JOURNAL OF PETROLOGY | VOLUME 53 | NUMBER 12 | PAGES 2441–2464 | 2012 | doi:10.1093/petrology/egs055

Martinique: a Clear Case for Sediment Melting and Slab Dehydration as a Function of Distance to the Trench

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RECEIVED AUGUST 30, 2011; ACCEPTED JULY 18, 2012
ADVANCE ACCESS PUBLICATION SEPTEMBER 9, 2012

In subduction zones, melting and dehydration of the subducted slab introduce material into the mantle wedge and modify its chemical and isotopic composition. As a consequence, island arc lavas differ significantly from mid-ocean ridge basalts and ocean island basalts. In some arcs, the composition of lavas is strongly influenced by the sedimentary material introduced with the slab; in others, magma composition is mainly affected by aqueous fluids released by the slab. The Lesser Antilles arc is known for its extreme continental-crust-like signature but for some Lesser Antilles lavas subducted sediments are barely involved and enrichment in fluid-mobile elements (Ba, U, Sr, Pb, etc.) is the dominant feature. Here we evaluate whether La/Sm is a quantitative proxy of sediment involvement in volcanic arcs, and we relate dehydration and melting processes to the temperature and pressure conditions of the slab. We use Martinique as a case study because in this island both dehydration and sediment melting fingerprints coexist. We measured major and trace elements for about 130 age-constrained samples, carefully chosen to cover all volcanic phases of Martinique (25 Ma to present). Using these results we demonstrate that: (1) weathering does not modify the La/Sm ratio; (2) fractional crystallization of amphibole and/or garnet does not increase La/Sm by more than 20%; (3) rare earth element transfer from wall-rock to magma during fractionation is not significant; (4) melting of the mantle source increases La/Sm by only about 20%. As a consequence, we show that the proportion of slab sediment incorporated in the mantle wedge controls the La/Sm ratio of the source. The observed correlations between La/Sm and Nd and Hf isotopic compositions indicate that the effect of sediment addition is the overwhelming factor: La/Sm is a good proxy for slab sediment proportion in Martinique. We observe a geographical gradient between slab dehydration and sediment melting on the island. Whereas lavas located on the western side of the island display a clear sedimentary input in their source, lavas located on the eastern side of the island, closer to the trench, are clearly influenced by dehydration of the subducted slab. In addition, the aqueous fluids clearly come from the subducted basalt and they did not interact with the overlying sediments. The influence of sediment added to the source of the magmas increases from the eastern part to the western part of the island. We relate this geographical change to the pressure and temperature conditions at the slab surface. Sediments probably cross their solidus under Martinique and hydrous melting is triggered. Finally, we show that under all volcanic arcs where the signature of sediments overwhelms the signature of fluids, the slab surface reaches P–T conditions that allow the subducted sediments to melt. Inversely, under most volcanic arcs where the signal of aqueous fluids dominates over sediment melts, the subducted slab is not hot enough for the sedimentary pile to melt.

KEY WORDS: *Lesser Antilles; slab dehydration; sediment melting; island arcs; subduction zones*

INTRODUCTION

Intra-oceanic arc lavas have chemical and isotopic characteristics that differ significantly from those of mid-ocean ridge basalts and ocean island basalts, and these features

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are attributed to the involvement of fluids or melts coming from the subducted slab. The aqueous or siliceous fluids added to the mantle wedge trigger partial melting to generate magmas that form the volcanic arc. Processes leading to the final composition of the lavas are numerous: they include melting conditions, fractional crystallization of the primary melt and surface alteration effects, and they are sometimes hard to distinguish. To understand and quantify the processes that take place during the genesis of a volcanic rock, elements with distinct behaviors are often used. Ba/Th, Sr/Th, U/Th and Pb/Ce were used by Turner *et al.* (1996), Hawkesworth *et al.* (1997), Turner & Foden (2001) and Elliott (2003) to highlight the role of hydrous fluids in the genesis of magmas in volcanic arcs. Radiogenic isotopes (Pb, Sr, Nd and Hf) are widely used to demonstrate the presence of subducted sediments in the source of volcanic arc lavas (Armstrong, 1971; White & Patchett, 1984; Woodhead, 1989; Miller *et al.*, 1994; Hawkesworth *et al.*, 1997; Class *et al.*, 2000; Marini *et al.*, 2005), but element ratios, such as Th/Yb (Woodhead *et al.*, 2001), Th/Ce (Hawkesworth *et al.*, 1997), La/Sm (Elliott, 2003), Th/Nb (Elliott, 2003) or Th/La (Plank, 2005), can also serve as proxies for slab sediment involvement in the petrogenesis of arc lavas. In the latter case, the underlying assumption is that these ratios are representative of the source composition and are not significantly affected by melting or fractional crystallization.

The Lesser Antilles arc occurs as a result of the subduction of Atlantic oceanic lithosphere beneath the Caribbean Plateau. The volcanic rocks of the Lesser Antilles arc are well known for their very large diversity of chemical and isotopic compositions (Dupré *et al.*, 1985; Davidson, 1987). Whereas the northern islands have rather ordinary arc compositions, the southern islands reach extreme 'crustal-like' isotopic compositions compared with other intra-oceanic arcs (White & Dupré, 1986). These characteristics have been attributed to variable input of slab-derived sediment within the magma source (Davidson, 1983; White & Dupré, 1986; Carpentier *et al.*, 2008), possibly enhanced by crustal-assimilation processes (Davidson, 1986; Davidson & Harmon, 1989; Thirlwall *et al.*, 1996). Martinique is located in the central part of the Lesser Antilles arc and has registered the most complete history of the arc (Coulon *et al.*, 1990; Germa *et al.*, 2010, 2011*b*). It is an important site because Martinique lavas alone (Davidson, 1983, 1986) cover most of the chemical and isotopic variability known in the Lesser Antilles arc. The very large range of isotopic compositions of the Martinique lavas has recently been interpreted as the consequence of the incorporation of variable proportions of slab-derived sediment within the mantle wedge (Labanieh *et al.*, 2010).

In this study we demonstrate that the proportion of added sediment controls the REE content of the magmas and that the impact on La/Sm of weathering, fractional crystallization and partial melting conditions is relatively minor. We also show that ratios of fluid-mobile elements to Th demonstrate that slab dehydration also occurs under Martinique. More specifically, we show the existence of spatial zonation of La/Sm, Ba/Th and U/Th across the island. Finally, we suggest that this zoning is related to the depth of the slab: slab sediments seem to cross their solidus under Martinique such that lavas nearer the trench do not show significant signs of sediment addition to their source whereas further away from the trench the sediments melt and contaminate the magma source.

GEOLOGICAL SETTING

The Lesser Antilles island arc (Fig. 1) developed in response to subduction of Atlantic oceanic lithosphere (which is part of the American plate) under the Caribbean Plateau. The direction of convergence is thought to be globally westward oriented but the exact direction is still not well constrained. Molnar & Sykes (1969) suggested an east–west direction for the North American plate relative to the Caribbean plate, whereas Jordan (1975), Minster & Jordan (1978) and Stein *et al.* (1988) argued for ESE–WNW motion of the North American plate, and Sykes *et al.* (1982), McCann & Sykes (1984), Dixon & Mao (1997) and DeMets *et al.* (2000) proposed that the North American plate moves in an ENE–WSW direction.

In the Lesser Antilles magmatism has occurred since the Late Oligocene (Germa *et al.*, 2011*a*) and is currently represented by active volcanoes on most islands. In the southern part of the arc volcanic eruptions have occurred almost continuously on each island, with volcanic centers overlapping both in space and time. In the northern part of the arc a distinct westward jump occurred ~7 Myr ago and the currently active northern islands are uniformly young (recent arc) and lie to the west of an inactive chain (old arc), the Limestone Caribbees (Nagle *et al.*, 1976; Briden *et al.*, 1979). The geographical jump of volcanic activity was attributed by Bouysse & Westercamp (1990) to subduction of an aseismic ridge that momentarily blocked the subduction, stopped volcanic activity for ~8 Myr and changed the dip of the slab before volcanism started again to the west in the northern part of the arc (e.g. in Saba, St Kitts, Montserrat and Guadeloupe). With its central position, Martinique has recorded the most complete history of the arc (Coulon *et al.*, 1990; Germa *et al.*, 2011*a*). On this island, the effect of the aseismic ridge subduction was only a small westward migration of volcanic activity and no significant gap in magma production is recorded: the 'recent arc' does not cover the 'old arc' and a third period of activity, called the 'intermediate arc', is also present.

Numerous distinct volcanic phases, each having different characteristics, make up the old, intermediate and recent

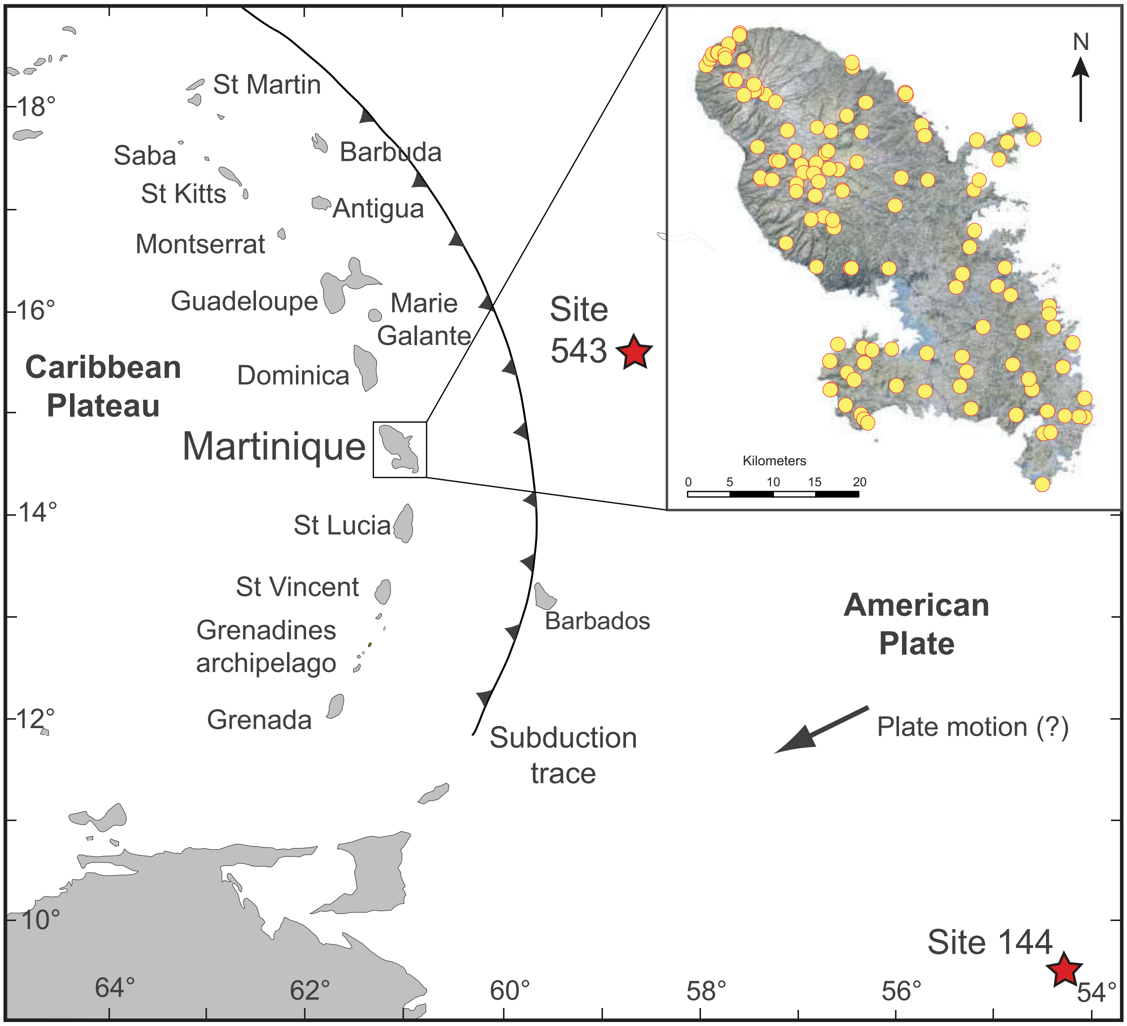

Fig. 1. Map of the Lesser Antilles region modified from Bouysse & Westercamp (1990). The two DSDP sites analyzed by Carpentier *et al.* (2008, 2009) are also shown (stars). The inset is a map of Martinique; the location of samples for which major and trace elements were determined are represented by circles. The direction of plate motion is that proposed by Sykes *et al.* (1982), McCann & Sykes (1984), Dixon & Mao (1997) and DeMets *et al.* (2000).

volcanic activity in Martinique. Westercamp *et al.* (1989) mapped and described all these volcanic phases and a simplified geological map based on their work is presented in Fig. 2. The old arc crops out on two peninsulas located in the east and the south of the island (Fig. 2). This consists of two volcanic phases: the Basal Complex (24·2–24·8 Ma) and the St Anne Series (20·8–24·8 Ma) (Westercamp *et al.*, 1989; Germa *et al.*, 2011*a*). The intermediate arc includes four main volcanic phases: the submarine Vauclin–Pitault phase 1 (16·1–8·5 Ma), the subaerial Vauclin–Pitault phase 2 (10·6–8·4 Ma), the S and SW volcanic phase (9·2–8·8 Ma) and the Gros Ilet volcanic phase (7·1 Ma) (Fig. 2). Finally, the recent arc includes six main phases: the submarine Jacob phase 1 (5·1–4·1 Ma), the subaerial Jacob phase 2 (3·01–1·53 Ma) (Germa *et al.*, 2010), the Trois Ilets phase (2·36–0·35 Ma), the Carbet phase (998–322 ka), the Conil phase (543–126 ka) and the currently active Pelée volcanic phase (126 ka to present) (Fig. 2) (Westercamp *et al.*, 1989; Germa *et al.*, 2011*b*).

PREVIOUS WORK

The Lesser Antilles is an extreme example among intra-oceanic volcanic arcs because of its very large diversity of chemical and isotopic compositions (White & Dupré, 1986; Davidson, 1987). The range defined by Pb, Sr and Nd isotopic ratios covers almost the entire range known for arc lavas and has been interpreted as the result of mixing processes between mantle and crustal components. However, the nature and origin of the crustal component have been the subject of debate in the literature.

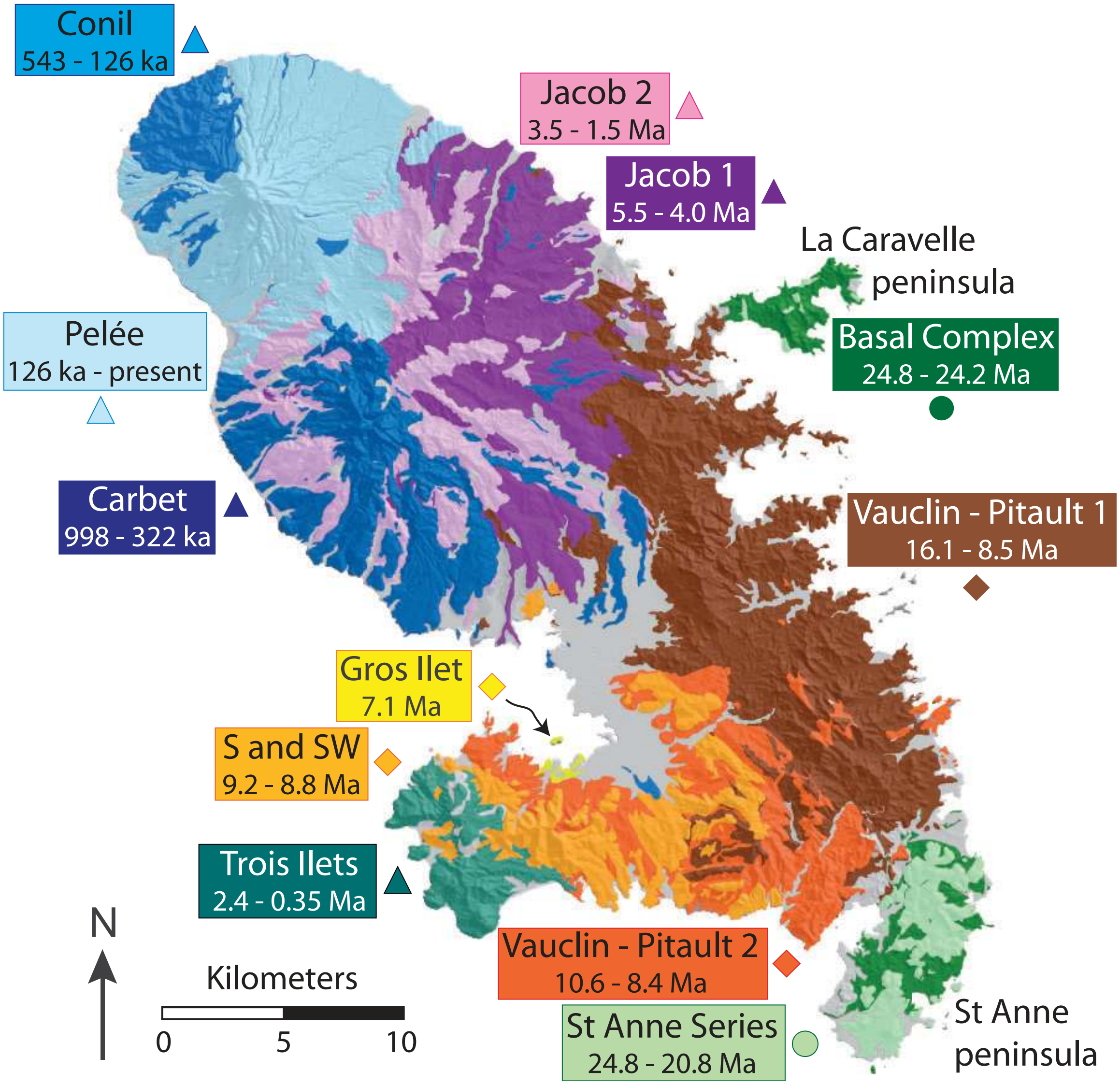

Fig. 2. Simplified geological map after Westercamp *et al.* (1989). Shades of green refer to old arc volcanic activity; brown, orange and yellow represent volcanic activity of the intermediate arc; and shades of blue and purple represent volcanic activity of the recent arc. The symbols next to the names of the volcanic phases are those used in subsequent figures to refer to the related volcanic phases. Ages of the volcanic phases are from Germa *et al.* (2010, 2011*a*, 2011*b*).

Davidson (1983), Dupré *et al.* (1985) and White & Dupré (1986) first suggested that sediments were incorporated within the magma source through dehydration or melting of the subducted slab. However, the sediments cored at Site 543 (Fig. 1) and analyzed by White & Dupré (1986) do not have Pb isotopic ratios radiogenic enough to represent a possible contaminant for the most radiogenic Lesser Antilles lavas found in the southernmost islands of the arc (from Martinique to Grenada). This led a number of workers (e.g. Davidson, 1986; Davidson & Harmon, 1989; Van Soest *et al.*, 2002) to suggest that sediments present within the Caribbean arc crust were assimilated by the magma during fractional crystallization in crustal magma chambers. Recently, a new study of sediments cored at Deep Sea Drilling Project (DSDP) Site 144 (Fig. 1) was published by Carpentier *et al.* (2008, 2009). Those workers showed that the Site 144 sediments have Sr, Nd, Hf and Pb isotopic compositions suitable to be the potential contaminant for the southern Lesser Antilles magmas. Finally, Labanieh *et al.* (2010) showed that addition of Site 144 sediments to the mantle wedge reproduced the composition of the Martinique lavas, whereas crustal assimilation processes did not reproduce the isotopic trends defined by the lavas from this island.

SAMPLING AND ANALYTICAL PROCEDURES

We collected 127 samples from throughout Martinique, selecting outcrops based on the freshness of the samples (see inset in Fig. 1) and with the aim of sampling all the effusive phases of Martinique. Samples were finely powdered in an agate mortar. Major and transition element contents were obtained by inductively coupled plasma–atomic emission spectrometry (ICP-AES) in Brest, following the procedure described by Cotten *et al.* (1995). Precisions on concentrations are 1% on the measured SiO_2 concentration, 2% on the other major elements, except P_2O_5 and MnO (6% on the measured concentration), and 5% on the transition elements.

Trace element concentrations were measured, after acid dissolution, by inductively coupled plasma–mass spectrometry (ICP-MS) using a PlasmaQuad2 + system and an Agilent 7500ce system at the University of Grenoble. Detailed analytical techniques have been described by Chauvel *et al.* (2011). Dissolution of about 100 mg of powder was performed in a HF–HNO_3 mixture in Teflon containers. Samples were diluted in 2% HNO_3 with a trace of HF and a multispike solution (Be, As, In, Tm and Bi) was added to each sample to monitor machine drift. Concentrations were obtained using the international rock standard BR to calibrate the signal and the values recommended by Chauvel *et al.* (2011) for the single trace element contents. AGV-1, BHVO-2 and BR24 were run as unknowns to validate the accuracy of our data and the results are provided in Supplementary Data file 1 (available for downloading at http://www.petrology.oxfordjournals.org), where they are compared with published values. Differences between our measured concentrations and the published values are less than 5% for most elements. In addition to checking the accuracy of our measurements, we checked the reproducibility of the data themselves by running total procedure duplicates ($n = 17$) and obtained values within 6% for all elements.

RESULTS

All major and trace element contents are given in Supplementary Data file 2, together with the precise location of the samples. Loss on ignition (LOI) is below 3% for more than 80% of our samples and does not exceed 6·1% (Fig. 3). Lavas range from basalt to rhyolite with SiO_2 between 47·3 and 71 wt % (See Supplementary Data file 2). $Na_2O + K_2O$ ranges from 2·3 to 6·9 wt % and all lavas plot in the subalkaline field in the total alkalis vs silica (TAS) diagram of Le Bas *et al.* (1991). All Martinique lavas show typical island arc trace element patterns (Fig. 4), with a clear enrichment in large ion lithophile elements (LILE; Perfit *et al.*, 1980), a depletion in Nb and Ta (Tatsumi *et al.*, 1986), and low Ce/Pb ratios (Hofmann *et al.*, 1986). Li contents show important variations and define a negative anomaly in the trace element patterns of submarine volcanic phases and a positive anomaly for subaerial volcanic phases.

The REE patterns display variable slopes, with La/Sm ranging from 1·29 to 6·10; these values are similar to previously published data (see Figs 3–5). Interestingly, the La/Sm ratios are negatively correlated with Nd and Hf isotopic ratios (Fig. 6) and positively correlated with Pb and Sr isotopic ratios (not shown).

WHAT CONTROLS THE REE CONTENT OF MARTINIQUE LAVAS?

To constrain the source of volcanic arc magmas we can use only geochemical tracers that are not significantly modified by magma-forming processes. This is the case for isotopic ratios, but it can also be the case for some trace element ratios if melting, fractional crystallization and alteration processes do not significantly modify their original values. For example, Th/Ce, Th/Nb, La/Sm and Th/La have been successfully used by numerous workers to demonstrate the addition of subducted sediments to the mantle wedge under various arcs worldwide (Hawkesworth *et al.*, 1997; Elliott, 2003; Plank, 2005). Here, we focus on the La/Sm ratio because hydrous fluids are generally represented using a ratio between a mobile element and Th as an immobile element (Ba/Th, Sr/Th, U/Th) and our aim is to decipher the relative role of hydrous fluids. However, one has to be cautious because processes other than slab sediment addition may modify the rare earth element (REE) content of the primary magmas and fractionate the ratio of light REE (LREE) to middle REE (MREE) and heavy REE (HREE) in arc lavas. We therefore need to quantify and correct for the effects of processes such as alteration, fractional crystallization (and crustal assimilation) and partial melting on the REE patterns of the arc lavas.

Island arc lavas are characterized by highly variable REE patterns ranging from depleted to very enriched in LREE. Among all island arcs, the Lesser Antilles belongs to a group in which La/Sm ratios are extraordinarily variable, with values ranging from 0·83 up to significantly higher than six (Fig. 7). The range of La/Sm ratios and particularly the high La/Sm values could be explained by a number of processes. Below, we evaluate and correct for the effect of (1) weathering processes under the prevailing tropical climate, (2) fractional crystallization of the magma on its way to the surface, (3) potential crustal assimilation, and (4) partial melting conditions in the mantle wedge to finally constrain the REE pattern of the source material.

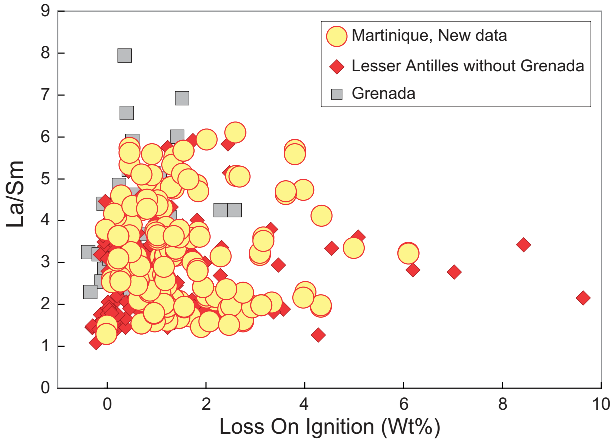

Fig. 3. La/Sm vs loss on ignition for Martinique lavas, Grenada and other Lesser Antilles lavas. Published data are from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/). Some lavas from the southern islands of the Lesser Antilles arc have higher La/Sm ratios but no LOI data were available for those samples.

Effect of weathering

All rocks discussed in this study have been carefully sampled and selected with freshness as a key objective. Low LOI values and petrological observations indicate that secondary processes have not significantly affected our samples: LOI is <3 wt % for most samples (Fig. 3) and secondary minerals such as chlorite have not been found during examination under the microscope. No correlation between La/Sm and LOI values for Martinique lavas appears in Fig. 3, and because LOI is a good proxy to discriminate between fresh and weathered samples (Chauvel *et al.*, 2005) the lack of correlation implies that weathering did not have a significant effect on the ratio of LREE in the studied samples. Similarly, there is no correlation between La/Sm and LOI for lavas from all the other Lesser Antilles islands (Fig. 3), suggesting that both at the island level and at the arc level weathering did not create changes in the ratio of LREE to MREE. This observation is consistent with the relatively immobile behavior of the REE during hydrothermal or metamorphic fluid–rock interaction at low fluid/rock ratios as described by Bau (1991) and Smith *et al.* (2008). Overall, we are therefore confident that the REE patterns of the studied Lesser Antilles lavas have not been modified by weathering processes.

Effect of fractional crystallization

Volcanic activity on Martinique has occurred in several phases with varying fractionation trends that need to be considered separately to evaluate the effect of crystal fractionation on the REE patterns of the lavas (Westercamp *et al.*, 1989). Figure 8 shows a plot of La/Sm vs SiO_2 content for Martinique lavas with each volcanic phase represented by a specific symbol. No correlation exists for most volcanic phases but three volcanic phases have higher La/Sm associated with higher SiO_2 contents (Carbet, Conil, Pelée); in addition, the sample from Gros Ilet volcanic phase also has a high La/Sm ratio (5·67) and a high SiO_2 content (67·4 wt %). The correlation between La/Sm and SiO_2 for the Carbet, Conil and Pelée lavas indicates that differentiation increases the slope of the REE patterns for these lavas and to obtain the primary magma REE pattern requires a proper correction.

Fractionating phases

Olivine, plagioclase and pyroxenes are widely involved during fractional crystallization of arc magmas, but their effect on the REE patterns is limited (Davidson *et al.*, 2007). This is why most volcanic phases of Martinique (St Anne, La Caravelle, Vauclin–Pitault, Jacob) show no variation in the slope of the REE pattern with increasing silica content. In contrast, amphibole and garnet can affect the shape of the REE pattern because garnet incorporates the HREE and amphibole preferentially incorporates the MREE with respect to both LREE and HREE (Davidson *et al.*, 2007). The correlation between La/Sm and SiO_2 defined by the Pelée, Conil and Carbet lavas, and the elevated La/Sm ratio of the garnet-bearing dacite from Gros Ilet could be explained by fractionation of amphibole and/or garnet. As shown in Fig. 5, the REE patterns of the Pelée, Conil and Carbet lavas are slightly U-shaped, a feature classically attributed to amphibole fractionation (Green & Pearson, 1985; Bottazzi *et al.*, 1999). This interpretation is confirmed by petrological observations (Supplementary Data file 3), which demonstrate the presence of amphibole phenocrysts in lavas from the Conil and Carbet volcanic phases. The presence of amphibole as a fractionating phase was also suggested by Davidson *et al.* (2007), who showed that the Pelée lavas define a negative correlation between Dy/Yb and SiO_2, which they attributed to the preferential partitioning of the MREE with respect to the HREE by amphibole. Our new data for the Pelée lavas confirm Davidson *et al.*'s (2007) observation and can also be extended to the Conil lavas (Fig. 9). In contrast, samples from the Carbet volcanic phase define a weak positive correlation in Fig. 9, a feature that can be interpreted, according to Davidson *et al.* (2007), as the result of garnet fractionation. We believe that both amphibole and garnet fractionation have modified the REE patterns of the Carbet lavas. The effect of garnet fractionation on Dy/Yb overwhelms the effect of amphibole fractionation and both minerals contribute to an increase of La/Sm. Finally, the geographically restricted and atypical garnet-bearing dacite of Gros Ilet has an extremely high Dy/Yb ratio, probably because of the fractionation of garnet, as can be suspected from the presence of garnet as phenocrysts in the lava.

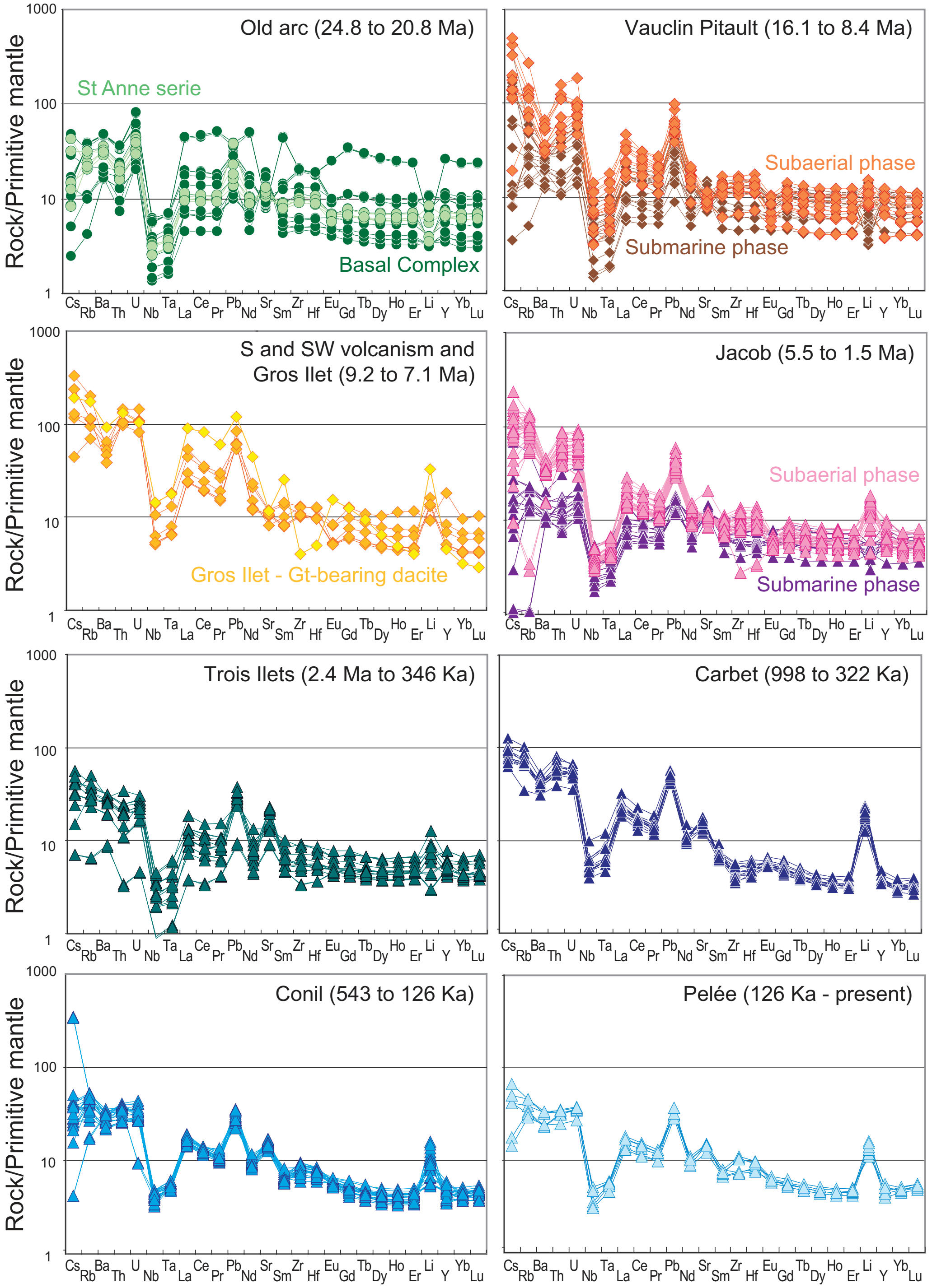

Fig. 4. Trace element patterns normalized to primitive mantle (McDonough & Sun, 1995) for the volcanic phases on Martinique, as defined by Westercamp *et al.* (1989). Symbols as in Fig. 2.

Impact of crystal fractionation

To calculate the impact of the fractionation of a mineral assemblage that includes amphibole (± garnet) we use the equation of Gast (1968) and a mineralogical assemblage consisting also of plagioclase, orthopyroxene and clinopyroxene (see Supplementary Data file 4). The proportions of minerals in the assemblage differ depending on the volcanic phase (Pelée, Conil or Carbet). For Pelée

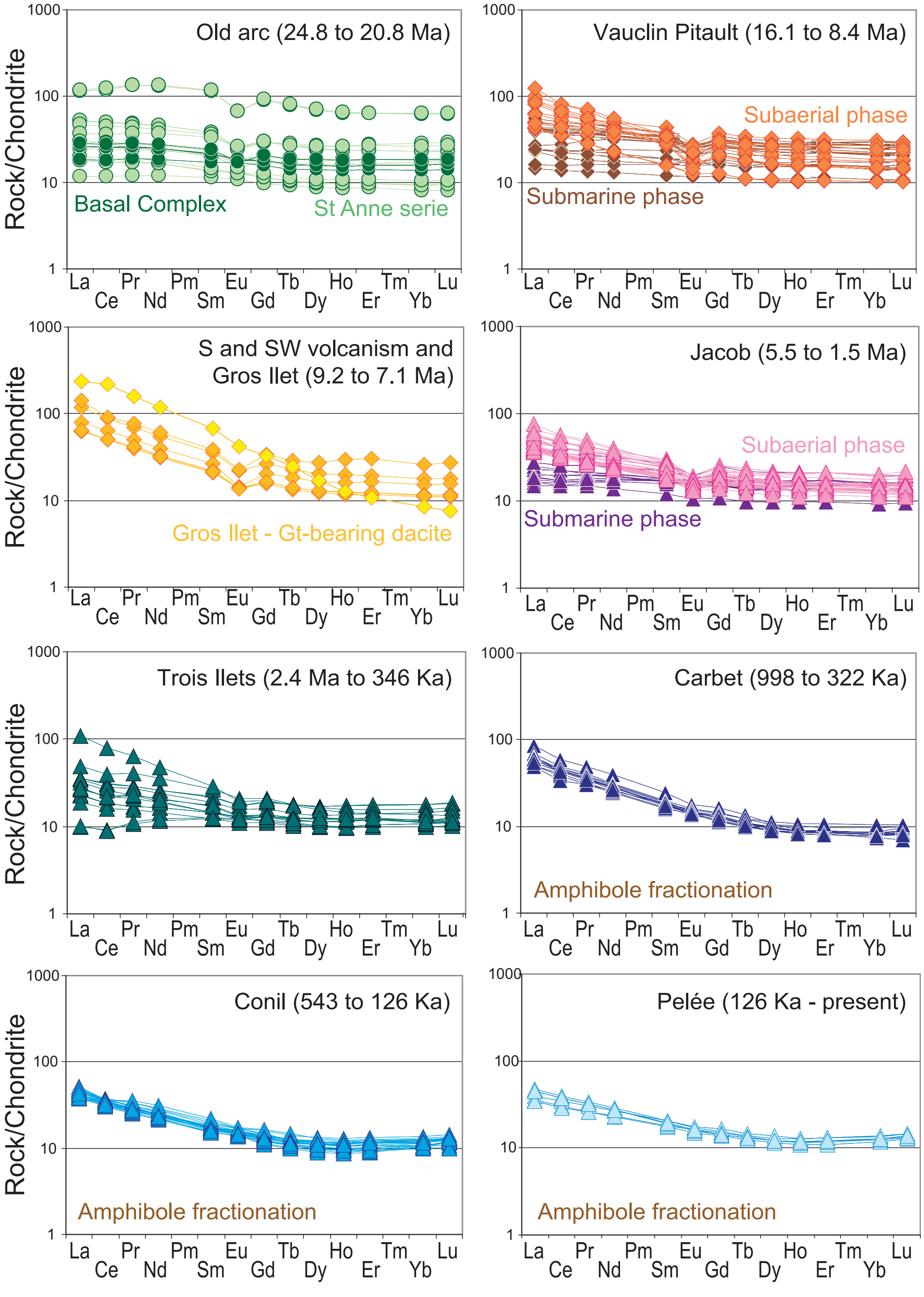

Fig. 5. REE patterns normalized to chondrite (Evensen *et al.*, 1978) for the volcanic phases on Martinique as defined by Westercamp *et al.* (1989). Symbols as in Fig. 2.

we use the proportion suggested by Davidson (1986); that is, 50% plagioclase, 35% hornblende, 10% orthopyroxene and 5% clinopyroxene (no garnet). For Conil, we tested two different mineral assemblages; one similar to that used for Pelée and the other one with slightly more amphibole. Finally, for Carbet lavas, we assume that the fractionating assemblage contains 5% garnet (see Fig. 10 and Supplementary Data file 4). For each volcanic series, we

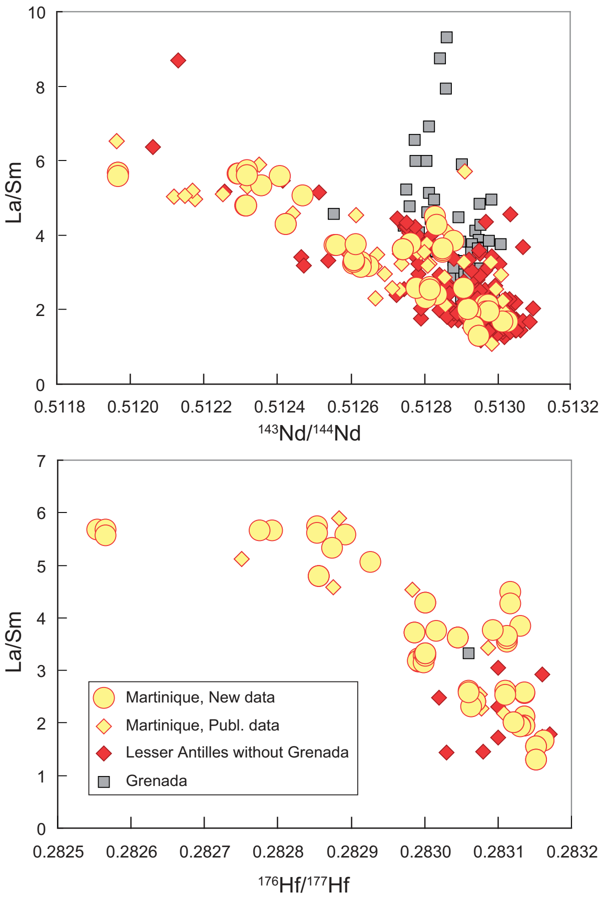

Fig. 6. La/Sm ratio vs Nd and Hf isotopic ratios for Martinique lavas, Grenada and other Lesser Antilles lavas. Published data are from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

use only one mineral assemblage to model fractional crystallization from parental to fractionated magma. This is justified by the observation and models proposed by Davidson & Wilson (2011): the trends defined by major elements do not show inflections, indicating that there are no sudden modal abundance changes in the fractionating mineral assemblage, and the models show little difference in phase proportions if fractionation of Pelée lavas is modeled in one or two stages (Davidson & Wilson, 2011). We assume that evolution from the primary to the parental magmas occurs through fractionation of a gabbroic assemblage (mostly olivine, plagioclase and pyroxene) that will have no significant impact on LREE/MREE ratios. Fractionation degrees (see Fig. 10) are estimated using ranges of SiO_2 concentrations and assuming that the parental magma has a silica content of about 51 wt %, a composition similar to that reported by Davidson & Wilson (2011) for their most primitive Pelée lavas and which they used as representative of the parental magma of the Pelée lavas. Finally, we used the partition coefficients published by Fujimaki *et al.* (1984) for plagioclase, hornblende, clinopyroxene and orthopyroxene, and those of Johnson (1994) for garnet (Supplementary Data file 4).

The combination of all these parameters leads to a decrease of La/Sm between the evolved lavas and the primary melts that ranges from 5 to 16% for Carbet magmas, from 4 to 20% for Conil lavas (depending on the mineral assemblage) and from 4 to 15% for Pelée lavas when the degree of fractional crystallization varies between 15 and 45% (see Supplementary Data file 4). In Fig. 10 we show the effect of the correction on the La/Sm ratio. It is important to note that we do not correct the silica contents (all corrected values would be equal to 51 %). The aim of the exercise is to demonstrate that no more positive or negative slopes exist after correction. Figure 10 shows clearly that the correction is efficient for Pelée lavas and Carbet lavas, and that the best correction is obtained for Conil lavas when 40% amphibole is present in the residual mineral assemblage.

The situation is more complex for the garnet-bearing dacite sampled in Gros Ilet. The very unusual chemical composition of this sample cannot be reproduced by simple fractional crystallization of a primary magma produced by mantle melting. Previous work showed that the fractionation process leading to its formation certainly involved garnet and amphibole (Westercamp, 1976). Both the mineral assemblage and the amount of fractional crystallization are not well constrained. However, we can reasonably assume that the Gros Ilet primary magma had a Dy/Yb ratio similar to that of the Martinique lavas that did not experience amphibole and garnet fractionation, at about 1·7 (Fig. 9). Depending on the amount of fractional crystallization (45–65%), the proportion of hornblende and garnet needed to change the Dy/Yb ratio from 3·1 (the value measured for the dacite) to 1·7 varies but we calculate that the primary magma had a La/Sm ratio only 6–17% lower than that of the garnet-bearing dacite itself (Supplementary Data file 4).

In summary, we estimate that for all lavas affected by hornblende and/or garnet fractionation (Pelée, Conil, Carbet and Gros Ilet), the primary magmas had La/Sm ratios systematically lower than the measured ratios. The difference varies depending on the presence or absence of garnet as a fractionating phase and on the amount of fractional crystallization, but overall, the decrease ranges from 4 to 20%. The vast majority of the erupted magmas in Martinique were not affected by hornblende or garnet fractionation and their La/Sm ratios are basically unchanged by crystal fractionation.

Crustal assimilation

Several researchers have proposed that crustal assimilation is a key process in the formation of Martinique lavas (Davidson, 1986, 1987; Davidson & Harmon, 1989; Thirlwall *et al.*, 1996; Van Soest *et al.*, 2002). These workers

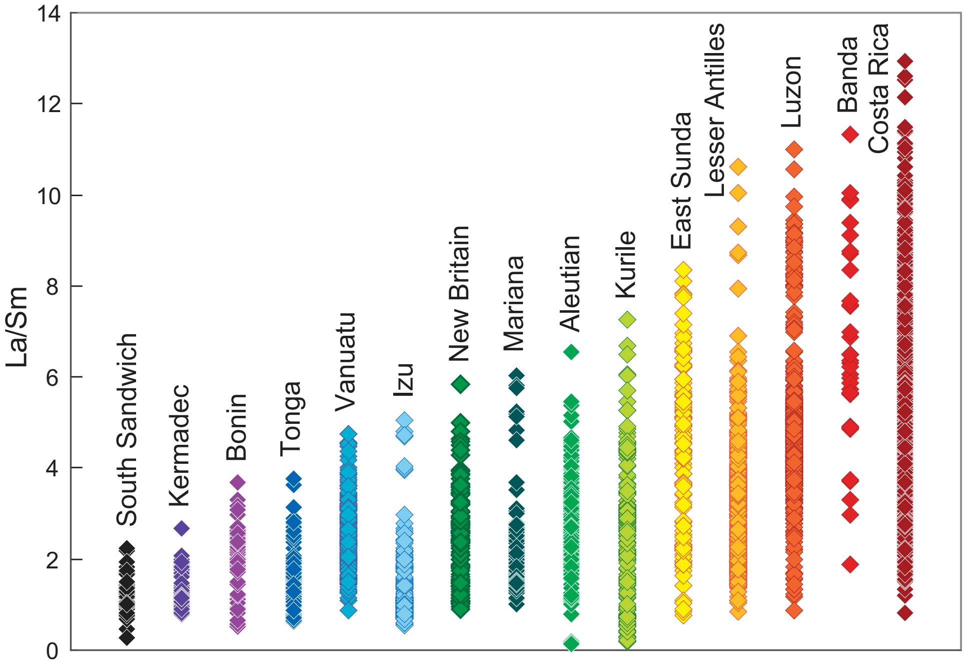

Fig. 7. Range defined by the La/Sm ratio of intra-oceanic arc lavas (South Sandwich, Kermadec, Bonin, Tonga, Vanuatu, Izu, New Britain, Mariana, Aleutian, Kurile, the easternmost islands of Sunda, Lesser Antilles, Luzon, Banda and Costa Rica). Data compilation from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

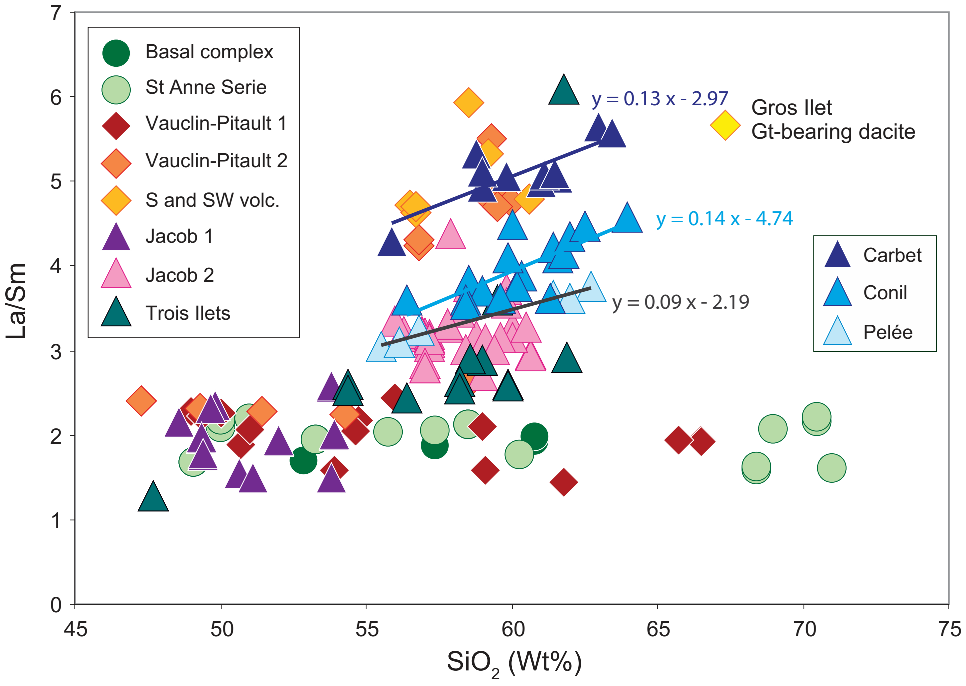

Fig. 8. La/Sm vs SiO$_2$ content for all volcanic phases in Martinique as defined by Westercamp *et al*. (1989). Symbols for each volcanic phase are as in Fig. 2.

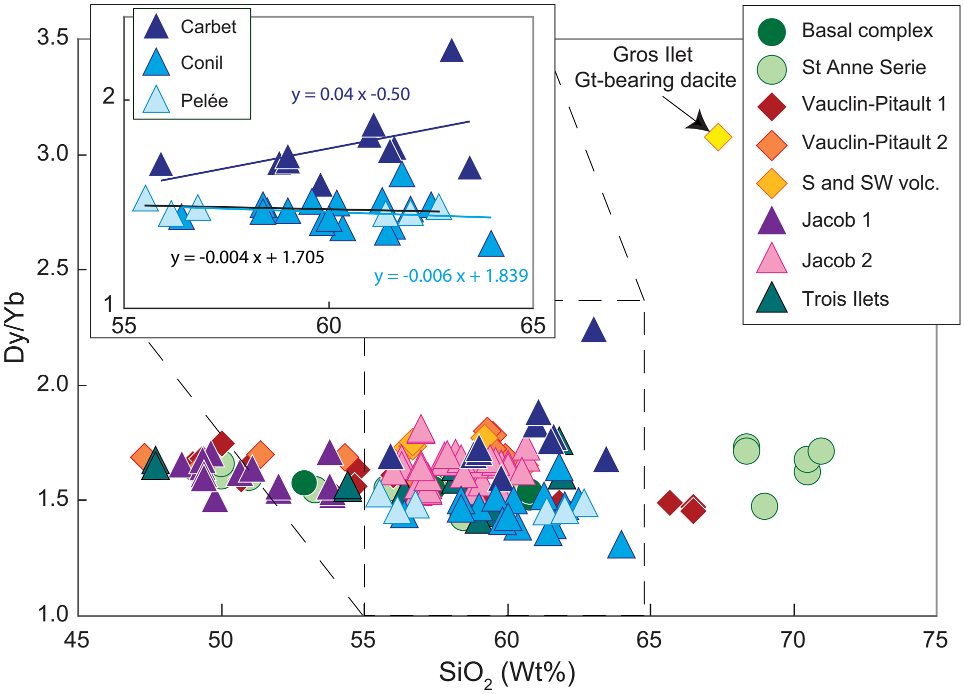

Fig. 9. Dy/Yb vs SiO$_2$ content for all volcanic phases on Martinique as defined by Westercamp *et al.* (1989). Symbols for each volcanic phase are as in Fig. 2.

argued that the high δ^{18}O reported for some lavas and the existence of correlations between radiogenic isotopic ratios and silica contents were proofs of significant impact of contamination by the underlying crust. Such a process could modify the REE patterns of the erupted magmas and this is why we need here to evaluate its possible impact.

The δ^{18}O data published in the 1980s and acquired on whole-rock samples (Davidson, 1985; Davidson & Harmon, 1989) defined a large range and reached values as high as 14·0, leading Davidson & Harmon (1989) to suggest that assimilation of crustal material during differentiation was the most likely interpretation. However, recently, Davidson & Wilson (2011) reported δ^{18}O data for plagioclase, clinopyroxene and orthopyroxene phenocrysts and showed that they define a much smaller range from 5·17 to 6·15, values that are indistinguishable from normal mantle values; the researchers concluded that the measurements on whole-rocks were not representative of the original magmas and were affected by secondary processes, as has been demonstrated previously by other authors for other locations (e.g. Eiler *et al.*, 2000).

The possibility that the large range of radiogenic isotopic ratios could be due to crustal assimilation by the ascending magmas has been discussed in detail by Labanieh *et al.* (2010). Here we briefly summarize the main points. Figure 11, modified from Labanieh *et al.* (2010), shows that the data define two distinct trends, one for the old and intermediate arc lavas and one for the recent lavas. Both trends can easily be reproduced by addition to the mantle wedge of sediments comparable with those present in front of the trench (Carpentier *et al.*, 2009). In contrast, crustal contamination models do not reproduce the observed trends. The modeled AFC curves always fall below the data, no matter which enriched end-member is selected [GLOSS; Plank & Langmuir, 1998); the average compositions of the sediments sampled in front of the arc at Site 144, Site 543 and Barbados (Carpentier *et al.*, 2008, 2009) or end-members determined using the best-fit trends through the lavas (Labanieh *et al.*, 2010)]. We are therefore confident that if crustal assimilation has occurred, it is not the process responsible for the large range of isotopic compositions. It could, however, be argued that crustal assimilation explains the observed correlation between La/Sm and silica content for the Carbet, Conil and Pelee volcanic phases as shown in Fig. 8. In Fig. 12 we show that no correlation exists between ^{143}Nd/^{144}Nd and SiO$_2$ for the Carbet and Pelée lavas and that the five samples from Conil might show a small decrease of ^{143}Nd/^{144}Nd with a SiO$_2$ increase from 57·5 to 60 wt %. If we extrapolate the Conil array to SiO$_2$ ≈51 wt %, we obtain a value of ^{143}Nd/^{144}Nd of 0·51305, which is much higher than the most depleted lava from Martinique. We believe that the trend defined by the Conil lavas in Fig. 12 is probably not significant because the range of SiO$_2$ is too small and the number of data

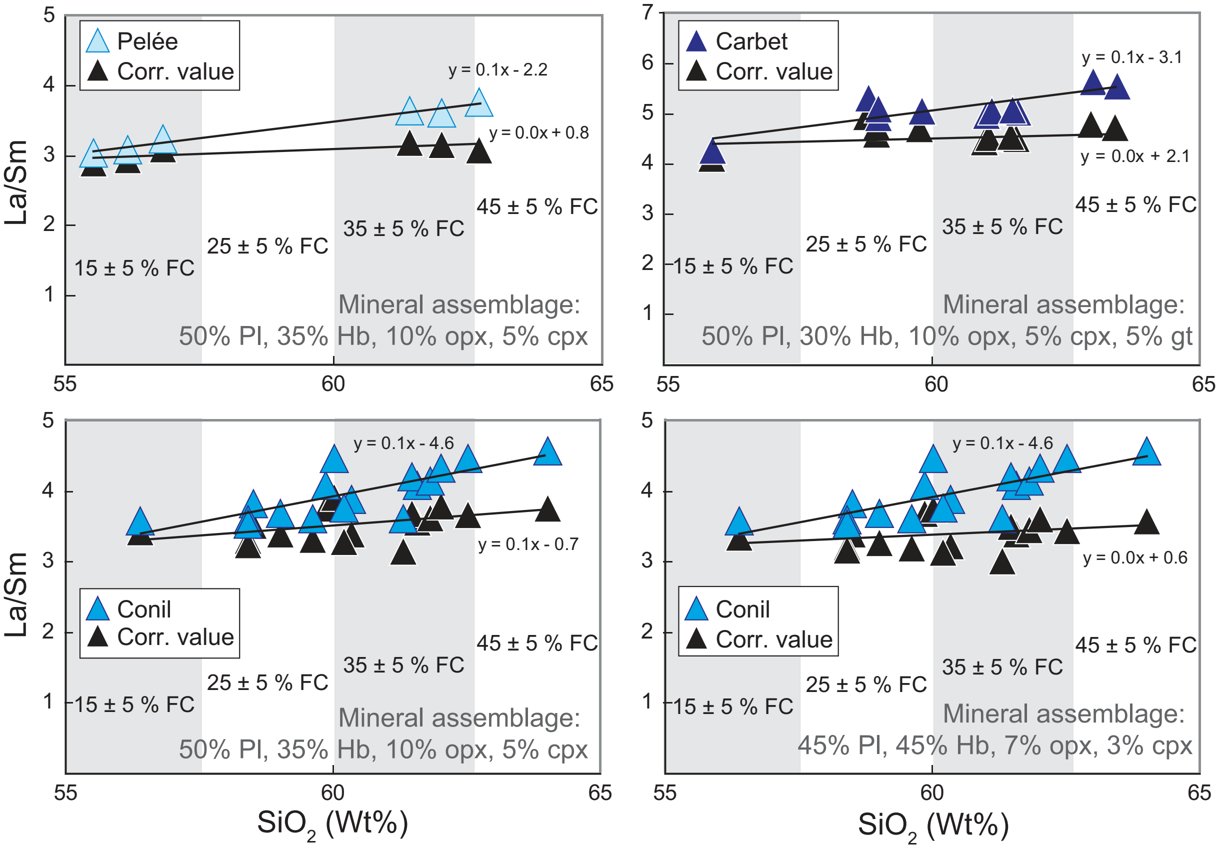

Fig. 10. La/Sm vs SiO_2 diagrams for Pelée, Carbet and Conil volcanic phases. Measured values are presented as triangles in shades of grey. The effect of fractional crystallization of a mineral assemblage containing amphibole ± garnet is calculated (see text for details) and the measured La/Sm ratios are corrected for the effect of 15%, 25%, 35% or 45% fractionation depending on the silica content of the lavas sampled in the Carbet, Conil, and Pelée volcanic phases (black triangles). Errors on the correction (±5% fractionation) are smaller than the black triangles. Even though the SiO_2 content of each lava should decrease when fractional crystallization is corrected for, we chose to keep the value measured in the lava itself so that the existence of a potential residual correlation can be seen in the figure.

points too limited. Overall, for Carbet, Conil and Pelée, it is unlikely that assimilation of crustal material has a significant impact on the REE content of the most evolved lavas and we believe that the correlated increases of La/Sm and SiO_2 seen in the Carbet, Conil and Pelée volcanic rocks are mainly controlled by fractionation of mineral assemblages containing hornblende (and garnet) as suggested and corrected for in the previous section (Fig. 10). Although the REE are not sequestered into the magma during fractionation and the large range of radiogenic isotopic compositions cannot be due to assimilation processes, this does not preclude the possibility that some assimilation of selected elements occurs. The Pelée and Carbet lavas define positive correlations when Pb isotopes are plotted as a function of silica content; this shows that some assimilation was associated with fractionation, but, as noted above, the assimilation process did not affect the REE or the high field strength elements (HFSE) as suggested by the absence of a correlation between $^{176}Hf/^{177}Hf$ and SiO_2 (not shown). Finally, as mentioned above, the garnet-bearing dacite from Gros Ilet has an extreme isotopic composition and a peculiar mineral assemblage. This exceptional lava might very well have been affected by contamination during fractionation; it needs to be considered with care as we do not know if or to what extent its composition needs to be corrected for assimilation.

Effect of partial melting conditions

Partial melting of mantle peridotite is known to generally enrich the LREE relative to the MREE and HREE in the resulting magma. Two main factors contribute to an increase in the La/Sm ratio: (1) low degrees of partial melting produce melts with higher La/Sm ratios than high-degree melting; (2) melting in the garnet stability field produces melts with higher LREE/HREE ratios than when melts are produced in the spinel (or plagioclase) stability field (Langmuir *et al.*, 1977). In the Lesser Antilles, the stable aluminous phase in the mantle source has been shown to

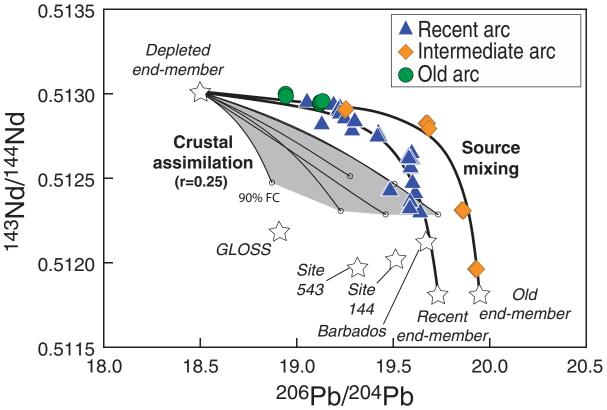

Fig. 11. ^{143}Nd/^{144}Nd vs ^{206}Pb/^{204}Pb diagram showing crustal assimilation (grey field) and source mixing (bold black curves) models. Distribution coefficients for AFC modeling are $D_{Pb} = 0{\cdot}61$ and $D_{Nd} = 0{\cdot}22$, and the ratio between assimilation rate and crystallization rate, *r*, is 0·25. Details of these models have been given by Labanieh *et al.* (2010).

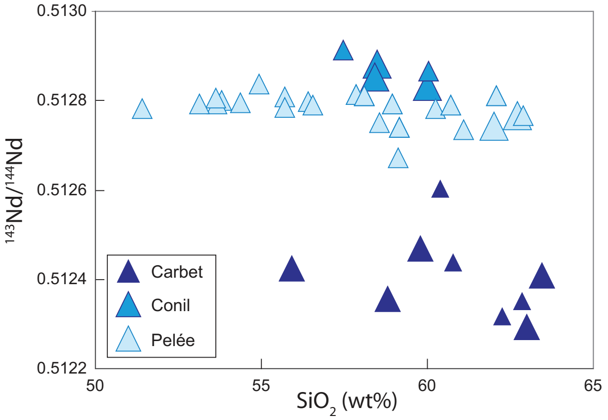

Fig. 12. ^{143}Nd/^{144}Nd vs SiO_2 diagram for the Carbet, Conil and Pelée lavas. Data are from Davidson (1986), Turner *et al.* (1996), Davidson & Wilson (2011) (small triangles) and the present study (large triangles).

be spinel (Pichavant *et al.*, 2002; Parkinson *et al.*, 2003; Pichavant & Macdonald, 2003; Smith *et al.*, 2008) and the melting degree has been estimated at 14–18% by Pichavant *et al.* (2002) and 10–20% by Bouvier *et al.* (2008). Such values are consistent with estimates by Plank & Langmuir (1988), Pearce & Parkinson (1993) and Hirose & Kawamoto (1995), who suggested 10–30% for all subduction-related magmas and who specified that volcanic arcs overlying thick lithosphere (as is the case for the Lesser Antilles arc) had lower partial melting degrees than arcs overlying thin lithosphere. Assuming melting of spinel peridotite and that the primary melts were produced by 10–20% melting, we calculate that the La/Sm enrichment factor between the solid source and the primary melt ranges from 1·10 to 1·43, with an average of 1·21 (see Fig. 13). These calculations were performed using the non-modal equilibrium melting equation of Shaw (1970). The mineral proportions in the solid source (a spinel-bearing peridotite) and those contributing to the melt, as well as partition coefficients, are given in Supplementary Data file 4.

Effect of sediment addition to the magma source

After removal of the effects of both fractional crystallization and partial melting on the La/Sm ratio of the magma, a large range still persists. In Fig. 13 we show that the magma sources still scatter between unity and about 3·9. Figure 13 also shows that the observed change in La/Sm ratio is clearly correlated with a change in Nd isotopic composition, suggesting that a component with elevated La/Sm and low ^{143}Nd/^{144}Nd contributes to varying degrees to the source of the magmas.

What we observe in Martinique is obviously not unique; a similar correlation was reported by Smith *et al.* (2008) for lavas from Bequia (one of the islands in the Grenadines archipelago; Fig. 1). This seems to be a general feature of the Lesser Antilles arc system (see Fig. 6 where both ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf vary with La/Sm). The only exception to this general rule is Grenada, where high and variable La/Sm ratios occur at elevated ^{143}Nd/^{144}Nd (Fig. 6). Indeed, the Grenada lavas appear to be an exception in many ways: the lavas are unusually mafic, alkali basalts erupted in several volcanic centers (Arculus, 1976), differentiation trends are unusual (Cawthorn *et al.*, 1973) and two very different types of basalt occur concurrently (C- and M-series lavas; Thirlwall and Graham, 1984, Thirlwall *et al.*, 1996). Finally, Shimizu & Arculus (1975) suggested that the variability in LREE at rather constant HREE could be attributed to small degrees of partial melting of a garnet-bearing lherzolite. These melting conditions could very well explain the significant difference between the lavas from Grenada and those from the other Lesser Antilles islands.

The very low ^{143}Nd/^{144}Nd reported for a number of Martinique lavas is typical of continental crust and given the tectonic context of the Lesser Antilles arc these values can be reasonably explained by the involvement of sedimentary material eroded from the neighbouring South American craton (Carpentier *et al.*, 2008, 2009). In Fig. 13, we report the data published by Carpentier *et al.* (2008, 2009) for sediments from Sites 144 and 543 as well as for the carbonate-free sediments from Site 144 (average for each unit; grey diamonds) because their compositions are consistent with the enriched end-member required by the mixing hyperbolas defined in Sr–Nd–Pb isotope space for the Martinique lavas [see Labanieh *et al.* (2010) for details]. These data define a broad field at low ^{143}Nd/^{144}Nd with a weighted average for the entire sedimentary column of

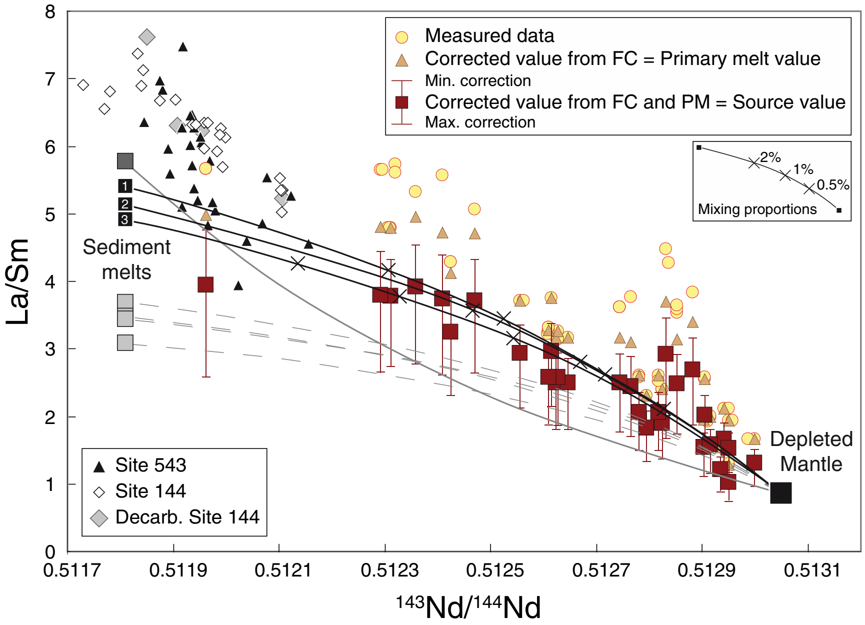

Fig. 13. Measured and calculated La/Sm ratios of Martinique lavas as a function of Nd isotope composition (Labanieh *et al.*, 2010). Circles represent measured data, triangles represent the La/Sm ratios after correction for fractional crystallization and squares represent values after correction for both fractional crystallization (FC) and partial melting (PM). Error bars include uncertainties on the degree of fractional crystallization and partial melting. Local sediments are represented as diamonds [Site 144 sediments: white diamonds, measured values; grey diamonds, carbonate-free values, calculated by virtually removing the carbonate for each unit; see Carpentier *et al.* (2009) for details] and black triangles (Site 543 sediments) (Carpentier *et al.*, 2008, 2009). The hyperbolas are the modeled mixing trends between a depleted mantle end-member (large black square) and various possible sediment end-members: bulk local sediments (dark grey square) or melts suggested by Hermann & Rubatto (2009) (black squares and light grey squares). The three sediment melts represented as black squares and labelled 1, 2 and 3 lead to mixing hyperbolas (black curves) that fit very well the trend defined by data corrected for fractional crystallization and partial melting. They correspond respectively to experiments at 4·5 GPa and 900°C, at 3·5 GPa and 900°C and at 4·5 GPa and 1050°C (Hermann & Rubatto, 2009). Black crosses correspond to mixing proportions: 0·5%, 1% and 2 % of sediment melts added to the mantle wedge.

La/Sm = 5·78. The continuous grey curve in Fig. 13 represents a mixing line between bulk Site 144 sediments and the mantle wedge [using the depleted mantle value of Salters & Stracke (2004)]. The curve does not go through the data and it always lies below the values representative of the mantle sources (squares in Fig. 13). In addition, the mixing array is concave whereas the calculated sources define a slightly convex trend. Mixing between bulk Site 144 sediments and the mantle wedge does not seem to reproduce well the array defined by the data.

In our previous study (Labanieh *et al.*, 2010), we demonstrated that no significant decoupling between Pb, Sr, Nd and Hf occurred in the subducted sedimentary material and we suggested that sediments comparable with those sampled at Site 144 could be incorporated in the magma sources through melting of the sedimentary cover on the subducted lithosphere. Such an interpretation was also proposed by Turner *et al.* (1996) and Hawkesworth *et al.* (1997). In Fig. 13 we show mixing lines between the mantle wedge [taken as the depleted mantle of Salters and Stracke (2004)] and the various compositions suggested by Hermann & Rubatto (2009) for hydrous melts of subducted sediment. For the sediment melts of Hermann & Rubatto (2009), we chose a Nd isotopic composition of 0·51181, a value selected by Labanieh *et al.* (2010) to fit the mixing curves in radiogenic isotope diagrams. All the mixing lines define convex curves and three of them (black curves) fit very well the inferred Martinique magma sources. Addition of sediment melt to the mantle wedge appears therefore to be a very plausible explanation for the correlated La/Sm and Nd isotopic ratios in the Martinique magma sources. The exact proportions of sediment melt added to the mantle wedge to explain the Martinique magma sources depend on the chosen composition of the hydrous melt, which varies with pressure, temperature and amount of water added in the experiments [see Hermann & Rubatto (2009)]. However, addition of about 2% sediment melt to the mantle wedge increases the La/Sm ratio from 0·87, the chosen mantle wedge value, to ~4; that is, the highest calculated value for the mantle source under Martinique. This calculated sediment melt contribution is consistent with our previous estimates based on the Nd, Hf, Pb and Sr isotopic systems alone (Labanieh *et al.*, 2010).

In summary, we show that fractional crystallization and partial melting modify the La/Sm ratios of Lesser Antilles lavas but that the key factor controlling these values is the amount of subducted sediment in the source. Whereas fractional crystallization and partial melting can increase the La/Sm ratio by up to 70%, depending on the nature of the residual phases and degree of partial melting, addition of a sedimentary component to the source can change the La/Sm ratio by a factor of about five, a change that is correlated with changes in both ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf. We are therefore confident that La/Sm can be considered as a good proxy for the amount of subducted sediment incorporated into the source of arc magma.

SEDIMENT MELTING VERSUS SLAB DEHYDRATION

Although the changes in La/Sm ratio seen in the lavas can be attributed to melting of subducted sediments, these do not preclude the possibility that dehydration of the subducted slab also occurs. As previously suggested by a number of workers, dehydration of the slab translates into elevated Ba/Th, U/Th or Sr/Th ratios in the lavas because Ba, U and Sr are preferentially incorporated into aqueous fluid phases (Condomines *et al.*, 1988; McDermott & Hawkesworth, 1991; Gill & Condomines, 1992; Hawkesworth *et al.*, 1997; Johnson & Plank, 1999) whereas Th is transferred efficiently from the slab only when sediment melts are involved (Hawkesworth *et al.*, 1997; Johnson & Plank, 1999; Plank, 2005).

Mapping of dehydration and melting processes

Turner *et al.* (1996) suggested that both slab dehydration and sediment melting processes occur in the Lesser Antilles arc, with an along-arc change from slab dehydration under the northern islands (high Ba and K relative to Th) towards sediment melting under the southern islands (high Ta/Zr and Sr isotopic ratios). Following the same logic, we show in Fig. 14 how Ba/Th and Sr/Th evolve relative to ^{143}Nd/^{144}Nd and ^{87}Sr/^{86}Sr in Martinique and more generally in the Lesser Antilles arc. Our new data for Martinique demonstrate that, in the same island, samples with high Ba/Th, Sr/Th, ^{143}Nd/^{144}Nd and low ^{87}Sr/^{86}Sr coexist with samples with low Ba/Th, Sr/Th, ^{143}Nd/^{144}Nd and high ^{87}Sr/^{86}Sr (Fig. 14). This strongly suggests that both melting of sediments and dehydration of a material with a radiogenic Nd isotopic composition occur under Martinique.

On the three maps shown in Fig. 15 we report, using a color scale, the ratios of La/Sm, Ba/Th and U/Th for all the Martinique samples. The geographical variations of the three ratios are obviously not randomly distributed. Samples located on the eastern side of the island have low La/Sm and high Ba/Th and U/Th ratios, whereas samples located on the western side of the island have high La/Sm associated with low Ba/Th and U/Th. In addition, all samples with elevated La/Sm are located in a narrow band less than 20 km wide. It is worth noting that this spatial gradient is not related to age, as the low La/Sm lavas on the eastern side of the island include volcanic rocks ranging in age from 25 to 4 Ma, whereas the high La/Sm lavas on the western side have ages ranging from 11 Ma to the present (see Fig. 2). As demonstrated in the previous section, changes in La/Sm reflect changes in the proportion of subducted sediment in the source; we can therefore conclude not only that more sediment is involved in the source of lavas on the western side of the island than on the eastern side, but also that they melt. In contrast, fluids produced by the dehydration of a slab component with low ^{87}Sr/^{86}Sr mainly control the transfer of material under the eastern side of the island.

Across-arc zoning in geochemical characteristics has been described in other arcs but always at the scale of an entire arc and back-arc system. Pearce *et al.* (2005) demonstrated for the Mariana arc system that the ‘shallow subduction component’ (i.e. aqueous fluids) is mostly present beneath the volcanic arc whereas the ‘deep subduction component’ (i.e. sediment melts) influences to different degrees both the back-arc basin and the arc. Hoogewerff *et al.* (1997) also showed that volcanoes of the eastern part of the Sunda arc define an across-arc zoning pattern, with LILE enrichment owing to aqueous fluids in the magmas erupted near the trench, whereas magmas erupted further away from the trench are influenced by siliceous melts. What we demonstrate here is that, at the scale of a single island and within less than 20 km, aqueous fluids control the geochemical signature of the magmas nearer the trench, whereas siliceous melts are dominant in the source of the magas further away from the trench.

Origin of the aqueous fluids and implications of the chemical zoning

One important question remains concerning the origin of the aqueous fluids: are they released by dehydration of the subducted sediments or by dehydration of the subducted basaltic oceanic crust? Turner *et al.* (1996), Hawkesworth *et al.* (1997) and Turner & Foden (2001) used plots of ^{87}Sr/^{86}Sr versus ratios such as Ba/Th to show that the Sr added to the source of the northern Lesser Antilles arc magmas by aqueous fluids has an unradiogenic composition of about 0·7035–0·704, a value that indicates that the fluids could be derived from partially altered oceanic crust or that they exchanged with depleted material in the mantle wedge (Turner *et al.*, 1996). Figure 14 shows that a similar isotopic composition occurs in lavas with high Ba/Th and Sr/Th from the eastern side of Martinique. Such a Sr isotopic composition does not correspond directly to any of the potential fluid sources: subducted sediments are far more radiogenic [GLOSS: 0·71730 (Plank & Langmuir, 1998); bulk

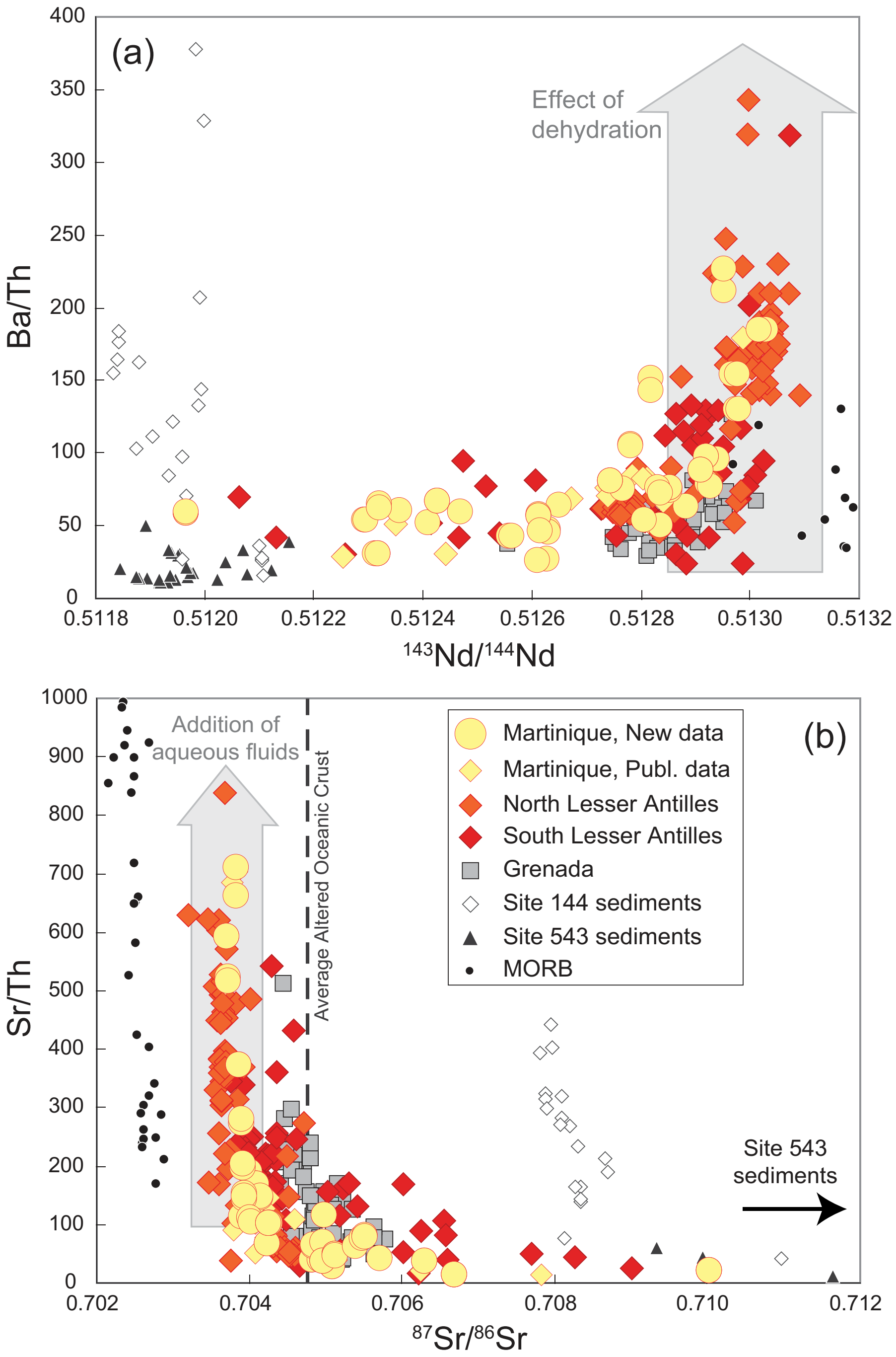

Fig. 14. Ba/Th vs Nd isotope composition (a) and Sr/Th vs Sr isotope composition (b) for Martinique lavas, Grenada (gray squares) and North and South Lesser Antilles island lavas. Published data are from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/). Local sediments are represented as white diamonds (Site 144 sediments) and black triangles (Site 543 sediments) (Carpentier *et al.*, 2008, 2009). It is important to note that the Site 144 sediments shown here correspond to measured values and not to the 'decarbonated sediment' because the Ba content in carbonates is so high that a 'decarbonated sediment' Ba content cannot be calculated. As a consequence, the range in Ba/Th displayed by these sediments in (a) is much larger than the probable range covered by the sediments that are effectively subducted and incorporated within the source of the Lesser Antilles arc magmas. Fresh Atlantic MORB between 30°N and 30°S are represented as black dots, and the dashed line in (b) represents the average altered oceanic crust value suggested by Staudigel *et al.* (1995). Most Site 543 sediments are off-scale in (b).

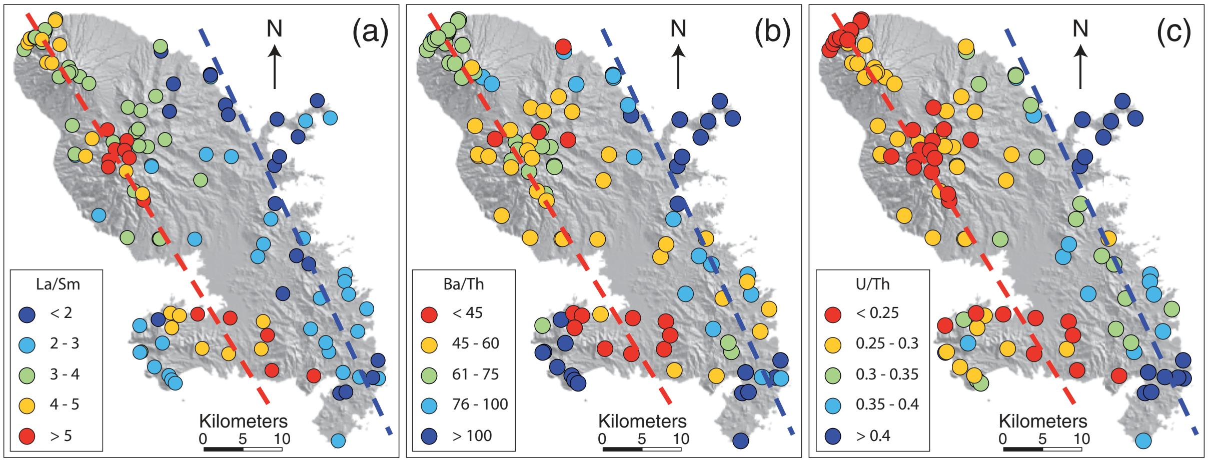

Fig. 15. Maps of Martinique showing the La/Sm, Ba/Th and U/Th zoning. The circles represent the location of the samples and the color of the circles refers to the value of La/Sm (a), Ba/Th (b) and U/Th (c). The blue dashed line represents the axis where La/Sm is uniformly low; the red dashed line represents the axis where La/Sm is variable and reaches high values.

Site 144 sediments: 0·708509; bulk Site 543 sediments: 0·715852 (Carpentier *et al.*, 2009)] and subducted oceanic crust is either less radiogenic [fresh Atlantic oceanic crust has $^{87}Sr/^{86}Sr < 0·703$) or more radiogenic ($^{87}Sr/^{86}Sr = 0·70475$ for average altered oceanic crust (Staudigel *et al.*, 1995)] (Fig. 14). Whether the fluids originate from a mixture of unaltered and altered portions of the subducted basaltic crust or from interactions between the subducting basaltic crust and the mantle wedge, the important observation is that subducted sediments cannot be the source of these fluids. In addition, fluids from the basaltic crust cannot have significantly interacted with its sedimentary cover because the effect on the Sr isotopic composition would be substantial. This is puzzling because the chemical zoning defined by the Martinique lavas indicates that the sediment melt signature shows up in lavas on the western side of the island, in a location further away from the trench compared with the lavas with the aqueous fluid signal. The geographical gradient shown in Fig. 15 indicates that sediments are indeed present on the top of the subducted basaltic crust when the latter dehydrates but they do not interact with the rising fluid (Fig. 16). This is even more puzzling because sediments such as those present in front of the trench (Carpentier *et al.*, 2008, 2009) are rich in water and should be a fertile source of aqueous fluids.

The nature of fluid processes in subduction zones proposed by Peacock (1990) can help answer these questions, as he suggested that most fluids present in the sediment pile are released beneath the accretionary prism through compaction of the sediments (expulsion of pore fluids) and low-grade metamorphic devolatilization reactions such as clay minerals breakdown or transformation of opal-A into quartz (Peacock, 1990) (Fig. 16). The primary source of H_2O at magma genesis depths would thus be the breakdown of hydrous minerals contained in the basaltic, gabbroic, and ultramafic layers of the oceanic crust (Peacock, 1990). Moreover, fluids migrating upward could travel along shear zones where interactions between aqueous fluids and sediments are limited (Fig. 16).

Slab geometry and dehydration versus melting

The most obvious explanation for the geographical zoning described above is that the depth of the subducted slab is the controlling factor. Only when the slab reaches sufficiently high pressure and temperature conditions can the sediments melt. Syracuse & Abers (2006) estimated that the depth of the subducted slab under Mont Pelée is 137 km, a value that translates into a pressure of about 4·5 GPa and a temperature of about 780°C if we use the D80 model $P-T$ path suggested by Syracuse *et al.* (2010) for the Lesser Antilles arc. Such a value is also consistent with the temperature suggested by Cooper *et al.* (2012) for the southern Lesser Antilles arc using constraints provided by H_2O/Ce ratios (Plank *et al.*, 2009). We can compare these estimated $P-T$ conditions with the experimental data of Hermann & Spandler (2008), who tracked how elements are released from subducted sediments under arcs. Those workers showed in their figure 9 that a major transition occurs at the $P-T$ conditions that prevail under Martinique, 4·5 GPa and 780°C; at lower temperatures transfer by aqueous fluids dominates, whereas hydrous melts prevail above this transition. In addition, they demonstrated that the aqueous fluid has low LILE

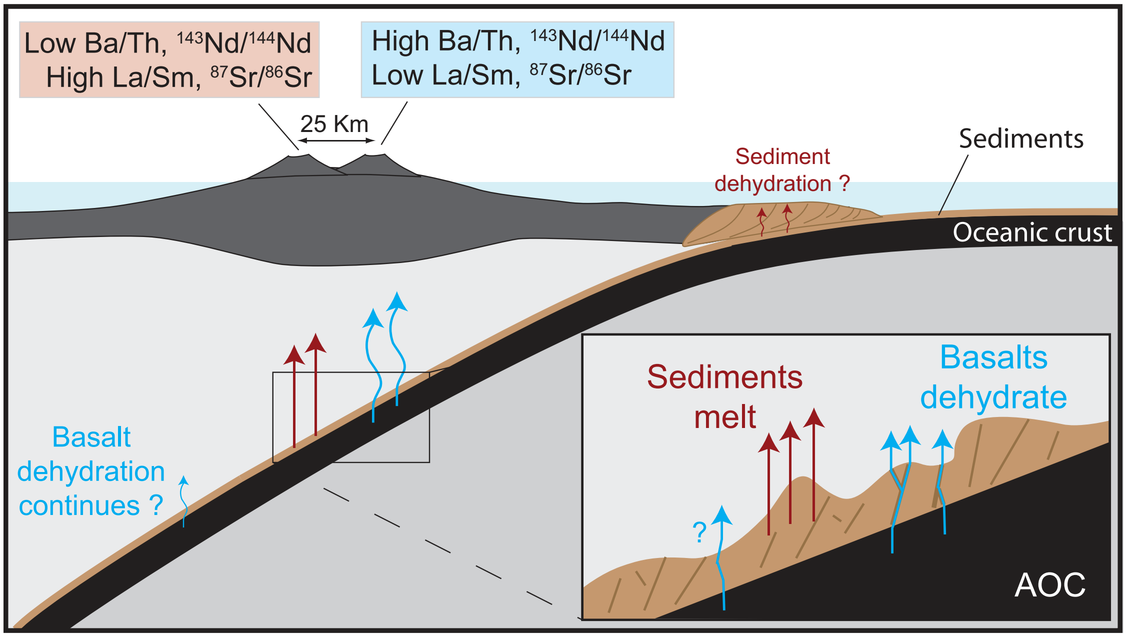

Fig. 16. Sketch representing the melting and dehydration processes that occur under Martinique. AOC stands for Altered Oceanic Crust. Dehydration of the basaltic crust occurs before melting of slab sediments. Fluids released do not interact with the sediments and probably rise along fractures. Sediment melts ascend through the mantle wedge without significant horizontal deviation.

contents, whereas the hydrous melts are rich in those elements. This is entirely consistent with the geographical gradient that we highlight in Fig. 15. We conclude therefore that in Martinique we observe a very rare case where the transition from aqueous fluid transport to hydrous melt transport is observed at the surface in volcanic products within a distance of less than 20 km and has remained unchanged over a period of about 25 Myr. In addition, the consistency between lava composition at the surface and P–T conditions at the slab surface suggests that melts ascend through the mantle wedge with no significant horizontal deviation. The predominance of vertical transport was recently suggested by Cooper *et al.* (2012) and our results provide an extra observation to support this suggestion.

The relationship between the P–T conditions of the slab and the surface expression of sediment melting can also explain the north–south chemical changes along the Lesser Antilles arc. According to Syracuse & Abers (2006) and Syracuse *et al.* (2010), the top of the slab is at about 122 km depth under the northern part of Lesser Antilles arc, whereas it is at about 141 km under the southern part of the arc (Table 1). Because the P–T paths are very similar in the northern and southern parts of the arc [D80 model described by Syracuse *et al.* (2010)], the slab under the northern Lesser Antilles islands may be a little too shallow to produce sediment melts whereas it is at the right depth under the southern part of the Lesser Antilles arc.

What about other island arcs?

In Fig. 17, we show that the negative correlation between La/Sm and Nd isotopic composition highlighted for the Lesser Antilles arc is also observed for other intra-oceanic arcs. Costa Rica, East Sunda and Luzon lavas have high La/Sm ratios (up to 10) at unradiogenic Nd isotopic compositions and the same negative correlation exists in arcs with lower La/Sm ratios and more radiogenic Nd isotopic compositions. For example, this is the case for Bonin and New Britain lavas (Fig. 17). The data suggest that for all these arcs the impact of sediment melting on the La/Sm ratio overwhelms other processes. However, some exceptions exist; for example, the lavas from the Aleutian, Vanuatu and Kermadec arcs, for which there is no correlation between La/Sm and Nd isotopic composition (not shown).

Figure 18 shows a compilation of data for a large number of intra-oceanic arc lavas plotted in Ba/Th vs La/Sm diagrams. East Sunda, Luzon and Banda volcanic arc lavas have variable La/Sm, reaching high values, but uniformly low Ba/Th ratios, a relationship typical of sediment melting. Conversely, Izu–Bonin–Mariana, Tonga–Kermadec and South Sandwich lavas reach high Ba/Th ratios but their La/Sm ratios are low, features consistent with slab dehydration. Finally, a few volcanic arcs (Costa Rica, Kurile, Aleutian, New Britain, Vanuatu and the Lesser Antilles) have lavas with high La/Sm and lavas with high Ba/Th but no lavas have both high La/Sm and high Ba/Th ratios. In these arcs, both slab dehydration and

Table 1: Comparison between P–T conditions under volcanic arcs and the sediment solidus

Arc	Slab surface			*T* of the solidus at *P* of slab surface (°C)	Can sediments melt?	Are there high La/Sm lavas?
	Depth (km)	*P* (GPa)	*T* (°C)			
Basalt dehydration related arcs						
Northern Lesser Antilles	122	4·0	740	750	NO	NO
Izu	134	4·2	720	760	NO	NO
Bonin	164	5·1	760	820	NO	NO
North Mariana	185	6·0	850	850	YES	NO
South Mariana	169	5·5	780	840	NO	NO
Tonga	123	4·0	700	750	NO	NO
Kermadec	171	5·5	770	840	NO	NO
South Sandwich	118	3·7	840	730	YES	NO
Sediment melting related arcs						
Southern Lesser Antilles	141	4·6	800	780	YES	YES
West Banda	126	4·0	750	750	YES	YES
East Banda	159	5·1	840	820	YES	YES
East Sunda	118*	3·7	730	730	YES	YES
Luzon	142	4·6	820	780	YES	YES

*Depth of East Sunda is an average of depths measured by Syracuse & Abers (2006) for the three easternmost islands of the section called Bali–Lombok.

The depth of the slab under each arc as well as the pressure and temperature conditions at these depths are from Syracuse *et al*. (2010). The temperature at which the sediments should melt at the corresponding pressure is from the sediment solidus determined by Hermann & Spandler (2008). The column 'Can sediments melt?' relates the actual temperature of the slab under the volcanic arc and the temperature at which sediments should melt. Concordance between the possibility for sediments to melt and the occurrence of high La/Sm lavas implies that *P*–*T* conditions at the slab surface can be related to surface observations.

sediment melting probably occur. This has already been pointed out by Class *et al.* (2000) for the Aleutian arc and is consistent with what Woodhead *et al.* (2001) described as 'sediments or sediment melts' versus 'slab-derived fluids' arcs using a Th/Yb vs Ba/La plot.

Following the same reasoning as for the Lesser Antilles arc, we can compare the *P*–*T* conditions under each of the two 'extreme' groups of arcs shown in Fig. 18 with the sediment solidus provided by Hermann & Spandler (2008) and determine if sediments present under the arc can potentially melt (see Table 1). As for Martinique and the Lesser Antilles, we use the D80 thermal model from Syracuse *et al.* (2010) because it is consistent with the temperatures determined by Cooper *et al.* (2012). The depth of the subducted slabs under the volcanic arcs are also from Syracuse *et al.* (2010) and the sediment solidus is that of Hermann & Spandler (2008). Theoretically, slab surfaces under volcanic arcs that show basalt dehydration effects (high Ba/Th and low La/Sm) should have a temperature too low for sediments to melt in significant proportions. This is the case for the Izu–Bonin, South Marianas, Tonga and Kermadec arcs (see Table 1). For example, the slab under the Izu arc is 134 km deep (Syracuse *et al.*, 2010), a depth corresponding to 4·2 GPa and 720°C according to the *P*–*T* path suggested by Syracuse *et al.* (2010) for this arc. At 4·2 GPa, sediments melt at a temperature of 760°C (Hermann & Spandler, 2008). Thus, under the Izu arc, the sediments are not at the right conditions to melt. This is also the case for other dehydration-related arcs but it does not apply to the Northern Mariana and South Sandwich arcs. The slab surface under the Northern Mariana arc is at a temperature at which sediments should melt and, indeed, Elliott *et al.* (1997) suggested that some sediment might melt, although most of the transfer from the slab to the mantle wedge occurs through aqueous fluids (Woodhead, 1989). The slab under the South Sandwich arc reaches high temperatures at low pressure [800°C at 3 GPa; see Syracuse *et al.* (2010)] and the sediment solidus is crossed before the slab reaches the level of the arc. Thus, under the South Sandwich arc, sediments may have already melted.

Under volcanic arcs with high La/Sm and low Ba/Th ratios, the slab surface should be hot enough for any

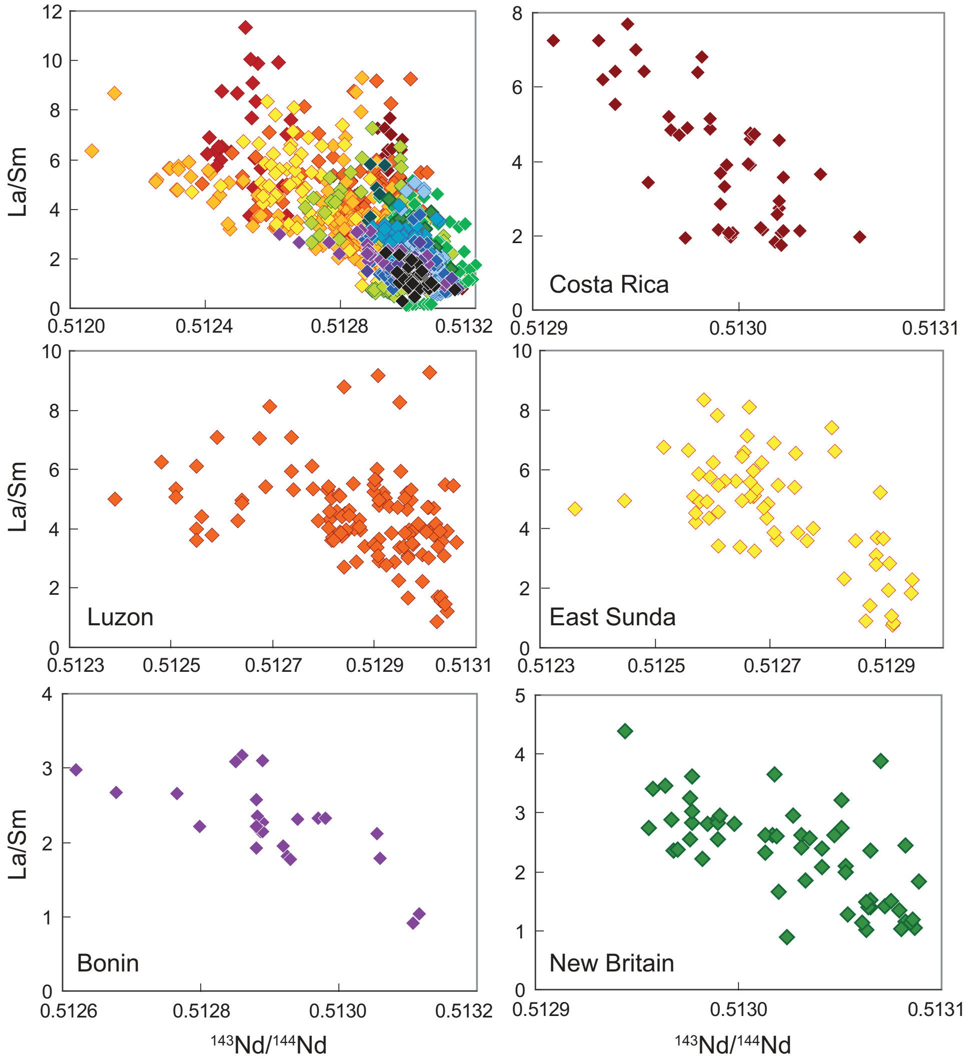

Fig. 17. La/Sm ratio as a function of Nd isotope composition for all intra-oceanic arcs (top left panel) and a selection of arcs: Costa Rica, Luzon, East Sunda, Bonin and New Britain. Data compilation from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

sediments present to melt. This is the case for all the arcs belonging to the sediment-related arcs group (see Table 1). Overall, the coherence between the *P–T* path of the slab surface, the sediment solidus and the geochemical characteristics of the lavas is extremely good. Thus, we believe that La/Sm and Ba/Th provide accurate information about element transport from the subducted basalt and its surface sediments. The amount of sediment added to the mantle wedge is related to the temperature of the slab, with a threshold determined by the sediment solidus and the capacity of hydrous melts to be formed. The chemical zoning that we observed in the Martinique lavas is probably rare and is due to the fact that the island formed exactly above the place where slab sediments heat up from temperatures lower than their solidus to temperatures higher than their solidus.

CONCLUSIONS

Using new chemical data for lavas from Martinique we quantify the relative role of weathering processes, fractional crystallization, intra-crustal assimilation, partial melting and sediment incorporation in the mantle wedge in influencing the slope of the REE patterns. We show that La/Sm ratios vary over a large range from 1·3 to 6·1. Weathering processes have basically negligible effect on the La/Sm ratio; when amphibole or garnet is involved in the crystallizing assemblage, fractional crystallization can change La/Sm by up to 24%, but for most lavas the effect is negligible; REE are not added from the wall-rocks to the magmas during fractionation processes, and partial melting increases La/Sm by only 21% relative to the ratio of the original source. Finally, we show that most of the

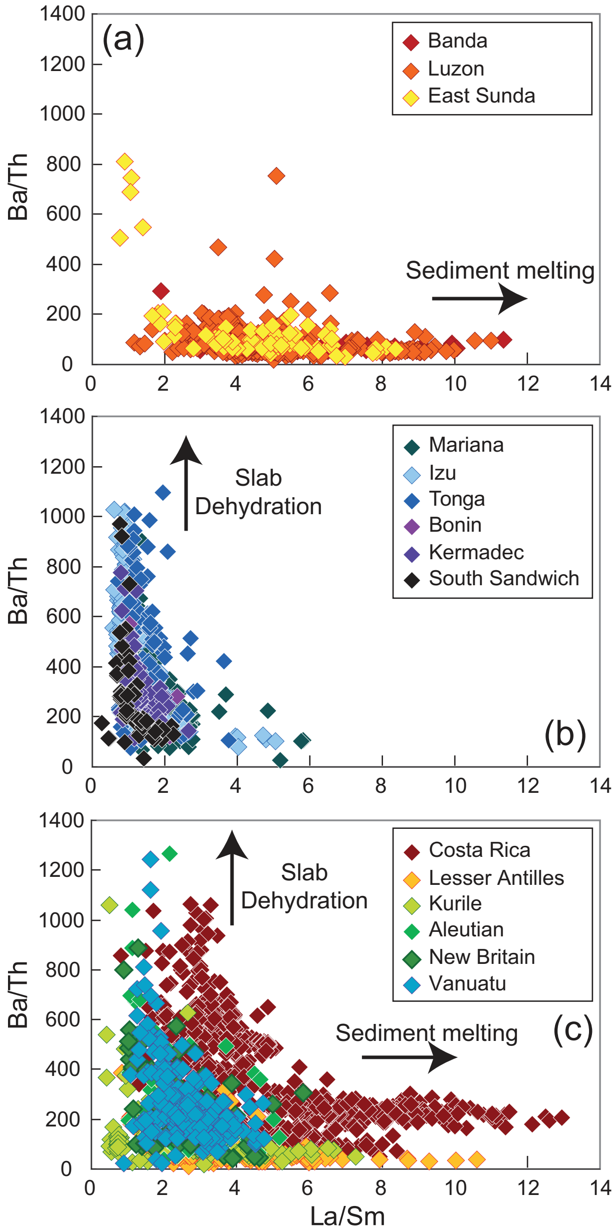

Fig. 18. Ba/Th as a function of La/Sm for all intra-oceanic arcs. (a) Volcanic arcs that mainly experience sediment melting (Banda, Luzon and East Sunda); (b) volcanic arcs that mainly experience slab dehydration (Izu–Bonin–Mariana, Tonga–Kermadec and South Sandwich). (c) Volcanic arcs where both sediment melting and slab dehydration occur (Costa Rica, Lesser Antilles, Kurile, Aleutian, New Britain and Vanuatu). Data compilation from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

range in La/Sm ratios depends on the amount and nature of subducted sediment incorporated into the mantle; the sedimentary component is added through a hydrous melt as opposed to an aqueous fluid. In Martinique, the La/Sm ratio is a proxy of the proportion of sediment involved in the genesis of the lavas.

Slab sediments are incorporated via melting under the western side of Martinique but dehydration processes also occur under the eastern side. Under that part of the island, aqueous fluids come from the basaltic oceanic crust and do not interact with the overlying sediments. We show that the Martinique lavas define a chemical spatial zoning pattern: lavas sampled on the eastern side of the island have systematically low values of La/Sm associated with high values of Ba/Th and U/Th, whereas high La/Sm and low Ba/Th and U/Th characterize lavas on the western side of the island. La/Sm is a proxy for the proportion of sediment incorporated into the mantle wedge, and Ba/Th and U/Th ratios are a proxy for basalt dehydration. The nature of the transfer agent, melting or dehydration, follows a clear geographical pattern. We relate the change in sediment involvement to the pressure and temperature conditions at the surface of the slab and suggest that sediments cross their solidus just under Martinique. This is a very rare case in which the transition from aqueous fluid transport to hydrous melt transport can be seen at the surface.

In the Lesser Antilles, as well as in many other intra-oceanic volcanic arcs, REE patterns represent an excellent proxy for the proportion of slab sediment in the mantle source. Arcs with high La/Sm ratios are defined as 'sediment-dominated' and are all related to slab *P*–*T* conditions that allow sediments to melt. Conversely, for most arcs with low La/Sm and high Ba/Th, and defined as 'fluid-dominated', the pressure and temperature at the slab surface are too low for sediments to melt.

ACKNOWLEDGEMENTS

We are very grateful to students and friends from former offices 349 and 310 for fruitful discussions. Technical help from Sarah Bureau and Christèle Poggi in the chemistry laboratory, and from Philippe Nonotte and Philippe Telouk on the mass spectrometers was greatly appreciated. We thank Gilles Chazot and Stefan Lalonde for their very useful comments on the paper. The paper has greatly benefited from the insightful comments from the reviewers R. Avanzinelli, J. Davidson and T. Plank, and we thank them for their time and constructive suggestions.

FUNDING

This work was financially supported by the Agence Nationale de la Recherche program 'UD Antilles'.

SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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