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Martinique: a clear case for sediment melting and slab dehydration as a function of distance to the trench

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Abstract:

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.

Keywords: Lesser Antilles ; slab dehydration ; sediment melting ; island arcs ; subduction zones

INTRODUCTION

Intra-oceanic arc lavas have chemical and isotopic characteristics that differ significantly from Mid-Ocean Ridge Basalts and Ocean Island Basalts, features 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, chemical 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 and Foden (2001), Elliott (2003) to highlight the role of hydrous fluids in the genesis of lavas 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, Class *et al.*, 2000, Hawkesworth *et al.*, 1997, Marini, 2005, Miller *et al.*, 1994, White & Patchett, 1984, Woodhead, 1989), 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 of slab sediment implication in the genesis of arc lavas. In the latter case, the underlying assumption is that these ratios are representative of source compositions and are not significantly affected by melting or fractional crystallization.

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

In this paper, we demonstrate that the proportion of added sediment controls the REE content of the lavas 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 over Th demonstrate that slab dehydration also occurs under Martinique Island. More specifically, we show the existence of a spatial zoning of La/Sm, Ba/Th and U/Th ratios in 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 Island so that lavas near the trench do not show significant signs of sediment addition to their source while further away from the trench sediments melt and contaminate magma sources.

GEOLOGICAL SETTING

The Lesser Antilles Volcanic Arc (Figure 1) developed in response to subduction of the Atlantic 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 and Sykes (1969) suggest a East – West direction for the North American plate relative to the Caribbean plate while Jordan (1975), Minster and Jordan (1978) and Stein et al. (1988) argue for a ESE - WNW motion of the North American plate and Sykes et al. (1982), McCann and Sykes (1984), Dixon and Mao (1997) and DeMets et al. (2000) propose that the North American plate moves along a ENE - WSW direction.

In the Lesser Antilles, magmatism has occurred since the Late Oligocene (Germa *et al.*, 2011a) and is currently represented by active volcanoes on most islands. In the southern part of the arc, volcanic eruptions 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 (Briden *et al.*, 1979, Nagle *et al.*, 1976). The geographical jump of volcanic activity was attributed by Bouysse and Westercamp (1990) to subduction of an aseismic ridge that momentarily blocked the subduction, stopped volcanic activity for about 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 Island recorded the most complete history of the arc (Coulon *et al.*, 1990, Germa *et al.*, 2011a). On this island, the effect of the aseismic ridge subduction was only a small westward migration of volcanic activity and no significant gap in lava 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, compose the old, intermediate and recent volcanic activity in Martinique Island. Westercamp et al. (1989) mapped and described all these volcanic phases and a simplified geological map based on their work is presented in Figure 2. The old arc outcrops on two peninsulas located on the East and the South of the Island (Figure 2). It consists of two volcanic phases: the Basal Complex (24.2-24.8 Ma) and the St Anne Series (20.8-24.8 Ma) (Germa *et al.*, 2011a, Westercamp *et al.*, 1989). The intermediate arc includes four main volcanic phases: the submarine Vauclin-Pitault phase 1 (16.1-8.5 Ma), the sub-aerial 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) (Figure 2). Finally, the recent arc includes six main phases: the submarine Jacob phase 1 (5.1-4.1 Ma), the sub-aerial 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 presently active Pelée volcanic phase (126 ka to present) (Figure 2) (Germa *et al.*, 2011b, Westercamp *et al.*, 1989).

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 (Davidson, 1987, White & Dupré, 1986). The range defined by Pb, Sr and Nd isotopic ratios covers almost the entire range known for arc lavas and they have 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. Davidson (1983), Dupré et al. (1985) and White and 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 (Figure 1) and analyzed by White and Dupré (1986) did 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 authors (e.g. Davidson (1986); Davidson and 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 magma chambers. Recently, a new study of sediments cored at DSDP Site 144 (Figure 1) was published by Carpentier et al. (2008, 2009). These authors showed that the Site 144 sediments had Sr, Nd, Hf and Pb isotopic compositions suitable to be the potential contaminant for the southern Lesser Antilles lavas. Finally, Labanieh et al. (2010) showed that addition of Site 144 sediments to the mantle wedge reproduced the composition of the Martinique Island lavas while crustal assimilation processes did not reproduce the trends defined by isotopic systems for lavas from this Island.

SAMPLING AND ANALYTICAL PROCEDURES

We collected 127 samples throughout Martinique Island, selecting outcrops based on the freshness of the samples (see inset in Figure 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 using an Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) in Brest and 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 using an ICP-MS PlasmaQuad2+ and an ICP-MS Agilent 7500ce at the University of Grenoble. Detailed analytical techniques are described in 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 traces 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 individual 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 file 1 where they are compared to 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 file 2, together with the precise location of samples. Loss on Ignition is below 3% for more than 80% of our samples and does not exceed 6.1% (Figure 3). Lavas range from basalt to rhyolite with SiO_2 between 47.3 and 71 wt% (See Supplementary file 2). Na_2O+K_2O ranges from 2.3 wt% to 6.9 wt% and all lavas belong to the subalkaline field as defined in the Total Alkali vs. Silica diagram (TAS) by Le Bas et al. (1991). All Martinique Island lavas show typical island arc trace element patterns (see Figure 4), with a clear enrichment in large-ion-lithophile elements (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 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, values similar to previously published data (see Figures 3, 4 and 5). Interestingly, the La/Sm ratios are negatively correlated with Nd and Hf isotopic ratios (Figure 6) and positively correlated with Pb and Sr isotopic ratios (not shown).

WHAT CONTROLS THE REE OF MARTINIQUE ISLAND LAVAS?

To constrain sources of volcanic arc magmas, we can only use geochemical tracers that are not significantly modified by magma forming processes. This is the case of isotopic ratios but it can also be the case of some trace element ratios if melting, fractional crystallization and alteration processes do not modify much their original values. For example, Th/Ce, Th/Nb, La/Sm and Th/La were successfully used by numerous authors to demonstrate the addition of subducted sediments to the mantle wedge under various arcs worldwide (Elliott, 2003, Hawkesworth *et al.*, 1997, 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 and aqueous fluids. However, one has to be cautious because processes other than slab sediment addition may modify the REE content and fractionate the ratio of LREE over MREE and 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 low values at 0.83 but also values significantly higher than 6 (Figure 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, (4) partial melting conditions in the mantle wedge to finally constrain the REE pattern of the source material.

Effect of weathering

All rocks presented in this study have been carefully sampled and selected with freshness as a key objective. Low Loss On Ignition (LOI) values and petrological observations indicate that secondary processes have not significantly affected our samples: LOI is below 3 Wt% for most samples (Figure 3) and secondary minerals such as chlorite could not be found during examination under the microscope. No correlation between La/Sm and LOI values for Martinique Island lavas appears in Figure 3 and since 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 coming from all other Lesser Antilles Islands (Figure 3) suggesting that both at the island level and at the arc level weathering did not create changes of LREE over MREE. This observation is consistent with the relatively immobile behavior of 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 Lesser Antilles lavas have not been modified by weathering processes.

Effect of fractional crystallization

Volcanic activity on Martinique Island occurred as several phases with varying fractionating trends that need to be considered individually 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 ratios versus SiO_2 contents of Martinique Island 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 to higher SiO_2 contents (Carbet, Conil, Pelée); in addition, the sample from Gros Ilet volcanic phase has a high La/Sm ratio (5.67) and a high SiO_2 content (67.4 wt%). The correlation existing between La/Sm and SiO_2 for 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 Island (St Anne, La Caravelle, Vauclin-Pitault, Jacob) show no variation in the slope of the REE with increasing silica contents. In contrast, residual amphibole and garnet can affect the shape of the REE pattern because garnet incorporates HREE and amphibole preferentially incorporates MREE over both LREE and HREE (Davidson *et al.*, 2007). The correlation between La/Sm and SiO_2 defined by Pelée, Conil and Carbet lavas, and the elevated La/Sm ratio of the garnet-bearing dacite could be explained by fractionation of amphibole and/or garnet. As shown in Figure 5, the REE patterns of Pelée, Conil and Carbet lavas are slightly U-shaped, a feature classically attributed to amphibole fractionation (Bottazzi *et al.*, 1999, Green & Pearson, 1985). This interpretation is confirmed by petrological observations (Supplementary file 3) that demonstrate the presence of amphibole phenocrysts in lavas from Conil and Carbet volcanic phases. The presence of amphibole as a fractionating phase is also suggested by Davidson et al. (2007) who show that Pelée lavas form a negative correlation between Dy/Yb and SiO_2 which they attribute to the preferential partitioning of middle REE over heavy REE by amphibole. Our new data for Pelée lavas confirm Davidson et al.'s observation and can also be extended to Conil lavas (Figure 9). In contrast, samples from Carbet volcanic phase define a positive correlation in Figure 9, feature that can be interpreted, according to Davidson et al. (2007), as the result of garnet fractionation. We believe that both amphibole and garnet modified the REE pattern of 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 due to fractionation of garnet as can be suspected from their presence as phenocrysts in the lava.

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 file 4). The proportions of minerals in the assemblage differ depending on the volcanic phase (Pelée, Conil or Carbet). For Pelée we use the proportion suggested by Davidson (1986), i.e. 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 Figure 10 and Supplementary file 4). For each volcanic series, we 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 and 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 primitive to the parental magma 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 figure 10) are estimated using ranges of SiO_2 concentrations and assuming that the parental magma should have a silica content of about 51 wt%, a composition similar to that measured by Davidson and Wilson (2011) for their most primitive Pelée lavas and which they used as representative of the parental magma of 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 file 4).

The combination of all these parameters leads to a decrease of La/Sm ratio between evolved lavas and 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 file 4). In figure 10, we show the effect of the correction on La/Sm ratios. 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 of negative slope exists 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 mineralogical 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 but previous work showed that the fractionation process leading to its formation certainly involved garnet and amphibole (Westercamp, 1976). Both the mineralogical assemblages 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 Martinique lavas that did not experience amphibole and garnet fractionation, at about 1.7 (Figure 9). Depending on the amount of fractional crystallization (45 to 65%), the proportion of hornblende and garnet needed to change the Dy/Yb ratio from 3.1 (value measured for the dacite) to 1.7 varies but we calculate that the primary magma had a La/Sm ratio only 6 to 17% lower than that of the garnet-bearing dacite itself (supplementary 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 melts 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 volcanics in Martinique Island was not affected by hornblende or garnet fractionation and their La/Sm ratios are basically unchanged by crystal fractionation.

Crustal assimilation

Several studies argued that crustal assimilation is a key process to understand the formation of Martinique Island lavas (Davidson, 1986, Davidson & Harmon, 1989, Davidson, 1987, Thirlwall *et al.*, 1996, Van Soest *et al.*, 2002). These authors argued that the high $\delta^{18}O$ 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 process could modify the REE pattern of erupted lavas and this is why we need here to evaluate its possible impact.

The $\delta^{18}O$ data published in the eighties 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 and Harmon (1989) to suggest that assimilation of crustal material during differentiation was the most likely interpretation. However, recently, Davidson and Wilson (2011) reported $\delta^{18}O$ 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 authors concluded that measurements on whole rock were not representative of the original magmas and were affected by secondary processes as had been demonstrated previously by other authors for other locations (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) but here we quickly summarize the main points. Figure 11, modified from Labanieh et al. (2010), shows that data define two distinct trends, one for the old and intermediate Martinique lavas and one for the recent Martinique lavas. Both trends can easily be reproduced by addition to the mantle wedge of sediments comparable to 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); average compositions of sediments sampled in front of the arc at Site 144, Site 543 and Barbados Island (Carpentier *et al.*, 2008, Carpentier *et al.*, 2009) or end-members determined using the best-fit lines through the lavas (Labanieh *et al.*, 2010)). We are therefore confident that if crustal assimilation occurred, it is not the process responsible of the large range of isotopic compositions. It could however be argued that crustal assimilation explains the observed correlation between La/Sm and silica contents of Carbet, Conil and Pelee volcanic phases as shown in figure 8. In figure 12, we show that no correlation exists between $^{143}Nd/^{144}Nd$ and SiO_2 for Carbet and Pelée lavas and that the five samples from Conil might show a small decrease of $^{143}Nd/^{144}Nd$ when SiO_2 increases from 57.5 to 60 Wt%. If we extrapolate the Conil array to $SiO_2 \approx 51$ wt%, we obtain a $^{143}Nd/^{144}Nd$ of 0.51305, value that is much higher than the most depleted lava of Martinique Island. We believe that the trend defined by the Conil lavas in figure 12 is probably not significant because the range of SiO_2 is too small and the number of data 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 volcanics are mainly controlled by fractionation of mineralogical assemblages containing hornblende (and garnet) as suggested and corrected for in the previous section (figure 10). Although REE are not assimilated by the magma during fractionation and the large range of radiogenic isotopic compositions cannot be due to assimilation processes, it does not preclude that some assimilation of selected elements occurs. Pelée and Carbet lavas define positive correlations when Pb isotopes are plotted as a function of silica contents; this shows that some assimilation was associated to fractionation, but as said above, assimilation processes did not affect the REE nor the HFSE as testified by the absence of 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 quite peculiar mineralogical assemblage. This exceptional lava might very well be affected by contamination during fractionation; it needs to be considered with care as we do not know if and to what extent its composition needs to be corrected from assimilation.

Effect of partial melting conditions

Partial melting of mantle peridotite is known to generally enrich LREE relative to MREE and HREE in the resulting magmas. 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 and (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 of the mantle source has been shown to be spinel (Parkinson *et al.*, 2003, Pichavant & Macdonald, 2003, Pichavant *et al.*, 2002, Smith *et al.*, 2008) and the melting degree has been estimated at 14 to 18% by Pichavant et al. (2002) and 10 to 20 % by Bouvier et al. (2008). Such values are consistent with estimates suggested by Plank and Langmuir (1988), Pearce and Parkinson (1993) and Hirose and Kawamoto (1995) who mentioned 10 to 30% for all subduction related magmas and who specified that volcanic arcs overlying thick lithosphere (as is the case with the Lesser Antilles arc) had partial melting degrees lower than arcs overlying thin lithosphere. Assuming melting of a spinel peridotite and primary melts produced by 10% to 20% melting, we calculate that the La/Sm enrichment factor between solid source and primary liquid ranges from 1.10 to 1.43 with an average of 1.21 (see Figure 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 file 4.

Effect of sediment addition to the magmas

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 figure 13, we show that the magma sources still scatter between 1 and about 3.9. Figure 13 also shows that the observed change of La/Sm ratio is clearly correlated to a change in Nd isotopic composition suggesting that a material with elevated La/Sm and low ^{143}Nd/^{144}Nd ratio contributes at varying degrees to the source of magmas.

What we observe in Martinique Island is obviously not unique since a similar correlation was reported by Smith et al. (2008) for lavas from Bequia (one of the Grenadines archipelago islands, see Figure 1). It seems to be a general feature of the Lesser Antilles arc system (see Figure 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 Island where high and variable La/Sm ratios exist at elevated ^{143}Nd/^{144}Nd (Figure 6). Indeed, Grenada Island lavas appear as an exception in many ways: 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 basalts occur concomitantly (C- and M-series lavas; Thirlwall et al. (1984, 1996)). Finally, Shimizu and 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 lavas from Grenada Island lavas and lavas from the other Lesser Antilles islands.

The very low ^{143}Nd/^{144}Nd measured for a number of Martinique Island lavas are typical of continental crust and given the tectonic context of the Lesser Antilles arc, these values can be reasonably explained by the presence of sedimentary material eroded from the neighbouring South-American craton (Carpentier *et al.*, 2008, Carpentier *et al.*, 2009). In figure 13, we report the data published by Carpentier et al. (2008, 2009) for sediments from Site 144 and Site 543 as well as 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 isotopic spaces by Martinique lavas (see Labanieh et al. (2010) for details). They define a broad field at low ^{143}Nd/^{144}Nd with a weighted average for the entire sedimentary column of La/Sm = 5.78. The solid grey curve in Figure 13 represents the mixing line between bulk Site 144 sediments and the mantle wedge (using the depleted mantle value of Salters and Stracke (2004)). The curve does not go through the data and it always lies below the values representative of the mantle sources (brown squares in Figure 13). In addition, the mixing array is concave while the calculated sources form a slightly convex trend (Figure 13). Mixing of bulk Site 144 sediments and 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 to those sampled at Site 144 could be incorporated in magma sources through melting of the sedimentary pile. Such interpretation was also suggested by Turner et al. (1996) and Hawkesworth et al. (1997). In figure 13 we show mixing lines between mantle wedge taken as the depleted mantle of Salters and Stracke (2004) and the various compositions suggested by Hermann and Rubatto (2009) for hydrous melts of sediments. For the sediment melts of Hermann and Rubatto (2009), we chose a Nd isotopic composition of 0.51181, value selected in Labanieh et al. (2010) to fit the mixing curves in radiogenic isotope diagrams. All mixing lines form convex curves and three of them (black curves) fit very well the inferred Martinique magma sources. Addition of sediment melts to the mantle wedge appears therefore as a very plausible explanation for the correlated La/Sm and Nd isotopic ratios in Martinique magma sources. The exact proportions of sediment melt added to the mantle wedge to explain Martinique magma sources depend on the chosen composition of the hydrous melt, which varies with pressure, temperature and amount of water added for the experiments (see Hermann and 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, i.e. the highest calculated value for sources under Martinique Island. This calculated sediment melt contribution is consistent with our previous estimates made using 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 the key factor controlling the values is the amount of subducted sediment in the source. While 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 5, change that is correlated with changes of both ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf ratios. We are therefore quite confident that La/Sm can be considered as a good proxy for the amount of sediments incorporated in the source of magmas.

SEDIMENT MELTING VERSUS SLAB DEHYDRATION

While the changes in La/Sm ratio seen in the lavas can be attributed to melting of subducted sediments, it does not preclude that dehydration of the subducted slab also occurs. As previously suggested by numerous authors, 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, Gill & Condomines, 1992, Hawkesworth *et al.*, 1997, Johnson & Plank, 1999, McDermott & Hawkesworth, 1991) while Th is only transferred efficiently from the slab when sediments 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 Figure 14 how Ba/Th and Sr/Th evolve relative to $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ in Martinique Island and more generally in the Lesser Antilles arc. Our new data on Martinique Island demonstrate that, in the same island, samples with high Ba/Th, Sr/Th, $^{143}Nd/^{144}Nd$ and low $^{87}Sr/^{86}Sr$ ratios coexist with samples with low Ba/Th, Sr/Th, $^{143}Nd/^{144}Nd$ and high $^{87}Sr/^{86}Sr$ ratios (Figure 14). This strongly suggests that both melting of sediments and dehydration of a material with radiogenic Nd isotopic composition occur under Martinique Island.

On the three maps shown in Figure 15 we report using a color scale the values of La/Sm, Ba/Th and U/Th ratios for all the Martinique samples. The geographic 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 while samples located on the western side of the island have high La/Sm ratios associated to low Ba/Th and U/Th ratios. In addition, all samples with elevated La/Sm ratios are located in a narrow band less than 20 km wide. It is worth noting that this spatial gradient is not related to age since the low La/Sm lavas on the eastern side of the island include volcanics ranging in age from 25 to 4 Ma while the high La/Sm lavas on the western side have ages ranging from 11 Ma to present (see figure 2). As demonstrated in the previous section, changes in La/Sm ratios reflect changes in the proportion of sediments in the source; we can therefore conclude not only that more sediments are 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 material with low $^{87}Sr/^{86}Sr$ mainly control the transfer of material under the eastern side of the island.

Across-arc zoning of 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 system that the “shallow subduction component”, i.e. aqueous fluids, is mostly present beneath the volcanic arc while the “deep subduction component”, i.e. sediment melts, influence 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 with LILE-enrichment due to aqueous fluids in the volcanoes located near the trench while volcanoes 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 signature of the lavas near the trench while siliceous melts prevail for the lavas away from the trench.

Origin of the aqueous fluids and implications of the chemical zoning

One important question remains as to 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) or Turner and Foden (2001) used plots of $^{87}Sr/^{86}Sr$ versus ratios such as Ba/Th to show that the Sr added to the northern Lesser Antilles arc lavas by aqueous fluids has an unradiogenic composition at about 0.7035 - 0.704, value that indicates that the fluids could derive 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 value occurs in lavas with high Ba/Th and Sr/Th on the eastern side of Martinique Island. 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 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)) (see Figure 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 the sedimentary pile because the effect on the Sr isotopic composition would be quickly huge. This is quite intriguing because the chemical zoning defined by 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 to the lavas with the aqueous fluids signal. The geographical gradient shown in figure 15 indicates that sediments are indeed present on top of the basaltic crust when the latter dehydrates but they do not interact with the rising fluid (Figure 16). This is even more puzzling because sediments such as those present in front of the trench (Carpentier *et al.*, 2008, Carpentier *et al.*, 2009) are rich in water and should be a fertile source of aqueous fluids.

The study of fluid processes in subduction zones proposed by Peacock (1990) can help answer these questions as he suggests 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) (Figure 16). Then, the primary source of H_2O at magma genesis depths, would 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 (Figure 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 and Abers (2006) estimated that the depth of the subducted slab under Mount 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 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 confront these estimated P-T conditions to the experimental data published by Hermann and Spandler (2008) who track how elements are released from subducted sediments under arcs. These authors show in their figure 9 that a major transition occurs at the P-T conditions that prevail under Martinique Island, 4.5 GPa and 780°C: at lower temperatures, transfer by aqueous fluids dominates while hydrous melts prevail above this transition. In addition, they also demonstrate that the aqueous fluid does not contain much LIL elements while the hydrous melts are rich in those elements. This is entirely consistent with the geographical gradient that we highlight in Figure 15. We conclude therefore that in Martinique Island, 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 unchanged over a period of about 25Myr. In addition, the consistency between lava composition at the surface of the island and P-T conditions at the slab surface suggest 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 extra observation to support this suggestion.

The relationship between P-T conditions of the slab and surface expression of sediment melting can also explain the North-South chemical changes along the Lesser Antilles arc. According to Syracuse and 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 while it is at about 141 km under the southern part of the arc (Table 1). Since 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 northern Lesser Antilles Islands may be a little too shallow to produce sediment melts while it is at the right depth under the southern part of the Lesser Antilles arc.

What about other island arcs?

In Figure 17, we show that the negative correlation between La/Sm and Nd isotopic compositions highlighted for the Lesser Antilles arc is also observed for other intra-oceanic arcs. Few examples are provided in Figure 17. 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. This is for example the case for Bonin and New Britain lavas (see Figure 17). It suggests that for all these arcs, the impact of sediment melting on the La/Sm ratio overwhelms other processes. However, some exceptions exist with, for example, the lavas from Aleutian, Vanuatu or Kermadec, for which no correlation occurs 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 versus 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. Inversely, 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 sediment melting occur. This was already pointed out by Class et al. (2000) for the Aleutian arc and it 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 Figure 18 with the sediment solidus provided by Hermann and Spandler (2008) and determine if sediments present under the arc can potentially melt (see table 1). As for Martinique Island 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). Depth of slabs under volcanic arcs are also from Syracuse et al. (2010) and the sediment solidus is that of Hermann and 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 of Izu, Bonin, South Marianas, Tonga and Kermadec arcs (see Table 1). For example, the slab under 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, sediments are not in 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 temperature under Northern Mariana is at the 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 or may be too hot.

Under volcanic arcs with high La/Sm and low Ba/Th ratios, the slab surface should be hot enough for sediments to melt. This is the case for all the arcs belonging to the sediment related arcs (see Table 1). Overall, the coherence between P-T paths of slab surface, sediment solidus and geochemical characteristics of lavas is extremely good. Thus, we believe that La/Sm and Ba/Th provide accurate information on the mean of element transport from the subducted basalt and sediments. The amount of sediments 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 discovered in Martinique Island 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 on Martinique Island we quantify the relative role of weathering processes, fractional crystallization, intra-crustal assimilation, partial melting and sediment incorporation in the mantle wedge to influence the slope of REE patterns. We show that the La/Sm ratios cover a large range from 1.3 to 6.1. Weathering processes have basically negligible effect on the La/Sm ratio; when amphibole or garnet are 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 wall rock to magmas during fractionation processes, and partial melting only increases La/Sm by 21% relative to the ratio of the solid source. Finally, we show that most of the range in La/Sm ratios depends on the amount and nature of subducted sediment incorporated into the mantle; the sedimentary component is added through hydrous melt as opposed to aqueous fluid. In Martinique Island, the La/Sm ratio is a proxy of the proportion of sediments involved in the genesis of the lavas.

Slab sediments are incorporated via melting under the western side of Martinique Island 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 Martinique lavas follow a chemical spatial zoning: 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 while high La/Sm and low Ba/Th and U/Th characterize lavas on the western side of the Island. La/Sm being a proxy for the proportion of sediments incorporated in the mantle wedge and Ba/Th and U/Th ratios being proxies for basalt dehydration, the nature of the transfer agent, melting or dehydration, follows a geographical gradient. We relate the change in sediment involvement to pressure and temperature conditions at the surface of the slab and suggest that sediments cross their solidus just under Martinique Island. This is a very rare case where 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 to the proportion of slab sediments in the source. Arcs with high La/Sm ratios and defined as “sediment-dominated” are all related to slab P-T conditions that allow sediments to melt. Inversely, under most arcs with low La/Sm and high Ba/Th, and defined as “fluid-dominated” the pressure and temperature conditions are too low for sediments to melt.

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FIGURE CAPTIONS

Figure 1:

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

Figure 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 volcanic activity of the recent arc. The symbols next to the names of volcanic phases are those used in the rest of the manuscript to refer to the related volcanic phases. Ages of volcanic phases are from Germa et al. (2011a, 2010, 2011b). Please refer to the on-line manuscript for all colored figures.

Figure 3:

La/Sm ratio versus Loss On Ignition of Martinique Island lavas (yellow dots), Grenada Island (gray squares) and other Lesser Antilles Island lavas (red diamonds). 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.

Figure 4:

Trace elements patterns normalized to primitive mantle (McDonough & Sun, 1995) for the different volcanic phases as defined by Westercamp et al. (1989) in Martinique Island. Symbols as in Figure 2.

Figure 5:

REE patterns normalized to chondrites (Evensen *et al.*, 1978) for the different volcanic phases as defined by Westercamp et al. (1989) in Martinique Island. Symbols as in Figure 2.

Figure 6:

La/Sm ratio versus Nd and Hf isotopic ratios for Martinique Island lavas (new data are represented by yellow dots and published data by yellow diamonds), Grenada Island (gray squares) and other Lesser Antilles Island lavas (red diamonds). Published data are from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

Figure 7:

Range defined by the La/Sm ratio of intra-oceanic arcs 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/).

Figure 8:

La/Sm ratio versus SiO_2 content of all volcanic phases as defined by Westercamp et al. (1989) in Martinique. Symbols for each volcanic phase are the same as in Figure 2. Carbet, Conil and Pelée volcanic phases are the three most recent phases present in Martinique. The garnet-bearing dacite from Gros Ilet is the most recent activity of the intermediate arc.

Figure 9:

Dy/Yb ratio versus SiO_2 content of all volcanic phases as defined by Westercamp et al. (1989) in Martinique. Symbols for each volcanic phase are as in Figure 2. Pelée and Conil volcanic phases define negative correlations while Carbet lavas define a positive correlation.

Figure 10:

La/Sm versus SiO_2 plots. Measured values are presented as triangles in shades of blue. The effect of fractional crystallization of a mineralogical assemblage containing amphibole ± garnet is calculated (see text for details) and measured La/Sm ratios are corrected from the effect of 15%, 25%, 35% or 45% fractionation depending on the silica content of lavas sampled in Carbet, Conil and Pelée volcanic phases (black triangles). Minimum and maximum corrections (±5% fractionation) are shown using the error bars around 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.

Figure 11:

$^{143}Nd/^{144}Nd$ versus $^{206}Pb/^{204}Pb$ diagram showing crustal assimilation (grey) and source mixing (black) models. Distribution coefficients for AFC modeling are $D_{Pb} = 0.61$ and $D_{Nd} = 0.22$ and the ratio between assimilation rate and crystallization rate, r, is 0.25. Details of these models are given in Labanieh et al. (2010).

Figure 12:

$^{143}Nd/^{144}Nd$ versus SiO_2 diagram showing Carbet, Conil and Pelée lavas. Data are from Davidson (1986), Davidson & Wilson (2011), Turner *et al.* (1996) (small triangles) and this study (large triangles).

Figure 13:

Measured and calculated La/Sm ratio of Martinique Island lavas as a function of measured Nd isotope ratios (Labanieh *et al.*, 2010). Yellow dots represent measured data, light brown triangles represent the La/Sm ratios after correction for fractional crystallization and brown squares represent values after correction for both fractional crystallization and partial melting. Error bars include uncertainties on the degree of fractional crystallization and partial melting. Local sediments are represented as diamonds (Site 144 sediments; measured values are represented as white diamonds and carbonate-free values (calculated by virtually removing the carbonate for each unit; see Carpentier et al. (2009) for details) as grey diamonds) and black triangles (Site 543 sediments) (Carpentier *et al.*, 2008, Carpentier *et al.*, 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 designated as 1, 2 and 3 lead to mixing hyperbolas (black curves) that fit very well the trend defined by data corrected from fractional crystallization and partial melting. They correspond respectively to experiments at 4.5GPa and 900°C, at 3.5GPa and 900°C and at 4.5GPa 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.

Figure 14:

Ba/Th ratio versus Nd isotopes (a) and Sr/Th versus Sr isotopes (b) for Martinique Island lavas (new data are represented as yellow dots and published data as yellow diamonds), Grenada Island (gray squares) and North and South Lesser Antilles Island lavas (orange and red diamonds respectively). 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, Carpentier *et al.*, 2009). It is important to note that the Site 144 sediments shown here correspond to measured values and not to the "decarbonated sediment" because Ba content in carbonates is so high that a "decarbonated sediment" Ba content cannot be calculated. As the consequence, the range displayed by these sediments in panel (a) is much larger than the probable range covered by the sediments that are effectively subducted and incorporated within Lesser Antilles lavas. Fresh Atlantic MORB between 30°N and 30°S are represented as black dots and the dashed line in panel (b) represents the average altered oceanic crust value suggested by Staudigel et al. (1995). Most Site 543 sediments are off-scale in panel (b).

Figure 15:

Maps of Martinique Island showing the La/Sm, Ba/Th and U/Th zoning. The dots represent the location of the samples and the color of the dots refers to the value of La/Sm (a), Ba/Th (b) and U/Th (c) ratios. Low La/Yb and high Ba/Th and U/Th are represented by blue dots while high La/Sm and low Ba/Th and U/Th are represented by red dots. The blue dashed line represent the axis where La/Sm is uniformly low while the red dashed line represent the axis where La/Sm is quite variable and reaches high values.

Figure 16:

Sketch representing melting and dehydration processes that occur under Martinique Island. Dehydration of the basaltic crust occurs before melting of slab sediments does. Fluids do not interact with sediments, they probably rise along fractures. Sediment melts ascend through the mantle wedge without significant horizontal deviation.

Figure 17:

La/Sm ratio as a function of Nd isotopic ratios for all intra-oceanic arcs (first panel) and a selection of 5 of these arcs: Costa Rica, Luzon, East Sunda (they have the highest La/Sm ratios of all intra-oceanic arc lavas) and Bonin and New Britain. Data compilation from Georoc (http://georoc.mpch-mainz.gwdg.de/georoc/).

Figure 18:

Ba/Th as a function of La/Sm for all intra-oceanic arcs. Volcanic arcs that mainly experience sediment melting (Banda, Luzon and East Sunda) are represented in inset (a). In inset (b), we represent volcanic arcs that mainly experience slab dehydration (Izu-Bonin-Mariana, Tonga-Kermadec and South Sandwich). Inset (c) shows 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/).

TABLE CAPTION

Table 1:

Comparison between P-T conditions under volcanic arcs and sediment solidus. The depth of the slab under each arc as well as pressure and temperature conditions at these depths are from Syracuse et al. (2010). Temperature at which sediments should melt at the corresponding pressure is from the sediment solidus provided by Hermann and Spandler (2008). The column named “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.

SUPPLEMENTARY FILE CAPTION

Supplementary file 1:

Average results obtained on n measurements of AGV-1, BHVO-2 and BR24 international standards together with Relative Standard Deviation and comparison between these averages and values recommended by Chauvel et al. (2011) for AGV-1 and BR24 and preferred literature values for BHVO-2 (see table 8 in Chauvel et al. (2011) and references therein)

Supplementary file 2:

Major and trace element contents and geographical coordinates of all volcanic phases of Martinique Island. Most of the samples have been accurately dated by Samper et al. (2008) and Germa et al. (2011a, 2010, 2011b) and represent all volcanic phases of Martinique Island, from the old lavas (24.8 Ma) to the recent lavas (present activity). Ages in italic were estimated using the geological map (Westercamp *et al.*, 1989). Pb, Sr, Nd and Hf isotopes measured on a selection of these samples and published in Labanieh et al. (2010) are also shown in the table.

Footnote:

Dup and Ter stand for complete duplicate and triplicate analyses, Rep stands for replicate analyses (one “mother solution” and two diluted solutions and measurements, see Chauvel et al. (2011)) and Rerun stands for duplicate measurements only.

Supplementary file 3:

Petrographic description of the studied samples. The type of lava is determined using a TAS diagram (Total Alkali vs. Silica; (Le Bas *et al.*, 1991)). Presence and relative proportions of each type of phenocryst are expressed as crosses, no cross corresponds to an absence of this type of phenocryst and four crosses correspond to an overwhelming presence of the mineral.

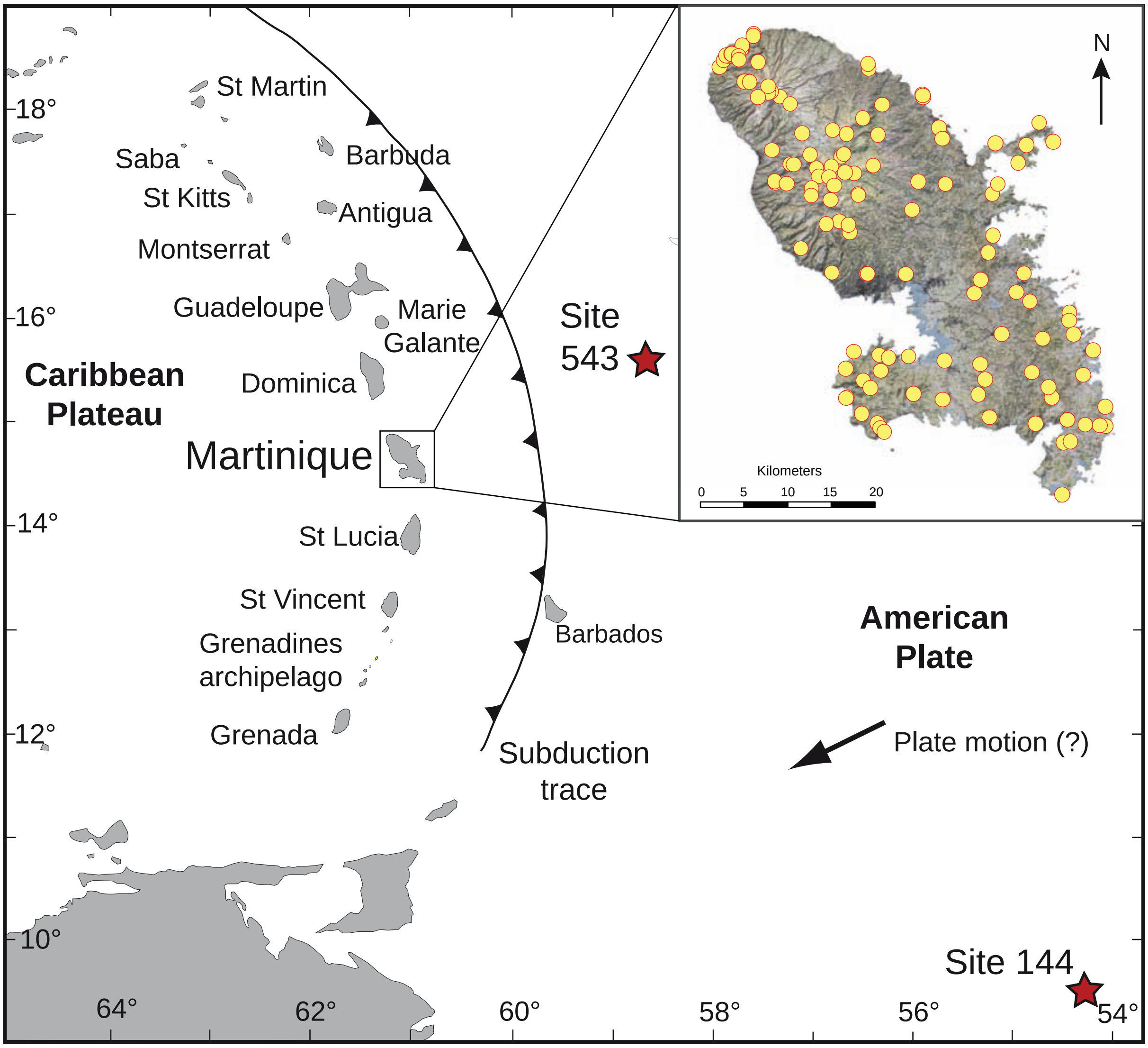
Supplementary file 4:

Parameters and calculations used for fractional crystallization and partial melting models.

Partition coefficients for plagioclase, hornblende, clinopyroxene and orthopyroxene in fractional crystallization models are from Fujimaki et al. (1984) and those for garnet are from Johnson (1994). Two mineral assemblages are suggested for Conil volcanic phase: model 1 is similar to that used for Pelée lavas and model 2 contains more hornblende. Degrees of fractionation, F, depend on the silica content of each lava (see figure 10). For the Gros Ilet sample, the mineral assemblage needed to decrease Dy/Yb from 3.1 to 1.7 depends heavily on the degree of fractionation. We envision three different assemblages for 45%, 55% and 65% of fractionation but these are highly unconstrained.

For partial melting models, partition coefficients between spinel, clinopyroxene, orthopyroxene, olivine and liquid are those suggested by Niu and Hékinian (1997). Mineral proportions in the solid source are those suggested by Stracke et al. (2006) and mineral fractions contributing to the melt are those used by Kinzler (1997). The negative value of mineral proportion contributing to the melt corresponds to a peritectic reaction. The numbers provided in the table correspond to an average degree of partial melting of 15%.

Figure 1



St Martin
18°
Saba
Barbuda
St Kitts
Antigua
Montserrat
16°
Guadeloupe
Marie
Galante
Site
543
Caribbean
Plateau
Dominica
Martinique
14°
St Lucia
St Vincent
Grenadines
archipelago
Barbados
American
Plate
12°
Grenada
Subduction
trace
Plate motion (?)
10°
Site 144
64°
62°
60°
58°
56°
54°
N
Kilometers
0
5
10
15
20

Figure 2

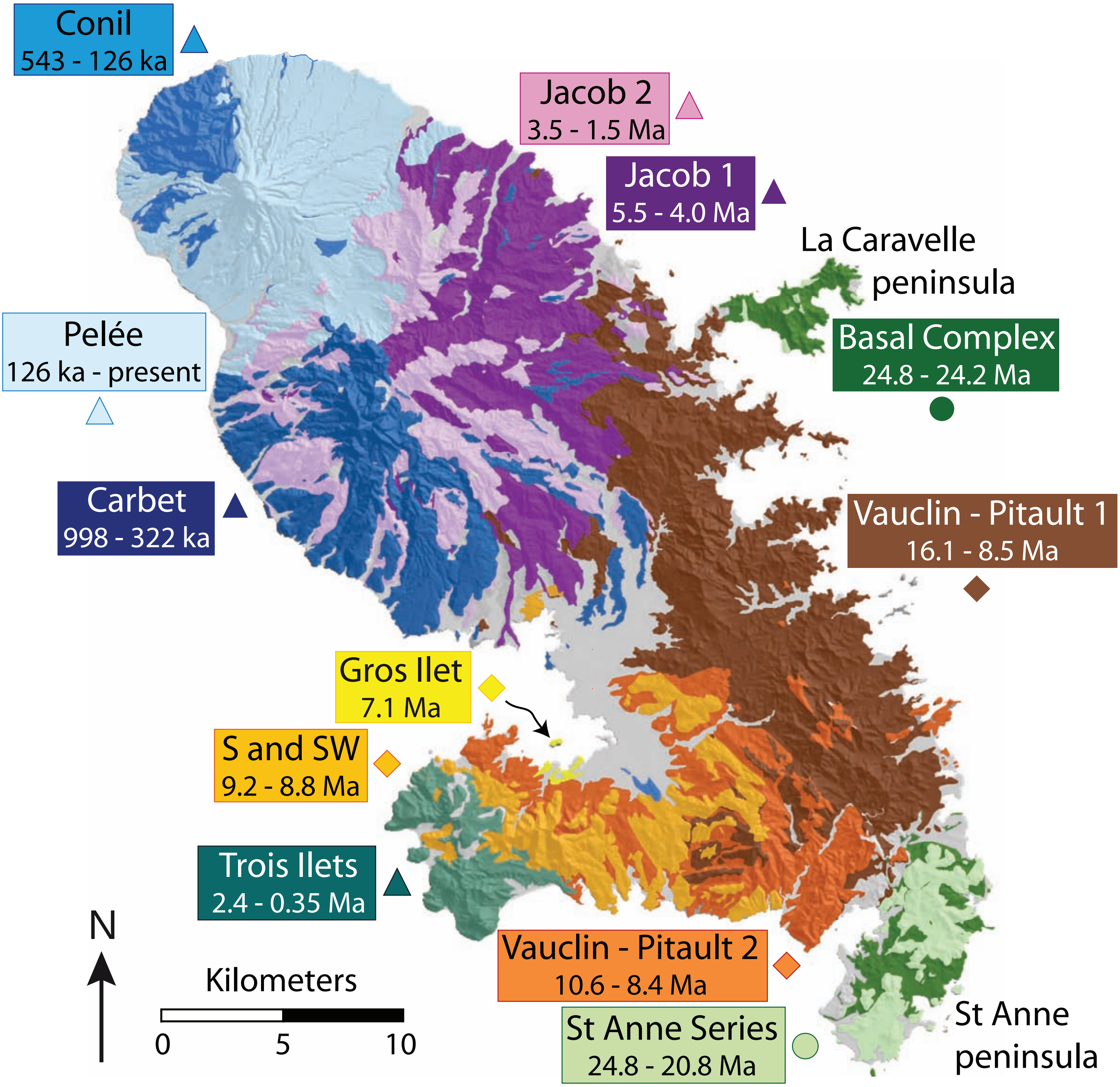
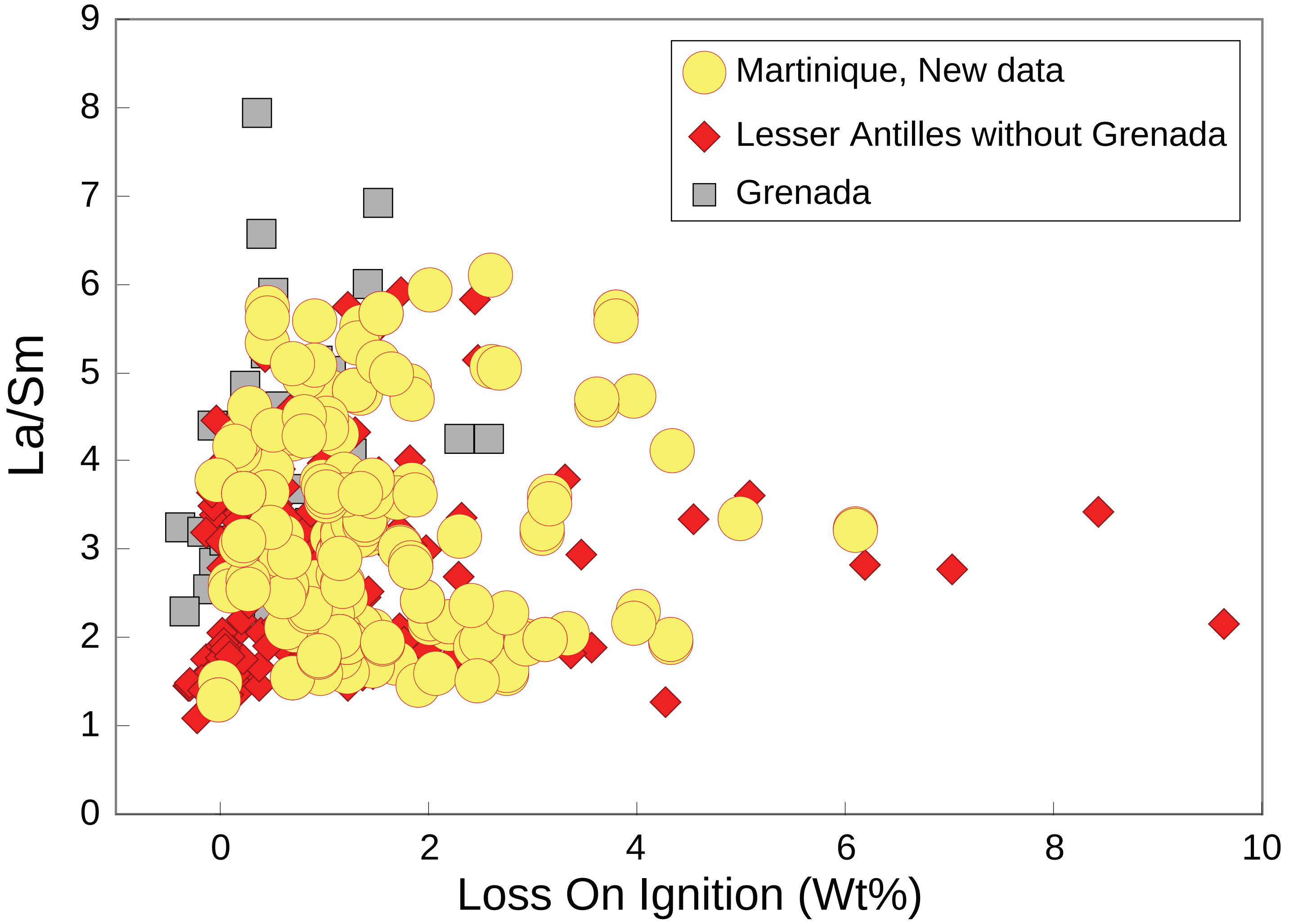

Conil
543 - 126 ka
Jacob 2
3.5 - 1.5 Ma
Jacob 1
5.5 - 4.0 Ma
La Caravelle
peninsula
Basal Complex
24.8 - 24.2 Ma
Pelée
126 ka - present
Carbet
998 - 322 ka
Vauclin - Pitault 1
16.1 - 8.5 Ma
Gros Ilet
7.1 Ma
S and SW
9.2 - 8.8 Ma
Trois Ilets
2.4 - 0.35 Ma
N
Kilometers
0
5
10
Vauclin - Pitault 2
10.6 - 8.4 Ma
St Anne Series
24.8 - 20.8 Ma
St Anne
peninsula

Figure 3



Martinique, New data
Lesser Antilles without Grenada
Grenada
La/Sm
Loss On Ignition (Wt%)
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10

Figure 4

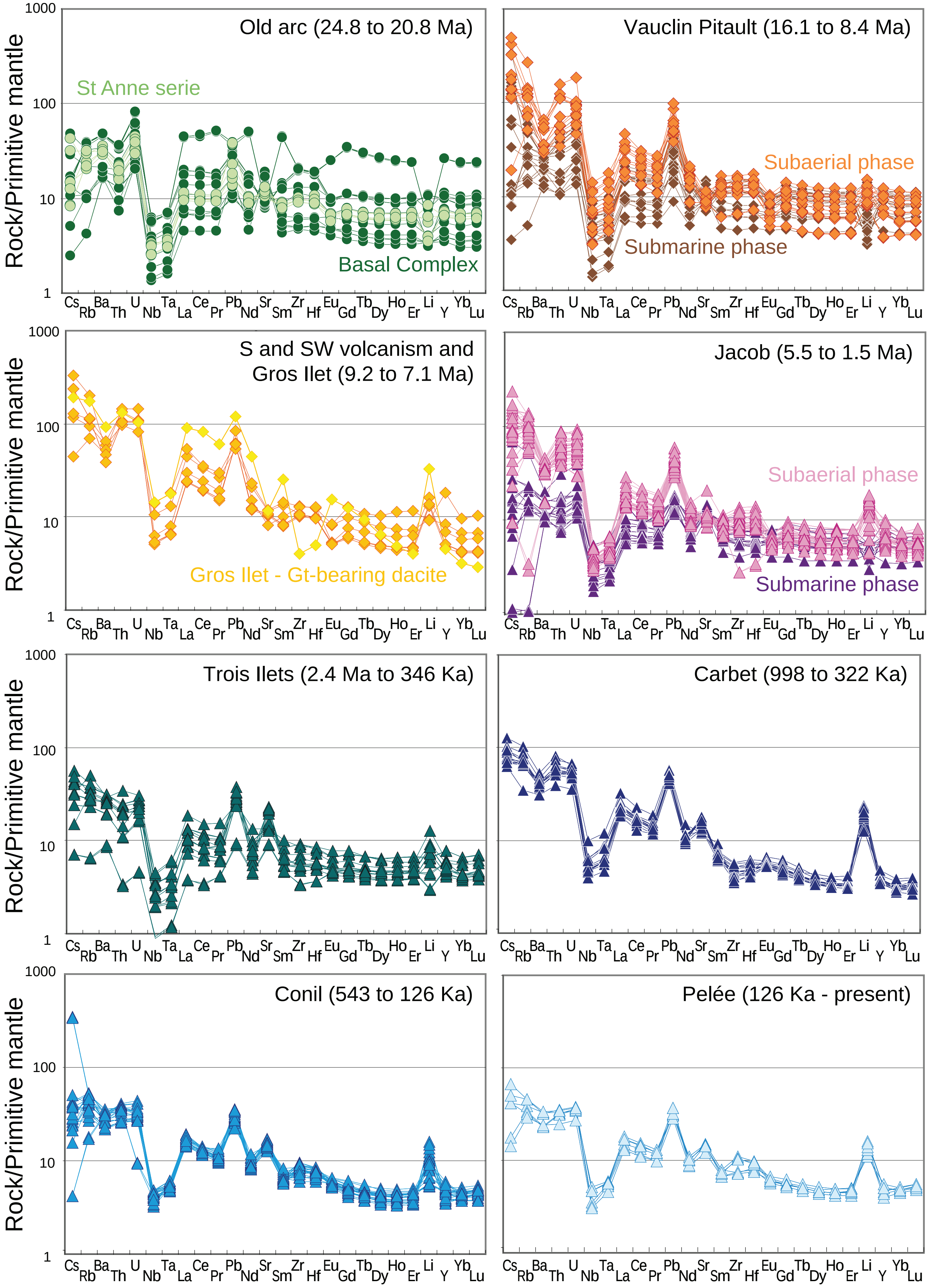

Old arc (24.8 to 20.8 Ma)
St Anne serie
Basal Complex
Vauclin Pitault (16.1 to 8.4 Ma)
Subaerial phase
Submarine phase
S and SW volcanism and Gros Ilet (9.2 to 7.1 Ma)
Gros Ilet - Gt-bearing dacite
Jacob (5.5 to 1.5 Ma)
Subaerial phase
Submarine phase
Trois Ilets (2.4 Ma to 346 Ka)
Carbet (998 to 322 Ka)
Conil (543 to 126 Ka)
Pelée (126 Ka - present)
Rock/Primitive mantle
1000
100
10
1
Cs Rb Ba Th U Nb Ta La Ce Pr Pb Nd Sr Sm Zr Hf Eu Gd Tb Dy Ho Er Li Y Yb Lu

Figure 5

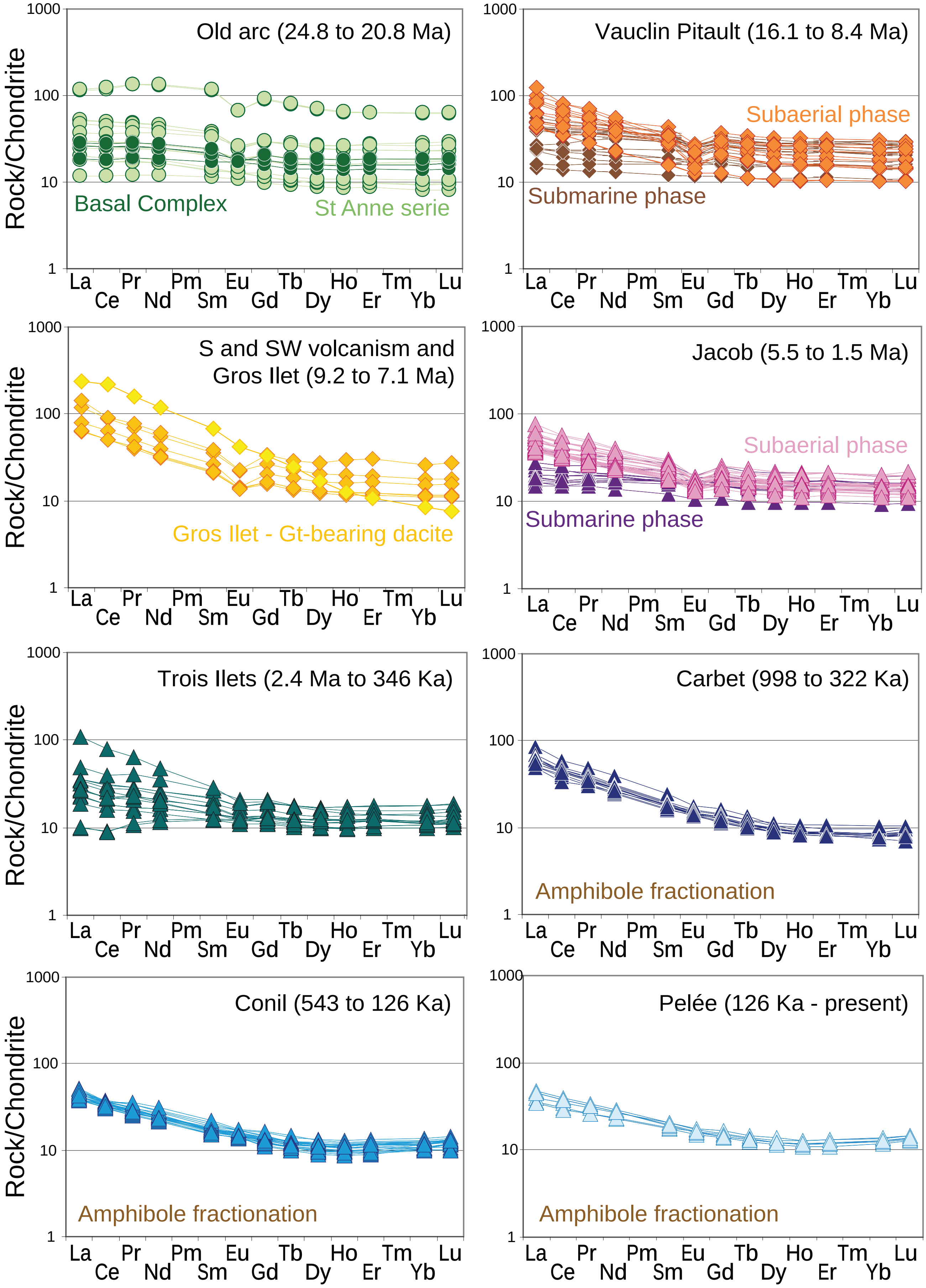

Rock/Chondrite
1000
100
10
1
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Old arc (24.8 to 20.8 Ma)
Basal Complex
St Anne serie
Vauclin Pitault (16.1 to 8.4 Ma)
Subaerial phase
Submarine phase
S and SW volcanism and Gros Ilet (9.2 to 7.1 Ma)
Gros Ilet - Gt-bearing dacite
Jacob (5.5 to 1.5 Ma)
Subaerial phase
Submarine phase
Trois Ilets (2.4 Ma to 346 Ka)
Carbet (998 to 322 Ka)
Amphibole fractionation
Conil (543 to 126 Ka)
Amphibole fractionation
Pelée (126 Ka - present)
Amphibole fractionation

Figure 6

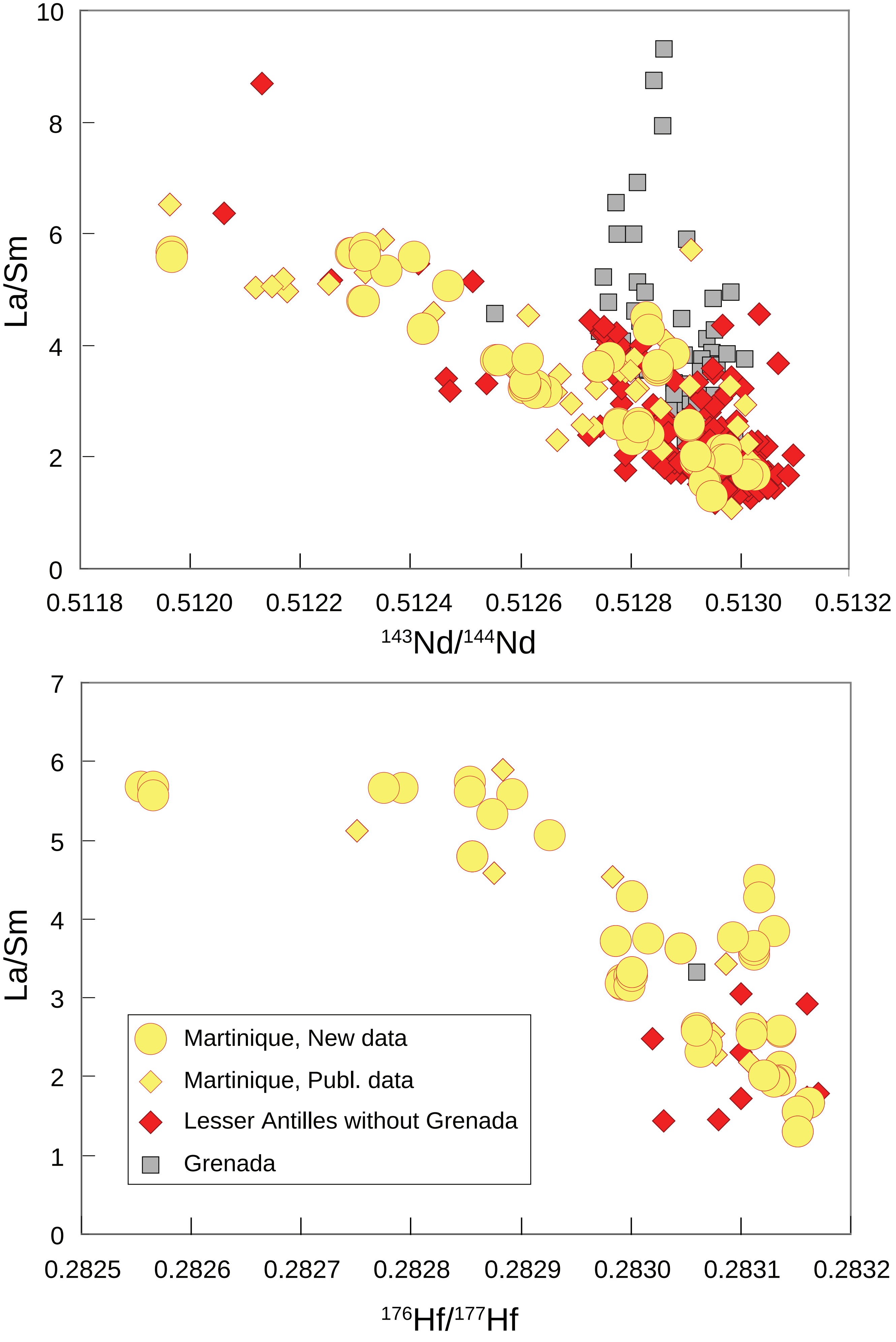

10
8
6
4
2
0
La/Sm
0.5118
0.5120
0.5122
0.5124
0.5126
0.5128
0.5130
0.5132
^{143}Nd/^{144}Nd
7
6
5
4
3
2
1
0
La/Sm
Martinique, New data
Martinique, Publ. data
Lesser Antilles without Grenada
Grenada
0.2825
0.2826
0.2827
0.2828
0.2829
0.2830
0.2831
0.2832
^{176}Hf/^{177}Hf

Figure 7

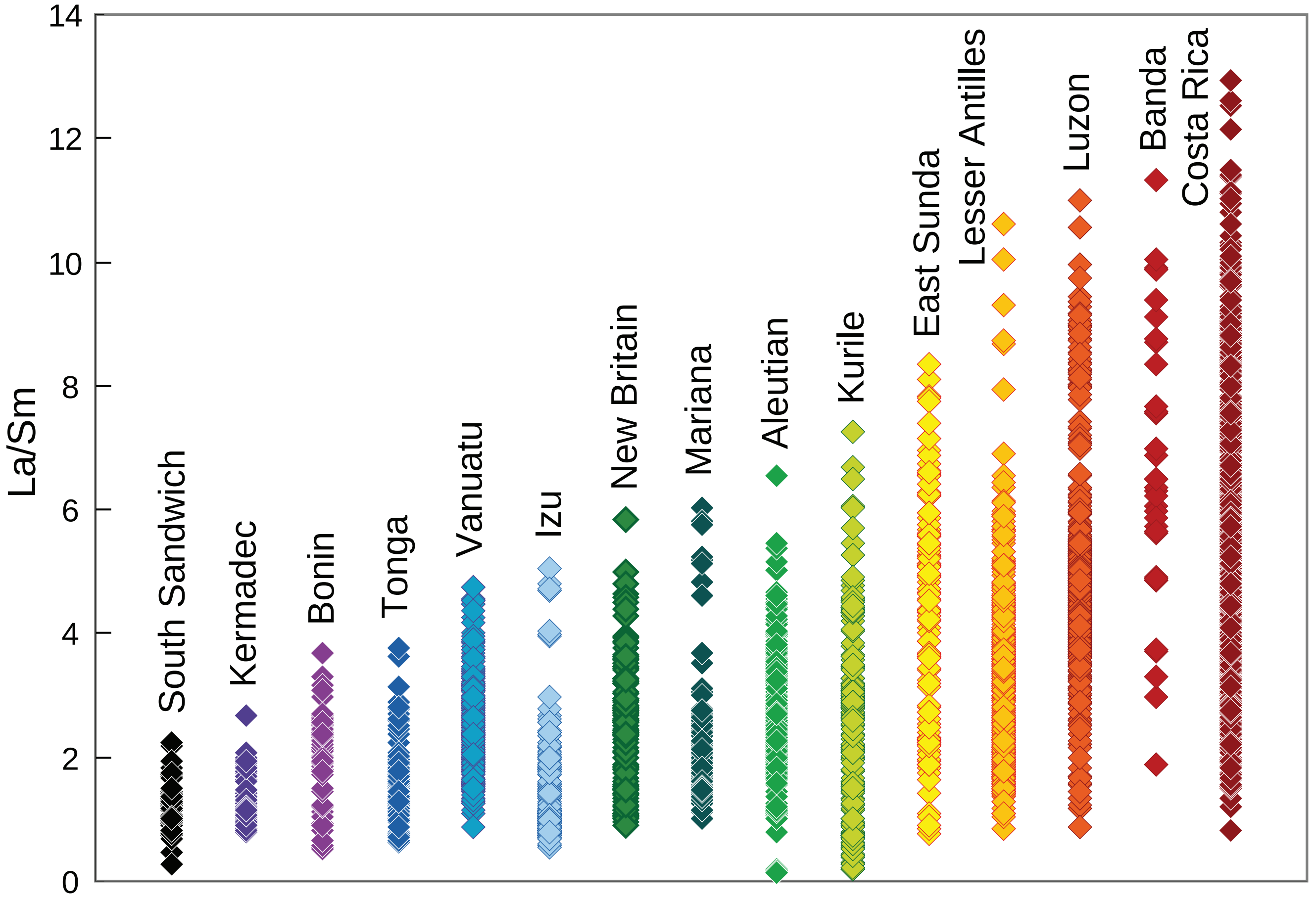
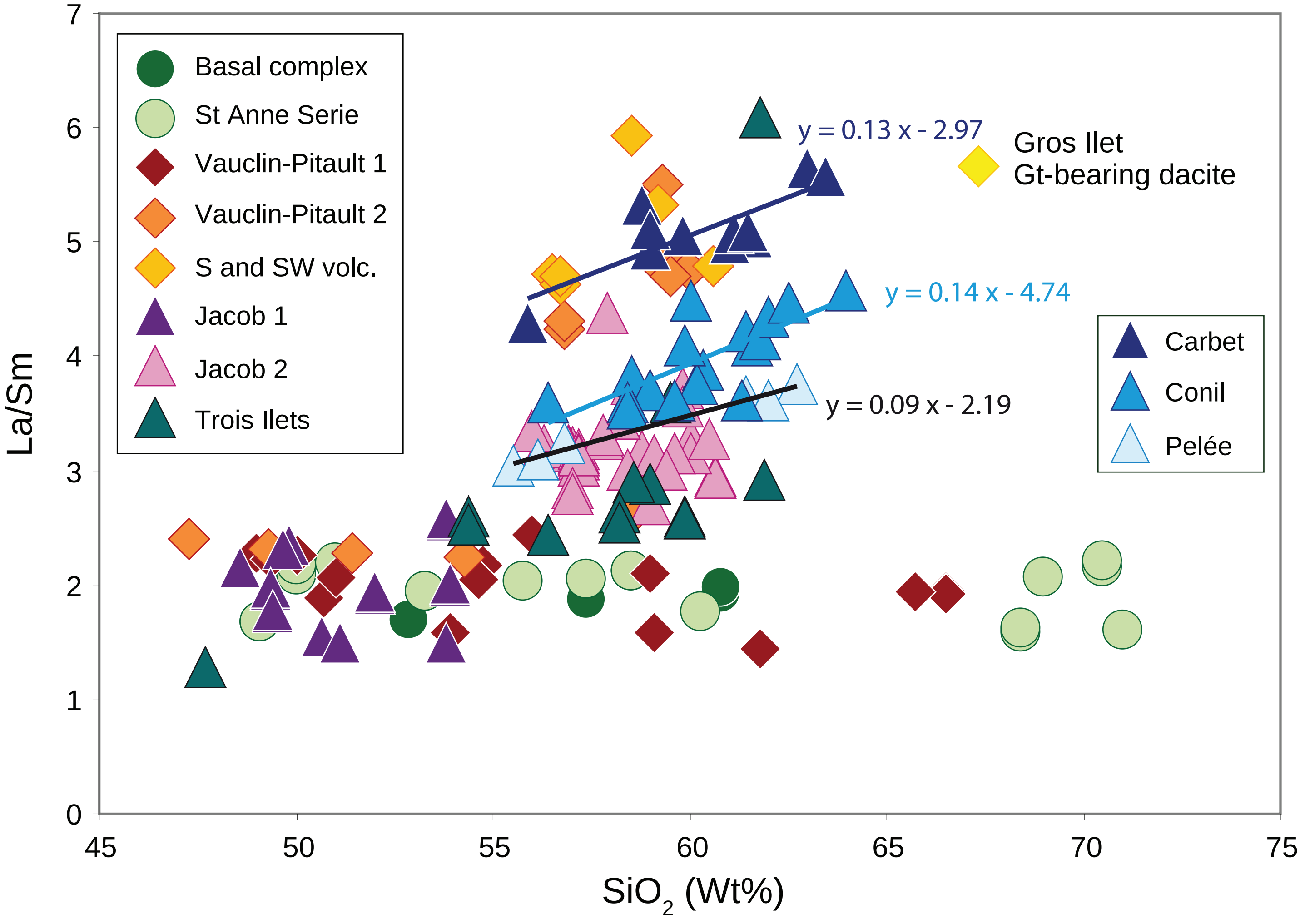
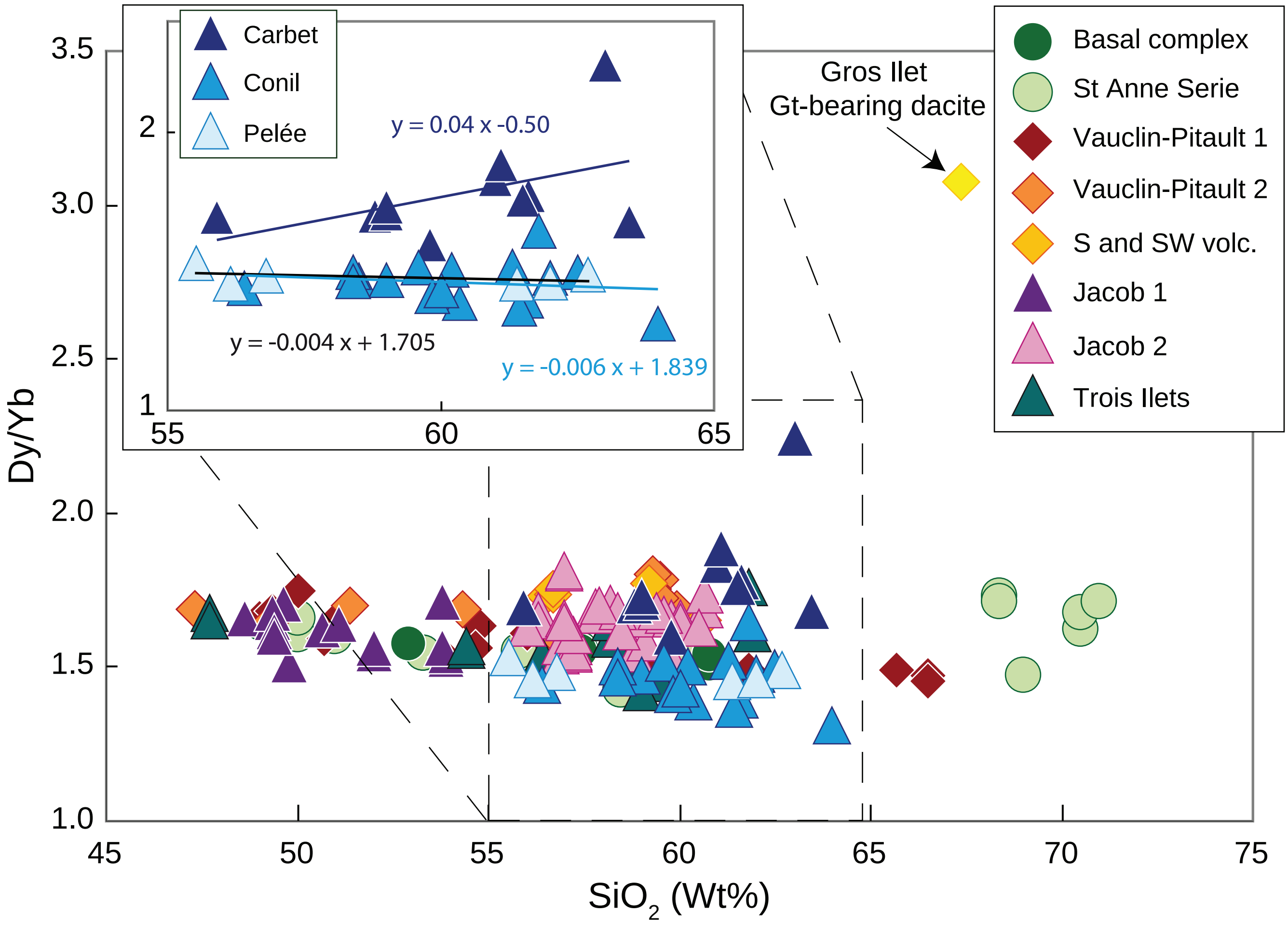

La/Sm
0
2
4
6
8
10
12
14
South Sandwich
Kermadec
Bonin
Tonga
Vanuatu
Izu
New Britain
Mariana
Aleutian
Kurile
East Sunda
Lesser Antilles
Luzon
Banda
Costa Rica

Figure 8



7
6
5
4
3
2
1
0
La/Sm
45
50
55
60
65
70
75
SiO_2 (Wt%)
Basal complex
St Anne Serie
Vauclin-Pitault 1
Vauclin-Pitault 2
S and SW volc.
Jacob 1
Jacob 2
Trois Ilets
y = 0.13 x - 2.97
Gros Ilet
Gt-bearing dacite
y = 0.14 x - 4.74
y = 0.09 x - 2.19
Carbet
Conil
Pelée

Figure 9



Carbet
Conil
Pelée
y = 0.04 x -0.50
y = -0.004 x + 1.705
y = -0.006 x + 1.839
2
1
55
60
65
Gros Ilet
Gt-bearing dacite
Basal complex
St Anne Serie
Vauclin-Pitault 1
Vauclin-Pitault 2
S and SW volc.
Jacob 1
Jacob 2
Trois Ilets
3.5
3.0
2.5
2.0
1.5
1.0
Dy/Yb
45
50
55
60
65
70
75
SiO_2 (Wt%)

Figure 10

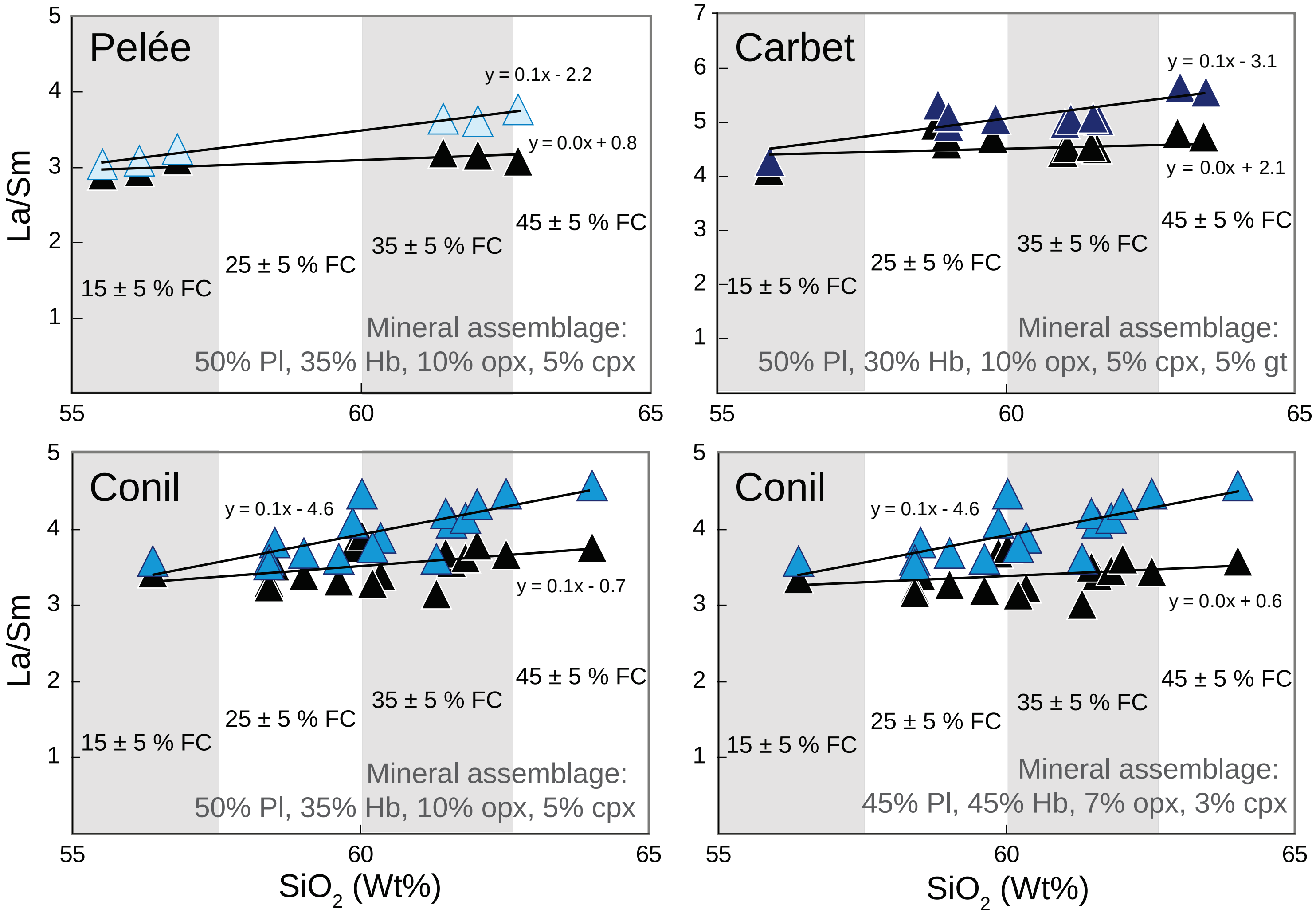

Pelée
y = 0.1x - 2.2
y = 0.0x + 0.8
45 ± 5 % FC
35 ± 5 % FC
25 ± 5 % FC
15 ± 5 % FC
Mineral assemblage:
50% Pl, 35% Hb, 10% opx, 5% cpx
Carbet
y = 0.1x - 3.1
y = 0.0x + 2.1
45 ± 5 % FC
35 ± 5 % FC
25 ± 5 % FC
15 ± 5 % FC
Mineral assemblage:
50% Pl, 30% Hb, 10% opx, 5% cpx, 5% gt
Conil
y = 0.1x - 4.6
y = 0.1x - 0.7
45 ± 5 % FC
35 ± 5 % FC
25 ± 5 % FC
15 ± 5 % FC
Mineral assemblage:
50% Pl, 35% Hb, 10% opx, 5% cpx
Conil
y = 0.1x - 4.6
y = 0.0x + 0.6
45 ± 5 % FC
35 ± 5 % FC
25 ± 5 % FC
15 ± 5 % FC
Mineral assemblage:
45% Pl, 45% Hb, 7% opx, 3% cpx
La/Sm
La/Sm
SiO$_2$ (Wt%)
SiO$_2$ (Wt%)
1
2
3
4
5
6
7
55
60
65

Figure 11

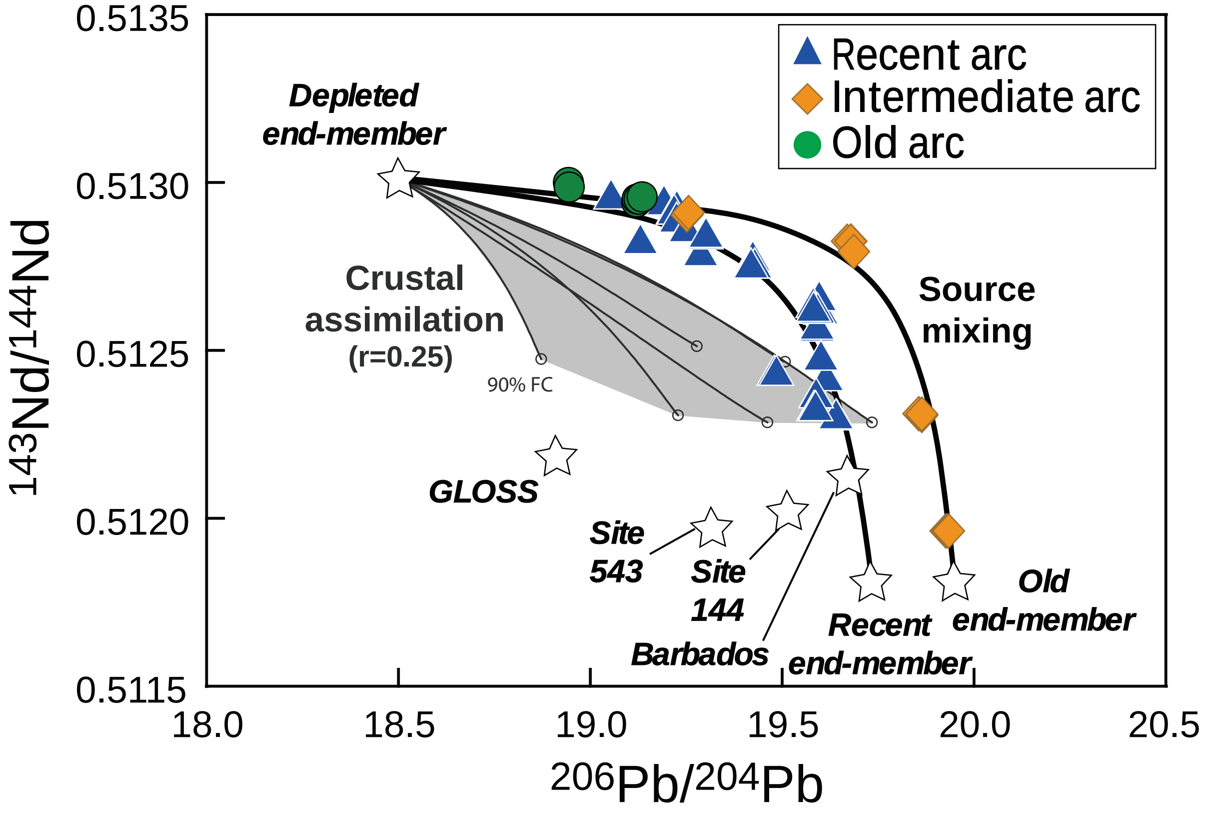

Recent arc
Intermediate arc
Old arc
Depleted end-member
Crustal assimilation (r=0.25)
90% FC
GLOSS
Site 543
Site 144
Barbados
Recent end-member
Old end-member
Source mixing
0.5135
0.5130
0.5125
0.5120
0.5115
18.0
18.5
19.0
19.5
20.0
20.5
$^{143}Nd/^{144}Nd$
$^{206}Pb/^{204}Pb$

Figure 12

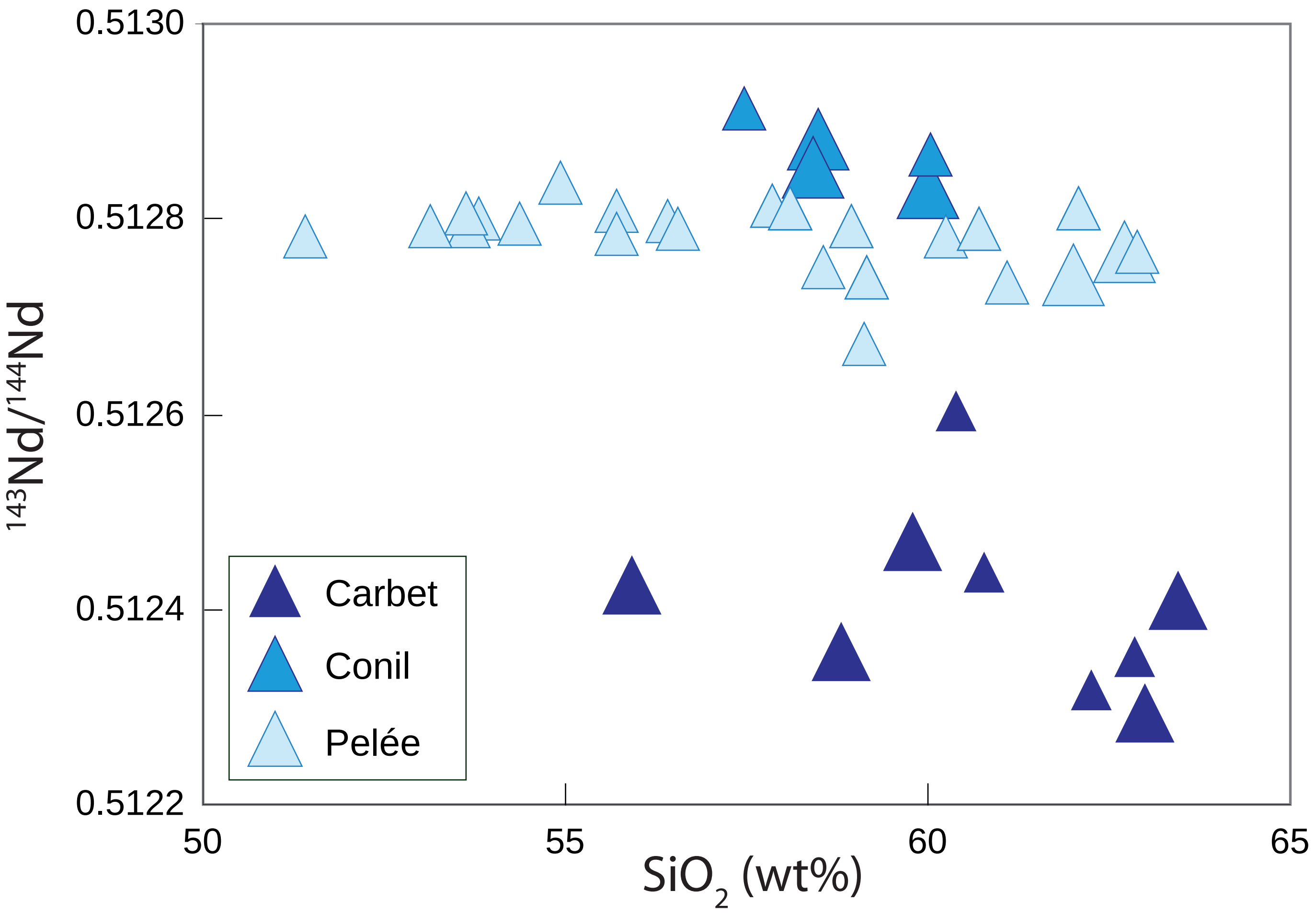

0.5130
0.5128
0.5126
0.5124
0.5122
$^{143}Nd/^{144}Nd$
50
55
60
65
SiO_2 (wt%)
Carbet
Conil
Pelée

Figure 13

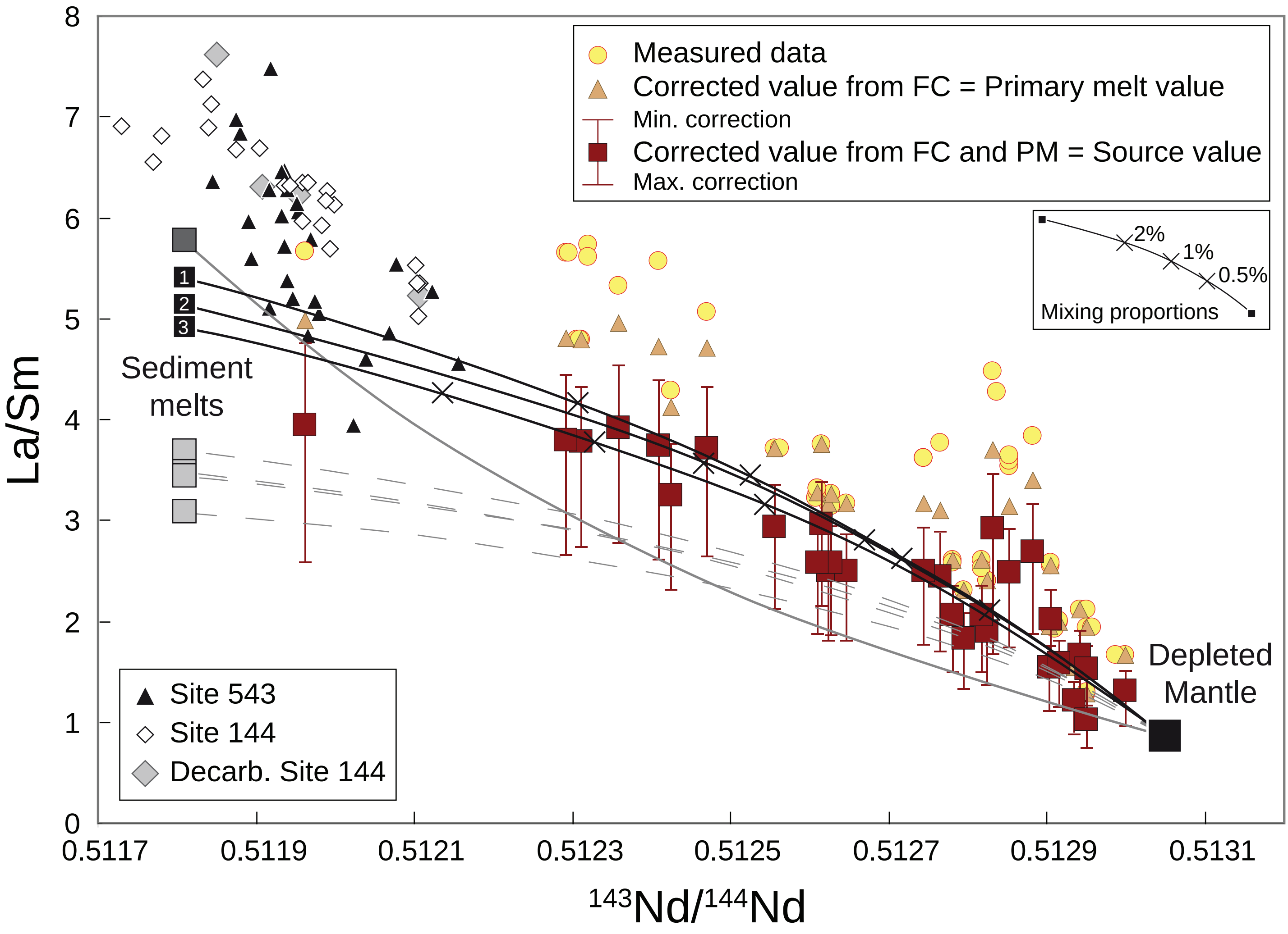

Measured data
Corrected value from FC = Primary melt value
Min. correction
Corrected value from FC and PM = Source value
Max. correction
2%
1%
0.5%
Mixing proportions
Site 543
Site 144
Decarb. Site 144
Sediment melts
1
2
3
Depleted Mantle
La/Sm
^{143}Nd/^{144}Nd
0
1
2
3
4
5
6
7
8
0.5117
0.5119
0.5121
0.5123
0.5125
0.5127
0.5129
0.5131

Figure 14

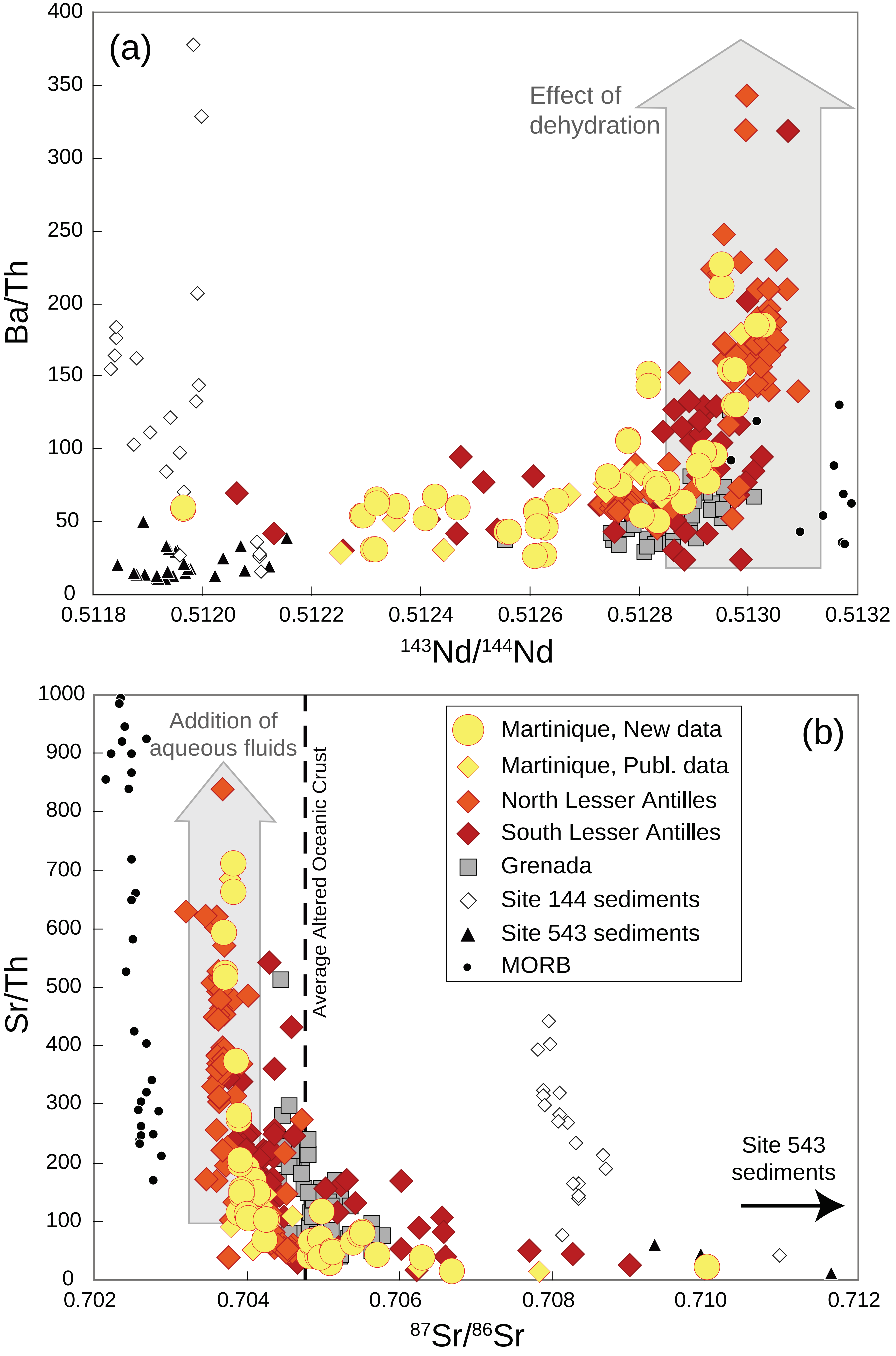

(a)
Effect of dehydration
Ba/Th
0
50
100
150
200
250
300
350
400
0.5118
0.5120
0.5122
0.5124
0.5126
0.5128
0.5130
0.5132
^{143}Nd/^{144}Nd
(b)
Addition of aqueous fluids
Average Altered Oceanic Crust
Martinique, New data
Martinique, Publ. data
North Lesser Antilles
South Lesser Antilles
Grenada
Site 144 sediments
Site 543 sediments
MORB
Site 543 sediments
Sr/Th
0
100
200
300
400
500
600
700
800
900
1000
0.702
0.704
0.706
0.708
0.710
0.712
^{87}Sr/^{86}Sr

Figure 15

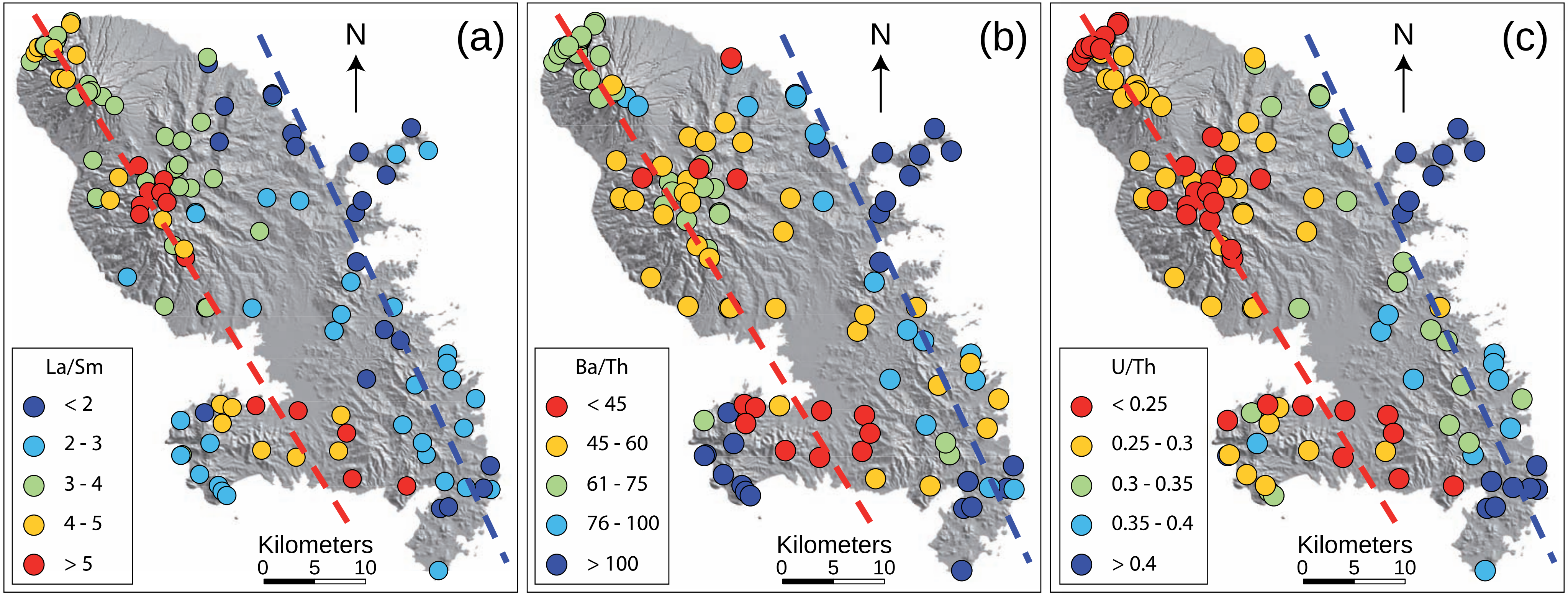

(a)
(b)
(c)
N
La/Sm
< 2
2 - 3
3 - 4
4 - 5
> 5
Ba/Th
< 45
45 - 60
61 - 75
76 - 100
> 100
U/Th
< 0.25
0.25 - 0.3
0.3 - 0.35
0.35 - 0.4
> 0.4
Kilometers
0
5
10

Figure 16

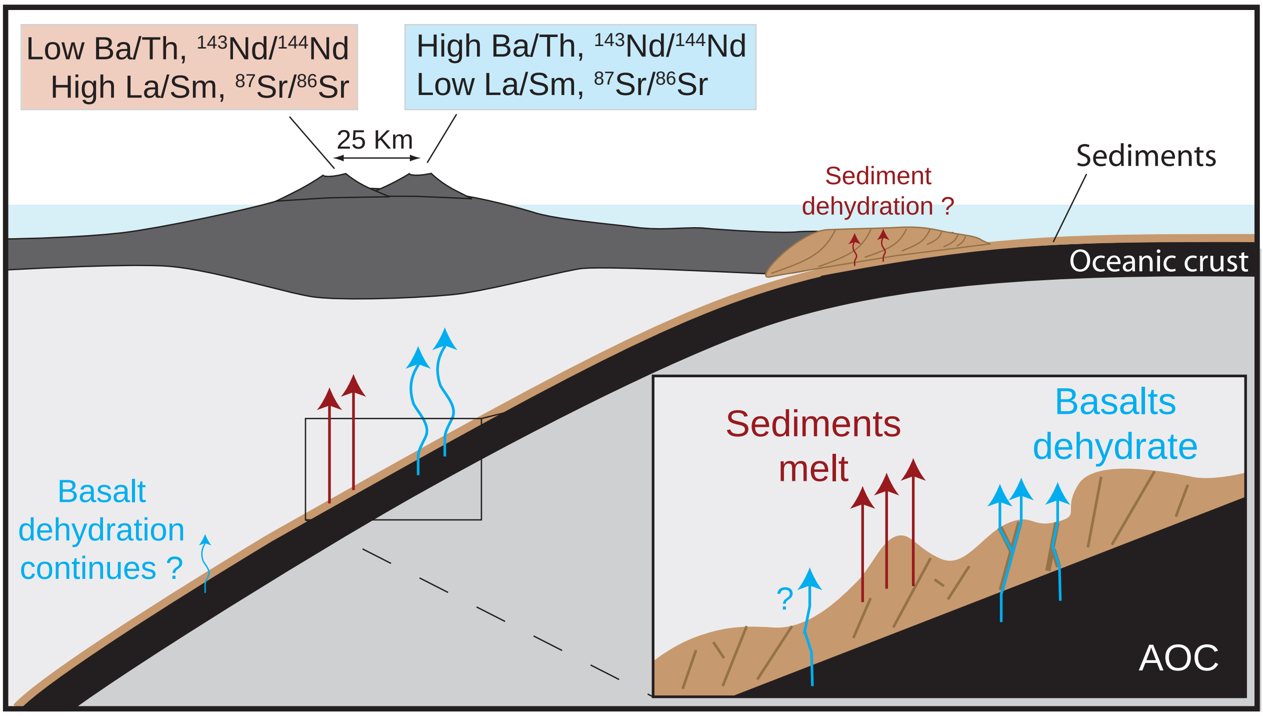

Low Ba/Th, ^{143}Nd/^{144}Nd
High La/Sm, ^{87}Sr/^{86}Sr
High Ba/Th, ^{143}Nd/^{144}Nd
Low La/Sm, ^{87}Sr/^{86}Sr
25 Km
Sediment dehydration ?
Sediments
Oceanic crust
Basalt dehydration continues ?
Sediments melt
Basalts dehydrate
?
AOC

Figure 17

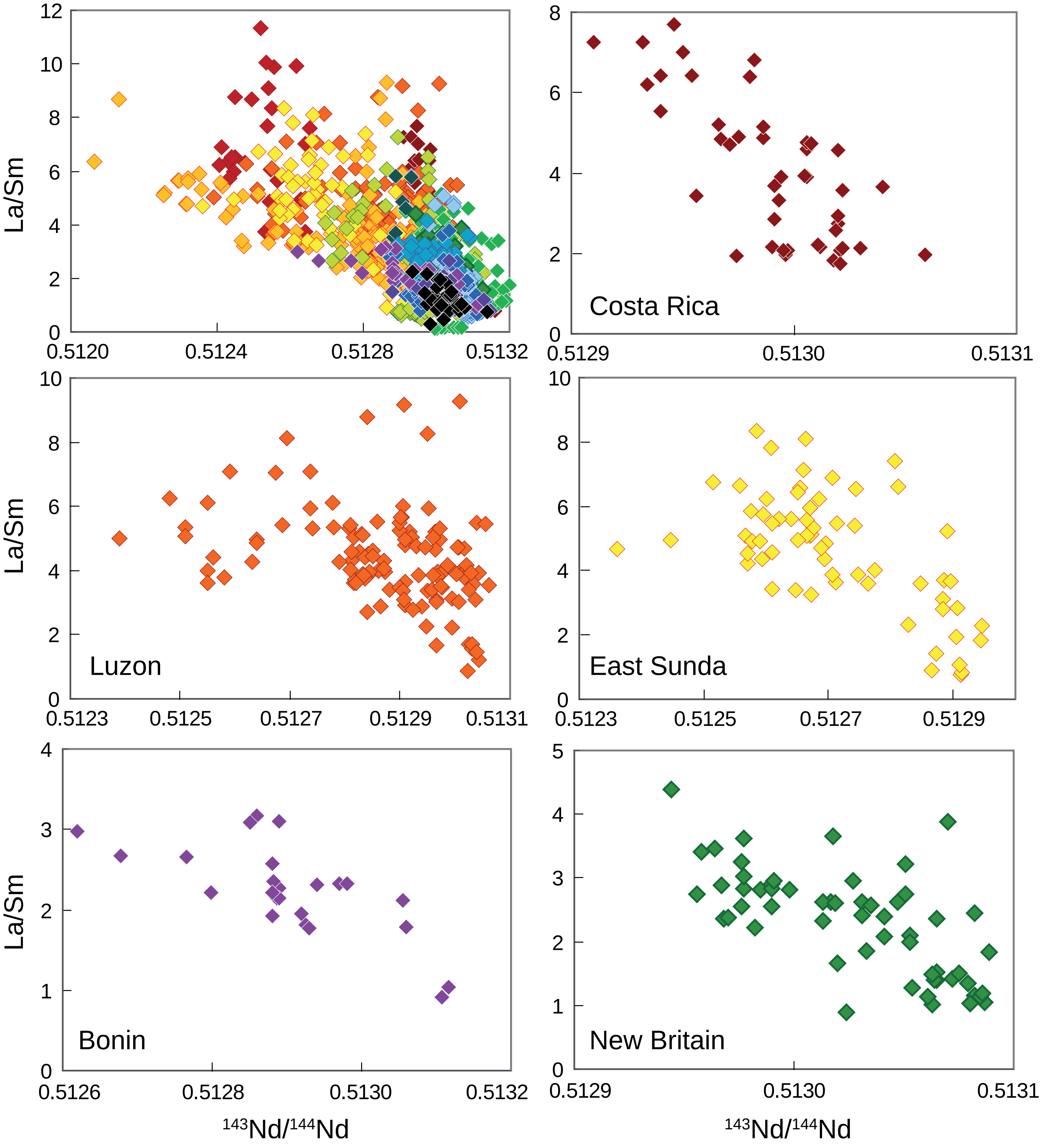
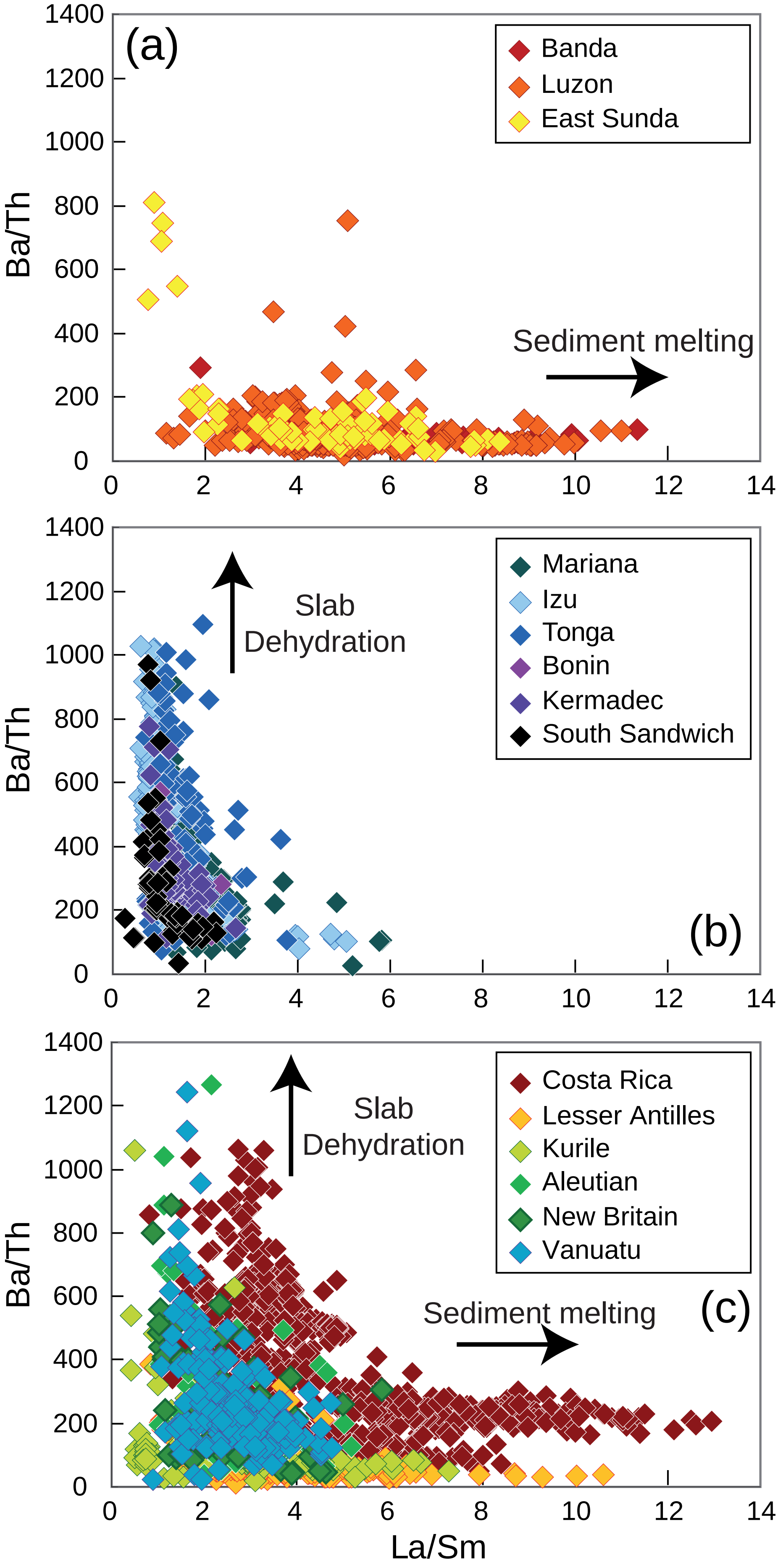

La/Sm
12
10
8
6
4
2
0
0.5120
0.5124
0.5128
0.5132
8
6
4
2
0
0.5129
0.5130
0.5131
Costa Rica
La/Sm
10
8
6
4
2
0
0.5123
0.5125
0.5127
0.5129
0.5131
Luzon
10
8
6
4
2
0
0.5123
0.5125
0.5127
0.5129
East Sunda
La/Sm
4
3
2
1
0
0.5126
0.5128
0.5130
0.5132
Bonin
5
4
3
2
1
0
0.5129
0.5130
0.5131
New Britain
^{143}Nd/^{144}Nd
^{143}Nd/^{144}Nd

Figure 18



(a)
Banda
Luzon
East Sunda
Sediment melting
Ba/Th
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
(b)
Mariana
Izu
Tonga
Bonin
Kermadec
South Sandwich
Slab Dehydration
Ba/Th
(c)
Costa Rica
Lesser Antilles
Kurile
Aleutian
New Britain
Vanuatu
Slab Dehydration
Sediment melting
Ba/Th
La/Sm

Table 1

Arc	**Slab surface** **Depth**	**Pressure**	**Temperature**	**T of the solidus at P of slab surface**	**Can sediments melt?**	**Are there high La/Sm lavas?**
	Km	Gpa	℃	℃		
		Syracuse et al. (2010)		*Hermann and Spandler (2006)*		
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 and Abers (2006) for the three easternmost islands of the section called Bali/Lombok