



Pb–Nd isotopic constraints on sedimentary input into the Lesser Antilles arc system

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ABSTRACT

The Lesser Antilles arc is a particularly interesting island arc because it is presently very active, it is located perpendicular to the South American continent and its chemical and isotopic compositions display a strong north–south gradient. While the presence in the south of a thick pile of sedimentary material coming from the old South American continent has long been suspected to explain the geochemical gradient, previous studies failed to demonstrate unambiguously a direct link between the arc lava compositions and the subducted sediment compositions.

Here, we present new Nd, Sm, Th, U and Pb concentrations and Nd–Pb isotopic data for over 60 sediments from three sites located in the fore arc region of the Lesser Antilles arc. New data for DSDP Site 543 drill core located east of Dominica Island complement the data published by White et al. [White, W.M., Dupré, B. and Vidal, P., 1985. Isotope and trace element geochemistry of sediments from the Barbados Ridge–Demerara Plain region, Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 49: 1875–1886.] and confirm their relatively uniform isotopic compositions (i.e., $^{206}\text{Pb}/^{204}\text{Pb}$ between 19.13 and 19.53). In contrast, data obtained on DSDP Site 144 located further south, on the edge of the South American Rise and on sediments from Barbados Island are much more variable ($^{206}\text{Pb}/^{204}\text{Pb}$ ranges from 18.81 to 27.69). The very radiogenic Pb isotopic compositions are found in a 60 m thick black shale unit, which has no age equivalent in the Site 543 drill core. We interpret the peculiar composition of the southern sediments as being due to two factors, (a) the proximity of the South American craton, which contributes coarse grain old detrital material that does not travel far from the continental shelf, and (b) the presence of older sediments including the thick black shale unit formed during Oceanic Anoxic events 2 and 3.

The north–south isotopic change known along the Lesser Antilles arc can be explained by the observed geographical changes in the composition of the subducted sediments. About 1% contamination of the mantle wedge by Site 543 sediments explains the composition of the northern islands while up to 10% sediments like those of Site 144 is required in the source of the southern island lavas. The presence of black shales in the subducted pile provides a satisfactory explanation for the very low $\Delta 8/4$ values that characterize the Lesser Antilles arc.

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1. Introduction

Magma in subduction zones results from melting of the mantle wedge, modified by material transferred from the subducted slab in hydrous fluids and/or partial melts. Thus, subducted oceanic crust and sediments are believed to influence the chemical composition of island arcs. Constraining the chemical composition of the input flux (i.e., subducted components) can therefore help understanding the role or such material in arc magma genesis.

Lavas in the Lesser Antilles arc (Fig. 1) exhibit a large range of Sr–Nd–Pb isotopic compositions which include the most radiogenic Pb isotopic compositions known for intra-oceanic arcs. They are also characterized by a pronounced chemical zoning from north to south along the arc

(Hawkesworth and Powell, 1980; White and Dupré, 1986; Davidson, 1987; Turner et al., 1996), with the highest Pb isotope ratios and lowest Nd isotope ratios being found in the southern islands (Fig. 1). Such characteristics have been attributed to variable input in the magmas of crustal material located either in the arc crust or in the subducted sedimentary pile (i.e., Davidson, 1987; White and Dupré, 1986; Davidson and Harmon, 1989; Thirlwall et al., 1996; Turner et al., 1996).

Previous geochemical studies of subducting sediments along the Lesser Antilles arc focused on one site drilled during DSDP Leg 78A, and on surface sediments from a large area in front of the Lesser Antilles trench (White et al., 1985). These authors suggested that the isotopic compositions of both surface and drilled sediments were strongly influenced by detrital input from the South American continent, in particular, the Guyana Precambrian shield via the Orinoco River (White et al., 1985). They also highlighted an increase in Pb isotope ratios in the surface sediments southward, toward the

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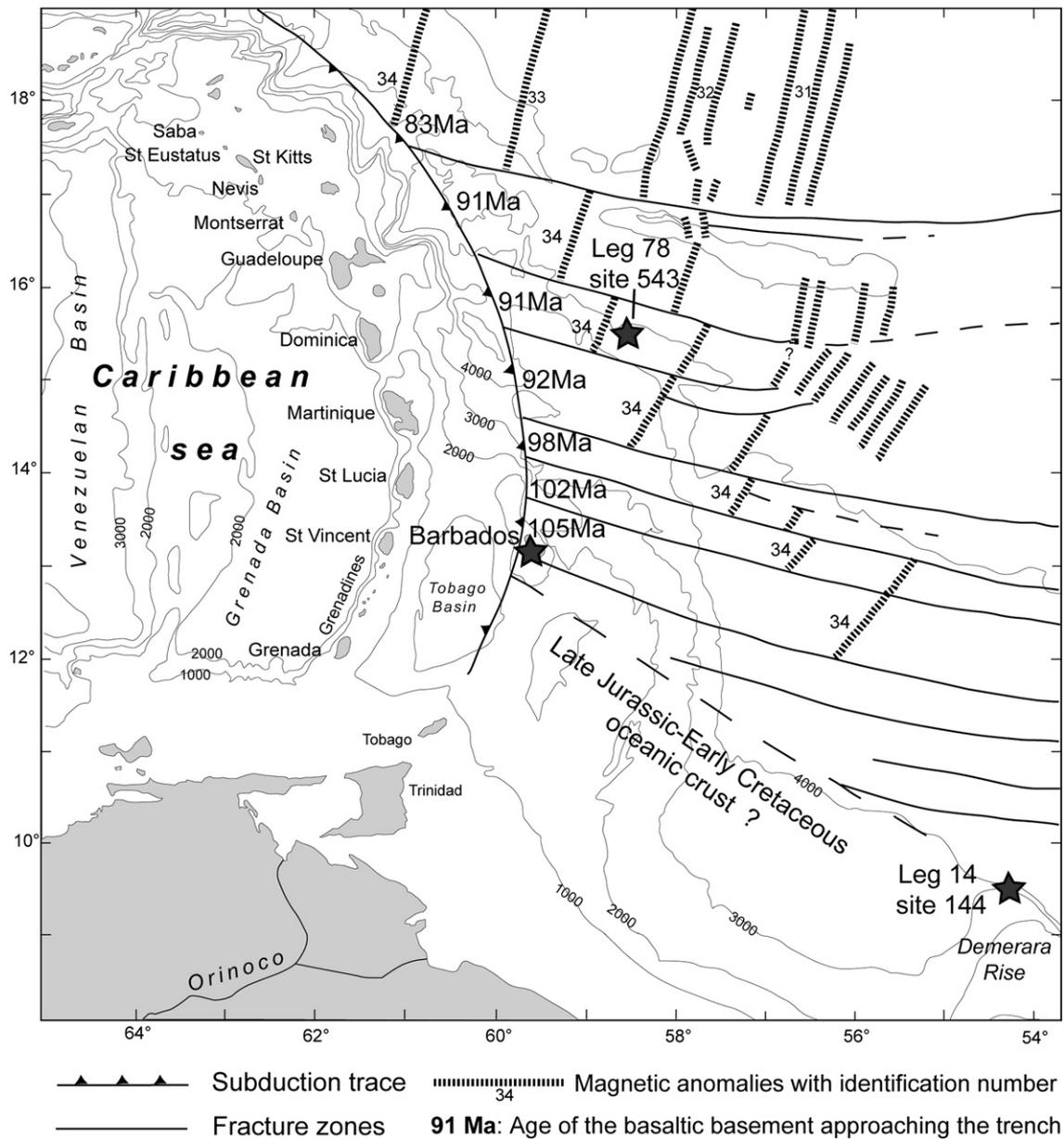


Fig. 1. Bathymetric map of the studied area showing the locations of the three sampled sites (DSDP 78A Site 543, DSDP 14 Site 144 and Barbados Island shown with stars). The major oceanic magnetic anomalies and fracture zones in the Atlantic crust are also shown (modified from Speed et al., 1984). The age of the subducting slab is indicated next to the trench and was calculated using a Cretaceous half-spreading rate of 2.2 cm/yr for the middle Atlantic ridge (Cogné and Humler, 2004) and the distance to the magnetic anomaly 34.

mouth of the Orinoco River, and attributed this gradient to an increasing input of radiogenic Pb derived from the shield.

However, when the isotopic compositions of Lesser Antilles lavas are compared with those of the soon-to-be subducted sediments of White et al. (1985), it appears clearly that some lavas from the southern islands have Pb isotope ratios that are more radiogenic than the sediments. While all studies agree that variable amounts (and/or compositions) of sediments are the cause of the observed geochemical variations, the manner in which the sedimentary signature was introduced into the lavas is still discussed: it could be “contamination” of the mantle wedge by subducted sediments as suggested by White and Dupré (1986), Vidal et al. (1991) and Turner et al. (1996), or it could be high-level contamination of the magmas by sediments intercalated within the arc crust as suggested by Thirlwall and Graham (1984), Davidson (1985, 1986, 1987), Davidson and Harmon (1989), Smith et al. (1996) and Thirlwall et al. (1996). White and Dupré (1986) suggested that sediments with more radiogenic Pb compositions

might exist in deep horizons south of Site 543, as observed in surface sediments (White et al., 1985) and their involvement in the source of magmas below the southern islands would explain the Pb-radiogenic signature of southern islands. Such sediments, with the required Pb-radiogenic composition, have not yet been identified; neither on the subducting plate nor in the sedimentary components of the arc crust (Thirlwall et al., 1996).

The aim of this work is therefore to determine whether a north-south chemical variation exists within the sediment cover on the subducting oceanic crust. We report new Nd–Pb isotope analyses on sediments from three sites: (a) DSDP 78A Site 543, which is located in front of Dominica Island. These data complement the pioneering results of White et al. (1985) which concentrated in the 230–280 m depth range of the sedimentary pile (b) Sediments drilled on the Demerara Rise at Site 144 during DSDP Leg 14 (see Fig. 1) at a latitude of about 9.4° N (c) Sediments from Barbados Island on the accretionary prism in front of St Vincent Island. The comparison between the three

sites should help to identify any north–south changes in the composition of sediments presently subducting along the arc.

2. Geological context

The Lesser Antilles arc lies at the eastern margin of the Caribbean plate and is related to the slow westward subduction of the Atlantic plate beneath the Caribbean plate (about 2 cm/yr, [Minster and Jordan, 1978](#)). Recent volcanism occurs from Saba in the north to Grenada, 800 km to the south ([Maury et al., 1990](#)) ([Fig. 1](#)).

The forearc region consists mainly of a large accretionary complex, the Barbados Ridge. In the southern part of the complex, sediments are more than 10 km thick and contain a large proportion of terrigenous turbidites. In contrast, in the north, the sediments are less than 1 km thick and predominantly pelagic ([Westbrook et al., 1984](#)). The main source of terrigenous sediments is the South American continent which is drained by the Orinoco and Amazon Rivers and the decreasing sediment thickness northward reflects the declining turbiditic input from the Orinoco ([Westbrook et al., 1984](#)).

Numerous seismic reflection profiles across the deformation front of the accretionary wedge have shown the existence of a strong reflector interpreted as a décollement surface between overthrust sediment and deeper sediment underthrust beneath the accretionary complex ([Biju-Duval et al., 1982](#); [Moore et al., 1982](#); [Westbrook et al., 1982](#); [Westbrook and Smith, 1983](#)). Only sediments located under the décollement have a chance to be subducted.

DSDP 78A Site 543 was drilled at 15°4 N ([Fig. 1](#)) and sampled a 410-m sequence of sediments overlying the Campanian (~82 Ma) basaltic basement. The incipient décollement is located at a depth of 170 m, in the Lower Miocene sequence ([Biju-Duval et al., 1984](#)) suggesting that only the lowermost 240 m of sediments are presently being subducted at this latitude. Further south, the stratigraphic level of the décollement is poorly constrained ([Westbrook et al., 1984](#)) and the age and depth range of the subducted sediments in the sediment pile is not well known.

[Speed et al. \(1984\)](#) compiled a magnetic map of the Atlantic Ocean floor in the area east of the Lesser Antilles (see [Fig. 1](#)) and showed that the well-identified Anomaly 34, which marks the end of the “Cretaceous quiet zone” at 84 Ma ([Lowrie and Alvarez, 1981](#)) is present at the trench level in the northern part of the arc but is displaced eastward farther south along the trench ([Fig. 1](#)). As a consequence, the crust entering the trench in the south of the arc is much older than in the northern part (see [Fig. 1](#)). In the northern part of the arc, the age of the subducting oceanic basement is about 83 Ma; in front of St Vincent, it is about 105 Ma and south of Barbados, the oceanic crust may be as old as Jurassic or Early Cretaceous ([Speed et al., 1984](#)). The sediments on top of the oceanic crust are therefore older in the south than in the north. Sediments drilled at Site 144 on the Demerara Rise ([Fig. 1](#)) have ages ranging from 115 Ma to 30 Ma and are time equivalents to sediments potentially subducted in front of the southern part of the arc system.

3. Sampling

The drilled samples recovered at DSDP 78A Site 543 and DSDP 14 Site 144 were obtained from the ODP repository at Lamont-Doherty Earth Observatory and samples from Barbados Island were collected in the field in July 2005. The locations of DSDP core samples, the geographical locations for Barbados samples, and the age and the lithology units for these samples are given in Supplemental files 1 to 3. In total, 24 samples from Site 543, 21 samples from Site 144 and 12 samples from Barbados were selected to represent the entire subducted sedimentary material.

3.1. DSDP 78A Site 543

At Site 543 ([Fig. 1](#)), a 410 m sequence of sediments and 44 m of ~80 Ma basaltic basement were drilled, at about 5630 m water depth.

Supplemental file 2 presents a simplified description of the lithostratigraphy at Site 543. Detailed description can be found in [Biju-Duval et al. \(1984\)](#). We only sampled the sediment pile located below the décollement found at about 170 m depth because only that part is underthrust beneath the accretionary wedge. The lithological characteristics are rather monotonous: the sediments consist mainly of pelagic clays and radiolarian clays and, with the exception of Unit 6, they are carbonate free. According to [Hemleben and Troester \(1984\)](#), almost all sediments were deposited well below the carbonate compensation depth (CCD), in a deep abyssal environment. Only Unit 6, which directly overlies the basaltic crust was deposited above the CCD, in a ridge crest environment. Ash layers are recognized in Unit 4 and persist upwards to the top of the drilled sequence, indicating an input of volcanic material as the Atlantic crust approached the Lesser Antilles arc.

3.2. DSDP 14 Site 144

Site 144 is located at the edge of the Guyana continental margin, on the northern slope of the Demerara Rise ([Fig. 1](#)). A 350 m thick sedimentary sequence was drilled at Site 144 during the DSDP Leg 14, at about 2960 m water depth (see Supplemental file 3). The oldest samples are early Albian (~115 Ma). Units 5 and 4, which consist mainly of terrigenous claystone, siltstone and sandstone with variable carbonate contents (30% on average), are considered to form the uppermost part of the syn-rift sequence linked to the opening of the Central Atlantic ([Hayes et al., 1972](#)). Unit 3 (~96 to 84 Ma) comprises laminated organic-rich black shales (total organic carbon up to 30%) with occasional calcareous layers (carbonate contents between 25 and 80%). Units 2 and 1 consist of Late-Cretaceous to Oligocene grey marl and chalk ooze with a carbonate content between 30 and 70%.

3.3. Barbados Island

Barbados Island is the only emergent part of the Barbados accretionary prism. Most of the island is covered by Pleistocene reef formations, but older strata outcrop in its north-eastern part. Two major formations have been distinguished in these strata, the Scotland and Oceanic Formations with ages of 57–35 Ma and 45–15 Ma, respectively ([Pudsey and Reading, 1982](#); [Biju-Duval et al., 1985](#)). We selected 8 samples of the fine to coarse grained facies of the Scotland Formation, which consists mainly of terrigenous claystones and sandstones that are classically interpreted as turbidites ([Pudsey and Reading, 1982](#); [Biju-Duval et al., 1985](#)). Four samples were selected from the Oceanic Formation which consists of mudstones, marls and chalks with locally ash layers. Sample descriptions are given in Supplemental file 1.

4. Analytical techniques

4.1. Trace elements

All samples were hand-crushed in an agate mortar. Trace element contents were obtained using inductively coupled plasma-mass spectrometry (ICP-MS) in Grenoble. About 100 mg of powder were dissolved in HF–HNO₃ mixtures (4:1) in Teflon containers. Complete dissolution was achieved by using steel jacketed PARR bombs for 7 days at 150 °C. Samples were then diluted in 2% HNO₃ to obtain a dilution factor of 2000. A multispike solution (⁹Be, ⁷⁵As, ¹¹⁵In, ¹⁶⁹Tm, ²⁰⁹Bi) was added to each sample to monitor machine drift. The external calibration curves were realised with standard BHVO-2 using the Grenoble reference values given in Supplemental file 4. During the course of this study, international rock standards (BR and AGV-1) and an in-house standard (Bora Bora 24) were analysed as unknown samples. Results obtained on these standards and the precision of our data, as evaluated from replicate analyses of these standards, are given

Table 1

Trace element concentrations and Nd and Pb isotope ratios measured in sediments from Site 543 (DSDP 78A), Site 144 (DSDP 14) and Barbados Island

	Lith. unit	Nd	Sm	Pb	Th	U	$^{143}\text{Nd}/^{144}\text{Nd} (\pm 2\sigma)$	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$
<i>Leg DSDP 78, Site 543</i>													
543 18 4W 15–17	3	23.4	4.83	12.9	8.69	1.22	0.512069±16	19.2083	0.0009	15.7305	0.0008	39.273	0.002
543 19 1W 97–98	4	23.1	5.04	13.9	7.66	1.19	0.512155±18						
543 20 3W 99–101	4	22.7	4.61	19.1	8.15	1.50	0.512123±21	19.1439	0.0014	15.7213	0.0012	39.212	0.003
DR							0.512138±21						
543 23 2W 73–75	4	32.8	6.28	22.2	16.5	1.72	0.511953±22	19.4023	0.0013	15.7725	0.0010	39.459	0.002
DR							0.511950±22						
543 24 2W 78–80	4	33.4	6.44	20.0	16.3	1.94	0.511952±21	19.4003	0.0016	15.7718	0.0014	39.448	0.004
DD							0.511939±20	19.3889	0.0012	15.7705	0.0012	39.448	0.003
543 25 2W 86–88	4	32.3	5.94	24.9	13.8	1.82	0.511935±14	19.3648	0.0016	15.7684	0.0014	39.399	0.003
543 26 1W 120–122	4	31.6	6.15	22.4	11.7	2.01		19.1260	0.0011	15.7129	0.0010	39.231	0.002
543 26 4W 27–29	4	28.4	5.48	21.5	12.1	1.8	0.511891±20	19.3572	0.0016	15.7799	0.0012	39.432	0.003
543 26 6W 27–29	5a	29.8	5.92	19.7	12.1	1.83	0.511969±21	19.3726	0.0014	15.7812	0.0012	39.409	0.003
543 27 2W 114–116	5a	26.3	5.16	12.6	11.4	1.62	0.511933±16	19.5075	0.0016	15.8241	0.0014	39.552	0.003
DD								19.5090	0.0016	15.8282	0.0014	39.555	0.003
543 28 3W 66–68	5a	28.7	5.82	19.9	12.4	1.39	0.511893±13	19.3112	0.0012	15.7963	0.0011	39.405	0.002
543 28 5W 66–68	5a	31.3	6.17	14.1	11.1	1.37	0.511939±18	19.5145	0.0014	15.8233	0.0012	39.531	0.003
543 29 4W 45–47	5a	33.1	6.71	11.3	10.5	1.33	0.511947±18	19.5323	0.0015	15.8370	0.0012	39.588	0.002
543 30 4W 53–55	5a	23.9	4.53	21.1	9.95	1.30	0.511845±21						
543 31 1W 76–78	5a	25.5	4.74	17.6	11.2	1.34	0.511880±16	19.5283	0.0021	15.8090	0.0016	39.420	0.004
543 32 3W 10–12	5a	17.2	3.25	12.4	8.28	1.08	0.511932±19	19.2254	0.0012	15.7613	0.0011	39.274	0.003
DD		16.9	3.31	12.4	8.15	1.02	0.511917±19	19.2235	0.0012	15.7604	0.0011	39.277	0.003
543 33 2W 71–73	5b	21.3	3.7	17.9	10.1	1.32	0.511918±14	19.1515	0.0017	15.7506	0.0012	39.239	0.003
543A 2 1W 116–118	5b	18.5	3.84	16.6	8.76	1.27	0.511916±14	19.1683	0.0011	15.7477	0.0010	39.054	0.002
DR							0.511898±17	19.1682	0.0016	15.7463	0.0011	39.054	0.002
543A 3 2W 12–14	5b	31.6	6.29	12.3	12.3	1.64	0.511979±15	19.5308	0.0020	15.7915	0.0016	39.452	0.004
DD		32.5	6.39	12.6	12.6	1.64	0.511974±21	19.5325	0.0011	15.7923	0.0009	39.455	0.002
543A 5 3W 47–49	5c	33.6	6.63	23.2	11.8	1.48	0.511936±17	19.2605	0.0012	15.7546	0.0010	39.329	0.002
DR							0.511929±24	19.2584	0.0013	15.7524	0.0013	39.324	0.003
543A 3 1W 75–77	5c	31.1	5.78	26.7	12.5	1.31	0.511875±17	19.2136	0.0016	15.7568	0.0011	39.316	0.003
543A 7 2W 100–102	6	53.6	11.4	18.2	9.49	0.702	0.512023±19	19.4646	0.0021	15.7778	0.0017	39.412	0.004
DR							0.511985±18	19.4638	0.0012	15.7766	0.0009	39.407	0.002
543A 8 1W 116–118	6	43.3	8.72	24.7	11.1	0.966	0.511965±17	19.3564	0.0013	15.7674	0.0010	39.376	0.002
DD		44.4	8.88	24.7	11.2	0.970							
543A 9 1W 45–46	6	42.3	8.72	24.1	6.92	0.812	0.512039±14	19.1567	0.0016	15.7246	0.0012	39.115	0.003
543A 10 1W 25–27	6	31.9	6.35	12.3	5.85	0.639	0.512077±16	19.1270	0.0013	15.7255	0.0011	39.157	0.002
<i>Leg DSDP 14, Site 144</i>													
144B 1 2W 11.5–13	1	26.0	4.85	15.8	10.7	1.41	0.511959±10	19.1351	0.0019	15.7426	0.0019	39.271	0.004
DD		26.1	5.15	16.7	11.6	1.55							
144B 2 2W 16.5–18	1	9.30	1.87	4.05	2.94	0.438	0.511959±13	19.4485	0.0026	15.7977	0.0019	39.427	0.004
144A 1 2W 11.5–14	1	10.6	2.02	6.68	3.93	0.658	0.511904±21	19.4449	0.0014	15.8145	0.0013	39.476	0.003
144B 3 2W 71.5–73	1	14.8	2.85	8.96	5.95	0.681	0.511935±25	19.4876	0.0021	15.8184	0.0016	39.475	0.005
DD								19.4924	0.0022	15.8185	0.0019	39.478	0.005
144A 2 2W 79–80.5	1	11.2	2.20	6.25	3.86	0.571	0.511942±12	19.3454	0.0026	15.7899	0.0023	39.312	0.006
144 1 4W 98–99	1	6.81	1.33	3.03	1.88	0.283	0.511998±14	19.4381	0.0030	15.7909	0.0024	39.255	0.005
DR							0.511979±20						
144 1 6W 71–72	1	6.94	1.39	2.35	1.85	0.298	0.511983±12	19.6580	0.0037	15.8383	0.0032	39.533	0.009
144 2 5W 93–95	1	11.5	2.20	8.07	4.56	0.673	0.511990±16	19.2102	0.0013	15.7352	0.0011	39.087	0.003
DD							0.512010±15						
144A 3 1W 79–80	2	17.8	3.34	7.68	7.11	0.965	0.511988±21	19.7053	0.0015	15.7959	0.0014	39.560	0.004
DD							0.511993±15	19.6914	0.0012	15.7939	0.0011	39.552	0.002
144A 3 3W 25–26	2	19.4	3.90	6.73	6.88	1.01	0.511994±13	19.7077	0.0019	15.8022	0.0014	39.570	0.003
DD								19.6994	0.0028	15.8021	0.0019	39.566	0.004
144A 3 3W 125–126	2	8.24	1.54	3.91	2.97	0.425	0.511780±13	19.6460	0.0020	15.8245	0.0018	39.555	0.004
144 3 1W 120–121	2	11.7	2.13	4.36	4.26	0.804	0.511730±14	20.0424	0.0030	15.8863	0.0028	39.862	0.006
144 3 2W 110–113.5	2	9.64	1.74	3.71	3.62	0.617	0.511770±17	19.9467	0.0019	15.8685	0.0015	39.720	0.004
144A 4 1W 140–144	2	24.1	4.73	9.00	8.61	2.32	0.511965±18	19.8287	0.0018	15.8566	0.0014	39.554	0.004
144A 5 1W 108–109	3	0.844	0.164	0.629	0.217	5.37	0.511841±14	27.6746	0.0033	16.2415	0.0018	39.693	0.004
DD								27.6913	0.0075	16.2339	0.0042	39.662	0.011
144A 5 1W 119–124	3	7.39	1.46	7.93	2.31	13.0	0.511843±16	21.2725	0.0041	15.8820	0.0029	39.423	0.007
DD		7.60	1.44	7.83	2.20	13.0		21.2760	0.0024	15.8804	0.0016	39.416	0.005
144A 5 CCW 0–1	3	8.67	1.65	6.6	2.07	14.6	0.511879±8	21.5472	0.0035	15.8915	0.0027	39.356	0.007
144A 6 1W 90–93	3	8.24	1.56	6.33	2.16	13.7	0.511832±22	21.6909	0.0022	15.9251	0.0016	39.422	0.004
DD								21.7282	0.0016	15.9297	0.0012	39.440	0.003
DR							0.511828±12						
144A 6 1W 125–130	3	9.34	1.80	4.54	2.11	12.6	0.511840±10	22.9249	0.0043	16.0080	0.0032	39.633	0.008
DD								22.8995	0.0027	15.9896	0.0024	39.577	0.006
144 4 2W 60–64	3	4.95	0.973	4.77	1.45	11.1	0.511875±14	21.5582	0.0021	15.8969	0.0015	39.313	0.004
144 5 1W 123–125	4	20.8	4.20	8.91	6.39	1.81	0.512107±16	19.0034	0.0010	15.7132	0.0009	39.035	0.002
DR								19.0028	0.0019	15.7118	0.0017	39.034	0.004
144 6 1W 46–48	5	15.4	3.02	5.35	4.26	1.33	0.512101±11	19.1781	0.0011	15.7107	0.0009	38.948	0.002
DD		13.5	2.70	5.60	4.88	1.32							
144 7 1W 80–82	5	27.6	5.40	14.0	8.42	1.84	0.512105±14	18.8081	0.0014	15.6848	0.0013	38.940	0.003
DD							0.512106±16						

Table 1 (continued)

	Lith. unit	Nd	Sm	Pb	Th	U	$^{143}\text{Nd}/^{144}\text{Nd} (\pm 2\sigma)$	$^{206}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$	
<i>Leg DSDP 14. Site 144</i>											
DR							0.512120±23				
144 7 1W 125–130	5	25.2	5.06	10.5	7.29	1.94	0.512105±13	18.9347	0.0015	15.6915	
144 8 2W 54–57	5	12.7	2.55	5.62	3.39	0.896		18.8183	0.0017	15.6815	
144 8 3W 130–135	5	26.9	5.5	13.3	8.19	1.61	0.512104±11	18.8030	0.0014	15.6842	
DD							0.512111±18	18.8117	0.0014	15.6868	
<i>Barbados Island</i>											
B-1	Oc Fm	11.0	3.41	5.30	2.01	2.10		19.5329	0.0016	15.6975	
B-2	Oc Fm	13.5	3.97	5.52	3.10	2.87	0.513045±15	19.6336	0.0012	15.7039	
B-4	Oc Fm	19.0	4.18	8.57	5.38	1.55	0.512387±19	19.3442	0.0012	15.7274	
B-7	Oc Fm	7.65	1.68	2.96	2.07	0.456	0.512240±19	19.2561	0.0030	15.7290	
B-6	Up Sc Fm	17.3	3.58	7.82	5.56	1.69	0.512089±16	19.5156	0.0011	15.7444	
B-10b	Up Sc Fm	77.9	18.2	9.30	7.86	3.59	0.512080±21	20.7433	0.0017	15.8790	
DR							0.512111±10				
B-10c	Up Sc Fm	29.6	5.21	14.0	12.2	2.85	0.512014±10	19.8778	0.0012	15.7930	
DR							0.511998±11				
B-11	Up Sc Fm	29.6	5.82	18.8	12.6	3.61	0.512041±19	19.9832	0.0015	15.8015	
B-8c	Lo Sc Fm	23.6	4.75	13.3	7.74	2.57	0.512127±21	19.5224	0.0013	15.7420	
B-8d	Lo Sc Fm	32.5	6.10	18.9	13.5	3.16	0.512091±16	19.6153	0.0009	15.7587	
B-12a	Lo Sc Fm	30.1	5.71	21.0	12.5	2.53	0.512217±14	19.3910	0.0017	15.7353	
B-12b	Lo Sc Fm	29.4	5.64	20.1	13.1	3.89	0.512174±18	19.4630	0.0013	15.7404	

DD stands for duplicate dissolution and DR for duplicate run. Nd isotope ratios are relative to the value recommended by Chauvel and Blichert-Toft (2001) for the Rennes Nd standard ($^{143}\text{Nd}/^{144}\text{Nd}=0.511961$, which corresponds to a La Jolla value of 0.511856). Uncertainties reported on the Nd isotope ratios are in-run errors ($2\sigma/\sqrt{n}$, where σ is the standard deviation and n the number of measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, generally 60). The Rennes Nd standard was run every second sample and its reproducibility (2σ) calculated on each analyses session (~20 analyses) is typically 30 ppm. Reproducibility calculated using complete duplicate analyses of 7 samples is $1.2 \cdot 10^{-5}$ (2σ) on the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (25 ppm) and is better than the average in-run errors. Pb isotope ratios are relative to NBS 981 values of $^{206}\text{Pb}/^{204}\text{Pb}=16.9405$, $^{207}\text{Pb}/^{204}\text{Pb}=15.4963$ and $^{208}\text{Pb}/^{204}\text{Pb}=36.7219$ (Galer and Abouchami, 1998). The NBS 981 standard was run every second sample and its reproducibility (2σ) calculated on the entire period of analyses is 150, 180 and 200 ppm for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios respectively (106 analysis). Reproducibility calculated using complete duplicate analyses of 8 samples, excluding the 4 duplicates of black shales (Site 144 – Unit 3), is 0.007 (370 ppm), 0.002 (130 ppm) and 0.011 (300 ppm) for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios respectively (2σ). The reproducibility of the black shale duplicates is not as good probably because of the strong heterogeneities of these samples.

in Supplemental file 4 where they are compared to values published by Wilson (1997), Lin et al. (2000), Raczek et al. (2000), Kelley et al. (2003), Marini et al. (2005) and Weis et al. (2005). Accuracy is estimated at 3% and precision on the concentrations is better than 5%.

4.2. Pb and Nd isotopes

Pb was isolated in Grenoble using the anion resin technique of Manhès et al. (1984). During the study, total procedural blank was <70 pg ($n=9$) and considered as negligible relative to the amount of Pb extracted. Rare earth elements were separated on 2 or 8 ml Biorad column filled with AG50W-X8 or AG50W-X12 cationic resin. Nd was isolated from the other REE on Ln-Spec resin using dilute HCl. Total procedure blank was <110 pg ($n=6$). Pb and Nd isotopic compositions were measured on a Nu Plasma MC-ICP-MS (from Nu Instruments) in Bruxelles. Pb isotopic compositions were measured in static multi-collection mode with a Thallium spike added to each sample to monitor mass fractionation (White et al., 2000). [Pb]/[Ti] ratios were almost constant at ~4 in all standard and sample solutions. The NBS 981 standard was run every second sample. As described by White et al. (2000) and Blichert-Toft et al. (2003), Pb isotope ratios were corrected by sample-standard bracketing to the NBS 981 TIMS values recommended by Galer and Abouchami (1998). Nd isotopic compositions were also measured using static multicollection. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized for mass fractionation to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$. The Rennes Nd standard was run systematically every second sample to apply the same sample bracketing technique as for Pb and using the Nd Rennes values recommended by Chauvel and Blichert-Toft (2001). More information is given in the footnote of Table 1.

5. Results

Trace element concentrations (Sm, Nd, Pb, Th and U) and isotope ratios (Nd and Pb) are given in Table 1. In Supplemental file 5, we report trace element and isotope averages calculated for each lithological unit for both DSDP sites. Also listed are grand averages

calculated for each DSDP site and the values recommended for Global Subducting Sediments (GLOSS) (Plank and Langmuir, 1998) and the Upper Continental Crust (UCC) (McLennan, 2001).

5.1. Trace element compositions

Trace element concentrations of Site 543 sediments do not display large variations and are comparable to previous data published by White et al. (1985). Nd concentrations vary from 17 to 53 ppm and Pb concentrations from 11 to 27 ppm (Table 1). No systematic differences between lithological units can be noticed (Supplemental file 5); the grand average composition is similar to GLOSS and UCC estimates (Supplemental file 5).

In contrast, sediments from Site 144 have more variable trace element concentrations (Table 1). In particular, the black shale unit (Unit 3) displays striking features. This unit has the lowest trace element concentrations (average Nd and Pb contents at 6.6 and 5.3 ppm respectively) but very high U concentrations (from 5.3 to 14.6 ppm with an average of 11.5 ppm) leading to very high U/Pb ratios (Supplemental file 5). Trace element concentrations in the other lithological units of Site 144 are generally more variable and lower relative to Site 543 sediments. Nd concentrations vary between 6.8 and 27 ppm, and Pb contents from 2.4 to 14 ppm, with Units 4 and 5 having the highest concentrations. At Site 144, Average trace element concentrations (excluding U) are lower than the averages of Site 543, GLOSS and UCC but elemental ratios, excluding U/Pb, are comparable (Supplemental file 5). The low trace element concentrations in Site 144 sediments compared to Site 543 or GLOSS, for roughly similar elemental ratios, are attributable to high carbonate contents in these sediments because carbonates are known to be poor in those trace elements (e.g. Plank and Langmuir, 1998). Similarly, variations in carbonate content explain the variability of trace element contents in Site 144 sediments.

Trace element concentrations of samples from Barbados Island also display large variations, with Nd ranging from 11 to 80 ppm and Pb from 3 to 21 ppm. The ashes and marls of the Oceanic Formation have lower

trace element concentrations than GLOSS, UCC and Site 543 sediments while samples from the Scotland Formation are generally richer. Their trace element ratios are generally intermediate between GLOSS and UCC values, with the exception of the U/Pb ratio, which is slightly higher.

5.2. Nd and Pb isotopic compositions

Variations of measured Nd and Pb isotope ratios of sediments with depth in Sites 144 and 543 are shown in Supplemental file 6 and Fig. 2. We also calculated Nd and Pb isotopic compositions at time of deposition and these values are also shown.

5.2.1. DSDP 78A, Site 543

Present-day Nd isotope ratios of Site 543 sediments define a small range between 0.51185 and 0.51215 (see Table 1 and Supplemental file 6) with the highest values being found in the bottom 20 m and the top 25 m of the core. Pb isotope ratios do not change systematically with depth and vary between 19.13 and 19.53 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.71 and 15.84 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 39.05 and 39.59 for $^{208}\text{Pb}/^{204}\text{Pb}$. As for trace element concentrations, there is no striking difference between lithological units (Supplemental file 5), and the range of isotopic compositions reported here is roughly similar to previous results of White et al. (1985), which were nevertheless focused on sediments collected between 230 and 280 m depth only. The average sediment pile has a Nd isotope ratio slightly lower than GLOSS, and Pb isotope ratios higher than GLOSS (Supplemental file 5). Initial Nd and Pb isotopic compositions follow paths similar to those of the present-day compositions (Supplemental file 6).

5.2.2. DSDP 14, Site 144

Nd isotope ratios of Site 144 sediments are quite similar to Site 543 sediments and range from 0.51173 to 0.51212 (Table 1 and Fig. 2) with

the highest values in the bottom Units 5 and 4, followed by low values in Unit 3 and the lower half of Unit 2. At 140 m depth, $^{143}\text{Nd}/^{144}\text{Nd}$ suddenly increases to 0.5120 and remains almost constant until the top of the pile. In contrast to Nd isotopes, Pb isotopic compositions of Site 144 sediments display very large variations through time. In Units 5 and 4, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are relatively low and constant (18.8 to 19.2) while they reach values as high as 27.69 in the black shales of Unit 3 (Fig. 2) and then abruptly decrease to values of 20.04–19.44 down in Units 2 and 1. While $^{207}\text{Pb}/^{204}\text{Pb}$ ratios follow the same pattern as $^{206}\text{Pb}/^{204}\text{Pb}$, this is not the case for $^{208}\text{Pb}/^{204}\text{Pb}$, which varies only between 38.89 and 39.86. When averages are calculated for individual units and for the entire sediment pile (see Supplemental file 5), Nd isotopes are quite similar to the average value of Site 543 sediments. In contrast, calculating an average value for the Pb isotope ratios is very difficult due to the huge isotopic range. Units 4 and 5 have average values similar to GLOSS, the black shale Unit 3 has extremely high $^{206-207}\text{Pb}/^{204}\text{Pb}$ ratios but moderate $^{208}\text{Pb}/^{204}\text{Pb}$, and Unit 2 has the highest $^{208}\text{Pb}/^{204}\text{Pb}$ (Supplemental file 5). Unit 1 displays intermediate values and is similar to the Site 543 average. The calculated Pb isotopic compositions of the average sedimentary pile are quite similar to those of Site 543 (Supplemental file 5), but because of the large heterogeneities of Site 144 sediments, the grand average calculated for Site 144 should be used with great caution.

When comparing present and initial Nd isotopic ratios as shown in Fig. 2, no large shift is observed, but this is not the case with the Pb isotopic system. For Units 1, 2, 4 and 5, the difference between measured and initial Pb isotopic ratios is small, but for the black shales of Unit 3, the difference between measured and initial $^{206-207}\text{Pb}/^{204}\text{Pb}$ ratios is very large, with the initial $^{206-207}\text{Pb}/^{204}\text{Pb}$ ratios being similar to those of the rest of the sediments (Fig. 2). Because of their very high U/Pb but normal Th/Pb ratios (Fig. 2 and Table 1), the organic-rich shales acquired in this short time-scale (~90 Ma), extremely radiogenic $^{206-207}\text{Pb}/^{204}\text{Pb}$ but unchanged $^{208}\text{Pb}/^{204}\text{Pb}$.

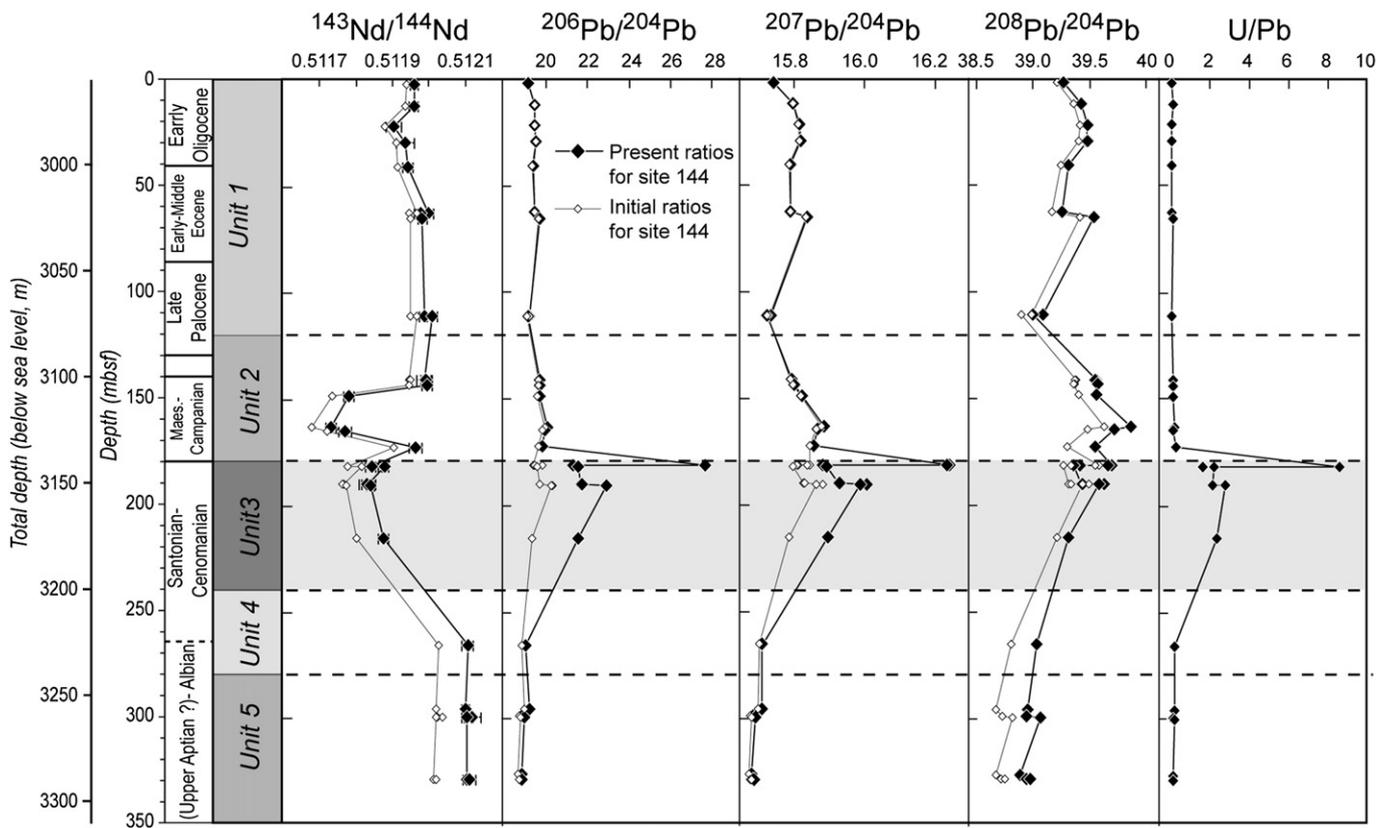


Fig. 2. Lithostratigraphic column of the sedimentary pile drilled at Site 144 showing the Nd and Pb isotopic compositions, and the U/Pb ratios of samples as a function of depth along the sedimentary pile. The units and ages are from Hayes et al. (1972). The analytical errors on the isotopic ratios are shown by horizontal bars for Nd but for Pb, they are smaller than the symbol size. The black symbols show the measured values while the white symbols correspond to the initial values calculated using the ages given in Supplemental file 1.

5.2.3. Barbados Island

Nd isotopic compositions of Barbados samples display larger variations than samples from the two drilling sites with $^{143}\text{Nd}/^{144}\text{Nd}$ ranging from 0.51201 to 0.51304 and $^{206}\text{Pb}/^{204}\text{Pb}$ ranges from 19.26 to 20.75 (Table 1). Samples from the Upper Scotland Formation have the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ and the highest Pb isotopic ratios while marls and ash from the Oceanic Formation display the highest Nd and the lowest Pb isotope ratios. Overall, the Barbados sediments have more radiogenic Pb isotopes than GLOSS. Finally, we did not calculate an average composition for the Barbados sediments because the analyzed samples only represent selected sampling sites on the island and their relative proportion is difficult to evaluate.

6. Discussion

6.1. Origin of the sediments

Sediments from DSDP Sites 543 and 144 and from Barbados were deposited in different paleo-environments. Sediments at Site 543 lie directly on the Atlantic basaltic crust, and (except for Unit 6) were deposited in a deep abyssal setting, below the CCD (Biju-Duval et al., 1984). They are carbonate free and consist mainly of pelagic and radiolarian clay. Their ages cover the period 82–17 Ma with the oldest sedimentary horizon being younger than the inferred age of the magnetic anomaly 34 (Fig. 1). In contrast, sediments at Site 144 were deposited at the edge of the South American margin, on the northern slope of the Demerara rise, in a shallower water environment (Fig. 1). Site 144 sediments were all deposited above the CCD, and carbonate contents range from 25 to 80% (Hayes et al., 1972). Units 1 and 2 cover a time period from 30 to 80 Ma and were deposited at the same time as the Site 543 sediments. This is not the case with the older units which have no time equivalent in Site 543: the black shales of Unit 3 have an age of ~96 to 84 Ma and the oldest units of the pile, Units 4 and 5, have ages between ~115 and ~98 Ma (Hayes et al., 1972). Site 144 therefore provides an older record of the sedimentation in the Atlantic Ocean than Site 543. In Barbados, the Scotland and Oceanic Formations were deposited between 57 and 15 Ma, at the same time as Units 4 and 5 of Site 543 and Unit 1 of Site 144. The mainly turbiditic Scotland Formation was probably deposited in a deep sea fan environment, while the Oceanic Formation may have been deposited in shallower environment, with minor clastic input (Pudsey and Reading, 1982; Biju-Duval et al., 1985).

In Fig. 3, we compare the Pb and Nd isotope ratios of sediments from the three sites with various oceanic sediments. Black shales are shown in the insets of the main diagrams because of their elevated $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, and they will be discussed separately. Compared to GLOSS (Plank and Langmuir, 1998), to other Atlantic surface sediments (Ben Othman et al., 1989; Abouchami and Zabel, 2003) and to average sedimentary piles in front of other major subduction zones (Plank and Langmuir, 1998), our sediments have very radiogenic Pb isotope ratios and unradiogenic Nd isotopic compositions (Fig. 3). These features suggest that they contain a much larger component of old continental material than the other oceanic sediments worldwide. Such characteristics can be attributed to the overwhelming contribution of radiogenic detrital materials coming from an old continental crust, the Brazilian and Guyana cratons. Indeed, hydrogenous material, which is usually rich in Pb and Nd and has a seawater isotopic composition (see Fig. 3) is a very minor component in the studied sediments (Hayes et al., 1972; Pudsey and Reading, 1982; Biju-Duval et al., 1984). In addition, the volcanogenic contribution is generally low in the two drill sites and their biogenic silica and calcium carbonate components are extremely poor in Pb and Nd. For example, Unit 2 of Site 144 is characterized by high CaCO_3 content (~50%), but also high Pb and low Nd isotope ratios that do not reflect the composition of the Atlantic seawater for which the carbonates formed (Fig. 3). Surprisingly, despite the large variety of

ages, depositional environments and lithologies, all local sediments define a linear array in Pb–Pb isotopic spaces (Fig. 3a,b) and a rough negative correlation in Nd–Pb space (Fig. 3c). Such relationships suggest mixing of components that remained identical through the 115 Ma of sedimentation.

In detail, the Barbados and Site 144 sediments have more heterogeneous compositions than Site 543 samples, which vary within the range previously reported by White et al. (1985). In the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot (Fig. 3a), two arrays can be distinguished: the “main array” defined by samples from Sites 543 and 144, and the “Barbados array”. As suggested by Pudsey and Reading (1982) on the basis of the sediment mineralogy, variations along the “Barbados array” can be

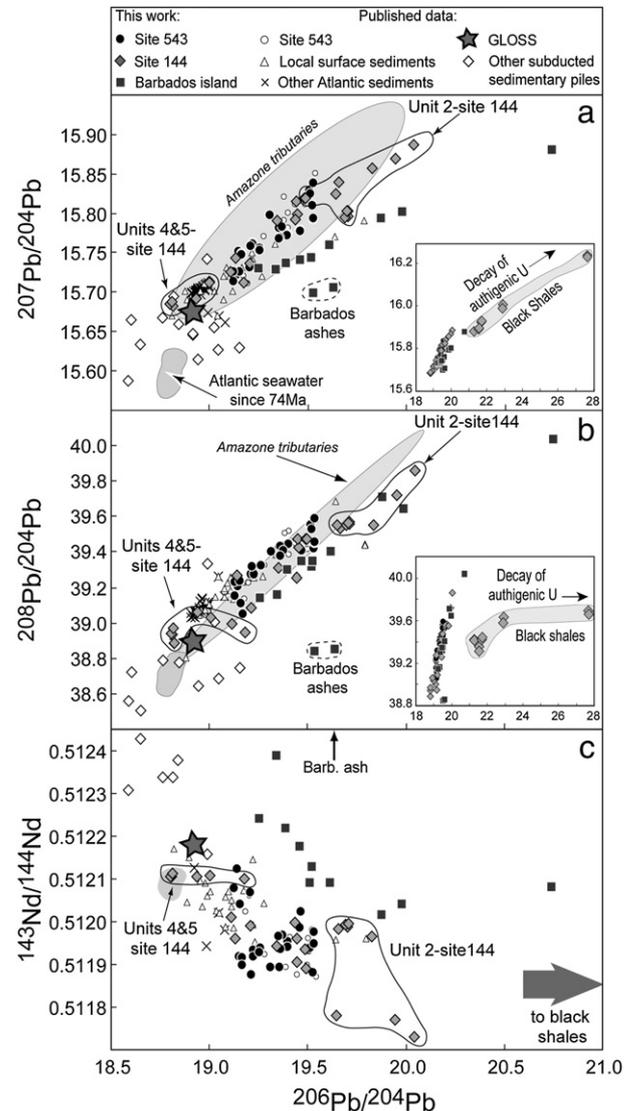


Fig. 3. $^{207}\text{Pb}/^{204}\text{Pb}$ (a), $^{208}\text{Pb}/^{204}\text{Pb}$ (b) and $^{143}\text{Nd}/^{144}\text{Nd}$ (c) vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams showing the results obtained for sites 543 and 144 samples, and for Barbados Island samples. Because of the extremely high Pb isotopic values of samples from the Site 144 black shale Unit, these samples are shown in the insets. Data published by White et al. (1985) on Site 543 and local surface sediments are also shown as well as the GLOSS estimate of Plank and Langmuir (1998) and data published by Abouchami and Zabel (2003) for Ceara Rise surface sediments (Western Atlantic) and by Ben Othman et al. (1989) for North Atlantic surface sediments. Average compositions of sedimentary piles in front of other major subduction zones (mainly Pacific Ring of Fire, Sandwich in Atlantic ocean, Java and Sunda in Indian ocean) and estimated by Plank and Langmuir (1998) are shown for comparison except in Fig. 3c where the most Nd radiogenic averages are not shown for scale reasons. The field for Amazon tributaries is from Allègre et al. (1996) and the field for North Atlantic seawater corresponds to data published by Burton et al. (1997) and O’Nions et al. (1998).

explained by binary mixing between detrital material with radiogenic Pb isotopic compositions from the South American continent and relatively unradiogenic volcanogenic material from the Lesser Antilles arc. The marls from the Oceanic Formation have the lowest Pb isotope ratios and the highest proportion of volcanogenic material while the clays and sandstones from the Scotland Formation have more radiogenic Pb ratios. We suspect that the radiogenic end of the Barbados array is controlled by the local input of the proto-Orinoco (Beck et al., 1990) during a period that lasted only 10–20 Ma.

The “main array”, defined by the sites 543 and 144 sediments, has a steeper slope than the Barbados array in Fig. 3a. The oldest sediments – Units 4 and 5 of Site 144, which have no time equivalent in Site 543 – have the least radiogenic compositions, while the most radiogenic values are found in Unit 2 of Site 144. The variations along this array cannot be attributed to mixtures of volcanogenic and continental materials because no volcanic material has been reported in Site 144 and particularly in Units 4 and 5. We suggest instead that heterogeneities in the continental material delivered by the Orinoco and Amazon, the two main rivers that drain the South American continent, explain the isotopic range seen in Fig. 3. No Pb isotopic data on suspended sediments for the Orinoco River are available in the literature but such data have been reported by Allègre et al. (1996) for suspended sediments of the Amazon River and by McDaniel et al. (1997) for the mud from the Amazon fan. While the present composition of the Amazon sediments is rather unradiogenic ($^{206}\text{Pb}/^{204}\text{Pb} < 19.2$), this is not the case of the tributaries that only drain the Guyana and Brazilian cratons (Allègre et al., 1996). More than 12 Ma ago, the Andes were not part of the drainage basin of the “Paleo-Amazon” (Hoorn et al., 1995) and we can assume that the average Pb isotopic composition of the sediments was higher and more variable than today. In Fig. 3a and b, we show that the field defined by these tributaries overlaps that of sites 144 and 543 sediments. Consequently, we interpret the “main array” as reflecting variable contributions of heterogeneous continental input delivered by Orinoco and Amazon rivers. The isotopic variability is larger in Site 144 sediments than in

Site 543 sediments because of the less efficient mixing processes associated to its proximity to the continental sources.

6.2. The black shales

A 60-m-thick sequence of black shales at Site 144, on the edge of the Demerara Plateau contains records of two major Oceanic Anoxic Events (OAE 2 and 3) (Arndt et al., 2006). The first, OAE 2 (~96–93 Ma), is widely distributed in the Atlantic basin and is recorded in both deep-ocean and marginal sea sediments (Arthur, 1979; de Gracianski et al., 1981); OAE 3 (~89–84 Ma) is geographically more restricted and apparently confined to shallow water environments (Arthur et al., 1990; Rey et al., 2004).

Our measurements show that these black shales are characterized by a strong U enrichment with U/Pb ratios varying between 1.6 and 8.5 (Fig. 2), a feature common in organic-rich sediments (Lange et al., 1977; Fisher et al., 2003; Lev and Filer, 2004; Brumsack, 2006). Such enrichment is due to early diagenesis under reducing conditions, a processes that removes U from seawater by reduction of dissolved U^{VI} to insoluble U^{IV} , which precipitates in organic-rich sediments (Anderson et al., 1989; Klinkhammer and Palmer, 1991). Within the limited time these sediments were on the ocean floor, their elevated U/Pb ratios produced extremely radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ but unchanged $^{208}\text{Pb}/^{204}\text{Pb}$ (Figs. 2 and 3). Similar phenomena have been reported for Paleozoic black shales (Fisher et al., 2003; Lev and Filer, 2004), but to our knowledge, we present the first Pb isotopic data illustrating this U-enrichment for Atlantic Cretaceous black shales. U, Th and Pb concentrations have been reported for other Atlantic Cretaceous black shales (Brumsack, 2006; Lange et al., 1977), and a similar U enrichment was observed at DSDP 41 Site 367 in the Cape Verde Basin. As these black shales were deposited in a deep-sea environment, below the CCD, we are very confident that a U-enriched black shale stratum of variable thickness is present everywhere on the Atlantic sea floor, and not just restricted to the continental margins. We suggest therefore that such a layer is present on the plate that is subducted in the Lesser Antilles

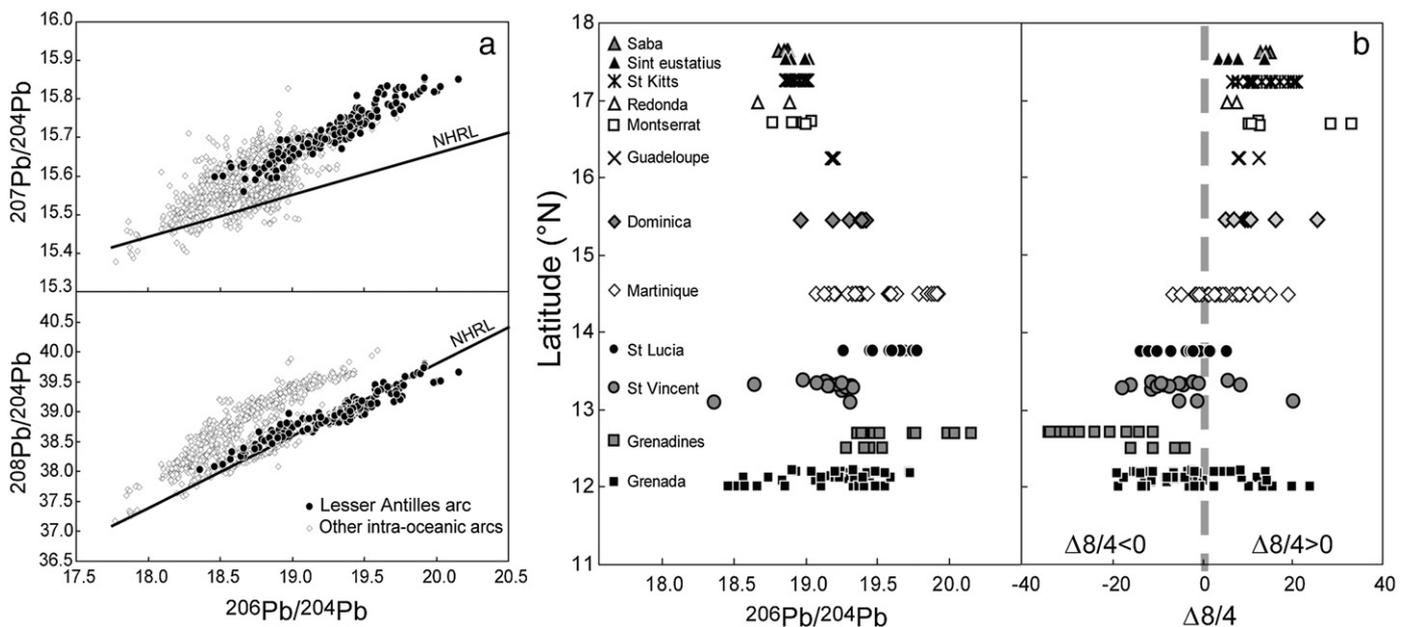


Fig. 4. a) Pb isotopic compositions of Lesser Antilles arc lavas compared to those from other intra-oceanic arcs. Published data for the Lesser Antilles lavas are from Armstrong and Cooper (1971), Thirlwall and Graham (1984), White and Dupré (1986), Davidson (1986, 1987), Vidal et al. (1991), Smith et al. (1996), Thirlwall et al. (1996), Turner et al. (1996), Heath et al. (1998), Chabaux et al. (1999), Thirlwall (2000). For the other intra-oceanic arcs lavas (Tonga-Kermadec, Sonde, Sandwich, Aleoutian, Izu-Bonin, Luzon, Banda arcs), data source is available on: <http://georoc.mpch-mainz.gwdg.de/georoc/>. The Northern hemisphere reference line (NHRL) defined by Hart (1984) is also shown; b) $^{206}\text{Pb}/^{204}\text{Pb}$ and $\Delta 8/4$ - vertical deviation of $^{208}\text{Pb}/^{204}\text{Pb}$ from the NHRL (Hart, 1984) – for lavas from the various islands in the Lesser Antilles arc plotted as a function of the island latitude. Same data sources as in Fig. 4a.

trench. Its location is directly related to the age of the oceanic crust, which must be 95 Ma old or older to carry the entire black shale sequence.

6.3. Relationship between subducted sediments and Lesser Antilles arc lava chemistry

During the past two decades, numerous studies have established the geochemical and isotopic variability of lavas from the Lesser Antilles arc (e.g. White and Dupré, 1986; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996; Turner et al., 1996; Heath et al., 1998; Van Soest et al., 1998, 2002). In particular, Pb isotopic compositions of Lesser Antilles arc lavas are characterized by large variations that span at least three quarters of the entire range of Pb isotopic compositions reported for arc lavas. Moreover, they reach highly radiogenic values compared to other arcs (Fig. 4a). These features have been interpreted in two different manners. Some authors (Thirlwall and Graham, 1984; Davidson, 1987; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996) suggest that the radiogenic characteristics of the lavas are inherited from interactions between the ascending lavas and the surrounding arc crust while other authors (White and Dupré, 1986; Turner et al., 1996) attribute the continental fingerprint to involvement of sediments in the mantle source of the volcanics.

A puzzling feature of the Lesser Antilles volcanics is the association of high $^{207}\text{Pb}/^{204}\text{Pb}$ and low $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 4a). In $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ space, Lesser Antilles lavas plot on the upper part of the island arc array, well above the Northern Hemisphere Reference Line (NHRL) of Hart (1984), while in $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ space, they plot at the bottom of the main array, on both sides of the NHRL (Fig. 4a). In addition, the Lesser Antilles arc is characterized by a north-to-south chemical zoning (Hawkesworth and Powell, 1980; White and Dupré, 1986; Davidson, 1987; Turner et al., 1996). In Fig. 4b, we plot $^{206}\text{Pb}/^{204}\text{Pb}$ and $\Delta 8/4$ (the vertical deviation of $^{208}\text{Pb}/^{204}\text{Pb}$ from the NHRL) of Lesser Antilles lavas as a function of latitude. Lavas from the northern part of the arc have relatively constant and unradiogenic Pb isotope ratios, and their $\Delta 8/4$ are positive. In contrast, lavas from the southern part exhibit more variable Pb isotope ratios with more radiogenic compositions and negative $\Delta 8/4$.

Using our sediment data, we can evaluate the potential influence of geographical changes in the subducted sediment composition on the north-to-south variations in Pb isotopic compositions along the arc. Fig. 5 displays Pb and Nd isotopic data for lavas from the northern and the southern islands as well as our new results on Site 543 sediments. Lavas from northern islands, shown as black triangles, display a much narrower range of Pb and Nd isotope ratios than those from the southern islands, and they form a much steeper array. They lie between the MORB field and the field defined by the Site 543 sediments, whereas the southern island lavas extend to Pb isotope ratios that are even higher than those measured in Site 543 sediments. In both Pb isotopic diagrams, the southern islands define a trend whose slope differs from that of the northern islands and does not intersect the Site 543 field. We suggest therefore that while the Site 543 sediments could explain the composition of the northern islands, they cannot explain those of the southern islands. In the following discussion, we will treat the two parts of the island arc separately.

6.3.1. The Northern group, from Saba to Dominica

The position of the northern islands between MORB and Site 543 sediments in Pb isotopic space can be modelled using a simple binary mixing calculation that takes into account the following observations: (1) Pb isotopic data for the northern island lavas define a funnel that roughly converges towards one point in the Atlantic MORB field. We assumed therefore that this point represents the isotopic composition of the local depleted mantle. (2) To account for the isotopic variability of northern islands lavas, we used as sediment end members the two ends

of the field defined by the sediments. (3) For simplicity, we performed a bulk solid–solid mixing calculation. Most probably, the subducted sediment component occurs as hydrous fluids or partial melts and it is no doubt enriched in Pb and Nd compared to the bulk sediments. If so, our estimates represent maximum sediment contributions. (4) We neglected the subducted basaltic crust component because the Nd and Pb isotopic compositions of basaltic crust drilled at Site 543 are quite similar to those of local depleted mantle (Fig. 5).

Our mixing model suggests that less than 1% sediment is required to produce the Pb and Nd isotope ratios measured in northern island basalts. Our estimation is equivalent to previous calculations for the northern lavas published by White and Dupré (1986), Davidson (1987) and Turner et al. (1996).

6.3.2. The southern group, from Martinique to Dominica

Most studies have focused on the southern half of the Lesser Antilles arc, and different interpretations of the north-to-south

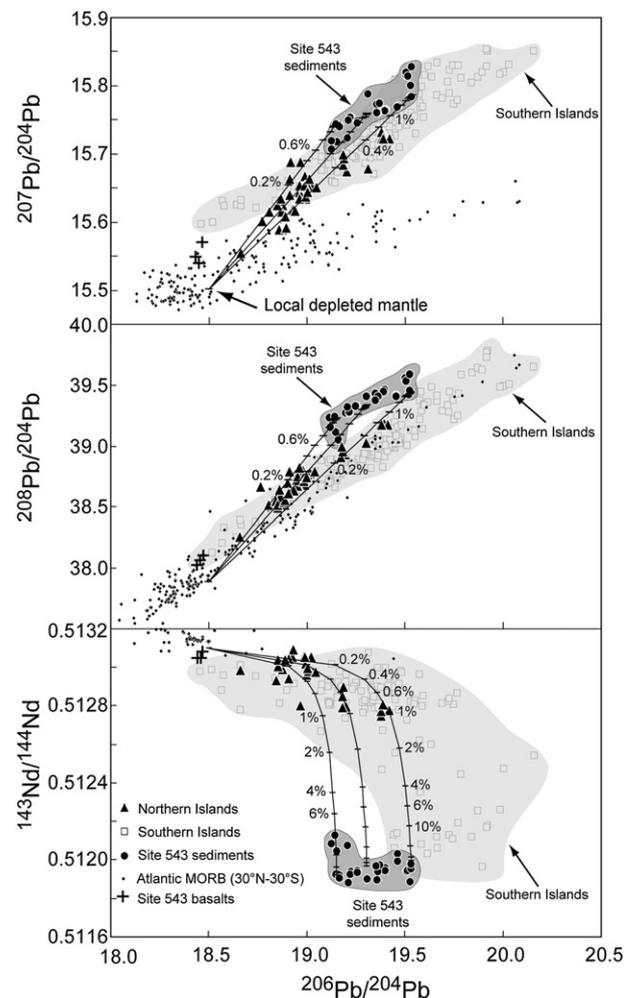


Fig. 5. Pb and Nd isotopic compositions of lavas from the northern and southern parts of the Lesser Antilles arc compared with those of Site 543 sediments and Atlantic MORB. The solid lines represent mixing curves between depleted mantle and Site 543 sediments. Ticks show the percentage of sediments in the mixture. Compositions of the end members used for the calculation: (1) depleted mantle: Nd=0.71 ppm, Pb=0.023 ppm (Salters and Stracke, 2004), $^{143}\text{Nd}/^{144}\text{Nd}=0.5131$, $^{206}\text{Pb}/^{204}\text{Pb}=18.5$, $^{207}\text{Pb}/^{204}\text{Pb}=15.5$ and $^{208}\text{Pb}/^{204}\text{Pb}=37.9$; (2) for the sediment end members, Nd and Pb concentrations are those of the average of the entire Site 543 sedimentary pile (see Supplemental file 5) and the isotopic compositions of the three end members are those of samples 543 33 2W 71–73, 543A 3 2W 12–14 and the average of Site 543 (see Table 1 and Supplemental file 5). Same data sources as in Fig. 4a for the Lesser Antilles arc and PETDB (<http://www.petdb.org/science.jsp>) for MORB data between 30°N and 30°S along the mid-Atlantic ridge. The isotopic compositions of Site 543 basalts are from White et al. (1985).

geochemical variations have been suggested. All studies agree that variable amounts of sediments can explain the geochemical variations but the way the sedimentary signature is acquired by the lavas differs: some authors suggest that sediments are involved both in the source of the lavas and as contaminants intercalated within the arc crust (Thirlwall and Graham, 1984; Davidson, 1985, 1986, 1987; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996). The arguments supporting contamination during fractional crystallization are mainly based on correlations between $\delta^{18}\text{O}$ on one hand and $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ on the other hand. Other authors think that contamination of the mantle wedge by subducted sediments is the major process (White and Dupré, 1986; Turner et al., 1996). However, White and Dupré (1986) recognized that some lavas from the southern part of the arc have Pb isotope ratios that are more radiogenic than the subducted sediments at Site 543 (see Fig. 5) and they suggested that sediments with more radiogenic Pb compositions must occur in deep horizons south of Site 543. They supported this hypothesis by noting that surface sediments show an increase in Pb isotope ratios toward the mouth of the Orinoco River (White et al., 1985). This debate has been going on for the last 20 yr and is still not solved. The aim of this paper is not to provide arguments for or against contamination of the lavas on their way to the surface but simply to evaluate the potential role of sediments similar to those drilled at Site 144 and collected on Barbados Island if they are subducted and involved in the genesis of the lavas in the southern part of the arc.

In the following sections, we use our new data on Site 144 and Barbados sediments to evaluate whether the presence of such sediments in the source of the southern islands lavas can account for their radiogenic Pb isotopic compositions and low $\Delta 8/4$ values.

6.3.3. Involvement of Site 144 sediments in the source of the southern islands

In Fig. 6, we display the Pb and Nd isotopic compositions of the southern part of the Lesser Antilles arc lavas and those of Site 144 sediments. The average composition of the sediment pile shown by a star lies at intermediate values and is clearly not the radiogenic end member required to explain the most radiogenic island arc lavas. However, two stratigraphic units, the marls from Unit 2 and the black shales from Unit 3 have sufficiently high Pb isotopic ratios to represent the radiogenic component. If only these two units were involved in the contamination of the mantle wedge, the composition of the southern islands volcanics could be explained. For it to happen requires that the most superficial Unit 1 does not contaminate the mantle wedge, suggesting that it is accreted to the sedimentary prism rather than subducted. Whereas the stratigraphic location of the décollement is well constrained in the north, this is not the case in this area (Westbrook et al., 1984) but considering the thickness of the accretionary prism it is not unreasonable.

In detail, Unit 2 has radiogenic Pb isotopic ratios and could represent the radiogenic component necessary to explain most of the southern island lavas; black shales of Unit 3, which have very high $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios but relatively low $^{208}\text{Pb}/^{204}\text{Pb}$, could represent a peculiar component also involved in the source of the southernmost islands. The black shales of Unit 3 have extremely low $\Delta 8/4$ values due to their high $^{206}\text{Pb}/^{204}\text{Pb}$ ratio at a given $^{208}\text{Pb}/^{204}\text{Pb}$ ratio, a feature that is characteristic of the southernmost islands (Figs. 4b and 6). As shown in Fig. 1, the age of the subducting plate increases from 83 Ma in the north to over 105 Ma in the south. The age of Unit 3 is well constrained to be between 95 and 84 Ma (Hayes et al., 1972). We therefore suggest that in the southern part of the arc, black shales like those of Unit 3 are part of the subducted sediments. This is not the case in the north where the oceanic crust is much younger.

To evaluate whether input of black shales in the source region of southern lavas could explain their isotopic compositions, we performed a simple binary mixing calculation with depleted mantle. Assumptions concerning the mantle wedge composition and the way

sediments are involved are similar to those described for the northern islands: the results are shown in Fig. 6. To account for the isotopic composition of the lavas with the highest $^{206}\text{Pb}/^{204}\text{Pb}$ values, as found on the Grenadines, a mixture of 18% black shales and 82% Unit 2 sediments is sufficient to create an appropriate sediment end member. In this particular case, about 6% sediment in the source of the lavas explains the most extreme Grenada and Grenadines lava compositions. At Site 144, the mass proportions of Units 2 and 3 are almost identical (Supplemental file 5) and a mixture of 18% black shales with 82% marls can occur without difficulties.

Due to the peculiar U enrichment of the black shales, their presence in the sedimentary component could be expected to have a significant effect on the Th/U and U/Pb ratios of the island arc lavas. An approximate quantification shows that the most contaminated mantle source would have a Th/U ratio of about 1.7 and a U/Pb ratio of about 0.48. By comparison, the southern island volcanics have extremely variable Th/U (≈ 1.5 –5) and U/Pb (≈ 0.1 –3) ratios that are compatible with the calculated source ratios but are most probably more controlled by dehydration, melting and fractionation processes than

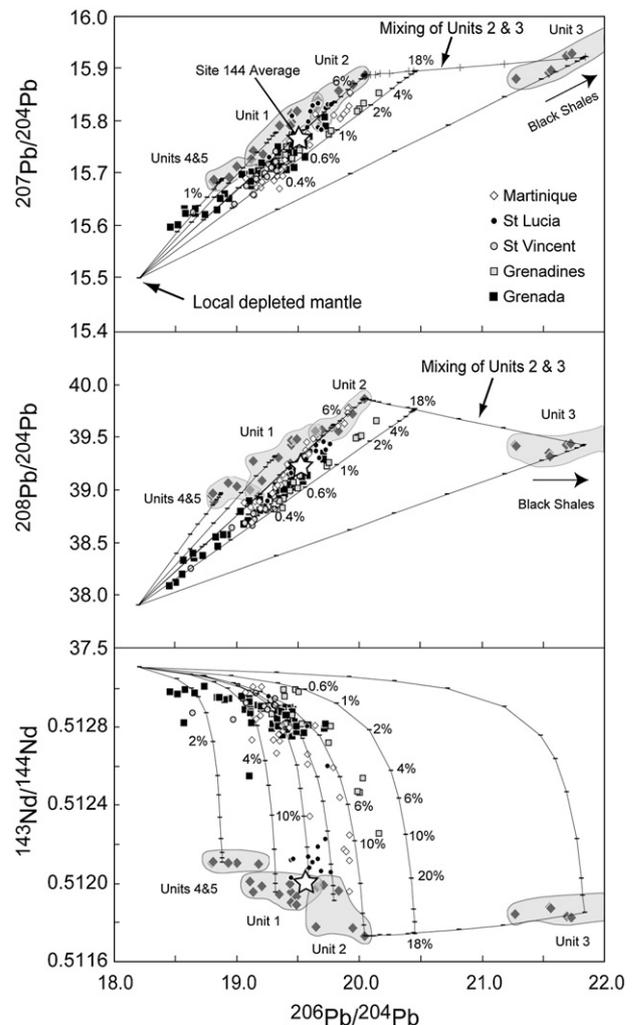


Fig. 6. Pb and Nd isotopic compositions of lavas from the southern part of the Lesser Antilles arc compared with those of Site 144 sediments. Data for samples from individual stratigraphic units are surrounded by a field. The solid lines represent mixing curves between local depleted mantle and Site 144 sediments grouped by stratigraphic units. Ticks show the percentage of sediments in the mixture. Compositions of the end members used for the calculations: (1) depleted mantle: Nd=0.71 ppm, Pb=0.023 ppm (Salters and Stracke, 2004), $^{143}\text{Nd}/^{144}\text{Nd}=0.5131$, $^{206}\text{Pb}/^{204}\text{Pb}=18.2$, $^{207}\text{Pb}/^{204}\text{Pb}=15.5$ and $^{208}\text{Pb}/^{204}\text{Pb}=37.9$; (2) for the sediment end members, we used the average of each unit and the average of the entire pile (see Supplemental file 5). Same data sources as in Fig. 4a for the Lesser Antilles arc.

by the source itself. An independent hint of the existence of black shales in the source of the southern volcanics is the north–south increase of non-mantle carbon flux and proportion of organic carbon as noticed by Van Soest et al. (1998).

Isotopic data reported for the other islands in the south (i.e., Martinique, St Lucia) all require a lower proportion of black shales in their source and the overall sediment contribution is always less than 20%. This value is very high and might be unacceptable from a petrological point of view. Several factors might reduce the proportion of sediments in the source of the arc lavas. First, we did a bulk mixing calculation and if the trace elements are removed from the sediments via a fluid phase or a partial melt, it is most likely that these phases are richer in trace elements than the starting sediment. Second, we performed that calculation using the bulk carbonate sediments as drilled at Site 144. If the carbonate fraction – which is very poor in REE and Pb and does not exist in sediments deposited below the CCD as is the case at Site 543 – is virtually removed from the sediments, the maximum sediment contribution to the source decreases from 20% to 10% for the most extreme cases of St Lucia and Martinique.

Our study is the first reporting Pb isotopic compositions on black shales produced during the Cretaceous Oceanic Anoxic Events and the impact of such deposits in other locations has not yet been evaluated. Similar deposits exist in other areas and in particular on the Caribbean plate where the OAE 3 was recognized in four different DSDP sites (Edgar et al., 1973), while the OAE 2 was not found because it is older than the emplacement of the Caribbean plateau (Sinton et al., 1998). We can therefore not exclude that such sediments are present within the crust under the Lesser Antilles arc. However, if black shales contaminated the Lesser Antilles lavas during their ascent through the Caribbean crust, the origin of the north–south Pb isotopic changes would still remain unclear because the black shales seem to be deposited all over the Caribbean plate. More generally, the presence of Cretaceous black shale units has been reported in other ocean basins (Sliter, 1989; Rullkötter et al., 1992) but none exists in any of the geochemically well characterized sites drilled in front of the main subduction zones (see Plank and Langmuir, 1998 and Plank et al., 2007 for further details). In the present situation, it is difficult to evaluate if similar effects can be found in other island arcs.

6.3.4. Involvement of Barbados sediments in the source of the southern islands

In Fig. 7, we show the isotopic compositions of the southern island lavas and those of the Barbados sediments. The Barbados sample with the most radiogenic Pb isotopes has higher Pb isotope ratios than the most radiogenic southern island lavas and having high $^{206}\text{Pb}/^{204}\text{Pb}$ ratio at moderate $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, it could correspond to the required radiogenic end member (Fig. 7). However, Barbados sediments alone cannot explain the composition of most lavas from Martinique, St Lucia, Grenadines and Grenada islands because their $^{207}\text{Pb}/^{204}\text{Pb}$ are generally lower at a given $^{206}\text{Pb}/^{204}\text{Pb}$ than the southern island lavas (Fig. 7); however, if mixed with sediments with relatively high $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, as is the case with Site 543 sediments, appropriate sedimentary end members can be calculated. In Fig. 7, we show mixing lines between the most radiogenic Site 543 sediments and the most radiogenic Barbados turbidite. For proportions of Barbados sediments varying between 0 and 80%, the required enriched end members can be reproduced. This sedimentary component is then mixed with depleted mantle to model the lava compositions using the same procedure as in Figs. 5 and 6. The maximum sedimentary contribution in the lava sources is 6% when using only Pb isotopes (see Fig. 7a and b) but increases to almost 20% when Pb and Nd isotopes are combined (see Fig. 7c). When modelling contamination of the mantle wedge with Site 144 sediments (Fig. 6), the elevated sedimentary contribution of 20% can be reduced to 10% by removing the carbonate fraction but this is not the case with the Barbados sediments because they are carbonate free. In summary, the

most extreme Barbados sediment mixed with Site 543 sediments can provide the required Pb-radiogenic end members. However, it can be argued that the required proportion of sediment in the lava sources is too high to be realistic. We therefore do not favour this model and prefer the involvement of Site 144 sediments to explain the isotopic compositions of the southern part of the Lesser Antilles arc.

7. Summary and conclusions

Our new measurements of Pb and Nd isotopic compositions of sediments from Barbados Island and two sites drilled in front of the Lesser Antilles arc system show that sediment compositions are strongly influenced by material from the continental crust. While Site 543 sediments have relatively uniform isotopic compositions, Site 144 sediments display a large range, particularly in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. The proximity of the South American craton explains some specificities of Site 144 sediments – very low $^{143}\text{Nd}/^{144}\text{Nd}$ and high $^{206-207-208}\text{Pb}/^{204}\text{Pb}$ ratios in some lithological units – while the presence of a U-rich black shales implies very extreme Pb isotopes.

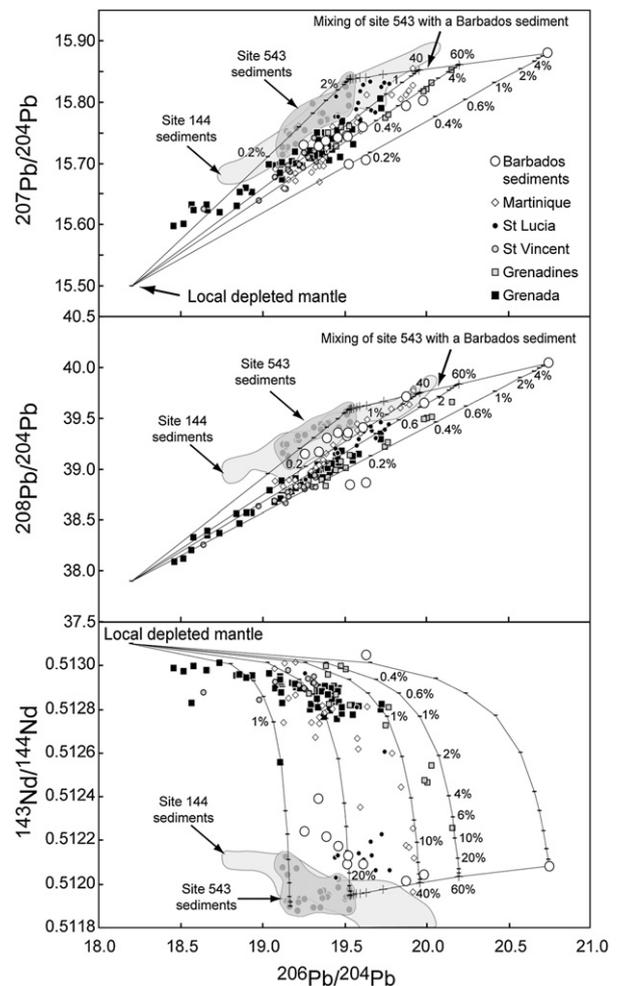


Fig. 7. Pb and Nd isotopic compositions of lavas from the southern part of the Lesser Antilles arc compared with those of Barbados island sediments. The compositions of Sites 543 and 144 sediments (excluding the black shales) are also shown. The solid lines represent mixing curves between local depleted mantle and Site 543 and Barbados Island sediments and the ticks show the percentage of sediments in the mixture. Compositions of the end members used for the calculations: (1) depleted mantle: same as in Fig. 6; (2) for the Site 543 sediment end members, Nd and Pb concentrations are those of the average sedimentary pile (see Supplemental file 5) and the isotopic compositions are those of samples 543 29 4W 45–47 and 543A 2 1W 116–118 (Table 1). For the Barbados sediment end member, we use the average Nd and Pb concentrations of Scotland formation sediments (Nd = 33.8 ppm and Pb = 15.4 ppm), and the isotopic compositions of sample B-10b (Table 1). Same data sources as in Fig. 4a for the Lesser Antilles arc.

Using data from Barbados and both sediment piles, we model the composition of the arc lavas by mixing local subducted sediment into the mantle wedge. In the northern part of the Lesser Antilles arc, the lava composition is satisfactorily reproduced by involving less than 1% sediments similar to those drilled in front of the arc at Site 543. The puzzling isotopic composition of the southern islands is reproduced by involving less than 10% sediments similar to those sampled further south at Site 144. The radiogenic Pb isotopes of the southern islands, as well as their low $\Delta 8/4$ values, are explained by the generally more radiogenic characteristics of Site 144 sediments and by the presence of the black shale unit in the subducting pile. The north–south isotopic variation of the Lesser Antilles arc seems therefore to result from the changing age and composition of the subducting material in front of the arc system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.04.036.

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