nd}$  in relative proximity to major riverine sources of Nd such as the Amazon River are therefore vital to understanding Nd exchange between particulate and dissolved phases in continental margin settings.

### 1.1 Archives of seawater $\varepsilon_{Nd}$

Fossilised fish teeth recovered from deep sea sediment cores are an ideal substrate for reconstructing past changes in  $\varepsilon_{Nd}$  values of ancient bottom waters. Fish teeth are found throughout the world's oceans and incorporate the majority of their Nd postmortem (>100 ppm Nd), during early diagenetic recrystallization of the biogenic apatite at the sediment-seawater interface. They are therefore resistant to late diagenetic overprinting (Martin and Scher, 2004). Analysis of Nd associated with authigenic Fe-Mn oxyhydroxides in marine sediments can also be used to extract bottom water Nd isotope compositions (Piotrowski et al., 2005), although care must be taken during sample processing (Elmore et al., 2011).

The only method by which  $\varepsilon_{Nd}$  values of surface waters have been successfully reconstructed to date is through the analysis of reductively cleaned planktonic foraminifera (Vance and Burton, 1999). However, because diagenetic ferromanganese coatings formed on the seafloor and in pore waters are extremely enriched in Nd (200 ppm) compared with biogenic calcite (0.1 ppm), these coatings must be effectively removed (Pomiès et al., 2002).  $\varepsilon_{Nd}$  records of cleaned planktonic foraminifera that have elevated Nd/Ca are likely compromised by incomplete removal (<98%) of ferromanganese coatings or reabsorption of Nd released during the cleaning process. For this reason, even cleaned foraminifera often exhibit  $\varepsilon_{Nd}$  values similar to bottom waters (Roberts et al., 2012; Tachikawa et al., 2014).

#### 1.2 Scope of this study

Here we assess evidence for changes in continental inputs from the Amazon River during the Oligocene-Miocene transition (OMT), through analysis of  $\epsilon_{Nd}$  in fish teeth, planktonic foraminifera, and the Fe-Mn oxyhydroxide and detrital fractions of sediments recovered from ODP Site 926 (Figure 1). The OMT is marked by a positive excursion (>1‰) in benthic foraminiferal  $\delta^{18}$ O at 23 Ma (Figure 2) that represents cooler deep-water temperatures and increased Antarctic ice volume associated with the so-called Mi-1 glaciation event (Pälike et al., 2006; Liebrand et al., 2011). We use our  $\epsilon_{Nd}$  data to assess the contribution of the Amazon as a source

- of Nd to the regional Equatorial Atlantic water mass signal at this site during this
- 122 interval of climatic variability, and discuss the implications of these data for
- interpretation of  $\varepsilon_{Nd}$  records in terms of water mass mixing.

### 124 2 Materials and methods

- 125 2.1 Geological setting and core chronology
- 126 Samples spanning the OMT were selected from sediment cores recovered from ODP
- 127 Leg 154, Site 926, Hole B (3°43.148'N, 42°54.507'W, ~3600 m water depth; Leg 154
- 128 Shipboard Scientific Party, 1995), situated approximately 800 km to the northeast of
- the mouth of the River Amazon (Figure 1). The geographic position and water-depth
- of Site 926 have not changed significantly since the Oligocene. Although there is no
- magnetostratigraphic age control available for ODP Leg 154 cores, a high quality
- orbital chronology is available for the Oligocene-Miocene sequence at ODP Site 926
- 133 (Pälike et al., 2006) and can be correlated to ODP Site 1090 on the Agulhas Ridge
- (Liebrand et al., 2011) where a high quality magnetostratigraphy is available (Figure
- 2; Channell et al., 2003). We apply the age model of Pälike et al. (2006).
- 136 2.2 Sample preparation
- 137 Sediment samples were dried in an oven at 50°C, then gently disaggregated in
- deionised water using a shaker table and washed over a 63 μm sieve. Tests (~1 mg) of
- the planktonic foraminifer *Dentoglobigerina venezuelana* were picked from the 355-
- 400 μm size fraction for trace element analysis (See Supplementary Information)
- following the morphotype description of Stewart et al., (2012). Larger samples of D.
- venezuelana (~25 mg) and a second species, Globigerina bulloides (~5 mg), were
- picked for Nd isotope analysis from the >355 µm size fraction. Additionally,
- fossilised fish teeth (and one fish bone sample) were taken for  $\varepsilon_{Nd}$  analysis. These
- samples consisted of an average of three individual teeth.

### 2.2.1 Detrital and authigenic Fe-Mn oxyhydroxide extraction

146

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

Dried and ground bulk sediment (~420-610 mg) was transferred into centrifuge tubes for processing. After an initial wash in MQ water and centrifuging, 15 ml of a reductive cocktail containing 0.05 M hydroxylamine hydrochloride, 15% acetic acid, and 0.01 M buffered EDTA was added following methods of Blaser et al. (2016), with reductive cocktail concentrations as used in Gutjahr et al. (2007). Samples were centrifuged and the supernatant was removed for purification of Nd from the Fe-Mn oxyhydroxide fraction. Another 25 ml of the reductive leaching solution was added to remove any remaining Fe-Mn oxyhydroxides (Gutjahr et al., 2007) in order to target the pure terrigenous signal without residual authigenic Nd contributions. After shaking for 24 hours, the supernatant was discarded following centrifuging and the sample was dried. Approximately 50 mg of the dried re-homogenised residue was first treated with concentrated HNO3 and 30% H2O2 for effective oxidation of organics. Dried samples were subsequently treated with aqua regia prior to pressure digestion in steel bombs (190°C over three days) in a mixture of concentrated HNO<sub>3</sub> and HF. Dried digested samples were treated three times with concentrated HNO<sub>3</sub> before conversion to chloride with HCl and column purification using procedures outlined in Section 2.2.3.

### 164 2.2.2 Foraminifera and fish tooth cleaning procedure

- All foraminifera and fish teeth samples were subject to cleaning prior to analysis
- using established methods (Rosenthal et al., 1999). Briefly, adhering clay particles
- were removed through repeated ultrasonication and rinsing with MQ water and
- methanol. Samples were then cleaned to remove ferromanganese oxide coatings and
- organic matter, and finally leached in weak acid to remove any re-adsorbed ions.
- 170 Foraminiferal calcite and fish teeth samples for isotopic analysis were dissolved in
- 171 0.075 M and 0.15 M HNO<sub>3</sub> respectively.

### 172 2.2.3 Separation of Nd from the sample matrix

- 173 Nd was separated from the sample matrix using a two-stage chromatography
- procedure. Sample solutions were dried down on a hotplate and then re-dissolved in

0.2 M HCl. This solution was then loaded onto a Teflon column containing 2.4 ml of Bio-Rad<sup>TM</sup> AG50W-X12 cation exchange resin. Matrix elements were removed by eluting with 4 M HCl. Rare earth elements were then collected in 6 M HCl. The recovered rare earth fraction was dried down, re-dissolved in 0.18 M HCl, and loaded onto a second cation exchange column containing 0.6 ml of Eichron<sup>TM</sup> Ln spec resin of particle size 50 to 100 μm. Residual Sr and approximately 90% of the Ce were first eluted with 8 ml of 0.18 M HCl, and the Nd fraction was collected by addition of a further 7 ml of 0.18 M HCl. The total procedural blank from the columns was 13 pg of Nd, which is typically <<1% of the sample size.

### 2.3 Analytical techniques

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

Details and results of analysis of Nd/Ca and Mn/Ca in foraminiferal calcite are shown in the Supplementary Information. The Nd isotopic composition of the fish teeth and foraminifera was determined by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS; ThermoFisher Neptune) at the University of Southampton, and the Nd isotopic composition of the sediment leaches and digests was carried out at GEOMAR in Kiel (MC-ICP-MS: ThermoFisher Neptune Plus). using the method of Vance and Thirwall (2002). Measured <sup>143</sup>Nd/<sup>144</sup>Nd ratios were corrected to a 146Nd/144Nd ratio of 0.7219 to remove mass bias effects (Wombacher and Rehkämper, 2003). The external reproducibility of our Nd isotope measurements, for Nd solutions of 25 to 50 ppb is better than  $\pm 0.16$  (n=37) and  $\pm 0.11$  (n=19)  $\epsilon$  units (2σ) in Southampton and Kiel, respectively. Corrected data were normalised by adjusting the average <sup>143</sup>Nd/<sup>144</sup>Nd ratio of the JNdi-1 Nd isotope standard measured during that analytical session to the accepted value of 0.512115 (Tanaka et al., 2000). <sup>143</sup>Nd/<sup>144</sup>Nd ratios (ε<sub>Nd(0)</sub>) were corrected for post-depositional ingrowth of <sup>143</sup>Nd from  $^{147}$ Sm ( $\varepsilon_{Nd(t)}$ ) using an initial  $^{147}$ Sm/ $^{144}$ Nd ratio of 0.1286 for fish teeth (Thomas et al., 2003) and 0.1412 for foraminifera, detrital and Fe-Mn oxyhydroxide samples (Vance et al., 2004). This adjustment is small for our samples (lowering  $\varepsilon_{Nd}$  by <0.17 units). All subsequent discussion refers to the adjusted  $\epsilon_{Nd(t)}$  values.

### 3 Results

204

205 In Figure 2 we compare our records of  $\varepsilon_{Nd}$  in the detrital fraction, Fe-Mn 206 oxyhydroxides (Table 1), fish teeth, and foraminifera (D. venezuelana, and G. 207 bulloides; Table 2) from ODP Site 926 with the benthic foraminiferal oxygen isotope 208 record from the same site (Figure 2 A; Pälike et al., 2006). We further compare these 209  $\varepsilon_{Nd}$  measurements to records of representative contemporaneous deep water  $\varepsilon_{Nd}$ 210 (Figure 1; Figure 2 B) from the North (Fe-Mn crust ALV539; O'Nions et al., 1998), 211 South (fish teeth from ODP Site 1090; Scher and Martin, 2008), and Equatorial 212 Atlantic Ocean (Fe-Mn crust ROM46; Frank et al., 2003). With the exception of the 213 North Atlantic Fe-Mn crust site ALV539 (depth 2.7 km) the water depths (and 214 palaeodepths) of all of these sites are similar to that of Ceara Rise (Figure 1). Despite 215 its slightly shallower depth, we assume that the  $\varepsilon_{Nd}$  of seawater at Site ALV539 is 216 typical of northern sourced deep water to Ceara Rise. 217 Most of our data for the detrital fraction from the OMT at Ceara Rise show distinctly 218 unradiogenic  $\varepsilon_{Nd}$  values with a baseline of around -18  $\varepsilon$  units. Four samples show 219 slightly more radiogenic values (around –16.5 ε units) at 22.4, 23.3, 23.6, and 24.1 220 Ma but the occurrence of these data points shows no clear correspondence to 221 structure in the benthic foraminiferal oxygen isotope stratigraphy from the same site. 222  $\varepsilon_{Nd}$  values for fish teeth are, on average, -14.5 and all data points are lower than 223  $-13.0 \epsilon$  units. The foraminiferal  $\epsilon_{Nd}$  records for D. venezuelana and G. bulloides are 224 generally within analytical uncertainty of one another and vary between -16.5 and -225 13.2 ε units. Compositions of the Fe-Mn oxyhydroxide fraction are within 0.26 ε 226 units of the foraminiferal  $\varepsilon_{Nd}$  values. Furthermore, the pattern of change seen in the 227 Fe-Mn oxyhydroxide and foraminiferal  $\varepsilon_{Nd}$  records is remarkably similar to that of 228 the fish teeth record. We therefore find no discernible difference between the fish 229 teeth, foraminifera, and Fe-Mn oxyhydroxide  $\varepsilon_{Nd}$  records, even during the large 230 oxygen isotope excursion corresponding to the Mi-1 glaciation event.

### 4 Discussion

231

- To assess the potential influence of input of riverine particulate material from the
- 233 Amazon to Ceara Rise, we first discuss the Nd isotope composition of the detrital
- fraction of the sediments. We then assess the impact of the Amazon on the Nd
- 235 isotopic composition of seawater in the western equatorial Atlantic across the OMT
- 236 by comparing Nd isotope compositions in the three different palaeo-seawater
- substrates.
- 238 4.1 Source of detrital sediments at Ceara Rise
- The Nd isotopic composition of the detrital fraction of the sediments is used to assess
- 240 the Nd isotopic signature of terrestrial material from the Amazon River reaching the
- 241 Ceara Rise during the OMT. Sediment particles delivered to the modern Amazon Fan
- from the River Amazon and its tributaries exhibit a wide range of  $\varepsilon_{Nd}$  values today
- 243 (from -8 to -22; Allègre et al., 1996), reflecting the variable age of the catchment
- bedrock (Figure 3 A). Unradiogenic  $\varepsilon_{Nd}$  values are observed in the eastern tributaries
- 245 (Tapajós tributary  $\varepsilon_{Nd} = -20$ , Trombetas tributary  $\varepsilon_{Nd} = -22$ ; Allègre et al., 1996),
- 246 which drain ancient cratonic sequences of the Guiana Shield (>2.3 Ga). By contrast,
- the western tributaries draining younger Phanerozoic sedimentary rocks have more
- radiogenic sedimentary particulate loads ( $\varepsilon_{Nd} \sim -8$ ). These eroded sediments from the
- east and west tributaries combine to give an intermediate  $\varepsilon_{Nd}$  value for the modern
- Amazon suspended sediment load output to the Atlantic Ocean, which has  $\varepsilon_{Nd} = -10$
- 251 (Allègre et al., 1996; McDaniel et al., 1997; Rousseau et al., 2015). These large
- regional distinctions in  $\varepsilon_{Nd}$  composition between geological terranes mean that
- 253 changes in drainage patterns have the potential to give rise to dramatic changes in the
- $\epsilon_{Nd}$  of riverine suspended sediments to the Atlantic Ocean.
- 255 The drainage of the Amazon during the Oligocene and Miocene is thought to have
- been very different from today because of the lower altitude of the Andes (Figure 3
- 257 B; Campbell et al., 2006; Figueiredo et al., 2009; Shephard et al., 2010). Stratigraphic
- records suggest that, prior to the middle-Miocene (Cunha et al., 1994; Eiras et al.,
- 259 1994), the Amazon Basin consisted of two catchments divided by the Purus Arch: the
- 260 Eastern Amazon basin to the east and the Pebas Wetlands to the west (Figueiredo et

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

al., 2009). Under this configuration, the outflow from the Amazon to the Atlantic would have originated almost exclusively from the Eastern Amazon Basin, which is underlain by the Guiana Shield and today yields very unradiogenic  $\varepsilon_{Nd}$  values for suspended loads, between -17 and -22 (Allègre et al., 1996). The low  $\varepsilon_{Nd}$  values recorded in the detrital fraction (-18  $\varepsilon$  units) that we document at Site 926, together with colour, grain-size and rare earth element logs of sediments recovered from other ODP Leg 154 sites (Dobson et al., 2001), all suggest that the Guiana Shield was the dominant source of terrigenous sediment to Ceara Rise throughout our study interval.

Four samples in our data set show higher  $\varepsilon_{Nd}$  in the detrital fraction (up to -16.5) and are interpreted to reflect the incorporation of detrital material from more radiogenic terranes adjacent to the ancient Guiana Shield. One possible source of more radiogenic Nd is the westerly Purus Arch (Figure 3 B). Changes in Amazon vegetation cover (e.g. van der Hammen and Hooghiemstra, 2000) and distribution of precipitation have been linked to global climate (Wang et al., 2004), as centres of tropical precipitation are often shifted meridionally away from the hemisphere of maximum cooling (Arbuszewski et al., 2013). Nearly all detrital  $\varepsilon_{Nd}$  values are slightly higher (more radiogenic) before the Mi-1 event than they are afterwards, but there is no obvious relationship between our detrital  $\varepsilon_{Nd}$  record and the benthic  $\delta^{18}$ O record across the OMT (Figure 2 A; Pälike et al., 2006), even during the Mi-1 glaciation. We therefore conclude that changes in the source of Amazonian terrigenous sediment to Site 926 during our study interval are not strongly modulated by processes coupled to changes in high latitude temperature and continental ice volume. On the other hand, our data indicate that measurement of detrital  $\varepsilon_{Nd}$  of more recent Ceara Rise sediments (e.g. McDaniel et al., 1997) could represent a powerful tool for determining the disputed timing of westward enlargement of the Amazon Basin to its modern configuration during the Miocene/Pliocene (Campbell et al., 2006; Figueiredo et al., 2009).

### 4.2 Nd in fish teeth and fossilised foraminifera at Ceara Rise

Of the data types presented here, those generated using fish teeth are commonly regarded as the most robust archive of changes in oceanic bottom water  $\epsilon_{Nd}$  because most of the Nd contained in fish tooth fluorapatite is acquired during early diagenesis on the seafloor (Martin and Haley, 2000; Martin and Scher, 2004). In our study,  $\epsilon_{Nd}$  data from planktonic foraminifera are strikingly similar to data from fish teeth and the authigenic Fe-Mn oxyhydroxide fraction, despite reductive cleaning that is expected to remove authigenic overgrowths from test calcite. While it is possible that the  $\epsilon_{Nd}$  value of surface water was identical to the  $\epsilon_{Nd}$  value of bottom water during the OMT, high Mn/Ca (>500  $\mu$ mol/mol) and Nd/Ca (>1  $\mu$ mol/mol) ratios measured in these foraminifera (see Supplementary Information) imply that the Nd in these samples more likely has an authigenic origin and is not representative of surface water (Pomiès et al., 2002; Tachikawa et al., 2014).

### 4.3 Sources of Nd to deep water at Ceara Rise

Fish teeth  $\epsilon_{Nd}$  records from South Atlantic ODP Sites 689, Maud Rise (Scher and Martin, 2004) and 1090, Agulhas Ridge (Scher and Martin, 2006; Figure 2 B) suggest that, during the OMT, Atlantic deep waters originating in the Southern Ocean had  $\epsilon_{Nd}$  values close to those of modern southern component water ( $\epsilon_{Nd} \sim -8$ ). Unradiogenic  $\epsilon_{Nd}$  values typical of modern northern component deep water (-13.5; principally North Atlantic Deep Water; Piepgras and Wasserburg, 1987; Lacan and Jeandel, 2005a) only appear in the marine sedimentary record in the late Neogene, following closure of the Central American Seaway (Burton et al., 1997). The  $\epsilon_{Nd}$  value of northern component deep water in the Miocene is estimated to have been much higher ( $\sim -10$ ; O'Nions et al., 1998; Scher and Martin, 2006) than its present day composition. Thus, simple mixing between northern and southern component deep waters cannot explain the low  $\epsilon_{Nd}$  that we document in fish teeth, planktonic foraminifera, and the authigenic Fe-Mn fraction of sediments from Site 926 ( $\sim -15$   $\epsilon_{Nd}$  units; Figure 2 B). Rather, the deep waters must be affected by input of very unradiogenic Nd from a regional source, a clear candidate being the River Amazon.

318

319

320

321

322

323

324

325

326

327

328

329

330

331

332

333

334

335336

337

338

339

340

341

342

343

344

345

346

Neodymium is exported from rivers to the oceans in three main phases, (i) dissolved Nd (Goldstein and Jacobsen, 1987), (ii) pre-formed oxides (Bayon et al., 2004), and (iii) Nd contained in detrital suspended particulate matter (Pearce et al., 2013). Various lines of evidence point to detrital particulate-bound supply as the major influence on deep water  $\varepsilon_{Nd}$  at Ceara Rise. First, dissolved Nd concentration in the modern Amazon Estuary is observed to increase in the mid-salinity zone and is accompanied by a shift in  $\varepsilon_{Nd}$  from riverine values (>-9) to values closer to the suspended load (<-10) (Rousseau et al., 2015). Therefore, Nd in the dissolved phase of Amazon river waters is extremely susceptible to alteration by Nd released from suspended particles during estuarine mixing. Second, if pre-formed Fe-Mn oxides were controlling the bottom water Nd isotope signature at Ceara Rise, this should be most clearly identifiable in isotopic differences between fish tooth- and Fe-Mn oxyhydroxide-derived  $\varepsilon_{Nd}$ . In such a scenario, the Fe-Mn oxyhydroxides would yield  $\varepsilon_{\rm Nd}$  values similar to the detrital composition (c.f. Bayon et al., 2004; Kraft et al., 2013). By contrast, the Nd incorporated into fish teeth is derived from bottom waters or pore fluids (Martin and Scher, 2004). Hence, our data indicate that pore fluid and bottom water  $\varepsilon_{Nd}$  at Ceara Rise differed from that of deep water in the central Atlantic (with  $\varepsilon_{Nd} \sim -10$ ; O'Nions et al., 1998). The most likely reason for this is partial dissolution of Amazon particulate material within Ceara Rise pore fluids (Lacan and Jeandel, 2005a; Carter et al., 2012; Pearce et al., 2013; Abbott et al., 2015a). Once delivered to Ceara Rise, this particulate-bound Nd is transferred to the overlying deep waters through dissolution or desorption, thus shifting the deep water signal regionally towards less radiogenic  $\varepsilon_{Nd}$  values. Discovery of this signal at a site more than 800 km from the outflow source, in 3.6 km water depth, indicates that this process is not restricted to the continental shelves and can operate further offshore if particle fluxes are high.

To assess the percentage contribution of detrital Amazon-derived Nd to deep water  $\epsilon_{Nd}$  at this site we compare fish tooth, foraminifera, and Fe-Mn oxyhydroxide data, with  $\epsilon_{Nd}$  measurements of the corresponding detrital fraction and open ocean seawater. In this analysis, we used the detrital measurement closest to the sample

depth of the fish tooth, foraminifera and leachate data where data from the same sample was not available (we note that our choice between detrital data from identical or adjacent samples for comparison to estimates of seawater  $\epsilon_{Nd}$  has little impact on the main findings of this study). Assuming that the  $\epsilon_{Nd}$  value of northern component water bathing Ceara Rise during the OMT was -10 (O'Nions et al., 1998), we calculate that the majority of the Nd in bottom waters at this site (average 64%) was derived from Amazon particulate material (Figure 2 C). Although we observe large amplitude variability in our down-core record (between 45% and 90%) that is likely related to variations in sediment sourcing from various Amazon tributaries (Figure 3), there is no clear link between short-term increases/decreases in the estimated fraction of Amazon particulate-derived Nd on the  $\epsilon_{Nd}$  signal of Ceara Rise bottom water and pronounced changes in high latitude climate inferred from benthic foraminiferal  $\delta^{18}$ O (Figure 2 A; Pälike et al., 2006).

We note that  $\varepsilon_{Nd}$  values for deep water of similar age and water depth to our samples derived from a Fe-Mn crust (ROM46) recovered from the central Equatorial Atlantic Ocean are also relatively unradiogenic (–11.5; Figure 2 B), and also cannot therefore be explained by simple mixing between northern and southern component deep waters (Frank et al., 2003). Such unradiogenic deep water  $\varepsilon_{Nd}$  at the ROM46 site, more than 1,000 km from land, prompted the authors to invoke additional sources of Nd including Saharan dust and also the Amazon River (Frank et al., 2003). Our new data from Ceara Rise support a far-reaching Amazon source for deep water Nd at the ROM46 site during the Oligocene-Miocene, given that this more distal central Atlantic site yields deep water  $\varepsilon_{Nd}$  values that fall between those observed at Ceara Rise and contemporaneous northern/southern component water.

4.4 Potential impact of regional terrestrial inputs on seawater  $\epsilon_{Nd}$  in the Neogene Ocean

The highly unradiogenic  $\varepsilon_{Nd}$  composition of suspended particulate material in the Amazon River during the OMT points to more restricted drainage than in the Amazon Basin today, with the dominant terrestrial input coming from the ancient

377

378

379

380

381

382

383

384

385

386

387

388

389

390

391

392

393

394

395

396

397

398

399

400

401

402

403

404

405

terrane of the Guiana Shield in the East Amazon Basin. The fingerprint of this highly unradiogenic sediment source on deep water  $\varepsilon_{Nd}$  is recognisable far from the Amazon outflow source, yielding values outside of the range defined by mixing of northern and southern component water masses in the Atlantic. This result is consistent with the findings of Abbott et al. (2015a), who suggest that seawater  $\varepsilon_{Nd}$  can be strongly affected by inputs of pore fluid Nd if the  $\varepsilon_{Nd}$  of those pore fluids is significantly offset from that of the overlying water mass.

In more recent geological times the flux and  $\varepsilon_{Nd}$  composition of the open deep Equatorial Atlantic water mass and Amazon weathering sources have changed. First, the sediment flux from the Amazon increased from the late Miocene to the Pliocene in conjunction with Andean uplift (Figueiredo et al., 2009). This uplift has also resulted in a larger modern Amazon drainage basin that now includes younger Phanerozoic sedimentary rocks (Figueiredo et al., 2009). As the  $\varepsilon_{Nd}$  of suspended sediments is strongly influenced by drainage pattern changes in the heterogeneous Amazon basin, broadening of the Amazon catchment westwards introduces suspended sediments with more radiogenic compositions ( $\varepsilon_{Nd} \sim -10$ ; Figure 3 A; Allègre et al., 1996; Rousseau et al., 2015). Second, the  $\varepsilon_{Nd}$  composition of northern component deep water became less radiogenic, starting at about 4 to 3 Ma in the late Neogene (Burton et al., 1997), and is now approximately -13.5 (Piepgras and Wasserburg, 1987). Both of these changes are in a direction that makes it more difficult to discern the influence of regional terrestrial sources from changes in northern/southern component water mass mixing despite the higher Amazon sediment fluxes. For example, a 60% contribution of Nd sourced from the Amazon detrital sediments to Ceara Rise today ( $\varepsilon_{Nd} = -10$ ; Allègre et al., 1996) would be enough to increase the seawater value by 2  $\epsilon$  units above the modern northern component water value. Such a change could be incorrectly interpreted to represent an increased contribution from southern sourced deep waters at this site.

Authigenic  $\varepsilon_{Nd}$  records for the last 25 thousand years from piston cores GEO B1515-1 and GEOB 1523-1 on Ceara Rise (Figure 1) show a much more radiogenic signal than we measure across the OMT, with values changing from about -10 at the last

glacial maximum to approximately -12 or -13 for the Holocene (Lippold et al., 2016). This Pleistocene to Holocene shift is interpreted to be the result of a change in water mass provenance at Ceara Rise, from predominantly Atlantic southern component water to more unradiogenic northern component water (Lippold et al., 2016). The Holocene Nd isotope compositions in these cores match modern seawater  $\varepsilon_{\rm Nd}$  (Piepgras and Wasserburg, 1987). We note however that these (de-)glacial deep water  $\varepsilon_{Nd}$  values are close to modern Amazon suspended sediment values. Therefore, a potential alternative explanation for these Pleistocene  $\varepsilon_{Nd}$  data could be a greater influence of the benthic sedimentary flux of Nd (~60% of total Nd) on deep water at Ceara Rise during the last glacial maximum. This could be due to increased exposure time to the benthic sedimentary Nd flux (e.g. Abbott et al., 2015a) during this time of more sluggish Atlantic oceanic overturning (Lippold et al., 2016). Yet because both an increased contribution of southern component water, and a higher flux of benthic (pore fluid) Nd, act to shift deep water  $\varepsilon_{Nd}$  towards more radiogenic values, the effect of enhanced Nd release from the particulate fraction at the last glacial maximum at Ceara Rise cannot be unambiguously resolved at this stage.

### 5 Conclusions

406

407

408

409

410

411

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429

430

431

432

433

434

435

We present  $\epsilon_{Nd}$  records in fossilised fish teeth, planktonic foraminifera and Fe-Mn oxyhydroxide substrates from Ceara Rise for the Oligocene-Miocene transition. Records from these three substrates are remarkably consistent with one another, implying that all three archives have acquired the  $\epsilon_{Nd}$  signature of bottom waters. Yet the  $\epsilon_{Nd}$  data that we have obtained are extremely unradiogenic (down to -15) in comparison to those for contemporaneous bottom waters in the Atlantic Ocean. They cannot therefore be explained by simple large-scale ocean mixing between northern and southern component Atlantic deep waters, both of which were significantly more radiogenic ( $\epsilon_{Nd}$  of -10 and -8 respectively). We suggest that bottom waters at Ceara Rise were strongly influenced by inputs of Nd derived from weathering of ancient cratonic rocks in the eastern Amazon drainage basin. The similarity between the fish teeth, planktonic foraminifera, and Fe-Mn oxyhydroxide Nd isotope records provides evidence for significant release of Nd from sedimentary particulate material from the

River Amazon during the OMT. Discovery of such a strong regional continental influence on deep waters, many hundreds of kilometres from source, suggests that boundary exchange processes can operate far from continental shelf regions (under high particle flux conditions). Caution must therefore be exercised in site selection and when interpreting seawater  $\varepsilon_{Nd}$  records in light of the vast distances across which major point sources of Nd may influence deep water  $\varepsilon_{Nd}$ . On the other hand, these techniques present an opportunity to investigate changes in sourcing of riverine-supplied Nd to the ocean associated with major tectonic and/or climatic change.

# 6 Acknowledgements

This work used samples provided by the (Integrated) Ocean Drilling Program (ODP), which is sponsored by the US National Science Foundation and participating countries under management of the Joint Oceanographic Institutions (JOI), Inc. We thank Walter Hale and staff at the Bremen Core Repository for their help in obtaining core material and also Guy Rothwell of BOSCORF for providing core top material for production of our in-house foraminiferal calcite standards. We thank Dieter Garbe-Schönberg (University Kiel) and Ana Kolevica (GEOMAR Kiel) for their help in detrital sample processing. We are indebted to Gavin Foster, Carrie Lear, Dan Murphy, Fred Le Moigne, Helen Griffin and Anya Crocker for their advice and helpful discussion of the manuscript. We also thank Derek Vance for assistance with deconvolution of Nd isotope data and Matt Cooper, Darryl Green and Andy Milton for their help with laboratory work. Three anonymous reviewers and the editor provided constructive reviews that improved an earlier version of the manuscript.

Financial support was provided by the UK Natural Environment Research Council, award # NE/D005108/1 to R.H.J and NE/K014137/1 and a Royal Society Research

460 Merit Award to P.A.W.

Figure 1: Location of ODP Leg 154 Site 926B Ceara Rise in relation to other deep water ε<sub>Nd</sub> records across the Oligocene-Miocene transition discussed in this study. Fe-Mn crust ALV539, 2,665 m water depth (O'Nions et al., 1998), Fe-Mn crust ROM46, 3,350 m water depth (Frank et al., 2003), Fish tooth record from ODP Site 1090, 3,700 m water depth

ALV539, 2,665 m water depth (O'Nions et al., 1998), Fe-Mn crust ROM46, 3,350 m water depth (Frank et al., 2003), Fish tooth record from ODP Site 1090, 3,700 m water depth (Scher and Martin, 2008). Colours correspond to line/marker colours in Figure 2. Inset shows location of ODP Site 926B in relation to the Amazon River mouth and piston core sites on Ceara Rise, GEOB 1515-1 (3,129 m water depth) and GEOB 1523-1 (3,292 m

water depth) used in the study by Lippold et al. (2016).

Figure 2:  $\varepsilon_{Nd}$  records across the Oligocene-Miocene transition at ODP Site 926. **A**. Benthic oxygen isotope record for this site (Pälike et al., 2006), **B**.  $\varepsilon_{Nd}$  values for fossilised fish teeth (green triangles), planktonic foraminifera *D. venezuelana* (blue circles) and *G. bulloides* (red circles), Fe/Mn oxyhydroxides (black diamonds), and the detrital fraction (squares). Deep water  $\varepsilon_{Nd}$  values for the South Atlantic (Scher and Martin, 2008), Equatorial Atlantic (Frank et al., 2003), and North Atlantic (O'Nions et al., 1998) at the OMT are also shown for comparison. Colour scale corresponds to that used in Figure 3 showing potential Amazon basin source rock  $\varepsilon_{Nd}$  ranges for Guiana Shield, Purus Arch and Phanerozoic sediments (Allègre et al., 1996). **C**. Estimated percentage of  $\varepsilon_{Nd}$  seawater signal at Ceara Rise coming from Amazon sources relative to northern component water during the OMT. Error bars represent the 2 standard error of each measurement. Magnetostratigraphic correlation from ODP Site 1090 in the South Atlantic (Billups et al., 2002; Channell et al., 2003).

Figure 3: Geology of the Amazon Basin. Star shows the position of ODP Site 926 on Ceara Rise. Panel A. Coloured squares (colour scale corresponds to that used in Figure 2) show  $\varepsilon_{Nd}$  values of modern suspended sediments in Amazon tributaries (Allègre et al., 1996). Shaded regions show basement lithology. Panel B. Amazon drainage during the Oligocene-Miocene. Black arrows and blue dashed line show, respectively, the inferred drainage pattern and catchment area at this time (Figueiredo et al., 2009; Shephard et al., 2010).

 Table 1:  $\epsilon_{Nd}$  measurements of detrital sediments and Fe/Mn oxyhydroxides from the Oligocene-Miocene transition of ODP Site 926. Ages are calculated using the age model of Pälike et al. (2006).  $\epsilon_{Nd}(0)$  denotes measured  $\epsilon_{Nd}$  values, and  $\epsilon_{Nd}(t)$  values have been adjusted for ingrowth of <sup>143</sup>Nd since the Oligocene (assumption: initial <sup>147</sup>Sm/<sup>144</sup>Nd ratio 0.1412 for detrital and Fe-Mn oxyhydroxide samples).

 Table 2:  $\epsilon_{Nd}$  measurements of fossilised fish teeth and planktonic foraminifera (*D. venezuelana* and *G. bulloides*) from the Oligocene-Miocene transition of ODP Site 926. Ages are calculated using the age model of Pälike et al. (2006).  $\epsilon_{Nd}(0)$  denotes measured  $\epsilon_{Nd}$  values, and  $\epsilon_{Nd}(t)$  values have been adjusted for ingrowth of <sup>143</sup>Nd since the Oligocene (assumption: initial <sup>147</sup>Sm/<sup>144</sup>Nd ratio 0.1286 for fish teeth and 0.1412 for foraminifera samples).

### 7 References

- Abbott, A.N., Haley, B.A., McManus, J., 2015a. Bottoms up: Sedimentary control of the deep North
- Pacific Ocean's εNd signature. Geology 43, 1035.
- Abbott, A.N., Haley, B.A., McManus, J., Reimers, C.E., 2015b. The sedimentary flux of dissolved rare
- earth elements to the ocean. Geochimica et Cosmochimica Acta 154, 186-200.
- Allègre, C.J., Dupré, B., Négrel, P., Gaillardet, J., 1996. Sr-Nd-Pb isotope systematics in Amazon and
- Congo River systems: constraints about erosion processes. Chemical Geology 131, 93-112.
- Arbuszewski, J.A., deMenocal, P.B., Cleroux, C., Bradtmiller, L., Mix, A., 2013. Meridional shifts of
- 513 the Atlantic intertropical convergence zone since the Last Glacial Maximum. Nature Geosci 6, 959-
- 514 962

505

- Arsouze, T., Dutay, J.C., Lacan, F., Jeandel, C., 2009. Reconstructing the Nd oceanic cycle using a
- 516 coupled dynamical biogeochemical model. Biogeosciences 6, 2829-2846.
- Bayon, G., German, C.R., Burton, K.W., Nesbitt, R.W., Rogers, N., 2004. Sedimentary Fe-Mn
- 518 oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic
- dissolved REE. Earth and Planetary Science Letters 224, 477-492.
- Billups, K., Channell, J.E.T., Zachos, J., 2002. Late Oligocene to early Miocene geochronology and
- paleoceanography from the subantarctic South Atlantic. Paleoceanography 17, 1004.
- Blaser, P., Lippold, J., Gutjahr, M., Frank, N., Link, J.M., Frank, M., 2016. Extracting foraminiferal
- seawater Nd isotope signatures from bulk deep sea sediment by chemical leaching. Chemical Geology
- 524 439, 189-204.
- 525 Burton, K.W., Ling, H.-F., O'Nions, R.K., 1997. Closure of the Central American Isthmus and its
- effect on deep-water formation in the North Atlantic. Nature 386, 382-385.
- 527 Campbell, K.E., Frailey, C.D., Romero-Pittman, L., 2006. The Pan-Amazonian Ucayali Peneplain, late
- Neogene sedimentation in Amazonia, and the birth of the modern Amazon River system.
- Palaeogeography, Palaeoclimatology, Palaeoecology 239, 166-219.
- Carter, P., Vance, D., Hillenbrand, C.D., Smith, J.A., Shoosmith, D.R., 2012. The neodymium isotopic
- 531 composition of waters masses in the eastern Pacific sector of the Southern Ocean. Geochimica et
- Cosmochimica Acta 79, 41-59.
- Channell, J.E.T., Galeotti, S., Martin, E.E., Billups, K., Scher, H.D., Stoner, J.S., 2003. Eocene to
- Miocene magnetostratigraphy, biostratigraphy, and chemostratigraphy at ODP Site 1090 (sub-
- Antarctic South Atlantic). Geological Society of America Bulletin 115, 607-623.
- 536 Cunha, P.R.C., Gonzaga, F.G., Coutinho, L.F.C., Feijó, F.J., 1994. Bacia do Amazonas, Boletim de
- Geociências da Petrobras. 8(1), pp. 47-55.
- Dobson, D.M., Dickens, G.R., Rea, D.K., 2001. Terrigenous sediment on Ceara Rise: a Cenozoic
- record of South American orogeny and erosion. Palaeogeography, Palaeoclimatology, Palaeoecology
- 540 165, 215-229.

Influence of the Amazon River on the Nd isotope composition of deep water in the western equatorial Atlantic during the Oligocene-Miocene transition

- 541 Eiras, J.F., Becker, C.R., Souza, E.M., Gonzaga, F.G., Silva, J.G.F., Daniel, L.M.F., Matsuda, N.S.,
- 542 Feijó, F.J., 1994. Bacia do Solimões, Boletim de Geociências da Petrobras. 8(1), pp. 17–22.
- 543 Elmore, A.C., Piotrowski, A.M., Wright, J.D., Scrivner, A.E., 2011. Testing the extraction of past
- 544 seawater Nd isotopic composition from North Atlantic deep sea sediments and foraminifera. Geochem.
- 545 Geophys. Geosyst. 12, O09008.
- 546 Figueiredo, J., Hoorn, C., van der Ven, P., Soares, E., 2009. Late Miocene onset of the Amazon River
- 547 and the Amazon deep-sea fan: Evidence from the Foz do Amazonas Basin. Geology 37, 619-622.
- 548 Frank, M., van de Flierdt, T., Halliday, A.N., Kubik, P.W., Hattendorf, B., Gunther, D., 2003.
- 549 Evolution of deepwater mixing and weathering inputs in the central Atlantic Ocean over the past 33
- 550 Myr. Paleoceanography 18, 1091.
- 551 Gibbs, R.J., 1967. The Geochemistry of the Amazon River System: Part I. The Factors that Control the
- 552 Salinity and the Composition and Concentration of the Suspended Solids. Geological Society of
- 553 America Bulletin 78, 1203-1232.
- 554 555 Goldstein, S.J., Jacobsen, S.B., 1987. The Nd and Sr isotopic systematics of river-water dissolved
- material: Implications for the sources of Nd and Sr in seawater. Chemical Geology: Isotope
- 556 Geoscience section 66, 245-272.
- 557 Goldstein, S.L., Hemming, S.R., 2003. Long-lived isotopic tracers in oceanography,
- 558 paleoceanography, and ice-sheet dynamics. Treatise on geochemistry 6, 453-489.
- 559 Gutjahr, M., Frank, M., Stirling, C.H., Klemm, V., van de Flierdt, T., Halliday, A.N., 2007. Reliable
- 560 extraction of a deepwater trace metal isotope signal from Fe-Mn oxyhydroxide coatings of marine
- 561 sediments. Chemical Geology 242, 351-370.
- 562 Jeandel, C., 1993. Concentration and isotopic composition of Nd in the South Atlantic Ocean. Earth
- 563 and Planetary Science Letters 117, 581-591.
- 564 Jeandel, C., Arsouze, T., Lacan, F., Téchiné, P., Dutay, J.C., 2007. Isotopic Nd compositions and
- 565 concentrations of the lithogenic inputs into the ocean: A compilation, with an emphasis on the
- 566 margins. Chemical Geology 239, 156-164.
- 567 Kraft, S., Frank, M., Hathorne, E.C., Weldeab, S., 2013. Assessment of seawater Nd isotope signatures
- 568 extracted from foraminiferal shells and authigenic phases of Gulf of Guinea sediments. Geochimica et
- 569 Cosmochimica Acta 121, 414-435.
- 570 Lacan, F., Jeandel, C., 2005a. Acquisition of the neodymium isotopic composition of the North
- 571 Atlantic Deep Water. Geochem. Geophys. Geosyst. 6, Q12008.
- 572 Lacan, F., Jeandel, C., 2005b. Neodymium isotopes as a new tool for quantifying exchange fluxes at
- 573 the continent-ocean interface. Earth and Planetary Science Letters 232, 245-257.
- 574 Liebrand, D., Lourens, L.J., Hodell, D.A., de Boer, B., van de Wal, R.S.W., Pälike, H., 2011. Antarctic
- 575 ice sheet and oceanographic response to eccentricity forcing during the early Miocene. Climate of the
- 576 Past 7, 869-880.
- 577 Lippold, J., Gutjahr, M., Blaser, P., Christner, E., de Carvalho Ferreira, M.L., Mulitza, S., Christl, M.,
- 578 Wombacher, F., Böhm, E., Antz, B., Cartapanis, O., Vogel, H., Jaccard, S.L., 2016. Deep water
- 579 provenance and dynamics of the (de)glacial Atlantic meridional overturning circulation. Earth and
- 580 Planetary Science Letters 445, 68-78.

Influence of the Amazon River on the Nd isotope composition of deep water in the western equatorial Atlantic during the Oligocene-Miocene transition

- Martin, E.E., Haley, B.A., 2000. Fossil fish teeth as proxies for seawater Sr and Nd isotopes.
- 582 Geochimica et Cosmochimica Acta 64, 835-847.
- Martin, E.E., Scher, H.D., 2004. Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad
- news and good news. Earth and Planetary Science Letters 220, 25-39.
- McDaniel, D.K., McLennan, S.M., Hanson, G.N., 1997. Provenance of Amazon Fan muds: constraints
- from Nd and Pb isotopes, in: Flood, R.D., Piper, D.J.W., Klaus, A., Peterson, L.C. (Eds.), Proceedings
- of the Ocean Drilling Program, Scientific Results, pp. 155: 169-176.
- 588 O'Nions, R.K., Frank, M., von Blanckenburg, F., Ling, H.F., 1998. Secular variation of Nd and Pb
- isotopes in ferromanganese crusts from the Atlantic, Indian and Pacific Oceans. Earth and Planetary
- 590 Science Letters 155, 15-28.
- 591 Osborne, A.H., Haley, B.A., Hathorne, E.C., Flögel, S., Frank, M., 2014. Neodymium isotopes and
- 592 concentrations in Caribbean seawater: Tracing water mass mixing and continental input in a semi-
- enclosed ocean basin. Earth and Planetary Science Letters 406, 174-186.
- Pälike, H., Frazier, J., Zachos, J.C., 2006. Extended orbitally forced palaeoclimatic records from the
- equatorial Atlantic Ceara Rise. Quat. Sci. Rev. 25, 3138-3149.
- Pearce, C.R., Jones, M.T., Oelkers, E.H., Pradoux, C., Jeandel, C., 2013. The effect of particulate
- dissolution on the neodymium (Nd) isotope and Rare Earth Element (REE) composition of seawater.
- Earth and Planetary Science Letters 369–370, 138-147.
- Piepgras, D.J., Wasserburg, G.J., 1987. Rare earth element transport in the western North Atlantic
- inferred from Nd isotopic observations. Geochimica et Cosmochimica Acta 51, 1257-1271.
- 601 Piotrowski, A.M., Goldstein, S.L., Hemming, S.R., Fairbanks, R.G., 2005. Temporal Relationships of
- 602 Carbon Cycling and Ocean Circulation at Glacial Boundaries. Science 307, 1933-1938.
- Pomiès, C., Davies, G.R., Conan, S.M.H., 2002. Neodymium in modern foraminifera from the Indian
- Ocean: implications for the use of foraminiferal Nd isotope compositions in paleo-oceanography.
- Earth and Planetary Science Letters 203, 1031-1045.
- Rempfer, J., Stocker, T.F., Joos, F., Dutay, J.-C., Siddall, M., 2011. Modelling Nd-isotopes with a
- 607 coarse resolution ocean circulation model: Sensitivities to model parameters and source/sink
- distributions. Geochimica et Cosmochimica Acta 75, 5927-5950.
- Roberts, N.L., Piotrowski, A.M., Elderfield, H., Eglinton, T.I., Lomas, M.W., 2012. Rare earth
- element association with foraminifera. Geochimica et Cosmochimica Acta 94, 57-71.
- Rosenthal, Y., Field, M.P., Sherrell, R.M., 1999. Precise determination of element/calcium ratios in
- calcareous samples using sector field inductively coupled plasma mass spectrometry. Anal. Chem. 71,
- 613 3248-3253.
- Rousseau, T.C.C., Sonke, J.E., Chmeleff, J., van Beek, P., Souhaut, M., Boaventura, G., Seyler, P.,
- Jeandel, C., 2015. Rapid neodymium release to marine waters from lithogenic sediments in the
- Amazon estuary. Nat Commun 6.
- 617 Scher, H.D., Martin, E.E., 2004. Circulation in the Southern Ocean during the Paleogene inferred from
- neodymium isotopes. Earth and Planetary Science Letters 228, 391-405.

Influence of the Amazon River on the Nd isotope composition of deep water in the western equatorial Atlantic during the Oligocene-Miocene transition

- 619 Scher, H.D., Martin, E.E., 2008. Oligocene deep water export from the North Atlantic and the
- development of the Antarctic Circumpolar Current examined with neodymium isotopes.
- Paleoceanography 23, PA1205.
- Scher, H.D., Martin, E.E., 2006. Timing and Climatic Consequences of the Opening of Drake Passage.
- 623 Science 312, 428-430.
- 624 Shephard, G.E., Muller, R.D., Liu, L., Gurnis, M., 2010. Miocene drainage reversal of the Amazon
- River driven by plate-mantle interaction. Nature Geoscience 3, 870-875.
- 626 Shipboard Scientific Party, 1995. Site 926, in: Curry, W.B., Shackleton, N.J., Richter, C, et al., (Ed.),
- Proceedings of the Ocean Drilling Program. Initial Reports. College Station, TX (Ocean Drilling
- 628 Program), pp. 154: 153-232.
- 629 Stewart, J.A., Wilson, P.A., Edgar, K.M., Anand, P., James, R.H., 2012. Geochemical assessment of
- 630 the palaeoecology, ontogeny, morphotypic variability and palaeoceanographic utility of
- "Dentoglobigerina" venezuelana. Marine Micropaleontology 84-85, 74-86.
- Stichel, T., Frank, M., Rickli, J., Haley, B.A., 2012. The hafnium and neodymium isotope composition
- of seawater in the Atlantic sector of the Southern Ocean. Earth and Planetary Science Letters
- 634 317,Äì318, 282-294.
- Tachikawa, K., Athias, V., Jeandel, C., 2003. Neodymium budget in the modern ocean and paleo-
- oceanographic implications. Journal of Geophysical Research 108, 3254.
- 637 Tachikawa, K., Piotrowski, A.M., Bayon, G., 2014. Neodymium associated with foraminiferal
- carbonate as a recorder of seawater isotopic signatures. Quat. Sci. Rev. 88, 1-13.
- Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Yuhara, M.,
- Orihashi, Y., Yoneda, S., Shimizu, H., Kunimaru, T., Takahashi, K., Yanagi, T., Nakano, T., Fujimaki,
- H., Shinjo, R., Asahara, Y., Tanimizu, M., Dragusanu, C., 2000. JNdi-1: a neodymium isotopic
- reference in consistency with LaJolla neodymium. Chemical Geology 168, 279-281.
- Thomas, D.J., Bralower, T.J., Jones, C.E., 2003. Neodymium isotopic reconstruction of late Paleocene
- early Eocene thermohaline circulation. Earth and Planetary Science Letters 209, 309-322.
- van der Hammen, T., Hooghiemstra, H., 2000. Neogene and Quaternary history of vegetation, climate,
- and plant diversity in Amazonia. Quat. Sci. Rev. 19, 725-742.
- Vance, D., Burton, K., 1999. Neodymium isotopes in planktonic foraminifera: a record of the response
- of continental weathering and ocean circulation rates to climate change. Earth and Planetary Science
- 649 Letters 173, 365-379.
- Vance, D., Scrivner, A.E., Beney, P., Staubwasser, M., Henderson, G.M., Slowey, N.C., 2004. The use
- of foraminifera as a record of the past neodymium isotope composition of seawater. Paleoceanography
- 652 19, PA2009.
- Vance, D., Thirlwall, M., 2002. An assessment of mass discrimination in MC-ICPMS using Nd
- isotopes. Chemical Geology 185, 227-240.
- Wang, X., Auler, A.S., Edwards, R.L., Cheng, H., Cristalli, P.S., Smart, P.L., Richards, D.A., Shen,
- 656 C.-C., 2004. Wet periods in northeastern Brazil over the past 210 kyr linked to distant climate
- anomalies. Nature 432, 740-743.

Influence of the Amazon River on the Nd isotope composition of deep water in the western equatorial Atlantic during the Oligocene-Miocene transition

- West, A.J., Galy, A., Bickle, M., 2005. Tectonic and climatic controls on silicate weathering. Earth
- and Planetary Science Letters 235, 211-228.
- Wilson, D.J., Piotrowski, A.M., Galy, A., McCave, I.N., 2012. A boundary exchange influence on
- deglacial neodymium isotope records from the deep western Indian Ocean. Earth and Planetary
- 662 Science Letters 341-344, 35-47.
- Wombacher, F., Rehkämper, M., 2003. Investigation of the mass discrimination of multiple collector
- 664 ICP-MS using neodymium isotopes and the generalised power law. Journal of Analytical Atomic
- Spectrometry 18.

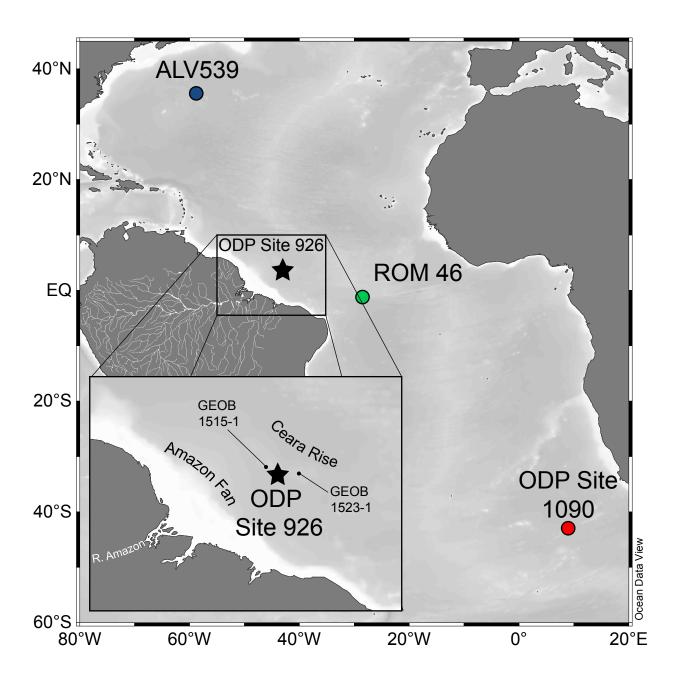


Figure 1: Location of ODP Leg 154 Site 926B Ceara Rise in relation to other deep water  $\varepsilon$ Nd records across the Oligocene-Miocene transition discussed in this study. Fe-Mn crust ALV539, 2,665 m water depth (O'Nions et al., 1998), Fe-Mn crust ROM46, 3,350 m water depth (Frank et al., 2003), Fish tooth record from ODP Site 1090, 3,700 m water depth (Scher and Martin, 2008). Colours correspond to line/marker colours in Figure 2. Inset shows location of ODP Site 926B in relation to the Amazon River mouth and piston core sites on Ceara Rise, GEOB 1515-1 (3,129 m water depth) and GEOB 1523-1 (3,292 m water depth) used in the study by Lippold et al. (2016).

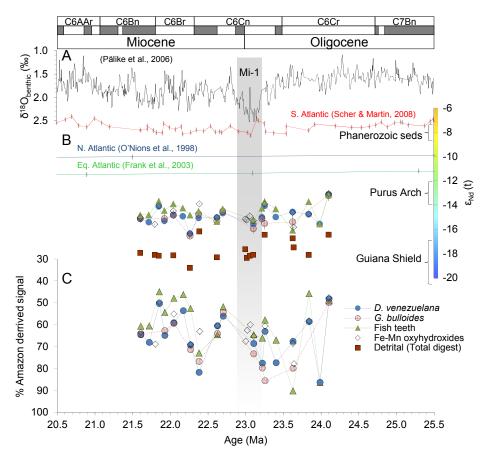


Figure 2:  $\epsilon_{Nd}$  records across the Oligocene-Miocene transition at ODP Site 926. A. Benthic oxygen isotope record for this site (Pälike et al., 2006), B.  $\epsilon_{Nd}$  values for fossilised fish teeth (green triangles), planktonic foraminifera *D. venezuelana* (blue circles) and *G. bulloides* (red circles), Fe/Mn oxyhydroxides (black diamonds), and the detrital fraction (squares). Deep water  $\epsilon_{Nd}$  values for the South Atlantic (Scher and Martin, 2008), Equatorial Atlantic (Frank et al., 2003), and North Atlantic (O'Nions et al., 1998) at the OMT are also shown for comparison. Colour scale corresponds that used in Figure 3 showing potential Amazon basin source rock  $\epsilon_{Nd}$  ranges for Guiana Shield, Purus Arch and Phanerozoic sediments (Allègre et al., 1996). C. Estimated percentage of  $\epsilon_{Nd}$  seawater signal at Ceara Rise coming from Amazon sources relative to northern component water during the OMT. Error bars represent the 2 standard error of each measurement. Magnetostratigraphic correlation from ODP Site 1090 in the South Atlantic (Billups et al., 2002; Channell et al., 2003).

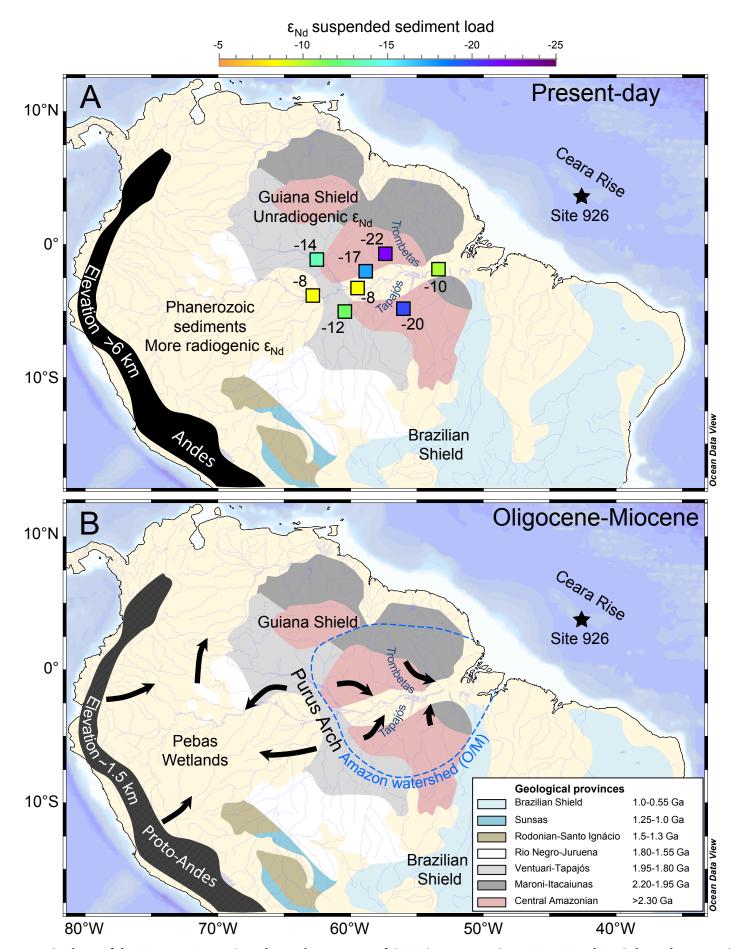


Figure 3: Geology of the Amazon Basin. Star shows the position of ODP Site 926 on Ceara Rise. Panel A. Coloured squares (colour scale corresponds to that used in Figure 2) show εNd values of modern suspended sediments in Amazon tributaries (Allègre et al., 1996). Shaded regions show basement lithology. Panel B. Amazon drainage during the Oligocene-Miocene. Black arrows and blue dashed line show, respectively, the inferred drainage pattern and catchment area at this time (Figueiredo et al., 2009; Shephard et al., 2010).

			Detrital (Total d	igest)		Fe-Mn oxyhydroxides						
ODP Sample Identification Site, Hole, Core, Section,		Depth	Age	$^{143}$ Nd/ $^{144}$ Nd	$\varepsilon_{Nd}(0)$	$\varepsilon_{Nd}(t)$		$^{143}$ Nd/ $^{144}$ Nd	$\varepsilon_{Nd}(0)$	$\varepsilon_{Nd}(t)$		
		(mbsf)	(Ma)	(normalised)				(normalised)				
Half, Int.							2SE				2SE	
926 B 46 4 W	40 - 50	427.8	21.61	0.511710	-18.10	-17.95	0.06	0.511859	-15.20	-15.04	0.05	
926 B 46 6 W	70 - 80	431.1	21.72									
926 B 47 1 W	65 - 67	433.1	21.80	0.511701	-18.27	-18.12	0.05	0.511831	-15.74	-15.59	0.06	
926 B 47 2 W	70 - 80	434.7	21.85	0.511698	-18.33	-18.17	0.05	0.511909	-14.21	-14.06	0.08	
926 B 47 4 W	10 - 20	437.1	21.93									
926 B 47 6 W	42 - 50	440.4	22.05	0.511700	-18.30	-18.15	0.06	0.511887	-14.64	-14.49	0.06	
926 B 48 2 W	72 - 80	444.4	22.17									
926 B 48 4 W	52 - 60	447.2	22.27	0.511647	-19.34	-19.18	0.05	0.511793	-16.49	-16.33	0.05	
926 B 48 6 W	91 - 100	450.6	22.38									
926 B 48 6 W	132 - 134	450.9	22.39	0.511800	-16.34	-16.19	0.05	0.511917	-14.06	-13.90	0.06	
926 B 49 4 W	109 - 120	457.3	22.62	0.511691	-18.47	-18.31	0.05	0.511860	-15.18	-15.02	0.04	
926 B 49 6 W	5 - 15	459.3	22.70									
926 B 50 4 W	102 - 105	466.9	23.00	0.511725	-17.81	-17.64	0.04	0.511852	-15.32	-15.16	0.05	
926 B 50 5 W	5.5 - 7.5	467.5	23.02	0.511688	-18.52	-18.36	0.05	0.511849	-15.39	-15.23	0.05	
926 B 50 5 W	111 - 114	468.5	23.06	0.511698	-18.34	-18.18	0.05	0.511866	-15.07	-14.90	0.04	
926 B 50 6 W	82 - 92	469.8	23.11	0.511702	-18.27	-18.10	0.04	0.511846	-15.45	-15.29	0.05	
926 B 51 2 W	35 - 45	472.9	23.22									
926 B 51 2 W	128 - 133	473.8	23.26	0.511786	-16.61	-16.45	0.05	0.511917	-14.07	-13.91	0.06	
926 B 51 5 W	53 - 60	477.6	23.40									
926 B 52 1 W	94 - 104	481.5	23.63	0.511771	-16.91	-16.75	0.06	0.511880	-14.79	-14.62	0.06	
926 B 52 1 W	141 - 143	481.9	23.64	0.511733	-17.66	-17.49	0.05	0.511818	-16.00	-15.83	0.05	
926 B 52 5 W	29 - 38	486.8	23.84	0.511700	-18.29	-18.12	0.05	0.511874	-14.90	-14.73	0.05	
926 B 53 1 W	35 - 44	490.6	23.99									
926 B 53 3 W	105 - 114	494.3	24.10	0.511786	-16.62	-16.44	0.04	0.511959	-13.24	-13.07	0.05	

Table 1:  $\epsilon_{Nd}$  measurements of detrital sediments and Fe/Mn oxyhydroxides from the Oligocene-Miocene transition of ODP Site 926. Ages are calculated using the age model of Pälike et al. (2006).  $\epsilon_{Nd}(0)$  denotes measured  $\epsilon_{Nd}$  values, and  $\epsilon_{Nd}(t)$  values have been adjusted for ingrowth of  $^{143}Nd$  since the Oligocene (assumption: initial  $^{147}Sm/^{144}Nd$  ratio 0.1412 for detrital and Fe-Mn oxyhydroxide samples).

				Fish teeth				D. venezuelana				G. bulloides			
ODP Sample Iden		Depth	Age	<sup>143</sup> Nd/ <sup>144</sup> Nd	$\varepsilon_{Nd}(0)$	$\varepsilon_{Nd}(t)$		<sup>143</sup> Nd/ <sup>144</sup> Nd	$\varepsilon_{Nd}(0)$	$\varepsilon_{Nd}(t)$		<sup>143</sup> Nd/ <sup>144</sup> Nd	$\varepsilon_{Nd}(0)$	$\varepsilon_{Nd}(t)$	
Site, Hole, Core, S	Section,	(mbsf)	(Ma)	(normalised)				(normalised)				(normalised)			
Half, Int.							2SE				2SE				2SE
926 B 46 4 W	40 - 50	427.8	21.61	0.511869	-15.00	-14.81	0.19	0.511854	-15.28	-15.13	0.22	0.511856	-15.26	-15.11	0.39
926 B 46 6 W	70 - 80	431.1	21.72	0.511869	-15.00	-14.81	0.18	0.511840	-15.56	-15.41	0.20				
926 B 47 1 W	65 - 67	433.1	21.80												
926 B 47 2 W	70 - 80	434.7	21.85	0.511928	-13.86	-13.67	0.17	0.511907	-14.26	-14.11	0.21				
926 B 47 4 W	10 - 20	437.1	21.93	0.511888	-14.63	-14.44	0.19	0.511846	-15.45	-15.30	0.23	0.511855	-15.27	-15.12	0.46
926 B 47 6 W	42 - 50	440.4	22.05	0.511916	-14.09	-13.90	0.19	0.511871	-14.96	-14.81	0.20	0.511870	-14.99	-14.83	0.31
926 B 48 2 W	72 - 80	444.4	22.17	0.511898	-14.43	-14.25	0.18	0.511865	-15.07	-14.92	0.27				
926 B 48 4 W	52 - 60	447.2	22.27	0.511868	-15.02	-14.83	0.19	0.511791	-16.52	-16.36	0.17	0.511782	-16.70	-16.55	0.25
926 B 48 6 W	91 - 100	450.6	22.38	0.511884	-14.70	-14.51	0.18	0.511858	-15.21	-15.06	0.23	0.511874	-14.90	-14.75	0.24
926 B 48 6 W	132 - 134	450.9	22.39												
926 B 49 4 W	109 - 120	457.3	22.62	0.511841	-15.56	-15.36	0.18	0.511860	-15.18	-15.03	0.16	0.511844	-15.48	-15.32	0.27
926 B 49 6 W	5 - 15	459.3	22.70	0.511895	-14.50	-14.31	0.20	0.511878	-14.82	-14.66	0.20	0.511886	-14.67	-14.51	0.19
926 B 50 4 W	102 - 105	466.9	23.00												
926 B 50 5 W	5.5 - 7.5	467.5	23.02												
926 B 50 5 W	111 - 114	468.5	23.06												
926 B 50 6 W	82 - 92	469.8	23.11	0.511847	-15.43	-15.23	0.26	0.511832	-15.72	-15.56	0.20	0.511813	-16.10	-15.94	0.40
926 B 51 2 W	35 - 45	472.9	23.22	0.511897	-14.46	-14.26	0.36	0.511861	-15.16	-15.00	0.25	0.511854	-15.30	-15.14	0.43
926 B 51 2 W	128 - 133	473.8	23.26	0.511924	-13.92	-13.72	0.24	0.511909	-14.23	-14.06	0.22	0.511834	-15.68	-15.52	0.50
926 B 51 5 W	53 - 60	477.6	23.40	0.511894	-14.52	-14.32	0.20	0.511861	-15.15	-14.99	0.24				
926 B 52 1 W	94 - 104	481.5	23.63	0.511803	-16.29	-16.09	0.16	0.511883	-14.72	-14.56	0.18	0.511841	-15.55	-15.39	0.71
926 B 52 1 W	141 - 143	481.9	23.64												
926 B 52 5 W	29 - 38	486.8	23.84	0.511924	-13.92	-13.72	0.25	0.511873	-14.92	-14.76	0.21				
926 B 53 1 W	35 - 44	490.6	23.99	0.511830	-15.77	-15.57	0.19	0.511832	-15.72	-15.56	0.24				
926 B 53 3 W	105 - 114	494.3	24.10	0.511953	-13.37	-13.16	0.26	0.511958	-13.27	-13.11	0.21	0.511952	-13.38	-13.21	0.45

Table 2:  $\epsilon_{Nd}$  measurements of fossilised fish teeth and planktonic foraminifera (*D. venezuelana* and *G. bulloides*) from the Oligocene-Miocene transition of ODP Site 926. Ages are calculated using the age model of Pälike et al. (2006).  $\epsilon_{Nd}(0)$  denotes measured  $\epsilon_{Nd}$  values, and  $\epsilon_{Nd}(t)$  values have been adjusted for ingrowth of <sup>143</sup>Nd since the Oligocene (assumption: initial <sup>147</sup>Sm/<sup>144</sup>Nd ratio 0.1286 for fish teeth and 0.1412 for foraminifera samples).