



The “zircon effect” as recorded by the chemical and Hf isotopic compositions of Lesser Antilles forearc sediments

Marion Carpentier ^{a,*}, Catherine Chauvel ^a, René C. Maury ^b, Nadine Mattielli ^c

^a Laboratoire de Géodynamique des Chaînes Alpines, CNRS, Université Joseph Fourier, BP 53, 38041 Grenoble, France

^b Domaines Océaniques, IUEM, UMR 6538, Université de Bretagne Occidentale, Place Nicolas Copernic, 29280 Plouzané, France

^c Département des Sciences de la Terre et de l'Environnement, Université Libre de Bruxelles, CP 160/02, Avenue FD. Roosevelt, 50, 1050 Bruxelles, Belgium

ARTICLE INFO

Article history:

Received 2 February 2009

Received in revised form 23 July 2009

Accepted 30 July 2009

Available online 18 September 2009

Editor: R.W. Carlson

Keywords:

oceanic sediments

Lesser Antilles

Hf–Sr isotopes

zircon effect

major and trace elements

ABSTRACT

Oceanic sediments contain the products of erosion of continental crust, biologic activity and chemical precipitation. These processes create a large diversity of their chemical and isotopic compositions. Here we focus on the influence of the distance from a continental platform on the trace element and isotopic compositions of sediments deposited on the ocean floor and highlight the role of zircons in decoupling high-field strength elements and Hf isotopic compositions from other trace elements and Nd isotopic compositions.

We report major and trace element concentrations as well as Sr and Hf isotopic data for 80 sediments from the Lesser Antilles forearc region. The trace-element characteristics and the Sr and Hf isotopic compositions are generally dominated by detrital material from the continental crust but are also variably influenced by chemical or biogenic carbonate and pure biogenic silica. Next to the South American continent, at DSDP Site 144 and on Barbados Island, sediments, coarse quartz arenites, exhibit marked Zr and Hf excesses that we attribute to the presence of zircon. In contrast, the sediments from DSDP Site 543, which were deposited farther away from the continental platform, consist of fine clay and they show strong deficiencies in Zr and Hf. The enrichment or depletion of Zr–Hf is coupled to large changes in Hf isotopic compositions ($-30 < \varepsilon_{\text{Hf}} < +4$) that vary independently from the Nd isotopes. We interpret this feature as a clear expression of the “zircon effect” suggested by Patchett and coauthors in 1984. Zircon-rich sediments deposited next to the South American continent have very low ε_{Hf} values inherited from old zircons. In contrast, in detrital clay-rich sediments deposited a few hundred kilometers farther north, the mineral fraction is devoid of zircon and they have drastically higher ε_{Hf} values inherited from finer, clay-rich continental material.

In the two DSDP sites, average Hf isotopes are very unradiogenic relative to other oceanic sediments worldwide ($\varepsilon_{\text{Hf}} = -14.4$ and -7.4) and they define the low Hf end member of the sedimentary field in Hf–Nd space. Their compositions correspond to end members that, when mixed with mantle, are able to reproduce the pattern of volcanic rocks from the Lesser Antilles. More generally, we find a relationship between Nb/Zr ratios and the vertical deviation of Hf isotope ratios from the Nd–Hf terrestrial array and we suggest that this relationship can be used as a tool to distinguish sediment input from fractionation during melting during the formation of arc lavas.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Worldwide oceanic sedimentation results from the combined effects of three main processes: the deposition of detrital grains of continental origin, the accumulation of biogenic materials derived from marine organisms and chemical precipitation of components dissolved in seawater. These processes are influenced by the location and mechanism of deposition, and the composition of the final sediment depends strongly on factors such as the distance to continental sources, the carbonate

compensation depth, the level of biological activity and the sedimentation rate, which all vary within individual ocean basins.

In the Lesser Antilles forearc on the Atlantic oceanic plate, the sedimentation rate is high and the authigenic component is low (Wright, 1984). In this region, two sediment-forming processes compete, the accumulation of biogenic material and input of detrital material from the nearby continental platforms. This area is thus a good target to study the composition of the detrital fraction and compare it to average upper continental crust. By selecting sites located at various distances from the continental shelf, we can investigate the geographical changes and relate them to sedimentary sorting – preferential deposition of coarser-grained material near the continent and dispersion of the finer clay-rich

* Corresponding author.

E-mail address: Marion.Carpentier@ujf-grenoble.fr (M. Carpentier).

fraction – during transport of the crustal material away from the continent. The Pb–Nd–Sr isotopic compositions of surface sediments in the Lesser Antilles forearc domain display a north–south geochemical gradient that White et al. (1985) attribute to a southward increase of detrital input supplied by the Orinoco River which drains the Guyana Precambrian shield. Our investigation extends this approach to a large set of trace element and Sr–Hf isotopic data obtained on sediments deposited over a period of about 115 Ma.

We analyzed sediments from three sites located in front of the Lesser Antilles island arc at distances of 340 km (Site DSDP 144), 480 km (Barbados Island) and 860 km (Site DSDP 543) from the South American continent. In a previous paper (Carpentier et al., 2008), we showed that changes of the Pb–Nd isotopic compositions of these sediments mimic the north–south isotopic variation along the Lesser Antilles island arc (White and Dupré, 1986). The northern sediments have relatively unradiogenic Pb compositions while the southern sediments have elevated values due to the proximity of the South American continent and to the presence of black shale layers with extreme Pb isotopic compositions.

Here, we report major and trace element concentrations as well as Hf and Sr isotopic compositions of about 80 sediments and examine these data together with the previously published Nd isotopic compositions. The main goal of the present paper is to use the geochemical data to help

understand the processes that control the compositions of oceanic sediments. We show that detrital input from the Southern American continent dominates the sedimentary budget for most elements in the entire area. In addition, we establish that fractionation of Zr and Hf relative to other trace elements is correlated with the distance to the continent and is related to the proportion of zircon-rich sands in the detrital fraction. Finally, we calculate the average sediment compositions for the three sites, compare them to GLOSS (Global Subducting Sediment; Plank and Langmuir, 1998), and evaluate the potential impact of these detrital sediments on the sources of magmas of the Lesser Antilles island arc, as they are introduced by the subduction into the mantle.

2. Geological background and sampling

The Atlantic oceanic plate approaches the Lesser Antilles trench from the east (Fig. 1) at a rate of about 2 cm/year (Minster and Jordan, 1978). Cretaceous crust is currently subducting beneath the volcanic arc and, because of the geometry of the arc–ridge system, its age increases from ca. 80 Ma in the north to more than 105 Ma in the south (Westbrook et al., 1984; Carpentier et al., 2008). The forearc region is dominated by a large accretionary complex, the Barbados Ridge, which is also characterized by a north–south gradient in lithology and thickness of the

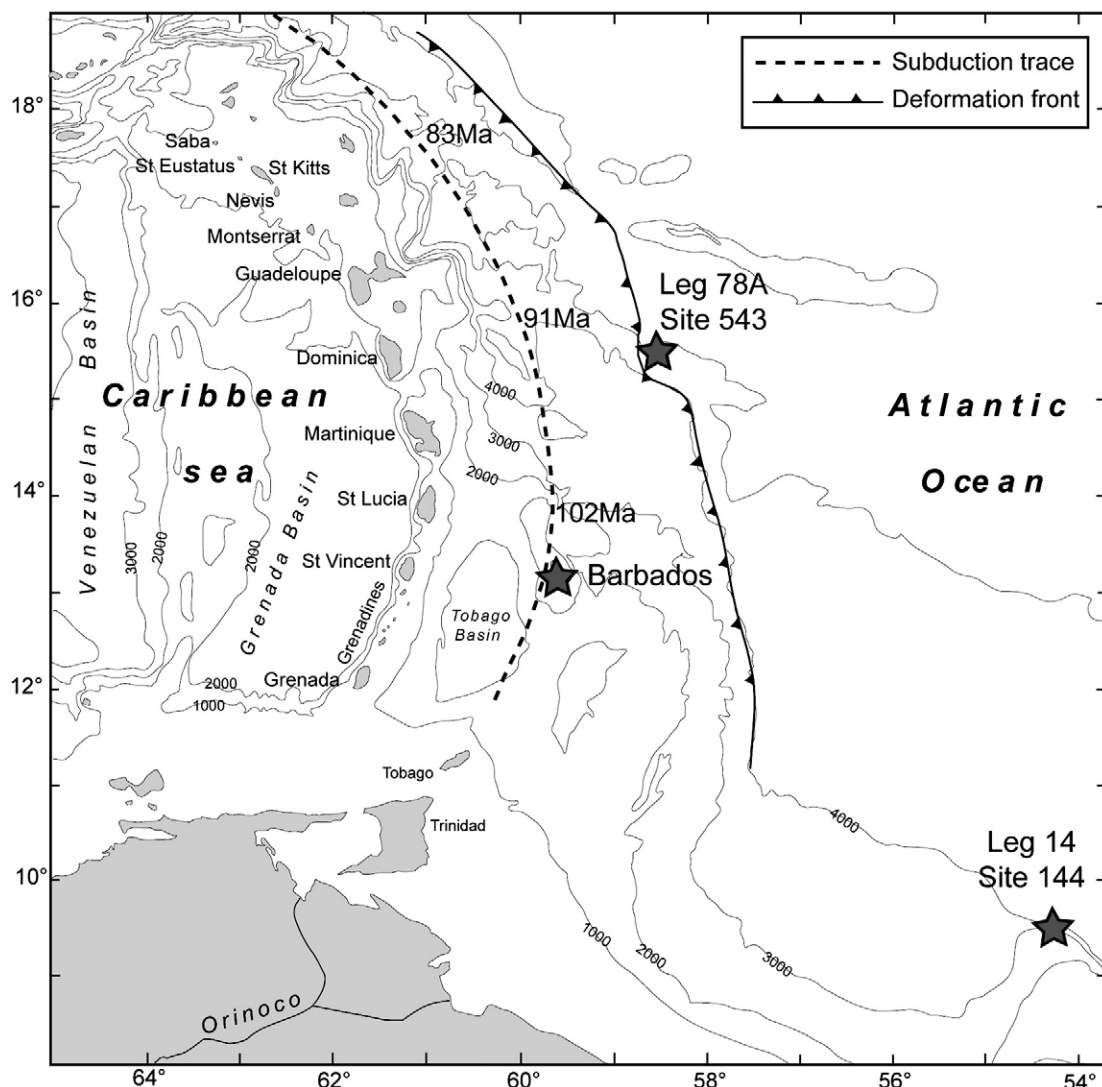


Fig. 1. Bathymetric map of the studied area showing the location of the three sampled sites (DSDP 78A Site 543, DSDP 14 Site 144 and Barbados Island), modified from Speed et al. (1984) and Carpentier et al. (2008). The age of the subducting slab is indicated next to the trench.

sediment pile. In the northern part of the forearc region, the sediments are less than 1 km thick and mainly pelagic. In its southern part, the sequence is more than 10 km thick and consists largely of terrigenous turbidites which are exposed in Barbados Island. The Amazon and Orinoco Rivers, which drain the South American continent, are the main source of terrigenous sediments in the area and the decreasing sediment thickness from south to north is probably due to the declining turbiditic input from these rivers (Westbrook et al., 1984).

Biju-Duval et al. (1984) documented the lithologies, ages and thickness of Atlantic sediments facing the trench in their study of core from Site 543 (Fig. 1) of DSDP Leg 78A. At this site, the 82 Ma old basaltic basement is overlain by a 410-m-thick sedimentary sequence that consists mainly of pelagic and radiolarian clays. A décollement surface at 170 m depth separates overthrust sediments from deeper sediments which are thought to be subducting beneath the accretionary prism (Westbrook, 1982; Moore et al., 1982; Biju-Duval et al., 1982; Westbrook and Smith, 1983).

Farther south, the age and nature of the sedimentary pile entering the trench is not as well constrained because no deep drilling has been done near the deformation front. The composition of sediments located in front of the southern part of the arc can be constrained, however, using samples from Barbados Island, which belongs to the accretionary prism, and from sediments cored at Site 144 (Leg DSDP 14) on the Demerara Plateau (Fig. 1). Both sites are located closer to the South American continent than Site 543.

Precise locations of samples from all three sites are given in Supplemental file 1, together with their estimated ages and lithological characteristics, locations within the DSDP cores and the geographical locations of the Barbados samples. The Nd and Pb isotopic compositions, as well as more detailed lithologies are reported by Carpentier et al. (2008). In Supplemental file 2, we show the sedimentary columns for the two DSDP sites, together with the mineralogical changes as a function of depth, as described by Hayes et al. (1972) and Biju-Duval et al. (1984).

Twenty-eight samples were selected to represent the diversity of sediment lithologies at Site 543, drilled at 5630 m water depth. All samples are located beneath the décollement level at 170 m depth and they were deposited below the carbonate compensation depth (CCD) (Hemleben and Troester, 1984) between ~82 and 16 Ma ago. The sediments consist mainly of clays and radiolarites, and the proportion of the silica biogenic component never exceeds 50% (Supplemental file 2a). The oldest unit, which immediately overlies the basaltic basement, contains some calcium carbonate, and volcanic ash layers were identified in the upper Miocene Unit 4.

Thirty-eight samples were selected from the 350-m-thick sediment pile drilled at Site 144, at 2960 m water depth. Calcium carbonate is a major constituent of all sediments (Supplemental file 2b). The oldest units 4 and 5 (~115 to 96 Ma), interpreted as syn-rift sequences (Hayes et al., 1972), consist of terrigenous claystones, sandstones with up to 40% detrital quartz and variable amounts of calcium carbonate (10 to 60%). They are overlain by a 60-m-thick “black shale” unit (~96 to 84 Ma) that recorded the Cretaceous Oceanic Anoxic Events 2 and 3 (Arndt et al., 2006). The upper two units consist of late Cretaceous to Oligocene chalks and marls containing up to 30% biogenic silica (derived from radiolarians and diatoms) at some levels (Supplemental file 2b).

Thirteen samples from Barbados Island were analyzed. Most of the island is covered by Pleistocene reef formations, but older sediments representing the emerged part of the Barbados accretionary prism outcrop in the northeastern part. These sediments belong to two main formations: the Scotland Formation (~57–35 Ma), which consists of terrigenous deposits that are interpreted as turbidites, and the Oceanic Formation (~45–15 Ma), which consists of marls and chalks with numerous intercalated volcanic ash layers (Pudsey and Reading, 1982; Biju-Duval et al., 1985). We selected 9 Scotland Formation samples ranging from fine-grained claystones to sandstones, and 4 samples from the Oceanic Formation (Supplemental file 1).

3. Analytical techniques

All samples were hand crushed in an agate mortar. Major element contents were determined at the SARM-CRPG (Nancy, France). Details about analytical procedures and uncertainties are available at <http://www.crpq.cnrs-nancy.fr/SARM/index.html>.

Trace element contents were measured using an ICP-MS in Grenoble. About 100 mg of powder were dissolved using a HF-HNO₃ (4:1) mixture in steel-jacketed Teflon PARR bombs for 7 days at 150 °C. The external calibration curves were realized with standard BHVO-2 using the Grenoble reference values given in Supplemental file 3a where they are compared with previously published data for BHVO-1 and BHVO-2. Results obtained on the international standards BR and AGV-1, and our in-house standard Bora Bora 24, which was analyzed repeatedly during the course of this study, are given in Supplemental file 3b, together with the precision of our data evaluated from replicated analyses of these standards. Accuracy is estimated at 3% and precision on the concentrations is usually better than 5% at the 2 σ level.

Sr and Hf isotope ratios were obtained from a common powder dissolution using HF-HNO₃ mixture in PARR bombs. Hf separation was achieved using a procedure modified from Blichert-Toft et al. (1997) in which the first separation step (HF leaching and fluoride precipitation) was replaced by a chromatographic isolation using a high capacity AG50-X12 cationic resin. During this step, a fraction containing Sr was collected to be further purified on a Sr-Spec column. Total procedure blanks were <85 pg for Hf ($n=7$) and <40 pg for Sr ($n=6$) and are negligible compared to the amount of Hf and Sr processed. Sr isotopic compositions were measured by TIMS (Triton, Finnigan) in Brest (France) using static multicollection mode. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were corrected for mass fractionation using $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$. The NBS 987 standard was run regularly and yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710246 ± 18 (2σ , $n=26$). Hf isotopic compositions were measured on a Nu Plasma MC-ICP-MS (from Nu Instruments) in Brussels (Belgium) using also static multicollection modes, $^{176}\text{Hf}/^{177}\text{Hf}$ were normalized to $^{179}\text{Hf}/^{177}\text{Hf}=0.7325$. The JMC 475 Hf standard was run every second sample and yielded a $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282168 ± 17 (2σ , $n=60$). Hf isotope ratios were corrected for bias using the JMC 475 Hf value recommended by Vervoort and Blichert-Toft (1999). More information is given in the footnote of Table 1.

4. Results

Major and trace element concentrations are given in Supplemental file 3c, while Sr and Hf isotope ratios are given in Table 1. SiO₂, CaO and Al₂O₃ contents as well as Sr and Hf isotopic compositions are plotted as a function of depth for Sites 144 and 543 and as a function of age for Barbados Island samples (Supplemental file 2). When all sediments are considered, CaO contents vary from 0.06 to 53.8%, Al₂O₃ from 0.31 to 20.6% and SiO₂ from 1.4 to 85.5%. These values are obviously correlated with the contents in biogenic carbonates, clays, and detrital quartz or biogenic silica of the sediments. More specifically, sediments from Site 144 generally display higher CaO contents than those from Site 543 and Barbados Island, due to the abundance of calcium carbonate (Fig. 2 and Supplemental file 3c). In contrast, sediments from Site 543 have generally high Al₂O₃ concentrations due to their high clay contents (Fig. 2). Except for the dolomite sample B-7, the Barbados sandstone and claystone samples are poor in CaO and display high SiO₂ and Al₂O₃ contents compared to the Site 144 samples (Fig. 2).

Trace element concentrations define large ranges with, for example, Cs and La contents varying from 0.1 to 8.3 ppm and from 1.4 ppm up to 46.3 ppm, respectively (Fig. 3). Most trace elements correlate with Al₂O₃, and thus the claystones from Site 543 and Barbados Island are generally enriched in trace element relative to the carbonate-rich sediments from Site 144 (Fig. 3).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary widely (Table 1). While Site 144 sediments have almost constant Sr isotope ratios around 0.7085, sediments from Barbados Island and Site 543 display much more variability and are

Table 1

Sr and Hf isotope ratios measured in sediments from Site 543 (DSDP 78A), Site 144 (DSDP 14) and Barbados Island.

	Depth (m)	Lith. unit	$^{87}\text{Sr}/^{86}\text{Sr}$	2 σ_m	$^{176}\text{Hf}/^{177}\text{Hf}$	2 σ_m	ϵ_{Hf}
<i>Leg DSDP 14, Site 144</i>							
144B 1 2W 11.5–13	2	1	0.710971	0.000006	0.282510	0.000013	–9.7
144B 2 2W 16.5–18	12	1	0.708090	0.000006	0.282462	0.000012	–11.4
144A 1 2W 11.5–14	22	1	0.708204	0.000007	0.282345	0.000009	–15.6
144A 1 2W 11.5–14 DD			0.708208	0.000005			
144B 3 2W 71.5–73	29	1	0.708343	0.000006	0.282355	0.000010	–15.2
144A 2 2W 79–80.5	41	1	0.708098	0.000007	0.282308	0.000013	–16.9
144 1 4W 98–99	62	1	0.707944	0.000007	0.282408	0.000012	–13.3
144 1 6W 71–72	65	1	0.707961	0.000005	0.282413	0.000015	–13.2
144 2 5W 93–95	111	1	0.708276	0.000006	0.282589	0.000015	–6.9
144 2 5W 93–95 DD			0.708277	0.000006			
144A 3 1W 79–80	141	2	0.708335	0.000006	0.282615	0.000014	–6.0
144A 3 1W 79–80 DD			0.708353	0.000005	0.282608	0.000010	–6.3
144A 3 3W 25–26	143	2	0.708343	0.000006	0.282534	0.000014	–8.9
144A 3 3W 125–126	144	2	0.708301	0.000006	0.282192	0.000017	–21.0
144 3 1W 120–121	163	2	0.708694	0.000006	0.282233	0.000014	–19.5
144 3 2W 110–113.5	165	2	0.708666	0.000006	0.282284	0.000011	–17.7
144A 4 1W 140–144	172	2	0.708136	0.000006	0.282411	0.000026	–13.2
144A 5 1W 108–109	181	3	0.707596	0.000007			
144A 5 1W 119–124	181	3	0.707871	0.000007			
144A 5 CCW 0–1	182	3	0.708077	0.000009			
144A 6 1W 90–93	190	3	0.707884	0.000006	0.282483	0.000014	–10.7
144A 6 1W 125–130	190	3	0.707904	0.000007			
144 4 2W 60–64	215	3	0.707806	0.000007	0.282428	0.000011	–12.6
144 5 1W 123–125	265	4	0.708556	0.000006	0.282482	0.000014	–10.7
144 5 1W 123–125 DD					0.282464	0.000009	–11.3
144 6 1W 46–48	295	5	0.709158	0.000007	0.282221	0.000009	–19.9
144 6 1W 46–48 DD	295	5	0.709145	0.000007			
144 7 1W 80–82	299	5	0.710830	0.000005	0.282387	0.000011	–14.1
144 7 1W 80–82 DD					0.282371	0.000012	–14.7
144 7 1W 125–130	299	5	0.709141	0.000006	0.282273	0.000011	–18.1
144 8 3W 130–135	328	5	0.710293	0.000007	0.282424	0.000014	–12.8
144 8 3W 130–135 DD					0.282461	0.000020	–11.5
<i>Leg DSDP 78A, Site 543</i>							
543 18 4W 15–17	174	3	0.714076	0.000005	0.282741	0.000021	–1.6
543 19 1W 97–98	181	4	0.711648	0.000007	0.282807	0.000013	0.8
543 20 3W 99–101	194	4	0.714467	0.000005	0.282766	0.000017	–0.7
543 20 3W 99–101 DD			0.714422	0.000007			
543 23 2W 73–75	220	4	0.718270	0.000007	0.282631	0.000014	–5.5
543 24 7W 24–26	230	4	0.720299	0.000006	0.282617	0.000013	–6.0
543 24 7W 24–26 DD					0.282630	0.000020	–5.5
543 25 2W 86–88	239	4	0.721363	0.000006	0.282596	0.000011	–6.7
543 26 1W 120–122	248	4	0.717401	0.000006	0.282702	0.000011	–3.0
543 26 4W 27–29	251	4			0.282468	0.000006	–11.2
543 26 6W 27–29	254	5a	0.719155	0.000006	0.282520	0.000012	–9.4
543 27 2W 114–116	259	5a	0.720598	0.000005	0.282477	0.000016	–10.9
543 27 2W 114–116 DD					0.282456	0.000011	–11.6
543 28 3W 66–68	269	5a	0.722171	0.000006	0.282499	0.000019	–10.1
543 28 5W 66–68	274	5a	0.720803	0.000006	0.282519	0.000015	–9.4
543 29 4W 45–47	280	5a	0.719727	0.000007	0.282539	0.000018	–8.7
543 30 4W 53–55	290	5a	0.722327	0.000006			
543 31 1W 76–78	295	5a	0.718082	0.000006	0.282452	0.000018	–11.8
543 32 3W 10–12	307	5a	0.718700	0.000006	0.282568	0.000015	–7.7
543 32 3W 10–12 DD			0.718765	0.000008	0.282562	0.000014	–7.9
543 33 2W 71–73	315	5b	0.716811	0.000007	0.282539	0.000013	–8.7
543A 2 1W 116–118	333	5b	0.715892	0.000007	0.282515	0.000013	–9.6
543A 3 2W 12–14	343	5b	0.713965	0.000007	0.282597	0.000011	–6.6
543A 3 2W 12–14 DD			0.713963	0.000008	0.282583	0.000009	–7.1
543A 5 3W 47–49	364	5c	0.722128	0.000006	0.282576	0.000013	–7.4
543A 3 1W 75–77	371	5c	0.721648	0.000007	0.282456	0.000011	–11.6
543A 7 2W 100–102	382	6	0.709933	0.000008	0.282506	0.000011	–9.9
543A 8 1W 116–118	390	6	0.731781	0.000006	0.282479	0.000012	–10.8
543A 9 1W 45–46	399	6	0.713139	0.000006	0.282495	0.000011	–10.3
543A 10 1W 25–27	408	6	0.709340	0.000006	0.282399	0.000010	–13.7
543A 10 1W 25–27 DD			0.709331	0.000005			
<i>Barbados Island</i>							
B-1		OF	0.705489	0.000006	0.283164	0.000010	13.4
B-2		OF	0.706098	0.000006	0.283164	0.000011	13.4
B-4		OF	0.708617	0.000007	0.282892	0.000011	3.8
B-7		OF	0.709154	0.000006			
B-6		USF	0.720589	0.000006	0.282178	0.000010	–21.5
B-6 DR					0.282167	0.000010	–21.8

(continued on next page)

Table 1 (continued)

	Depth (m)	Lith. unit	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma_m$	$^{176}\text{Hf}/^{177}\text{Hf}$	$2\sigma_m$	ε_{Hf}
<i>Barbados Island</i>							
B-10b		USF	0.715313	0.000007	0.281935	0.000011	−30.1
B-10b DR					0.281942	0.000009	−29.8
B-10c		USF	0.722074	0.000007	0.282431	0.000011	−12.5
B-10c DR					0.282431	0.000012	−12.5
B-11		USF	0.726101	0.000006	0.282215	0.000011	−20.2
B-8c		LSF	0.714112	0.000007	0.282387	0.000010	−14.1
B-8d		LSF	0.715282	0.000006	0.282590	0.000009	−6.9
B-12a		LSF	0.715175	0.000006	0.282655	0.000011	−4.6
B-12b		LSF	0.717746	0.000006	0.282560	0.000010	−8.0

DD stands for duplicate dissolution and DR for duplicate run. Lithological units are given in Supplemental file 2 and OF, USF and LSF stand for Oceanic, Upper and Lower Scotland Formations. Uncertainties reported on the Sr and Hf isotope ratios are in-run errors ($2\sigma/\sqrt{n}$, where σ is the standard deviation and n the number of measured ratios, generally 110 for Sr, and 60 for Hf). Hf isotope ratios are given relative to the value recommended by Vervoort and Blichert-Toft (1999) for the JMC 475 Hf standard ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$). Reproducibility calculated using complete duplicate analyses of 8 samples is 0.000019 (2σ) on the measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and 0.000030 (2σ) on the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. ε_{Hf} values were calculated using $^{176}\text{Hf}/^{177}\text{Hf}_{\text{CHUR}} = 0.282785$ (Bouvier et al., 2008).

generally more radiogenic, with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.70549 up to 0.72610 in Barbados and from 0.70933 to 0.73178 at Site 543 (Fig. 4 and Table 1). The uniform $^{87}\text{Sr}/^{86}\text{Sr}$ values measured on Site 144 sediments are similar to values estimated for Cretaceous to Oligocene seawater (−0.707 to 0.708; Jones et al., 1994) (see Fig. 4 and Supplemental file 2b) and most probably result from buffering of the isotopic compositions by the overwhelming presence of calcium carbonate that precipitated from seawater. Site 543 sediments define a different trend in Fig. 4 and the observed range is similar to that reported by White et al. (1985) on the same core. The lowest and highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are found at the bottom of the sedimentary pile, and no systematic change through time occurs (Supplemental file 2a). However, in the unit located just below the décollement, a clear decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ appears to be related to increasing proportion of volcanic ash from the island arc (Supplemental file 2a). Most Site 543 sediments are more radiogenic than the average Upper Continental Crust (UCC) and Global Subducting Sediment (GLOSS) estimates, suggesting a higher-than-average proportion of old crustal material in

their source. Finally, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Barbados sediments vary from 0.70549 up to 0.72610. While ashes and marls of the Oceanic Formation are relatively unradiogenic (<0.70915), the claystones and sandstones

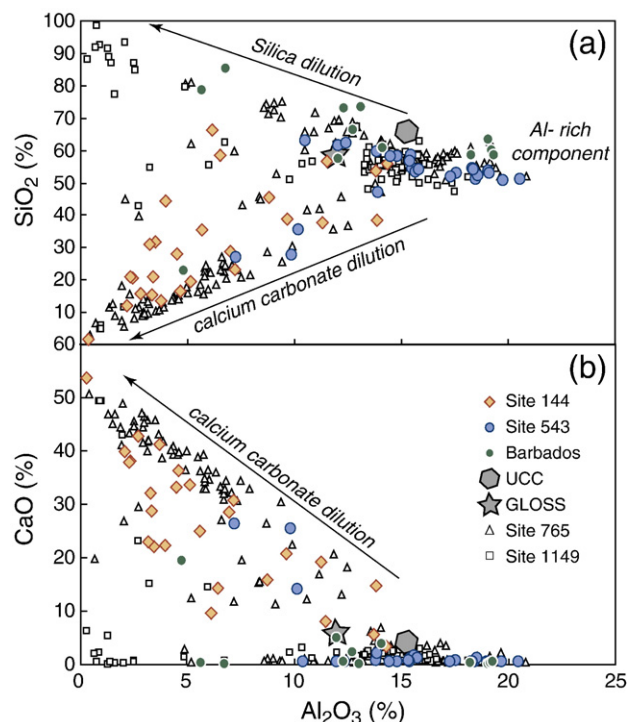


Fig. 2. a) SiO_2 and b) CaO vs. Al_2O_3 diagrams showing data for Site 543, Site 144 and Barbados. Also shown are data published by Plank and Ludden (1992) for ODP Site 765 sediments and by Plank et al. (2007) for ODP Site 1149 sediments as well as the GLOSS (Plank and Langmuir, 1998) and the UCC (McLennan, 2001) values.

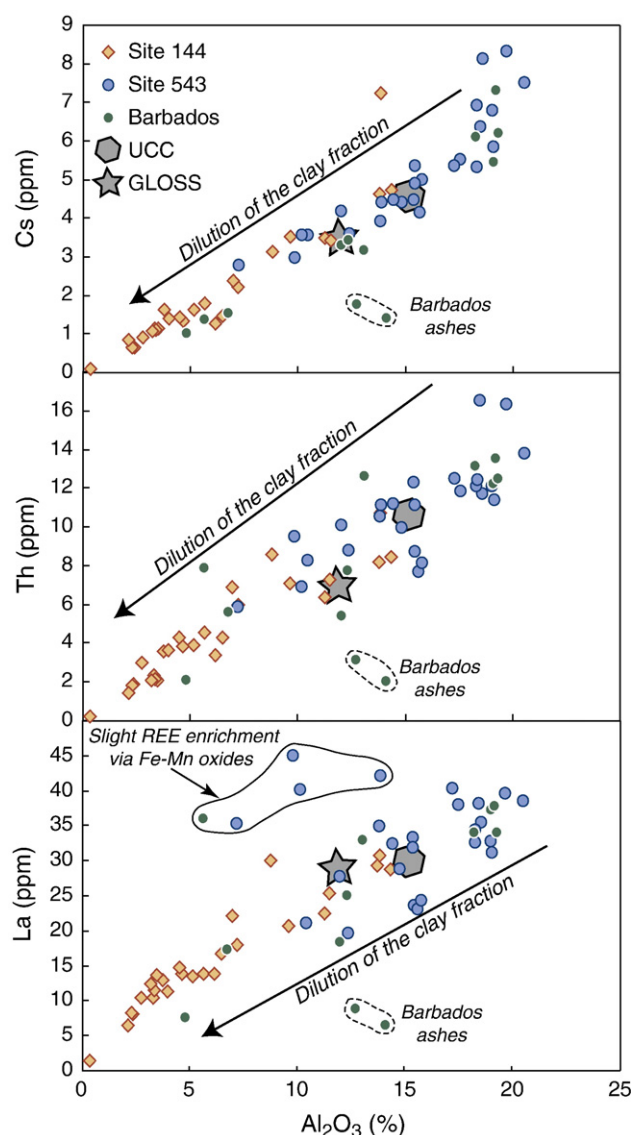


Fig. 3. Cs, Th and La vs. Al_2O_3 diagrams showing the results obtained for Sites 543 and 144 samples and for Barbados Island samples. GLOSS (Plank and Langmuir, 1998) and UCC (McLennan, 2001) are also shown. Samples with a slight REE enrichment due to the presence of Fe–Mn oxides are highlighted.

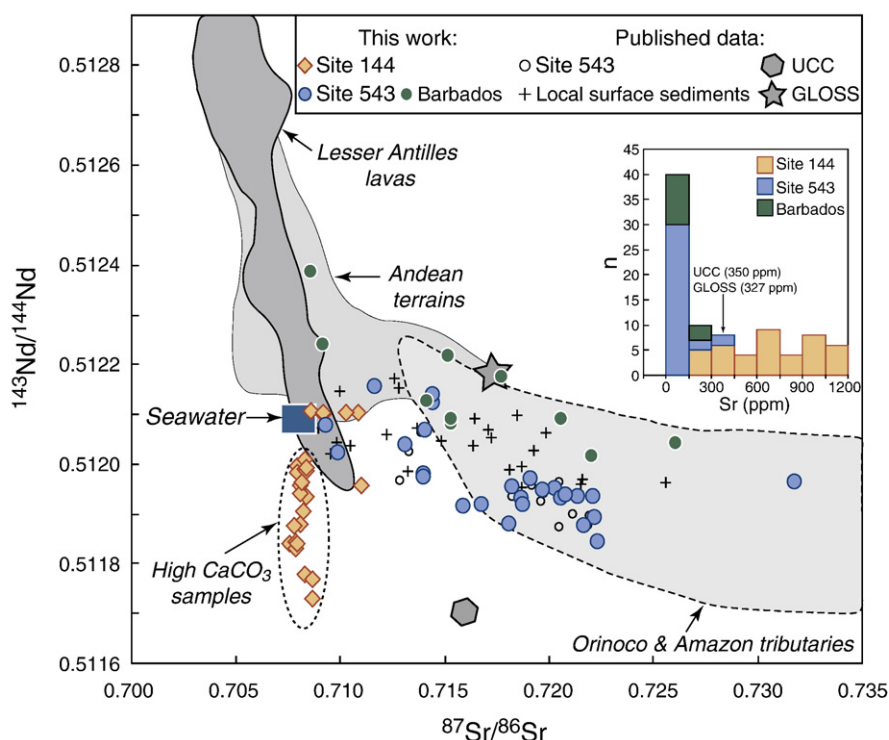


Fig. 4. Nd and Sr isotopic compositions of sediments from DSDP Sites 543 and 144 and Barbados Islands. The inset shows a histogram of Sr concentrations in the analyzed samples. Data published by White et al. (1985) on Site 543 and local surface sediments, as well as GLOSS (Plank and Langmuir, 1998) and average UCC (Goldstein et al., 1984; Goldstein and Jacobsen, 1988) are also shown. The field for late Cretaceous to Miocene North Atlantic seawater was built using Nd isotopic compositions from Burton et al. (1997) and O'Nions et al. (1998) and Sr isotopic compositions from Jones et al. (1994). Lesser Antilles arc and Andean terrains fields were built using data compilation available on: <http://georoc.mpch-mainz.gwdg.de/georoc/>, while Sr–Nd isotopic compositions of sediments from Orinoco and Amazon tributaries are from Allègre et al. (1996) and Parra et al. (1997).

of the Scotland Formation have much higher values (Table 1, Supplemental file 2c), comparable to those measured for Site 543 sediments.

$^{176}\text{Hf}/^{177}\text{Hf}$ ratios also define a large range (0.28194 to 0.28317) that corresponds to 43 ϵ_{Hf} units (Table 1 and Fig. 5). Both the highest and the lowest ratios are found in the Barbados samples: the ash samples

have an ϵ_{Hf} of +14.0 while the sandstone sample B-10b from the Scotland Formation has an ϵ_{Hf} of –29.0. In contrast, the Site 543 and 144 sediments define a narrower range, of 15 ϵ_{Hf} units. At Site 144, $^{176}\text{Hf}/^{177}\text{Hf}$ ratios do not vary systematically through time and both the highest and lowest values (ϵ_{Hf} of –4.9 and –20.2) are found in the same stratigraphic unit (Supplemental file 2b). Site 543 sediments are

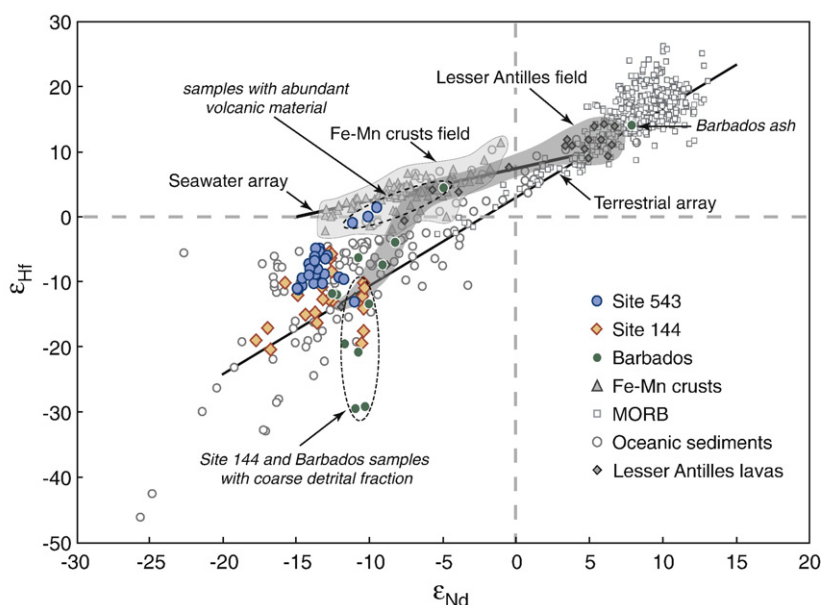


Fig. 5. Nd and Hf isotopic compositions of sediments from Sites 543, 144 and Barbados Island. MORB compositions are from Salters (1996), Salters and White (1998), Chauvel and Blichert-Toft (2001) and the database compiled by Agraniér et al. (2005). Data for Fe–Mn crusts and nodules are from Albarède et al. (1997), Godfrey et al. (1997), Albarède et al. (1998), David et al. (2001) and van der Fliedert et al. (2006). Oceanic sediment compositions are from Vervoort et al. (1999), Vlastélic et al. (2005), Prytulak et al. (2006), van der Fliedert et al. (2007), Chauvel et al. (2009) and Bayon et al. (2009). The Lesser Antilles data are from White and Patchett (1984), Vidal et al. (1991) and Woodhead et al. (2001). The Seawater and Terrestrial array are from Albarède et al. (1998) and Vervoort et al. (1999) respectively.

generally more radiogenic than Site 144 sediments. While most of the pile has relatively constant ε_{Hf} (−13.1 to −8.8), the uppermost samples have more radiogenic values (ε_{Hf} up to +1.9) that are most probably influenced by volcanic ash in these sediments (Table 1, Supplemental file 2a). When compared to the Nd–Hf “terrestrial array” of Vervoort et al. (1999) in Fig. 5, our data plot in the unradiogenic part of the diagram suggesting that relatively old crustal material was the dominant source of Hf in these sediments. In detail, the majority of samples are located above the array and both the Barbados samples and part of the Site 144 samples define a vertical trend towards very low ε_{Hf} values.

5. Discussion

5.1. Chemical variations controlled by dilution of the clay fraction by carbonates and silica

The Lesser Antilles forearc sediments define an extremely large range of major element compositions that is easily explained by dilution of a clay-rich fraction with two different components. In the SiO_2 vs Al_2O_3 plot (Fig. 2a), all data plot within a triangle defined by three components: an Al-rich component, a “pure” silica component and a carbonate component in which both Al_2O_3 and SiO_2 are absent (Fig. 2b). Alumina is typically associated with the detrital clay fraction, while the silica end member is either of biogenic or detrital origin. In the Barbados sediments, silica is mainly present as detrital quartz grains (Pudsey and Reading, 1982) as demonstrated by the trend shown in Fig. 2a which illustrates the variation from SiO_2 -rich (up to 85%) coarse-grained sandstones to Al_2O_3 -rich (up to 19%) fine-grained claystones (Supplemental file 3c). In Site 543 sediments, the variation is related to the abundance of biogenic silica (radiolarites, Supplemental file 2a). At Site 144, dilution of the Al-rich component is due to calcium carbonates (Fig. 2b) and CaO contents can reach 50%.

The dilution of the detrital clay fraction by the silica- and calcium-rich components has consequences for the distribution of other elements. The high Pearson correlation coefficients between Al_2O_3 and most trace elements (Supplemental file 4) show that the latter are preferentially concentrated into the clay fraction. Fig. 3 shows concentrations of selected trace elements as a function of Al_2O_3 contents. In all three cases, the strong positive linear correlation illustrates the high Pearson correlation coefficients given in Supplemental file 4. Concentrations of Cs, Th and La vary from very low values (nearly 10 times lower than UCC) in the carbonate-rich samples from Site 144 to values much higher than UCC in claystones from Barbados and Site 543 (Fig. 3). The trace-element variations within Site 144 sediments are mostly due to dilution of the clay fraction by calcium carbonate and pure silica (biogenic in both the top chalk unit and the black shale unit, and detrital in the older units, see Supplemental file 2b). In contrast, in Site 543 and Barbados sediments, variations of Cs, Th and La contents are related to dilution by pure silica, which is biogenic at Site 543 and detrital at Barbados. The two volcanic ashes from Barbados are exceptions and have very low trace element contents given their Al_2O_3 concentrations (Fig. 3).

A few trace elements, namely U and Sr, do not follow the overall dilution trends. In sediments from Barbados, Site 543, and part of Site 144, the correlation between U and Al_2O_3 suggests that U is associated with the clay fraction and is therefore of detrital origin. However, in the carbonate-rich black shale unit from Site 144 (Unit 3), U concentrations are extremely high, varying from 5.4 to 14.6 ppm. Carpentier et al. (2008) attributed such high U contents to strongly reducing conditions during the anoxic event that accompanied the deposition of these shales (Anderson et al., 1989; Klinkhammer and Palmer, 1991). Sr concentrations are also extremely variable (from 35 to 1150 ppm, Supplemental file 3c). In Barbados and most Site 543 sediments, where carbonate is absent, Sr is associated with the detrital fraction and diluted by both biogenic silica and detrital quartz. In contrast, sediments from Site 144,

and to a lesser extent, sediments from the oldest unit of Site 543, contain high proportions of calcium carbonate and are clearly Sr enriched compared to UCC (Fig. 4-inset).

Such Sr enrichment causes a decoupling of the Nd and Sr isotopic compositions, and the Site 144 sediments define a vertical trend in Fig. 4 because the Sr is buffered by Sr from seawater. All other samples, as well as local surface sediments (White et al., 1985), display a “normal” scattered negative correlation in Sr–Nd isotopic space reflecting mixing of various materials derived from the South American continent and from the Lesser Antilles arc (Fig. 4).

5.2. Impact of the “zircon effect” on the high-field strength elements

Although the concentrations of most trace elements can be explained by dilution of the clay fraction by either carbonate or pure silica, this is not the case of the high-field strength elements.

5.2.1. Relationship between Nb (Ta), Zr (Hf) and Al_2O_3

In Fig. 6a, we show that Nb behaves like most other trace elements (see Fig. 3 for comparison) and correlates strongly with Al_2O_3 . The same applies for Ta, which varies together with Nb at a constant ratio of 14.6. The Nb– Al_2O_3 correlation exists not only for the studied sediments (correlation coefficient of 0.88, Supplemental file 4) but also for other oceanic sediments sampled in diverse environments all over the globe. The average Nb/ Al_2O_3 ratio of our sediments is 0.79, a value similar to the UCC and GLOSS ratios (Plank and Langmuir, 1998; McLennan, 2001) but a few samples have quite different ratios. For instance, the two Barbados ashes have very low values typical of arc lavas (0.16), while several Barbados sediments and one Site 144 sample plot significantly above the main trend in Fig. 6a. Because these sediments also have excess Ti, we attribute the Nb excess to the presence of detrital rutile in these samples.

This is not the case for the Fe–Mn sediments from Sites 595/6, located in the Pacific basin, where high Nb contents are attributed to scavenging from seawater by Fe–Mn oxides in an unusually low sedimentation rate environment (Chan et al., 2006). As a whole, the histogram of our new data, together with published Nb/ Al_2O_3 ratios of oceanic sediments, defines a Gaussian curve (Fig. 6b) with a median value of 0.78, which is very close to the upper continental crust value of 0.79. This feature suggests that most oceanic sediments have the same Nb/ Al_2O_3 ratio as UCC, as already highlighted by Plank and Langmuir (1998) who suggested a value of 0.75 for GLOSS.

The relationship between Zr (and Hf) and Al_2O_3 in the studied sediments is more complex (Fig. 6c), as shown by the correlation coefficient of 0.48 (Supplemental file 4). Two types of sediment can be distinguished: a first group in which Zr and Al_2O_3 are positively correlated, and a second in which the two elements vary independently. The first group includes all Site 543 sediments and some Site 144 and Barbados samples, all of which have a clay-rich detrital fraction. Their Zr/ Al_2O_3 ratio does not vary much (4.6 to 9) and is always lower than the UCC value of 12.5 (McLennan, 2001), indicating a systematic deficiency in Zr (Fig. 6c). This is not the case of the second group, in which Zr and Al are uncorrelated and where Zr/ Al_2O_3 ratios are identical to or higher than that of UCC (up to 67). All these samples contain a coarse detrital fraction with abundant quartz (See Supplemental file 2b for Site 144 and Pudsey and Reading, 1982 for Barbados). We suggest that their Zr excess is due to the presence of zircon in the heavy mineral assemblage associated with the quartz-rich sands.

When worldwide oceanic sediments are considered, the same observation can be made: most sediments have a Zr/ Al_2O_3 ratio lower than the UCC value and only few samples have elevated Zr/ Al_2O_3 ratios (Fig. 6c). Some of these are turbidites that contain zircon-rich layers, like the Site 765 sediments in the Indian Ocean near the Australian margin (Plank and Ludden, 1992). Others are Fe–Mn rich sediments that contain a Zr-rich hydrogenous component (Plank and Langmuir, 1998; Chan et al., 2006) as is the case for some Site 595/6 samples (Fig. 6c). When our new Zr/ Al_2O_3 values are plotted as a histogram together with published ratios

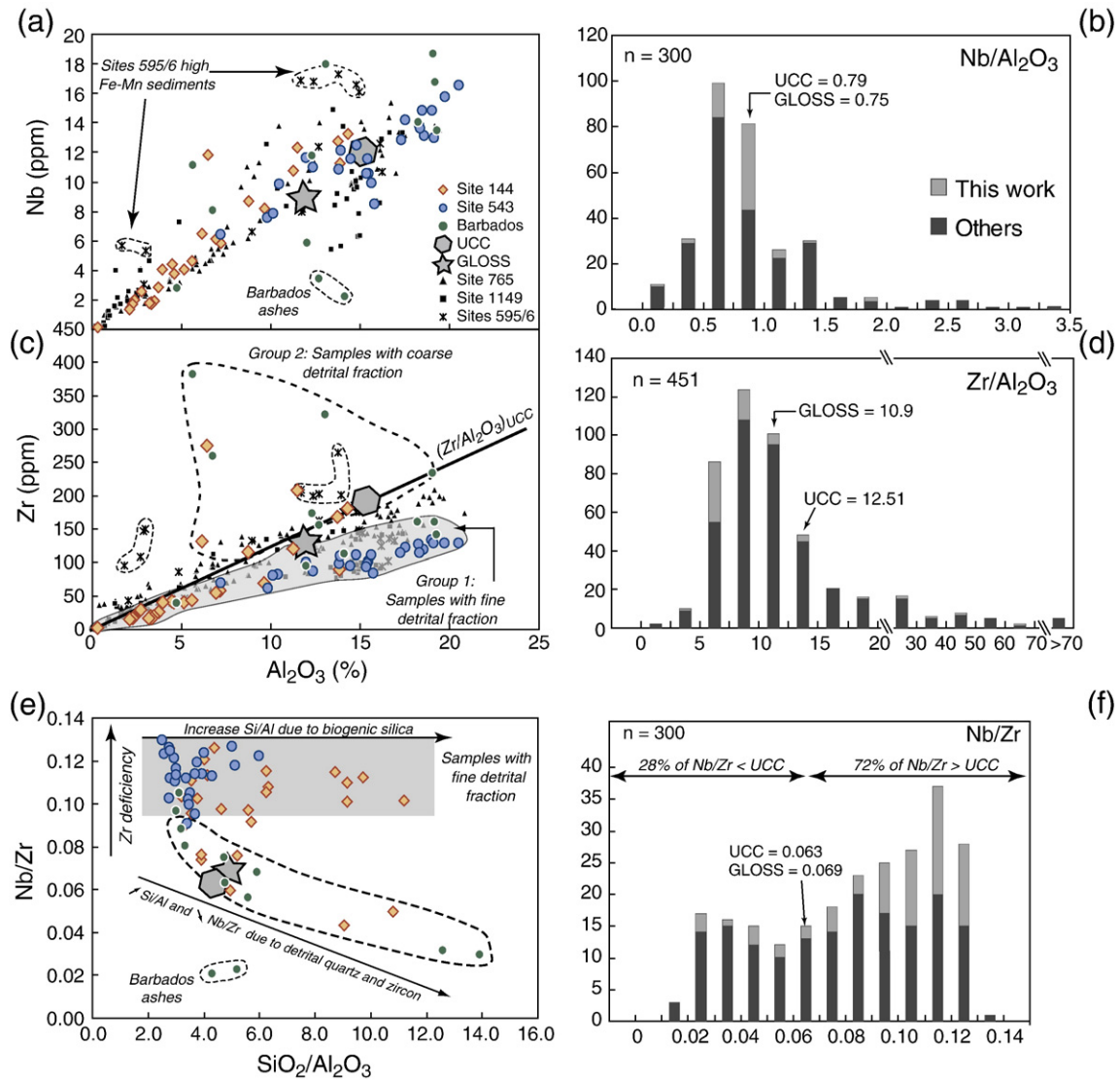


Fig. 6. Plots of Nb and Zr as a function of Al_2O_3 and SiO_2 showing the decoupling of the HFSE. a) Nb vs. Al_2O_3 , b) histogram of the Nb/Al_2O_3 ratio, c) Zr vs. Al_2O_3 , d) histogram of the Zr/Al_2O_3 ratio, e) Nb/Zr vs. SiO_2/Al_2O_3 and f) histogram of the Nb/Zr ratio. Results for Site 543, Site 144 and Barbados samples are plotted together with those of Site 765, Site 1149 and Sites 595/596 (Plank and Ludden, 1992; Plank and Langmuir, 1998; Chan et al., 2006; Plank et al., 2007). GLOSS and UCC compositions are from Plank and Langmuir (1998) and McLennan (2001) respectively. The histograms include all data shown in panels a, and e plus data for sediments from Sites 701 and 183 (Chan et al., 2006), Site 266 (Vlastélic et al., 2005), Site 174 (Prytulak et al., 2006), Site 262 (Vroon et al., 1995), deep sea turbidites of McLennan et al. (1990) and for Ben Othman et al. (1989) surface sediments (data of Plank and Langmuir, 1998).

(Fig. 6d), they define a Gaussian curve with a median value of 10.1, which is significantly lower than the upper-crustal estimate of 12.51 (McLennan, 2001). In fact 72% of the sediments plotted in this histogram have a Zr/Al_2O_3 ratio lower than the UCC ratio. The best explanation for this striking feature is the “zircon effect” first recognized by Patchett et al. (1984). These authors assumed that zircon is the main Zr and Hf reservoir in both the continental crust and in coarse-grained detrital sediments. During alteration and erosion of the continental crust, zircon is very resistant to chemical alteration, and most of the Zr and Hf are sequestered in zircons which are deposited in sands near the continental margins (Patchett et al., 1984). Other elements such as the REE, Al, and alkalis are mostly contained in the clay fraction, which, being finer, is transported farther away from the continent and deposited in deeper waters. The low Zr/Al_2O_3 ratios of most oceanic sediments results from the decoupling of Zr and Hf from other elements.

5.2.2. The Nb/Zr ratio of oceanic sediments

Because zircons control the Zr and Hf budget in sediments but not their Nb concentrations, significant and large changes of the Nb/Zr ratio

may occur. Fig. 6e shows the relationship between Nb/Zr and SiO_2/Al_2O_3 in the Lesser Antilles sediments. The Site 543 sediments, together with some Barbados and Site 144 samples, define a broad horizontal band with Nb/Zr ratios higher than those of upper crust and variable SiO_2/Al_2O_3 ratios. The mineral compositions of these sediments explain the trend because the zircon-poor claystones have high Nb/Zr ratios, and the variable amounts of biogenic silica account for the changes of SiO_2/Al_2O_3 from crustal values to very high ratios (see Supplemental file 2 for the mineralogy of individual samples). In contrast, a second group of samples, which includes the detrital units of Site 144 and most Barbados sediments, defines a negative correlation in Fig. 6e. We attribute the decrease of Nb/Zr as SiO_2/Al_2O_3 increases to higher proportions of quartz- and zircon-rich sands in the sediments. When the Nb/Zr ratios of all oceanic sediments are plotted in a histogram (Fig. 6f), a bimodal distribution can be observed with sandy sediments having ratios lower than 0.06, and fine-grained sediments having an average Nb/Zr ratio of about 0.11. Three quarters of the oceanic sediments have Nb/Zr ratios higher than the upper-crust and GLOSS values (Fig. 6f). The calculated average Nb/Zr ratio is 0.082 but the dispersion is such that the standard deviation is 36% of the total range (at 1σ level).

5.2.3. The “zircon effect” on the Nd–Hf isotopes

If zircon is the main carrier of Hf and Zr, then variable proportions of zircons in sediments will influence the relationship between Hf and Nd isotopes. In Hf–Nd isotopic space (Fig. 5), almost all our samples plot in the continental domain of the terrestrial array (Vervoort et al., 1999). Because both silica and calcium carbonate biogenic components are poor in REE and HFSE (e.g. Plank and Langmuir, 1998; Vlastélic et al., 2005; Olivier and Boyet, 2006), the Nd and Hf isotopic compositions of bulk sediments are mainly those of their detrital fraction. On the basis of Nd and Pb isotopic compositions of the same set of samples, Carpentier et al. (2008) suggested that the Guyana and Brazilian cratons were the main sources of continental material to Lesser Antilles forearc sediments since the Cretaceous. The low ε_{Hf} of the sediments supports this interpretation because negative ε_{Hf} values require derivation from old continental crust (Fig. 5). However, a few samples have high ε_{Hf} values relative to their ε_{Nd} values and one ash sample has an extremely high value that plots within the MORB field (Fig. 5). These exceptional samples contain volcanogenic material from the Lesser Antilles, either as a pure component (sample B-2 from a Barbados ash layer) or mixed with detrital material from the South American continent (samples from Site 543 and Barbados, Supplemental file 2a; Pudsey, 1984; Carpentier et al., 2008). Mixing of variable amounts of high ε_{Hf} – ε_{Nd} arc volcanic ashes with the continental detrital fraction explains the intermediate position of the data points in Fig. 5.

In all other sediments, the detrital fraction is dominated by the terrigenous input from the South American continent, and the data are scattered between the seawater (Albarède et al., 1998) and terrestrial arrays (Vervoort et al., 1999), with no obvious correlation between Hf and Nd isotopes (Fig. 5). When considered in detail, two major trends related to the mineralogy of the sediments become evident: the clay-rich sediments from Sites 543 and 144 and from Barbados define a cluster above the terrestrial array of Vervoort et al. (1999) (Fig. 5) while the zircon-rich sediments from both Site 144 and Barbados define a vertical trend with variable ε_{Hf} at near-constant ε_{Nd} . We attribute the large range of Hf isotopes at constant Nd to the presence in these sediments of variable amounts of zircon with highly unradiogenic Hf, rather than to variation of the Hf isotopic composition of their continental sources.

To further test the effect of zircon on the decoupling of Hf–Nd isotopes in the sediments from Sites 543, 144 and Barbados, we compare their Nb/Zr ratios with their vertical deviation of ε_{Hf} from the terrestrial array of

Vervoort et al. (1999) ($\Delta\varepsilon_{\text{Hf}}$) in Fig. 7. For all oceanic sediments (with the exception of Fe–Mn crusts and pure volcanogenic material), the Nb/Zr ratio is an excellent indicator of the “zircon effect”, with high ratios in zircon-poor sediments and low ratios in zircon-rich sediments. Fig. 7 shows that although the correlation between Nb/Zr ratios and $\Delta\varepsilon_{\text{Hf}}$ in the studied sediments is excellent, two parallel trends can be distinguished.

The main array includes the vast majority of the samples and displays a strong positive correlation (correlation coefficient of 0.92). The zircon-poor, clay-rich sediments from Sites 543 and 144 define the high Nb/Zr-high $\Delta\varepsilon_{\text{Hf}}$ end member, and the zircon-rich, coarse detrital fractions from Barbados and Site 144 define the low Nb/Zr-low $\Delta\varepsilon_{\text{Hf}}$ end of the array. The clay-rich sediments are characterized by a Zr (and associated Hf) deficiency and inherit their radiogenic Hf isotopic composition from minerals with high Lu/Hf ratio. In contrast, the sandy sediments, which have low Nb/Zr ratios, are characterized by Zr and Hf excesses due to the presence of zircons. Their strongly negative $\Delta\varepsilon_{\text{Hf}}$ is due to the time-integrated low Lu/Hf ratio of this mineral. This relation between Nb/Zr and $\Delta\varepsilon_{\text{Hf}}$ supports previous suggestions made by Vervoort et al. (1999), van der Fliedert et al. (2007), Chauvel et al. (2008) and Bayon et al. (2009) who attributed the decoupling of Nd from Hf isotopes in the sedimentary systems to the zircon effect. The slope of the array in Fig. 7 depends on the average age of the detrital material in the sediments. Large differences in $\Delta\varepsilon_{\text{Hf}}$ can only develop if the detrital fraction is old enough to create divergence of ε_{Hf} between the zircon- and clay-rich fractions.

The five samples containing volcanic ashes define a distinct trend with low Nb/Zr ratio and high ε_{Hf} . The Barbados volcanic ash falls in the middle of the island arc field in Fig. 7, while the other four samples define a mixing array between this ash and the clay-rich high Nb/Zr – $\Delta\varepsilon_{\text{Hf}}$ sediments. The composition of the entire group of samples is consistent with the presence of volcanic glass, as recognized in petrographic studies (Supplemental file 2a and Pudsey and Reading, 1982).

5.3. Averages of the three studied sites

We calculated the average compositions of the two sedimentary piles drilled at Sites 543 and 144 using the method of Plank et al. (2007) (see Table 2 for a summary and Supplemental file 3d for the detailed calculations). Sediments at Site 144 were deposited at shallow water depth on the Demerara rise (Fig. 1) and are carbonate-rich, unlike

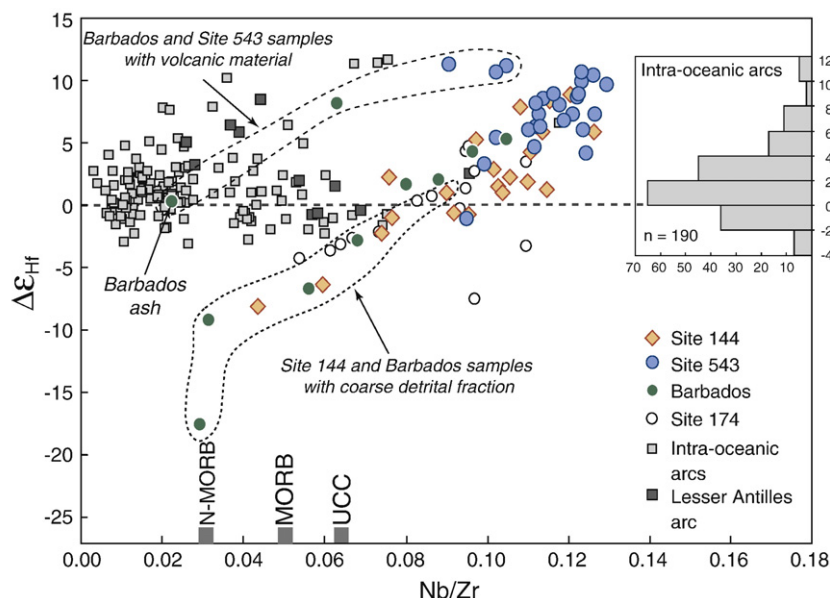


Fig. 7. Vertical deviation of ε_{Hf} from the terrestrial array of Vervoort et al. (1999) ($\varepsilon_{\text{Hf}} = 1.36\varepsilon_{\text{Nd}} + 2.95$) as expressed by $\Delta\varepsilon_{\text{Hf}}$ vs. Nb/Zr ratio of sediments from Sites 543, 144 and Barbados Island. Also shown are sediments from Site DSDP 174 (Prytulak et al., 2006) intra-oceanic island arcs. Data for Lesser Antilles lavas are from White and Patchett (1984), Vidal et al. (1991) and Woodhead et al. (2001) and those from other intra-oceanic arcs (Tonga–Kermadec, Sunda, Sandwich, Aleoutian, Izu–Bonin, Mariana, New Britain, Luzon, Banda arcs) come from GEOROC (<http://georoc.mpch-mainz.gwdg.de/georoc/>). Average UCC, MORB and N-MORB Nb/Zr ratios are from McLennan (2001), Su (2002) and Hofmann (1988).

Table 2

Averages calculated for major and trace element and Sr, Hf, Nd and Pb isotopic compositions for DSDP Sites 543 and 144 sediments and for Barbados Island sediments.

	Bulk Site 543 (n = 28)	Bulk Site 144 (n = 38)	Carbonate-free Site 144 (n = 38)	Barbados (n = 11)
SiO ₂ (%)	51.9	35.2		63.7
Al ₂ O ₃	15.5	6.88		13.2
Fe ₂ O ₃	6.66	3.03		3.86
MnO	0.26	0.05		0.04
MgO	2.36	1.12		2.41
CaO	3.21	24.1		2.67
Na ₂ O	1.79	1.50		1.36
K ₂ O	1.81	1.09		1.59
TiO ₂	0.58	0.40		0.72
P ₂ O ₅	0.16	0.20		0.09
LOI	16.0	27.0		10.4
Li (ppm)	59.9	24.0	38.3	40.4
Rb	66.7	39.8	67.0	57.1
Sr	110	656	n. d.	103
Y	26.1	16.2	22.2	21.0
Zr	104	83.8	138	174
Nb	11.8	6.42	10.8	11.8
Cs	5.09	2.26	3.80	3.90
Ba	230	894	n. d.	329
La	33.4	16.9	25.6	26.0
Ce	80.6	31.2	50.5	51.6
Pr	8.16	3.89	5.99	6.31
Nd	30.6	14.8	22.6	23.3
Sm	6.04	2.91	4.43	4.55
Eu	1.27	0.660	0.988	0.924
Gd	5.15	2.62	3.84	3.91
Tb	0.821	0.412	0.611	0.637
Dy	4.55	2.38	3.49	3.71
Ho	0.926	0.499	0.730	0.776
Er	2.63	1.45	2.10	2.30
Yb	2.44	1.36	2.00	2.32
Lu	0.374	0.213	0.310	0.361
Hf	2.79	2.15	3.56	4.78
Ta	0.819	0.444	0.748	0.885
Pb	18.7	7.24	11.5	13.1
Th	10.9	4.74	7.69	8.97
U	1.39	2.94	4.90	2.39
⁸⁷ Sr/ ⁸⁶ Sr	0.715852	0.708509		0.71
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.282560	0.282362	0.282361	0.282327
ϵ_{Hf}	−7.9	−15.0	−15.0	−16.2
¹⁴³ Nd/ ¹⁴⁴ Nd	0.511966 [1]	0.512014 [1]	0.512021 [2]	0.512122 [2]
ϵ_{Nd}	−13.1 [1]	−12.2 [1]	−12.0 [2]	−10.1 [2]
²⁰⁶ Pb/ ²⁰⁴ Pb	19.3150 [1]	19.5158 [1]	19.4917 [2]	19.6740 [2]
²⁰⁷ Pb/ ²⁰⁴ Pb	15.7671 [1]	15.7650 [1]	15.7625 [2]	15.7650 [2]
²⁰⁸ Pb/ ²⁰⁴ Pb	39.347 [1]	39.220 [1]	39.213 [2]	39.456 [2]

For the two DSDP Sites, the bulk composition was calculated combining the isotopes, major and trace element contents and mass proportion of each unit (given in Supplemental file 3d) as recommended by Plank et al. (2007). The average for the carbonate-free Site 144 was calculated by virtually removing the carbonates in each unit; the carbonate contents were estimated from the CaO concentrations. The average for Barbados was calculated by giving the same weight to all samples, but excluding the two ash samples because their occurrences are probably very sporadic. Details of the calculation procedures are given in Supplemental file 3d. [1] Carpentier et al. (2008); [2] Calculated in the present study using the isotopic data of Carpentier et al. (2008); n. d.: not determined.

sediments deposited at greater water depth (below the CCD) on the Atlantic oceanic seafloor. Thus we estimated a bulk trace element and isotopic composition for the non-carbonate fraction of the Site 144 sedimentary pile by numerically removing the carbonate using the procedure given in Supplemental file 3d footnote. Although we also calculated an average composition of Barbados sediments, this average is less well constrained because the analyzed samples are from selected sampling sites on the island and their relative proportions are difficult to estimate.

The averages are given in Table 2 and are plotted relative to UCC values in Fig. 8. Because both Site 543 and GLOSS are dominated by

terrigenous materials derived from upper continental crust (Plank and Langmuir, 1998), the Site 543 bulk composition is generally very similar to GLOSS (Fig. 8a). Exceptions are the relatively strong negative Sr and Ba anomalies of Site 543 (Fig. 8a) that are probably inherited from the detrital source rocks. Our Site 543 bulk composition is also quite similar to Plank and Langmuir's (1998) estimate of the composition of sediments entering the northern part of the Lesser Antilles arc (Fig. 8a), the only differences being the higher values for HFSE elements in their estimate. The Site 144 bulk pattern is nearly parallel to Site 543 pattern on Fig. 8b, but concentrations are generally lower due to dilution by calcium carbonate. This pattern also displays positive Sr, U and Ba anomalies, related respectively to carbonate, U-enriched black shale and biogenic material. The carbonate-free Site 144 bulk composition is about 1.6 times richer than the measured values but the pattern remains below that of Site 543 (Fig. 8b). The exceptions are U, which is 2 times that of Site 543 due to the presence of the black shale unit, and Zr and Hf, which are enriched in the zircon-bearing lowest units of Site 144. Finally, the average for Barbados is strikingly similar to the carbonate-free Site 144 bulk composition (Fig. 8b) but with even higher Zr and Hf concentrations due to the abundance of zircon-rich sandstones. Both the Barbados estimate and the carbonate-free Site 144 bulk composition are markedly different from the estimate of Plank and Langmuir (1998) for the Southern Antilles sediments (Fig. 8b). The discrepancy is best explained by the differences in methods used to obtain the averages. Plank and Langmuir (1998) combined their northern Antilles sediment average with data obtained on a single surface sample from the southern part of the Lesser Antilles forearc analyzed by Ben Othman et al. (1989)

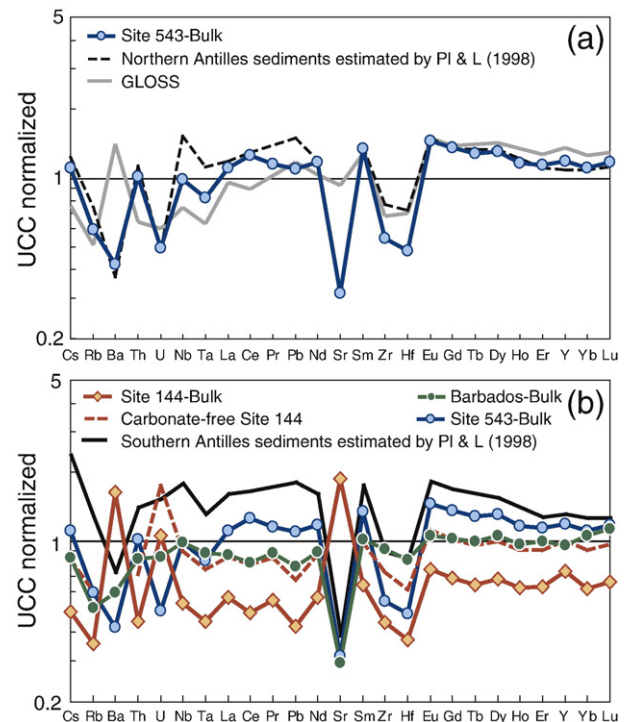


Fig. 8. UCC (McLennan, 2001) normalized trace element patterns for (a) Bulk Site 543 (Table 2) compared with GLOSS and the Northern Antilles sediments estimate of Plank and Langmuir (1998); (b) Bulk Site 144 average together with the carbonate-free Site 144 average and the Barbados average (Table 2) compared with the Southern Antilles sediments estimate of Plank and Langmuir (1998). Bulk Site 543 is also shown for comparison. The lower concentrations in carbonate-free Site 144 and Barbados relative to Site 543 come from lower proportion of clay over quartz ($\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 5$ vs. ~ 3.3). The Plank and Langmuir (1998) estimate for the southern sediments is also much higher than our averages. Because Plank and Langmuir (1998) estimated their southern average using one clay-rich sample analyzed by Ben Othman et al. (1989) and combining it to their northern estimate, their bulk southern average has a very low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.7. We therefore suggest that the high proportion of clay fraction in their estimate explains their systematically higher trace element concentrations.

(see Fig. 8 caption). Our new extensive dataset is more representative of the subducted pile.

Average Sr and Hf isotope ratios are also given in Table 2, together with the values for Nd and Pb isotopes of Carpentier et al. (2008). They all have a distinctly “continental” signature. The Site 543 bulk composition has a $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.71585, which is similar to the average UCC ratio of 0.716 estimated by Goldstein and Jacobsen (1988). The average for Site 144, on the other hand, is overwhelmed by seawater carbonates that buffer the Sr budget. In addition, both Site 543 and Site 144 have unradiogenic Hf isotopic compositions ($\epsilon_{\text{Hf}} = -7.4$ and -14.4 , respectively, Table 2). These values are particularly low when compared to the mean Hf isotopic composition ($\epsilon_{\text{Hf}} = +2 \pm 3$) for subducting sediments recently estimated by Chauvel et al. (2008). This feature is readily explained by the unusually large contribution of old detrital material to the Lesser Antilles forearc sediments, compared to worldwide oceanic sediments.

In summary, the Lesser Antilles forearc sediments from Sites 543 and 144 are characterized by a dominant input from continental material, and represent the continental end member of the entire spectrum defined by soon-to-be-subducted oceanic sediments. However, the two sites are not identical in composition, and their differences can be used to model the contribution of various types of sediments to the sources of arc lavas.

5.4. Nd–Hf isotopes in the subducting sediments and the Lesser Antilles lavas

Numerous studies have highlighted the strong geochemical and isotopic changes of lava composition from north to south along the Lesser Antilles arc (Hawkesworth and Powell, 1980; White and Dupré, 1986; Davidson, 1987; Turner et al., 1996). The lavas from the northern islands (from Saba to Dominica) have relatively constant and unradiogenic Pb isotopes. In contrast, Pb isotope ratios of lavas from the southern islands (from Martinique to Grenada) display very strong variations and reach highly radiogenic values. These variations are usually attributed to changes in the composition and/or amount of the subducted sediments (White and Dupré, 1986; Vidal et al., 1991; Turner et al., 1996; Carpentier et al., 2008) and/or to interactions during magma

ascent with sedimentary rocks in the arc crust (Thirlwall and Graham, 1984; Davidson, 1987; Thirlwall et al., 1996; Smith et al., 1996). Carpentier et al. (2008) suggested on the basis of Pb–Nd isotopic data that sediments from Site 543 represent an appropriate radiogenic end member to explain the lava compositions of the northern islands, while Site 144 and Barbados sediments, located in the south of the forearc region, have the appropriate composition to explain the southern island lavas.

Fig. 9 displays the Nd and Hf isotopic compositions of lavas from the Lesser Antilles, together with those of Sites 543–144 and Barbados sediments. Although the available Hf data for the Lesser Antilles arc are very limited, their range is large compared to other intra-oceanic arcs (Fig. 9). In addition, some St Lucia lavas (Vidal et al., 1991) have ϵ_{Hf} and ϵ_{Nd} values that are much lower than in any other intra-oceanic arc. White and Patchett (1984) and Vidal et al. (1991) attributed these unradiogenic Nd and Hf isotopic compositions to contamination of the mantle wedge by subducted sediments. In contrast, Woodhead et al. (2001) preferred high level crustal contamination as an explanation of the Hf isotopic compositions of some Martinique lavas.

The studied forearc sediments plot at the unradiogenic end of the Lesser Antilles array (Fig. 9) and could thus represent the unradiogenic material required to explain the lava compositions. However, the number of analyzed lavas is so small that it is difficult to evaluate whether a north–south gradient exists in Nd–Hf isotopic space (Fig. 9). Indeed, the Hf isotopic compositions of the northern islands (from Saba to Dominica) and those of the southernmost islands (from St Vincent to Grenada) are quite similar and relatively radiogenic (Fig. 9). However, the lowest Hf isotope ratios are found in lavas from Martinique and St Lucia islands (Fig. 9), which are both located in the southern part of the arc (Fig. 1) and are characterized by crustal-like Pb–Nd–Sr isotopes (White and Dupré, 1986; Vidal et al., 1991; Turner et al., 1996).

While Site 543 and 144 sediments have comparable average Nd isotopic compositions, the average Hf isotopic composition of Site 144 is significantly less radiogenic than that of Site 543 (Fig. 9). In addition, sediments from Site 144 and Barbados display generally lower Nb/Zr ratios associated with lower $\Delta\epsilon_{\text{Hf}}$ (Fig. 7) due to the

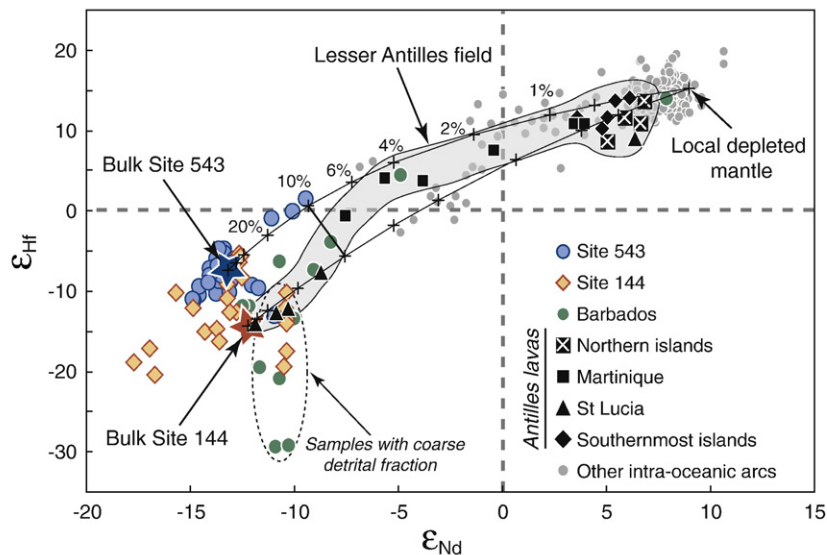


Fig. 9. Nd and Hf isotopic compositions of Lesser Antilles lavas compared to those of sediments from Sites 543 and 144 and Barbados Island. Published data for the Lesser Antilles lavas are from White and Patchett (1984), Vidal et al. (1991) and Woodhead et al. (2001). Northern islands are Saba, St Kitts, Montserrat and Guadeloupe islands, while southernmost islands are St Vincent, Grenadines and Grenada islands. The sediments Nd isotopic compositions are from Carpentier et al. (2008). Hf and Nd isotopic compositions of lavas from other intra-oceanic arcs come from GEOROC: (<http://georoc.mpch-mainz.gwdg.de/georoc/>). The solid lines represent mixing curves between local depleted mantle and two sedimentary end members. Ticks show the percentage of sediments in the mixture. Compositions of the end members used for the calculations: (1) depleted mantle: Nd = 0.713 ppm, Hf = 0.199 ppm (Salters and Stracke, 2004) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.5131$, $^{176}\text{Hf}/^{177}\text{Hf} = 0.2832$, (2) for the sedimentary end members, we used the average of Site 543 sediments and the carbonate-free Site 144 average (Table 2).

presence of zircons in some units. It might, therefore, be possible to distinguish two mixing trends. Assuming that Site 543 sediments are involved in the northern island lava genesis, the mixing array between these sediments and mantle wedge should correspond to the upper part of the Lesser Antilles field in Nd–Hf isotopic space (Fig. 9). Similarly the average composition of Site 144, should define the mixing array for the lower part of the Lesser Antilles field. However, in the southern part of the arc, the situation is complex because zircons are the carrier of the unradiogenic Hf signature. Given the low solubility of zircon in aqueous fluids (Ayers and Watson, 1991; Kovalenko and Ryzhenko, 2009), the unradiogenic Hf of the southern sediments should not be transmitted to the magma source in the mantle wedge if aqueous fluid is the dominant transport medium from slab to mantle. If this is so, the southern island lavas should not differ strongly from the northern islands, particularly if the proportion of sediment is low. In contrast, if the temperature of the subducted slab is sufficient for the sediments and the zircons to melt (Hermann and Rubatto, 2009; Dufrane et al., 2009), the unradiogenic Hf carried by the zircons will be transmitted to the mantle wedge and then to the lavas. In this case, the southern islands should lie on the lower part of the Lesser Antilles Hf–Nd field.

Using the few available data on the Lesser Antilles arc, we modeled bulk mixing of depleted mantle with the two average sediment piles (Fig. 9) and we tried to reproduce the island arc field. The mixing hyperbolas show that the compositions of lavas from both the northern islands and from St Vincent to Grenada in the south require no more than 1% bulk sediment in the mantle–sediment mixture (Fig. 9). About 8% sediment is needed to explain the lowest ε_{Hf} – ε_{Nd} lava of Martinique Island. The situation is more complex for the St Lucia Soufrière lavas whose compositions are clearly shifted toward the Site 144 field, an observation consistent with the southward position of this island. Using the Site 144 average, between 15 and 60% sediment is required in the mixture, a proportion that seems excessive in view of the unremarkable chemical composition of these potassic calc-alkaline andesites and dacites (Vidal et al., 1991). An alternative is to use the Site 144 sediment with the lowest ε_{Hf} and ε_{Nd} as an end member. This considerably reduces the percentage of sediments involved in the St Lucia magmas but the model is presently unconstrained. Alternatively, the evolved dacites might have been contaminated on their way to the surface.

5.5. Impact of recycled sediments on arcs and mantle

In broader terms, the subduction of sediments affects both the composition of the arc lavas and the average composition of the mantle. The process creates large chemical and isotopic heterogeneities because of the extreme and variable compositions of the sediments that differ significantly from that of the mantle. With their very unradiogenic isotopic compositions, the Lesser Antilles forearc sediments represent the continental end member of the entire spectrum defined by subducted oceanic sediments. Their Hf isotope ratios correlate well with their Nb/Zr ratios, as shown in Fig. 7. In this figure, the field for island arc volcanics is located at very low Nb/Zr ratios (~ 0.02), and relatively high $\Delta\varepsilon_{\text{Hf}}$ (see histogram shown in inset of Fig. 7). The very low average Nb/Zr ratio is puzzling because this ratio normally increases during partial melting and the lavas always have higher Nb/Zr than their source. The island arc ratio is significantly lower than in MORB and N-MORB suggesting that their source is either more depleted than normal depleted mantle or a mineral phase such as rutile preferentially retains Nb (Hermann and Rubatto, 2009 and references therein). The positive average $\Delta\varepsilon_{\text{Hf}}$ for island arcs suggests that sediments mixed into the mantle wedge source have generally high Hf isotope ratios relative to their Nd isotopic compositions. To explain the general features of the island arc lavas, two possibilities can be envisioned: in the first case, the majority of subducted sediments have positive $\Delta\varepsilon_{\text{Hf}}$ values, a feature

consistent with their generally low Zr/ Al_2O_3 and high Nb/Zr (see Fig. 6). The complementary zircon-rich sediments must then remain at or near the continent, and only the clay-rich fraction is transferred via subduction into the source of the lavas. In the second case, if average oceanic sediments have $\Delta\varepsilon_{\text{Hf}} \sim 0$, then the zircons could be retained in the slab or could be residual during melting of the mantle wedge, and only the high $\Delta\varepsilon_{\text{Hf}}$ mineral fraction is involved in the genesis of island arc lavas. In the former case, the sedimentary residue recycled back in the mantle would have high Nb/Zr and high $\Delta\varepsilon_{\text{Hf}}$; in the latter, the mantle would acquire the “zircon signature”. The two processes would have quite different effects on the long-term evolution of the Earth mantle because of the diverging evolution through time of these two sedimentary packages.

6. Conclusions

Our study of sediments from the Lesser Antilles forearc region shows that their chemical and isotopic compositions are mainly controlled by a detrital sedimentary component that is variably diluted by biogenic silica or carbonate. Site 543 in the north is dominated by Al-rich detrital clays with high concentrations of most trace elements and contains only a small fraction of biogenic sediment. Farther to the south and closer to the South American continent, at Site 144 and Barbados, sediments have generally lower trace-element concentrations due to variable but significant dilution of the clay fraction by carbonate and pure silica (biogenic and detrital).

The “zircon effect” is strongly visible in variations of Zr and Hf contents, of Nb/Zr ratios and of the Hf isotope compositions of sediments from the three sites. In the clay-rich sediments in the north, Zr and Hf contents are low, whereas in the coarse sands in the south, the presence of zircons leads to strong enrichments in Zr and Hf. The depletion or excess of Zr and Hf correlates with $\Delta\varepsilon_{\text{Hf}}$, the vertical deviation of Hf isotopic compositions from the terrestrial Hf–Nd isotopic array of Vervoort et al. (1999): fine, clay-rich and Zr-poor sediments plot above the Terrestrial array, a position that indicates that their Hf came from a source with a high time-integrated Lu/Hf ratio. In contrast, Zr and Hf enrichment due to zircon in the coarse detrital fractions produces lower Hf isotopic ratios in the sands which plot well below the Terrestrial array.

Sediments from the entire Lesser Antilles arc have unradiogenic Hf isotopic compositions compared to worldwide oceanic sediments, a difference we attribute to an unusually large component of old detrital material in the sediments that are subducting into this very crustal-like intra-oceanic island arc. We speculate that the trace-element and isotopic differences between sediments from the northern and the southern sites are transmitted to the compositions of the arc lavas: a systematic difference in $\Delta\varepsilon_{\text{Hf}}$ between the northern and the southern part of the arc should be observed but more data on the arc volcanics are required to confirm our suggestion. More generally, the long-term recycling of heterogeneous sedimentary material will create diversity and isotopic heterogeneity in the terrestrial mantle.

Acknowledgements

Sites DSDP 543 and 144 samples were kindly provided by the ODP repository of the Lamont-Doherty Earth Observatory. Sylvain Campillo is thanked for his help in the lab in Grenoble as well as Claire Bassoullet and Jeroen de Jong for analytical assistance during TIMS and MC-ICP-MS measurements in Brest and Bruxelles respectively. Discussions with Nick Arndt and Dominique Weis improved style and content. We are grateful to the two anonymous reviewers and to the editor Rick Carlson for their very constructive comments made on the manuscript. This work was supported by funding from the Dyeti CNRS program and the ANR project “UDAntilles” while travel to Brussels was financed by Egide.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2009.07.043](https://doi.org/10.1016/j.epsl.2009.07.043).

References

- Agranier, A., et al., 2005. The spectra of isotopic heterogeneities along the mid-Atlantic Ridge. *Earth Planet. Sci. Lett.* 238, 96–109.
- Albarède, F., Goldstein, S.L., Dautel, D., 1997. The neodymium isotopic composition of manganese nodules from the Southern and Indian oceans, the global oceanic neodymium budget, and their bearing on deep ocean circulation. *Geochim. Cosmochim. Acta* 61 (6), 1277–1291.
- Albarède, F., Somonetti, A., Vervoort, J.D., Blichert-Toft, J., Abouchami, W., 1998. A Hf–Nd isotopic correlation in ferromanganese nodules. *Geophys. Res. Lett.* 25 (20), 3895–3898.
- Allègre, C.J., Dupré, B., Nègre, P., Gaillardet, J., 1996. Sr–Nd–Pb isotope systematics in Amazon and Congo River systems: Constraints about erosion processes. *Chem. Geol.* 131, 93–112.
- Anderson, R.F., Fleisher, M.Q., LeHuray, A.P., 1989. Concentration, oxidation state, and particle flux of uranium in the Black Sea. *Geochim. Cosmochim. Acta* 53, 2215–2224.
- Arndt, S., Brumsack, H.J., Wirtz, K.W., 2006. Cretaceous black shales as active bioreactors: a biogeochemical model for the deep biosphere encountered during ODP Leg 207 (Demerara Rise). *Geochim. Cosmochim. Acta* 70, 408–425.
- Ayers, J.C., Watson, E.B., 1991. Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry. *Philos. Trans. R. Soc.* 335, 365–375.
- Bayon, G., et al., 2009. Hf and Nd isotopes in marine sediments: constraints on global silicate weathering. *Earth Planet. Sci. Lett.* 277, 318–326.
- Ben Othman, D., White, W.M., Patchett, J., 1989. The geochemistry of marine sediments, island arc magma genesis, and crust–mantle recycling. *Earth Planet. Sci. Lett.* 94, 1–21.
- Biju-Duval, B., Quélé, P.L., Mascle, A., Renard, V., Valéry, P., 1982. Multibeam bathymetric survey and high resolution seismic investigations on the Barbados ridge complex (Eastern Caribbean): a key to the knowledge and interpretation of an accretionary wedge. *Tectonophysics* (86), 275–304.
- Biju-Duval, B., et al., 1984. Initial Reports of the Deep Sea Drilling Project 78A. U.S. Government Printing Office, Washington, 848 pp.
- Biju-Duval, B., et al., 1985. The terrigenous and pelagic series of Barbados island: Paleocene to middle Miocene slope deposits accreted to the Lesser Antilles margin. In: Mascle, A. (Ed.), *Géodynamique des Caraïbes*. Technip, Paris, pp. 187–197.
- Blichert-Toft, J., Chauvel, C., Albarède, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector–multiple collector ICP–MS. *Contrib. Mineral. Petrol.* 127, 248–260.
- Bouvier, A., Vervoort, J.D., Patchett, P.J., 2008. The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet. Sci. Lett.* 273, 48–57.
- Burton, K.W., Ling, H.F., O’Nions, R.K., 1997. Closure of the Central American Isthmus and its effect on the deep-water formation in the North Atlantic. *Nature* 386, 382–385.
- Carpentier, M., Chauvel, C., Mattielli, N., 2008. Pb–Nd isotopic constraints on sedimentary input into the Lesser Antilles arc system. *Earth Planet. Sci. Lett.* 272, 199–211.
- Chan, L.H., Leeman, W.P., Plank, T., 2006. Lithium isotopic composition of marine sediments. *Geochim. Geophys. Geosyst.* 7 (6), Q06005. [doi:10.1029/2005GC001202](https://doi.org/10.1029/2005GC001202).
- Chauvel, C., Blichert-Toft, J., 2001. A hafnium isotope and trace element perspective on melting of the depleted mantle. *Earth Planet. Sci. Lett.* 190, 137–151.
- Chauvel, C., Lewin, E., Carpentier, M., Arndt, N.T., Marini, J.-C., 2008. Role of recycled oceanic basalt and sediment in generating the Hf–Nd mantle array. *Nature Geoscience* 1, 64–67.
- Chauvel, C., Marini, J.-C., Plank, T., Ludden, J.N., 2009. Hf–Nd input flux in the Izu–Mariana subduction zone and recycling of subducted material in the mantle. *Geochim. Geophys. Geosyst.* 10 (1), Q10001. [doi:10.1029/2008GC002101](https://doi.org/10.1029/2008GC002101).
- David, K., Frank, M., O’Nions, R.K., Belshaw, N.S., Arden, J.W., 2001. The Hf isotope composition of global seawater and the evolution of Hf isotopes in the deep Pacific Ocean from Fe–Mn crusts. *Chem. Geol.* 178, 23–42.
- Davidson, J.P., 1987. Crustal contamination versus subduction zone enrichment: examples from the Lesser Antilles and implications for mantle source compositions of island arc volcanic rocks. *Geochim. Cosmochim. Acta* 51, 2185–2198.
- DuFrane, A.S., Turner, S., Dosseto, A., van Soest, M., 2009. Reappraisal of fluid and sediment contributions to Lesser Antilles magmas. *Chem. Geol.* 265, 272–278.
- Eggins, S.M., et al., 1997. A simple method for the precise determination of > 40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. *Chem. Geol.* 134, 311–326.
- Erbacher, J., Mosher, D.C., Malone, M.J., 2004. Proceedings of the Ocean Drilling Program, Initial Reports, 207. Ocean Drilling Program, College Station.
- Godfrey, L.V., et al., 1997. The Hf isotopic composition of ferromanganese nodules and crusts and hydrothermal manganese deposits: Implications for seawater Hf. *Earth Planet. Sci. Lett.* 151, 91–105.
- Goldstein, S.L., Jacobsen, S.B., 1988. Nd and Sr isotopic systematics of river water suspended material: implications for crustal evolution. *Earth Planet. Sci. Lett.* 87, 249–265.
- Goldstein, S.L., O’Nions, R.K., Hamilton, P.J., 1984. A Sm–Nd isotopic study of atmospheric dusts and particulates from major river systems. *Earth Planet. Sci. Lett.* 70, 221–236.
- Hawkesworth, C.J., Powell, M., 1980. Magma genesis in the Lesser Antilles island arc. *Earth Planet. Sci. Lett.* 51, 297–308.
- Hayes, D.E., et al., 1972. Initial Reports of the Deep Sea Drilling Project 14. U.S. Government Printing Office, Washington.
- Hemleben, C., Troester, J., 1984. Campanian–Maestrichtian deep-water foraminifers from Hole 543A, Deep Sea Drilling Project. In: Biju-Duval, B., Moore, J.C. (Eds.), *Initial Reports of the Deep Sea Drilling Project 78A*. U.S. Government Printing Office, Washington, pp. 509–524.
- Hermann, J., Rubatto, D., 2009. Accessory phase control on the trace element signature of sediment melts in subduction zones. *Chem. Geol.* 265, 512–526.
- Hofmann, A.W., 1988. Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* 90, 297–314.
- Jones, C.E., Jenkyns, H.C., Coe, A.L., Hesselbo, S.P., 1994. Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochim. Cosmochim. Acta* 58 (14), 3061–3074.
- Kelley, K.A., Plank, T., Ludden, J., Staudigel, H., 2003. Composition of altered oceanic crust at ODP Sites 801 and 1149. *Geochim. Geophys. Geosyst.* 4 (6), 8910. [doi:10.1029/2002GC000435](https://doi.org/10.1029/2002GC000435).
- Klinkhammer, G.P., Palmer, M.R., 1991. Uranium in the oceans: where it goes and why. *Geochim. Cosmochim. Acta* 55 (1799–1806).
- Kovalenko, N.I., Ryzhenko, B.N., 2009. Comparative study of the solubility of zircon and baddeleyite. *Geochim. Int.* 47, 405–413.
- Lin, S., He, M., Hu, S., Yuan, H., Gao, S., 2000. Precise determination of trace elements in geological samples by ICP–MS using compromise conditions and fine matrix-matching strategy. *Anal. Sci.* 16, 1291–1296.
- McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochim. Geophys. Geosyst.* 2, 2000GC000109.
- McLennan, S.M., Taylor, S.R., McCulloch, M.T., Maynard, J.B., 1990. Geochemical and Nd–Sr isotopic composition of deep sea turbidites: Crustal evolution and plate tectonic associations. *Geochim. Cosmochim. Acta* 54, 2015–2050.
- Minster, J.F., Jordan, T.H., 1978. Present-day plate motions. *J. Geophys. Res.* 83, 5331–5351.
- Moore, J.C., Biju-Duval, B., Bergen, J.A., 1982. Offscraping and underthrusting of sediment of the deformation front of the Barbados Ridge: Deep Sea Drilling Project Leg 78A. *Geol. Soc. Am. Bull.* 93, 1065–1077.
- Olivier, N., Boyet, M., 2006. Rare earth and trace elements of microbialites in Upper Jurassic coral- and sponge- microbialite reefs. *Chem. Geol.* 230, 105–123.
- O’Nions, R.K., Frank, M., von Blanckenburg, F., Ling, H.F., 1998. Secular variation of Nd and Pb isotopes in ferromanganese crusts from the Atlantic, Indian and Pacific oceans. *Earth Planet. Sci. Lett.* 155, 15–28.
- Parra, M., Faugères, J.C., Grousset, F., Pujol, C., 1997. Sr–Nd isotopes as tracers of finegrained detrital sediments: the south-Barbados accretionary prism during the last 150 kyr. *Mar. Geol.* 136, 225–243.
- Patchett, P.J., White, W.M., Feldmann, H., Kienlitz, S., Hofmann, A.W., 1984. Hafnium/rare earth element fractionation in the sedimentary system and crustal recycling into the Earth’s mantle. *Earth Planet. Sci. Lett.* 1984, 365–378.
- Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* 145, 325–394.
- Plank, T., Ludden, J.N., 1992. Geochemistry of sediment in the Argo Abyssal Plain at Site 765: a continental margin reference section for sediment recycling in subduction zones. In: Gradstein, F.M., Ludden, J.N. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, 123. Ocean Drilling Program, College Station, pp. 167–189.
- Plank, T., Kelley, K.A., R.W., M., Stern, L.Q., 2007. Chemical composition of sediments subducting at the Izu–Bonin trench. *Geochim. Geophys. Geosyst.* 8 (4), Q04116. [doi:10.1029/2006GC001444](https://doi.org/10.1029/2006GC001444).
- Prytulak, J., Vervoort, J.D., Plank, T., Yu, C., 2006. Astoria Fan sediments, DSDP site 174, Cascadia Basin: Hf–Nd–Pb constraints on provenance and outburst flooding. *Chem. Geol.* 233, 276–292.
- Pudsey, C.J., 1984. X-ray mineralogy of Miocene and older sediments from Deep Sea Drilling Project Leg 78A. In: Biju-Duval, B., Moore, J.C. (Eds.), *Initial Reports of the Deep Sea Drilling Project 78A*. U.S. Government Printing Office, Washington, pp. 325–356.
- Pudsey, C.J., Reading, H.G., 1982. Sedimentology and structure of the Scotland group, Barbados. *Geol. Soc. Lond., Spec. Pub.* 10, 291–308.
- Raczek, I., Stoll, B., Hofmann, W., Jochum, K.P., 2000. High-precision trace element data for USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, DTS-1, DTS-2, GSP-1 and GSP-2 by ID-TIMS and MIC-SSMS. *Geostand. Newsl.* 25 (1), 77–86.
- Salter, V.J.M., 1996. The generation of mid-ocean ridge basalts from the Hf and Nd isotope perspective. *Earth Planet. Sci. Lett.* 141, 109–123.
- Salter, V.J.M., Stracke, A., 2004. Composition of the depleted mantle. *Geochim. Geophys. Geosyst.* 5 (5), Q05004. [doi:10.1029/2003GC000597](https://doi.org/10.1029/2003GC000597).
- Salter, V.J.M., White, W.M., 1998. Hf isotope constraints on mantle evolution. *Chem. Geol.* 145, 447–460.
- Smith, T.E., Thirlwall, M.F., Macpherson, C.G., 1996. Trace element and isotopic geochemistry of the volcanic rocks of Bequia, Grenadine Islands, Lesser Antilles arc: a study of subduction enrichment and intra-crustal contamination. *J. Petrol.* 37 (1), 117–143.
- Speed, R.C., et al., 1984. Lesser Antilles arc and adjacent terranes, Atlas 10, Ocean Margin drilling Program, Regional Atlas Series: Marine Science International, Woods Hole, Massachusetts. 27 sheets pp.
- Su, Y. J., 2002. Mid-ocean Ridge Basalt Trace Element Systematics: Constraints From Database Management, ICP–MS Analyses, Global Data Compilation and Petrologic Modeling. Thesis, Columbia University, 472 pp.
- Thirlwall, M.F., Graham, A.M., 1984. Evolution of the high-Ca, high-Sr C-series basalts from Grenada, Lesser Antilles: the effects of intra-crustal contamination. *J. Geol. Soc. Lond.* 141 (427–445).
- Thirlwall, M.F., Graham, A.M., Arculus, R.J., Harmon, R.S., Macpherson, C.G., 1996. Resolution of the effects of crustal assimilation, sediment subduction, and fluid transport in island arc magmas: Pb–Sr–Nd–O isotope geochemistry of Grenada, Lesser Antilles. *Geochim. Cosmochim. Acta* 60 (23), 4785–4810.
- Turner, S., et al., 1996. U-series isotopes and destructive plate margin magma genesis in the Lesser Antilles. *Earth Planet. Sci. Lett.* 142, 191–207.

- van der Flierdt, T., Hemming, S.R., Goldstein, S.L., Abouchami, W., 2006. Radiogenic isotope fingerprint of Wilkes Land-Adélie Coast Bottom Water in the circum-Antarctic Ocean. *Geophys. Res. Lett.* 33. doi:10.1029/2006GL026020.
- van der Flierdt, T., et al., 2007. Global neodymium-hafnium isotope systematics revisited. *Earth Planet. Sci. Lett.* 259, 432–441.
- Vervoort, J.D., Blichert-Toft, J., 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochim. Cosmochim. Acta* 63, 533–556.
- Vervoort, J.D., Patchett, P.J., Blichert-Toft, J., Albarède, F., 1999. Relationships between Lu–Hf and Sm–Nd isotopic systems in the global sedimentary system. *Earth Planet. Sci. Lett.* 168, 79–99.
- Vidal, P., Guen, Le, de Kerneizon, M., Maury, R.C., Dupré, B., White, W.M., 1991. Large role of sediments in the genesis of some Lesser Antilles and dacites (Soufrière, St Lucia): isotopic constraints. *Bull. Soc. Géol. Fr.* 162 (6), 993–1002.
- Vlastélic, I., Carpentier, M., Lewin, E., 2005. Miocene climate change recorded in the chemical and isotopic (Pb, Nd, Hf) signature of the Southern Ocean sediments. *Geochem. Geophys. Geosyst.* 6 (1), Q03003. doi:10.1029/2004GC000819.
- Vroon, P.Z., Van Bergen, M.J., Klaver, G.J., White, W.M., 1995. Strontium, neodymium, and lead isotopic and trace-element signatures of the East Indonesian sediments: provenance and implications for Banda Arc magma genesis. *Geochim. Cosmochim. Acta* 59 (12), 2573–2598.
- Weis, D., Kieffer, B., Maerschalk, C., Pretorius, W., Barling, J., 2005. High-precision Pb–Sr–Nd–Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials. *Geochem. Geophys. Geosyst.* 6 (2), Q02002. doi:10.1029/2004GC000852.
- Westbrook, G.K., 1982. The Barbados Ridge Complex: tectonics of a mature forearc system. *Geol. Soc. Lond., Spec. Pub.* 10, 275–290.
- Westbrook, G.K., Smith, M.J., 1983. Long décollements and mud volcanoes: evidence from the Barbados Ridge Complex for the role of high pore-fluid pressure in the development of an accretionary complex. *Geology* 11, 279–283.
- Westbrook, G.K., Mascle, A., Biju-Duval, B., 1984. Geophysics and the structure of Lesser Antilles Forearc. In: Biju-Duval, B., Moore, J.C.J. (Eds.), *Initial Reports of the Deep Sea Drilling Program 78A*. U.S. Government Printing Office, Washington, pp. 23–28.
- White, W.M., Dupré, B., 1986. Sediment subduction and magma genesis in the Lesser Antilles: isotopic and trace element constraints. *J. Geophys. Res.* 91 (B6), 5927–5941.
- White, W.M., Patchett, P.J., 1984. Hf–Nd–Sr isotopes and incompatible element abundances in island arcs: implications for magma origins and crust–mantle evolution. *Earth Planet. Sci. Lett.* 67, 167–185.
- White, W.M., Dupré, B., Vidal, P., 1985. Isotope and trace element geochemistry of sediments from the Barbados Ridge-Demerara Plain region, Atlantic ocean. *Geochim. Cosmochim. Acta* 49, 1875–1886.
- Wilson, S.A., 1997. Data compilation for USGS reference material BHVO-2. Hawaiian Basalt. USGS Open File Report.
- Woodhead, J.D., Hergt, J.M., Davidson, J.P., Eggins, S.M., 2001. Hafnium isotope evidence for “conservative” element mobility during subduction zone processes. *Earth Planet. Sci. Lett.* 192 (3), 331–346.
- Wright, A., 1984. Sediment distribution and depositional processes operating in the Lesser Antilles intraoceanic island arc, eastern Caribbean. In: Biju-Duval, B., Moore, J.C. (Eds.), *Initial Reports of the Deep Sea Drilling Program 78A*. U.S. Government Printing Office, Washington, pp. 301–324.