

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

Anne H. Osborne<sup>1</sup>, Derrick R. Newkirk<sup>2,3</sup>, Jeroen Groeneveld<sup>4</sup>, Ellen E. Martin<sup>2</sup>, Ralf Tiedemann<sup>5</sup>, and Martin Frank<sup>1</sup>

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

---

---

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 [ *Journal of Marine Research*, 2009;

## 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 [Lund, 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 [Lund, 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) [Lund, 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, [Lund, 2003]), bathed today in relatively oxygen-depleted waters characterized by low  $\delta^{13}\text{C}$  signatures originating from mid-depths in the north Pacific [Lund, 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 [Lund, 1998], [Lund, 2007], [Lund, 2006, 2010], and [Lund, 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 [Lund, 2006].

### 2.3. Sample Preparation and Isotope Analysis

Fossil fi

Mixed planktonic foraminifera weighing 25 to 50 mg were crushed between two glass plates and

2010: , --

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  $\epsilon_{Nd}$  signatures. There are no published seawater  $\epsilon_{Nd}$  data for the Caribbean to date, but profiles in the western equatorial Atlantic [Lyle et al., 1987] and at Demerara Rise [Lyle et al., 2014] show that the core of AAIW today has an  $\epsilon_{Nd}$  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  $\epsilon_{Nd}$  value of  $-10.5$  [Lyle 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 ( $\epsilon_{Nd}$  between  $-8$  and  $-9$   $\epsilon_{Nd}$ ) [Lyle et al., 2009; Lyle 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 ( $\epsilon_{Nd} = -10.7$ )

but are presented and compared with the foraminifera data in the supporting information (Figure S2). In contrast, fish teeth and foraminiferal  $\epsilon_{\text{Nd}}$  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 [Klein 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  $^{206}\text{Pb}/^{204}\text{Pb}$ , between 15.62 and 15.64 for  $^{207}\text{Pb}/^{204}\text{Pb}$ , and between 38.66 and 38.78 for  $^{208}\text{Pb}/^{204}\text{Pb}$ ).

from ~ 7 Ma onward [ *Journal of Geology*, *117*, 2009]

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

The Miocene-Pliocene record (Figure 5) shows that the majority of the change in deep Caribbean  $\epsilon_{Nd}$  away from Pacific-like compositions had already taken place prior to about 7 Ma [ *McManis et al., 2009*] but that the trend toward less radiogenic  $\epsilon_{Nd}$  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  $\epsilon_{Nd}$  signal. The key question is therefore whether the  $\epsilon_{Nd}$  records reflect the continued but decreasing influence of Pacific waters



[Stouffer et al., 2009; Stouffer et al., 2012] we argue that it is unlikely that the  $\epsilon_{Nd}$  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  $\epsilon_{Nd}$  and the composition of seawater in the deep Caribbean is another potential factor contributing to the Pliocene  $\epsilon_{Nd}$  trend. Despite the relatively long

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

Finally, the Pliocene Caribbean  $\epsilon_{Nd}$  records also show variability on shorter timescales (Figure 4). Planktonic  $\delta^{18}O$  records [Linsley et al., 2001] and sea surface salinity reconstructions [Linsley et al., 2005; Linsley et al., 2006, 2008; Linsley et al., 2006] indicate that the CAS had shoaled to ~ 100 m by ~ 4.2 Ma. The intermediate water  $\epsilon_{Nd}$  record from uncleaned planktonic foraminifera for Site 1000 is plotted together with the ice volume-corrected  $\delta^{18}O$  gradient between

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 [Lippert et al., 2009], when the CAS closed for major deep water exchange.

## 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, *Earth and Planetary Science Letters*, **170**, 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, *Earth and Planetary Science Letters*, **221**, 2725–2744.

- 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 and Planetary Science Letters*, **367**, 163–174.
- Jacobsen, S. B., and G. J. Wasserburg (1980), Sm-Nd evolution of chondrites, *Earth and Planetary Science Letters*, **51**, 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, *Earth and Planetary Science Letters*, **257**, 156–164.
- Johns, W. E., T. L. Townsend, D. M. Fratantoni, and W. D. Wilson (2002), On the Atlantic inflow to the Caribbean Sea, *Journal of Geophysical Research*, **107**, C02001, doi:10.1029/2001JC001811.
- 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, *Journal of Geophysical Research*, **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

- 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, *Earth and Planetary Science Letters*, 307(1-2), 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, *Estuaries and Coasts*, 29(1), 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 and Planetary Science Letters*, 170(4), 381–396.
- Rickli, J., M. Frank, and A. N. Halliday (2009), The hafnium-neodymium isotopic composition of Atlantic seawater, *Earth and Planetary Science Letters*, 288(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, *Earth and Planetary Science Letters*, 297(1-2), 75–78.
- Roberts, N. L., A. M. Piotrowski, H. Elderfield, T. I. Eglington, and M. W. Lomas (2012), Rare earth element association with foraminifera, *Earth and Planetary Science Letters*, 357(1-2), 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, *Earth and Planetary Science Letters*, 288(1-2), 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, *Earth and Planetary Science Letters*, 181(3-4), 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, *Earth and Planetary Science Letters*, 288(2), 269–283.
- Schaule, B. K., and C. C. Patterson (1981), Lead concentrations in the northeast Pacific—Evidence for global anthropogenic perturbations, *Earth and Planetary Science Letters*, 56(1), 97–116.
- Scher, H. D., and E. E. Martin (2004), Circulation in the Southern Ocean during the Paleogene inferred from Nd isotopes, *Earth and Planetary Science Letters*, 221(1-2), 391–405.
- Schlitzer, R. (2011), Ocean Data View. [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 and Planetary Science Letters*, 243(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<sub>2</sub> records, *Earth and Planetary Science Letters*, 297(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, *Earth and Planetary Science Letters*, 397(1-2), 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 Leg 201*, 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, *Earth and Planetary Science Letters*, 243(1-2), 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, *Earth and Planetary Science Letters*, 297(1-2), PA2202, doi:10.1029/2008PA001645.