AGU PUBLICATIONS

Paleoceanography

RESEARCH ARTICLE
10.1002/2014PA002676

Key Points:
- Seawater Nd and Pb isotope records for the Pliocene Caribbean and EEP
- Caribbean Nd isotope composition became more UNADW-like during the Pliocene
- Short-term changes support link between CAS closure and strength of AMOC

Supporting Information:
- Readme
- Text S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Table S1
- Table S2
- Table S3
- Table S4

Correspondence to:
A. H. Osborne,
aosborne@geomar.de

Citation:
Osborne, A. H., D. R. Newkirk, J. Groeneveld, E. E. Martin, R. Tiedemann, and M. Frank (2014), The seawater neodymium and lead isotope record of the final stages of Central American Seaway closure, *Paleoceanography*, *29*, 715–729, doi:10.1002/2014PA002676.

Received 26 MAY 2014
Accepted 12 JUN 2014
Accepted article online 16 JUN 2014
Published online 12 JUL 2014

The seawater neodymium and lead isotope record of the final stages of Central American Seaway closure

Anne H. Osborne[1], Derrick R. Newkirk[2,3], Jeroen Groeneveld[4], Ellen E. Martin[2], Ralf Tiedemann[5], and Martin Frank[1]

[1]GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany, [2]Department of Geological Sciences, University of Florida, Gainesville, Florida, USA, [3]Now at ExxonMobil Production Company, Houston, Texas, USA, [4]Center for Marine Environmental Sciences (MARUM), University of Bremen, Bremen, Germany, [5]Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

Abstract The shoaling and final closure of the Central American Seaway (CAS) resulted in a major change of the global ocean circulation and has been suggested as an essential driver for strengthening of Atlantic Meridional Overturning Circulation (AMOC). The exact timing of CAS closure is key to interpreting its importance. Here we present a reconstruction of deep and intermediate water Nd and Pb isotope compositions obtained from fossil fish teeth and the authigenic coatings of planktonic foraminifera in the eastern equatorial Pacific (Ocean Drilling Program (ODP) Site 1241) and the Caribbean (ODP Sites 998, 999, and 1000) covering the final stages of CAS closure between 5.6 and 2.2 Ma. The data for the Pacific site indicate no significant Atlantic/Caribbean influence over this entire period. The Caribbean sites show a continuous trend to less radiogenic Nd isotope compositions during the Pliocene, consistent with an enhancement of Upper North Atlantic Deep Water (UNADW) inflow and a strengthening of the AMOC. Superimposed onto this long-term trend, shorter-term changes of intermediate Caribbean Nd isotope signatures approached more UNADW-like values during intervals when published reconstructions of seawater salinity suggested complete closure of the CAS. The data imply that significant deep water exchange with the Pacific essentially stopped by 7 Ma and that shallow exchange, which still occurred at least periodically until approximately 2.5 Ma, may have been linked to the strength of the AMOC but did not have any direct effect on the intermediate and deep Caribbean Nd isotope signatures through mixing with Pacific waters.

1. Introduction

The progressive closure of the Central American Seaway (CAS) resulted in a major reorganization of ocean circulation, which has been controversially reported as both promoting and hindering major intensification of Northern Hemisphere Glaciation in the late Pliocene [*Berggren and Hollister*, 1974; *Berger and Wefer*, 1996; *Driscoll and Haug*, 1998; *Haug and Tiedemann*, 1998; *Molnar*, 2008]. The most direct effect of CAS closure was a reduced supply of low salinity Pacific water to the North Atlantic and an increase in Caribbean sea surface salinities [*Keigwin*, 1982; *Keller et al*., 1989; *Haug et al*., 2001; *Steph et al*., 2006; *Groeneveld et al*., 2008]. Ocean Circulation Model (OCM) simulations indicate that a decrease in surface water buoyancy in the North Atlantic promoted the production of North Atlantic Deep Water (NADW) and a more vigorous Atlantic Meridional Overturning Circulation (AMOC) [*Maier-Reimer et al*., 1990; *Mikolajewicz and Crowley*, 1997; *Schneider and Schmittner*, 2006; *Lunt et al*., 2008; *Zhang et al*., 2012]. Benthic δ^{13}C data and the abundance of the carbonate sand fraction in the deep Caribbean suggest that the AMOC reached peak strength at 3.6 Ma [*Haug and Tiedemann*, 1998]. Benthic δ^{13}C data from the intermediate depth Caribbean also support a strong AMOC between 4 and 3 Ma [*Steph et al*., 2010]. *Haug et al*. [2001] interpreted differences between planktonic δ^{18}O records on either side of the CAS as a shoaling of the seaway to ~100 m water depth by 4.2 Ma, which is supported by an increase in the salinity contrast between surface waters in the eastern equatorial Pacific (EEP) and the Caribbean from ~4.5 Ma onward [*Groeneveld*, 2005; *Groeneveld et al*., 2006, 2008; *Steph et al*., 2006]. However, there is also land-based geological evidence for a much earlier isolation of the Pacific from the Caribbean at ~15 Ma [*Kirby et al*., 2008; *Montes et al*., 2012a, 2012b], a discrepancy that remains to be resolved. The strength of the AMOC in OCM reconstructions increases dramatically in response to the final few hundred meters of CAS shoaling [*Schneider and Schmittner*, 2006; *Lunt et al*., 2008; *Zhang et al*., 2012].

©2014. American Geophysical Union. All Rights Reserved.

Therefore, it is critical to reconstruct not only the timing of final complete CAS closure but also the restriction of the seaway to deep and intermediate waters in order to test how CAS closure was linked to AMOC strength. Here we reconstruct seawater Nd and Pb isotope compositions in the eastern equatorial Pacific and the deep and intermediate Caribbean for a detailed investigation of the final stages of CAS closure, which may have been interrupted by intermittent reopenings as a result of either tectonics or ice volume changes [*Sarnthein et al*., 2009; *De Schepper et al*., 2013].

The isotopic compositions of dissolved Nd and Pb in seawater are water mass tracers that are independent of biological and thermodynamic modifications and have been successfully applied in paleoceanographic studies on different timescales [e.g., *Burton et al*., 1997; *Abouchami et al*., 1999; *Rutberg et al*., 2000; *Piotrowski et al*., 2004, 2005, 2009; *Gourlan et al*., 2008; *Gutjahr et al*., 2007, 2008, 2009]. The Nd isotope signatures of water masses reflect rock type and age of the continental landmasses adjacent to the regions of water mass formation, whereas in the case of Pb isotopes the weathering regime also plays a major role. The residence times of Nd (200–1000 years) [*Tachikawa et al*., 1999; *Arsouze et al*., 2009; *Rempfer et al*., 2011] and Pb (50–200 years) [*Schaule and Patterson*, 1981; *von Blanckenburg and Igel*, 1999] in seawater are similar to or shorter than the global ocean mixing time of ~1500 years [e.g., *Broecker and Peng*, 1982], so that measurable differences between basins, basin regions, and, in the case of Nd isotopes, water masses are preserved [e.g., *Piepgras and Wasserburg*, 1980].

On million year timescales coarse-resolution deep water Nd and Pb isotope signatures have been extracted from ferromanganese crusts. Crust "Blake" was recovered from intermediate water depths of 800 m within the pathway of the modern Gulf Stream and revealed a pronounced trend toward less radiogenic isotope compositions between 8 and 5 Ma [*Frank et al*., 1999; *Reynolds et al*., 1999]. In particular, the change in the isotopic composition of Pb was interpreted as a decreased supply of Pacific deep and intermediate waters to the Caribbean due to the shoaling CAS, rather than an increase in contributions from the Southern Ocean [*Reynolds et al*., 1999]. At the same time, ferromanganese crust records from the deep Pacific indicated no changes in the inflow of Atlantic or Caribbean water masses [*Ling et al*., 1997, 2005; *Frank et al*., 1999].

Acid-reductive leaching of bulk sediment has been considered a reliable way to extract the deep water Nd and Pb isotope composition from authigenic Fe-Mn coatings of bulk sediments and to produce high-resolution records of past seawater [e.g., *Rutberg et al*., 2000; *Piotrowski et al*., 2004, 2005; *Gutjahr et al*., 2007, 2008, 2009]. However, recent studies have shown that at some locations this method may also release Nd from detrital material, thus compromising the results [*Roberts et al*., 2010; *Elmore et al*., 2011; *Piotrowski et al*., 2012; *Wilson et al*., 2013]. In contrast, authigenic coatings formed on handpicked sedimentary planktonic foraminifera can be analyzed to minimize detrital contribution and have been shown to reliably record the Nd isotope signature of bottom waters [*Roberts et al*., 2010, 2012; *Tachikawa et al*., 2014]. Another alternative approach is to use fish teeth that after deposition in the sediments rapidly incorporate bottom water Nd and are subsequently unaffected by further diagenetic processes [*Martin and Scher*, 2004]. Fish teeth records from the Miocene deep Caribbean show a major change away from Pacific Nd isotope compositions starting at ~ 11 Ma, which continued into the early Pliocene [*Newkirk and Martin*, 2009].

Although uncleaned planktonic foraminifera and fish teeth have been shown to reliably record seawater Nd isotope signatures [*Martin and Scher*, 2004; *Roberts et al*., 2010], they are not suitable archives for seawater Pb isotope signatures [*Basak et al*., 2011], whereas the bulk sediment leachates are still considered reliable archives for seawater Pb isotope compositions. We therefore measured down core and core top Nd isotope compositions of bulk sediment leachates, fish teeth, and planktonic foraminifera, as well as of the detrital fraction in order to determine the most reliable approach for each site to extract deep water radiogenic Nd isotope signatures in the study area.

We present new Nd and Pb isotope records for the period between 5.6 and 2.2 Ma for Ocean Drilling Program (ODP) sites in the Caribbean (998, 999, and 1000) and in the eastern equatorial Pacific (1241) (Figure 1). Not only are these sites more proximal to the region of final CAS closure and offer a higher time resolution than those of published ferromanganese crusts, they have also been extensively studied for a range of other paleoceanographic parameters [*Haug and Tiedemann*, 1998; *Haug et al*., 2001; *Bickert et al*., 2004; *Steph et al*., 2006, 2010; *Groeneveld et al*., 2008; *Newkirk and Martin*, 2009; *Seki et al*., 2010; *De Schepper et al*., 2013].

©2014. American Geophysical Union. All Rights Reserved.

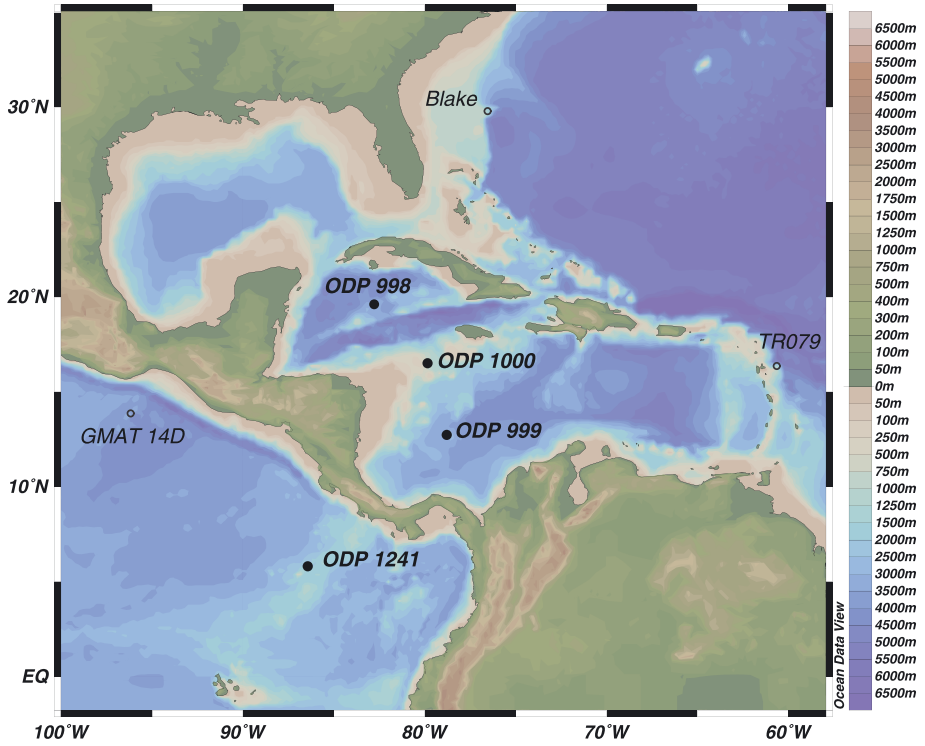

Figure 1. Location of ODP sites (filled circles) and ferromanganese crusts (open circles) referred to in the text. Blake and TR079 [*Reynolds et al*., 1999]; GMAT 14D [*Frank et al*., 1999]. Map produced using Ocean Data View [*Schlitzer*, 2011].

2. Materials and Methods

2.1. Sample Sites and Hydrological Setting

Pliocene to early Pleistocene Nd isotope records were obtained from ODP Sites 998, 999, and 1000 in the Caribbean and ODP Site 1241 in the eastern equatorial Pacific (Figure 1). Core top samples from nearby locations were measured for calibration purposes (Table S1 and Figure S1 in the supporting information). ODP Site 999 (12°45′N, 78°44′W, 2828 m water depth) is located on Kogi Rise in the deep Colombian Basin [*Sigurdsson et al*., 1997] and ODP Site 998 (19°39′N, 82°56′W, 3180 m water depth) was drilled on the Cayman Rise between the Yucatan Basin and the Cayman Trough. Deep waters entering the Caribbean from the Atlantic must pass across the relatively shallow sills of the Antilles Island Arc, which reach a maximum depth of ~ 1900 m [*Johns et al*., 2002] and thus only allow inflow of Upper North Atlantic Deep Water (UNADW) today. Shallower ODP Site 1000 (16°33′N, 79°52′W, 916 m water depth) is well placed for recording changes at intermediate water depths in the Caribbean and is at present under the influence of Antarctic Intermediate Water (AAIW) [*Wüst*, 1964]. Pacific ODP Site 1241 is located on the northern slope of the Cocos Ridge in the Guatemala Basin (5°51′N, 86°24′W, 2027 m, [*Mix et al*., 2003]), bathed today in relatively oxygen-depleted waters characterized by low $\delta^{13}C$ signatures originating from mid-depths in the north Pacific [*Tsuchiya and Talley*, 1998].

2.2. Age Models

We present data for the time interval 5.6 to 2.2 Ma, with a resolution of between 50 and 100 kyr, using age models established by *Haug and Tiedemann* [1998], *Tiedemann et al*. [2007], *Steph et al*. [2006, 2010], and *Kameo and Bralower* [2000]. The benthic foraminifer isotope records of Caribbean Sites 999 and 1000 have previously been correlated to Atlantic Site 925/926 and to the 1241 age model, thus allowing direct comparisons of paleoceanographic changes between these three sites [*Steph et al*., 2006].

2.3. Sample Preparation and Isotope Analysis

Fossil fish teeth from Site 1000 were ultrasonicated in de-ionized water to remove any particles and inspected under the microscope to check that the cleaning was successful. Fish teeth from Site 998 and 999 were not cleaned prior to dissolution [*Martin et al*., 2010]. Fish teeth from the three sites were dissolved in a 1:1 or 1:3 mixture of concentrated HNO_3 and concentrated HCl.

©2014. American Geophysical Union. All Rights Reserved.

Mixed planktonic foraminifera weighing 25 to 50 mg were crushed between two glass plates and ultrasonicated repeatedly in de-ionized water and once with methanol to remove clays. After a final rinse in de-ionized water, samples were examined under the microscope and any remaining detrital particles were removed with a single paintbrush bristle. Samples were left to dissolve overnight in 0.3 M HNO_3.

Bulk sediment samples were leached following the procedure described by *Gutjahr et al*. [2007], modified by *Stumpf et al*. [2010]. In brief, 3 g of dried and powdered sediment were rinsed twice in de-ionized water, then shaken with 15% acetic acid/1 M Na acetate buffer (hereafter referred to as "buffered acetic acid solution") for 2.5 h, and then centrifuged and shaken again overnight after addition of fresh buffered acetic acid solution to remove carbonate. The samples were then triple rinsed in de-ionized water and shaken with NaOH-buffered 0.05 M hydroxylamine hydrochloride/15% acetic acid solution (hereafter referred to as "HH leach solution") for 1 h. The supernatant containing the seawater derived Nd and Pb fractions of the ferromanganese coatings of the particles was collected and prepared for ion exchange chemistry. In addition, selected samples were leached in the HH leach solution for a further 12 h to ensure complete removal of the oxides, triple-rinsed in de-ionized water, and then dried down. Fifty milligrams of this residual detrital fraction was completely dissolved in a mixture of HF and HNO_3.

Samples were processed through ion exchange columns following standard procedures to separate and purify Pb, Sr, and Nd (see supporting information for further details).

Isotope measurements were performed on Nu Plasma Multiple Collector Inductively Coupled Mass Spectrometer (MC-ICPMS) at GEOMAR and at the University of Florida (UF). Analyses at UF were performed using a time-resolved analysis technique [*Kamenov et al*., 2008]. The $^{143}Nd/^{144}Nd$ results were mass bias corrected to a $^{146}Nd/^{144}Nd$ ratio of 0.7219 and normalized to the accepted $^{143}Nd/^{144}Nd$ of 0.512115 for the JNdi-1 standard [*Tanaka et al*., 2000]. The Nd isotopic signature is reported as ε_{Nd}, which corresponds to the deviation of a measured $^{143}Nd/^{144}Nd$ of a sample from the Chondritic Uniform Reservoir value of 0.512638 [*Jacobsen and Wasserburg*, 1980] ($\varepsilon_{Nd} = \{(^{143}Nd/^{144}Nd)_{sample}/(^{143}Nd/^{144}Nd)_{CHUR} -1\} \times 10{,}000$). External reproducibility (2σ) at GEOMAR was between 0.16 and 0.71 ε_{Nd} units; the 2σ error at UF was 0.27 ε_{Nd} units. Procedural Nd blanks at GEOMAR were ≤ 250 pg Nd for leachates, ≤ 50 pg Nd for total dissolutions, ≤ 20 pg Nd for foraminifera, and ≤ 120 pg Nd for fish teeth, equivalent to ≤ 1%, ≤ 0.1%, ≤0.08%, and ≤ 0.6% of total amount of samples, respectively. The total blank for fish teeth samples measured at UF was 14 pg Nd.

The Pb isotope ratios were measured at GEOMAR by a standard-sample bracketing method [*Albarede et al*., 2004] using the National Institute of Standards and Technology (NIST) SRM981 standard and its widely accepted isotopic composition [*Abouchami et al*., 1999]: $^{208}Pb/^{204}Pb = 36.7219$; $^{207}Pb/^{204}Pb = 15.4963$; $^{206}Pb/^{204}Pb = 16.9405$; $^{208}Pb/^{206}Pb = 2.1677$; and $^{207}Pb/^{206}Pb = 0.9147$. External reproducibility was monitored using a SPEX Pb standard solution and gave the following 2σ error, expressed in ppm: $^{208}Pb/^{204}Pb = 188$ to 591; $^{207}Pb/^{204}Pb = 159$ to 447; $^{206}Pb/^{204}Pb = 163$ to 279; $^{208}Pb/^{206}Pb = 73$ to 303; and $^{207}Pb/^{206}Pb = 38$ to 163. Procedural Pb blanks were always ≤ 500 pg, equivalent to 9% of the total sample for a few samples with very low Pb concentrations. However, for the vast majority, the Pb blank represented ≤ 4% of the total sample. Moreover, those samples with potentially higher blank influence are not shifted toward Pb isotope compositions typical for European anthropogenic sources (17.82, 15.62, and 37.72 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, respectively [*Veron and Church*, 1997]).

The Sr isotope ratios were also measured at GEOMAR and were mass bias corrected to a $^{86}Sr/^{88}Sr$ ratio of 0.1194, after correction for Kr and Rb interferences. The samples were normalized to the widely accepted value of NIST SRM987 standard with an $^{87}Sr/^{86}Sr$ of 0.710245. External reproducibility was monitored using an Alfa Aesar Sr standard solution as an internal standard and was between 21 and 67 ppm (2σ) for leachates and 115 ppm (2σ) for total dissolution. Procedural Sr blanks were ≤2.18 ppb for leachates and ≤ 0.03 ppb for total dissolution, equivalent to ≤ 2.72% and ≤ 0.06%, respectively.

3. Results and Discussion

3.1. Reliable Extraction of the Seawater Signal

Prior to interpreting down core data an evaluation of the different extraction methods for each site is crucial given that significant offsets have previously been observed between different methods applied to the same samples depending on the type of sediment, in particular when volcanic material is involved [*Roberts et al*.,

©2014. American Geophysical Union. All Rights Reserved.

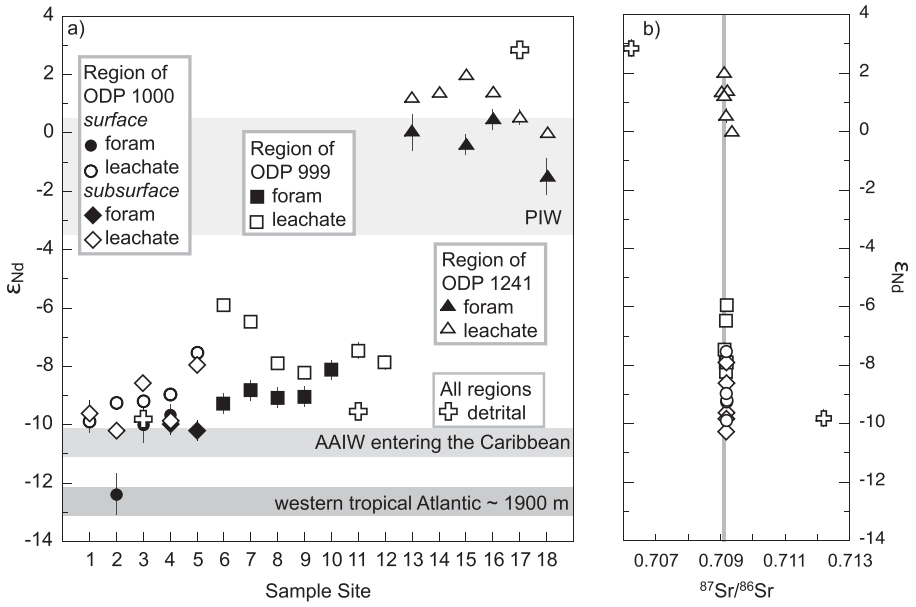

Figure 2. (a) Values of ε_{Nd} for core top uncleaned planktonic foraminifera (filled symbols) and leachates (open symbols) and the detrital fraction (open crosses) in the region of ODP Sites 1000, 999, and 1241. Numbers on the *x* axis refer to Sites in Table S1 and Figure S1. Errors of 2σ are indicated by the gray bars but in most cases are smaller than symbol size. Horizontal shading indicates ε_{Nd} signatures of water masses: PIW [*Piepgras and Wasserburg*, 1982; *Piepgras and Jacobsen*, 1988], AAIW entering the Caribbean, and western tropical Atlantic ~1900 m [*Piepgras and Wasserburg*, 1987; *Huang et al*., 2014]. (b) $^{87}Sr/^{86}Sr$ versus ε_{Nd} for core top leachate and detrital samples. Symbols as before. The composition of modern seawater Sr [*McArthur et al*., 2001] is indicated by the vertical line.

2010; *Elmore et al*., 2011], or in shelf settings supplied with river-borne detrital particles that carry preformed ferromanganese coatings [*Kraft et al*., 2013]. Indeed, all of the core top samples from the regions of Sites 999, 1000, and 1241 show more radiogenic ε_{Nd} signatures of the leachates than of the uncleaned planktonic foraminifera (from now on referred to as "foraminifera") (Table S1a and Figure 2a).

The average foraminiferal Nd isotope composition of core top samples from the region of ODP Site 1241 ($\varepsilon_{Nd} = -0.35$) is within the expected range for modern Pacific Intermediate Water (PIW) (0 ± 0.5 to -3 ± 0.5) [*Piepgras and Wasserburg*, 1982; *Piepgras and Jacobsen*, 1988] and is therefore considered a reliable archive of bottom water ε_{Nd}. The average leachate value ($\varepsilon_{Nd} = 1.1$), however, is offset toward the signature of the detrital fraction ($\varepsilon_{Nd} = 2.9$) and suggests that the leaching procedure partially dissolved the volcanogenic detrital material present. Consequently, only the foraminiferal record is applied for interpretation.

The foraminifera in the region of ODP Site 1000 (916 m) should have recorded the ε_{Nd} signature of AAIW, which is the deepest water mass present at this location [*Wüst*, 1964]. The average value of core top leachate samples in the region of ODP Site 1000 ($\varepsilon_{Nd} = -9.0$) is 1.7 ε_{Nd} units more radiogenic than the average foraminiferal composition ($\varepsilon_{Nd} = -10.7$). Additional samples were taken from the subsurface sediment close to Site 1000 at 18 to 20 cm and 30 to 32 cm below the sediment surface (Table S1a and Figure 2a). The average leachate value ($\varepsilon_{Nd} = -9.2$) for these subsurface samples is also more radiogenic than the average foraminiferal composition ($\varepsilon_{Nd} = -10$), although the difference between the two archives is smaller than at the surface. The detrital composition in the region of ODP Site 1000 is relatively unradiogenic (-9.8 ε_{Nd}), implying that a minor, radiogenic component, most likely of volcanic origin, was attacked during the leaching procedure, analogous to the findings of *Wilson et al*. [2013] for sediments from the western Indian Ocean. An alternative source of Nd may be preformed ferromanganese coatings acquired in local rivers, which would be expected to affect bulk leachate isotope compositions but not those of the foraminifera [*Kraft et al*., 2013]. One possible candidate is the Magdalena, which is the largest river draining directly into the Caribbean and delivers approximately 150 MT/yr of sediment to the basin [*Restrepo et al*., 2006]. This sediment is characterized by an ε_{Nd} of -8.3 [*Goldstein et al*., 1984]. However, the distance between the mouth of the Magdalena River and the region of Site 1000 is more than 900 km and further work to characterize the origin

©2014. American Geophysical Union. All Rights Reserved.

of detrital particles and the composition of other local rivers is necessary before firm conclusions can be drawn about the probable cause of offset between bulk leachate and foraminiferal ε_{Nd} signatures. There are no published seawater ε_{Nd} data for the Caribbean to date, but profiles in the western equatorial Atlantic [*Piepgras and Wasserburg*, 1987] and at Demerara Rise [*Huang et al*., 2014] show that the core of AAIW today has an ε_{Nd} signature between −11.2 and −10.1 prior to entering the Caribbean. A hydrogenetic ferromanganese crust layer from a water depth between 600 and 950 m water depth in the eastern Caribbean gave an ε_{Nd} value of −10.5 [*Frank et al*., 2006]. It is noted that these signatures are significantly less radiogenic than the composition of AAIW close to its source region in the Southern Ocean (ε_{Nd} between −8 and −9 ε_{Nd}) [*Rickli et al*., 2009; *Stichel et al*., 2012] due to mixing and dilution of AAIW with less radiogenic Atlantic water masses prior to entering the Caribbean basin. Near Site 1000, the average core top foraminiferal composition ($\varepsilon_{Nd} = -10.7$) not only falls within the range of AAIW compositions expected at Caribbean latitudes, it is also within error of the seawater ε_{Nd} signature at 1000 m at the Demerara Rise ($\varepsilon_{Nd} = -10.6$) [*Huang et al*., 2014] and we thus conclude that the foraminifera reliably recorded ambient seawater with an Atlantic ε_{Nd} signature.

The Caribbean Basin at deeper ODP Site 999 is today dominated by UNADW. The average value of bulk leachate ε_{Nd} for core top samples in the region of Site 999 ($\varepsilon_{Nd} = -7.3$) is 1.6 ε_{Nd} units more radiogenic than the average foraminiferal value ($\varepsilon_{Nd} = -8.9$). The detrital fraction is relatively unradiogenic ($\varepsilon_{Nd} = -9.5$), suggesting again that a minor, easily leachable component (such as volcanic ash) caused the radiogenic offset of the leachate data. Preformed ferromanganese coatings from the Magdalena River could not fully account for leachate ε_{Nd} values more radiogenic than −8.3 [*Goldstein et al*., 1984]. The composition of western tropical Atlantic seawater at depths comparable to the deepest sills connecting the Atlantic and the Caribbean (~1900 m) [*Johns et al*., 2002] is between −13.1 and −12.1 ε_{Nd} [*Piepgras and Wasserburg*, 1987; *Huang et al*., 2014]. Therefore, it is clear that the seawater signal as recorded by foraminifera at Site 999 ($\varepsilon_{Nd} = -8.9$) is at least 3 ε_{Nd} units more radiogenic than expected if Nd isotopes in the deep Caribbean were a strictly conservative Atlantic water mass tracer. We have no reason to expect that the foraminiferal isotope signal is offset from the bottom water ε_{Nd} signature, and the good agreement between foraminiferal and fish teeth ε_{Nd} signatures in the down core samples (next section) support this conclusion and the reliability of both archives.

One of the main factors contributing to the 3 ε_{Nd} unit shift compared to incoming Atlantic water is most likely the sluggish and discontinuous deep water replenishment in the Caribbean [*Parr*, 1937; *Dietrich*, 1939; *Wüst*, 1963, 1964; *Gordon*, 1967; *MacCready et al*., 1999; *Johns et al*., 2002]. This led to extreme and unrealistically radiogenic Nd isotope data for Caribbean deep waters in a recent modeling study [*Sepulchre et al*., 2014]. A location with an analogous setting is the Angola Basin, where there is a ~2 ε_{Nd} unit offset of the Nd isotope composition of the deep and intermediate waters compared to that expected for NADW [*Rickli et al*., 2009], which was attributed to the remineralization of particulate organic matter of the Congo River and boundary exchange with the sediments of the West African margin. For that location, it was further postulated that the weak density stratification at depth and the long residence time of the deep waters enabled diffusive mixing of the low ε_{Nd} signal from deep waters into the overlying intermediate and shallow waters [*Rickli et al*., 2009]. The Caribbean is even more limited by the maximum sill depth of ~1900 m for inflowing deep waters [*Johns et al*., 2002]. Furthermore, the water mass structure below 2000 m in the modern Caribbean is essentially homogenous [*Gordon*, 1967], and there is evidence for a deep cyclonic flow [*Joyce et al*., 2001]. Interaction with volcanic sediments in the southern and eastern parts of the Caribbean is thus expected to modify the Nd isotope composition of the incoming UNADW toward more radiogenic values. The combined effects of diffusion and cyclonic flow will homogenize the more radiogenic ε_{Nd} signature throughout the basin below 2000 m.

It is noted that the leachate $^{87}Sr/^{86}Sr$ compositions of all core top samples are very close to seawater [*McArthur et al*., 2001] and are markedly different from that of the detrital fraction in each region (Table S1b and Figure 2b, see also supporting information). The observation that core top leachate ε_{Nd} is most likely not a pure seawater signature corroborates the conclusion that the $^{87}Sr/^{86}Sr$ composition alone is not sufficient to determine the presence or absence of nonseawater contributions to leachate ε_{Nd} signatures [*Gutjahr et al*., 2007].

In summary, the offset toward more radiogenic ε_{Nd} signatures of core top bulk leachate samples indicates contributions from easily leachable or dissolvable detrital phases or contributions from preformed ferromanganese coatings. The downcore bulk leachate records that we produced for these sites are thus not used for paleoceanographic interpretations, despite the fact that they show very similar patterns in many cases,

©2014. American Geophysical Union. All Rights Reserved.

but are presented and compared with the foraminifera data in the supporting information (Figure S2). In contrast, fish teeth and foraminiferal ε_{Nd} values are considered reliable, and we will therefore base our interpretations only on these data.

3.2. Pliocene Pb Isotope Evolution of the Eastern Equatorial Pacific and the Caribbean

The Pliocene seawater Pb isotope signatures obtained from the bulk sediment leachates at Site 1241 are more radiogenic than the deep Pacific as recorded by ferromanganese crust GMAT 14D [*Frank et al*., 1999] (Table S3a and Figure 4). Variations in the seawater Pb composition at Site 1241 were small (between 18.79 and 18.88 for $^{206}Pb/^{204}Pb$, between 15.62 and 15.64 for $^{207}Pb/^{204}Pb$, and between 38.66 and 38.78 for $^{208}Pb/^{204}Pb$) but show an overall decrease from 4.17 to 2.45 Ma. The Pb isotope composition of the detrital fraction varied little during the Pliocene and shows somewhat higher $^{206}Pb/^{204}Pb$ (between 18.90 and 18.93) and $^{208}Pb/^{204}Pb$ (between 38.76 and 38.80) than seawater as well as $^{207}Pb/^{204}Pb$ ratios (between 15.63 and 15.64) similar to seawater.

Dissolved Pb has a residence time of less than 200 years in the Pacific [*Schaule and Patterson*, 1981] and is useful as a tracer of regional weathering inputs and water mass changes in the eastern equatorial Pacific. Given there is good agreement between the Nd isotope signatures of the leachates and those in fish teeth or foraminifera (Sites 1241 and 999), we conclude that the Pb isotope composition of the leachates also recorded bottom water signatures, which, however, was strongly controlled by regional weathering contributions. The short-term variability in the leachate Pb and Nd isotope signatures at Site 1241 is weakly correlated ($R^2 = 0.39$ for ε_{Nd} and $^{206}Pb/^{204}Pb$). Similarities between the evolutions of Pb isotopes and ε_{Nd} in ferromanganese crusts in the equatorial Pacific have previously been reported and have been attributed to terrigenous inputs and exchange with the South American continental margin [*Frank et al*., 1999]. There is also evidence for continuous supply of eolian material to the region of Site 1241 from South America throughout the late Neogene, transported by the Southeast trade winds [*Hovan*, 1995]. The similarity of the weak trends suggests that both the Pb and Nd isotope records of deep waters at Site 1241 were mainly controlled by regional weathering inputs. Comparison with the composition of rocks from the Pacific margins places Site 1241 seawater and detrital fraction Pb isotope compositions within the overlapping fields of the Andean Arc, the Galapagos, and the Central American Arc (Figure S4), consistent with the probable transport of eolian material from South America.

For the Caribbean we assume that the residence time of dissolved Pb is about 50 years, similar to that in the Atlantic [*Schaule and Patterson*, 1981; *von Blanckenburg and Igel*, 1999; *Frank*, 2002]. The Pb isotope composition of seawater at Site 999 should be sensitive to changes of regional weathering inputs into the Caribbean. Seawater $^{206}Pb/^{204}Pb$ (19.06 to 19.16), $^{207}Pb/^{204}Pb$ (15.70 to 15.71), and $^{208}Pb/^{204}Pb$ (39.04 to 39.10) ratios from Site 999 exhibited very little change between 5.23 and 2.57 Ma and were significantly more radiogenic than ferromanganese crusts from intermediate depths in the western Atlantic [*Reynolds et al*., 1999] (Table S3b and Figure 4). The Pb isotope composition of the detrital fraction was even more radiogenic than that of the leachates (between 19.28 and 19.45 for $^{206}Pb/^{204}Pb$, between 15.73 and 15.74 for $^{207}Pb/^{204}Pb$, and between 39.23 and 39.36 for $^{208}Pb/^{204}Pb$) but also does not display any significant trends. The detrital Pb isotope composition at Site 999 can be explained by a mixture of inputs from the Antilles and the Orinoco River, whereas the seawater Pb isotope composition was similar to the northwest Atlantic but also was constantly influenced by weathering contributions from the above sources (Figure S4). The combined seawater and detrital Pb isotope records thus document that there were no major changes in weathering inputs during the investigated period of time.

3.3. Pliocene Seawater Nd Isotope Evolution of the Eastern Equatorial Pacific

The range of seawater ε_{Nd} compositions at Site 1241 was remarkably small and essentially invariant during the Pliocene (−0.32 to 1.67) (Figure 3a). Fish teeth records from the same core showed a similar composition during the Miocene [*Newkirk and Martin*, 2009] (Figure 5). Although there is evidence for regional contributions to the seawater Pb and Nd budget in the eastern equatorial Pacific (section 3.2), it is unlikely that interaction with volcanogenic sediments in the CAS completely overprinted or masked any significant inflow from the Caribbean, given that the ε_{Nd} signature of Site 1241 remained constant even during times of most pronounced changes in ε_{Nd} recorded at Sites 998 and 999 between 12 and 10 Ma ago [*Newkirk and Martin*, 2009] (Figure 5). Any significant contribution from Caribbean waters, which were ~7 ε_{Nd} units more negative than Site 1241

©2014. American Geophysical Union. All Rights Reserved.

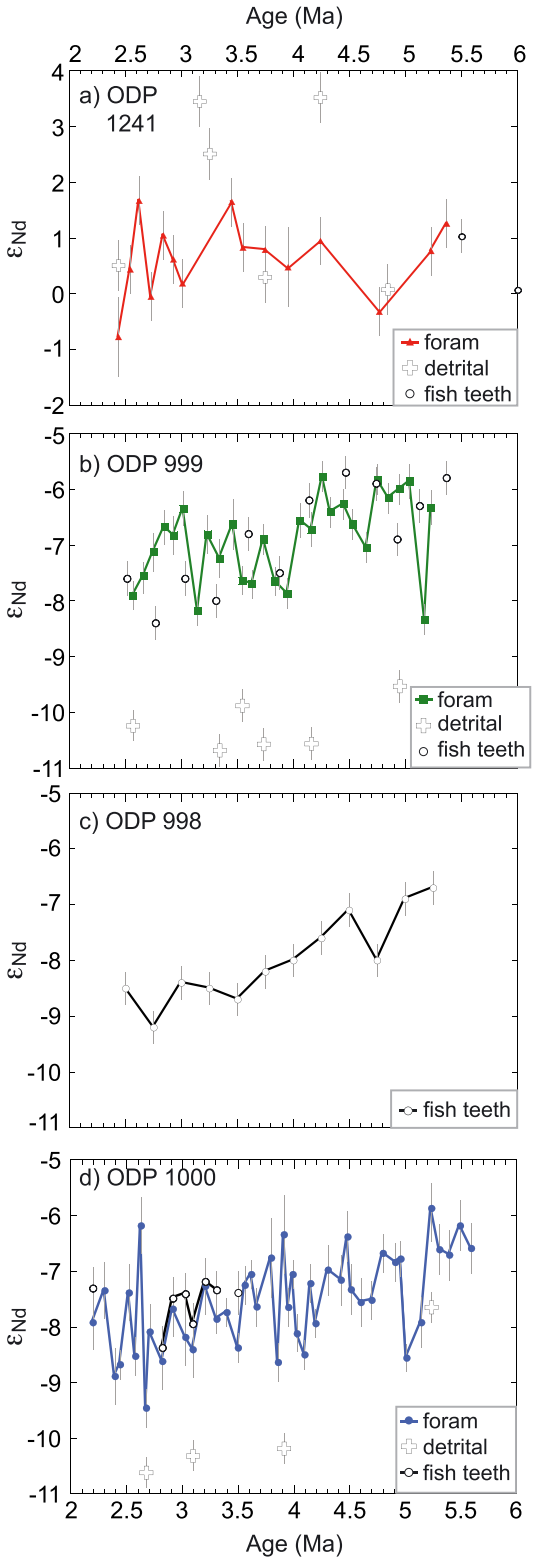

Figure 3. ε_{Nd} composition of uncleaned planktonic foraminifera (foram), detrital fraction, and fish teeth. Fish teeth data for ODP Site 1241 from *Newkirk and Martin* [2009]. Errors of 2σ are indicated by the gray bars.

from ~7 Ma onward [*Newkirk and Martin*, 2009] would most likely have perturbed the ε_{Nd} signature of the eastern equatorial Pacific to a measureable degree, even at 2000 m water depth, due to vertical transport processes such as observed by *Grasse et al.* [2012]. Taking into account the movement of Site 1241 away from the equator and the Galapagos hot spot since the Late Miocene as well as deepening of the site location by several hundred meters to the present depth of 2027 m [*Mix et al.*, 2003], we can confidently conclude that by the start of the Site 1241 record at 11.2 Ma the CAS had shoaled to at least ~1800 m and thus prevented advection of unradiogenic Caribbean/Atlantic seawater at the paleodepth levels of Site 1241. In fact, given that vertical transport processes to greater depths cannot be ruled out [*Grasse et al.*, 2012] and modeling simulations suggest that any significant westward transport of deep water from the Atlantic only occurred when a sill depth greater than 1000 m existed [*Nisancioglu et al.*, 2003; *Schneider and Schmittner*, 2006], the Site 1241 ε_{Nd} record [*Newkirk and Martin*, 2009; this work] would also be consistent with shoaling to at least 1000 m by 11.2 Ma, in agreement with diverging benthic foraminiferal assemblages in the Atrato basin from ~12 Ma onward [*Duque-Caro*, 1990].

3.4. Pliocene Evolution of the Deep and Intermediate Water Nd Isotope Composition of the Caribbean Basin

The seawater ε_{Nd} signature at Site 999 obtained from the foraminifera underwent relatively large short-term fluctuations ranging from −5.8 to −8.3 ε_{Nd} throughout the Pliocene. Overall, there was a trend toward less radiogenic compositions during that time reflected by average signatures that were 0.8 ε_{Nd} units less radiogenic after 4 Ma (Figures 3 and 5). The trend is also clearly seen in the fish teeth record. The least radiogenic foraminifera-derived seawater ε_{Nd} compositions of Site 999 (−8.3 at 5.18 Ma and −8.2 at 3.15 Ma) fall within the range of the deep Caribbean core top compositions (−8.10 to −9.27). The fish teeth record of Site 998, which ranges from −6.7 to −9.2 ε_{Nd}, also shows a trend toward less radiogenic values during the Pliocene, but is consistently 0.5 to 2 ε_{Nd} units less radiogenic than that of Site 999. The intermediate depth ε_{Nd} signature at Site 1000 generally falls between the two deep Caribbean sites, again with relatively large fluctuations (between −5.9 and −9.5 ε_{Nd}) within a general trend toward less radiogenic Nd isotope signatures. Past seawater ε_{Nd} at Site 1000

©2014. American Geophysical Union. All Rights Reserved.

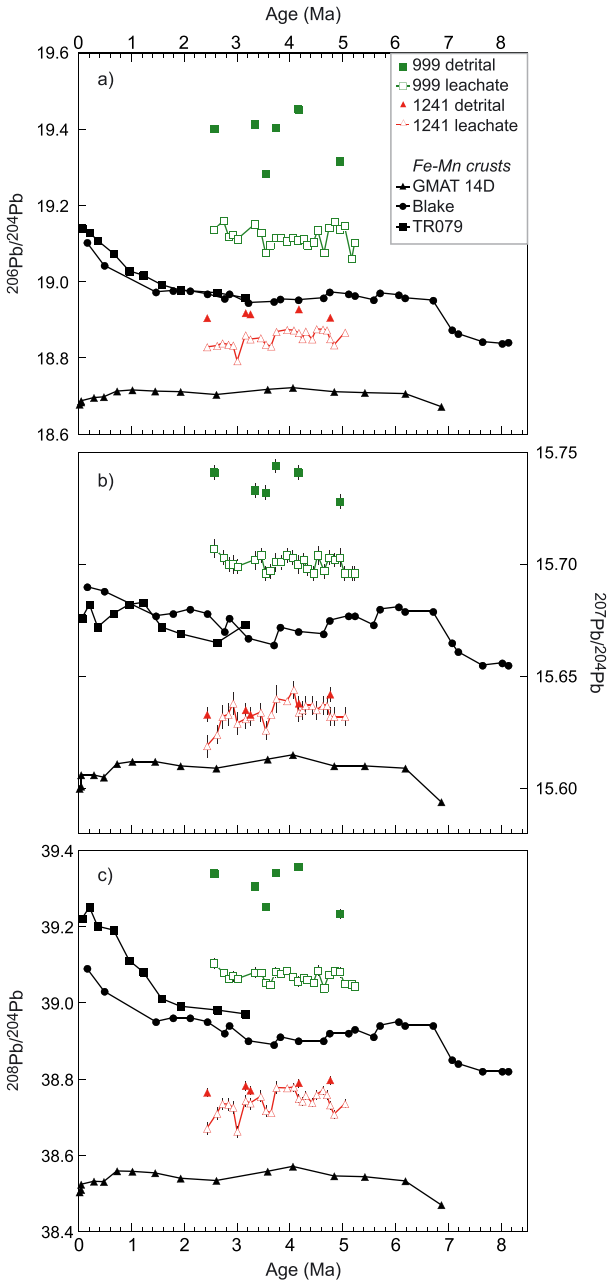

Figure 4. (a) $^{206}Pb/^{204}Pb$, (b) $^{207}Pb/^{204}Pb$, and (c) $^{208}Pb/^{204}Pb$ values for Sites 999 and 1241. Errors of 2σ are indicated by the gray bars but in many cases are smaller than symbol size. Also shown are Fe-Mn crust data from GMAT 14D [*Frank et al.*, 1999], Blake [*Reynolds et al.*, 1999], and TR079 [*Reynolds et al.*, 1999]. Symbols are the same for all plots.

approached, but did not reach, the range of the unradiogenic intermediate depth core top compositions (−9.7 to −12.4 ε_{Nd}).

The Miocene-Pliocene record (Figure 5) shows that the majority of the change in deep Caribbean ε_{Nd} away from Pacific-like compositions had already taken place prior to about 7 Ma [*Newkirk and Martin*, 2009] but that the trend toward less radiogenic ε_{Nd} signatures continued throughout the Pliocene. Leachate and detrital Pb isotope compositions (Figure 4) do not indicate that any significant change in weathering inputs during the Pliocene contributed to a change in the deep Caribbean seawater ε_{Nd} signal. The key question is therefore whether the ε_{Nd} records reflect the continued but decreasing influence of Pacific waters entering through the closing CAS, changes in ocean circulation within the Atlantic basin, or variations in the intensity of exchange with the boundary sediments of the Caribbean.

3.4.1. Northern Versus Southern Sources of Deep and Intermediate Waters

Haug and Tiedemann [1998] argued that a continuous increase in the percentage of sand in the total carbonate of Site 999 after 4.6 Ma was caused by a decrease of the advection of corrosive AAIW into the Caribbean and that this resulted from increased UNADW production in the North Atlantic. They did not consider Pacific waters contributing directly to the deep Caribbean. In order to test this hypothesis based on our Caribbean seawater ε_{Nd} records, we need to consider the Nd isotopic composition of AAIW and UNADW during the Pliocene and whether changes in the proportions of these water masses may have produced the measured ε_{Nd}, without the need for admixture of radiogenic ε_{Nd} from the Pacific. In the modern Atlantic Ocean adjacent to the Caribbean, the salinity and potential temperature of waters at 1800 m is consistent with a mixture of 85% UNADW, 10% AAIW, and 5% Mediterranean Outflow Water (MOW) [*Kawase and Sarmiento*, 1986; *de Menocal et al.*, 1992]. Taking the end-member ε_{Nd} values of each of these water masses in their source regions (Table 1), the ε_{Nd} at this water depth is expected to be ~ −12.8, a value which is in good agreement with nearby seawater ε_{Nd} profiles [*Piepgras and Wasserburg*, 1987; *Huang et al.*, 2014].

The ε_{Nd} signature of NADW recorded by ferromanganese crusts in the deep NW Atlantic showed values near −11 prior to 4 Ma and became gradually less radiogenic toward the end of the Pliocene (~ −12) [*Burton et al.*, 1999]. To date there is no published ε_{Nd} record of Pliocene AAIW upstream of the Caribbean in the Atlantic. Available Pliocene ferromanganese crust data from the tropical Atlantic and the Southern Ocean do

©2014. American Geophysical Union. All Rights Reserved.

Table 1. End-Member ε_{Nd} Compositions

	Modern	Pliocene
PIW	0 to −3[a]	0 to −1.5[b]
AAIW	−8 to −9[c]	unknown
NADW	−13.5[d]	−11.5 to −12[e]
MOW	−9.4[f]	−8.2 to −8.9[g, h]

[a] *Piepgras and Wasserburg* [1982] and *Piepgras and Jacobsen* [1988].
[b] This study.
[c] *Rickli et al.* [2009] and *Stichel et al.* [2012].
[d] *Piepgras and Wasserburg* [1987].
[e] *Burton et al.* [1999].
[f] *Tachikawa et al.* [2004].
[g] *Ivanovic et al.* [2013].
[h] Late Miocene value.

unfortunately not reflect intermediate waters and crust TR079 from the Antilles slope at a water depth of 2000 m most likely recorded a mixed signature of northern and southern component waters [*Reynolds et al.*, 1999]. For the following calculations, we will use the composition of modern AAIW ε_{Nd} close to its source area in the Southern Ocean (−8 and −9) [*Rickli et al.*, 2009; *Stichel et al.*, 2012] but will discuss how changes of this end-member composition could have affected the Caribbean seawater composition. The composition of MOW at the end of the Miocene was −8.2 to −8.9 ε_{Nd} [*Ivanovic et al.*, 2013], consistent with a ferromanganese crust record from about 700 m depth in the eastern Atlantic close to Gibraltar [*Muiños et al.*, 2008] and thus was at the most 1.2 ε_{Nd} units more radiogenic than it is today (−9.4) [*Tachikawa et al.*, 2004]. It is not possible to distinguish between MOW and AAIW based on ε_{Nd} alone given that a decrease of the intermediate depth Caribbean ε_{Nd} signature may represent a decrease in the admixture of either or both of these water masses. However, it is noted that there were significant differences in the geometry of the Mediterranean-Atlantic connection in the late Miocene and early Pliocene compared to today [e.g., *Hsu et al.*, 1977; *Ivanovic et al.*, 2013] and it is therefore very difficult to estimate the proportion of MOW that would have reached the Caribbean. Given that, similar to today, the fraction of MOW was very small, we assume the MOW contribution to have been constant during the Pliocene [*Muiños et al.*, 2008].

Our core top record near Site 999 shows that the deep Caribbean ε_{Nd} today is about 3 ε_{Nd} units more radiogenic than the incoming Atlantic seawater due to exchange with the Caribbean boundary sediments. We assume that there was also an offset of 3 ε_{Nd} units during the Pliocene and a potential change in this offset will be considered separately. If the deep Caribbean was 100% UNADW, we would consequently expect a composition of ~ −8 ε_{Nd} at the start of the Pliocene, decreasing to ~ −9 at the end of the Pliocene (3 ε_{Nd} units more radiogenic than −11 to −12 as recorded by ferromanganese crusts that grew within UNADW in the deep NW Atlantic [*Burton et al.*, 1999]). Similarly, if the deep Caribbean was 100% AAIW, we would expect a composition of between −5 and −6 ε_{Nd} (3 ε_{Nd} units more radiogenic than −8 to −9 [*Rickli et al.*, 2009; *Stichel et al.*, 2012]). Clearly, our deep Caribbean seawater ε_{Nd} records from Sites 999 and 998 are within this range of −5 to −9 ε_{Nd} for the entire Pliocene, and the overall trend toward less radiogenic ε_{Nd} is consistent with an increase in the admixture of UNADW, most likely at the expense of AAIW [*Haug and Tiedemann*, 1998].

In contrast to deep Site 999, based on the core top results (section 3.1), we would not expect the foraminifera ε_{Nd} record at shallow Site 1000 to be offset from Atlantic values at the same depth. The most radiogenic compositions (up to −5.9 ε_{Nd}) are more radiogenic than modern AAIW [*Rickli et al.*, 2009; *Stichel et al.*, 2012]. The composition of AAIW in its source region in the Southern Ocean is a mixture of Pacific and North Atlantic inputs and has been shown to be significantly more radiogenic (−6.4 ± 0.4 ε_{Nd}) during Heinrich event 1, when the strength of AMOC was likely much reduced [*Robinson and van de Flierdt*, 2009]. Based on the Site 1000 record alone, it is not possible to determine whether there was a direct input of Pacific water into the intermediate Caribbean via an open CAS or whether the ε_{Nd} composition reflects a more radiogenic AAIW composition. However, similarities in the trend (Figure 5) in both the intermediate and deep Caribbean ε_{Nd} records support a common mechanism, which is most likely an increase in the proportion of UNADW relative to AAIW given that the deep Caribbean already exhibited a major departure from Pacific compositions by 7 Ma [*Newkirk and Martin*, 2009],

If AAIW was indeed more radiogenic in the Pliocene than it is today, then the amount of AAIW relative to UNADW would be proportionally lower for a given deep Caribbean ε_{Nd}. If AAIW was less radiogenic than −10 ε_{Nd}, then the majority of the record prior to 4 Ma cannot be explained by changes in the relative proportions of AAIW and UNADW alone. Until the composition of AAIW during the Pliocene can be reconstructed, this will remain an open question. However, based on the similarity of Late Eocene and modern intermediate water ε_{Nd} compositions in the Atlantic sector of the Southern Ocean [*Scher and Martin*, 2004;

©2014. American Geophysical Union. All Rights Reserved.

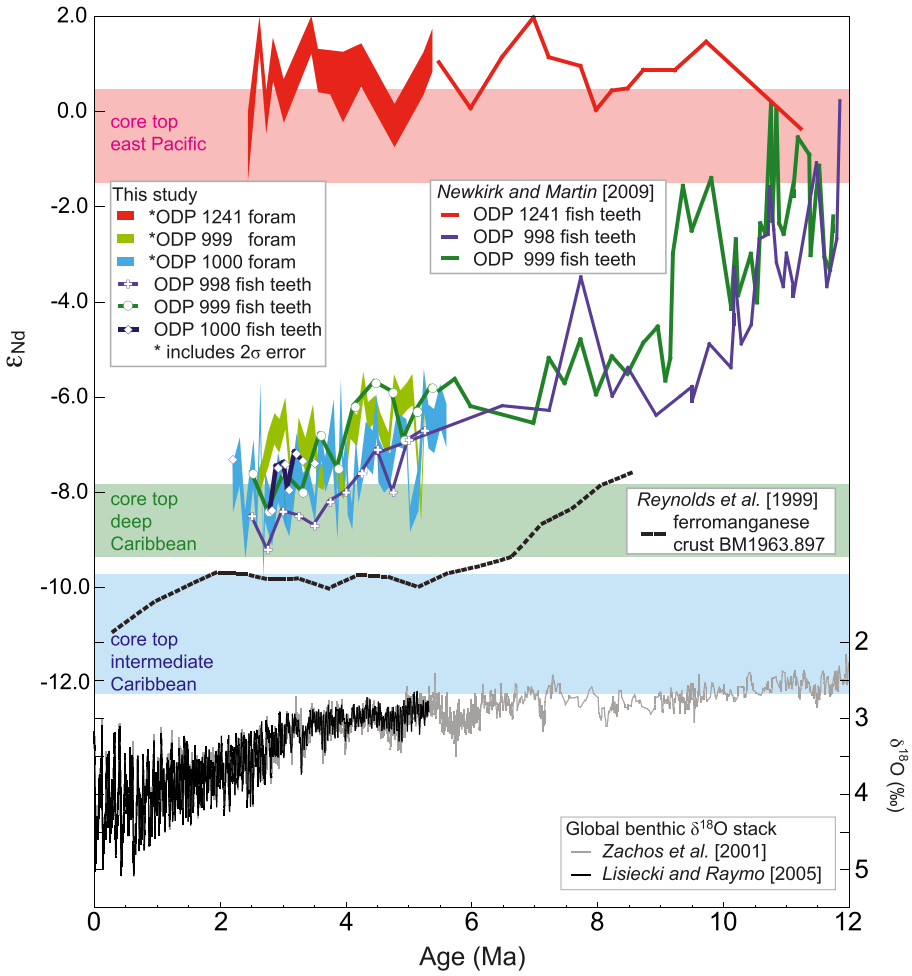

Figure 5. Compilation of ε_{Nd} data for ODP Sites 1241, 998, 999, and 1000 from this study and *Newkirk and Martin* [2009]. Colored horizontal bars indicate the core top foraminifera ε_{Nd} results. Also shown is the ε_{Nd} of ferromanganese crust BM1963.897, taken from ~850 m water depth on the Blake Plateau [*Reynolds et al.*, 1999] and the global benthic $\delta^{18}O$ stack of *Zachos et al.* [2001] and *Lisiecki and Raymo* [2005].

Rickli et al., 2009; *Stichel et al.*, 2012] we argue that it is unlikely that the ε_{Nd} signature of AAIW was significantly less radiogenic than −9 at its source and that there is consequently no need to invoke any volumetrically important admixture of Pacific water to the deep Caribbean.

3.4.2. Residence Time of Nd and Exchange With the Margin Sediments

A change in the offset between incoming Atlantic seawater ε_{Nd} and the composition of seawater in the deep Caribbean is another potential factor contributing to the Pliocene ε_{Nd} trend. Despite the relatively long residence time of waters in the deep Caribbean (~150 years below 1800 m) [*Joyce et al.*, 2001], the present-day deep water Nd isotope composition obtained from the core top foraminifera (Figure 2a) is much less radiogenic than that of the surrounding margins [e.g., *Jeandel et al.*, 2007; *Sepulchre et al.*, 2014]. If the magnitude of the offset has been linked to the length of time that a unit of water was in contact with the margins, then an increase in the rate of deep water renewal may be expected to shift deep Caribbean compositions toward less radiogenic, more Atlantic-like ε_{Nd} signatures.

With the exception of the apparent 2 ε_{Nd} unit step to less radiogenic signatures at 4 Ma in the lower resolution Site 999 fish teeth record, our Caribbean ε_{Nd} records (Figure 5) show no major step change, but rather a general, continuous trend toward less radiogenic ε_{Nd} throughout the Pliocene. This pattern is consistent with a gradual increase in the strength of AMOC [*Haug and Tiedemann*, 1998; *Steph et al.*, 2010], which would be expected to both increase the proportion of UNADW relative to AAIW and to decrease the residence time of deep water in the Caribbean.

©2014. American Geophysical Union. All Rights Reserved.

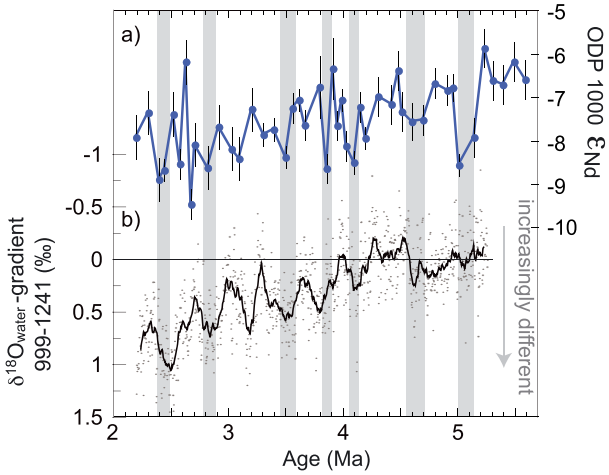

Figure 6. (a) Uncleaned planktonic foraminifera ε_{Nd} for Site 1000. (b) Difference in salinity between the Caribbean and the eastern equatorial Pacific, line is the 25 point running average [*Groeneveld*, 2005]. Gray bars indicate episodes of less radiogenic ε_{Nd} in the Site 1000 record that correspond to maxima in the salinity difference record.

3.4.3. Short-Term Nd Isotope Variability of Caribbean Intermediate and Deep Waters

Finally, the Pliocene Caribbean ε_{Nd} records also show variability on shorter timescales (Figure 4). Planktonic $\delta^{18}O$ records [*Haug et al.*, 2001] and sea surface salinity reconstructions [*Groeneveld*, 2005; *Groeneveld et al.*, 2006, 2008; *Steph et al.*, 2006] indicate that the CAS had shoaled to ~ 100 m by ~ 4.2 Ma. The intermediate water ε_{Nd} record from uncleaned planktonic foraminifera for Site 1000 is plotted together with the ice volume-corrected $\delta^{18}O$ gradient between the Caribbean (Site 999) and the EEP (Site 1241) (Figure 6) [*Groeneveld*, 2005]. A difference of 1‰ between Sites 999 and 1241 developed during the Pliocene, interrupted by episodes of reduced $\delta^{18}O$ gradients, which have been attributed to reconnection across the CAS either as a result of local tectonics/volcanics or of ice volume-related changes in sea level [*Sarnthein et al.*, 2009; *De Schepper et al.*, 2013]. Ocean circulation models consistently show an intensification of the AMOC with a closed CAS (see *Zhang et al.* [2012] for a multimodel comparison). A closed CAS prevented relatively fresh Pacific surface and subsurface waters from reaching the North Atlantic and consequently promoted NADW formation and enhancement of the AMOC [*Schneider and Schmittner*, 2006]. Although our seawater ε_{Nd} record of Site 1000 has a much lower time resolution than the $\delta^{18}O$ records of *Groeneveld* [2005], larger $\delta^{18}O$ gradients and thus closed CAS conditions were generally associated with less radiogenic ε_{Nd} signatures, in particular during the early and mid-Pliocene (Figure 6). A higher-resolution Nd isotope record would be required to test whether this relationship is robust. Nevertheless, our ε_{Nd} record presented here supports the idea of a close link between periodic CAS closure and enhanced NADW formation and advection into the Caribbean. In contrast, during periods of a periodically open shallow CAS the intermediate water ε_{Nd} signatures became more radiogenic, consistent with a decrease in the amount of UNADW relative to AAIW.

4. Conclusions

The deep water ε_{Nd} signature recorded by Site 1241 was highly radiogenic and essentially invariable during the late Miocene and Pliocene (this work and *Newkirk and Martin* [2009]). This is consistent with little or no advection of Atlantic waters into the deep eastern equatorial Pacific over this entire period of time in agreement with model predictions [*Maier-Reimer et al.*, 1990; *Mikolajewicz et al.*, 1993; *Schneider and Schmittner*, 2006; *Zhang et al.*, 2012], suggesting that the CAS had shoaled to at least 1800 m, and most likely to 1000 m by 11.2 Ma.

Intermediate and deep Caribbean seawater Nd isotope values generally became less radiogenic during the Pliocene, which was not a consequence of changes in weathering inputs as evidenced by unchanged seawater and detrital Pb isotope compositions of the same samples. If boundary exchange processes were operating similarly to today and created an ~3 ε_{Nd} offset between inflowing waters and Caribbean waters, the decreasing trend in the Caribbean ε_{Nd} data during most of the Pliocene is best explained by a relative increase in UNADW and decrease in AAIW inflow, in agreement with previous studies [*Haug and Tiedemann*, 1998]. If boundary exchange processes are related to the residence time of deep waters in the Caribbean, then the trend is also consistent with an increased rate of deep water renewal. Short-term variability in the early to mid-Pliocene ε_{Nd} record appears to have covaried with the salinity difference between the Caribbean and the EEP surface waters [*Groeneveld*, 2005], whereby less radiogenic ε_{Nd} signatures are consistent with enhanced Atlantic inflow linked to a strengthened AMOC during periods of complete CAS closure.

©2014. American Geophysical Union. All Rights Reserved.

Overall, the observed Pliocene changes in Caribbean circulation related to the final closure of the CAS were smaller than during the Miocene between 12 and 7 Ma ago [*Newkirk and Martin*, 2009], when the CAS closed for major deep water exchange.

Acknowledgments
The data for this paper are available in the supporting information Tables S1–S4. This work was funded through an Alexander von Humboldt Fellowship (AO) and German Science Foundation (DFG) project FR1198/8-1 (MF) as well as National Science Foundation (NSF) grant OCE-0451170 (EEM). Sample material used in the project was provided by ODP, the Lamont-Doherty Core Repository of the Lamont-Doherty Earth Observatory, the University of Rhode Island and GEOMAR. Funding for the curation of marine geological samples at URI came from NSF grant OCE-644625. We thank two anonymous reviewers for their constructive comments and Heiko Paelike for editorial handling.

References

Abouchami, W., S. J. G. Galer, and A. Koschinsky (1999), Pb and Nd isotopes in NE Atlantic Fe-Mn crusts: Proxies for trace metal paleosources and paleocean circulation, *Geochim. Cosmochim. Acta*, *63*(10), 1489–1505.

Albarede, F., P. Telouk, J. Blichert-Toft, M. Boyet, A. Agranier, and B. Nelson (2004), Precise and accurate isotopic measurements using multiple-collector ICPMS, *Geochim. Cosmochim. Acta*, *68*(12), 2725–2744.

Arsouze, T., J. C. Dutay, F. Lacan, and C. Jeandel (2009), Reconstructing the Nd oceanic cycle using a coupled dynamical-biogeochemical model, *Biogeosciences*, *6*(12), 2829–2846.

Basak, C., E. E. Martin, and G. D. Kamenov (2011), Seawater Pb isotopes extracted from Cenozoic marine sediments, *Chem. Geol.*, *286*, 94–108.

Berger, W. H., and G. Wefer (1996), Expeditions into the past: Paleoceanographic studies in the South Atlantic, in *The South Atlantic: Present and Past Circulation*, edited by G. Wefer et al., pp. 363–410, Springer-Verlag, Berlin Heidelberg.

Berggren, W. A., and C. D. Hollister (1974), Paleogeography, paleobiology, and the history of circulation of the Atlantic Ocean, in *Studies in Paleoceanography*, *Soc. Econ. Paleont. Mineral. Spec. Publ.*, vol. 20, edited by W. W. Hay, pp. 126–186, SEPM, Tulsa, Okla.

Bickert, T., G. H. Haug, and R. Tiedemann (2004), Late Neogene benthic stable isotope record of Ocean Drilling Program Site 999: Implications for Caribbean paleoceanography, organic carbon burial, and the Messinian Salinity Crisis, *Paleoceanography*, *19*, PA1023, doi:10.1029/2002PA000799.

Broecker, W. S., and T. H. Peng (1982), *Tracers in the Sea*, 690 pp., Eldigio Press, Palisades, N. Y.

Burton, K. W., H. F. Ling, and R. K. O'Nions (1997), Closure of the Central American Isthmus and its effect on deep-water formation in the North Atlantic, *Nature*, *386*(6623), 382–385.

Burton, K. W., D. C. Lee, J. N. Christensen, A. N. Halliday, and J. R. Hein (1999), Actual timing of neodymium isotopic variations recorded by Fe-Mn crusts in the western North Atlantic, *Earth Planet. Sci. Lett.*, *171*(1), 149–156.

de Menocal, P. B., D. W. Oppo, R. G. Fairbanks, and W. L. Prell (1992), Pleistocene $\delta^{13}C$ variability of North Atlantic intermediate water, *Paleoceanography*, *7*(2), 229–250, doi:10.1029/92PA00420.

De Schepper, S., J. Groeneveld, B. D. A. Naafs, C. Van Renterghem, J. Hennissen, M. J. Head, S. Louwye, and K. Fabian (2013), Northern Hemisphere glaciation during the globally warm early late Pliocene, *PLoS One*, doi:10.1371/journal.pone.0081508.

Dietrich, G. (1939), Das Amerikanische Mittelmeer, *Z. Gesellsch. Erdkunde*, *3–4*, 108–130.

Driscoll, N. W., and G. H. Haug (1998), A short circuit in thermohaline circulation: A cause for Northern Hemisphere glaciation?, *Science*, *282*(5388), 436–438.

Duque-Caro, H. (1990), Neogene stratigraphy, paleoceanography and paleobiogeography in northwest South America and the evolution of the Panama seaway, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *77*(3–4), 203–234.

Elmore, A. C., A. M. Piotrowski, J. D. Wright, and A. E. Scrivner (2011), Testing the extraction of past seawater Nd isotopic composition from North Atlantic marine sediments, *Geochem., Geophys., Geosyst.*, *12*, Q09008, doi:10.1029/2011GC003741.

Frank, M. (2002), Radiogenic isotopes: Tracers of past ocean circulation and erosional input, *Rev. Geophys.*, *40*(1), 1001 doi:10.1029/2000RG000094.

Frank, M., B. C. Reynolds, and R. K. O'Nions (1999), Nd and Pb isotopes in Atlantic and Pacific water masses before and after closure of the Panama gateway, *Geology*, *27*(12), 1147–1150.

Frank, M., H. Marbler, A. Koschinsky, T. van de Flierdt, V. Klemm, M. Gutjahr, A. N. Halliday, P. W. Kubik, and P. Halbach (2006), Submarine hydrothermal venting related to volcanism in the Lesser Antilles: Evidence from ferromanganese precipitates, *Geochem. Geophys. Geosyst.*, *7*, Q04010, doi:10.1029/2005GC001140.

Goldstein, S. L., R. K. O'Nions, and P. J. Hamilton (1984), A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems, *Earth Planet. Sci. Lett.*, *70*, 221–236.

Gordon, A. L. (1967), Circulation of the Caribbean Sea, *J. Geophys. Res.*, *72*(24), 6207–6223, doi:10.1029/JZ6072i6024p06207.

Gourlan, A. T., L. Meynadier, and C. J. Allegre (2008), Tectonically driven changes in the Indian Ocean circulation over the last 25 Ma: Neodymium isotope evidence, *Earth Planet. Sci. Lett.*, *267*(1–2), 353–364.

Grasse, P., T. Stichel, R. Stumpf, L. Stramma, and M. Frank (2012), The distribution of neodymium isotopes and concentrations in the Eastern Equatorial Pacific: Water mass advection versus particle exchange, *Earth Planet. Sci. Lett.*, *353*, 198–207.

Groeneveld, J. (2005), Effect of the Pliocene closure of the Panamanian gateway on Caribbean and east Pacific sea surface temperatures and salinities by applying combined Mg/Ca and $d^{18}O$ measurements (5.6–2.2 Ma), PhD thesis, Faculty of Mathematics and Natural Sciences, Christian Albrechts University, Kiel, Germany.

Groeneveld, J., S. Steph, R. Tiedemann, D. Garbe-Schoenberg, D. Nürnberg, and A. Sturm (2006), Pliocene mixed layer oceanography for Site 1241, using combined Mg/Ca and $d^{18}O$ analyses of *Globigerinoides sacculifer*, *Proc. ODP, Scientific Results*, *202*, 1–27.

Groeneveld, J., D. Nürnberg, R. Tiedemann, G. J. Reichart, S. Steph, L. Reuning, D. Crudeli, and P. Mason (2008), Foraminiferal Mg/Ca increase in the Caribbean during the Pliocene: Western Atlantic Warm Pool formation, salinity influence, or diagenetic overprint?, *Geochem. Geophys. Geosyst.*, *9*, Q01P23, doi:10.1029/2006GC001564.

Gutjahr, M., M. Frank, C. H. Stirling, V. Klemm, T. van de Flierdt, and A. N. Halliday (2007), Reliable extraction of a deepwater trace metal isotope signal from Fe-Mn oxyhydroxide coatings of marine sediments, *Chem. Geol.*, *242*(3–4), 351–370.

Gutjahr, M., M. Frank, C. H. Stirling, L. D. Keigwin, and A. N. Halliday (2008), Tracing the Nd isotope evolution of North Atlantic deep and intermediate waters in the Western North Atlantic since the Last Glacial Maximum from Blake Ridge sediments, *Earth Planet. Sci. Lett.*, *266*(1–2), 61–77.

Gutjahr, M., M. Frank, A. N. Halliday, and L. D. Keigwin (2009), Retreat of the Laurentide ice sheet tracked by the isotopic composition of Pb in western North Atlantic seawater during termination 1, *Earth Planet. Sci. Lett.*, *286*(3–4), 546–555.

Haug, G. H., and R. Tiedemann (1998), Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation, *Nature*, *393*(6686), 673–676.

Haug, G. H., R. Tiedemann, R. Zahn, and A. C. Ravelo (2001), Role of Panama uplift on oceanic freshwater balance, *Geology*, *29*(3), 207–210.

Hovan, S. A. (1995), Late Cenozoic atmospheric circulation intensity and climatic history recorded by eolian deposition in the eastern equatorial Pacific ocean, Leg 138, *Proc. ODP, Scientific Results*, *138*, 615–625.

Hsu, K. J., L. Montardert, D. Bernoulli, M. B. Cita, A. Erickson, R. E. Garrison, R. B. Kidd, F. Mèlierés, C. Müller, and R. Wright (1977), History of the Mediterranean salinity crisis, *Nature*, *267*, 399–403.

Huang, K.-F., D. W. Oppo, and W. B. Curry (2014), Decreasing influence of Antarctic intermediate water in the tropical Atlantic during North Atlantic cold events, *Earth Planet. Sci. Lett.*, *389*, 200–208.

©2014. American Geophysical Union. All Rights Reserved.

Ivanovic, R. F., R. Flecker, M. Gutjahr, and P. J. Valdes (2013), First Nd isotope record of Mediterranean-Atlantic water exchange through the Moroccan Rifian Corridor during the Messinian Salinity Crisis, *Earth Planet. Sci. Lett.*, *368*, 163–174.
Jacobsen, S. B., and G. J. Wasserburg (1980), Sm-Nd evolution of chondrites, *Earth Planet. Sci. Lett.*, *50*, 139–155.
Jeandel, C., T. Arsouze, F. Lacan, P. Techine, and J. C. Dutay (2007), Isotopic Nd compositions and concentrations of the lithogenic inputs into the ocean: A compilation, with an emphasis on the margins, *Chem. Geol.*, *239*, 156–164.
Johns, W. E., T. L. Townsend, D. M. Fratantoni, and W. D. Wilson (2002), On the Atlantic inflow to the Caribbean Sea, *Deep-Sea Res. Part I-Oceanogr. Res. Pap.*, *49*(2), 211–243.
Joyce, T. M., A. Hernandez-Guerra, and W. M. Smethie (2001), Zonal circulation in the NW Atlantic and Caribbean from a meridional World Ocean Circulation Experiment hydrographic section at 66°W, *J. Geophys. Res.*, *106*(C10), 22,095–22,113, doi:10.1029/2000JC000268.
Kamenov, G., M. Perfit, P. A. Mueller, and I. R. Jonasson (2008), Controls on magmatism in an island arc environment: Study of lavas and sub-arc xenoliths from the Tabar-Lihir-Tanga-Feni island chain, Papua New Guinea, *Contrib. Mineral. Petrol.*, *155*, 635–656, doi:10.1007/s00410-007-0262-0.
Kameo, K., and T. J. Bralower (2000), Neogene calcareous nannofossil biostratigraphy of sites 998, 999 and 1000, Caribbean Sea, *Proc. ODP, Scientific Results*, *165*, 3–17.
Kawase, M., and J. L. Sarmiento (1986), Circulation and nutrients in middepth Atlantic waters, *J. Geophys. Res.*, *91*(C8), 9749–9770, doi:10.1029/JC091iC08p09749.
Keigwin, L. (1982), Isotopic paleoceanography of the Caribbean and East Pacific: Role of Panama uplift in late neogene time, *Science*, *217*, 350–353.
Keller, G., C. E. Zenker, and S. M. Stone (1989), Late Neogene history of the Pacific-Caribbean gateway, *J. South Am. Earth Sci.*, *2*, 73–108.
Kirby, M. X., D. S. Jones, and B. J. MacFadden (2008), Lower Miocene stratigraphy along the Panama Canal and its bearing on the Central American Peninsula, *PLoS One*, *3*(7), e2791, doi:10.1371/journal.pone.0002791.
Kraft, S., M. Frank, E. C. Hathorne, and S. Weldeab (2013), Assessment of seawater Nd isotope signatures extracted from foraminiferal shells and authigenic phases of Gulf of Guinea sediments, *Geochim. Cosmochim. Acta*, *121*, 414–435.
Ling, H. F., K. W. Burton, R. K. O'Nions, B. S. Kamber, F. von Blanckenburg, A. J. Gibb, and J. R. Hein (1997), Evolution of Nd and Pb isotopes in Central Pacific seawater from ferromanganese crusts, *Earth Planet. Sci. Lett.*, *146*, 1–12.
Ling, H. F., S. Y. Jiang, M. Frank, H. Y. Zhou, F. Zhou, Z. L. Lu, X. M. Chen, Y. H. Jiang, and C. D. Ge (2005), Differing controls over the Cenozoic Pb and Nd isotope evolution of deepwater in the central North Pacific Ocean, *Earth Planet. Sci. Lett.*, *232*, 345–361.
Lisiecki, L. E., and M. E. Raymo (2005), A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records, *Paleoceanography*, *20*, PA1003, doi:10.1029/2004PA001071.
Lunt, D. J., P. J. Valdes, A. Haywood, and I. C. Rutt (2008), Closure of the Panama Seaway during the Pliocene: Implications for climate and Northern Hemisphere glaciation, *Clim. Dyn.*, *30*(1), 1–18.
MacCready, P., W. E. Johns, C. G. Rooth, D. M. Fratantoni, and R. A. Watlington (1999), Overflow into the deep Caribbean: Effects of plume variability, *J. Geophys. Res.*, *104*(C11), 25,913–25,935, doi:10.1029/21999JC900206.
Maier-Reimer, E., U. Mikolajewicz, and T. Crowley (1990), Ocean General Circulation Model Sensitivity Experiment with an open Central American Isthmus, *Paleoceanography*, *5*(3), 349–366, doi:10.1029/PA005i003p00349.
Martin, E. E., and H. D. Scher (2004), Preservation of seawater Sr and Nd isotopes in fossil fish teeth: Bad news and good news, *Earth Planet. Sci. Lett.*, *220*, 25–39.
Martin, E. E., S. W. Blair, G. D. Kamenov, H. D. Scher, E. Bourbon, C. Basak, and D. N. Newkirk (2010), Extraction of Nd isotopes from bulk deep sea sediments for paleoceanographic studies on Cenozoic time scales, *Chem. Geol.*, *269*, 414–431.
McArthur, J. M., R. J. Howarth, and T. R. Bailey (2001), Strontium Isotope Stratigraphy: LOWESS Version 3—Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age, *J. Geol.*, *109*, 155–170.
Mikolajewicz, U., and T. J. Crowley (1997), Response of a coupled ocean/energy balance model to restricted flow through the central American isthmus, *Paleoceanography*, *12*(3), 429–441, doi:10.1029/1096PA03542.
Mikolajewicz, U., E. Maier-Reimer, T. J. Crowley, and K. Y. Kim (1993), Effect of Drake and Panamanian Gateways on the circulation of an ocean model, *Paleoceanography*, *8*(4), 409–426, doi:10.1029/1093PA00893.
Mix, A. C., R. Tiedemann, P. Blum, and L. S. Party (2003), Site 1241, proceeding of the ocean drilling program, initial reports, *202*.
Molnar, P. (2008), Closing of the Central American Seaway and the ice age: A critical review, *Paleoceanography*, *23*, PA2201, doi:10.1029/2007PA001574.
Montes, C., et al. (2012a), Evidence for middle Eocene and younger land emergence in central Panama: Implications for Isthmus closure, *Geol. Soc. Am. Bull.*, *124*, 780–799.
Montes, C., G. Bayona, A. Cardona, D. M. Buchs, C. A. Silva, S. Morón, N. Hoyos, D. A. Ramírez, C. A. Jaramillo, and V. Valencia (2012b), Arc-continent collision and orocline formation: Closing of the Central American seaway, *J. Geophys. Res.*, *117*, B04105, doi:10.1029/2011JB008959.
Muiños, S. B., M. Frank, C. Maden, J. R. Hein, T. van de Flierdt, S. M. Lebreiro, L. Gaspar, J. H. Monteiro, and A. N. Halliday (2008), New constraints on the Pb and Nd isotopic evolution of NE Atlantic water masses, *Geochem., Geophys. Geosyst.*, *9*, Q02007, doi:10.1029/2007GC001766.
Newkirk, D. R., and E. E. Martin (2009), Circulation through the Central American Seaway during the Miocene carbonate crash, *Geology*, *37*(1), 87–90.
Nisancioglu, K. H., M. E. Raymo, and P. H. Stone (2003), Reorganization of Miocene deep water circulation in response to the shoaling of the Central American Seaway, *Paleoceanography*, *18*(1), 1006 doi:1010.1029/2002PA000767.
Parr, A. E. (1937), A contribution to the hydrography of the Caribbean and Cayman Seas, based upon the observations made by the research ship *Atlantis*, 1933–1934, *Bull. Bingham Oceanogr. Collection*, *5*(4), 1–110.
Piepgras, D. J., and S. B. Jacobsen (1988), The isotopic composition of neodymium in the North Pacific, *Geochim. Cosmochim. Acta*, *52*(6), 1373–1381.
Piepgras, D. J., and G. J. Wasserburg (1980), Neodymium isotopic variations in seawater, *Earth Planet. Sci. Lett.*, *50*(1), 128–138.
Piepgras, D. J., and G. J. Wasserburg (1982), Isotopic composition of neodymium in waters from the Drake Passage, *Science*, *217*(4556), 207–214.
Piepgras, D. J., and G. J. Wasserburg (1987), Rare-earth element transport in the Western North Atlantic inferred from Nd isotopic observations, *Geochim. Cosmochim. Acta*, *51*(5), 1257–1271.
Piotrowski, A. M., S. L. Goldstein, S. R. Hemming, and R. G. Fairbanks (2004), Intensification and variability of ocean thermohaline circulation through the last deglaciation, *Earth Planet. Sci. Lett.*, *225*(1–2), 205–220.
Piotrowski, A. M., S. L. Goldstein, S. R. Hemming, and R. G. Fairbanks (2005), Temporal relationships of carbon cycling and ocean circulation at glacial boundaries, *Science*, *307*(5717), 1933–1938.
Piotrowski, A. M., V. K. Banakar, A. E. Scrivner, H. Elderfield, A. Galy, and A. Dennis (2009), Indian Ocean circulation and productivity during the last glacial cycle, *Earth Planet. Sci. Lett.*, *285*, 179–189.
Piotrowski, A. M., A. Galy, J. A. L. Nicholl, N. Roberts, D. J. Wilson, J. A. Clegg, and J. Yu (2012), Reconstructing deglacial North and South Atlantic deep water sourcing using foraminiferal Nd isotopes, *Earth Planet. Sci. Lett.*, *357–358*, 289–297.

©2014. American Geophysical Union. All Rights Reserved.

Rempfer, J., T. F. Stocker, F. Joos, J.-C. Dutay, and M. Siddall (2011), Modelling Nd-isotopes with a coarse resolution ocean circulation model: Sensitivities to model parameters and source/sink distributions, *Geochim. Cosmochim. Acta*, *75*(20), 5927–5950.
Restrepo, J. D., P. Zapata, J. M. Díaz, J. Garzón-Ferreira, and C. B. García (2006), Fluvial fluxes into the Caribbean Sea and their impact on coastal ecosystems: The Magdalena River Columbia, *Global Planet. Change*, *50*, 33–49.
Reynolds, B. C., M. Frank, and R. K. O'Nions (1999), Nd- and Pb-isotope time series from Atlantic ferromanganese crusts: Implications for changes in provenance and paleocirculation over the last 8 Myr, *Earth Planet. Sci. Lett.*, *173*(4), 381–396.
Rickli, J., M. Frank, and A. N. Halliday (2009), The hafnium-neodymium isotopic composition of Atlantic seawater, *Earth Planet. Sci. Lett.*, *280*(1–4), 118–127.
Roberts, N. L., A. M. Piotrowski, J. F. McManus, and L. D. Keigwin (2010), Synchronous deglacial overturning and water mass source changes, *Science*, *327*, 75–78.
Roberts, N. L., A. M. Piotrowski, H. Elderfield, T. I. Eglinton, and M. W. Lomas (2012), Rare earth element association with foraminifera, *Geochim. Cosmochim. Acta*, *94*, 57–71.
Robinson, L. F., and T. van de Flierdt (2009), Southern Ocean evidence for reduced export of North Atlantic Deep Water during Heinrich event 1, *Geology*, *37*, 195–198.
Rutberg, R. L., S. R. Hemming, and S. L. Goldstein (2000), Reduced North Atlantic Deep Water flux to the glacial Southern Ocean inferred from neodymium isotope ratios, *Nature*, *405*(6789), 935–938.
Sarnthein, M., G. Bartoli, M. Prange, A. Schmittner, B. Schneider, M. Weinelt, N. Andersen, and D. Garbe-Schonberg (2009), Mid-Pliocene shifts in ocean overturning circulation and the onset of Quaternary-style climates, *Clim. Past*, *5*(2), 269–283.
Schaule, B. K., and C. C. Patterson (1981), Lead concentrations in the northeast pacific—Evidence for global anthropogenic perturbations, *Earth Planet. Sci. Lett.*, *54*(1), 97–116.
Scher, H. D., and E. E. Martin (2004), Circulation in the Southern Ocean during the Paleogene inferred from Nd isotopes, *Earth Planet. Sci. Lett.*, *228*, 391–405.
Schlitzer, R. (2011), Ocean Data Viel. [Available at http://odv.awi.de.]
Schneider, B., and A. Schmittner (2006), Simulating the impact of the Panamanian seaway closure on ocean circulation, marine productivity and nutrient cycling, *Earth Planet. Sci. Lett.*, *246*(3–4), 367–380.
Seki, O., G. L. Foster, D. N. Schmidt, A. Mackensen, K. Kawamura, and R. D. Pancost (2010), Alkenone and boron-based Pliocene pCO(2) records, *Earth Planet. Sci. Lett.*, *292*(1–2), 201–211.
Sepulchre, P., T. Arsouze, Y. Donnadieu, J.-C. Dutay, C. Jaramillo, J. Le Bras, E. Martin, C. Montes, and A. J. Waite (2014), Consequences of shoaling of the Central American Seaway determined from modeling Nd isotopes, *Paleoceanography*, *29*, 176–198, doi:10.1002/2013PA002501.
Sigurdsson, H., R. M. Leckie, G. D. Acton, and S. S. Party (1997), Site 999, in *Proceedings of the Ocean Drilling Program, Initial Reports*, edited by H. Sigurdsson, R. M. Leckie, and G. D. Acton, pp. 131–230, Ocean Drilling Program, College Station, Tex.
Steph, S., R. Tiedemann, M. Prange, J. Groeneveld, D. Nürnberg, L. Reuning, M. Schulz, and G. H. Haug (2006), Changes in Caribbean surface hydrography during the Pliocene shoaling of the Central American Seaway, *Paleoceanography*, *21*, PA4221, doi:10.1029/2004PA001092.
Steph, S., R. Tiedemann, M. Prange, J. Groeneveld, M. Schulz, A. Timmermann, D. Nürnberg, C. Rühlemann, C. Saukel, and G. H. Haug (2010), Early Pliocene increase in thermohaline overturning: A precondition for the development of the modern equatorial Pacific cold tongue, *Paleoceanography*, *25*, PA2202, doi:10.1029/2008PA001645.
Stichel, T., M. Frank, J. Rickli, and B. A. Haley (2012), The hafnium and neodymium isotope composition of seawater in the Atlantic sector of the Southern Ocean, *Earth Planet. Sci. Lett.*, *317*, 282–294.
Stumpf, R., M. Frank, J. Schönfeld, and B. A. Haley (2010), Late Quaternary variability of Mediterranean Outflow Water from radiogenic Nd and Pb isotopes, *Quat. Sci. Rev.*, *29*(19–20), 2462–2472.
Tachikawa, K., C. Jeandel, and M. Roy-Barman (1999), A new approach to the Nd residence time in the ocean: The role of atmospheric inputs, *Earth Planet. Sci. Lett.*, *170*(4), 433–446.
Tachikawa, K., M. Roy-Barman, A. Michard, D. Thouron, D. Yeghicheyan, and C. Jeandel (2004), Neodymium isotopes in the Mediterranean Sea: Comparison between seawater and sediment signals, *Geochim. Cosmochim. Acta*, *68*, 3095–3106.
Tachikawa, K., A. M. Piotrowski, and G. Bayon (2014), Neodymium associated with foraminiferal carbonate as a recorder of seawater isotopic signatures, *Quat. Sci. Rev.*, *88*, 1–13.
Tanaka, T., et al. (2000), JNdi-1: A neodymium isotopic reference in consistency with LaJolla neodymium, *Chem. Geol.*, *168*(3–4), 279–281.
Tiedemann, R., A. Sturm, S. Steph, S. P. Lund, and J. S. Stoner (2007), Astronomically calibrated timescales from 6 to 2.5 Ma and benthic isotope stratigraphies, Site 1236, 1237, 1239 and 1241, *Proc. Ocean Dril. Prog*, *202*, 1–69.
Tsuchiya, M., and L. D. Talley (1998), A Pacific hydrographic section at 88 degrees W: Water-property distribution, *J. Geophys. Res.*, *103*(C6), 12,899–12,918, doi:10.1029/12897JC03415.
Veron, A. J., and T. M. Church (1997), Use of stable lead isotopes and trace metals to characterize air mass sources into the eastern North Atlantic, *J. Geophys. Res.*, *102*(D23), 28,049–28,058, doi:10.1029/97JD01527.
von Blanckenburg, F., and H. Igel (1999), Lateral mixing and advection of reactive isotope tracers in ocean basins: Observations and mechanisms, *Earth Planet. Sci. Lett.*, *169*(1–2), 113–128.
Wilson, D. J., A. M. Piotrowski, A. Galy, and J. A. Clegg (2013), Reactivity of neodymium carriers in deep sea sediments: Implications for boundary exchange and paleoceanography, *Geochim. Cosmochim. Acta*, *109*, 197–221.
Wüst, G. (1963), On the stratification and circulation in the cold water sphere of the Antillean-Caribbean Basins, *Deep Sea Res.*, *10*, 165–187.
Wüst, G. (1964), *Stratification and Circulation in the Antillean-Caribbean Basins, Part 1, Spreading and Mixing of the Water Types With an Oceanographic Atlas*, 201 pp., Columbia Univ. Press, New York.
Zachos, J., M. Pagani, L. Sloan, E. Thomas, and K. Billups (2001), Trends, rhythms, and aberrations in global climate 65 Ma to present, *Science*, *292*(5517), 686–693.
Zhang, X., et al. (2012), Changes in equatorial Pacific thermocline depth in response to Panamanian seaway closure: Insights from a multi-model study, *Earth Planet. Sci. Lett.*, *317*, 76–84.

©2014. American Geophysical Union. All Rights Reserved.