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Neodymium isotopes and concentrations in Caribbean seawater: Tracing water mass mixing and continental input in a semi-enclosed ocean basin

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ABSTRACT

We present the first full water column Nd isotope (ε_{Nd}) and concentration data for Caribbean seawater, as well as for stations close to the Orinoco River mouth and in the Florida Straits. The surface inflow into the southeastern Caribbean via the Guyana Current is characterized by an ε_{Nd} signature of −10.9, which is a consequence of the mixing of relatively unradiogenic ε_{Nd} signatures (−13.6) supplied by the Orinoco River with contributions from the Amazon River (∼−10). Despite the proximity to land, sub-surface and intermediate waters within the Caribbean largely retain the ε_{Nd} signatures of their source water masses in the Atlantic. In contrast, the deep waters of the Caribbean show ε_{Nd} signatures at least 3 ε_{Nd} units more radiogenic than the inflowing Upper North Atlantic Deep Water (UNADW). A ε_{Nd} shift from −13 to −9.7 can be explained by addition of radiogenic Nd to the deep Caribbean through weathering inputs from land. However, in order to balance such large shifts in ε_{Nd} with at the same time modest increases in Nd concentrations, Nd must also be removed from seawater within the basin. It is suggested that the long residence time of deep waters in the Caribbean allows significant interaction of seawater with sinking particles and seafloor sediments resulting in more radiogenic values. These findings have implications for the use of ε_{Nd} as a proxy for paleocirculation in restricted basins, in which the residence times of the deep waters are long.

1. Introduction

The radiogenic isotope composition of neodymium in seawater has been used extensively as a modern water mass tracer and in palaeoceanography (e.g. Frank, 2002; Goldstein and Hemming, 2003). Nd is supplied to the oceans through weathering of continental rocks (Frank, 2002). Its average oceanic residence time is 400–2000 years (Arsouze et al., 2009; Rempfer et al., 2011; Tachikawa et al., 1999), comparable to the duration of global ocean mixing (Broecker and Peng, 1982). Variations in the $^{143}Nd/^{144}Nd$ ratio of source rocks, usually reported as ε_{Nd} [$\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd_{measured})/(^{143}Nd/^{144}Nd_{CHUR}) - 1] \times 10{,}000$, where CHUR is the chondritic uniform reservoir, with a value of 0.512638 (Hamilton et al., 1983; Jacobsen and Wasserburg, 1980)], are caused by the decay of ^{147}Sm to ^{143}Nd and are a consequence of the age and the Sm/Nd composition of the source rocks. For example, North Atlantic Deep Water (NADW) has a relatively unradiogenic ε_{Nd} signature (−13.5, Piepgras and Wasserburg, 1987), reflecting the old, continental crust surrounding its source areas. In contrast, water masses originating in the Southern Ocean have a more radiogenic ε_{Nd} signature (−7 to −9, Jeandel, 1993; Piepgras and Wasserburg, 1982; Stichel et al., 2012), a result of the admixture of Pacific waters that contain more radiogenic Nd from the young, mantle-derived rocks around the Pacific rim (Amakawa et al., 2004, 2009; Piepgras and Jacobsen, 1988).

A recent compilation of seawater ε_{Nd} data confirms that water mass mixing can explain much of the distribution of ε_{Nd} in the intermediate and deep open ocean, distal from continental influence (Lacan et al., 2012). However, when the Nd isotope composition is modeled using only surface water compositions as a boundary condition, seawater ε_{Nd} in the deep Pacific and Southern Oceans is less radiogenic than observations, which means that a further source of radiogenic Nd to the deep ocean is required in addition to the fluvial and eolian inputs at the sea surface (Jones et al., 2008). While Nd is not supplied to seawater by hydrothermal sources (German et al., 1990; Halliday et al., 1992), possible mechanisms for the addition of radiogenic Nd

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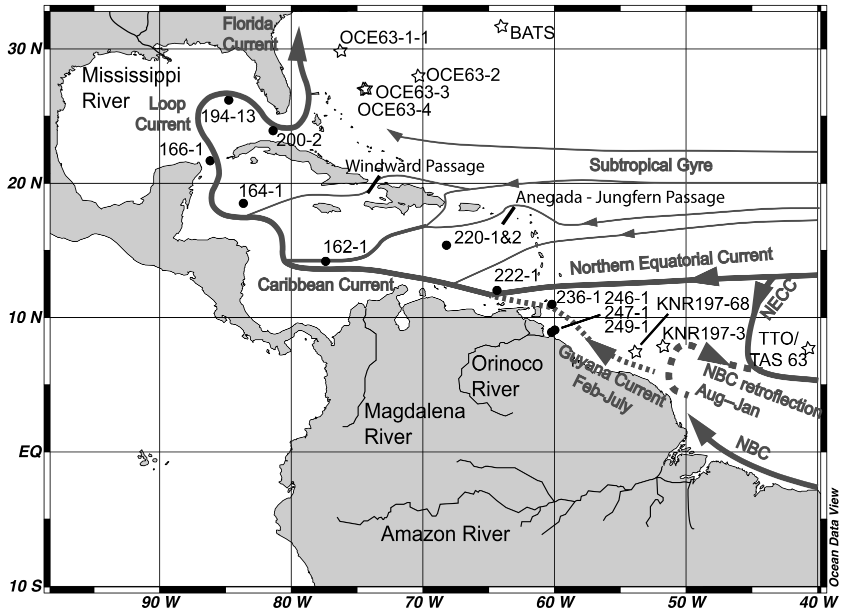

Fig. 1. Map showing location of sample stations in this study (filled circles) and published data (open stars, OCE63 stations, Piepgras and Wasserburg, 1980; TTO/TAS 63, Piepgras and Wasserburg, 1987; BATS, Pahnke et al., 2012; KNR197 stations, Huang et al., 2014). Depiction of major surface currents and rivers after Hellweger and Gordon (2002), Jouanno et al. (2008), Lumpkin and Garzoli (2005), Schott et al. (1988) and Steph et al. (2006). NBC, North Brazil Coastal Current; NECC, Northern Equatorial Counter Current. Map produced using Ocean Data View (Schlitzer, 2011).

at depth are submarine discharge of groundwaters (Johannesson and Burdige, 2007), partial dissolution of sinking riverine or dust particles (e.g. Albarède and Goldstein, 1992; Henry et al., 1994; Sholkovitz and Szymczak, 2000), or release from sea floor sediments or pore waters (e.g. Elderfield and Sholkovitz, 1987). Furthermore, a number of studies have shown that ε_{Nd} can be modified by interaction with sediments or continent derived particles, particularly at ocean margins (e.g. Grenier et al., 2013; Jeandel et al., 1998, 2007; Lacan and Jeandel, 2001, 2004a, 2004b, 2004c, 2005a, 2005b; Wilson et al., 2012). This process is poorly understood and has been termed boundary exchange in cases where the Nd concentration remains unchanged (e.g. Lacan and Jeandel, 2001).

Here we present the first ε_{Nd} and Nd concentration data for Caribbean seawater. The Caribbean is an ideal study area for investigating the extent to which Nd isotopes can be used as a water mass tracer in a semi-enclosed ocean basin. Comparable data have so far only been published for the Baltic Sea (Andersson et al., 1992; Chen et al., 2013), the Arctic Ocean (Andersson et al., 2008; Porcelli et al., 2009) and the Mediterranean (Tachikawa et al., 2004). The setting of the Caribbean is unique in that the rocks along the volcanic dominated continental margins of the Caribbean are characterized by much more radiogenic ε_{Nd} signatures than those generally surrounding the North Atlantic (Fig. A1). Consequently there is a large Nd isotopic difference of 15–20 ε_{Nd} units between the Atlantic water masses flowing into the Caribbean and the volcanic rocks of Central America and the Caribbean islands. Particles of volcanic origin have been shown to readily dissolve and release Nd to seawater (Pearce et al., 2013), making Caribbean seawater highly sensitive to continental inputs. Furthermore, restricted exchange of deep waters with the Atlantic and the absence of deep water formation within the Caribbean or the Gulf of Mexico result in a relatively long residence time of ∼150 years for waters below ∼1800 m depth (Joyce et al., 1999). Finally, Caribbean surface waters integrate inputs from two of the world's largest rivers, the Amazon and the Orinoco, while a third major river, the Magdalena, drains directly into the basin. Together, these three rivers account for nearly 20% of the global fluvial discharge (Hu et al., 2004; Müller-Karger et al., 1989) and we examine their impact on ε_{Nd} signatures and Nd concentrations in the Caribbean.

2. Methods

The samples of this study were taken during Meteor Cruise 78, Leg 1 in February and March 2009 (Fig. 1). Full details of sample collection and preparation are provided in the Supplementary material.

Nd concentrations were measured on an Agilent 7500ce ICP-MS connected to an online preconcentration seaFAST system (Elemental Scientific Inc., Nebraska, USA) as detailed in Hathorne et al. (2012). The accuracy of this technique has been confirmed through participation in the GEOTRACES intercalibration study (van de Flierdt et al., 2012). External precision (2σ) for Nd concentration measurements was 9.3% measured without using the buffer clean up column (Hathorne et al., 2012).

Nd isotope compositions were measured on a Nu Plasma MC-ICPMS at Oregon State University. Samples were corrected for instrumental mass bias to $^{146}Nd/^{144}Nd = 0.7219$. All $^{143}Nd/^{144}Nd$ ratios of the samples were normalized to the accepted literature value of 0.512115 for standard JNdi-1 (Tanaka et al., 2000), which was measured repeatedly during each of the measurement sessions and guarantees accuracy of the measurements. The external reproducibility (2σ) was also monitored using a second, SpecPure standard solution, which was measured at the same concentration as the most dilute sample solutions (15 ppb). The internal errors were always smaller than the external reproducibility (Table 1). For those samples measured more than once, the larger error of either the SpecPure standard or of the repeat analyses of selected samples is reported here (Table 1). Problems with instrument sensitivity resulted in relatively low beam intensities and the external reproducibility of the data reported in this study is thus poorer than that commonly reported for samples with similar concentrations. Nevertheless, the data are accurate and valid within the reported uncertainties and allow the first study of the distribution of Nd isotope compositions in Caribbean seawater.

Table 1
Potential temperature, salinity, potential density, dissolved oxygen content, ε_{Nd} and Nd concentrations of samples in this study. Results in bold type are the average of two repeat measurements.

Station (Number, Location, Date, Depth)	Depth (m)	θ (°C)	Salinity (psu)	Potential density (kg m^{-3})	[O_2] (mg L^{-1})	$^{143}Nd/^{144}Nd$	Internal error	ε_{Nd}[a]	2σ[b]	Nd (pM kg^{-1})	Water mass
Station 162-1	10	not measured	not measured	not measured	not measured	**0.512156**	6.12E–06	**−9.40**	1.21	18.63	CW
14°12.60′N, 77°23.40′W	35	26.21	36.19	23.87	4.15	**0.512140**	8.05E–06	**−9.71**	0.75	16.72	CW
24.02.2009, 4033 m	70	25.59	36.82	24.53	4.11	**0.512113**	6.90E–06	**−10.25**	0.64	15.43	SUW
	120	22.73	36.92	25.47	3.22	0.512236	8.71E–06	−7.84	0.73	14.94	SUW
	225	17.43	36.32	26.43	3.07	0.512098	5.95E–06	−10.54	0.73	15.81	EDW
	675	6.75	34.76	27.27	2.64	0.512094	7.01E–06	−10.61	0.73	15.82	AAIW
	1000	4.97	34.92	27.61	3.78	**0.512388**	1.13E–05	**−4.87**	0.64	15.52	
	1500	4.21	34.95	27.73	4.34	0.512213	6.71E–06	−8.30	0.73	16.84	UNADW
	2000	3.97	34.96	27.76	4.42	**0.512203**	6.32E–06	**−8.48**	0.64	18.07	UNADW
	3000	3.92	34.96	27.76	4.42	**0.512187**	7.12E–06	**−8.80**	0.64	21.40	UNADW
	4033	3.91	34.96	27.76	4.40	**0.512207**	7.46E–06	**−8.40**	0.64	20.19	UNADW
Station 164-1	10	26.43[c]	35.86[c]	not measured	not measured	**0.512134**	5.05E–06	**−9.83**	0.64	21.82	CW
"Mysteriosa Bank"	40	26.29	35.77	23.53	4.24	0.512130	5.35E–06	−9.91	0.73	16.64	CW
18°30.42′N, 83°38.66′W	80	26.21	35.91	23.66	4.17	**0.512138**	6.63E–06	**−9.74**	0.64	17.03	CW
26.02.2009, 1172 m	150	24.50	36.89	24.92	3.55					15.34	SUW
	249	18.11	36.42	26.34	3.03					16.02	EDW
	551	9.35	35.06	27.11	2.59					16.75	
	702	7.19	34.85	27.27	2.72					16.09	AAIW
	1173	4.49	34.94	27.69	4.35	**0.512155**	7.93E–06	**−9.43**	0.75	15.02	
Station 166-1	11	not measured	not measured	not measured	not measured	**0.512240**	7.23E–06	**−7.76**	0.64	16.83	CW
21°40.79′N, 86°9.92′W	40	26.17	35.87	23.64	4.24	**0.512087**	8.28E–06	**−10.74**	0.75	16.70	CW
28.02.2009, 1541 m	80	25.72	36.34	24.13	3.77					14.95	CW
	111	21.59	36.81	25.71	3.09					14.87	SUW
	200	17.87	36.40	26.38	3.13	**0.512130**	7.75E–06	**−9.91**	0.64	15.37	EDW
	506	9.80	35.14	27.10	2.61	**0.512136**	9.46E–06	**−9.80**	1.68	17.21	
	751	6.64	34.86	27.36	2.92					17.11	AAIW
	1470	4.27	34.95	27.72	4.46					16.66	UNADW
Station 194-13	10	not measured	not measured	not measured	not measured					18.76	
26°12.18'N, 84°43.88'W	30	20.64[d]	36.18[d]	25.49[d]	2.53[d]	**0.512228**	5.84E–06	**−7.99**	0.64	17.74	
07.03.2009, 538 m	50	20.69	36.48	25.70	4.65	**0.512235**	1.29E–05	**−7.86**	1.13	16.57	WP?
	90	20.62	36.47	25.72	4.59	**0.512188**	6.55E–06	**−8.78**	0.94	17.27	WP?
	150	16.80	36.20	26.48	2.65					14.49	NCW
	300	11.14	35.34	27.02	2.54	**0.512160**	6.56E–06	**−9.32**	0.75	17.10	NCW
	400	9.72	35.15	27.12	2.53	0.512118	6.24E–06	−10.15	0.73	17.09	
	531	7.91	34.96	27.25	2.64	**0.512155**	1.04E–05	**−9.42**	1.13	16.60	
Station 200-2	40	25.00	35.98	24.08	3.41					16.34	
23°56.58′N, 81°22.96′W	80	24.65	36.44	24.54	4.10	**0.512125**	9.49E–06	**−10.00**	0.75	14.51	SUW
08.03.2009, 1143 m	96	24.15	36.81	24.97	3.37	**0.512226**	8.44E–06	**−8.05**	1.13	17.35	SUW
	140	21.47	36.43	25.45	4.52	0.512258	9.13E–06	−7.40	0.73	17.22	WP?
	220	18.44	36.47	26.29	2.82	0.512168	6.11E–06	−9.17	0.73	16.42	EDW
	230	18.23	36.47	26.34	3.27	0.512121	5.79E–06	−10.08	0.73	16.12	EDW
	285	16.04	36.10	26.59	2.69	0.512162	7.07E–06	−9.28	0.73	16.02	NCW
	310	15.10	35.95	26.69	2.89					17.29	NCW
	550	8.83	35.05	27.18	2.53	0.512143	5.29E–06	−9.65	1.07	16.94	
	800	5.93	34.90	27.48	3.24	0.512176	5.26E–06	−9.01	1.07	17.78	
	950	5.34	34.91	27.57	3.57	0.512185	5.78E–06	−8.85	1.07	16.06	
	1149	4.55	34.94	27.68	4.20	0.512177	8.67E–06	−8.99	1.07	14.56	
Station 220-1 and 220-2	10	26.20	35.60	23.42	2.70	0.512121	6.28E–06	−10.09	1.07	20.90	CW
15°24.00′N, 68°12.00′W	60	26.10	35.70	23.53	4.29	0.512114	5.02E–06	−10.22	1.07	20.30	CW
16.03.2009, 4484 m	90	26.33	36.74	24.24	4.09	0.512101	5.08E–06	−10.47	1.07	18.16	CW
	136	22.24	36.96	25.64	3.36	0.512088	6.12E–06	−10.73	1.07	17.21	SUW
	210	17.44	36.37	26.46	3.41	0.512129	6.10E–06	−9.93	1.07	16.00	EDW
	485	8.97	34.97	27.10	2.61	0.512081	4.41E–06	−10.87	1.07	17.13	
	686	6.68	34.76	27.27	2.76	**0.512088**	1.40E–05	**−10.74**	0.48	18.14	AAIW
	1983	3.94	34.97	27.76	4.64	**0.512164**	1.42E–05	**−9.24**	0.48	18.36	UNADW
	2680	3.89	34.97	27.77	4.60	**0.512206**	1.88E–05	**−8.43**	0.48	18.10	UNADW
	3487	3.88	34.97	27.77	4.59	**0.512187**	4.53E–06	**−8.80**	0.62	19.03	UNADW
	4482	3.87	34.97	27.77	4.63	**0.512166**	1.24E–05	**−9.21**	0.48	21.06	UNADW
Station 222-1	10	26.4[e]	35.7[e]	not measured	not measured	**0.512108**	1.59E–05	**−10.34**	0.48	19.53	CW
12°1.48′N, 64°28.70′W	30	26.56	35.72	23.40	4.25	**0.512124**	1.37E–05	**−10.02**	0.48	19.68	CW
18.03.2009, 1026 m	55	25.72	36.38	24.16	3.96	**0.512070**	1.42E–05	**−11.09**	0.48	16.19	CW
	75	22.33	36.83	25.52	3.12	**0.512080**	1.69E–05	**−10.88**	0.48	16.11	SUW

Table 1 (*continued*)

Station (Number, Location, Date, Depth)	Depth (m)	θ (°C)	Salinity (psu)	Potential density ($kg\,m^{-3}$)	$[O_2]$ ($mg\,L^{-1}$)	$^{143}Nd/^{144}Nd$	Internal error	ε_{Nd}[a]	2σ[b]	Nd ($pM\,kg^{-1}$)	Water mass
	140	18.39	36.46	26.29	2.96	**0.512106**	1.13E−05	**−10.37**	0.48	15.56	EDW
	230	14.61	35.82	26.69	2.83	**0.512077**	5.24E−06	**−10.95**	0.62	16.68	NCW
	750	6.16	34.75	27.34	2.89	**0.512071**	7.46E−06	**−11.05**	1.02	17.68	AAIW
	1016	4.85	34.92	27.63	3.95	**0.512145**	5.15E−06	**−9.61**	0.62	16.58	
Station 236-1	10	not measured	not measured	not measured	not measured					21.51	CW
11°0.80′N, 60°12.08′W	30	27.21	34.66	22.39	2.47	**0.512082**	4.93E−06	**−10.85**	0.62	18.20	CW
22.03.2009, 1587 m	110	23.81	36.77	25.04	3.42	**0.512063**	8.96E−06	**−11.21**	0.99	16.29	SUW
	440	8.44	34.82	27.07	2.57	**0.512037**	6.17E−06	**−11.73**	0.99	16.97	
	750	5.48	34.66	27.35	2.96					17.37	AAIW
	1000	5.32	34.89	27.55	3.67	**0.512069**	9.69E−06	**−11.10**	0.99	17.80	
	1530	4.06	34.98	27.77	5.36	**0.511990**	7.52E−06	**−12.65**	0.99	16.24	UNADW
Station 246-1	10	27.92[f]	34.52[f]	not measured	not measured	**0.512119**	6.21E−06	**−10.13**	0.99	23.55	GC
9°10.01′N, 59°54.04′W	30	26.93	36.27	23.70	4.17	**0.511947**	1.88E−05	**−13.48**	0.99	17.07	
25.03.2009, 64 m	50	24.72	36.41	24.49	3.76	**0.511987**	1.06E−05	**−12.71**	0.99	13.96	
Station 247-1	10	27.66	34.60	not measured	not measured	**0.512097**	6.66E−06	**−10.56**	0.99	24.13	GC
9°6.01′N, 59°57.00′W	30	26.88	36.21	not measured	not measured	**0.512010**	1.21E−05	**−12.26**	0.99	17.03	
25.03.2009, 58 m	50	deepest is 42 m				**0.512002**	1.24E−05	**−12.41**	0.99	12.76	
Station 249-1	0	28.69[f]	29.56[f]	not measured	not measured	**0.511948**	6.12E−06	**−13.45**	0.62	58.93	Orinoco
8°56.49′N, 60°12.66′W	0	28.69[f]	29.56[f]	not measured	not measured	**0.511939**	6.13E−06	**−13.63**	0.62	57.15	Orinoco
25.03.2009, 14 m	0	28.69[f]	29.56[f]	not measured	not measured	**0.511954**	6.08E−06	**−13.35**	0.62	59.84	Orinoco
BUCKET	0	28.69[f]	29.56[f]	not measured	not measured	**0.511933**	6.00E−06	**−13.76**	0.62	53.74	Orinoco

[a] Corrected to Tanaka et al. (2000). Bold type indicates the average of two measurements.
[b] 2σ external reproducibility is calculated from repeated measurements of the SpecPure standard solution. For those samples with repeat measurements, the larger error of either the SpecPure standard or of the repeat analyses is reported.
[c] Average of 10 m and 10.1 m RBR XR-420 CTD measurements at stations 164-6 and 164-7 (Schönfeld et al., 2011).
[d] Measurement taken at 31 m water depth.
[e] 10 m RBR XR-420 CTD measurement at station 222-6 (Schönfeld et al., 2011).
[f] Shipboard thermosalinograph, taken at 3.5 m water depth (Schönfeld et al., 2011).

3. Hydrographic setting

3.1. Surface and thermocline waters

The major feature of the surface circulation is the Caribbean Current (Fig. 1). The upper 80 m of the Caribbean Current is relatively fresh Caribbean Water (CW, Fig. 2, density $\sigma_\theta \leq 25.5\ kg\,m^{-3}$) consisting of Atlantic surface waters and Amazon and Orinoco river water (Hellweger and Gordon, 2002; Wüst, 1964) transported into the Caribbean by the Guyana Current (Gordon, 1967).

The position of the ITCZ strongly influences the proportion of Amazon and Orinoco waters reaching the Caribbean (Müller-Karger et al., 1989). Samples in this study were taken during February and March, when the ITCZ was in a southerly position (0–5°S) (Philander and Pacanowski, 1986) and the Guyana Current transported both Amazon and Orinoco waters into the Caribbean. The ITCZ begins its northward migration in May, reaching its most northerly position in August (6–10°N) (Philander and Pacanowski, 1986). This results in the establishment of a cyclonic circulation cell southeast of the Lesser Antilles (Johns et al., 2002), which effectively blocks the Guyana Current between August and January, so that the North Brazil Coastal Current (NBC, Fig. 1), including Amazon river waters, is retroflected eastwards, forming the Northern Equatorial Counter Current (NECC) (Hu et al., 2004; Johns et al., 2002; Müller-Karger et al., 1989).

Between about 80 and 180 m water depth there is the high salinity layer of the Subtropical Under Water (SUW, Fig. 2, salinity >36.5 psu) (Wüst, 1964), which forms by excess evaporation in the tropical and subtropical gyres and enters the Caribbean via the Northern Equatorial Current (Johns et al., 2002; Wüst, 1964). Together, CW and SUW form the permanent Caribbean thermocline (temperature $\theta > 20$ °C) (Metcalf, 1976; Wüst, 1964) and both water masses were present at all Caribbean stations.

In contrast, our hydrographic profiles show that CW was either absent or already heavily modified in the uppermost waters of Stations 194-13 and 200-2, in the Gulf of Mexico and Florida Straits, respectively (Fig. 2). SUW was only present at Station 200-2 between ∼80 to 100 m water depth and was not encountered at Station 194-13. The dissolved oxygen profile in the Florida Straits Station (200-2) (Fig. A2) is similar to that of the Windward Passage (Schmitz and Richardson, 1991; Roemmich, 1981) and it is therefore possible that North Atlantic water supplied via this passage (labeled 'Windward Passage' in Fig. 2) was the source of the relatively low salinity layer between 110 and 250 m water depth at Station 200-2. This lower salinity, high oxygen layer is also present in Station 194-13, although it occurs at shallower depths (∼50–100 m) and its upper part was not found.

3.2. Intermediate waters

Sub-thermocline waters (∼20–12 °C) in the Caribbean mainly form in the North Atlantic (Schmitz and Richardson, 1991; Stalcup and Metcalf, 1972) and move westward across the Caribbean Basin under the influence of the Caribbean Current (Wüst, 1964). The well-oxygenated Eighteen Degree Water (EDW) (Worthington, 1959), defined as all waters between 17 and 19 °C (Worthington, 1976), is usually present between 200 and 400 m water depth,

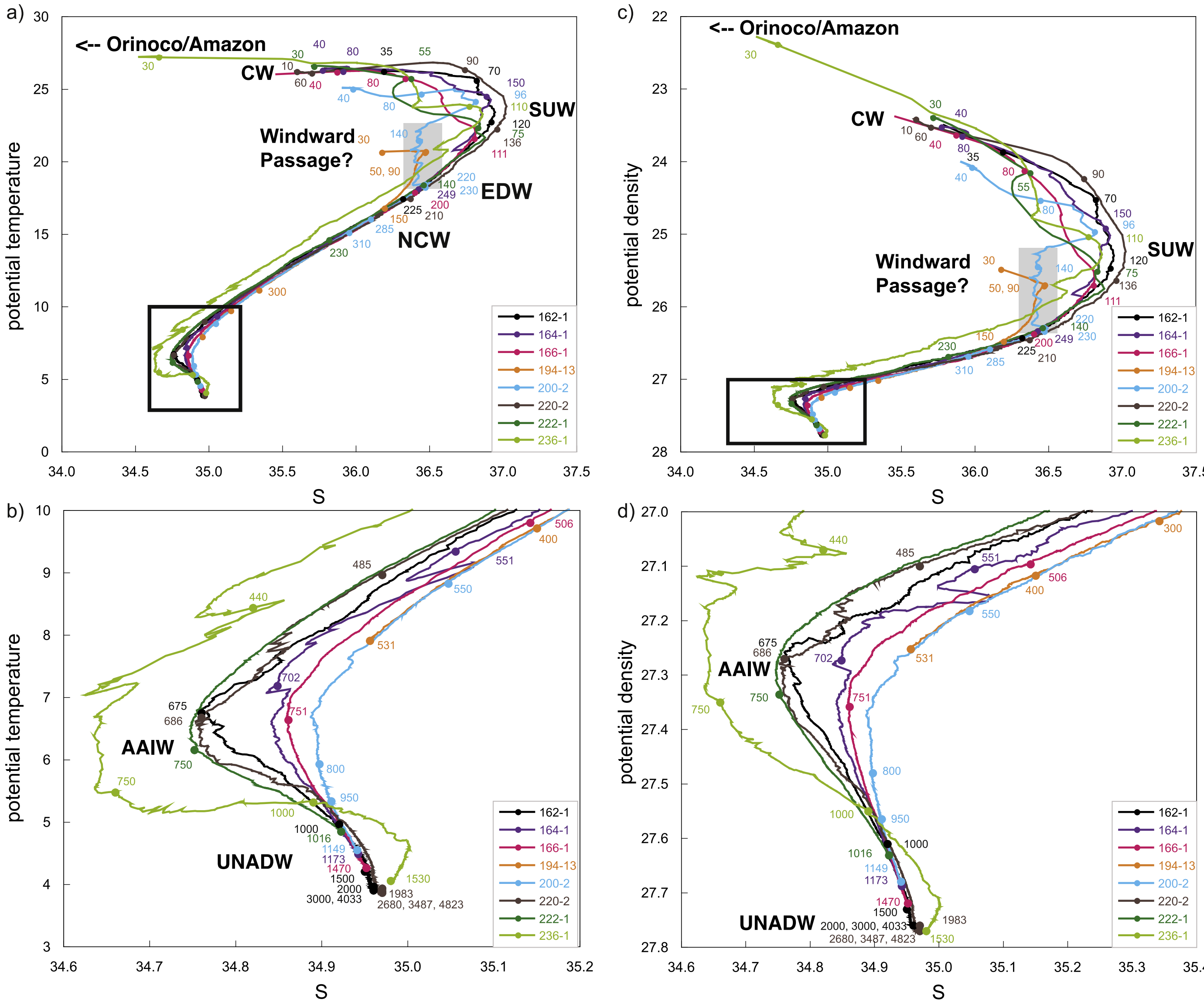

Fig. 2. (a) Potential temperature (°C) versus salinity at the sampling stations. Samples are indicated by colored dots and are labeled with their water depth (m). Black rectangle shows area of zoom (b). (c) Potential density (kg m^{-3}) versus salinity for same stations as (a). Black rectangle shows area of zoom (d). Water mass labels are CW, Caribbean Water; SUW, subtropical under water; EDW, Eighteen Degree Water from the Sargasso Sea (Worthington, 1959, 1976); NCW, North Atlantic Central Water; AAIW, Antarctic intermediate water and UNADW, upper north Atlantic deep water. The grey box indicates a low salinity layer that may originate from the North Atlantic and enter the Caribbean via the Windward Passage.

apart from the winter months when it extends to the surface in its formation region in the western North Atlantic subtropical gyre (Forget et al., 2011). EDW enters the Caribbean via the Windward Passage (Schmitz and Richardson, 1991) and is observed more prominently in the northern Antilles region than in the south (Metcalf et al., 1973).

Salinity in the Caribbean decreases steadily to a minimum at ∼750 m (Fig. 2). This low salinity layer is most prominent in the southeastern Caribbean and can be traced as far west as the Yucatan Basin and denotes the advection of Antarctic Intermediate Water (AAIW) from the South Atlantic (Wüst, 1964).

3.3. *Deep waters*

Deep water composition and structure in the Caribbean are controlled by the sills of the passages through the Antilles Island arc, the deepest of which are the Anegada-Jungfern (∼1900 m) and Windward (∼1700 m) passages (Fig. 1). Inflowing Atlantic waters, approximately equivalent in depth to the core of Upper North Atlantic Deep Water (UNADW, 1500–1700 m, Weiss et al., 1985), fill the basins of the Caribbean from their deepest points (∼4500–5500 m) to ∼1800 m (Wüst, 1964). Renewal of deep water is slow (Stalcup et al., 1975; Sturges, 1975) and the residence time of deep waters below ∼1800 m is ∼150 years (Joyce et al., 1999). A deep cyclonic flow pattern prevails in the Caribbean basin (Joyce et al., 2001) and the adjoining Gulf of Mexico (DeHaan and Sturges, 2005), where the deep water residence time is even higher at ∼250 years (Rivas et al., 2005). Apart from slow diffusion and mixing with overlying layers (Rivas et al., 2005), waters below the depth of the Florida Sill (∼800 m) return to the Caribbean via the Yucatan Passage before exiting to the North Atlantic through the deepest Antilles passages (Sturges, 2005).

3.4. *Orinoco transect*

Three shallow stations (maximum depth 64 m) were sampled near to the mouth of the Boca Grande, the main outlet of the Orinoco River. The most detailed profile (247-1, Fig. 3) showed a

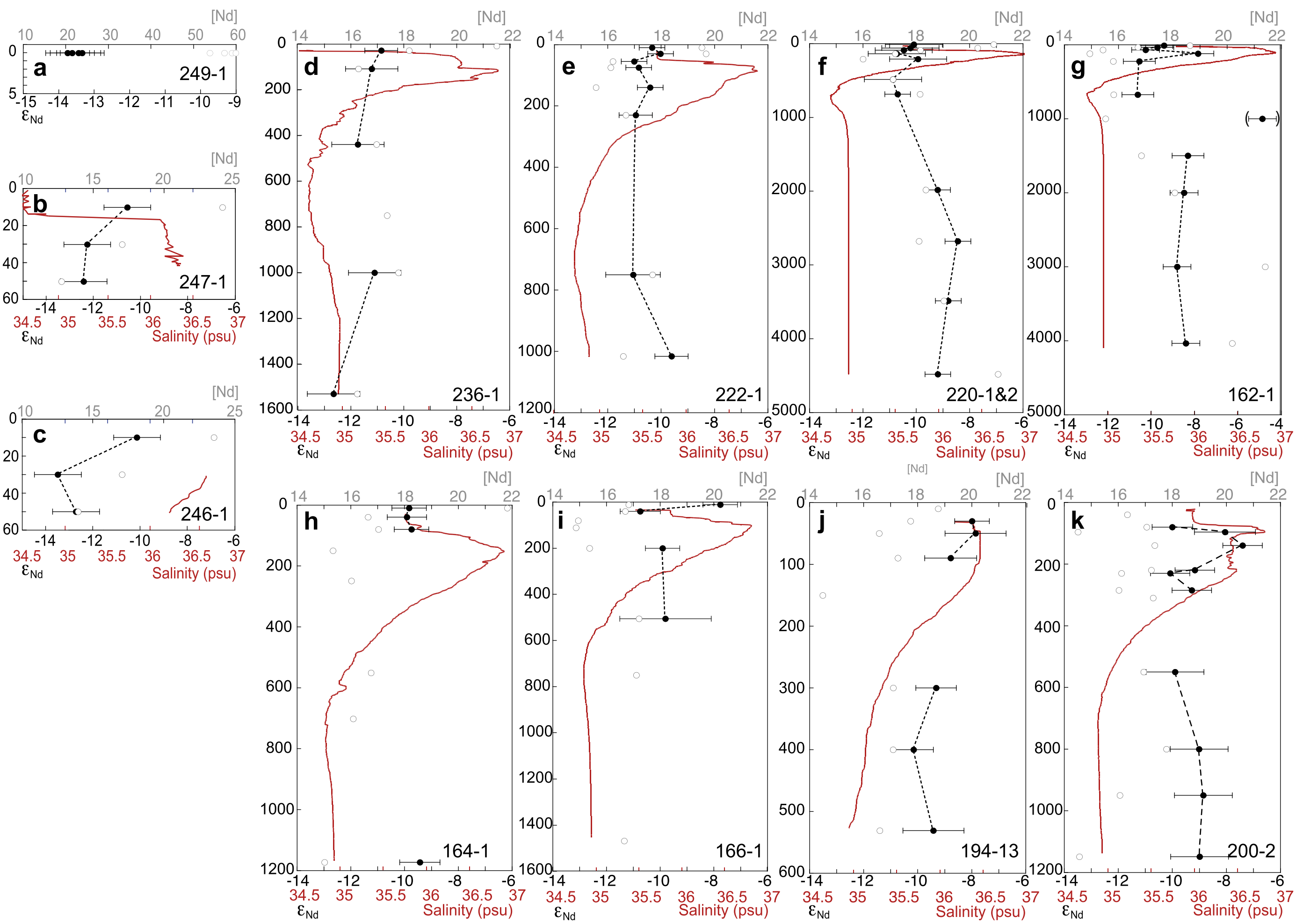

Fig. 3. Profiles of ε_{Nd}, [Nd] (in pmol kg^{-1}) and salinity for all stations.

15 m thick low salinity layer (34.5 psu) overlying a more saline layer (36.3 psu). The low salinity layer corresponds to a mixture of Orinoco river water and Amazon river water that had been transported northwestward by the Guyana Current.

4. Results

Neodymium isotope compositions (ε_{Nd}) and Nd concentrations [Nd] are reported in Table 1 along with θ, S, σ_θ and [O_2]. If the hydrographic properties recorded at a sample depth allow a particular water mass to be clearly identified, this is indicated in the table and in Fig. 4.

4.1. Surface waters

At Station 249-1, closest to the mouth of the Boca Grande, the average ε_{Nd} of surface waters is −13.6 (Fig. 3a) and thus the least radiogenic of all surface waters measured in this study. The concentration of Nd is also highest at Station 249-1 (57.4 pmol kg^{-1}) and thus clearly influenced by the Orinoco discharge as supported by low salinities recorded by the ship's thermosalinometer (29.6 psu, Schönfeld et al., 2011). [Nd] in the uppermost surface waters of Stations 246-1 and 247-1 decrease to ∼24 pmol kg^{-1} and ε_{Nd} averages −10.4. The underlying waters have less radiogenic ε_{Nd}, averaging −12.3 at Station 246-1 and −13.1 at Station 247-1 (Figs. 3b, c). The drop in ε_{Nd} is also reflected in a rapid decrease in [Nd] with depth to an average of 13.3 pmol kg^{-1} at 50 m.

Surface water entering the Caribbean, as recorded at Station 236-1, has an ε_{Nd} = −10.9 and [Nd] = 18.2 to 21.5 pmol kg^{-1} (Fig. 3d). The ε_{Nd} of CW within the Caribbean ranges from −11.0 to −9.4, with the exception of Station 166-1, where ε_{Nd} = −7.8 was measured at 11 m water depth (Fig. 3i). The [Nd] is generally highest in the uppermost sample of each station (maximum within the Caribbean is 21.8 pmol kg^{-1}) and decreases to a subsurface minimum within the upper 100–200 m, below which concentrations essentially stay constant.

Two distinct groups of ε_{Nd} compositions were measured for samples from within the high salinity SUW layer. At Stations 236-1, 222-1 and 220-1&2, ε_{Nd} is between −10.7 and −11.2 (Figs. 3d, e, f). In contrast, at station 162-1 in the central Colombia Basin ε_{Nd} is −10.3 at 70 m depth and becomes considerably more radiogenic (ε_{Nd} = −7.8) at 120 m depth in the core of the SUW (Fig. 3g). A similar pattern is seen at Florida Straits Station 200-2, where ε_{Nd} is −10 at 80 m and −8.1 at 96 m depth (Fig. 3k). The [Nd] in SUW at all stations is between 14.5 and 17.4 pmol kg^{-1}.

Although it is not clear if the relatively low salinity near-surface layers at Stations 194-13 and 200-2 (Fig. 2) have the same source, ε_{Nd} signatures and Nd concentrations in these samples are similar (Station 200-2, 140 m; Station 194-13, 50 and 90 m, ε_{Nd} between −7.4 and −8.8 and [Nd] between 16.6 and 17.3 pmol kg^{-1}). The ε_{Nd} composition of the shallowest sample measured at Station 194-13 (30 m) also falls within this range (ε_{Nd} = −8) (Fig. 3j).

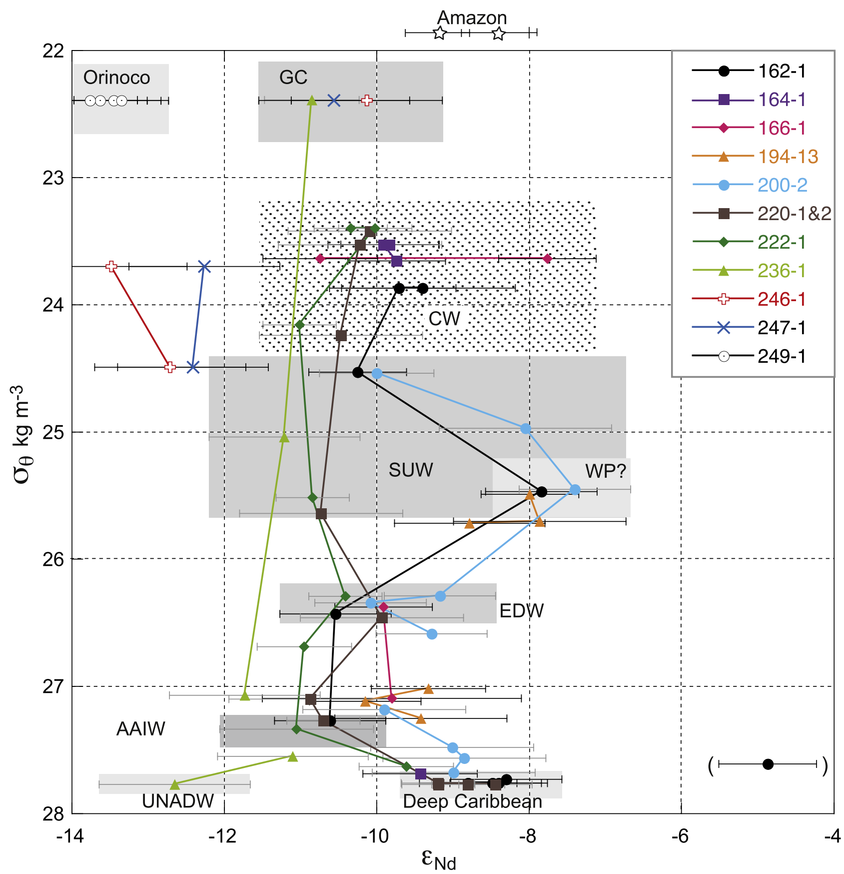

Fig. 4. Potential density versus ε_{Nd} for all stations. For near-surface samples where potential density was not measured, the value for the nearest underlying sample was taken, except for Stations 246-1, 247-1 and 249-1, where the shallowest samples have been plotted at the same potential density as the uppermost sample from Station 236-1. Potential density for the 30 m and 50 m samples at Station 247-1 was not measured and are plotted at the same potential densities as the 30 m and 50 m samples from nearby Station 246-1. The isotopic composition of Amazon River water is also indicated (open stars, Stordal and Wasserburg, 1986) but is not plotted on the potential density scale. Shading highlights the samples associated with different water masses, as determined from their hydrographic properties. Labels as before, except WP? water delivered via the Windward Passage.

4.2. Intermediate waters

The EDW has a narrow range of ε_{Nd} (−9.2 to −10.4) and [Nd] between 15.4 and 16.4 pmol kg^{-1}. Samples with lower temperatures between 12–17 °C show ε_{Nd} signatures ranging from −9.3 to −11 and [Nd] from 14.5 to 17.3 pmol kg^{-1}.

The three samples measured in the core of AAIW have very similar ε_{Nd} (−10.6 to −11). The [Nd] in AAIW ranges from 15.8 to 18.1 pmol kg^{-1}. Intermediate depth waters in the Florida Straits show slightly more radiogenic ε_{Nd} between −9 and −9.9 and [Nd] between 14.5 and 17.8 pmol kg^{-1}.

The sample at 1000 m depth at Station 162-1 in the central Colombia Basin is by far the most radiogenic of the entire data set ($\varepsilon_{Nd} = -4.9$) (Fig. 3g). Unlike the other samples in the Caribbean, it does not fall on the mixing line between AAIW and deeper water ε_{Nd}. As we have no analytical reason to exclude this data point, it is included in brackets in Figs. 3g and 4, but we will not further interpret it due to potential contamination.

4.3. Deep waters

Samples taken from waters deeper than 1500 m are significantly more radiogenic (ε_{Nd} between −8.3 and −9.2) than the 1530 m depth sample at Station 236-1 ($\varepsilon_{Nd} = -12.7$) representing the Atlantic inflow signature. [Nd] increases in the deep Caribbean to a maximum of 21 pmol kg^{-1}.

5. Discussion

5.1. Orinoco River and Guyana Current

The composition of surface waters closest to the Boca Grande river mouth indicates that dissolved Nd supplied by this branch of the Orinoco River is highly unradiogenic ($\varepsilon_{Nd} = -13.6$) (Fig. 3a). There are no published data for Orinoco River water itself but our result is, within error, identical to Lower Orinoco River sediments ($\varepsilon_{Nd} = -13.9$) (Goldstein et al., 1997) and to the least radiogenic detrital seafloor sediments measured on the Barbados Ridge and Demerara Rise, assumed to be of Orinoco and Amazon origin (White et al., 1985). Dissolved REEs in river water are rapidly removed from the dissolved fraction upon entering estuaries (Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Martin et al., 1976; Porcelli et al., 2009; Sholkovitz, 1993; Sholkovitz and Elderfield, 1988). Sea surface salinity at Station 249-1 is 29.6 psu (Schönfeld et al., 2011) and [Nd] is 57.4 pmol kg^{-1}. The concentration of dissolved Nd at similar salinities close to the Amazon river mouth is ∼40 pmol kg^{-1}, which is a factor of 10 lower than [Nd] measured at the mouth of the Amazon in waters at a salinity of 0.03 psu (Sholkovitz, 1993). Therefore, although [Nd] is high at Station 249-1, it is likely that the vast majority of REE removal from the Orinoco dissolved load had already occurred further upstream.

Further removal of Nd is likely responsible for the 50% decrease in [Nd] in the surface waters between Station 249-1 and 246-/247-1 to ∼24 pmol kg^{-1} (Fig. 3b, c). There is also a change to more radiogenic ε_{Nd} at 10 m water depth at Stations 246-1 and 247-1 (-10.4), which suggests mixing with Nd supplied by the Amazon River ($\varepsilon_{Nd} = -8.4$ to -9.2, Stordal and Wasserburg, 1986) and transported by the Guyana Current. The samples were taken in March, when the ITCZ was in a southerly position and the NBC continued in northwesterly direction along the South American Coast and entrained Amazon waters into the Guyana Current (Fig. 1). A similar composition to that of Stations 246-1 and 247-1 was recorded further downstream in the surface waters of Station 236-1 ($\varepsilon_{Nd} = -10.9$) (Fig. 3d). Remarkably, samples below the halocline at Stations 246-1 and 247-1 are significantly less radiogenic than those from 10 m depth (ε_{Nd} averages -12.3 at 246-1 and -13.1 at 247-1) and have much lower [Nd] (12 to 14 $pmol\,kg^{-1}$) (Fig. 3b, c). This composition is similar to that measured at Station 249-1 and to results of an earlier study at the Demerara Rise (White et al., 1985), which may indicate a contribution of unradiogenic ε_{Nd} signatures released from Orinoco River sediment particles. However, [Nd] is not elevated and the isotopic composition is also similar to that of a recently published seawater ε_{Nd} profile above Demerara Rise to the east of the Orinoco river mouth (Fig. 1, KNR197-68), which showed an $\varepsilon_{Nd} = -12.6$ at 50 m water depth (Huang et al., 2014). Despite short-term variability, Atlantic surface seawater away from the shelf was shown to have a relatively unradiogenic ε_{Nd} of -13.9 and moderate [Nd] (18 kg^{-1}) (Piepgras and Wasserburg, 1987), suggesting that the profiles of Stations 246-1 and 247-1 reflect Atlantic seawater overlain by a low salinity layer containing contributions from Amazon and Orinoco river water.

5.2. Caribbean surface water

Surface waters in the Caribbean are systematically enriched in Nd compared to underlying waters (Fig. 3). For the majority of the surface samples, ε_{Nd} is between -11.0 and -9.4, (Fig. 4) and is consistent with the advection of dissolved Nd from the Amazon/Orinoco via the Guyana Current. It is also expected that dissolved Nd from the Magdalena River, the sediments of which have an $\varepsilon_{Nd} = -8.3$ (Goldstein et al., 1984), would contribute to the surface water signal, particularly near Station 162-1. In this area a coastal counter current flowing eastward along the northern coast of South America merges with the westward flowing Caribbean Current to produce a broad plume of total suspended sediment in surface waters, which moves northwards and encompasses Station 162-1 (Bassin, 1976). Although the surface water ε_{Nd} signature is not distinctly different from the other CW samples, there is a change towards a more radiogenic ε_{Nd} signature at 120 m (-7.8) (Fig. 3g). It is noted that Station 162-1 also showed an excursion to radiogenic ε_{Nd} (-4.9) at 1000 m, which would not be predicted from simple water mass mixing, and as such, the region close to the outflow of the Magdalena River and its shelf sediments warrants further investigation in order to confirm these numbers and investigate the processes involved.

The sample from 11 m water depth at Station 166-1 in the Yucatan Channel is more radiogenic ($\varepsilon_{Nd} = -7.8$) than all other Caribbean surface water samples (Fig. 4) while the 40 m sample falls within the typical CW ε_{Nd} range (-10.7) (Fig. 4), suggesting that surface waters were affected by local inputs. The Yucatan Peninsula is a large limestone platform and therefore an unlikely source of radiogenic ε_{Nd}. The GEOROC compilation (Fig. A1), however, indicates the presence of radiogenic rocks in central and eastern Cuba, which are a potential source for the signal at Station 166-1, although surface currents would also be expected to transport water from this region to Station 164-1, which shows no excursion to more radiogenic values in the upper water column (Figs. 3h and 4). Likewise, the absence of radiogenic ε_{Nd} compositions in the surface waters of the other Caribbean stations argues against a significant contribution of radiogenic Nd to the surface ocean from the Antilles Arc volcanic rocks (Fig. A1).

5.3. Subtropical under water

Despite similarities in temperature and salinity, SUW in the southeastern Caribbean has a distinctly less radiogenic ε_{Nd} (-10.7 to -11.2) than in the central Caribbean ($\varepsilon_{Nd} = -7.8$) and in the Florida Straits ($\varepsilon_{Nd} = -8.1$) (Fig. 4). One factor contributing to this difference may be the different sources of SUW transported into the Caribbean. The Northern Equatorial Current moves waters westward into the Caribbean basin (Fig. 1). This current travels along the southern part of the anticyclonic subtropical gyre and the northern part of the cyclonic tropical gyre; the average latitude of the boundary between the two gyres is 15°N (Wilson and Johns, 1997). Fig. 1 shows the locations of stations within the two gyres. Station TTO/TAS 63, within the cyclonic tropical gyre, has $\varepsilon_{Nd} = -12.6$ at 200 m water depth (Piepgras and Wasserburg, 1987). In the subtropical gyre, ε_{Nd} is -9.6 at 50 m at station OCE 63-1-1, – (Piepgras and Wasserburg, 1980) and -10.1 at 75 m at BATS (Pahnke et al., 2012). In a more complete profile further to the North (All 109-1 Stn30, not shown), ε_{Nd} is -9.4 at 200 m water depth (Piepgras and Wasserburg, 1987). It is therefore reasonable to expect that SUW originating from the subtropical gyre is more radiogenic than that entering from the south. However, this cannot fully explain a signal of $-7.8\varepsilon_{Nd}$ at Station 162-1 or $-8.1\varepsilon_{Nd}$ at Station 200-2. As previously mentioned, no firm conclusions can be made about contributions from the Magdalena River, which would be expected to have $\varepsilon_{Nd} = -8.3$ (Goldstein et al., 1984). Signatures in the range -7.4 to $-8.8\varepsilon_{Nd}$ at Stations 194-13 and 200-2 are associated with $[O_2]$ greater than 4.5 $mg\,L^{-1}$ (Figs. 3 and A2). As discussed in Section 3.1, high $[O_2]$ is also observed in waters entering via the Windward Passage (Roemmich, 1981) and appears to be transferred to the Florida Straits (Schmitz and Richardson, 1991). Radiogenic ε_{Nd} compositions between $+2$ and $+14$ were obtained for volcanic rocks from eastern Cuba (Fig. A1). No data are available for northwestern Haiti but the geology of the region (Draper et al., 1995) includes rock types that typically have highly radiogenic ε_{Nd}. More seawater data are needed before firmer conclusions can be reached about any addition of or exchange with radiogenic Nd sources in the Windward and other Antilles passages.

5.4. Eighteen degree water and 12–17 °C water

Water samples taken from the 17–19 °C temperature range which defines EDW (Worthington, 1976) have ε_{Nd} signatures between -9.2 and -10.4 (Fig. 4) and show essentially no difference from the composition of seawater at 200 to 400 m in the western North Atlantic subtropical gyre ($\varepsilon_{Nd} = -9.4$ to -10.6, Piepgras and Wasserburg, 1987). In the water mass comprising the 12–17 °C temperature range, only three samples were obtained. The two samples from the northerly Stations 194-13 and 200-2 ($\varepsilon_{Nd} = -9.3$) are more radiogenic than the one from the southeasterly Station 222-1 ($\varepsilon_{Nd} = -11$) (Fig. 4). These results are consistent with intermediate waters in the northerly stations originating in the subtropical gyre, and intermediate waters in the southwest Caribbean originating in the tropical gyre, similar to the circulation pathway of SUW.

5.5. Antarctic intermediate water

AAIW within the Caribbean has a narrow range of compositions ($\varepsilon_{Nd} = -10.6$ to -11) (Fig. 4) and is within the error of measurements from stations in the western North Atlantic at Demerara Rise (-10.1 to -10.7, Huang et al., 2014). No sample was measured

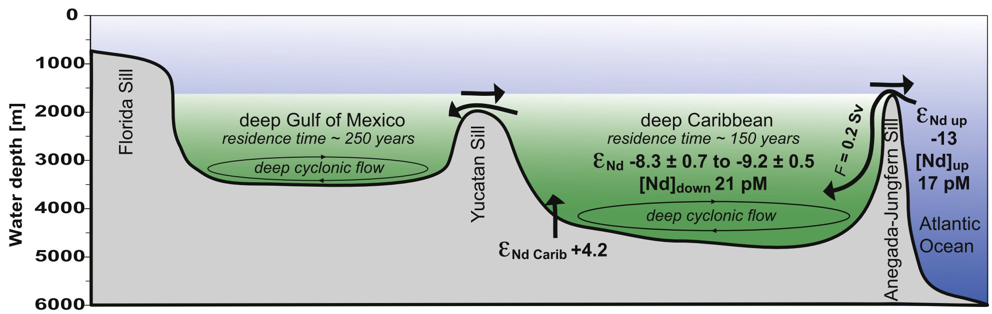

Fig. 5. Schematic of the major features of deepwater circulation and Nd composition in the Caribbean and Gulf of Mexico. ε_{Nd} up and $[Nd]_{up}$, Atlantic Nd composition and concentration at ∼1800 m (Piepgras and Wasserburg, 1987; Tachikawa et al., 2004). F, average deepwater inflow rate (Fratantoni et al., 1997; Joyce et al., 1999; MacCready et al., 1999; Stalcup et al., 1975; Sturges, 1975; Worthington, 1955). $\varepsilon_{Nd\,Carib}$, average composition of lithogenic sources to the Caribbean (GEOROC database, 2012). Deep Caribbean residence time from Joyce et al. (1999); deep Gulf of Mexico residence time from Rivas et al. (2005).

from the core of AAIW at Station 236-1, but measurements taken above and below show ε_{Nd} signatures of −11.7 and −11.1, respectively and are thus also consistent with the Huang et al. (2014) profiles. It appears that AAIW, as identified by the salinity minimum (Fig. 2), retains its relatively unradiogenic ε_{Nd} composition during its passage through the Caribbean. This is also confirmed by data ($\varepsilon_{Nd} = -10.6$) obtained from a hydrogenetic ferromanganese crust layer at 600–900 m water depth on the Caribbean basin side of the northern Lesser Antilles (Frank et al., 2006). It is also clear from both the salinity and ε_{Nd} data that AAIW is no longer discernable as a distinct water mass in the Florida Straits (Figs. 2 and 4), which potentially complicates the interpretation of paleoceanographic records from the region (Xie et al., 2012).

5.6. Upper North Atlantic deep water

Unlike AAIW, which retains its Atlantic-derived ε_{Nd} characteristics during its transit through the Caribbean until it cannot be distinguished any more based on hydrographic properties due to mixing, our data suggest that ε_{Nd} in deep waters is modified by addition from and/or exchange with local, radiogenic sources. Prior to entering the Caribbean the deep waters at Station 236-1 carry an ε_{Nd} of −12.7 at 1530 m water depth, which is intermediate between the nearest 'open ocean' data point for UNADW at Station TTO/TAS 63 ($\varepsilon_{Nd} = -13.3$ at 1990 m, Piepgras and Wasserburg, 1987) and a sample measured at 2000 m water depth near the Demerara Rise (−12.0, Huang et al., 2014). Inside the Caribbean basin, the deepest waters generally have ε_{Nd} between −8.3 and −9.2, at least 3 epsilon units more radiogenic than incoming Atlantic waters (Fig. 4). Concentrations of dissolved Nd increase in the deep basin to 21 $\mathrm{pmol\,kg^{-1}}$, similar to surface water concentrations in the Caribbean (Fig. 3). Release of Nd from dissolving particles is thought to be mainly responsible for this typical increase in concentration with depth (e.g. de Baar et al., 1985; Elderfield, 1988).

Three important conditions are responsible for the difference in the behavior of AAIW from that of UNADW in the Caribbean. First, AAIW enters the Caribbean through at least eight passages deeper than 800 m, whereas overflow into the abyssal Venezuela and Colombia basins only occurs via the Anegada-Jungfern sill (Johns et al., 2002). There is insufficient buoyancy loss within the Caribbean to allow deep water formation (MacCready et al., 1999; Schmitt et al., 1989). Second, intermediate waters (of which AAIW is at the lower boundary), flow through the Caribbean at a rate of ∼5 Sv (Schmitz and Richardson, 1991) whereas deep water replenishment in the deep Caribbean is sporadic and averages only ∼0.2 Sv (Fratantoni et al., 1997; Joyce et al., 1999; MacCready et al., 1999; Stalcup et al., 1975; Sturges, 1975; Worthington, 1955). Third, waters deeper than the Florida Sill (∼800 m) can only leave the Caribbean and Gulf of Mexico by mixing and diffusion with overlying water (Rivas et al., 2005) or by return flow through the deeper Caribbean passages (Sturges, 2005).

Given that no deep water forms within the Caribbean or Gulf of Mexico, other processes must account for the addition of radiogenic Nd to the deep waters. Possible processes are the release of Nd from sinking river or dust particles, interaction of seawater with sediments deposited on the Caribbean shelves and sea-floor, release of Nd from pore waters, and submarine groundwater discharge (e.g. Albarède and Goldstein, 1992; Elderfield and Sholkovitz, 1987; Grenier et al., 2013; Henry et al., 1994; Jeandel et al., 1998; Johannesson and Burdige, 2007; Lacan and Jeandel, 2001, 2005a, 2005b; Rickli et al., 2009; Sepulchre et al., 2014; Sholkovitz and Szymczak, 2000; Siddall et al., 2008). To calculate how much of the change in ε_{Nd} in the deep Caribbean can be accounted for by addition of radiogenic Nd from within the basin, we follow the approach of Lacan and Jeandel (2001). If addition was the only process modifying the incoming water, then the following equation should be balanced:

$$\varepsilon_{Nd\,result} = \Big\{[Nd]_{up} \times F \times \varepsilon_{Nd\,up} + \big([Nd]_{down} - [Nd]_{up}\big) \times F \times \varepsilon_{Nd\,Carib}\Big\} / \big([Nd]_{down} \times F\big) \quad (1)$$

where $\varepsilon_{Nd\,result}$ is the isotopic composition of seawater in the deep Caribbean, $[Nd]_{up}$ and $\varepsilon_{Nd\,up}$ are the concentration and isotopic composition of incoming seawater respectively, $[Nd]_{down}$ is the concentration of Nd in the deep Caribbean, $\varepsilon_{Nd\,Carib}$ is the composition of lithogenic sources within the Caribbean and F is the rate of deep water renewal.

The inputs to the deep Caribbean are depicted in Fig. 5. The deepest water entering the Caribbean consists of 85% UNADW, 10% AAIW and 5% MOW (de Menocal et al., 1992; Kawase and Sarmiento, 1986). The Nd isotope composition (and Nd concentration) of this water mass is therefore calculated as 85% contribution of −13.3 (17 $\mathrm{pmol\,kg^{-1}}$), 10% of −11.8 (15 $\mathrm{pmol\,kg^{-1}}$) (Piepgras and Wasserburg, 1987), and 5% −9.4 (17 $\mathrm{pmol\,kg^{-1}}$) (Tachikawa et al., 2004). Discounting the small differences in [Nd], this mixture brings water into the deep Caribbean with an $\varepsilon_{Nd\,up} = -13$ and $[Nd]_{up} = 17\ \mathrm{pmol\,kg^{-1}}$. Within the deep Caribbean, $[Nd]_{down} = 21\ \mathrm{pmol\,kg^{-1}}$. The replenishment rate, F, of deep waters in the Caribbean, is taken to be 0.2 Sv (Fratantoni et al., 1997; MacCready et al., 1999; Stalcup et al., 1975; Sturges, 1975; Worthington, 1955), therefore $3.6 \times 10^6\ \mathrm{g\,yr^{-1}}$ Nd are added to the basin. The average ε_{Nd} of lithogenic sources in the Caribbean and Gulf of Mexico ($\varepsilon_{Nd\,Carib}$) is taken from the GEOROC database (+4.2, Fig. A1). Deep cyclonic flow within the Caribbean basin (Joyce et al., 2001) and the Gulf of Mexico (DeHaan and Sturges, 2005), as well as exchange between the basins (Rivas et al., 2005; Sturges, 2005) homogenize the ε_{Nd} signature of the deep waters.

Eq. (1) gives $\varepsilon_{Nd\,result} = -9.7$, i.e. the addition of Nd from lithogenic sources with an average ε_{Nd} of +4.2 is within error

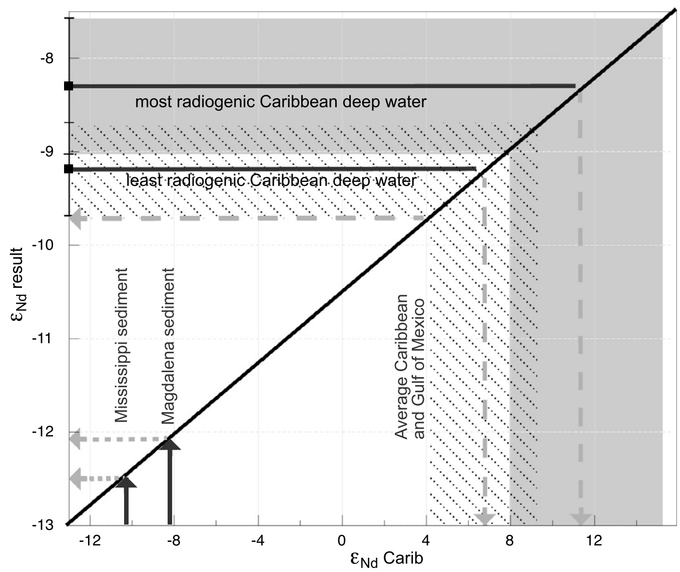

Fig. 6. Graphical depiction of Eq. (1) (Lacan and Jeandel, 2001) for the deep Caribbean. Incoming water with $\varepsilon_{\text{Nd up}} = -13$ and $[\text{Nd}]_{\text{up}} = 17$ pmol kg^{-1} (de Menocal et al., 1992; Piepgras and Wasserburg, 1983, 1987) is modified by the addition of Nd with composition $\varepsilon_{\text{Nd Carib}}$. The average ε_{Nd} of continental rocks surrounding the Caribbean and Gulf of Mexico is +4.2 (GEOROC database), which could produce a deep Caribbean composition ($\varepsilon_{\text{Nd result}}$) of −9.2. Horizontal black lines indicate the least and most radiogenic seawater compositions of the deep Caribbean measured in this study and the diagonal hatched area and grey shaded area show the 2σ external reproducibility for these measurements respectively. Vertical dashed grey lines and the associated hatching and shading show the compositions of $\varepsilon_{\text{Nd Carib}}$ required to produce the observed range of ε_{Nd} in the deep Caribbean. Also shown are the compositions of sediment in the Magdalena and Mississippi Rivers (Goldstein et al., 1984).

of the least radiogenic sample in the deep Caribbean ($-9.2 \pm 0.5\varepsilon_{\text{Nd}}$) (Fig. 6). To account for the most radiogenic deep water ε_{Nd} measured, the average composition of the sources would have to be at least $+8\varepsilon_{\text{Nd}}$. While it has been observed that volcanogenic material readily releases Nd on contact with seawater (Pearce et al., 2013), it is likely that even the average ε_{Nd} in the GEOROC database (+4.2) is heavily weighted towards radiogenic, volcanogenic rock samples and does not include, for example, carbonate platforms which formed from seawater and are therefore likely to have a significantly less radiogenic Nd composition, albeit at low concentrations. Thus an average contribution of material with $\varepsilon_{\text{Nd}} = +8$ is not realistic. Other possible sources are the Magdalena and Mississippi rivers, which have sediments with $\varepsilon_{\text{Nd}} = -8.3$ and -10.9 respectively (Goldstein et al., 1984) and could account for a shift in the deep Caribbean seawater composition to $-12.1\varepsilon_{\text{Nd}}$ at most (Fig. 6).

The majority of seawater samples from the deep Caribbean have $\varepsilon_{\text{Nd}} > -9.7$. In order to produce the observed shift in ε_{Nd} without exceeding the increase in [Nd], there needs to be removal of unradiogenic Nd and addition of radiogenic ε_{Nd} at the same time. Sinks for Nd in the deep ocean include adsorption to ferromanganese coatings of the particles, ferromanganese crusts, and nodules that form at the sediment/seawater interface. Nd released from seafloor sediments or sinking particles may be adsorbed or re-precipitated onto those same particles, i.e. by 'reversible scavenging' (Siddall et al., 2008) or by a 'boundary exchange' process (Arsouze et al., 2009; Lacan and Jeandel, 2005a, 2005b; Rempfer et al., 2011). This re-deposited Nd may have the same ε_{Nd} as released from the particles or may be a mixture with laterally transported Nd. Nd may also have been released at one location and be transported to another, where the hydrographic properties are different, before re-precipitation or adsorbtion occurs. Similar processes have been observed in the deep semi-enclosed Arctic basin (Andersson et al., 2008; Porcelli et al., 2009).

The amount of Nd supplied to and recycled within the oceans is poorly constrained (Rempfer et al., 2011) as it is inherently difficult to quantify rates of removal and release from sinking particles and seafloor sediments. Sepulchre et al. (2014) presented a modeling experiment of the Nd isotope composition of the Caribbean as a function of a closed Panama seaway. Their results suggested a highly radiogenic Nd isotope composition near $\varepsilon_{\text{Nd}} = 0$ for Caribbean deep water, most likely a consequence of an overestimation of the release of Nd from continent derived particles and an underestimation of the horizontal velocities of the deep waters in the Caribbean basin.

Our data from the Caribbean allow a semi-quantitative estimate of the amount of uptake and release required to balance the Nd budget in the deep basin. Taking $+4.2\varepsilon_{\text{Nd}}$ to be the upper limit for the radiogenic Nd isotope endmember composition of Nd sources within the Caribbean and Gulf of Mexico, and assuming that Nd with this composition has already been added to the incoming water to increase the concentration to 21 pmol kg^{-1} and to change the composition to $-9.7\varepsilon_{\text{Nd}}$, a minimum of 5.3 ± 2.7 pmol kg^{-1} would need to be removed and replaced by Nd with $\varepsilon_{\text{Nd}} = +4.2$ in order to change the ε_{Nd} of dissolved Nd in the deep Caribbean to the most radiogenic value of -8.3 ± 0.7. With a replenishment rate of 0.2 Sv (Worthington, 1955; Stalcup et al., 1975; Sturges, 1975; Fratantoni et al., 1997; MacCready et al., 1999), this equates to $4.8 \pm 2.5 \times 10^6$ g Nd yr^{-1} if all Caribbean deep water were to obtain this most radiogenic value.

Both deepest seawater profiles in this study are from the center of the Caribbean basin and therefore likely represent an integrated signal of all sources to the deep Caribbean. There, core-top foraminifera coatings from ~3000 m have an average ε_{Nd} signature of −8.9 (Osborne et al., 2014), consistent with the signatures of the deepest waters of the two deepest profiles at Stations 220-1&2 and 162-1. In contrast, the surface scrapings of a hydrogenetic ferromanganese crust from 2000 m in the central Caribbean has $\varepsilon_{\text{Nd}} = -11.6$ (Whiteley, 2000), significantly less radiogenic than the present day seawater Nd isotope composition at equivalent water depth (Fig. 3). The ferromanganese crust surface, however, integrates the seawater ε_{Nd} over tens of thousands of years and it may well be that the composition of seawater was less radiogenic in the past. On the other hand, the crust may provide evidence for heterogeneity of sources and sinks of Nd within the Caribbean. A key region for future study would be the Magdalena River fan, given that other studies have found evidence for significant release of Nd from river-borne particles (Bayon et al., 2004; Kraft et al., 2013; Rickli et al., 2009). It would thus be expected that sediments from the Magdalena River release significant amounts of Nd to the surrounding waters with an $\varepsilon_{\text{Nd}} = -8.3$ (Goldstein et al., 1984).

In summary, we suggest that owing to the long residence time of deep waters in the Caribbean and Gulf of Mexico (Joyce et al., 1999; Rivas et al., 2005), the ε_{Nd} of the incoming Atlantic water mixes with Nd released from sinking or deposited particles, or their coatings, and that some of this Nd is re-precipitated or adsorbed at the same time resulting in an average $\varepsilon_{\text{Nd}} = -8.4$ and [Nd] = 21 pmol kg^{-1} for Caribbean deep waters.

6. Conclusions

This work presents the first ε_{Nd} and Nd concentration data for seawater in the Caribbean, as well as in the Florida Straits and for surface water stations close to the Orinoco River mouth.

Waters dominated by the Orinoco River close to its mouth are characterized by an unradiogenic ε_{Nd} signature of −13.6 and [Nd] = 57 pmol kg^{-1} at a salinity of 29.6 psu (Schönfeld et al., 2011), indicating substantial removal of Nd in the Orinoco estuary. The

Guyana Current has an $\varepsilon_{Nd} = -10.9$ and [Nd] = 22 pmol kg^{-1} when it enters the Caribbean. Where Amazon/Orinoco plume water contributes to surface waters in the Caribbean, ε_{Nd} is mostly within −9.4 to −11 and [Nd] is ∼20 pmol kg^{-1}.

SUW in the southern and eastern parts of the Caribbean shows ε_{Nd} consistent with supply from the tropical Atlantic gyre; SUW in the northern Caribbean and Florida Straits is more radiogenic consistent with values from the subtropical Atlantic gyre. The EDW ε_{Nd} signature is similar to that measured in its source area between 200 and 400 m in the subtropical gyre (Piepgras and Wasserburg, 1980, 1987). Water in the temperature range of 12–17 °C shows a separation between a South Atlantic source in the southeastern Caribbean and a North Atlantic source in the Florida Straits.

AAIW has a narrow range of compositions ($\varepsilon_{Nd} = -10.6$ to −11) in the Caribbean, which is within error of the composition at the nearest available sites in the western Atlantic (Huang et al., 2014; Piepgras and Wasserburg, 1987). Neither the AAIW salinity minimum nor the relatively unradiogenic ε_{Nd} composition is seen in the Florida Straits, documenting that AAIW is not a major component of intermediate waters in the northernmost part of the study area today.

Deep waters in the Caribbean are more radiogenic ($\varepsilon_{Nd} = -8.3$ to −9.2) than the incoming mix of UNADW, AAIW and MOW ($\varepsilon_{Nd} = -13$, de Menocal et al., 1992; Piepgras and Wasserburg, 1983, 1987). Within error, the least radiogenic deep water compositions can be explained by addition of Nd from radiogenic source rocks around the Caribbean and Gulf of Mexico, although this is likely an upper limit as the average ε_{Nd} extracted from the data in the GEOROC database is biased towards volcanogenic, and therefore radiogenic, material. The long residence time of deep waters in the Caribbean and Gulf of Mexico (Joyce et al., 1999; Rivas et al., 2005) allows Nd in deep waters to partly adopt the average ε_{Nd} of all sedimentary and particulate sources of the basin whereas we show that this must at the same time also be accompanied by uptake (adsorption) of Nd by particles and thus removal from the water column (boundary exchange).

In summary, surface and intermediate waters flow through the Caribbean with essentially unchanged ε_{Nd} whereas deep waters are strongly modified. This finding has general implications for paleoceanographic studies in restricted basins, where the composition of seawater is sensitive to its residence time within the basin.

Contributions

A.O. processed and interpreted the data; B.H. and E.H. analyzed the samples; A.O., B.H., E.H, S.F. and M.F. jointly discussed the data and wrote the paper.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.09.011.

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