



HAL
open science

Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas

Yan Hu, Fang-Zhen Teng, Catherine Chauvel

► **To cite this version:**

Yan Hu, Fang-Zhen Teng, Catherine Chauvel. Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas. *Geochimica et Cosmochimica Acta*, 2021, 295, pp.98-111. 10.1016/j.gca.2020.12.013 . hal-03327741

HAL Id: hal-03327741

<https://hal.science/hal-03327741>

Submitted on 27 Aug 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Journal Pre-proofs

Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas

Yan Hu, Fang-Zhen Teng, Catherine Chauvel

PII: S0016-7037(20)30726-2
DOI: <https://doi.org/10.1016/j.gca.2020.12.013>
Reference: GCA 12014

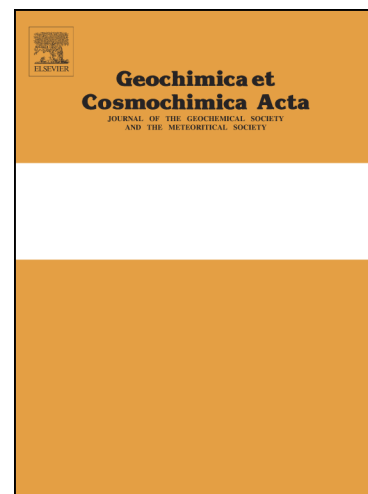
To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 13 June 2020
Accepted Date: 16 December 2020

Please cite this article as: Hu, Y., Teng, F-Z., Chauvel, C., Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas, *Geochimica et Cosmochimica Acta* (2020), doi: <https://doi.org/10.1016/j.gca.2020.12.013>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.



Potassium isotopic evidence for sedimentary input to the mantle source of Lesser Antilles lavas

Yan Hu^{a*}, Fang-Zhen Teng^{a*}, Catherine Chauvel^{b,c}

^aIsotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA

^bUniversité de Paris, Institut de Physique du Globe de Paris, CNRS, F-75005 Paris, France

^cUniversité Grenoble Alpes, ISTerre, CNRS, F-38041 Grenoble, France

Abstract: 232 words

Text: 5759 words

Figures: 6

Tables: 2

Submit to *GCA*

Revised version R2

(December, 2020)

*Corresponding authors:

Emails: yanhu@uw.edu (Y.H.); fteng@uw.edu (F.-Z.T.)

Abstract

Arc magmas derived from mantle melting often have trace element and isotopic signatures that indicate crustal contributions. The origin and extent of crustal contributions are critical constraints for quantifying crust-mantle recycling at subduction zones; however, it is difficult to distinguish between inputs from the downgoing oceanic slabs and that of the over-riding arc crust. Here we present a novel study using stable potassium (K) isotopes to fingerprint the long-debated crustal signatures in lavas from Martinique Island, Lesser Antilles arc. We find $\delta^{41}\text{K}$ of Martinique lavas varies from -0.66 to 0.01‰ and correlates with chemical parameters and radiogenic isotope ratios. These correlations cannot be produced by assimilation of arc crust during magma ascent. Rather, they reflect mantle sources that have been modified by the input of subducted sediments. Most lavas display a strong negative correlation between $\delta^{41}\text{K}$ and radiogenic isotopic compositions, from typical mantle values of -0.37‰ to much lower values of -0.66‰ , suggesting the addition of $<1\%$ to 5% subducted sediments to their mantle sources. Notable divergence in this correlation occurs for three samples with variably high $\delta^{41}\text{K}$ (-0.28 to 0.01‰), which is likely caused by the addition of isotopically heavy K-bearing fluids derived from slab dehydration. Our study indicates that a substantial fraction of large ion lithophile elements, including K in arc magmas and thus nascent crust, is inherited from subducted crust; K isotopes are useful tracers of this cycling process.

Keywords: potassium isotopes; subduction zone magmatism; crustal recycling; Lesser Antilles arc; Martinique Island

1. Introduction

Subduction zones are the essential sites of crust-mantle recycling, where new crust is produced via arc magmatism, and old crust is returned to the mantle with descending slabs of oceanic lithosphere. The subducting oceanic plate is geochemically distinct from the mantle because alteration by low-temperature hydrothermal fluids leads to a significant addition of volatiles (e.g., H₂O and CO₂) and seawater alkalis (K, Rb, Cs). In addition, sediments deposited on oceanic crust contain abundant large-ion lithophile elements (LILEs) that are incompatible during mantle melting and thus are concentrated in the continental crust (e.g., K, Rb, Sr, Cs, and Ba). As subduction proceeds, the oceanic plate dehydrates, or less frequently, melts, in response to increased pressure and temperature. The LILEs hosted in altered oceanic crust and sediments are then released into the overlying mantle wedge by fluids or melts and transferred to partial melting zones to give rise to arc magmas. En route to the surface, arc magmas may interact with and assimilate arc crust in the overlying plate. These various crustal components impart continental-like trace element and isotopic signatures to mantle-derived arc magmas (Ryan and Chauvel, 2014, and references therein). Distinguishing the various crustal contributions is at the center of the debate over the origin of arc magmas that is important for understanding the formation of continental crust and the development of long-term heterogeneities in the deep mantle.

The main controversial topics related to the presence of crustal input in arc lavas include: 1) whether crustal material is involved mainly as slab addition to the sub-arc mantle source prior to melting, or via assimilation of arc crust during magma ascent to the surface; 2) whether slab components are dominated by subducted sediments or basaltic crust; 3) how crustal components are transferred to partial melting regions; and 4) to what extent crustal components contribute to the composition of arc magmas. Such debates are best exemplified in studies of lavas erupted along the Lesser Antilles arc, where the Atlantic oceanic lithosphere is slowly subducting beneath the Caribbean Plate. The Lesser Antilles lavas represent a compositionally enriched endmember among global intra-oceanic arcs, containing continental crust-like Sr, Nd, Pb, Hf isotopic compositions and stable O, Li, B, and Mo isotopic compositions that have been attributed to either incorporation of slab-derived components to their mantle sources (e.g., Davidson, 1983; White and Dupré, 1986; Carpentier et al., 2008; DuFrane et al., 2009; Bouvier et al., 2010; Labanieh et al., 2010, 2012; Tang et al., 2014; Freymuth et al., 2016; Gaschnig et al., 2017) or assimilation of sediments in the arc crust (e.g., Davidson, 1985, 1986; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996; van Soest et al., 2002; Bezard et al., 2015).

This paper presents a novel study using K isotopic systematics to constrain the origin, nature, and size of crustal components in Lesser Antilles arc lavas. Enrichment in K and other LILEs is one of the defining characteristics of arc magmas when compared to mid-ocean ridge basalts (MORBs). These enrichments provide a key argument for slab inputs to arc magmas because LILEs are highly concentrated in the crust, particularly upper continental crust, whereas they are depleted in the mantle. Recent advances in K isotope geochemistry suggested negligible K isotope fractionations at mantle temperatures, and the majority (90%) of oceanic basalts reported by Tuller-Ross et al. (2019a,b) have similar $\delta^{41}\text{K}$ values averaging at $-0.43 \pm 0.09\text{‰}$ (2SD) despite a

few outliers that may be related to subducted components in their mantle sources (see Fig. S1 in Hu et al., 2020). Fractionation of K isotopes is substantially greater in low temperature environments. As an example, the global ocean is well-constrained to have a uniform and high $\delta^{41}\text{K}$ value of $0.12 \pm 0.07\text{‰}$ (Hille et al., 2019; Wang et al., 2020) whereas secondary clays and riverine sediments typically have $\delta^{41}\text{K}$ values lower than that of the ambient mantle due to leaching of heavy K during continental weathering (Li et al., 2019; Chen et al., 2020; Huang et al., 2020; Teng et al., 2020). Our recent study of sediments entering the Lesser Antilles trench, as sampled by Deep Sea Drilling Project (DSDP) Sites 144 and 543, detected unusually low $\delta^{41}\text{K}$ values among global sediment compositions (Fig. 1) (Hu et al., 2020). The $\delta^{41}\text{K}$ values of lower than -0.7‰ are unlikely to be caused by subaerial continental weathering alone, given that a wide survey by Huang et al. (2020) has not detected such low $\delta^{41}\text{K}$ values for upper continental crust sediments that underwent similar, or higher degrees of weathering. Addition of K from seawater after sediments entering the ocean is thus required, during which light K isotopes are commonly preferred by authigenic minerals within the sediments (Hu et al., 2020). These sediments thus provide a distinct, isotopically light K source that can be used to identify subducted sedimentary contributions to the Lesser Antilles lavas.

Here we report high-precision K isotopic data for a suite of arc lavas from Martinique Island in the central Lesser Antilles arc. We find large $\delta^{41}\text{K}$ variation in the lavas that is linked to sedimentary inputs. We assess where, how, and to what extent sediments are incorporated to the Martinique lavas by comparing the K isotopic compositions of the lavas to that of local subducting sediments (Hu et al., 2020), coupled with previously published chemical and radiogenic isotopic data for these lavas and sediments (Carpentier et al., 2008, 2009; Labanieh et al., 2010). Given that Martinique lavas record all major eruptive stages of the Lesser Antilles arc and encompass almost its full range of compositional variation (Labanieh et al., 2010, 2012; Germa et al., 2011), the inferred crustal inputs to Martinique lavas have broader implications for the compositional gradient in lavas erupted along the Lesser Antilles arc.

2. Geological background and samples

The Lesser Antilles (Fig. 1) is an intra-oceanic arc extending approximately 750 km along the eastern margin of the Caribbean plate; it was formed by westward subduction of the Atlantic lithosphere with ages that range from ca. 80 Ma in the north to older than 105 Ma in the south (Westbrook et al., 1984; Carpentier et al., 2008). The arc has been volcanically active since late Oligocene (~ 25 Ma, Germa et al., 2011). North of Dominica Island, the arc diverts to an active volcanic branch (~ 7 Ma to present) lying west of an extinct older branch. This westward shift of the northern part of the volcanic front has been attributed to subduction of an aseismic ridge that led to a halt to volcanic activity for ~ 8 Ma and a change in slab dip angle (Bouysse and Westercamp, 1990). During this period, however, volcanic eruptions continued on Martinique Island, and erupted lavas built the central part of the island. More recent eruptions added lavas to the eastern part of the island. As a result, Martinique Island contains a complete volcanic history of the arc (25 Myrs, Coulon et al., 1991).

Lavas erupted along the arc display a prominent transition in radiogenic isotope ratios, from primitive compositions typical of islands in the north to strongly enriched signatures that resemble continental crust in the south (e.g., Macdonald et al., 2000). Sedimentary input also varies along the arc (Westbrook et al., 1984; Carpentier et al., 2008). The Orinoco and Amazon Rivers that drain South American continent deliver abundant terrigenous sediments to the southern part of the arc, and form a large accretionary complex, i.e., the Barbados Ridge, in the forearc region. The terrigenous input thins towards the north where pelagic sediments become dominant. Representative sediment sections are drilled at DSDP Sites 144 and 543 (see Fig. 1). Their geochemical compositions are well established in the literature (White and Dupre, 1986; Carpentier et al., 2008, 2009); these studies found that sediments recovered from Site 144 in the south display more heterogeneous and more “crustal-like” radiogenic isotopic compositions than those recovered from Site 543 in the north.

The Lesser Antilles is an exceptional arc for assessing the relative roles of source contamination versus upper crustal assimilation. Locally the high fluxes of subducting terrigenous sediments eroded from the ancient South America continent could impart a strong sediment signature to the mantle sources. Assimilation of sediments overthrust in the upper plate is also possible if the Lesser Antilles has been developed on the older Aves arc crust or its forearc region (Bouysse et al., 1985; Davidson and Harmon, 1989). While sediments of such an origin are reported in the basement rocks exposed on Grenada, the southernmost island along this arc (Speed and Larue, 1985), they are not documented in islands north of St. Lucia (Larue et al., 1991; van Soest et al., 2002). It thus remains unclear what is the volumetric importance of intercalated sediments in the crust on which the Lesser Antilles arc as a whole is built.

High-precision K isotopic ratios are analyzed for 23 Martinique arc lavas that include those from the old arc (24.8 to 20.8 Ma), through the intermediate arc (16.1 to 7.1 Ma), to the recent arc (5.1 Ma to present). These samples were selected by Labanieh et al. (2010, 2012) from 127 collected samples to include only the freshest lavas of each eruptive phase of Martinique Island. No secondary minerals such as chlorite have been detected under the petrographic microscope, and samples that are analyzed for K isotopes have loss on ignition (LOI) below 2 wt.%. Three samples with clear submarine eruption origin are excluded due to their anomalously high $\delta^7\text{Li}$ values that may reflect interaction with seawater (Tang et al., 2014).

The geochemistry of the 23 fresh lavas has been investigated in detail by Labanieh et al., (2010, 2012). They are medium-K, calc-alkaline basalts, basaltic andesites, and andesites with K_2O contents varying from 0.29 to 1.9 wt.%. In addition to typical features of arc magmas (e.g., LILE enrichment, low Ce/Pb ratios, and Nb-Ta depletion), their Sr-Nd-Pb-Hf isotopic compositions form mixing hyperbolas between a depleted mantle endmember and an enriched endmember that has a composition within the range of sediment core samples analyzed by Carpentier et al. (2008, 2009) for DSDP Sites 144 and 543. The well-defined hyperbolas allowed Labanieh et al. (2010) to recognize two enriched sediment endmembers with slightly different Pb, Sr, and Hf isotopic compositions. Their subsequent work using trace element ratios along with radiogenic isotopes also identified inputs from slab dehydration, in particularly to the mantle sources of eastern

Martinique lavas (Labanieh et al., 2012). The presence of subducted sediments in the mantle sources is also reflected in their Li, Mo, and Ce isotopic compositions (Tang et al., 2014; Bellot et al., 2015; Gaschnig et al., 2017).

3. Analytical Methods

Potassium isotopic analyses were carried out in the Isotope Laboratory at the University of Washington, Seattle. Chemical procedures were performed in class-100 vented laminar flow hoods in a class-10,000 clean laboratory. Milli-Q water, double distilled acids, and Savillex screw-top Teflon beakers were used to minimize blank level. Sample powders were dissolved with a combination of Optima-grade concentrated HF-HCl-HNO₃ and heated on a hotplate until complete dissolution. Following the purification procedure of Xu et al. (2019), dried samples were refluxed with 0.5 N HNO₃ then passed twice through column chemistry in a 0.5 N HNO₃ medium. The columns are Bio-Rad Poly-Prep polyethylene columns that are packed with 2 mL pre-cleaned Bio-Rad AG 50W-X8 cation exchange resin (200-400 mesh).

Potassium isotopic compositions of purified samples were measured on a Nu Plasma II multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) using standard-sample bracketing method (Hu et al., 2018). To reduce the formation of argon-based interferences, the instrument was run at reduced radio-frequency (RF) power and the sample solutions were introduced using a DSN-100 desolvation nebulizer system. The residual Ar interferences are resolved using a high-mass-resolution source slit, with ⁴¹K⁺ and ³⁹K⁺ being measured simultaneously on interference-free peak shoulders. A blank was measured at the beginning of each analytical session and was subtracted from the measured ion beams. Potassium isotopic data are reported relative to the bracketing standard SRM 3141a from National Institute of Standards and Technology (NIST):

$$\delta^{41}\text{K} (\text{‰}) = \left\{ \frac{({}^{41}\text{K}/{}^{39}\text{K})_{\text{sample}}}{({}^{41}\text{K}/{}^{39}\text{K})_{\text{NIST SRM 3141a}}} - 1 \right\} \times 1000$$

To evaluate data accuracy, two USGS standards (JB-1 basalt and AGV-1 andesite) were processed and analyzed. They yield $\delta^{41}\text{K}$ values that agree with recommended values (Table 1). The sample-standard sequence was repeated N times (N = 4-8) for a given sample and the reported K isotopic composition is the average of the N repeat analyses. Uncertainties are reported as both 2SD (standard deviation) of repeated N analyses for one sample, and 95% c.i. (confidence interval) calculated from the 2SD of the $\delta^{41}\text{K}_{\text{standard}}$ and are corrected by Student's t factor (Platzner, 1997). Since bracketing standards have been measured many times more than any given sample during an analytical session, we argue that the 95% c.i. reported here is more robust than 2SE (standard error) calculated from the 2SD of a given sample (e.g., Teng et al., 2015). Furthermore, the 95% c.i. reflects not only the precision but also the accuracy of the method, verified by analyses on (1) high-purity KNO₃ solutions (Spex CertiPrep K), (2) synthetic solutions made from single element ICP standards to match natural rock compositions, (3) mixed solutions of KNO₃ with proportional additions of natural rock matrices, and (4) international rock standards; all purified by column

chemistry (Xu et al., 2019). The 95% c.i. is typically better than 0.06‰ based on multiple measurements of K standard solutions and rock standards, as well as duplicate analyses of purified sample solutions (Hu et al., 2018 and this study).

4. Results

The K isotopic compositions of Martinique lavas are reported in Table 1. There is no apparent dependence of $\delta^{41}\text{K}$ on rock types, with $\delta^{41}\text{K}$ varying from -0.47 to 0.01 ‰ in four basalts, -0.55 to -0.28 ‰ in three basaltic andesites, and -0.66 to -0.20 ‰ in 16 andesites, respectively (Fig. 2A). Furthermore, the K isotopic compositions of Martinique lavas do not vary systematically with eruption age (Fig. 2B). The three old arc samples have similar $\delta^{41}\text{K}$ values between -0.44 and -0.37 ‰, while the three intermediate arc samples display a large variation from -0.66 to 0.01 ‰, and the 17 recent arc samples fall between -0.55 and -0.20 ‰. Among all analyzed samples, sample IAR has the lowest SiO_2 (47.7 wt%) and K_2O (0.29 wt%) on a volatile-free basis; it also has a LOI value of -0.01 ‰, suggesting it is the most primitive and fresh sample within the suite. The $\delta^{41}\text{K}$ value of this arc basalt is -0.38 ‰, falling within the oceanic basalt range of -0.43 ± 0.09 ‰ (Tuller-Ross et al., 2019a,b). This value is taken to represent the mantle wedge composition beneath Martinique Island. When compared to this sample, the majority of the arc lavas are isotopically lighter except for three samples with high and variable $\delta^{41}\text{K}$ values of -0.28 to 0.01 ‰.

The K isotopic compositions of Martinique lavas can also be compared with published data on continental sediments and subducting marine sediments, which are two potential sources of crustal input that imparted highly enriched radiogenic isotopic compositions to the Martinique lavas (Fig. 2C and D). Overall, Martinique lavas span a wide range of $\delta^{41}\text{K}$ that is comparable to sedimentary material from upper continental crust. By contrast, they are isotopically heavier than most of the subducting sediments drilled at DSDP Site 144 and 543 (Fig. 2C). Apart from the three high- $\delta^{41}\text{K}$ lavas, samples vary from mantle-like $\delta^{41}\text{K}$ values at -0.37 ‰ to considerably lower values of -0.66 ‰ with increasing K_2O and ϵCe . In both cases (Fig. 2C and D) they trend towards local subducting sediments.

5. Discussion

The wide and systematic variation of K isotopic compositions in the Martinique lavas could result from a variety of processes, including post-eruption alteration, igneous differentiation, crustal assimilation, and modification of their mantle sources by subducted slab-derived components. These processes are discussed in detail below, followed by implications.

5.1. Negligible role of post-eruption alteration and igneous differentiation

Low-temperature fluid-rock interaction can lead to substantial K isotopic variations in erupted lavas (Tuller-Ross et al., 2019a; Hu et al., 2020; Santiago Ramos et al., 2020). To minimize effects from post-eruption alteration, our samples were selected after careful petrographic examination to insure the absence of secondary minerals (Labanieh et al., 2010, 2012). Samples with a submarine

origin and those with LOI values higher than 2 wt.% are excluded for K isotope analyses. This selection criteria limits the effects of weathering on the K isotopic compositions of the studied lavas because LOI is more sensitive than alkali elements to chemical weathering of basalts (Chauvel et al., 2005). The $\delta^{41}\text{K}$ values of the 23 Martinique lavas do not correlate with their LOI values (Fig. 3) or eruptive ages (Fig. 2B) but vary systematically with their chemical and radiogenic isotopic compositions (Figs. 2 and 4-6). Taken together, these observations indicate that the large K isotopic variations (-0.66 to 0.01%) in the Martinique lavas are not caused by post-eruption alteration.

Magmatic differentiation is unlikely to produce the range of $\delta^{41}\text{K}$ measured in Martinique lavas either. As a large cation that is highly incompatible during mantle melting, K^+ is sequestered in melts during partial melting, thereby it inherits the $\delta^{41}\text{K}$ signature from its mantle source with negligible fractionation. This is supported by recent theoretical calculations showing that equilibrium fractionation between silicate melts and minerals is less than 0.1% at 1100°C (Zeng et al., 2019). In addition, $\delta^{41}\text{K}$ data of globally-distributed oceanic basalts from Tuller-Ross et al. (2019a,b) cluster around $-0.43 \pm 0.09\%$ (see Fig. S1 in Hu et al., 2020). These observations suggest no resolvable K isotope fractionation during mantle partial melting. Subsequent differentiation of the Martinique magmas occurred via fractional crystallization of plagioclase, olivine, and pyroxene (e.g., Davidson, 1986; Labanieh et al., 2010, 2012). These minerals are not structurally compatible with K, and hence the differentiation process is not expected to exert strong control over the K isotopic compositions of Martinique lavas. This inference is consistent with the lack of correlation between $\delta^{41}\text{K}$ and SiO_2 as well as studies of Iceland's Hekla volcanics that conclude no resolvable K isotope fractionation during basalt-to-rhyolite differentiation (Fig. 2A). On the other hand, the systematic correlations between $\delta^{41}\text{K}$ and radiogenic isotopic compositions (Figs. 4 and 6) are indicative of mixing between isotopically distinct components rather than fractional crystallization, given that radiogenic isotopes are unaffected by mineral crystallization.

5.2. Crustal input as the primary cause of $\delta^{41}\text{K}$ variation in Martinique lavas

The two main sources of crustal inputs to arc magmas are 1) subducted oceanic crust and sediments that modify the mantle wedge prior to partial melting, and 2) overriding arc crust with intercalated sediments assimilated during magma ascent. It remains highly debated which of these two sources leads to the prominent continental signatures in the Lesser Antilles lavas. Part of the complexity arises from the possibility that forearc sediments of the extinct Aves arc may persist beneath the currently active Lesser Antilles arc (Davidson and Harmon, 1989; Bezard et al., 2014).

Previous analyses of sediments cored at DSDP Site 543, north of Martinique, yielded radiogenic Pb isotope ratios that are not sufficiently enriched to explain the most extreme Pb isotopic compositions in lavas from the southern arc (Davidson, 1986; Davidson and Harmon, 1989; van Soest et al., 2002). White and Dupré (1986) proposed that sediments deposited further south may contain more radiogenic Pb, where the Orinoco River delivers abundant turbiditic sediments eroded from the Archean Guiana Highland (White et al., 1985). By contrast, others argued that sediments with enriched radiogenic isotopic compositions are assimilated within the

arc crust, which is based on elevated bulk-rock $\delta^{18}\text{O}$ that is concomitant with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and decreasing $^{143}\text{Nd}/^{144}\text{Nd}$ (Davidson, 1985, 1986; Davidson and Harmon, 1989). However, $\delta^{18}\text{O}$ data reported later for mineral phenocrysts in the Lesser Antilles lavas display largely mantle-like values (Davidson and Wilson, 2011), suggesting that the bulk-rock $\delta^{18}\text{O}$ enrichment may be an artifact due to secondary enrichments during post-eruption alteration. While there is no direct evidence that sediments having required radiogenic isotopic ratios are present in local arc crust, Carpentier et al. (2008) discovered highly radiogenic Pb isotopic compositions in black shale units of sediments cored at DSDP Site 144, south of Martinique. These subducting sediments hence provide an adequate source to modify the mantle composition of Lesser Antilles lavas in its southern part (Hawkesworth et al., 1979; Hawkesworth and Powell, 1980; White and Dupré, 1986; Carpentier et al., 2008; Labanieh et al., 2010, 2012).

5.2.1. Subducted slab as the source of crustal input

The substantial $\delta^{41}\text{K}$ variation revealed in Martinique lavas strongly indicates that the crustal input to these lavas reflects slab-derived materials added to their mantle sources rather than contamination by crustal materials within the local arc. First of all, there is no known high- $\delta^{41}\text{K}$ continental source to explain the three Martinique lavas that have $\delta^{41}\text{K}$ higher than the mantle (Fig. 2C). Second, the known low- $\delta^{41}\text{K}$ values for crustal material are restricted to highly weathered shale samples (e.g., Huang et al., 2020). These highly weathered materials are commonly present in mature continental crust whereas they are absent in juvenile arc crust. In contrast to continental sediments, marine sediments seaward of the Lesser Antilles arc have unusually low $\delta^{41}\text{K}$ values (Fig. 2C). If such sediments are present in the arc crust, they may be assimilated into the ascending Martinique magmas. However, the process of simultaneous crustal assimilation and fractional crystallization (AFC) cannot reproduce the variation in $\delta^{41}\text{K}$ with $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 4A). Similarly, binary mixtures of primitive magmas with such sediments within the arc crust (i.e., crustal mixing) cannot explain the observed trend (Fig. 4A). These processes nevertheless produce a reasonable fit between $\delta^{41}\text{K}$ and Sr-Nd-Hf isotopes (Fig. 4B-D), but require unrealistically high proportions (40-90%) of sediment addition that cannot be reconciled with the major element compositions of the lavas. Crustal assimilation also failed to explain the well-defined radiogenic isotope mixing hyperbolas shown by Labanieh et al. (2010) and the low $\delta^7\text{Li}$ values of Martinique lavas (Tang et al., 2014).

The subducting Atlantic plate provides a potential source for the isotopically distinct K added to Martinique lavas. The slab surface temperature beneath Martinique Island ($\sim 780^\circ\text{C}$ at 4.5 GPa, Syracuse and Abers, 2010) is lower than that required to trigger melting of the basaltic crust (Schmidt and Poli, 2014). Indeed, Martinique lavas do not display the high Sr/Y ratio and Sr concentration that are expected in the case of addition of basaltic melts. Therefore, any contribution of basaltic crust to the Martinique magmas would be derived from dehydration fluids. The top basaltic sequence cored at DSDP Site 543A is pervasively altered, displaying alkali metal enrichments typically seen in altered oceanic crust (Bougault et al., 2000). Although altered seafloor basalts may not necessarily be enriched in heavy K isotopes, as indicated by recent

analyses of a western Pacific basement drill core (Hu et al., 2020; Santiago Ramos et al., 2020), dehydration of basaltic crust during subduction could strongly fractionate K isotopes and release heavy K into the fluid phase (Liu et al., 2020). In addition to basaltic crust, dehydration reactions could occur in metamorphosed sediments in overlapping pressure-temperature regions (e.g., Konrad-Schmolke et al., 2016), preferentially releasing heavy K isotopes from both basaltic crust and sediments due to similar solid-fluid fractionation. This is consistent with the Pb and Sr isotopic compositions of the three high- $\delta^{41}\text{K}$ lava samples that suggest a non-negligible sedimentary input (Fig. 4A and B). Therefore, slab-derived fluids from basalt and sediment dehydration are a likely source of heavy K isotopes for the three high- $\delta^{41}\text{K}$ lava samples. The variations of $\delta^{41}\text{K}$ in these three samples could reflect varying proportions of fluid additions from basaltic crust versus sediments, given the stronger correlations of $\delta^{41}\text{K}$ with Pb and Sr isotopes than with Nd and Hf isotopes (Fig. 4). Serpentinite dehydration is another possible source of fluids as inferred from the heavy Mg isotopic compositions in this suite of Martinique lavas (Teng et al., 2016). Given that serpentinite is formed from olivine alteration, fluids released from serpentinite are expected to be enriched in Mg but depleted in K. While these fluids would not affect the K isotopic compositions of the mantle wedge, they may facilitate melting of the subducted sediments.

The majority of the Martinique lavas has $\delta^{41}\text{K}$ values lower than that of the most primitive sample IAR, which is taken to represent the K isotopic composition of the local mantle. Therefore, slab-derived fluids alone cannot explain their K isotopic compositions and an isotopically light K source is required. Marine sediments approaching the Lesser Antilles trench are a suitable source of the light K because they have anomalously low $\delta^{41}\text{K}$ values compared to continental sediments (Fig. 2C). Although sediment dehydration could have released a minor fraction of K to form isotopically heavy dehydration fluids, this solid-fluid fractionation should not have a significant effect on the K isotopic compositions of residual sediments because most K is expected to be retained in the sediments by abundant clay and feldspar. For example, Busigny et al. (2003) studied fluid-mobile elements in oceanic metasediments exhumed from the western Alps, and they found no significant dehydration loss of these elements to at least the depth of arc magma production. Taking the highly fluid-mobile alkali metal Li for comparison, limited Li isotope fractionation occurs during progressive dehydration of metapelites and schists from sub-greenschist to granulite facies metamorphism (Teng et al., 2007; Qiu et al., 2011a,b). It is therefore reasonable to assume that the K isotopic compositions of sediments subducted beneath the Lesser Antilles arc are largely unaffected by dehydration during subduction. In addition, while it is possible that both slab-derived fluids and sediment melts contributed to the mantle sources of some lavas, the influence of sediment melts would dominate over fluids due to orders of magnitude higher K contents in the sediment melts.

There is a significant increase in sediment thickness and turbiditic component toward the south of the trench due to proximity to the Archean South American continent (White et al., 1985). Martinique Island is situated in the middle of the arc, and the nature of its sedimentary input can be examined by relationship between $\delta^{41}\text{K}$ and U/K because this ratio is not affected by magmatic processes but reflects source features. The low- $\delta^{41}\text{K}$ Martinique lavas display a decreasing trend

in $\delta^{41}\text{K}$ with increasing U/K, indicating a dominant contribution from sediments cored at the southern DSDP Site 144, particularly the U-rich, low- $\delta^{41}\text{K}$ black shale units (Fig. 5A). These units were formed during major Oceanic Anoxic Events (OAE 2, 93.5 Ma, e.g., Turgeon and Creaser, 2008); they are missing at DSDP site 543 because oceanic crust in the northern part of the Lesser Antilles arc is too young to have undergone these events (Carpentier et al., 2008). Most Martinique lavas fall on a binary mixing trend between the mantle and bulk Site 144 sediment, with up to 5% of sediment addition (Fig. 5A).

5.2.2. Sediment melts into the lava sources

Sediments can be incorporated to sub-arc mantle either as bulk solids or as partial melts, which can be distinguished using Th/Nd ratio (e.g., DuFrane et al., 2009). Both Th and rare earth elements are mainly associated with subducted sediments (e.g., Plank and Langmuir, 1993; Hawkesworth et al., 1997; Plank, 2005) with limited mobility during low-temperature hydrothermal alteration of oceanic crust (Staudigel et al., 1996; Kelley et al., 2003) and metamorphic dehydration during subduction (e.g., Brenan et al., 1995; Arculus et al., 1999; Becker et al., 1999, 2000). Compared to Nd, Th has a stronger preference for melts over solids; thus, sediment melts have higher Th/Nd than the bulk sediments. In addition to source enrichments by sediments, however, partial melting and magmatic differentiation also elevate the Th/Nd ratios of lavas; therefore, these effects need to be accounted for prior to using the Th/Nd ratios of the lavas to represent their mantle sources. Labanieh et al. (2012) provided a detailed correction method for La/Sm assuming that the primary magmas were formed by 10-20% melting. Using the mineral modal abundance in their calculation, we calculate that the Th/Nd in the primary magmas are enriched by a factor of approximately 1.2 compared to their mantle sources. The corrected Th/Nd display a negative correlation with $\delta^{41}\text{K}$, which corresponds to a decrease in $\delta^{41}\text{K}$ within an increased sediment contribution (Fig. 5B). This mixing trend requires the low- $\delta^{41}\text{K}$ sediment component to have a Th/Nd ratio higher than the bulk sediment cored at DSDP Site 144, indicating that the subducted sediments are added as partial melts. Using experimentally determined bulk partition coefficients for sediment melting at 800°C (Johnson and Plank, 2000), such melts are estimated to have formed by ~ 50% of melting. The lava data fall close to the binary mixing curve between the mantle and sediment melts, with the isotopically lightest lava sample requiring ~ 10% input of sediment melts. This estimate is higher than that assessed from the correlation between $\delta^{41}\text{K}$ and U/K, which is attributable to uncertainties related to element partition coefficients during partial melting of sediments and mantle, as well as during fractional crystallization.

A more accurate estimate for sediment contribution can be obtained from correlations of $\delta^{41}\text{K}$ with radiogenic isotopic compositions because these are not affected by partial melting and crystallization processes. Based on well-defined mixing hyperbolas of radiogenic isotopic compositions, Labanieh et al. (2010) provides tight constraints on the Sr-Nd-Pb-Hf isotopic compositions of the mantle and sediment end members involved in the sources of Martinique lavas, and identified two enriched endmembers with slightly different Pb, Sr, and Hf isotopic compositions for old and recent lavas. The strong and systematic correlations between $\delta^{41}\text{K}$ and

these radiogenic isotopic compositions indicate that the variation in $\delta^{41}\text{K}$ reflects mixing of different proportions of a common sediment endmember with the mantle endmember rather than heterogeneous $\delta^{41}\text{K}$ added from sediments. The weighted average $\delta^{41}\text{K}$ of sedimentary sections drilled at DSDP Site 144 (Hu et al., 2020) is taken to represent the bulk K isotopic composition of the sediment endmembers. Using these values, binary mixing of the mantle and sediment components can reproduce the negative correlations between $\delta^{41}\text{K}$ and Pb-Sr-Nd-Hf isotopic compositions for Martinique lavas, except for the three high- $\delta^{41}\text{K}$ samples that requires an isotopically heavy K input from dehydration fluids (Fig. 6). Based on these correlations, the estimated proportion of sediment contribution varies from $< 1\%$ to 5% , which agrees with the estimation based on $\delta^{41}\text{K}$ vs. U/K correlation (Fig. 5A). These estimations are similar to those proposed by White and Dupré (1986) and Labanieh et al. (2010) constrained from radiogenic isotopes, and Tang et al. (2014) from Li isotopes, of the Lesser Antilles lavas, whereas they are significantly lower than some previous estimations of up to 10-20% of sediment addition that are based on elemental data of erupted lavas (e.g., Turner et al., 1996) or radiogenic isotope data of subducting sediments (Carpentier et al., 2008).

5.3. Implications for geochemical gradient along the Lesser Antilles arc

The Martinique samples analyzed here cover a long magmatic history and large compositional variability; therefore, crustal inputs to Martinique lavas have broader implications for the Lesser Antilles arc. Along the arc, there is a well-recognized transition in lava composition, with those from the northern islands having a typical oceanic mantle composition whereas those from the central and south islands display a progressively crustal-like signature (e.g., Macdonald et al., 2000). This transition may reflect a change in slab input along the arc.

The Martinique lavas contain $\delta^{41}\text{K}$ values both higher and lower than the average mantle value, which suggests modification of their mantle sources by discrete fluid and melt components from the subducted sediments. The preservation of high- $\delta^{41}\text{K}$ fluid signature in Martinique lavas cannot be reconciled with the mélange diapir model proposed for Lesser Antilles, which involves physical mixing of dehydration fluids, bulk sediment, and mantle prior to partial melting (Nielsen and Marschall, 2017). Based on a more comprehensive mapping of La/Sm, Ba/Th, and U/Th ratios over the Martinique Island, Labanieh et al. (2012) suggested that sediment melts mainly contributed to lavas erupted on western Martinique whereas dehydration fluids contributed to those erupted on eastern and southwestern Martinique due to a shallower slab depth and insufficient temperatures for triggering sediment melting. Due to limited numbers of high- $\delta^{41}\text{K}$ samples ($n = 3$), no apparent correlation between their $\delta^{41}\text{K}$ and geological locations are observed. Nevertheless, the three high- $\delta^{41}\text{K}$ samples are located within regions of high Ba/Th that are indicative of a dominate input of slab fluids compared to sediment melts. In addition to Martinique Island, the control of slab geometry on sediment melting versus slab dehydration likely exerts across the entire Lesser Antilles. Therefore, the fluid signature is likely to be more prominent in the north Lesser Antilles due to a lower slab-top temperature by $\sim 50^\circ\text{C}$ (Syracuse et al., 2010).

For the central to south Lesser Antilles arc, sediment melts likely dominate the arc signature, whereby the size of crustal signature may increase towards the south of the arc due to a systematic increase in sediment thickness and highly weathered turbiditic components derived from the South American continent (White et al., 1985). The extent of sediment addition estimated from K isotopes is $\leq 5\%$; thus, a considerably greater sediment input toward the south of the arc is not necessary. On the other hand, correlations between $\delta^{41}\text{K}$ and U/K in Martinique lavas indicate an essential contribution from subducted black shale units to the mantle wedge. These units, which only occur in the southern part of the arc, are also the key component required to explain the extremely radiogenic Pb isotopic compositions in some lavas (Carpentier et al., 2008). Therefore, the along-arc compositional gradient of arc lavas is more likely a reflection of differing compositions of subducted sediments into the mantle wedge.

6. Conclusions

This study analyzed K isotopes in Martinique lavas from the Lesser Antilles arc to address the ongoing debate regarding how mantle-derived arc magmas obtain their crustal signatures. Our results suggest that subducted slab materials are the primary source of the crustal signatures instead of contamination during magma ascent through the crust. The majority of Martinique lavas have $\delta^{41}\text{K}$ varying from mantle-like values of -0.37‰ to variably lowered values (down to -0.66‰), indicating mixing of their mantle sources with $<1\%$ to 5% local subducting sediments that have unusually low $\delta^{41}\text{K}$ values. The correlation between $\delta^{41}\text{K}$ and the Th/Nd ratio suggests that the mantle was mixed with melts from sediments rather than bulk solid sediments. Three lavas have $\delta^{41}\text{K}$ values (-0.28 to 0.01‰) that are higher than the mantle and are attributed to input of slab-derived fluids. This study is the first example of using stable K isotopes to trace active sediment recycling at subduction zones, and it highlights the role of subducted ancient crustal materials in determining the composition of juvenile crust.

Acknowledgements

We thank Ronald S. Sletten and Roberta L. Rudnick for constructive discussions. Insightful comments from three anonymous reviewers and associate editor Dr. Ralf Halama are gratefully acknowledged. This is IGP contribution n° 4176.

References

- Arculus R.J., Lapiere H. and Jaillard E. (1999) Geochemical window into subduction and accretion processes: Raspas metamorphic complex, Ecuador. *Geology* **27**, 547-550.
- Becker H., Jochum K.P. and Carlson R.W. (1999) Constraints from high-pressure veins in eclogites on the composition of hydrous fluids in subduction zones. *Chem Geol* **160**, 291–308.
- Becker H., Jochum K.P. and Carlson R.W. (2000) Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. *Chem. Geol.* **163**, 65–99.

- Bellot N., Boyet M., Doucelance R., Pin C., Chauvel C. and Auclair D. (2015) Ce isotope systematics of island arc lavas from the Lesser Antilles. *Geochim Cosmochim Acta* **168**, 261–279.
- Bezard R., Schaefer B.F., Turner S., Davidson J.P. and Selby D. (2015) Lower crustal assimilation in oceanic arcs: Insights from an osmium isotopic study of the Lesser Antilles. *Geochim Cosmochim Acta* **150**, 330–344.
- Bougault H., Joron J.L., Maury R.C., Bohn M. Tardy M. and Biju-Duval B. (1984) Basalts from the Atlantic crust west of the Barbados Ridge (Site 543, Leg 78A): Geochemistry and mineralogy. In *Initial Reports. DSDP. 78A* (eds. Biju-Duval B. et al.), pp 401–410. U.S. Gov. Print. Off.
- Bouysse P. and Westercamp D. (1990) Subduction of Atlantic aseismic ridges and Late Cenozoic evolution of the Lesser Antilles island arc. *Tectonophysics* **175**, 349–390.
- Bouvier A.-S., Métrich, M. and Deloule E. (2010) Light elements, volatiles, and stable isotopes in basaltic melt inclusions from Grenada, Lesser Antilles: Inferences for magma genesis. *Geochem Geophys Geosys* **11**, doi:10.1029/2010GC003051.
- Brenan J.M., Shaw H.F. and Ryerson F.J. (1995) Experimental evidence for the origin of lead enrichment in convergent-margin magmas. *Nature* **378**, 54–56.
- Busigny V., Cartigny P., Philippot P., Ader M. and Javoy M. (2003) Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (western Alps, Europe). *Earth Planet Sci Lett* **215**, 27–42.
- Carpentier M., Chauvel C. and Mattielli N. (2008) Pb–Nd isotopic constraints on sedimentary input into the Lesser Antilles arc system. *Earth Planet Sci Lett* **272**, 199–211.
- Carpentier M., Chauvel C., Maury R.C. and Mattielli N. (2009) The “zircon effect” as recorded by the chemical and Hf isotopic compositions of Lesser Antilles forearc sediments. *Earth Planet Sci Lett* **287**, 86–99.
- Chauvel C., Dia A.N., Bulurde M., Chabaux F., Durand S., Ildefonse P., Gerard M., Deruelle B. and Ngounouno I. (2005) Do decades of tropical rainfall affect the chemical compositions of basaltic lava flows in Mount Cameroon? *J Volcanol Geotherm Res* **141**, 195–223.
- Chen H., Liu X.-M. and Wang K. (2020) Potassium isotope fractionation during chemical weathering of basalts. *Earth Planet Sci Lett* **539**, doi.org/10.1016/j.epsl.2020.116192.
- Coulon C., Dupuy C., Dostal J. and Escalant M. (1991). Spatial and temporal evolution of the volcanism of Martinique (Lesser Antilles). Petrogenetic implications. *Bulletin de la Société Géologique de France* **162**, 1037–1047.
- Davidson J.P. (1983) Lesser Antilles isotopic evidence of the role of subducted sediment in island arc magma genesis. *Nature* **306**, 253–256.
- Davidson J.P. (1985) Mechanisms of contamination in Lesser Antilles island arc magmas from radiogenic and oxygen isotope relationships. *Earth Planet Sci Lett* **72**, 163–174.
- Davidson J.P. (1986) Isotopic and trace element constraints on the petrogenesis of subduction-related lavas from Martinique, Lesser Antilles. *J Geophys Res* **91**, 5943–5962.
- Davidson J.P. and Harmon R.S. (1989) Oxygen isotope constraints on the petrogenesis of volcanic arc magmas from Martinique, Lesser Antilles. *Earth Planet Sci Lett* **95**, 255–270.
- Davidson J.P. and Wilson M. (2011) Differentiation and Source Processes at Mt Pelée and the Quill; Active Volcanoes in the Lesser Antilles Arc. *J Petrol* **52**, 1493–1531.
- DePaolo D.J. (1981) Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth Planet Sci Lett* **53**, 189–202.
- DuFrane S.A., Turner S., Dosseto A. and van Soest M. (2009) Reappraisal of fluid and sediment contributions to Lesser Antilles magmas. *Chem Geol* **265**, 272–278.
- Freyruth H., Elliott T., van Soest M. and Skora S. (2016) Tracing subducted black shales in the Lesser Antilles arc using molybdenum isotope ratios. *Geology* **44**, 987–990.
- Fujimaki H., Tatsumoto M. and Aoki K. (1984) Partition coefficients of Hf, Zr and REE between phenocrysts and groundmasses. *J Geophys Res* **89**, B662–B672.

- Gaschnig R.M., Reinhard C.T., Planavsky N.J., Wang X., Asael D. and Chauvel C. (2017) The molybdenum isotope system as a tracer of slab input in subduction zones: An example from Martinique, Lesser Antilles Arc. *Geochem Geophys Geosys* **18**, 4674–4689.
- Germa A., Quidelleur X., Labanieh S., Chauvel C. and Lahitte P. (2011) The volcanic evolution of Martinique Island: Insights from K–Ar dating into the Lesser Antilles arc migration since the Oligocene. *J Volcanol Geotherm Res* **208**, 122–135.
- Hawkesworth C.J., O'Nions R.K. and Arculus R.J. (1979) Nd and Sr isotope geochemistry of island arc volcanics, Grenada, Lesser Antilles. *Earth Planet Sci Lett* **45**, 237–248.
- Hawkesworth C.J. and Powell M. (1980) Magma genesis in the lesser Antilles island arc. *Earth Planet Sci Lett* **51**, 297–308.
- Hawkesworth C.J., Turner S.P., McDermott F., Peate D.W. and van Calsteren P. (1997) U–Th isotopes in arc magmas: implications for element transfer from the subducted crust. *Science* **276**, 551–555.
- Hille M., Hu Y., Huang T.-Y. and Teng F.-Z. (2019) Homogeneous and heavy potassium isotopic composition of global oceans. *Sci Bull* **64**, 1740–1742.
- Hu Y., Chen X.-Y., Xu Y.-K. and Teng F.-Z. (2018) High-precision analysis of potassium isotopes by HR-MC-ICPMS. *Chem Geol* **493**, 100–108.
- Hu Y., Teng F.-Z., Plank T. and Chauvel C. (2020) Potassium isotopic heterogeneity in subducting oceanic plates. *Sci Adv*, 6: eabb2472. <https://doi.org/10.1126/sciadv.abb2472>
- Huang T.-Y., Teng F.-Z., Rudnick, R.L., Chen X.-Y., Hu Y., Liu Y.-S. and Wu F.-Y. (2020) Heterogeneous potassium isotopic composition of the upper continental crust. *Geochim Cosmochim Acta* **278**, 122–136.
- Johnson M.C. and Plank T. (2000) Dehydration and melting experiments constrain the fate of subducted sediments. *Geochem Geophys Geosys* **1**, doi.org/10.1029/1999GC000014.
- Labanieh S., Chauvel C., Germa A., Quidelleur X. and Lewin E. (2010) Isotopic hyperbolas constrain sources and processes under the Lesser Antilles arc. *Earth Planet Sci Lett* **298**, 35–46.
- Labanieh S., Chauvel C., Germa A. and Quidelleur X. (2012) Martinique: a Clear Case for Sediment Melting and Slab Dehydration as a Function of Distance to the Trench. *J Petrol* **53**, 2441–2464.
- Langmuir C.H., Vocke R.D., Hanson G.N. (1978) A general mixing equation with applications to Icelandic basalts. *Earth Planet Sci Lett* **37**, 380–392.
- Larue D.K., Smith A.L., Schellekens J.H. (1991) Oceanic island arc stratigraphy in the Caribbean region: don't take it for granite. *Sed Geol* **74**, 289–308.
- Li S., Li W., Beard B.L., Raymo M.E., Wang X., Chen Y. and Chen J. (2019) K isotopes as a tracer for continental weathering and geological K cycling. *Proc Natl Acad Sci USA* **116**, 8740–8745.
- Liu H., Wang K., Sun W.D., Xiao Y., Xue Y.Y. and Tuller-Ross B. (2020) Extremely light K in subducted low-T altered oceanic crust: Implications for K recycling in subduction zone. *Geochim Cosmochim Acta* **277**, 206–223.
- Kelley K.A., Plank T., Ludden, J.N. and Staudigel H. (2003) The composition of altered oceanic crust at ODP sites 801 and 1149. *Geochem Geophys Geosys* **4**, doi: 10.1029/2002GC000435.
- Konrad-Schmolke M., Halama R. and Manea V.C. (2016) Slab mantle dehydrates beneath Kamchatka – Yet recycles water into the deep mantle. *Geochem. Geophys. Geosys.* **17**, 2987–3007.
- Macdonald R., Hawkesworth C.J. and Heath E. (2000) The Lesser Antilles volcanic chain: a study in arc magmatism. *Earth-Sci Rev* **49**, 1–76.
- Nielsen S.G. and Marschall H.R. (2017) Geochemical evidence for mélange melting in global arcs. *Sci Adv* **3**, e1602402.
- Niu Y. and Hékinian R. (1997) Basaltic liquids and harzburgitic residues in the Garrett Transform: a case study at fast-spreading ridges. *Earth Planet Sci Lett* **146**, 243–258.
- Pareno C.A., Jacobsen S.B., Wang K. (2017) K isotopes as a tracer of seafloor hydrothermal alteration. *Proc Natl Acad Sci USA* **114**, 1827–1831.
- Palme, H. and O'Neill, H.S.C. (2014) 3.1 - Cosmochemical Estimates of Mantle Composition, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford, pp. 1–39.

- Plank T. and Langmuir C.H. (1993) Tracing trace elements from sediment input to volcanic output at subduction zones. *Nature* **362**, 739–743.
- Plank T. (2005) Constraints from Thorium/Lanthanum on sediment recycling at subduction zones and the evolution of the continents. *J. Petrol.* **46**, 921–944.
- Plank, T. (2014) 4.17 - The Chemical Composition of Subducting Sediments, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry* (Second Edition). Elsevier, Oxford, pp. 607–629.
- Platzner I.T. (1997) Applications of isotope ratio mass spectrometry in *Modern Isotope Ratio Mass Spectrometry*. vol. 1, pp. 403–447.
- Qiu L., Rudnick R.L., Ague J.J. and McDonough W.F. (2011a) A lithium isotopic study of sub-greenschist to greenschist facies metamorphism in an accretionary prism, New Zealand. *Earth Planet Sci Lett* **301**, 213–221.
- Qiu L., Rudnick R.L., McDonough W.F. and Bea F. (2011b) The behavior of lithium in amphibolite- to granulite-facies rocks of the Ivrea-Verbano Zone, NW Italy. *Chem Geol* **289**, 76–85.
- Ryan, J.G. and Chauvel, C. (2014) 3.13 - The Subduction-Zone Filter and the Impact of Recycled Materials on the Evolution of the Mantle, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry* (Second Edition). Elsevier, Oxford, pp. 479–508.
- Santiago Ramos D.P., Morgan L.E., Lloyd N.S. and Higgins J.A. (2018) Reverse weathering in marine sediments and the geochemical cycle of potassium in seawater: insights from the K isotopic variation ($^{41}\text{K}/^{39}\text{K}$) of deep-sea pore-fluids. *Geochim Cosmochim Acta* **236**, 99–120.
- Santiago Ramos D.P., Coogan L.A., Murphy J.G. and Higgins J.A. (2020) Low-temperature oceanic crust alteration and the isotopic budgets of potassium and magnesium in seawater. *Earth Planet Sci Lett* **541**, 116290.
- Schmidt, M.W. and Poli, S. (2014) 4.19 - Devolatilization During Subduction, in: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry* (Second Edition). Elsevier, Oxford, pp. 669–701.
- Smith T.E., Thirlwall M.F. and Macpherson C. (1996) Trace element and isotope geochemistry of the volcanic rocks of Bequia, Grenadine Islands, Lesser Antilles arc: a study of subduction enrichment and intra-crustal contamination. *J Petrol* **37**, 117–143.
- Speed R.C. and Larue D.K. (1985) Tectonic evolution of Eocene turbidites of Grenada. In *Symposium géodynamique des Caraïbes* (pp. 101–108).
- Staudigel H., Plank T., White W.M. and Schmincke H. (1996) Geochemical fluxes during seafloor alteration of the upper oceanic crust: DSDP Sites 417 and 418. In: Bebout, G.E. and Kirby, S.H. (eds) SUBCON: Subduction from Top to Bottom. Geophysical Monograph, American Geophysical Union 96, 19–38.
- Syracuse E.M., van Keken P.E. and Abers G.A. (2010) The global range of subduction zone thermal models. *Phys Earth Planet Inter* **183**, 73–90.
- Tang M., Rudnick R.L. and Chauvel C. (2014) Sedimentary input to the source of Lesser Antilles lavas: A Li perspective. *Geochim Cosmochim Acta* **144**, 43–58.
- Teng F.-Z., McDonough W.F., Rudnick R.L. and Wing B.A. (2007) Limited lithium isotopic fractionation during progressive metamorphic dehydration in metapelites: a case study from the Onawa contact aureole, Maine. *Chem Geol* **239**, 1–12.
- Teng F.-Z., Li W.-Y., Ke S., Yang W., Liu S.-A., Sedaghatpour F., Wang S.-J., Huang K.-J., Hu Y., Ling M.-X., Xiao Y., Liu X.-M., Li X.-W., Gu H.-O., Sio C. K., Wallace D. A., Su B.-X., Zhao, Chamberlin J., Harrington M. and Brewer A. (2015) Magnesium isotopic compositions of international geological reference materials. *Geostand Geoanalyst Res* **39**, 329–339.
- Teng F.-Z., Hu Y. and Chauvel C. (2016) Magnesium isotope geochemistry in arc volcanism. *Proc Natl Acad Sci USA* **113**, 7082–7087.
- Teng F.-Z., Hu Y., Ma J. and Wei G. (2020) Potassium isotope fractionation during continental weathering and implications for global K isotopic balance. *Geochim Cosmochim Acta* **278**, 261–271.
- Thirlwall M.F., Graham A.M., Arculus R.J., Harmon R.S. and Macpherson C.G. (1996) Resolution of the effects of crustal assimilation, sediment subduction, and fluid transport in island arc magmas:

- Pb–Sr–Nd–O isotope geochemistry of Grenada, Lesser Antilles. *Geochim Cosmochim Acta* **60**, 4785–4810.
- Tuller-Ross B., Marty B., Chen H., Kelley K.A., Lee H. and Wang K. (2019a) Potassium isotope systematics of oceanic basalts. *Geochim Cosmochim Acta* **259**, 144–154.
- Tuller-Ross B., Savage P.S., Chen H. and Wang K. (2019b) Potassium isotope fractionation during magmatic differentiation of basalt to rhyolite. *Chem Geol* **525**, 37–45.
- Turgeon S.C. and Creaser R.A. (2008) Cretaceous oceanic anoxic event 2 triggered by a massive magmatic episode. *Nature* **454**, 323–326.
- Turner S., Hawkesworth C., van Calsteren P., Heath E., Macdonald R. and Black S. (1996) U-series isotopes and destructive plate margin magma genesis in the Lesser Antilles. *Earth Planet Sci Lett* **142**, 191–207.
- van Soest M.C., Hilton D.R., Macpherson C.G. and Matthey D.P. (2002) Resolving sediment subduction and crustal contamination in the Lesser Antilles island arc: A combined He–O–Sr isotope approach. *J Petrol* **43**, 143–170.
- Wang K., Close H.G., Tuller-Ross B. and Chen H. (2020) Global average potassium isotope composition of modern seawater. *ACS Earth Space Chem* **4**, 1010–1017.
- Westbrook G.K., Mascle A. and Biju-Duval B. (1984) Geophysics and the structure of Lesser Antilles forearc. In: Biju-Duval, B., Moore, J.C. (Eds.), Initial Reports of the Deep Sea Drilling Program 78A. U.S. Government Printing Office, Washington, pp. 23–28.
- White W.M., Dupré B. and Vidal P. (1985) Isotope and trace element geochemistry of sediments from the Barbados Ridge-Demerara Plain region, Atlantic Ocean. *Geochim Cosmochim Acta* **49**, 1875–1886.
- White W.M. and Dupré B. (1986) Sediment subduction and magma genesis in the Lesser Antilles: Isotopic and trace element constraints. *J Geophys Res* **91**, 5927–5941.
- Xu Y.-K., Hu Y., Chen X.-Y., Huang T.-Y., Sletten R.S., Zhu D. and Teng F.-Z. (2019) Potassium isotopic compositions of international geological reference materials. *Chem Geol* **513**, 101–107.
- Zeng H., Rozsa V.F., Nie N.X., Zhang Z., Pham T.A., Galli G. and Dauphas N. (2019) Ab Initio calculation of equilibrium isotopic fractionations of potassium and rubidium in minerals and water. *ACS Earth Space Chem* **3**, 2601–2612.

Figure captions

Figure 1. Bathymetric map (GeoMapApp, www.geomapapp.org) showing the location of Martinique Island and DSDP Sites 144 and 543 in the Lesser Antilles region, modified from Labanieh et al. (2010). The Martinique Island is enlarged in the upper-right panel with sampling locations color-coded by the age of the lavas: blue for recent arc, green for intermediate arc, and orange for old arc. The lower-right panel is a histogram showing the unusually low $\delta^{41}\text{K}$ values in the Lesser Antilles subducting sediments compared to global dataset. Data are from Hu et al. (2020).

Figure 2. $\delta^{41}\text{K}$ of Martinique lavas plotted versus (A) SiO_2 , (B) eruptive age, (C) K_2O , and (D) ϵCe . SiO_2 and K_2O contents and ages are from Labanieh et al. (2010), ϵCe values are from Bellot et al. (2015). The $\delta^{41}\text{K}$ of the most primitive lava (sample IAR) is taken to represent the K isotopic composition of the local mantle. $\delta^{41}\text{K}$ data plotted for comparison also include Iceland's Hekla lavas (Tuller-Ross et al., 2019b), continental sedimentary materials (Huang et al., 2020), and local subducting sediments (Hu et al., 2020). For local subducting sediments, carbonate-free K_2O

concentrations are plotted because the sediments entering the southern Antilles trench were predominantly deposited above the Carbonate Compensation Depth (CCD) (Plank, 2014). The three lavas with heavy K isotopes are shown in dark blue; they are likely affected by sediment-derived fluids (see text for discussion). $\delta^{41}\text{K}$ data of the Martinique lavas are reported in Table 1. $\delta^{41}\text{K}$ uncertainties are 95% c.i. in this and following figures.

Figure 3. $\delta^{41}\text{K}$ vs. loss on ignition (LOI) of Martinique lavas. LOI values are from Labanieh et al. (2010).

Figure 4. $\delta^{41}\text{K}$ versus Pb-Sr-Nd-Hf isotopic compositions in Martinique lavas. The red square represents the primitive basalt, and the yellow stars represent the sediment components. The black and red curves are modeled K isotopic variation during processes of assimilation-fractional crystallization, and binary mixing between primitive basalts and sediments within the arc crust (i.e., crust mixing), respectively; both with 10% increment. See Table 2 for modeling details.

Figure 5. $\delta^{41}\text{K}$ versus (A) U/K and (B) Th/Nd in Martinique lavas. The black curve represents binary mixing between the mantle (red square) and the bulk sediment from Site 144 (yellow star) with 1% increment. Mantle $\delta^{41}\text{K}$ value is based on the most primitive lava (sample IAR). Sediment $\delta^{41}\text{K}$ data are from Hu et al. (2020). The U, Th, Nd, and K concentrations of the mantle are from Palme and O'Neill (2014); for Martinique lavas, they are from Labanieh et al. (2010) and for subducting sediments are from Carpentier et al. (2009). The Th/Nd ratios measured in lavas are corrected for effect of fractional crystallization, using partition coefficient of Nd from Fujimaki et al. (1984): 0.1487 for plagioclase, 0.1828 for clinopyroxene, 0.0279 for orthopyroxene, and 1.012 for hornblende, and partition coefficient of Th from <https://earthref.org/KDD/e:90/>: 0.01 for plagioclase, 0.10 for clinopyroxene, 0.14 for orthopyroxene and 0.16 for hornblende. These ratios are then corrected for the effect of partial melting, using partition coefficient of Nd from Niu and Hékinian (1997): 0.0059 for olivine, 0.3030 for clinopyroxene, 0.0163 for orthopyroxene, and 0.0008 for spinel, and partition coefficient of Th from <https://earthref.org/KDD/e:90/>: 0.0001 for olivine, 0.0085 for clinopyroxene, 0.0007 for orthopyroxene and 0.0003 for spinel. The calculation follows supplementary data file 4 from Labanieh et al. (2012). Sediment melt composition was calculated using the bulk partition coefficients (at 800°C) from Johnson and Plank (2000): 1.45 for Th and 4.41 for Nd.

Figure 6. $\delta^{41}\text{K}$ versus Pb-Sr-Nd-Hf isotopic compositions for Martinique lavas. The black curves represent source mixing between mantle and sediment components. Numbers along the curves indicate the % of sediment component added. See Table 2 for modeling details. The three high- $\delta^{41}\text{K}$ lavas are characterized by enriched Pb-Sr isotope ratios and subdued Nd-Hf isotope ratios, suggesting a possible fluid input of isotopically heavy K from sediment dehydration.

Table 1. Potassium isotopic compositions of rock standards and Martinique arc lavas.

Sample	Rock type	Age (ka)	K ₂ O (wt%)	LOI (wt%)	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	²⁰⁶ Pb/ ²⁰⁴ Pb	¹⁷⁶ Hf/ ¹⁷⁷ Hf	δ ⁴¹ K (‰)	2SD (‰)	95% c.i. (‰)	N
Standards												
JB-1	B								-0.41	0.06	0.03	7
Rec. value									-0.42	0.06	0.04	9
AGV-1	A								-0.42	0.07	0.04	7
Rec. value									-0.45	0.05	0.02	19
Arc lavas												
Recent arc												
06MT50	A	1.929	0.98	0.23	0.704269	0.512744	19.4160	0.283046	-0.45	0.04	0.07	4
duplicate									-0.42	0.03	0.04	7
average									-0.43		0.03	
06MT51	A	1.929	1.01	-0.02	0.704261	0.512766	19.4235	0.283093	-0.42	0.04	0.03	8
06MT40	A	189	0.85	0.82	0.704014	0.512832	19.3014	0.283117	-0.40	0.07	0.08	4
duplicate									-0.40	0.04	0.05	6
average									-0.40		0.04	
06MT37	BA	322	0.74	1.12	0.704986	0.512426	19.4802	0.283002	-0.55	0.04	0.03	7
04MT07	A	341	1.07	0.46	0.705482	0.512359	19.5894	0.282874	-0.43	0.02	0.04	6
06MT18	A	346	0.73	1.03	0.703931	0.512853	19.2506	0.283113	-0.20	0.04	0.03	8
06MT28	A	543	0.95	1.2	0.703901	0.512882	19.2263	0.283131	-0.41	0.07	0.04	6
duplicate									-0.42	0.05	0.03	7
average									-0.42		0.03	
IAR	B	640	0.29	-0.01	0.703821	0.512951	19.0545	0.283152	-0.38	0.05	0.03	8
06MT21	A	893	1.33	0.92	0.705718	0.512410	19.6166	0.282893	-0.53	0.08	0.04	8
06MT36	A	998	1.47	1.55	0.706307	0.512293	19.6448	0.282793	-0.48	0.07	0.05	7
duplicate									-0.48	0.04	0.04	7
average									-0.48		0.03	
06MT61	BA	1175	0.64	0.1	0.703716	0.512818	19.1318	0.28311	-0.28	0.07	0.03	7
06MT55	A	1332	0.87	1.19	0.704157	0.512782	19.2893	0.28306	-0.43	0.05	0.04	6
06MT14	A	1530	1.27	0.99	0.705131	0.512616	19.5857	0.283016	-0.55	0.07	0.04	6

duplicate									-0.51	0.06	0.04	7
average									-0.53		0.03	
06MT19	A	1750	1.27	1.4	0.705120	0.512612	19.5904	0.283002	-0.46	0.09	0.04	6
duplicate									-0.45	0.02	0.03	7
average									-0.45		0.03	
06MT04	A	1870	1.49	1.33	0.704972	0.512629	19.5847	0.282999	-0.53	0.04	0.04	6
06MT10	A	2111	1.69	1.85	0.705098	0.512558	19.5970	0.282987	-0.47	0.04	0.04	5
06MT13	A	2550	1.21	1.17	0.704960	0.512650	19.6018	0.282991	-0.46	0.04	0.04	8
Intermediate arc												
06MT60	A	8760	1.9	1.29	0.706689	0.512318	19.8770	0.282856	-0.67	0.09	0.04	7
duplicate									-0.66	0.06	0.04	7
average									-0.66		0.03	
06MT71	B	10300	0.74	0.93	0.704936	0.512806	19.7037	0.283064	-0.01	0.09	0.06	4
duplicate									0.00	0.09	0.04	7
duplicate									0.01	0.06	0.04	7
average									0.01		0.02	
06MT69	B	10640	0.77	1.95	0.704831	0.512837	19.6896	0.28307	-0.47	0.05	0.03	7
Old arc												
06MT54	BA	20800	0.86	1.23	0.704092	0.512973	19.1876	0.283137	-0.45	0.09	0.05	5
duplicate									-0.44	0.07	0.03	7
average									-0.44		0.03	
06MT53	A	23400	0.57	1.36	0.704014	0.512967	19.1900	0.283137	-0.40	0.05	0.03	7
06MT68	B	24800	0.49	1.47	0.703701	0.513030	18.9866	0.283163	-0.37	0.06	0.04	6

The age, K₂O, LOI, and Sr-Nd-Pb isotopic data are from Labanieh et al. (2010).

Abbreviation for rock type: B = Basalt, BA = Basaltic Andesite, A = Andesite.

2SD represent two times standard deviation of N repeated analyses of a sample.

95% c.i. represents 95% confidence interval calculated from 2SD of all measurements on bracketing standard (NIST SRM 3141a) during a session.

N represents the number of repeated analyses on a sample solution during a session.

Duplicate represents repeat instrumental analysis on the same purified K solution during different sessions.

The average value and associated error are error-weighted average calculated from Isoplot.

Rec. value is recommended value from Xu et al. (2019).

Table 2. Modeling parameters and end-member compositions for binary mixing and assimilation-fractional crystallization (AFC).

	Crustal mixing (CM) and AFC				Source mixing		
	Primitive magma	Sediment component		D (AFC)	Mantle	Sediment component	
		Recent	Old			Recent	Old
K ₂ O, wt%	0.29	1.84	1.84	0.09	0.03	1.84	1.84
Sr, ppm	178	220	530	3.2	15.5	220	530
Nd, ppm	5.5	22.6	22.6	0.22	0.713	22.6	22.6
Pb, ppm	1.34	7.9	13	0.61	0.02	7.9	13
Hf, ppm	1.04	3.4	4.3	0.093	0.199	3.4	4.3
$\delta^{41}\text{K}$	-0.38	-0.74	-0.74		-0.38	-0.74	-0.74
⁸⁷ Sr/ ⁸⁶ Sr	0.70360	0.70887	0.71047		0.70346	0.70887	0.71047
¹⁴³ Nd/ ¹⁴⁴ Nd	0.51301	0.51181	0.51181		0.51301	0.51181	0.51181
²⁰⁶ Pb/ ²⁰⁴ Pb	18.5	19.734	19.948		18.5	19.734	19.948
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.28316	0.28230	0.28240		0.28316	0.28230	0.28240

The trace element and radiogenic isotopic compositions of the mantle and sediment components are taken from values provided in Labanieh et al. (2010).

D values for Sr, Nd, Pb and Hf are from Labanieh et al. (2010), and for K is calculated from D values listed on <https://earthref.org/KDD/e:19/> assuming a mineral assemblage suggested by Labanieh et al. (2010), which consists of 60% plagioclase ($D_K = 0.151$), 15% olivine ($D_K = 0$), 13% clinopyroxene ($D_K = 0.0178$), and 12% orthopyroxene ($D_K = 0.014$).

The K₂O content of the mantle is from Palme and O'Neill (2014). The K₂O of the sediment components are from Plank (2014), which is based on the bulk composition of DSDP site 144 sediments reported in Carpentier et al. (2009) and recalculated to a carbonate-free composition.

K₂O content and $\delta^{41}\text{K}$ value of the most primitive lava sample (IAR) are taken to represent primitive magma values.

The $\delta^{41}\text{K}$ of the sediment component is calculated from K₂O-weighted average for sediment samples measured from DSDP Site 144. Sediment $\delta^{41}\text{K}$ data are reported in Hu et al. (2020).

The AFC equations are from DePaolo (1981), assuming an assimilation/crystallization ratio (r) of 0.25 as suggested by Smith et al. (1996).

The binary mixing equations are from Langmuir et al. (1978).