frontiers in Earth Science

ORIGINAL RESEARCH
published: 25 May 2021
doi: 10.3389/feart.2021.682583

Isotopic Compositions of Plagioclase From Plutonic Xenoliths Reveal Crustal Assimilation Below Martinique, Lesser Antilles Arc

J. R. Brown[1], G. F. Cooper[2], G. M. Nowell[1], C. G. Macpherson[1], I. Neill[3] and J. Prytulak[1]*

[1]Department of Earth Sciences, Durham University, Durham, United Kingdom, [2]School of Earth and Ocean Sciences, Cardiff University, Cardiff, United Kingdom, [3]School of Geographical and Earth Sciences, University of Glasgow, Glasgow, United Kingdom

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***Correspondence:**
J. R. Brown
joshua.r.brown@durham.ac.uk

Specialty section:
This article was submitted to Petrology, a section of the journal Frontiers in Earth Science

Received: *18 March 2021*
Accepted: *11 May 2021*
Published: *25 May 2021*

Citation:
Brown J R, Cooper GF, Nowell GM, Macpherson CG, Neill I and Prytulak J (2021) Isotopic Compositions of Plagioclase From Plutonic Xenoliths Reveal Crustal Assimilation Below Martinique, Lesser Antilles Arc. Front. Earth Sci. 9:682583. doi: 10.3389/feart.2021.682583

The chemical and isotopic compositions of volcanic arc lavas often show evidence for involvement of a sedimentary component during magma genesis. Determining where this sedimentary component is added to arc magmas is of vital importance for constraining the extent to which sediments and volatiles are recycled at subduction zones. Lavas from Martinique in the Lesser Antilles arc have wide ranging isotopic compositions extending to highly radiogenic values (e.g. $^{87}/Sr/^{86}Sr$ up to ~0.710) that could, in principle, be explained by sediment addition to the mantle source or by crustal assimilation in the upper plate. We use Sr isotopic compositions of plagioclase from Martinique plutonic xenoliths to provide evidence supporting the crustal assimilation hypothesis. Plagioclase from plutonic xenoliths formed in the mid-crust (~12 km) show a restricted range of unradiogenic Sr isotope ratios ($^{87}Sr/^{86}Sr$ = 0.7041–0.7042) whereas plagioclase from upper crustal plutonic xenoliths (~6 km) show greater intra-sample variation and more radiogenic Sr isotopic compositions up to $^{87}Sr/^{86}Sr$ = 0.7047. This trend is also observed in plutonic xenolith whole rock $^{87}Sr/^{86}Sr$. Combined, these results indicate that the range of Sr isotope compositions becomes larger and more radiogenic in Martinique magmas as a result of sediment assimilation at shallow crustal levels. This is supported by Assimilation-Fractional Crystallization modeling, which shows that assimilation of chemically and isotopically heterogenous crustal sediments can produce the isotopic variation in Martinique plutonic xenoliths and lavas. Our results highlight the importance of constraining crustal contributions from the upper plate before using arc lava geochemistry to quantify sediment and volatile recycling at subduction zones and assessing potential heterogeneity of arc mantle sources.

Keywords: crustal sediment assimilation, plutonic xenoliths, strontium isotopes, lesser antilles arc, plagioclase, martinique

INTRODUCTION

The chemical and isotopic compositions of arc magmas are generally considered to reflect contributions from the mantle wedge combined with fluids and/or melts derived from subducting oceanic crust and sediments (e.g. Kelemen et al., 2003 and references therein). Many arc magmas have trace element and isotopic compositions displaced from MORB toward crustal compositions (e.g. Davidson et al., 2005), which may be explained by input from the subducting slab, or assimilation of arc crust during magma ascent and storage. Geochemical constraints upon the relative importance of slab vs. upper plate contributions to arc magmas have clear implications for understanding sediment recycling at subduction zones. Trace element contents of lavas have been combined with estimates of the trace element input from subducting sediments to perform mass balance calculations to determine the extent of sediment recycling (e.g. Plank and Langmuir, 1993). However, modification of trace element concentrations in arc lavas by assimilation of crustal material can cause misleading estimates of the amount of sediment recycled into the mantle. Similar calculations have been used to assess recycling of volatiles e.g. CO_2 at subduction zones (Bebout et al., 2014 and references therein). Assimilation of crustal sediments also modifies the volatile budget of arc magmas (e.g. Chadwick et al., 2007; Deegan et al., 2010), which in turn affects eruption explosivity, hence it is vital to constrain the relative contributions of the overlying vs. subducting plate to quantify recycling in arc systems.

Lavas from the intra-oceanic Lesser Antilles arc (LAA, **Figure 1**) are notable for their extreme range in radiogenic isotopic compositions, extending from MORB-like signatures to highly radiogenic, "*crustal/sedimentary*" values (**Figure 2**; Davidson, 1985; Davidson, 1986; Davidson et al., 1987; Davidson and Harmon, 1989; Van Soest, 2000; Labanieh et al., 2010; Bezard et al., 2014). Lavas show radiogenic isotopic variation both along the arc and at individual volcanic centers (**Figure 3**). Lavas from the island of Martinique span the whole Sr, Nd and Pb isotopic range of the arc (**Figures 2**, **3**, Nd isotopes not shown), and therefore provide an ideal suite to investigate the cause(s) of these variations.

The large isotopic variation in the LAA, and in particular Martinique lavas, has been interpreted as the result of variable sediment addition (White and Dupre, 1986; Davidson et al., 1987; Carpentier et al., 2008). However, there exists significant debate as to whether the sedimentary component is 1) added to the mantle wedge from subducting sediments (White and Dupre, 1986; Carpentier et al., 2008; Labanieh et al., 2010; Labanieh et al., 2012; Hu et al., 2021), or 2) incorporated during magma ascent and storage in the upper plate, *via* assimilation of unsubducted crustal sediments (Davidson, 1985, Davidson, 1986; Davidson et al., 1987; Davidson and Harmon, 1989; Smith et al., 1996; Van Soest et al., 2002; Davidson and Wilson, 2011; Bezard et al., 2014).

The majority of previous studies have used whole rock radiogenic isotopic compositions of arc lavas to assess the origin of the crustal signature, but there are potential issues with this approach. Crystals formed in different parts of a magma plumbing system record the isotopic composition of the magmas from which they grew. Whole rock compositions average the isotopic signatures of individual components e.g. crystals and groundmass, hence evidence for changes in isotopic composition of magmas during storage in the crust (recorded by the crystals) may be lost. The use of lavas may also

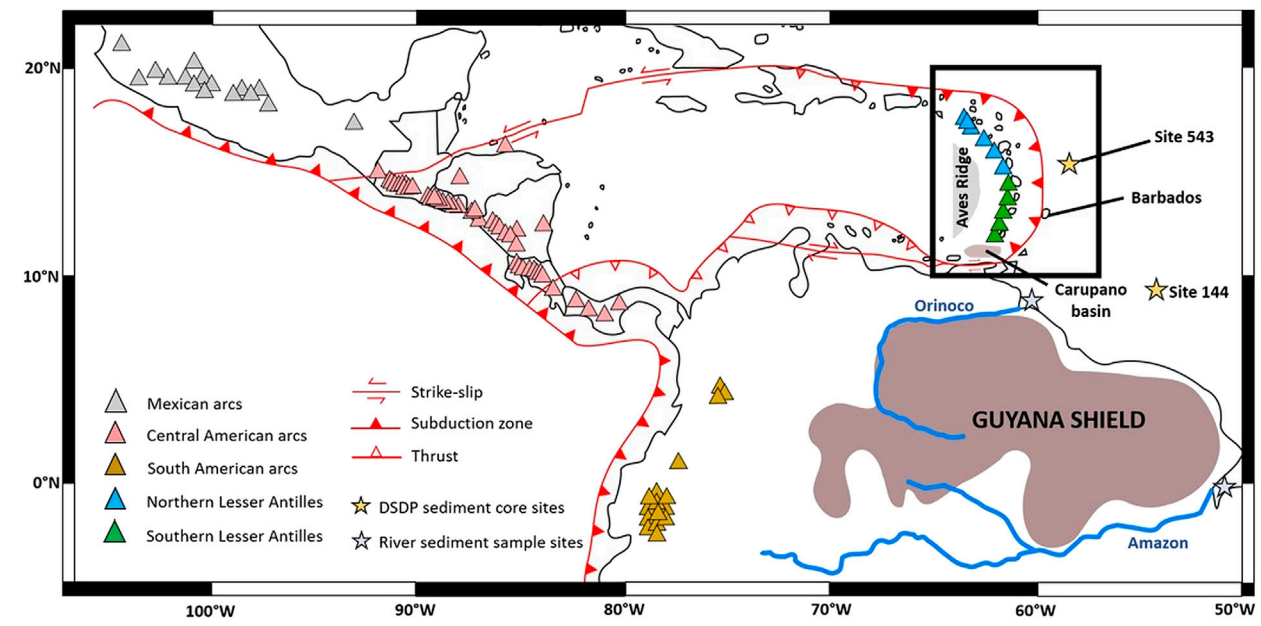

FIGURE 1 | Tectonic setting of Lesser Antilles arc (outlined by black box) and nearby arcs in Central-South America. The sampling sites of sediments discussed in *Potential Sediment Sources* are labeled. Locations of Site 543 and Site 144 from Carpentier et al. (2008). Locations for Orinoco and Amazon samples from Allegre et al. (1996); Parra et al. (1997) and Rousseau et al. (2019).

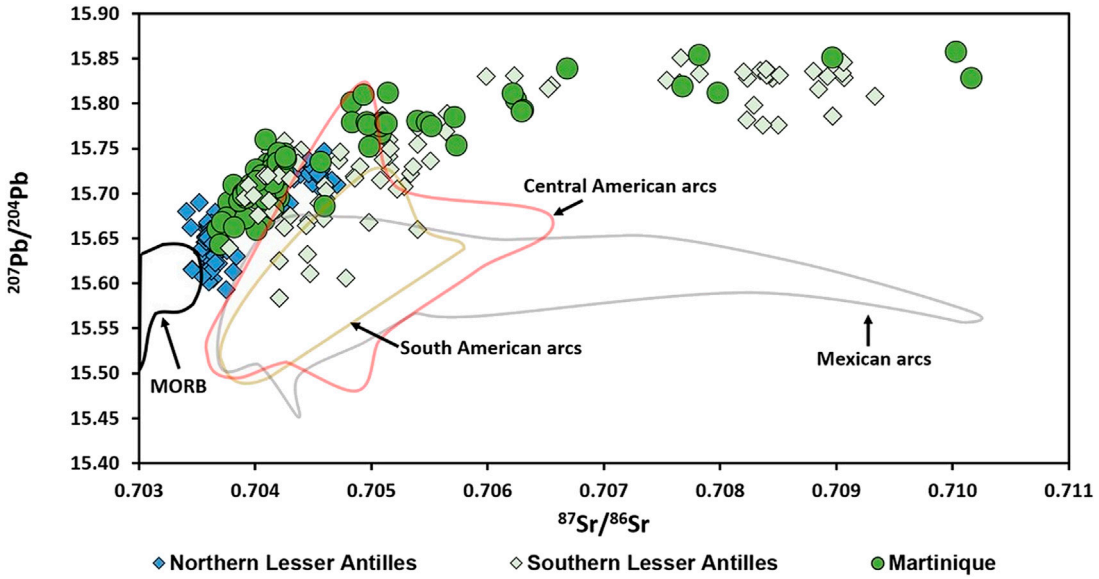

FIGURE 2 | $^{87}Sr/^{86}Sr$ vs. $^{207}Pb/^{204}Pb$ of lavas from the Lesser Antilles arc, compared to nearby arcs from Central-South America shown in **Figure 1**. For all data points, uncertainty (2 SE) is smaller than symbol size. Northern Lesser Antilles = Saba to Dominica. Southern Lesser Antilles = Martinique to Grenada (Martinique data shown separately). **Data sources:** Northern Lesser Antilles—Van Soest et al. (2002); Lindsay et al. (2005); Toothill et al. (2007); DuFrane et al. (2009); Davidson and Wilson (2011). Southern Lesser Antilles–Thirlwall and Graham (1984); Davidson (1986); White and Dupre (1986); Smith et al. (1996); Thirlwall et al. (1996); Turner et al. (1996); Heath et al. (1998); Labanieh et al. (2010); Huang et al. (2011); Bezard et al. (2014). Southern American, Central American and Mexican arc data from the Georoc database (http://georoc.mpch-mainz.gwdg.de/georoc/). MORB data from the PetDB database (www.earthchem.org/petdb) for Mid-Atlantic Ridge basalts 30° either side of the equator. Labanieh et al. (2010) found that the difference between measured and age corrected isotope ratios for the oldest lavas in the arc (~25 Ma, from Martinique) was negligible. Since majority of lavas in the LAA are much younger than 25 Ma, age correction is considered negligible by majority of authors and would not alter the trend shown.

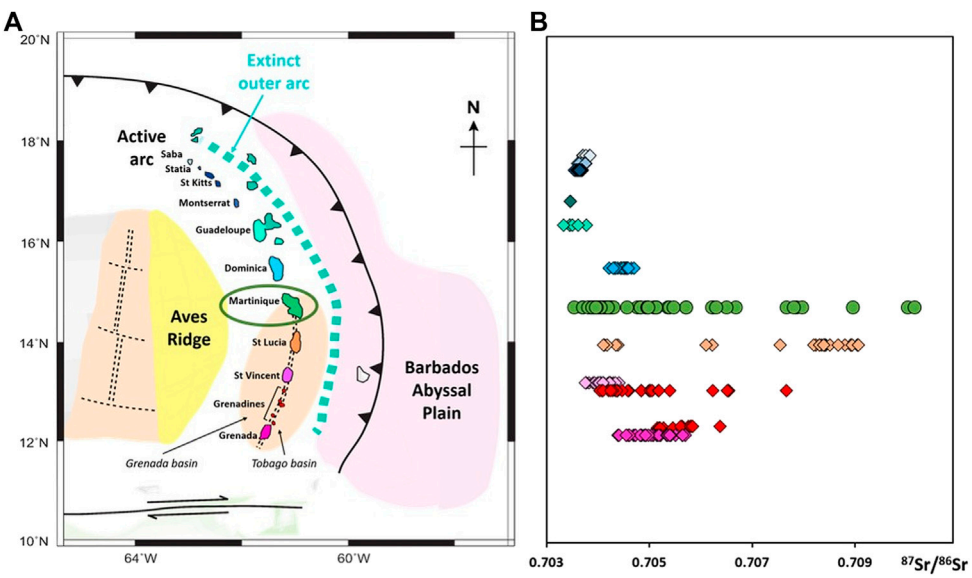

FIGURE 3 | (A) Map of Lesser Antilles arc (region marked by black outlined box on **Figure 1**) modified from Allen et al. (2019). **(B)** Compilation of along arc variation in $^{87}Sr/^{86}Sr$ of lavas. For all data points, uncertainty (2 SE) is smaller than symbol size. Data sources are the same as **Figure 2**. Note that the same along arc trends are also observed in the Nd and Pb isotopic systems.

be problematic since late stage processes such as magma mixing and/or subaerial alteration have the potential to overprint processes occurring deeper in the crust (e.g. Davidson et al., 2007). In addition, the mid to lower crust of the upper plate is probably a key location for the differentiation of arc lavas (e.g. the "Deep Crustal Hot Zone" of Annen et al., 2006). Finally, arc lavas travel from their mantle

source through the crust before they are erupted. Even when fresh arc lava chemistry unambiguously indicates a sedimentary component, it is extremely challenging to determine where that component was incorporated.

To overcome these ambiguities, this study explores plagioclase from plutonic xenoliths and their Sr isotopic compositions. The LAA is notable for its abundant plutonic xenoliths (e.g., Arculus and Wills, 1980; Melekhova et al., 2019), which represent deeper parts of the magmatic plumbing system. We focus on samples from Martinique due to its well-established variability in whole rock lava compositions and compare our findings with the more isotopically restricted island of St Vincent (**Figure 3**). These Martinique plutonic xenoliths record crystallization conditions at 21—6 km depth in the crust (Cooper et al., 2016; Melekhova et al., 2019) and, therefore, have the potential to record the isotopic composition of magmas throughout the crust. Previous studies have employed the $^{87}Sr/^{86}Sr$ isotopic composition of plagioclase phenocrysts in erupted lavas to assess crustal assimilation at arc volcanoes (e.g. Davidson et al., 2007; Bezard et al., 2014; Ginibre and Davidson, 2014; Waight and Tornqvist, 2018). Plagioclase is ubiquitous in Lesser Antilles plutonic xenoliths. Strontium concentrations in plagioclase are high (generally >250 μg/g, Cooper et al., 2016), thus precise $^{87}Sr/^{86}Sr$ measurements can be achieved on microgram sized pieces extracted from crystals (Charlier et al., 2006). Here, we determine the Sr isotopic composition of crystal domains within individual plagioclase crystals in plutonic xenoliths from a range of depths in the arc crust. We aim to test whether or not the plutonic roots of Martinique already display a radiogenic Sr isotopic composition. A radiogenic composition (similar to the higher $^{87}Sr/^{86}Sr$ lavas) is expected if subducted sediments are incorporated into the mantle source, whereas less radiogenic compositions would support a dominant role for crustal contamination within the upper plate.

MATERIALS AND METHODS

Sample Suite

Plutonic xenoliths were collected between 2008 and 2017 during a series of field campaigns to the Lesser Antilles. Five plutonic xenoliths from Martinique (MQ1, MQ6, MQ35, MQ48, and MQ59) and one from St Vincent (VS36) were chosen as the focus of this study. These samples form part of a wider sample set characterized in terms of petrology, mineral chemistry and whole rock major and trace elements by Cooper et al. (2016) and Tollan et al. (2012), providing key context for plagioclase isotopic analyses. We also present whole rock Sr, Nd, and Pb isotope data for 15 of the characterized Martinique plutonic xenoliths to give further context to our plagioclase Sr isotope data. Samples were collected *ex situ*, mostly from river beds on the flanks of volcanic edifices. The Martinique xenoliths are inferred to be derived from eruptions of either Mt Pelee (0–126 ka) or Mt Conil (127–550 ka), the most recent phases of volcanic activity on the island (Germa et al., 2011; Cooper et al., 2016). The St Vincent xenolith is inferred to have been erupted at La Soufriere volcano (<3.6 ka, Heath et al., 1998; Tollan et al., 2012).

Samples show good textural equilibration (120° grain contacts, minor or no evidence for deformation). The relative equilibration depths of selected xenoliths were estimated by mineral geobarometry and comparison to experimental studies (Cooper et al., 2016; Melekhova et al., 2019). Calculated depths vary from 21 to 6 km, though large uncertainty exists on these estimates (typically ~6 km). This suggests that the plutonic xenoliths represent portions of the magmatic plumbing system covering the middle to upper crust.

Plagioclase from Martinique lava sample M8321 ($^{87}Sr/^{86}Sr$ = 0.706246; Davidson, 1986) were also analyzed for Sr isotopic composition. This is one of the most radiogenic Martinique lavas with plagioclase crystals large enough for isotopic analysis. The lava is from the emergent/subaerial phase of the Intermediate arc, dated at 9.2–8.4 Ma (Germa et al., 2011), in a period when the most radiogenic (highest $^{87}Sr/^{86}Sr$) lavas in Martinique were erupted (Davidson, 1986; Labanieh et al., 2010).

Sampling and Analytical Techniques

Details of sample and target crystal selection, micro-milling and analytical procedures are outlined briefly below and are described in detail in **Supplementary Files S1,S2**. All laboratory procedures were carried out at Durham University, in the G.J. Russell Electron Microscopy Facility and the Arthur Holmes Isotope Geology Laboratory.

Plutonic Xenolith Sample Selection

A subset of the plutonic xenoliths characterized by Cooper et al. (2016), with a variety of mineral assemblages, were chosen for plagioclase isotopic analyses. Selected plagioclase crystals cover a range of anorthite contents (**Supplementary File S1 and Table S1.1**). The plutonic xenolith from St Vincent was included to compare a nearby volcanic center with restricted isotopic variation (Heath et al., 1998; **Figure 3**).

Optical microscopy of 100 μm thick sections was used to identify suitable plagioclase crystals for micro-milling and isotopic analysis. Potential target crystals were defined as containing minimal cracks and inclusions, and distinct core and rim zones if present. Electron backscatter imaging (BSE) and chemical mapping using a Hitachi SU70 SEM was used to confirm the presence/lack of chemical zoning (details in **Supplementary File S1**). BSE images and chemical maps were then assessed to identify the most suitable plagioclase domain(s) for microanalysis.

Micro-Milling

Material was recovered from plagioclase *in situ*, using a New Wave Micromill. The micro-milling and sample recovery procedure closely followed Charlier et al. (2006) except that to maximize sample recovery trenches were milled rather than a series of conical holes as in the former study. Sampling trenches were 60 μm deep and of sufficient length to yield ≥3 ng Sr for analysis, based on calculations of volume of material removed during milling and assuming a minimum Sr concentration of 250 μg/g (based on plagioclase Sr concentration data from Cooper et al., 2016). During micromilling, care was taken to avoid inclusions wherever possible.

Chemical Separation and Measurement

Milled material was digested using 150 µl Teflon distilled (TD) 29 M HF:50 µl TD 16 M HNO_3 and refluxed overnight on a hotplate at 100°C. The solution was then evaporated to incipient dryness at 100°C and the residue taken up in 50 µl TD 16 M HNO_3. This solution was returned to the hotplate for 90 min, evaporated, and re-dissolved in 50 µl TD 16 M HNO_3. The solution was evaporated, taken up in 400 µl TD 3 M HNO_3 and refluxed at 100°C prior to Sr separation.

Strontium separation closely follows the procedure outlined in Charlier et al. (2006). Briefly, Sr was separated and purified *via* two passes through pre-cleaned Eichrom Sr spec resin. Samples were loaded on to the resin in 400 µl TD 3 M HNO_3. Matrix elements were eluted with 3 × 250 µl TD 3 M HNO_3 followed by Sr elution with 400 µl Milli-Q water. The Sr solutions were subsequently evaporated at 100°C. All samples and standards were analyzed for Sr isotope ratios on a Thermo Fisher Scientific Triton Plus Thermal ionization Mass Spectrometer (TIMS). Full details of the measurement protocol are given in **Supplementary File S2**.

External precision and accuracy were assessed *via* multiple measurements of NIST Sr standard NBS 987 throughout the period of analyses, of varying load sizes from 1 to 10 ng (i.e. of similar size to the samples). The average $^{87}Sr/^{86}Sr = 0.710259 \pm 0.000031$ (2σ, n = 33) agrees well with the accepted value of $^{87}Sr/^{86}Sr = 0.710248 \pm 0.000023$ 2σ (Thirlwall, 1991). Method accuracy was also assessed *via* seven repeat analyses of ~10 ng Sr loads of USGS reference material BCR-2. To avoid potential heterogeneity with the BCR-2 powder a single large digestion was made from which repeat 10 µl aliquots were taken and diluted with 390 µl TD 3 M HNO_3 prior to Sr separation. The average $^{87}Sr/^{86}Sr = 0.705041 \pm 0.000063$ (2σ, n = 7) agrees within uncertainty of the value of $^{87}Sr/^{86}Sr = 0.705013 \pm 0.000010$ 2σ obtained with TIMS analyses of BCR-2 by Weis et al. (2006).

Total procedural blanks measured 5–20 pg (n = 6) and column blanks 3–50 pg (n = 9), with all but one below 25 pg. Concentration checks on aliquots of sample solutions taken after Sr separation indicated that majority of samples contained >3 ng Sr, therefore blanks are typically <1% of sample size and any blank correction would be negligible.

Whole Rock Sr-Nd-Pb Isotopes

The plutonic xenoliths analyzed for major and trace element compositions by Cooper et al. (2016) were previously powdered and whole rock Sr, Nd, and Pb isotopes were determined on these powders using standard HF dissolution techniques and established column separation and measurement techniques. A more detailed description, including standard data, is found in **Supplementary File S2**.

RESULTS

Petrography

Petrography and Classification of Xenoliths

Plutonic xenoliths are identified as either "cumulates" or "non-cumulate gabbros" based on chemical and textural characteristics (Cooper et al., 2016). If the whole rock and mineral chemistry (and texture) are consistent with the xenolith originating as a subtractive assemblage it is identified as a cumulate. Otherwise, xenoliths are identified as non-cumulate gabbros (NCG), indicative of origin as solidified equivalents of potentially eruptible lavas, formed "without movement of crystals relative to host melts" (Cooper et al., 2016; Cooper et al., 2019). Based on these definitions, this study analyzed the Sr isotopic composition of plagioclase in four cumulates and two NCG's. Mineral phases include plagioclase (Pl), clinopyroxene (CPX), orthopyroxene (OPX), amphibole (Hornblende, Amph/Hbl), olivine (Ol), and oxides (Ox), which is typical of Lesser Antilles plutonic xenolith assemblages (Arculus and Wills, 1980; Tollan et al., 2012; Stamper et al., 2014; Cooper et al., 2016, Cooper et al., 2019; Melekhova et al., 2019). Xenoliths are classified based on mineral assemblage using the scheme of Streckeisen (1976), and textural features. Those in which plagioclase were analyzed cover almost the full range of plutonic xenolith types from Martinique identified by Cooper et al. (2016). The single investigated lava is a two-pyroxene andesite typical of Martinique (e.g. intermediate subaerial lavas from Davidson, 1986).

A detailed petrographic description of each sample is given in **Supplementary File S1**. The classification and petrographic observations listed for each plutonic xenolith sample are summarized from Cooper et al. (2016) and Tollan et al. (2012), supplemented by additional details on the characteristics of plagioclase, including SEM images showing the crystals selected for isotopic analysis.

How Representative are Selected Plagioclase?

Plagioclase crystals were chosen primarily for their suitability for micromilling, and care was taken to ensure that selected crystals were representative of each sample. All crystals analyzed from cumulates are characterized by a lack of zonation (excluding minor overgrowth rim zones too narrow to be targeted by micro-milling). Examples of typical unzoned cumulate plagioclase are shown in **Figure 4**. Where multiple plagioclase size populations were observed, e.g. MQ48, crystals from both populations were targeted. In NCG's, about half of the plagioclase crystals display normal zoning (examples shown in **Figure 4**), which provided an opportunity to assess changes in isotopic composition during their crystallization. All crystals selected from these samples display normal zoning, with both cores and rims analyzed. The three plagioclase crystals selected from lava M8321 display the three different zoning patterns (described in **Supplementary File S1**). In this sample cores, rims, and bulk groundmass were analyzed.

Geochemical Results

Plagioclase Sr isotopic data is presented in **Table 1** and plutonic xenolith whole rock Sr, Nd, and Pb isotopic data in **Table 2**. Rb/Sr ratios are very low (<0.01) in plutonic xenolith whole rock and plagioclase, and the maximum sample age is estimated at 25 Ma, hence age correction is negligible, with the exception of the M8321 groundmass data (see **Supplementary File S2** for age correction details).

Martinique Cumulate Plagioclase

Unzoned plagioclase from Martinique cumulates show a restricted range of unradiogenic Sr isotope ratios across all three samples ($^{87}Sr/^{86}Sr$ = 0.704059–0.704221) (**Figures 5**, **6**). Cumulate plagioclase $^{87}Sr/^{86}Sr$ slightly exceeds whole rock values (**Figure 6**).

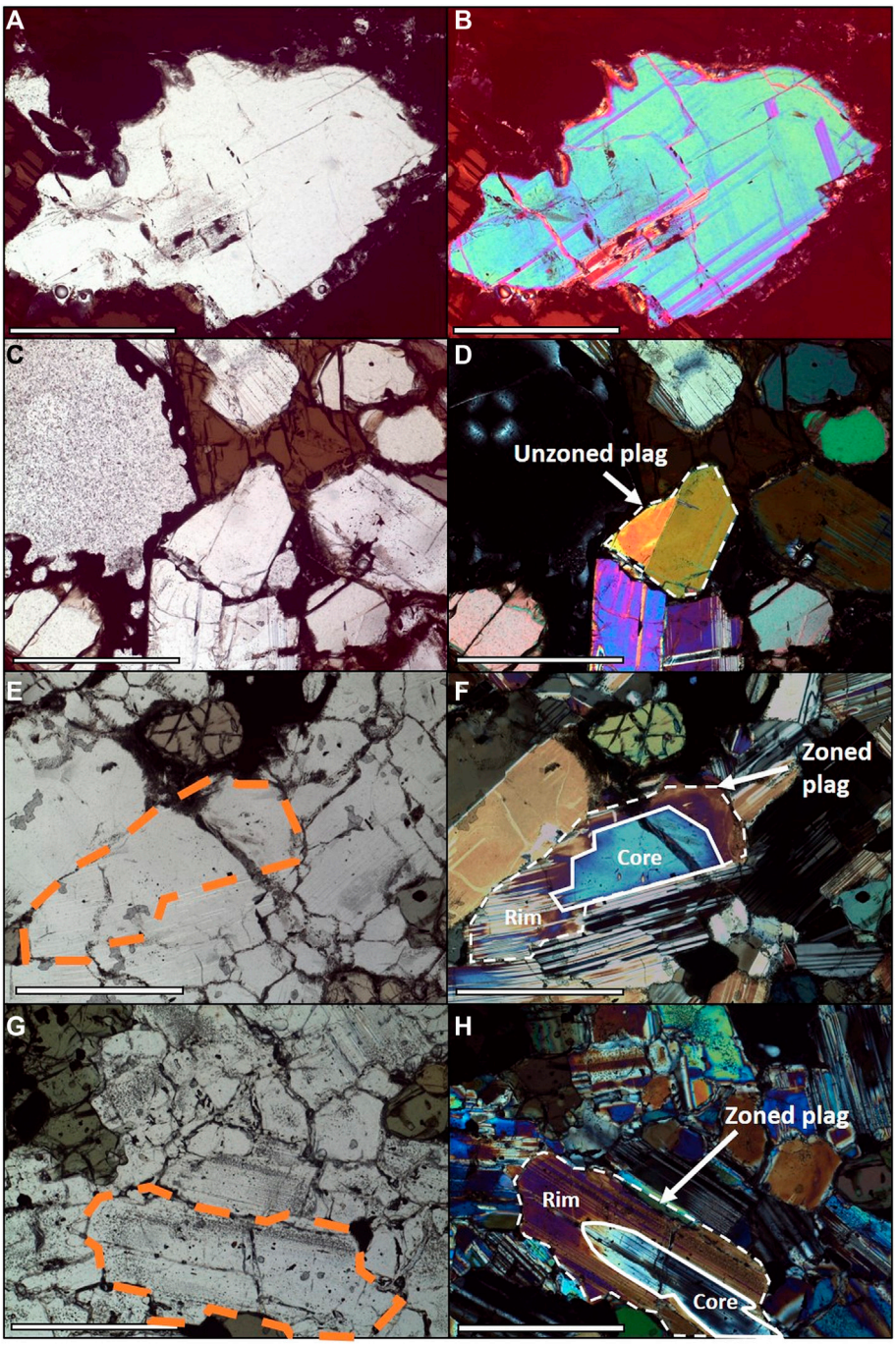

FIGURE 4 | (A) and **(B)** Typical unzoned cumulate plagioclase from sample MQ59. **(C)** and **(D)** Typical unzoned cumulate plagioclase from sample MQ48. **(E)** and **(F)** Typical zoned plagioclase in NCG sample MQ35. **(G)** and **(H)** Typical zoned plagioclase in NCG sample MQ6. Orange outlines in **(E)** and **(G)** highlight labeled zoned plagioclase in **(F)** and **(H)**. Images **(A), (C), (E)**, and **(G)** in PPL, **(B), (D,) (F)**, and **(H)** in XPL. White scale bar = 1 mm. Unusually high birefringence colors in XPL images are due to the 100 μm thickness of the sections.

Martinique Non-Cumulate Gabbro Plagioclase

Plagioclase cores from both NCG samples show greater intra-sample Sr isotopic variation than those of unzoned plagioclase in cumulates (**Figures 5**, **6**). MQ6 cores show a wider range in $^{87}Sr/^{86}Sr$ (0.703820–0.704334) than MQ35 cores (0.704576–0.704770). Within samples, plagioclase rim compositions show a more limited range in $^{87}Sr/^{86}Sr$ than cores (MQ6 = 0.703943–0.704058, MQ35 = 0.704622–0.704718) (**Figures 5**, **6**). No systematic variation in $^{87}Sr/^{86}Sr$ between core and rim is present in either sample. Notably, plagioclase in MQ35 is more radiogenic than that of cumulates. In

TABLE 1 | $^{87}Sr/^{86}Sr$ of individual plagioclase in cumulates, and core and rim zones of plagioclase in NCG's and lava. Whole rock $^{87}Sr/^{86}Sr$ also shown if available. Lava whole rock value from Davidson, (1986). SE = standard error.

Sample type	Sample and crystal no.	$^{87}Sr/^{86}Sr$	2 SE	Whole rock $^{87}Sr/^{86}Sr$
Cumulates	VS36—C1	0.703974	0.000012	—
	VS36—C2	0.704000	0.000008	—
	VS36—C3	0.703927	0.000011	—
	VS36—C4	0.703859	0.000038	—
	VS36—C5	0.703933	0.000007	—
	MQ1—C1	0.704191	0.000008	—
	MQ1—C2	0.704121	0.000006	—
	MQ1—C3	0.704202	0.000013	—
	MQ59—C1	0.704067	0.000006	0.704009
	MQ59—C2	0.704221	0.000014	—
	MQ59—C3	0.704077	0.000013	—
	MQ59—C4	0.704059	0.000009	—
	MQ59—C5	0.704077	0.000011	—
	MQ48—C1	0.704113	0.000020	0.703983
	MQ48—C2	0.704087	0.000012	—
	MQ48—C3	0.704086	0.000024	—
	MQ48—C4	0.704179	0.000010	—
NCG	MQ6 C1 core	0.703820	0.000012	—
	MQ6 C2 core	0.704055	0.000020	—
	MQ6 C3 core	0.703989	0.000014	—
	MQ6 C4 core	0.704334	0.000030	—
	MQ6 C1 rim	0.703943	0.000022	—
	MQ6 C2 rim	0.704058	0.000014	—
	MQ6 C3 rim	0.703971	0.000012	—
	MQ6 C4 rim	0.703996	0.000014	—
	MQ35 C1 core	0.704770	0.000014	0.704562
	MQ35 C2 core	0.704622	0.000009	—
	MQ35 C3 core	0.704576	0.000009	—
	MQ35 C1 rim	0.704718	0.000014	—
	MQ35 C2 rim	0.704622	0.000010	—
	MQ35 C3 rim	0.704692	0.000013	—
Andesitic lava	M8321 C1 core	0.706157	0.000016	0.706246
	M8321 C2 core	0.706219	0.000014	—
	M8321 C3 core	0.706259	0.000056	—
	M8321 C2 rim	0.706229	0.000021	—
	M8321 C3 rim	0.706185	0.000028	—
	M8321 GM1 9.2 Ma	0.706261	0.000007	—
	M8321 GM2 9.2 Ma	0.706286	0.000005	—
	M8321 GM3 9.2 Ma	0.706261	0.000012	—
	M8321 GM1 8.4 Ma	0.706282	0.000007	—
	M8321 GM2 8.4 Ma	0.706307	0.000005	—
	M8321 GM3 8.4 Ma	0.706282	0.000012	—

MQ35 $^{87}Sr/^{86}Sr$ in plagioclase is equivalent to or exceeds the whole rock value (**Figure 6**).

Martinique Andesitic Lava Plagioclase

Cores and rims in plagioclase from the andesitic lava (M8321) show a narrow range in $^{87}Sr/^{86}Sr$ (cores = 0.706157–0.706259, rims = 0.706185–0.706229), close to or within uncertainty of the whole rock value (**Figure 7**). Core-rim pairs have indistinguishable Sr isotopic compositions within uncertainty. Groundmass $^{87}Sr/^{86}Sr$ defines a very narrow range (0.706282–0.706307 corrected to 8.4 Ma, 0.706261–0.706286 corrected to 9.2 Ma).

St Vincent Cumulate Plagioclase

Unzoned plagioclase crystals from a single St Vincent cumulate (VS36) have restricted and unradiogenic Sr isotope ratios ($^{87}Sr/^{86}Sr$ = 0.703859–0.704000), with slightly less radiogenic compositions than Martinique cumulate plagioclase (**Figure 6**).

Martinique Plutonic Xenolith Whole Rock Data

Martinique cumulates show a narrow range in whole rock $^{87}Sr/^{86}Sr$ and unradiogenic compositions ($^{87}Sr/^{86}Sr$ = 0.703859–0.704087, **Figures 6**, **8**). NCG's show a wider range in whole rock $^{87}Sr/^{86}Sr$ and extend to slightly more radiogenic compositions ($^{87}Sr/^{86}Sr$ = 0.704069–0.704562, **Figures 6**, **8**).

Cumulates also show a restricted whole rock Nd isotopic range ($^{143}Nd/^{144}Nd$ = 0.512740–0.512830) which extends to slightly more unradiogenic compositions than NCG's ($^{143}Nd/^{144}Nd$ = 0.512790–0.512904) (**Figure 8**). Cumulate whole rock Pb isotopic compositions vary from $^{206}Pb/^{204}Pb$ = 19.11991–19.30179, $^{207}Pb/^{204}Pb$ = 15.68074–15.72108, and $^{208}Pb/^{204}Pb$ =

TABLE 2 | Whole rock $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ of cumulates and NCG's. SE = standard error.

Sample type	Sample	$^{87}Sr/^{86}Sr$	2 SE	$^{143}Nd/^{144}Nd$	2 SE	$^{206}Pb/^{204}Pb$	2 SE	$^{207}Pb/^{204}Pb$	2 SE	$^{208}Pb/^{204}Pb$	2 SE
Cumulates	MQ44	0.703863	0.000008	0.512764	0.000031	19.21881	0.00059	15.69934	0.00074	38.97973	0.00232
	MQ48	0.703983	0.000010	0.512740	0.000049	19.16035	0.00071	15.69339	0.00070	38.91686	0.00233
	MQ42	0.703984	0.000010	0.512760	0.000032	19.15504	0.00056	15.69051	0.00052	38.91513	0.00178
	MQ61	0.703913	0.000011	0.512820	0.000023	19.20034	0.00063	15.71063	0.00054	38.98981	0.00167
	MQ43	0.704087	0.000010	0.512784	0.000016	19.30179	0.00106	15.72108	0.00110	39.06616	0.00340
	MQ28	0.703859	0.000010	0.512818	0.000029	19.15996	0.00057	15.70016	0.00058	38.92992	0.00196
	MQ10	0.703932	0.000010	0.512784	0.000015	19.15353	0.00074	15.68784	0.00074	38.91756	0.00214
	MQ12	0.704046	0.000009	0.512830	0.000007	19.91055	0.00065	15.75423	0.00059	39.04088	0.00201
	MQ30	0.703920	0.000011	0.512803	0.000018	19.11991	0.00065	15.68074	0.00064	38.88149	0.00181
	MQ59	0.704009	0.000009	0.512804	0.000020	19.21250	0.00061	15.70008	0.00068	38.97948	0.00194
NCG	MQ2	0.704171	0.000011	0.512904	0.000010	19.28292	0.00069	15.71803	0.00064	39.05094	0.00201
	MQ45	0.704178	0.000010	0.512822	0.000012	19.41224	0.00066	15.73765	0.00066	39.17373	0.00198
	MQ35	0.704562	0.000010	0.512790	0.000009	19.40569	0.00063	15.73735	0.00063	39.16694	0.00216
NCG (mushy)	MQ20	0.704083	0.000010	0.512832	0.000008	19.33140	0.00076	15.72662	0.00069	39.10648	0.00219
	MQ67	0.704069	0.000010	0.512852	0.000011	19.29855	0.00079	15.71064	0.00081	39.04603	0.00252

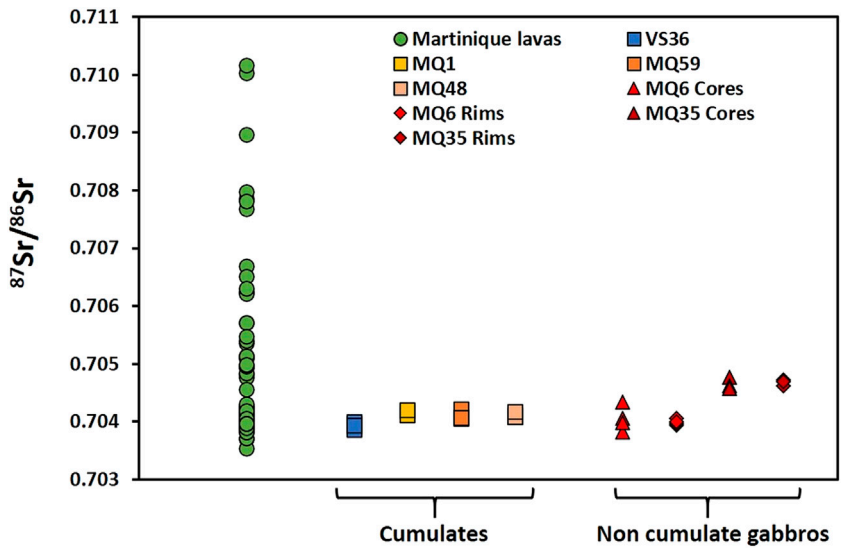

FIGURE 5 | $^{87}Sr/^{86}Sr$ of individual plagioclase in cumulates, and core and rim zones of plagioclase in NCG's, compared with the whole rock $^{87}Sr/^{86}Sr$ range of Martinique lavas. Lava data from Davidson (1986) and Labanieh et al. (2010). For all data points, uncertainty (2 SE) is smaller than symbol size.

38.88149–39.06616 (**Figure 8**), excluding sample MQ12, which represents a clear outlier with anomalously high $^{206}Pb/^{204}Pb$ (19.91055) and $^{207}Pb/^{204}Pb$ (15.75423). NCG's show a slightly more radiogenic range in whole rock Pb isotopic compositions (**Figure 8**), with $^{206}Pb/^{204}Pb$ = 19.28292–19.41226, $^{207}Pb/^{204}Pb$ = 15.71064–15.73765, and $^{208}Pb/^{204}Pb$ = 39.04603–39.17373.

DISCUSSION

The new Sr isotopic data from plutonic xenoliths is used to test whether the crustal/sedimentary component in Martinique lavas is introduced from the subducting slab or upper plate crust. We first discuss the chemical characteristics of potential sediment sources on the subducting plate and in the arc crust. We then explain how the data supports the crustal sediment assimilation hypothesis. Assimilation-Fractional Crystallization modeling is used to attempt to quantify the amount of sediment addition and provide constraints on the type of sediments assimilated. Finally, the wider implications of these findings for magma genesis and subduction zone recycling processes in the LAA and other arcs are discussed.

Potential Sediment Sources

If a sediment component is responsible for the range of isotopic compositions measured in Martinique lavas, then it must have more radiogenic Sr and Pb and less radiogenic Nd isotope compositions than the most extreme Martinique lava (**Figure 8A**). The lithological and chemical characteristics of

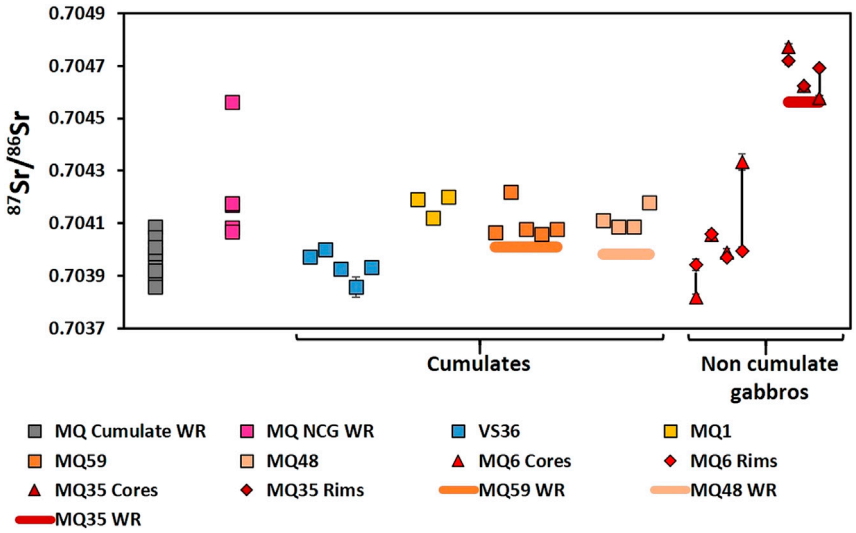

FIGURE 6 | Details of $^{87}Sr/^{86}Sr$ variation in cumulate and NCG plagioclase. The whole rock $^{87}Sr/^{86}Sr$ range for Martinique cumulates and NCG's is plotted for comparison. Whole rock data for individual samples shown as colored bars (bar width covers uncertainty). Where visible, black bars show uncertainty (2 SE), otherwise uncertainty is smaller than symbol size. Core-rim pairs are joined by tie lines.

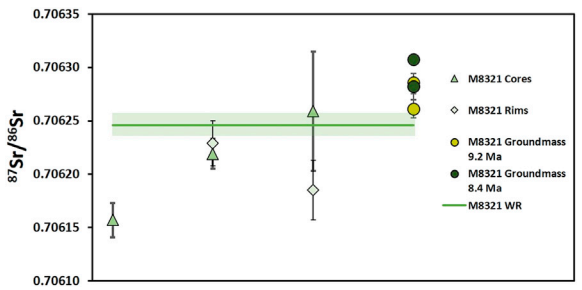

FIGURE 7 | Details of $^{87}Sr/^{86}Sr$ variation in lava sample M8321. The whole rock value from Davidson (1986) is plotted for comparison. Black and gray bars (and green box around the WR value) show uncertainty (2 SE).

the two main potential sediment sources—the slab and the arc crust—are discussed below.

Subducting Slab

Potential analogues to sediments subducting below the Lesser Antilles arc (LAA) come from Deep Sea Drilling Program (DSDP) Sites 543 and 144 in the Atlantic Ocean, and Barbados (Carpentier et al., 2008; Labanieh et al., 2010; **Figure 1**). These sediments are probably similar to those subducted based on their location and age relative to the age of oceanic crust at the trench (Carpentier et al., 2008). Sediments at DSDP Site 543 (<16–82 Ma) are mostly carbonate-free pelagic clays, in contrast to DSDP Site 144 sediments (29–104 Ma) which are mostly calcareous and include a distinctive black shale unit (Carpentier et al., 2008). Sediments from both sites contain a component of South American continental material delivered by the Amazon and Orinoco rivers (**Figure 1**; Carpentier et al., 2008). The variation in radiogenic isotopic composition of Site 543 and Site 144 sediments with depth is presented and compared with the isotopic range of Martinique lavas in **Figure 9**. Both Site 543 and Site 144 contain sediments with sufficiently radiogenic Sr and unradiogenic Nd isotopic compositions to represent a viable end member for Martinique lavas, while Site 144 sediments also have adequately radiogenic Pb isotopic compositions.

Sediments from Barbados include carbonate poor terrigenous claystones and sandstones, marls and chalks, with ages between 57 and 15 Ma (Carpentier et al., 2008). They are mixtures of detrital material from South America and volcanigenic material from the LAA and surrounding arcs (Carpentier et al., 2008; Carpentier et al., 2009). The radiogenic isotopic compositions of Barbados sediments are compared with Martinique lavas in **Figure 8**. Carpentier et al. (2008) noted that a mixture of the most radiogenic Barbados and Site 543 compositions represents a suitable sediment end member for Martinique (and Lesser Antilles) lavas.

Arc Crust

Recent tectonic models based on seismic and magnetic data show that the arc crust below the southern LAA (Martinique to Grenada) consists of oceanic crust and sedimentary cover of the formerly contiguous Grenada and Tobago basins (**Figure 3**) (Aitken et al., 2011; Allen et al., 2019). Fragments of dismembered Jurassic-Palaeocene age oceanic island arc terranes may also be present in the LAA basement (Neill et al., 2013). Tectonic reconstructions suggest that the region currently occupied by the southern LAA has been a site of sediment deposition since the Eocene (Escalona and Mann, 2011), supporting the idea that the arc, active since 25 Ma (Germa et al., 2011), was built through Grenada-Tobago basin sediments. These sediments comprise the upper few km of crust, thickening away from the centers of arc

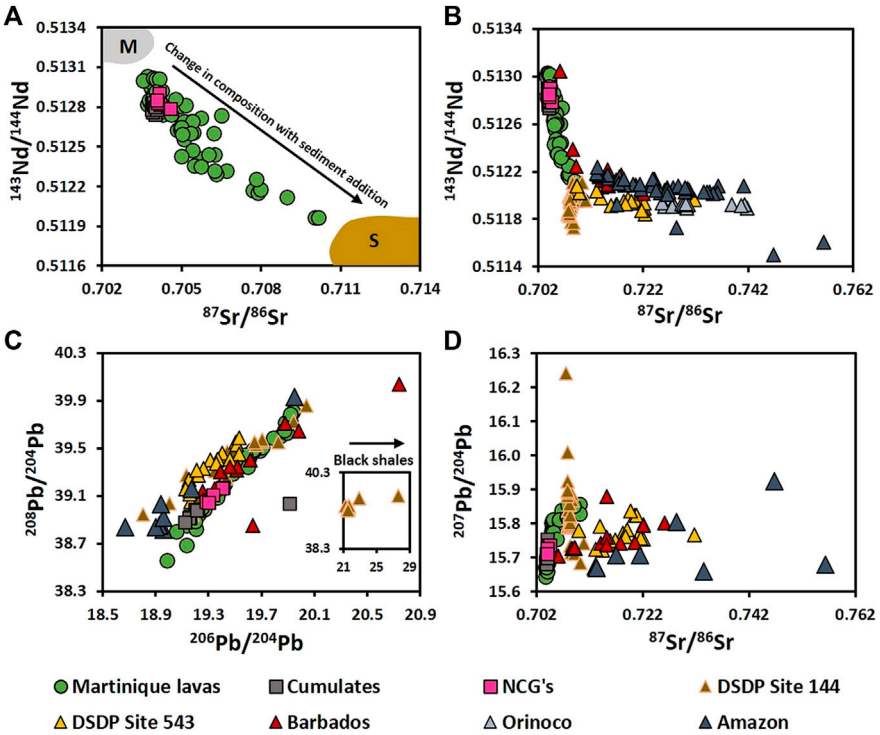

FIGURE 8 | (A) Whole rock $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$ for Martinique lavas and plutonic xenoliths (this study), with schematic fields for mantle (M) and sediment (S) end members. As shown, a suitable sediment end member is likely to have more radiogenic Sr and less radiogenic Nd than the lavas. **(B), (C), and (D)** $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$, $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$, and $^{87}Sr/^{86}Sr$ vs. $^{207}Pb/^{204}Pb$, respectively, for Martinique lavas and plutonic xenoliths (this study), potential equivalents to subducted sediments (Site 543, Site 144, Barbados) and sediments from the Orinoco and Amazon rivers. Inset in **C)** shows data for black shale unit of Site 144. For all data points, uncertainty (2 SE) is smaller than symbol size. **Data sources:** Martinique lavas—Davidson (1986), Labanieh et al. (2010). Site 543, Site 144 and Barbados—Carpentier et al. (2008); Carpentier et al. (2009). Amazon—Allegre et al. (1996); Parra et al. (1997); Viers et al. (2008); Rousseau et al. (2019). Orinoco—Parra et al. (1997); Rousseau et al. (2019).

magmatism, reaching total thicknesses of 13–14 km (Aitken et al., 2011).

To the best of our knowledge, sediment samples from the Grenada and Tobago basins are not available, hence the type and chemical characteristics of the sediments cannot be directly constrained. However, Aitken et al. (2011) used seismic data to identify sedimentary lithologies in the two basins *via* correlation with well logs in the Carupano Basin (**Figure 1**), to the south, and uplifted sediments on the Grenadine Islands considered equivalent to deep Grenada basin sediments (Speed et al., 1993). Lithologies include turbidites, pelagic siltstones and marls, limestones, and shales (Aitken et al., 2011). Similar lithologies, along with a greater shale component and minor sandstone, are present in the Carupano Basin (Ysaccis, 1997). These studies suggest that sediments in the southern LAA crust are likely to be highly heterogeneous.

Data from modern sediments derived from the same sources as Grenada-Tobago basin sediments can provide constraints on the isotopic composition of sediments in LAA crust. From the Eocene to mid-Miocene (49–11.2 Ma), Grenada-Tobago basin sediments were sourced from the South American continent (Aitken et al., 2011). Sediment derived from uplifted Andean terranes and the Guyana shield was supplied by the proto-Maracaibo and Orinoco rivers (Xie et al., 2010; Escalona and Mann, 2011; Rojas-Agramonte et al., 2017). The present-day Orinoco and Amazon rivers also drain the Andes and Guyana shield (Rojas-Agramonte et al., 2017; Rousseau et al., 2019), hence the isotopic composition of sediments from these rivers is likely to be analogous to the sediments in the LAA crust.

The Amazon and Orinoco rivers drain old cratonic material with suspended sediment and clay typically having highly radiogenic $^{87}Sr/^{86}Sr$ (0.7132–0.7564) and unradiogenic $^{143}Nd/^{144}Nd$ (0.5122–0.5115) (Allègre et al., 1996; Parra et al., 1997; Viers et al., 2008; Rousseau et al., 2019) (**Figure 8B**). The limited Pb isotope data are typically less radiogenic than most Martinique lavas, though highly radiogenic samples ($^{206}Pb/^{204}Pb$ = 19.95, $^{207}Pb/^{204}Pb$ = 15.924, $^{208}Pb/^{204}Pb$ = 39.93) have been reported (Allègre et al., 1996) (**Figures 8C,D**). Based on these data, it is plausible that sediments within LAA crust have the highly radiogenic Sr and Pb, and unradiogenic Nd isotopic compositions required to produce the isotopic variation in Martinique lavas. Since sediments at Sites 543 and 144 also include material from the Amazon and Orinoco (Carpentier et al., 2008), sediments of similar lithologies and isotopic compositions to those of the fore-arc are expected in the arc crust. Overall, the wide range of isotopic compositions in potential equivalents to sediments in the arc crust combined with a range of potential lithologies suggests that the arc crust is

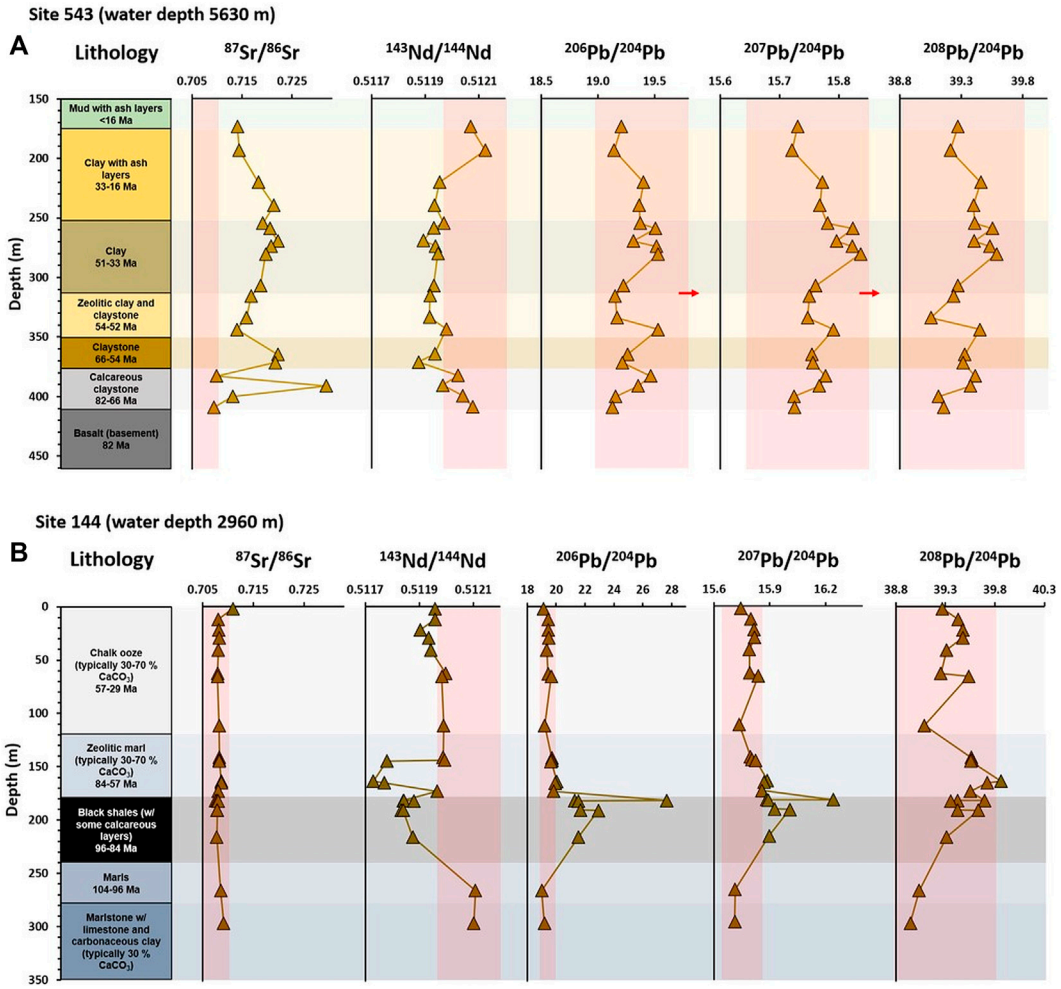

FIGURE 9 | (A): Radiogenic isotopic compositions of DSDP Site 543 sediments, modified from Carpentier et al. (2008). **(B):** Radiogenic isotopic compositions of DSDP Site 144 sediments, modified from Carpentier et al. (2008). Pink bar indicates isotopic range of Martinique lavas (data sources as per **Figure 8**). For all data points, uncertainty (2 SE) is smaller than symbol size. Red arrows in **(A)** indicate that range of lavas exceeds the scale shown on the plot.

chemically and isotopically heterogenous. Both recycled subducted and unsubducted crustal sediments provide viable isotopic components in Martinique lavas specifically and lavas of the Lesser Antilles more generally. Thus, chemical characteristics of lavas alone cannot be used to distinguish whether the sediment component is incorporated by recycling into the mantle source or crustal assimilation of sediments.

Cumulate Isotopic Compositions Support Crustal Assimilation of Sediments

Plutonic xenoliths from Martinique are considered to represent portions of an open crystal mush system (Cooper et al., 2016), which consists predominantly of cumulates in the mid-crust and NCG's in the upper crust. If the Sr isotopic variation observed in Martinique lavas is produced by varying sediment input to the mantle source (e.g., Carpentier et al., 2008; Labanieh et al., 2010), then a similar isotopic range would also be expected in mid-crustal magmas. To a first order, the unradiogenic and extremely restricted Sr isotopic range determined for individual cumulate plagioclase crystals (**Figure 6**) indicates that mid-crustal magmas beneath Martinique have not yet been modified significantly by sediment addition. The same logic can be applied to the wider cumulate whole rock $^{87}Sr/^{86}Sr$ data. The plagioclase and whole rock data support the hypothesis that isotopic heterogeneity and extreme radiogenic compositions of Martinique lavas are produced by assimilation of sediments at shallower crustal levels.

For comparison, plagioclase from a St Vincent cumulate also show unradiogenic Sr isotopic compositions close to those of Martinique cumulates (**Figures 5**, **6**). Tollan et al. (2012), used oxygen isotopes to show that St Vincent cumulates experienced negligible crustal contamination, suggesting that their isotopic composition should reflect the mantle source. St Vincent cumulate plagioclase have slightly lower $^{87}Sr/^{86}Sr$ than those from Martinique, suggesting that the two islands are fed by mantle sources with similar, but not identical, compositions.

This conclusion was also reached by Davidson and Wilson (2011) and Bezard et al. (2015) in studies of primitive Lesser Antilles lavas. Unlike Martinique, lavas on St Vincent do not extend to highly radiogenic isotopic compositions (**Figure 3**) and the impact of crustal assimilation is considered minimal (Heath et al., 1998). Since there are only subtle differences in the isotopic compositions inferred for the mantle sources of the two islands, the wider isotopic range of Martinique lavas is better explained by assimilation of crustal sediments.

Inferences About Assimilation From Isotopic Heterogeneity of Shallow Non-Cumulate Gabbros and Lavas

Non-cumulate gabbros are considered plutonic equivalents of potentially eruptible lavas that crystallized within the 27 km thick Martinique crust at shallower levels than the cumulates (Cooper et al., 2016). Evidence for upper crustal crystallization comes from comparing natural mineral assemblages and compositions to those from experimental studies. These comparisons suggest crystallization of NCGs between 2 and 4 kbar (Martel et al., 1999; Cooper et al., 2016; Melekhova et al., 2019), corresponding to depths of approximately 6–12 km (vs. ~12 km or greater for cumulates).

If the isotopic composition of a magma is inherited from its mantle source and subsequent evolution of that magma remains a closed system, crystals within the same rock should show minimal radiogenic isotopic variation. In contrast, intra-sample isotopic variation among crystals is characteristic of an open system, involving, for example, crustal assimilation (e.g., Baker et al., 2000). The isotopic diversity recorded by NCG plagioclase cores (particularly MQ6, **Figure 6**) may therefore indicate sediment assimilation during crystallization. In NCG sample MQ35, the presence of both cores and rims with significantly more radiogenic $^{87}Sr/^{86}Sr$ than cumulates again suggests that magmas can acquire more radiogenic compositions during crystal growth at shallow crustal levels.

In both NCG samples, more evolved plagioclase rims show less isotopic variation than cores and have Sr isotopic compositions within the range defined by the associated cores. We propose the following processes to explain this trend. Emplacement of new magma into the upper crust, in contact with crustal sediments, leads to sediment assimilation and crystallization of plagioclase cores. Assimilation of variable amounts of sediment, or sediments with different isotopic compositions, could produce an isotopically heterogenous magma resulting in crystallization of isotopically heterogenous plagioclase. Alternatively, isotopic variation among plagioclase cores may reflect crystallization at different times during progressive contamination of the newly emplaced magma.

Plagioclase rims may have crystallized from a more evolved, more isotopically homogenous melt that interacted with the pre-existing plagioclase cores. Other Martinique plutonic xenoliths contain evidence for percolating evolved melts (Cooper et al., 2016) and plutonic xenoliths from Statia in the northern LAA contain melt inclusions ranging in composition from basalt to rhyolite (Cooper et al., 2019). These lines of evidence suggest that it is plausible for plagioclase formed during an initial phase of crystallization (accompanied by assimilation) to interact with more evolved melts in the Martinique magma plumbing system. The fact that NCG plagioclase rims have Sr isotopic compositions within the range defined by the cores from the same sample suggests that in this scenario, the rim-forming melts were contaminated with crust to a similar extent to the core forming melts, hence were likely sourced from nearby regions of the crystal mush in the upper crust.

The most radiogenic Sr isotopic signatures in the LAA are observed in Martinique lavas. Sample M8321 represents one of the more radiogenic lavas, with a whole rock isotopic composition of $^{87}Sr/^{86}Sr = 0.706246$. Plagioclase crystals from M8321 have $^{87}Sr/^{86}Sr$ close to the whole rock value (**Figure 7**) and are significantly more radiogenic than NCG plagioclase (**Figure 6**). This suggests that the magma from which they are derived had assimilated more sediment, or a more radiogenic sediment, than the magmas that crystallized the NCGs. M8321 plagioclase crystals show either normal, reverse, or both normal and reverse zoning, a feature commonly observed in Martinique lavas and interpreted as evidence for mixing shortly before eruption (Coulon et al., 1984; Bourdier et al., 1985; Gorgaud et al., 1989). The indistinguishable Sr isotopic composition of analyzed core-rim pairs (**Figure 7**) suggests that all components involved in this mixing probably had similar Sr isotopic compositions. Plagioclase crystals show only very minor isotopic disequilibrium with the bulk groundmass and have isotopic compositions close to or within uncertainty of the whole rock value, consistent with an origin as true phenocrysts grown in the final erupted melt (or mixed melts).

If the minimal isotopic variation between plagioclase cores, rims and groundmass in M8321 was considered in isolation, then it could be argued that the radiogenic isotopic composition of this lava was inherited from the mantle source. However, by combining this observation with the isotopic data from plutonic xenoliths, we argue that shallow level assimilation is the dominant process controlling isotopic variation in Martinique lavas. Lava M8321 is quite evolved (approx. 58 wt % SiO_2) and increasing $^{87}Sr/^{86}Sr$ generally correlates with increasing SiO_2 in Martinique lavas (Davidson, 1986; Davidson and Wilson, 2011). As discussed by Bezard et al. (2014), this would require a fortuitous process linking the extent of source contamination and magmatic differentiation for isotopic variation to be produced by subducted sediment addition alone.

Quantifying the Addition of Sedimentary Components

Previous estimates of the amount of sediment addition required to generate the radiogenic isotopic compositions of Martinique and Lesser Antilles lavas are based on Sr, Nd, Pb and oxygen isotope data and calculated using binary mixing models. These studies estimate that bulk addition of up to 20–40% sediment in either the mantle source (Carpentier et al., 2008; Labanieh et al., 2010) or within the crust (Davidson and Harmon, 1989; Bezard et al., 2014) explains the *most extreme* Lesser Antilles lava

TABLE 3 | Sr-Nd-Pb isotopic compositions and concentrations of end members used in AFC modeling. Data sources: Bulk Site 543, Bulk Site 144, Bulk Barbados, Most extreme Barbados—Carpentier et al. (2008); Carpentier et al, (2009). Bezard 50:50 Bulk 543:144—Bezard et al. (2015). Average Orinoco—average of samples from Parra et al. (1997) and Rousseau et al. (2019) (n = 15). Most and least radiogenic Amazon—Allegre et al. (1996), Rousseau et al. (2019). Primitive magma—Ile a Ramiers high Mg basalt from Labanieh et al. (2010), (2012). Depleted mantle—Salters and Stracke, (2004). End members in italics represent sediment/crustal end members.

End member	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Sr (μg/g)	Nd (μg/g)	Pb (μg/g)
Bulk Site 543	0.71585	0.511966	19.315	15.767	39.347	110	30.6	18.7
Bulk Site 144	0.70851	0.512014	19.516	15.765	39.220	656	14.8	7.24
Bulk Barbados	0.71642	0.512122	19.674	15.765	39.456	103	23.3	13.1
Bezard 50:50 Bulk 543:144	0.71218	0.511990	19.415	15.766	39.284	383	22.7	13
Average Orinoco	0.73198	0.511920	—	—	—	107	31	—
Most radiogenic Amazon	0.75640	0.511500	19.950	15.924	39.930	97	17	42
Least radiogenic Amazon	0.71319	0.512185	18.670	15.675	38.84	97	17	42
Most extreme Barbados	0.71531	0.512080	20.740	15.879	40.037	85	77.9	9.3
Hypothetical crust	0.71280	0.511700	20.030	15.879	39.920	110	40	15
Hypothetical crust 2	0.71280	0.511500	20.000	15.879	39.950	217	32	20
Parental magma	0.70380	0.512951	19.055	15.662	38.802	181	5.8	1.41
Depleted mantle	0.70270	—	—	—	—	9.8	—	—

compositions. Here we use Assimilation-Fractional Crystallization (AFC) modeling to assess whether crustal sediment assimilation can produce the Sr-Nd-Pb isotopic variation in Martinique lavas and estimate the amount of sediment assimilation required.

Assimilation-Fractional Crystallization Modeling End Members and Parameters

Mid-crustal cumulates from Martinique crystallize from magmas that have undergone prior olivine fractionation at depth (Cooper et al., 2016). This suggests that parental magmas to NCGs and lavas, ascending to the upper crust from the mid-crust or deeper, are likely to have higher Sr concentrations than primary mantle melts, because Sr is incompatible in olivine. Therefore, we model sediment addition to a parental magma rather than a primary mantle melt composition. The Ile a Ramiers basalt, the least evolved lava erupted in Martinique (~12% MgO, Labanieh et al., 2010), is a reasonable approximation for parental magmas ascending to the upper crust. Its Sr isotopic composition of $^{87}Sr/^{86}Sr \sim 0.7038$ is consistent with the isotopic composition of Martinique primitive magmas calculated by Davidson and Wilson (2011), and is close to the least radiogenic value measured in this study (NCG sample MQ6). Hence the composition of the Ile a Ramiers basalt is used here to represent magmas prior to upper crustal sediment assimilation, hereon referred to as "parental magmas."

End member compositions used in AFC models are given in **Table 3**. In *Arc Crust*, we argue that LAA crustal sediments are likely to be both lithologically and chemically heterogenous, based on the best available constraints. This heterogeneity is emphasized by the wide range of potential crustal sediment compositions shown in **Figure 8**. To represent a lithologically and chemically heterogenous crust, eight different potential sediment end members were considered. These include the average Sr-Nd-Pb isotopic compositions of sediments from DSDP Sites 543 and 144, and from Barbados. We also include the 50:50 mixture of bulk Site 543 and bulk Site 144 sediments that Bezard et al. (2015) suggested were involved in St Lucia magmatism. Potential highly radiogenic crustal end members are represented by the average composition of sediments from the Orinoco (from Parra et al., 1997; Rousseau et al., 2019) and the most extreme composition from Barbados (Carpentier et al., 2008; Carpentier et al., 2009). Amazon sediments show a wide range of very radiogenic compositions (e.g. $^{87}Sr/^{86}Sr$ = 0.7132–0.7564, Allègre et al., 1996). The minimum and maximum isotopic compositions were used as additional potential crustal end members, with concentrations equal to the average of Amazon sediments [Sr and Pb from Allègre et al. (1996); Nd from Rousseau et al. (2019)]. The end member compositions in **Table 3** are plotted relative to Martinique lavas and the isotopic range of sediments potentially equivalent to those in the arc crust in **Figure 10**.

The fractionating assemblage used in the AFC models was that of NCG sample MQ6 (**Supplementary File S1**), which closely resembles the phenocryst assemblage of the lavas (e.g. Coulon et al., 1984; Davidson and Wilson, 2011). Bulk partition coefficients were calculated for this modal mineralogy using the mineral-melt partition coefficients listed in **Supplementary File S3**.

Modeling and Quantifying Crustal Assimilation

Results of AFC models, calculated using the equations of De Paolo (1981), are plotted in **Figures 10**, **11**, with details of the calculations given in **Supplementary File S3**. The value of r (rate of assimilation/rate of crystal fractionation) was set at 0.3, similar to previous AFC models for LAA lavas (e.g., Smith et al., 1996; Labanieh et al., 2010). An additional sediment end member ("Hypothetical crust" in **Table 3**) was also modeled in order to reproduce the most extreme (most radiogenic Sr and Pb, most unradiogenic Nd) lava compositions. This end member (plotted on **Figure 10**) lies within the range of potential arc crust sediment isotopic compositions identified in *Arc Crust* (**Figures 8**, **10**) and hence represents a reasonable approximation for an assimilant. Combined, the AFC models for the various crustal end members cover most of the observed isotopic variation in Martinique lavas (**Figure 11**). This suggests that Martinique lava isotopic compositions can be explained by assimilation of crustal sediments with a range of isotopic and chemical compositions,

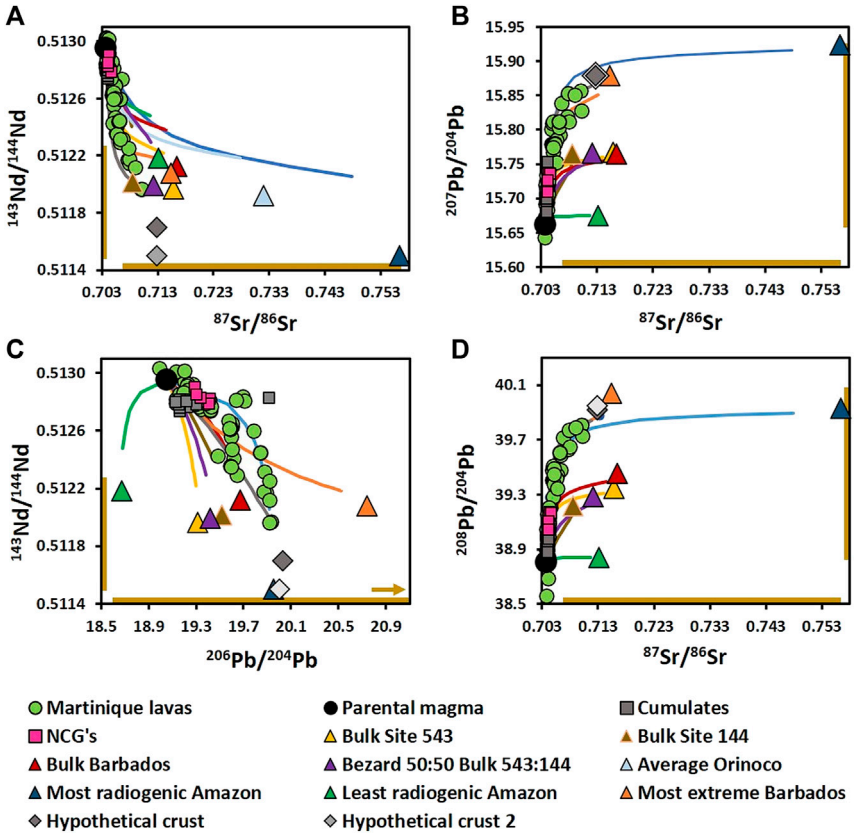

FIGURE 10 | (A) $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$, **(B)** $^{87}Sr/^{86}Sr$ vs. $^{207}Pb/^{204}Pb$, **(C)** $^{206}Pb/^{204}Pb$ vs. $^{143}Nd/^{144}Nd$ and **(D)** $^{87}Sr/^{86}Sr$ vs. $^{208}Pb/^{204}Pb$, for Martinique lavas, plutonic xenoliths (this study) and end members used in AFC modeling from **Table 3**. Data sources as per **Table 3** and **Figure 8**. For all data points, uncertainty (2 SE) is smaller than symbol size. Brown bars along axes show range of isotopic compositions of sediments potentially equivalent to those in the arc crust from **Figure 8**. Colored curves correspond to AFC models for each crustal end member, shown in detail in **Figure 11**.

with individual lavas having assimilated different crustal sediments.

The sediment end members considered represent only a few possible assimilants, which theoretically could lie anywhere within the range of sediment compositions outlined in **Figures 8**, **10**. Since the LAA crust has yet to be directly sampled, its actual isotopic composition remains to be determined but it is possible that sediments with more extreme isotopic compositions than those considered here could also exist within the arc crust.

To quantify the amount of crustal assimilation required to produce the isotopic compositions of Martinique lavas, we employed the method of Aitcheson and Forrest (1994). This method solves the AFC equations of De Paolo (1981) to determine the crust/magma ratio ρ (mass of crust assimilated/mass of original magma), which can be converted into a proportion of crust assimilated. If the isotopic and elemental compositions of the original magma and assimilant are defined, then the crust/magma ratio can be calculated for a *lava of a given isotopic composition*. We calculated the crust/magma ratio for the Martinique lava with the most extreme isotopic composition to determine the maximum amount of crustal sediment assimilated by Martinique lavas (details of the calculation given in **Supplementary File S3**). Assimilation of 28% sediment with the composition of the "Hypothetical crust" end member is required to produce the most extreme Martinique lava composition. To illustrate the effect of a chemically and isotopically heterogenous crust, we generated an alternative sediment end member ("Hypothetical crust two" in **Table 3**) which also reproduces the isotopic composition of the most extreme Martinique lava with only 23% assimilation (**Supplementary File S3**). This end member also has isotopic compositions within the potential range for crustal sediments shown on **Figures 8**, **10**. These results show that the amount of crustal assimilation required varies depending on the composition of crust being assimilated.

Previous estimates of the amount of sediment addition (whether to the mantle source or *via* crustal assimilation) required to produce the most extreme Martinique lava composition are similar to our calculated values of 23–28%. Given the wide range of potential assimilant compositions, the proportion of crustal sediment assimilated by Martinique lavas cannot be accurately quantified. However, 28% should be treated as a maximum amount, with most lavas likely experiencing significantly less assimilation. Our new AFC modeling, combined with the constraints from plutonic xenoliths on where assimilation takes place, clearly demonstrates that

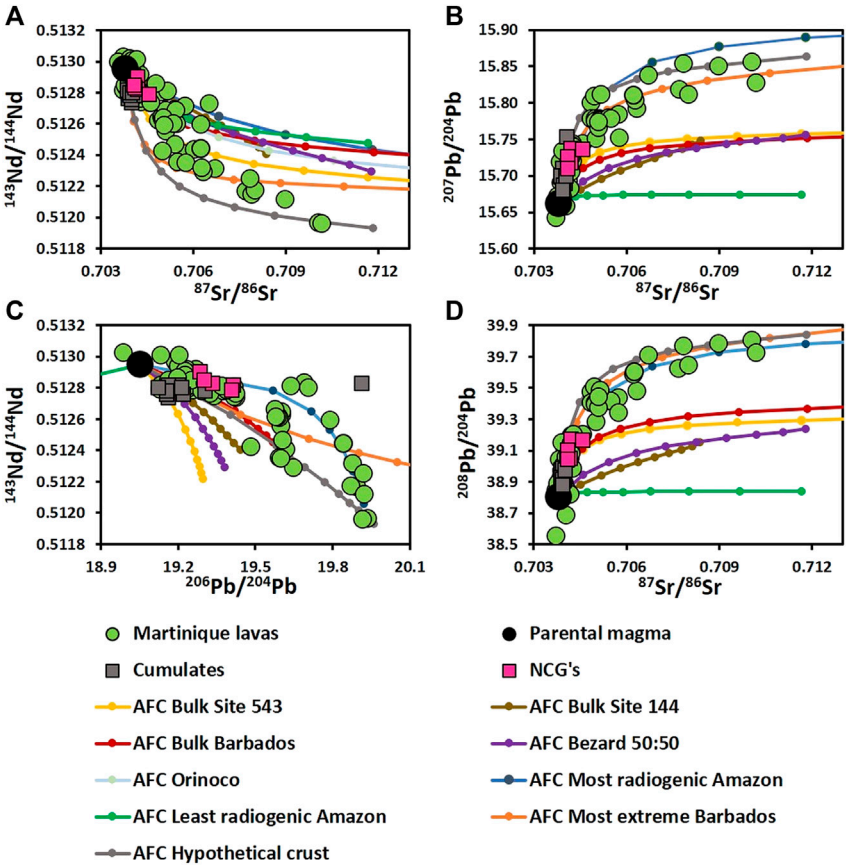

FIGURE 11 | (A) $^{87}Sr/^{86}Sr$ vs. $^{143}Nd/^{144}Nd$, **(B)** $^{87}Sr/^{86}Sr$ vs. $^{207}Pb/^{204}Pb$, **(C)** $^{206}Pb/^{204}Pb$ vs. $^{143}Nd/^{144}Nd$ and **(D)** $^{87}Sr/^{86}Sr$ vs. $^{208}Pb/^{204}Pb$, for Martinique lavas and plutonic xenoliths (this study). Data sources as per **Table 3** and **Figure 8**. For all data points, uncertainty (2 SE) is smaller than symbol size. Each colored curve corresponds to an AFC model using a different crustal end member from **Table 3** as the assimilant composition (see legend). Each point along the curves represents an increment of 10% fractional crystallization, up to a maximum of 90%. Details of AFC model calculations are given in **Supplementary File S3**.

isotopic variation in Martinique lavas is best explained by assimilation of isotopically and chemically heterogenous sediments in the upper crust.

Sediment Addition to the Mantle Source?

Although the evidence presented supports crustal assimilation at shallow crustal levels as the dominant process responsible for the large isotopic range and radiogenic compositions of Martinique lavas, this does not preclude the involvement of subducted sediment in generating the compositions of the parental magmas and cumulates, which are more radiogenic in terms of Sr isotopes than typical depleted mantle. As such, the amount of subducted sediment addition to the mantle source required to produce parental magma and cumulate plagioclase Sr isotopic compositions was calculated. A binary mixing approach was used for simplicity. The average depleted mantle composition of Salters and Stracke (2004) was used as the mantle end member. Potential subducted sediment end members were represented by average compositions of DSDP Site 543, DSDP Site 144 and Barbados sediments (**Table 3**).

The Sr isotopic composition of Martinique parental magmas ($^{87}Sr/^{86}Sr$ = 0.7038) allows a maximum of ~0.8% bulk sediment addition to the mantle source (**Figure 12**). This value agrees well with the <1% subducted sediment contribution to parental magmas at Mt Pelee, Martinique estimated by Davidson and Wilson (2011). Cumulate plagioclase compositions allow a maximum of 1–1.2% bulk sediment addition to the mantle source (**Figure 12**). The slightly higher $^{87}Sr/^{86}Sr$ of the cumulates relative to parental magma could be explained by minor variations in sediment input to the mantle source. Alternatively, the parental and cumulate forming magmas may have been affected by minor assimilation, either of deep sediments or oceanic crustal material, which underlies Grenada-Tobago basin sediments (Aitken et al., 2011; Allen et al., 2019). Since the maximum sediment contribution to the parental magma is <1% (regardless of where sediment addition occurs), this composition can still be considered a reasonable proxy for Martinique magmas prior to upper crustal assimilation. It should be noted that the Nd and Pb isotopic compositions of the parental magma also require <1% sediment contribution (when modeled as above for Sr isotopic composition).

Wider Significance

Our study of Martinique lavas *in conjunction* with plutonic xenoliths places important spatial constraints on the location where the crustal/sedimentary isotopic signatures of Martinique lavas are

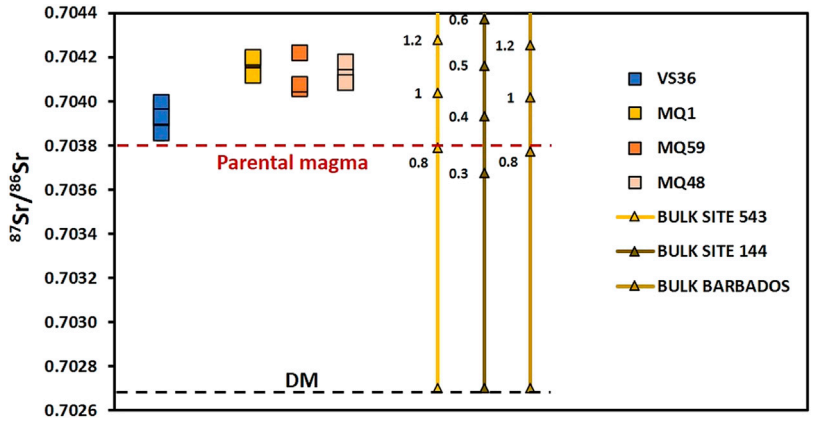

FIGURE 12 | $^{87}Sr/^{86}Sr$ of cumulate plagioclase compared with single component mixing lines between depleted mantle and potential subducted sediment end members. The subducted sediment end member from **Table 3** corresponding to each mixing line is shown in the legend. Labeled tickmarks represent percentage sediment addition to mantle source. Data sources as per **Table 3**. Dashed line labeled DM = depleted mantle [$^{87}Sr/^{86}Sr = 0.70270$, from Salters and Stracke (2004)]. Red dashed line shows Martinique parental magma composition ($^{87}Sr/^{86}Sr = 0.70380$). Where visible, black bars show uncertainty (2 SE), otherwise uncertainty is smaller than symbol size.

introduced, which simply cannot be derived from studies of lavas alone. We have shown that the crustal/sedimentary signatures are almost entirely inherited from AFC processes taking place in the upper crust, with only a very minor role for subducted sediment in the mantle source. Application of the approach applied here may reveal a greater role for crustal assimilation than previously considered in other arc systems where lava geochemistry is currently interpreted to reflect source processes. If crustal contributions are underestimated, relative contributions from the subducting slab and mantle will be overestimated, which has major implications for quantifying element and sediment recycling at subduction zones. Improved constraints on crustal contributions could also be utilized to re-assess the composition and heterogeneity of arc mantle source regions, by correcting lava compositions for the effects of crustal assimilation.

The latest tectonic model for the evolution of the LAA (Allen et al., 2019) corroborates evidence for crustal sediment assimilation in Martinique. The model suggests that an outer arc was active east of the current arc from 40 to 25 Ma. A back-arc basin formed during this period, extending from the present-day location of Dominica south to Grenada. Around 22 Ma, the arc migrated west and the southern volcanic centers of the current Lesser Antilles arc (Martinique to Grenada) were subsequently built through the back-arc basin crust (oceanic crust and sediments), separating it into the Grenada and Tobago basins (**Figure 3**). Evidence for crustal contamination in Martinique (and other southern LAA islands) demonstrates that magma interacted with the thick sediment pile of the Grenada-Tobago basins. In other arc settings where the tectonic evolution is less well constrained, the methods employed in this study could be used to identify shallow crustal sediment assimilation and thereby indicate the presence of sediments within the arc crust. This information could be used to infer the past locations of sedimentary basins/depocenters, which could be incorporated into tectonic models for arc development and may also indicate potential locations of hydrocarbon bearing sediments.

In an alternative scenario, isotopic studies of plutonic xenoliths from other arcs may prove a less effective means of recognizing crustal assimilation than in the LAA. The proximity of the LAA to the South American continental margin has resulted in a component of the arc crust composed of sediments which, based on available constraints, can be assumed to have highly radiogenic isotopic compositions. The contrast in isotopic compositions between crustal sediments and primitive magmas makes sediment assimilation easily detected in the LAA and may be unique among arcs. Upper plate crustal sediments elsewhere may not have such highly radiogenic or diverse compositions resulting in a less obvious geochemical signature of assimilation.

Recent studies have demonstrated that volatile fluxes from arc volcanoes (e.g. He and CO_2) contain contributions from crustal sediments (e.g. Troll et al., 2012; Yu et al., 2016; Aiuppa et al., 2017; Mason et al., 2017). Therefore, it is likely that volatile contents and compositions of magmas in volcanic arcs are modified by crustal sediment assimilation. This highlights the importance of considering and accurately quantifying volatile contributions from upper plate crust in models of volatile recycling at subduction zones. If volatiles added in the crust are mistakenly attributed to the subducted component, the contribution from the downgoing slab to arc volatile output could be significantly overestimated, resulting in misleadingly elevated volatile recycling efficiency estimates. Finally, addition of volatiles to magmas at shallow crustal levels may influence the typically explosive eruptive behavior of LAA volcanoes, as has been suggested for other arc volcanoes e.g. Merapi (Deegan et al., 2010).

CONCLUSION

The Sr isotopic composition of plagioclase from plutonic xenoliths has been used to evaluate the origin of the wide

isotopic range and highly radiogenic compositions of Martinique lavas. Through this approach it has been possible to distinguish between competing hypotheses where the compositions of the lavas result from variations in subducted sediment addition to the mantle source vs. assimilation of unsubducted, shallow, crustal sediments. Unzoned plagioclase crystals from mid-crustal cumulate xenoliths show restricted ranges of unradiogenic Sr isotope ratios. In contrast, cores of zoned plagioclase crystals from upper-crustal NCG xenoliths are characterized by wider intra-sample Sr isotopic ranges than cumulate plagioclase. Some NCG plagioclase crystals have both core and rim compositions with more radiogenic $^{87}Sr/^{86}Sr$ than mid-crustal cumulates. Whole rock Sr isotopic compositions follow the same pattern, with cumulates showing restricted, unradiogenic $^{87}Sr/^{86}Sr$ and NCG's extending to slightly more radiogenic values. Combined, these results support the hypothesis that Martinique magmas acquire more radiogenic compositions and isotopic diversity *via* assimilation of *in situ* sediment in the upper crust. Consistent with the best available constraints for crustal sediment composition, AFC modeling demonstrates that the isotopic variation in Martinique lavas can be produced by assimilation of chemically and isotopically heterogenous crust. The novel approach used here could be applied to other arc systems to assess the relative roles of subducted sediment and crustal contributions which in turn would have significant implications for understanding arc mantle source compositions and quantifying sediment and volatile recycling at subduction zones.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

JP, GC, CM, and IN devised the project. JB and GC performed petrographic analyses, JB performed SEM analyses. JB, GC and GN carried out sample preparation and isotopic analyses. All authors contributed to interpretation of the data and writing of the manuscript.

FUNDING

This research was funded by a NERC IAPETUS DTP PhD scholarship to JB and the NERC VoiLA project (Grant Number NE/K010824/1 from the Natural Environment Research Council) (www.voila.ac.uk).

ACKNOWLEDGMENTS

The authors would like to thank all members of the NERC VoiLA consortium and project partners for discussions during the course of this project both in the United Kingdom and during the 2019 consortium workshop in the Lesser Antilles. E. Melekhova is thanked in particular for initial discussions of the existing plutonic xenolith suite. B. Rogers is thanked for her contribution to testing and refining low concentration TIMS Sr isotopic analyses. Ian Chaplin and Sophie Edwards are thanked for thin section preparation. We are grateful to Leon Bowen for his support with SEM analyses.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.682583/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.