AGU PUBLICATIONS

Geochemistry, Geophysics, Geosystems

RESEARCH ARTICLE

10.1002/2017GC007085

Special Section:
FRONTIERS IN GEOSYSTEMS: Deep Earth - Surface Interactions

Key Points:
- Mo isotopes are useful tracers for subducted sediment contributions to arc magmas
- Secular changes in the Mo isotope composition of arc lavas from Martinique reflect changes in the isotope composition of incoming sediment
- Mo isotopic fractionation during removal of Mo from the subducting slab is not required to explain isotopic systematics of the arc lavas

Correspondence to:
R. Gaschnig,
richard_gaschnig@uml.edu

Citation:
Gaschnig, R. M., Reinhard, C. T., Planavsky, N. J., Wang, X., Asael, D., & Chauvel, C. (2017). The molybdenum isotope system as a tracer of slab input in subduction zones: An example from Martinique, Lesser Antilles Arc. *Geochemistry, Geophysics, Geosystems, 18*. https://doi.org/10.1002/2017GC007085

Received 22 JUN 2017
Accepted 5 DEC 2017
Accepted article online 9 DEC 2017

The Molybdenum Isotope System as a Tracer of Slab Input in Subduction Zones: An Example From Martinique, Lesser Antilles Arc

Richard M. Gaschnig[1], Christopher T. Reinhard[2], Noah J. Planavsky[3], Xiangli Wang[3], Dan Asael[3], and Catherine Chauvel[4]

[1]Department of Environmental, Earth and Atmospheric Sciences, University of Massachusetts Lowell, Lowell, MA, USA, [2]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA, [3]Department of Geology and Geophysics, Yale University, New Haven, CT, USA, [4]ISTerre, University Grenoble Alpes, CNRS, Grenoble, France

Abstract Molybdenum isotopes are fractionated by Earth-surface processes and may provide a tracer for the recycling of crustal material into the mantle. Here, we examined the Mo isotope composition of arc lavas from Martinique in the Lesser Antilles arc, along with Cretaceous and Cenozoic Deep Sea Drilling Project sediments representing potential sedimentary inputs into the subduction zone. Mo stable isotope composition (defined as δ^{98}Mo in ‰ deviation from the NIST 3134 standard) in lavas older than ~7 million years (Ma) exhibits a narrow range similar to and slightly higher than MORB, whereas those younger than ~7 Ma show a much greater range and extend to unusually low δ^{98}Mo values. Sediments from DSDP Leg 78A, Site 543 have uniformly low δ^{98}Mo values whereas Leg 14, Site 144 contains both sediments with isotopically light Mo and Mo-enriched black shales with isotopically heavy Mo. When coupled with published radiogenic isotope data, Mo isotope systematics of the lavas can be explained through binary mixing between a MORB-like end-member and different sedimentary compositions identified in the DSDP cores. The lavas older than ~7 Ma were influenced by incorporation of isotopically heavy black shales into the mantle wedge. The younger lavas are the product of mixing isotopically light sedimentary material into the mantle wedge. The change in Mo isotope composition of the lavas at ~7 Ma is interpreted to reflect the removal of the Cretaceous black shale component due to the arrival of younger ocean crust where the age-equivalent Cretaceous sediments were deposited in shallower oxic waters. Isotopic fractionation of Mo during its removal from the slab is not required to explain the observed systematics in this system.

1. Introduction

Subduction zones are key features in the ongoing differentiation of the Earth. They serve both to produce new continental crust through arc magmatism and to pollute the mantle with crustal materials (e.g., Ryan & Chauvel, 2014). These crustal materials include both oceanic crust produced at mid-ocean ridges and a sedimentary cover that includes materials derived both from continents and from the water column. All of this material is subjected to chemical transformations that are unique to the Earth's surface, such as chemical weathering and low temperature hydrothermal alteration. Stable isotopic tracers that experience fractionation under such circumstances therefore may offer unique insights into mass transfer between the subducting slab, mantle wedge, and magmatic arc. Understanding these fluxes is crucial to broader questions surrounding the origin of continental crust and different mantle geochemical reservoirs.

The molybdenum (Mo) stable isotope system has been investigated over the last few years as a potentially useful new tool for tracing the input of different components of subducting slabs into arc magmas, since different types of sediment and altered oceanic basalt can exhibit distinct Mo isotopic signatures (Freymuth et al., 2015, 2016; König et al., 2016; see review in Willbold & Elliott, 2017). While the Mo isotope compositions of rocks from several arcs appear to differ systematically depending on whether significant subducted sediment melting occurs, mismatches between characterized subduction zone inputs and arc outputs have been taken to suggest that Mo experiences isotope fractionation when leaving the slab and therefore does not directly record the isotope composition of the inputs (Freymuth et al., 2015; König et al., 2016). However, these studies have generally been conducted at the whole-arc scale, and have not looked at the potential for variability at a single eruptive center or the potential for temporal patterns in isotope variability.

In this contribution, we present Mo isotope data for a suite of lavas from the island of Martinique in the Lesser Antilles arc, which contains a ~25 Ma record of arc volcanism and shows evidence for both ocean crust dehydration and sediment melting in magma petrogenesis. We also compare these results to data obtained for sediments recovered from two Deep Ocean Drilling Program sites on the downgoing oceanic plate that can be taken to represent the sedimentary input to the subduction zone. We show that, while different subgroups of Martinique lavas show different Mo isotope ranges and covariation with radiogenic isotopes, all Mo isotope systematics can be explained by mixing between a mantle end-member and sediment compositions present in the downgoing slab, and Mo isotopic fractionation at the slab-mantle interface is not required to explain the observed covariations. By extension, mafic arc lavas in sediment-rich subduction environments may provide a record of the average Mo isotope composition of ocean sediments that is preserved in the geologic record long after the sediments depart the Earth's surface.

2. Background

2.1. Previous Work on Martinique

The Lesser Antilles is an island arc system formed by the westward subduction of Atlantic oceanic lithosphere beneath the Caribbean Plateau. It has been active since the Oligocene Epoch (e.g., Macdonald et al., 2000). The arc is broadly divisible into a northern and southern segment, each with distinctive histories. The northern segment experienced a rearward jump of the magmatic axis around 7 Ma, attributed to the subduction of an aseismic ridge and resulting changes in slab angle (Bouysse & Westercamp, 1990). This led to the development of a new volcanic front west of the original island chain. In contrast, the southern segment of the arc (e.g., southward of ~14°N) has remained fixed. Magma Sr, Nd, and Pb isotopic compositions also differ significantly between the segments. Northern magmas are isotopically primitive and closer to typical island arcs whereas the southern magmas have enriched isotopic signatures, approaching the composition of continental crust (e.g., Davidson, 1987; White & Dupré, 1986).

Martinique is located at the juncture of the northern and southern arc segments. Here, the axis of arc magmatism migrated only a small distance westward. This increased the size of Martinique and gave it a broad east to west age zonation preserving ~25 Ma of arc history (Germa et al., 2011) rather than resulting in the construction of a new island further west, as happened in the northern Lesser Antilles. Martinique has also featured heavily in a long-running debate over the source of isotopic diversity in the Lesser Antilles. Many workers have emphasized the importance of upper plate crustal assimilation (e.g., Bezard et al., 2015a, 2015b; Davidson, 1986; Smith et al., 1997). Other workers have argued that the observed isotopic diversity can be explained solely by differing amounts of subducted sediment melt and slab dehydration input into the mantle wedge (e.g., Carpentier et al., 2008, 2009; Labanieh et al., 2010, 2012; Tang et al., 2014; Teng et al., 2016; White & Dupré, 1986). In addition to the release of discrete melts and fluids from the slab, incorporation of mélange diapirs from the slab into the mantle wedge followed by melting of the mixture has also been proposed to explain isotopic systematics of the Lesser Antilles (Nielsen & Marschall, 2017; see also Marschall & Schumacher, 2012), although the unusually isotopically enriched compositions of Martinique do not entirely adhere to the expected geochemical covariations predicted by this model.

Of particular relevance to this work is the geochemical survey of Martinique by Labanieh et al. (2010, 2012). These workers found that Martinique lavas form well-defined radiogenic isotope mixing hyperbolas but that older samples (7.1–25 Ma) project to a slightly different end-member than younger samples ($\leq$ 5.1 Ma). Both of these hyperbolas project to isotopically enriched end-members that overlap with the range of isotopic compositions found in the DSDP sediment samples characterized by Carpentier et al. (2008, 2009). This model of sediment melting or incorporation into the mantle wedge has been further supported by Li isotope data for the same samples presented by Tang et al. (2014). Labanieh et al. (2012) also noted that trace elements ratios traditionally used to distinguish between subducted sediment melting and slab dehydration influences vary systematically based on location on the island. Lavas on the east side of the island and on the tip of the southwestern peninsula show influence of slab fluids whereas those in the central and northwest parts of the island show influence of sediment melting.

2.2. The Mo Isotope System and Its Application to Subduction Processes

Molybdenum is a transition metal that has the ability to exist in several valence states, with +4 and +6 being the most common. When oxidized to a +6 state, Mo (in the form of MoO_4^{-2} at circumneutral pH) is highly soluble, meaning that chemical weathering of the continents under oxidizing conditions will lead to significantly greater export of Mo to the ocean relative to weathering under anoxic atmospheric conditions (e.g., Kendall et al., 2017). For this reason, the concentration of Mo in ancient ocean sediments has served as an important paleoredox indicator (e.g., Anbar et al., 2007; Scott et al., 2008).

Molybdenum has seven stable isotopes and capture of oxidized Mo in sediments has the ability to induce isotopic fractionation, measured as δ^{98}Mo ([$\delta^{98}\text{Mo} = (^{98}\text{Mo} / {}^{95}\text{Mo}_{\text{sample}} / {}^{98}\text{Mo} / {}^{95}\text{Mo}_{\text{standard}}) - 1] \times 1{,}000$). Capture of dissolved seawater Mo by Fe-Mn oxides significantly favors light isotopes, as does nonquantitative reduction of Mo in suboxic or mildly anoxic sedimentary environments (Arnold et al., 2004; Barling et al., 2001; Siebert et al., 2003). On the other hand, alteration of oceanic crust by seawater appears to result in the preferential sequestration of heavy Mo isotopes (Freymuth et al., 2015; McManus et al., 2002).

Isotopic fractionation of Mo during high-temperature processes is also possible. Greber et al. (2011) reported isotopic fractionation during the formation of hydrothermal molybdenite deposits. In a study of the Kos Plateau Tuff, Voegelin et al. (2014) found that hornblende and biotite incorporated lighter isotopes of Mo preferentially and their crystallization during differentiation drove the magma to higher δ^{98}Mo values. Greber et al. (2014) also reported evidence of Mo isotope fractionation during fractional crystallization and fluid exsolution in granitic magma. On the other hand, Yang et al. (2015) reported no evidence of Mo isotope fractionation with igneous differentiation at the Hekla volcano in Iceland, although this is a "dry" magmatic system that does not crystallize biotite or hornblende. In summary, these findings suggest that differentiation of hydrous magmas is also capable of producing measurable Mo isotopic variation, although the magnitude of this variation is less than that observed in low-temperature settings associated with redox-dependent processes.

The creation of isotopically distinct pools of "surface Mo" in sediments and altered oceanic crust that are then subducted has led to interest in whether Mo isotopes can be used as tracers in studies of arc magmatism (see review in Willbold & Elliott, 2017). Freymuth et al. (2015) considered the Mo isotope composition of mafic lavas from the Marianas arc and compared them to DSDP sedimentary and basaltic oceanic crust samples from the downgoing Pacific plate. They found that the lavas and uppermost altered portions of the downgoing ocean crust have Mo isotopic compositions heavier than unaltered MORB but the majority of sediments are lighter than MORB. With the support of Pb isotopic data, they argued that the Mo isotope signature of the lavas reflected Mo-rich fluids expelled from the minimally altered portions of the subducting basaltic crust and that expulsion of these fluids resulted in isotopic fractionation favoring heavy isotopes in the fluids and lighter isotopes in a residual phase. König et al. (2016) measured the compositions of mafic arc lavas from several localities around the world and reported a large range of ~0.8‰, including many samples with δ^{98}Mo values much lower than MORB. They related differences in δ^{98}Mo to the relative importance of slab dehydration versus sediment melting, with the former resulting in fluids with isotopically heavy Mo and a residue with lighter Mo (analogous to Freymuth et al., 2015) and the latter resulting in the breakdown of the residual phases and release of isotopically light Mo.

Freymuth et al. (2016) recently presented Mo isotopic data on mafic lava samples from the entire length of the Lesser Antilles along with data for sediment from DSDP Site 144. This sample suite included a single sample from Martinique, which yielded a δ^{98}Mo value similar to MORB, but all of the other islands yielded results that were isotopically heavier, with the heaviest values found in samples from islands north of Martinique. Even heavier isotope compositions were observed in Cretaceous black shales from the DSDP site and the authors argued that incorporation of sediments such as these into the mantle wedge was the cause of the higher-than-MORB δ^{98}Mo values seen in the lavas. The comparatively anomalous nature of the Martinique sample was attributed to assimilation of suboxic sediments embedded in the arc-hosting upper plate.

Mo has long been considered to mirror the behavior of Ce in the mantle (Sims et al., 1990) and the Ce/Mo ratio has been used as a proxy for preferential transport of Mo off of the slab or preferentially retention in a residual mineral (Freymuth et al., 2015, 2016; König et al., 2016). Freymuth et al. (2016) noted that while northern Lesser Antilles lavas exhibited δ^{98}Mo values that could be explained by the incorporation of black shales or their melts into the mantle wedge, the lavas exhibited high Ce/Mo, whereas the DSDP black shales exhibited Ce/Mo < 1. This discrepancy was explored in the melting experiments of Skora et al. (2017), which found that different residual mineral phases control the budgets of Mo and Ce during melting, with a major dependence on redox conditions and carbonate content. These authors concluded that melting of the Site 144 black shales could not produce the Ce/Mo values seen in the Lesser Antilles lavas but that a hypothetical mix of black shales and Ca-poor marine clays and terrigenous sediments could explain the lava compositions.

The Freymuth et al. (2016) study of the Lesser Antilles and the studies from other arcs described above were generally reconnaissance studies that considered a small number of samples distributed along the entire length of the arc. Here, we focus on a single arc volcanic island with a ~25 Ma preserved history and a large sample suite already well characterized for the major radiogenic isotope systems and several stable isotope systems. This complements the regional studies and provides an additional window on the processes controlling Mo and its isotopes in arc systems and may ultimately also provides new insights into the potential to use the Mo isotope composition of arcs to track deep marine redox evolution.

3. Methods

3.1. Samples

The Martinique lava samples studied here are primarily basaltic to andesitic in composition, with the exception of one dacitic sample. The lavas have ages ranging from ~25 to ~0 Ma. Deep Sea Drilling Project sediment samples come from two sites (Figure 1). DSDP Leg 14, Site 144 is from the edge of the Demerara Rise, about 1,000 km SE of Martinique. Samples range in age from Oligocene to Early Cretaceous; they are uniformly carbonate-rich and include marlstone, black shale, and chalk ooze (Hayes et al., 1972). DSDP Leg 78A

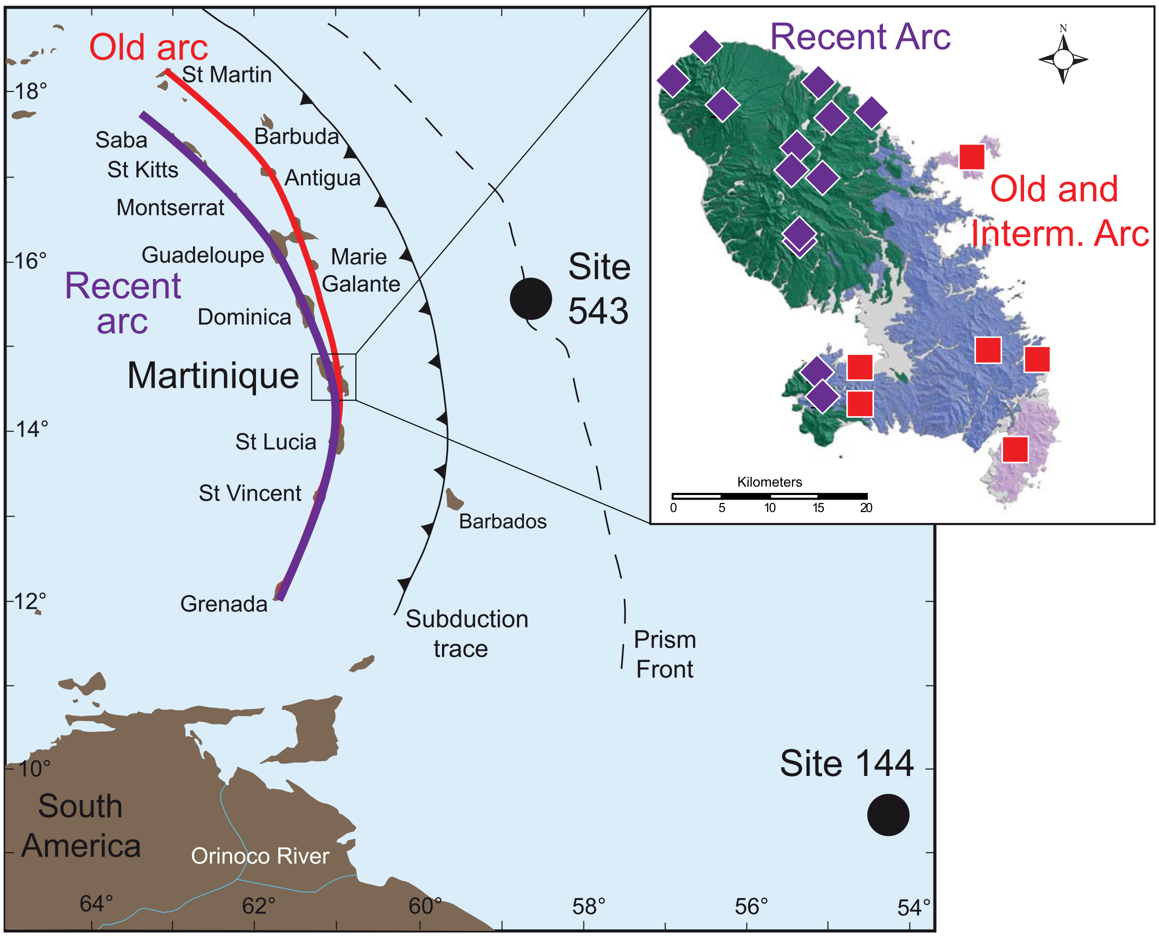

Figure 1. Map of the Lesser Antilles arc, showing DSDP sites, and inset of Martinique, showing lava sample locations (modified from Labanieh et al., 2010). For the sake of simplicity, the term "Old Arc" used in this paper will combine the Intermediate and Old Arc portions of the island shown in the inset.

Site 543 is from about ~270 km NE of Martinique. Samples range from Oligocene to Late Cretaceous and consist primarily of pelagic and radiolarian clays, with the youngest two samples containing some volcanic ash (Biju-Duval & Moore, 1984).

The lava samples studied here have been previously characterized for their major and trace element compositions and their Sr, Nd, Pb, and Hf isotope compositions by Labanieh et al. (2010, 2012). Only samples that showed no sign of alteration (as reported by Labanieh et al., 2012) were chosen for Mo isotope characterization. Sediment samples were previously characterized for major and trace element compositions and Sr, Nd, Pb, and Hf isotope compositions by Carpentier et al. (2008, 2009). Many of both the lavas and sediments have also been characterized for their Li (Tang et al., 2014), Ce (Bellot et al., 2015), and Mg (Teng et al., 2016) isotope compositions.

3.2. Sample Digestion and Mo Separation

Lava samples were digested on the hot plate in screw-top beakers in 3 mL of concentrated HF + 0.5 mL of concentrated HNO_3 at 140°C for 2 days and then evaporated. Sediments samples, which may contain zircon, were digested with the same acid mixture at high pressure in Parr bombs for 2 days at 140°C, before being unsealed and evaporated. Both types of sample materials were then dissolved in 3 mL of concentrated HCl + 1 mL of concentrated HNO_3 and heated overnight with the beakers capped before being evaporated. The resulting salts were dissolved in 4 mL of 6*M* HCl, with a small aliquot being taken to determine the concentration of Mo by ICP-MS in order to ensure a constant sample-spike ratio for isotope work. Aliquots of samples were taken and combined with a ^{97}Mo – ^{100}Mo double spike (spike used in Asael et al., 2013) in proportions designed to double the Mo concentration of the mixture.

Mo was isolated using the two-step chromatography procedure outlined in Asael et al. (2013). Samples were first loaded on anion exchange columns in HCl and washed to remove most of the sample matrix elements before being eluted. The Mo cut was then further purified on cation exchange columns to separate any remaining Fe.

3.3. Molybdenum Isotope Analysis

Molybdenum isotope analyses were conducted on a Thermo NeptunePlus MC-ICP-MS at the Yale Metal Geochemistry Center. Solutions were introduced with an ApexIR desolvating nebulizer and analyzed in static mode, with ^{91}Zr and ^{99}Ru being monitored in addition to the isotopes of Mo. Samples were analyzed in groups of three and bracketed by analyses of the NIST 3134 Mo standard and periodic analyses of the Johnson Matthey Specpure Mo plasma standard (also known as RochMo2). Data were reduced using a modified approach of Siebert et al. (2001).

All δ^{98}Mo values are reported per mil relative to the NIST 3134 standard (Goldberg et al., 2013), which is set to 0—following recent studies of igneous applications of the Mo isotope system (e.g., Bezard et al., 2016; Freymuth et al., 2015, 2016; König et al., 2016). Four analyses of three separately digested aliquots of the USGS reference material BHVO-2 yield a mean δ^{98}Mo value of $-0.08 \pm 0.03‰$ (2σ) (Table 1), which is within range of the values reported by Burkhardt et al. (2014), Hin et al. (2013), Li et al. (2014), König et al. (2016), Bezard et al. (2016), Freymuth et al. (2016), Zhao et al. (2016), and Liang et al. (2017). One analysis of the USGS reference material W-2 yielded a δ^{98}Mo value of $-0.04 \pm 0.08‰$ (2σ), which overlaps with the values given by Burkhardt et al. (2014), Zhao et al. (2016), and Bezard et al. (2016). External reproducibility of the Mo isotope standard was $\pm$ 0.04‰ (2σ).

4. Results

4.1. Lavas

Figure 2 shows that δ^{98}Mo results for the Martinique lavas vary systematically with age. These variations occur on the same time scale as the variations in radiogenic isotope compositions reported by Labanieh et al. (2010). Consequently, we will use the same terminology, describing samples older and younger than ~7 Ma as the "Old" and "Recent Arc," respectively. Samples from the Old Arc can be split into two groups based on both δ^{98}Mo and location. More western samples have δ^{98}Mo values of +0.06 to 0.08 and samples from the easternmost part of the island have δ^{98}Mo values from −0.11 to −0.15. Samples from the Recent Arc show a much larger δ^{98}Mo range and are also isotopically lighter on average. δ^{98}Mo values range from

Table 1
Mo Isotope Results

Sample	Latitude	Longitude	Age (Ma)	Lithology	Unit	[Mo] – isotope dilution	δ^{98}Mo NIST3134	2sigma
Lavas								
Younger lavas								
06MT10	14.7361	−61.0591	2.1	Andesite	Jacob 2	1.01	−0.18	0.09
06MT14	14.7686	−61.0863	1.5	Andesite	Jacob 2	0.65	−0.36	0.06
06MT18	14.8372	−61.2177	0.35	Andesite	Conil	0.57	−0.52	0.06
06MT23	14.7988	−61.0497	0.49	Basaltic andesite	Jacob 1	0.53	−0.35	0.05
06MT28	14.8717	−61.1820	0.54	Andesite	Conil	0.78	−0.41	0.08
06MT30	14.7449	−61.0920	3	Basaltic andesite	Jacob 2	0.66	−0.88	0.06
06MT32	14.8354	−61.0635	5.1	Basalt	Jacob 1	0.43	−0.23	0.06
06MT34	14.8065	−61.0075	4.1	Basaltic andesite	Jacob 1	0.84	−0.06	0.11
06MT37	14.6751	−61.0845	0.322	Basaltic andesite	Carbet	1.11	−0.28	0.05
06MT50	14.8109	−61.1673	0	Andesite	Pelee	0.71	−0.09	0.08
Older lavas								
06MT72	14.5394	−61.0224	7.10	Dacite	Gros Ilet	0.28	0.08	0.09
06MT60	14.5009	−61.0173	8.76	Andesite	SSW volc	0.70	0.09	0.18
06MT71	14.5456	−60.8324	10.3	Basalt	Vauclin Pitault 2	1.03	−0.11	0.08
06MT69	14.5575	−60.8846	10.8	Basalt	Vauclin Pitault 2	0.88	−0.15	0.08
06MT54	14.7391	−60.9095	20.8	Basaltic andesite	Saint Anne	0.42	0.06	0.07
06MT68	14.4520	−60.8556	24.8	Basalt	Saint Anne	0.28	−0.15	0.10
Offshore Sediments								
Site 144								
144-9			34	Chalk ooze	Unit 1	0.53	−0.47	0.07
144-12			41	Chalk ooze	Unit 1	0.20	−0.65	0.08
144-20			70	Zeolitic greenish gray marl	Unit 2	0.20	−0.61	0.09
144-28			90	Black and olive marl	Unit 3	97.54	0.49	0.06
144-33			104	Quartzose marlstone with shelly limestone and carbonaceous clay	Unit 5	0.70	0.63	0.10
144-34			106	Quartzose marlstone with shelly limestone and carbonaceous clay	Unit 5	0.41	−0.57	0.07
144-35			110	Quartzose marlstone with shelly limestone and carbonaceous clay	Unit 5	0.43	−0.19	0.09
Grand average[a]						17.29	0.47	
SITE 543								
543-4			26	Radiolarian clay with ashy layers	Unit 4	3.75	−0.54	0.06
543-7			31.5	Radiolarian clay with ashy layers	Unit 4	2.16	−0.75	0.07
543-8			36	Mn-stained radiolarian clay	Unit 5a	9.62	−0.68	0.19
543-10			50	Mn-stained radiolarian clay	Unit 5a	6.25	−1.06	0.06
543-12			52	Zeolitic clay and claystone	Unit 5b	11.51	−0.37	0.05
543-19			55	Claystone	Unit 5c	4.64	−0.63	0.06
543-24			82	Calcareous ferruginous claystone	Unit 6	5.38	−1.12	0.06
Grand average[a]						6.08	−0.70	
References materials								
BHVO-2, digest #1						4.20	−0.08	0.05
BHVO-2, digest #2, 1st aliquot						3.84	−0.07	0.06
BHVO-2, digest #2, 2nd aliquot						3.88	−0.06	0.06
BHVO-2, digest #3						3.63	−0.10	0.07
Mean							−0.08	0.03
W-2						0.45	−0.04	0.08

[a]Grand average takes into account thickness and density of each stratigraphic unit, after Carpentier et al. (2008).

−0.06 to −0.88‰ (Figure 2). Molybdenum concentrations determined by isotope dilution range from 1.11 to 0.28 ppm and do not vary systemically between the Old and Recent Arc samples (Figure 3).

4.2. Sediments

Sediments from Site 144 yield a bimodal distribution of δ^{98}Mo values (Figures 4 and 5). A Turonian marl and an Albian quartzose marlstone with interbedded limestone and carbonaceous clay are anomalously heavy,

Table 2
Mixing End-Members

End-member	Mo (ppm)	δ^{98}Mo	Sr (ppm)	$^{87}Sr/^{86}Sr$	Nd (ppm)	ε_{Nd}	Pb (ppm)	$^{206}Pb/^{204}Pb$
Depleted MORB source with low [Mo][a]	0.025	−0.16	17	0.7036	0.7	7.4	0.02	18.50
Depleted MORB source with high [Mo][a]	0.17	−0.16	17	0.7036	0.7	7.4	0.02	18.50
DSDP Site 543 sediments, grand average	6.1	−0.70	110	0.7090	31	−13.0	19	19.32
DSDP Site 144 sediments, grand average[b]	11	0.52	656	0.7085	23	−12.0	7	19.52

Note. ε_{Nd} calculated with Bouvier et al. (2008) chondrite parameters.
[a]Low [Mo] from Salters and Stracke (2004); high [Mo] from Liang et al. (2017).
[b][Mo] and δ^{98}Mo grand averages for Site 144 sediments includes both new data presented here and published data of Freymuth et al. (2016).

with δ^{98}Mo values of +0.49 and +0.63‰, while the other Cretaceous marls and marlstones and Cenozoic samples chalk ooze samples range from −0.19 to −0.65‰ (Figures 4 and 5). One of the isotopically heavy samples has an extremely high Mo concentration (97.5 ppm) while all other samples have concentrations less than 1 ppm. The range in Mo isotope compositions and concentrations mirrors that reported by Freymuth et al. (2016) for other samples from this site. Site 543 samples, consisting of clays and claystones, differ from those from Site 144 in that they yield consistently light δ^{98}Mo values, ranging from −0.37 to −1.12‰ (Figures 4 and 5). Molybdenum concentrations from Site 543 samples range from 11.5 to 2.16 ppm.

Using the approach of Carpentier et al. (2008) and considering the thickness and density of each sedimentary unit, we can calculate grand averages of the Mo concentration and isotope composition of the sediment sequence at each site (Table 2). We include the data reported by Freymuth et al. (2016) for Site 144 in the grand average for that site. The concentration and δ^{98}Mo value for Site 144 is 11.0 ppm and +0.52‰, respectively, whereas the concentration and δ^{98}Mo value for Site 543 is 6.1 ppm and −0.70‰, respectively. Site 144 shows extreme enrichment of Mo in sedimentary Unit 3 (roughly 200 times greater than other units) and in general shows huge isotopic variability. Therefore, the grand average for Site 144 should be utilized with caution.

5. Discussion

5.1. δ^{98}Mo of Martinique Lavas Compared to Other Lesser Antilles Islands and Other Arcs

Lavas from Martinique show an extreme diversity in Mo isotope compositions, with δ^{98}Mo values spanning ∼1.8‰ in total and significant differences between the Old and Recent Arc lavas. Lavas from the Old Arc overlap in δ^{98}Mo composition with results from other islands in the Lesser Antilles (Freymuth et al., 2016). Old Arc samples from the extreme eastern part of Martinique have δ^{98}Mo values resembling the Lesser Antilles islands to the north of Martinique reported by Freymuth et al. (2016), and these values also overlap with the depleted MORB mantle (Figure 3) (Bezard et al., 2016; Liang et al., 2017). Old Arc samples from the more western parts of Martinique have the heaviest Mo isotope compositions seen on Martinique, with values resembling the southern islands of the Lesser Antilles (Figure 3) (Freymuth et al., 2016). On the other hand, many of the Recent Arc samples extend to much lighter values than either the other Lesser Antilles or MORB. These compositions extend to, and in one case exceed, the lowest δ^{98}Mo values for arc lavas reported in the literature (König et al., 2016). The anomalously light δ^{98}Mo values seen elsewhere are characteristic of arc systems where subducted sediment is melting (König et al., 2016).

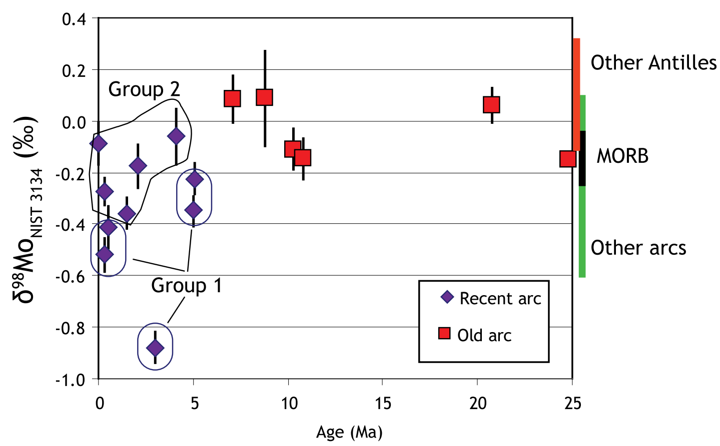

Figure 2. δ^{98}Mo versus age for the lava samples from Martinique. Samples older than ∼6 Ma tend to have a heavier isotopic composition than the younger ones. Bars on right side of plot represent δ^{98}Mo ranges found in the literature for MORB (black) (Bezard et al., 2016), the other Lesser Antilles islands (Freymuth et al., 2016), and other arcs (Voegelin et al., 2014; Freymuth et al., 2015; König et al., 2016), excluding two anomalously high and one anomalously low δ^{98}Mo values from Bezard et al. (2016) and König et al. (2016), respectively.

5.2. Origins of δ^{98}Mo Signal in DSDP Sediments

The sediments from the two DSDP cores differ greatly in lithology and bulk geochemistry, reflecting a mixture of carbonate and terrigenous material at Site 144 and pelagic material at Site 543, but the post-Turonian sediments of both cores are all isotopically light (Figure 5).

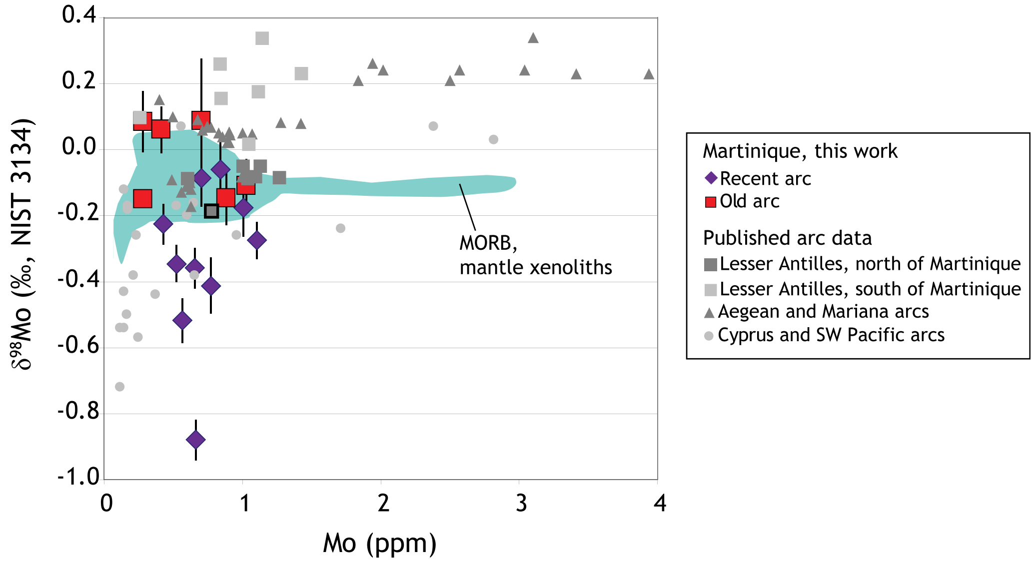

Figure 3. δ^{98}Mo versus Mo concentration for Martinique lavas. The Recent Arc lavas have light isotope compositions, distinct from other islands in the Lesser Antilles and several other arcs sampled worldwide. Published data sources for other arc rocks: others islands in the Lesser Antilles and one sample (bold outline) from Martinique (Freymuth et al., 2016); Kos (Voegelin et al., 2014); Mariana Islands (Freymuth et al., 2015); and the southwest Pacific and Cyprus (König et al., 2016). MORB and mantle xenolith field from Bezard et al. (2016) and Liang et al. (2017).

This probably reflects deposition in relatively well-oxygenated waters with light Mo isotopes scavenged from the water column by Fe/Mn-oxide mineral phases. On the other hand, the older Upper and the Lower Cretaceous sediments (present only at Site 144) yield δ^{98}Mo values that are both negative and positive. One of the samples (144-28) with a positive δ^{98}Mo value is from a black shale unit deposited around the time of

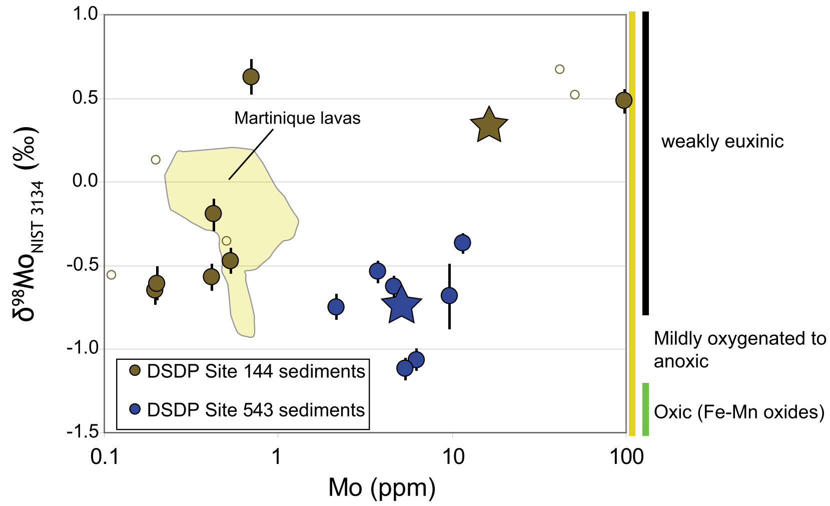

Figure 4. δ^{98}Mo versus Mo concentration for the DSDP sediments, shown in comparison to the Martinique lavas. (Note the use of the log scale on the *x* axis in contrast to Figure 3). Site 543 samples have consistently moderate Mo concentrations and light Mo isotope compositions whereas the Site 144 samples (including those from Freymuth et al., 2016, shown as open brown circles) are much more variable. Some of the Cretaceous samples from Site 144 have extreme Mo enrichment and heavier Mo isotopic compositions whereas other Cretaceous and all Cenozoic samples show light Mo isotope compositions. Large stars are grand average compositions for the two sites. Vertical bars on the right show range of Mo isotope compositions seen in marine sediments deposited under different redox conditions (Kendall et al., 2017 and references therein).

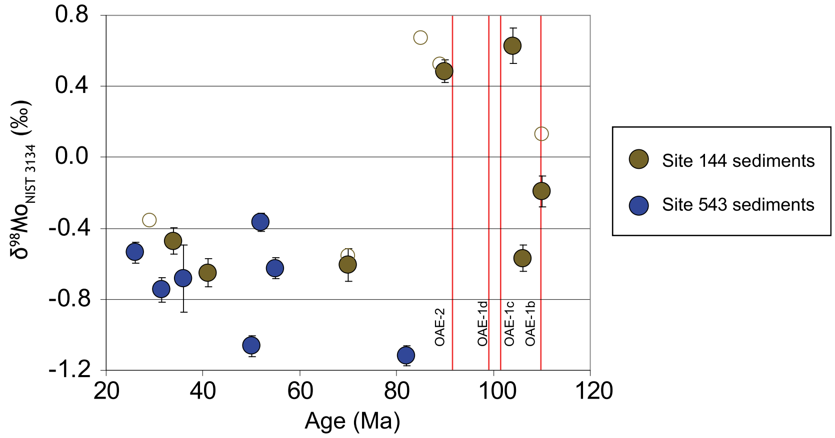

Figure 5. δ^{98}Mo values versus age for DSDP sediments. Although lithologies differ greatly between the cores, post-Turonian sediments from the two cores yield similarly negative δ^{98}Mo values indicative of oxidized Mo scavenged from the water column. The older Cretaceous sediments recovered only at Site 144 record both relatively oxic depositional intervals with negative δ^{98}Mo values and more anoxic conditions, including during Ocean Anoxic Event 2, indicated by positive δ^{98}Mo values. Open brown circles are data for Site 144 from Freymuth et al. (2016). OAE events after Leckie et al. (2002).

Ocean Anoxic Event-2 and is strongly enriched in both Mo and U. This suggests deposition under more reducing conditions, under which δ^{98}Mo of sediments can begin to approach the much heavier δ^{98}Mo values characteristic of seawater. Although seawater has a δ^{98}Mo of $\sim$2.0‰ today and the black shale sampled here has a value of 0.49, Goldberg et al. (2016) has suggested that the δ^{98}Mo of ocean water was as low as 0.6% during OAE-2, which would be consistent with euxinic (anoxic and sulfidic) water column conditions during the deposition of this sample. Another Cretaceous sample from Site 144 (144-33) has a slightly heavier Mo isotope composition but lacks the extreme Mo and U enrichment seen in sample 144-28. This sample could reflect deposition under conditions that were anoxic but not euxinic, and the remaining Cretaceous samples yielding negative δ^{98}Mo values were probably deposited under conditions that were at least mildly oxygenated.

5.3. Origin of δ^{98}Mo Variability in Martinique Lavas

The expansive range of Mo isotope compositions seen in the Martinique lavas, coupled with the great isotope heterogeneity documented in published radiogenic studies (see above) indicates that multiple components are involved in the genesis of these lavas. However, evidence for Mo variation due to fractional crystallization has been documented in another arc system (Voegelin et al., 2014) so the potential for this effect needs to first be considered before evaluating what ingredients are needed in the recipe for Martinique's lavas.

5.3.1. Do Variations in Lava δ^{98}Mo Reflect Magma Sources or the Effects of Igneous Differentiation?

Studies of the effects of magmatic differentiation on Mo isotope composition have produced differing results. The work most relevant to our sample suite is the study on arc volcanics at Kos by Voegelin et al. (2014), who found that hornblende and biotite separates in dacite had lighter Mo isotope compositions than the bulk rock values. It therefore stands to reason that crystallization and removal of these phases in a similarly hydrous arc magmatic system such as Martinique might lead to heavier Mo isotope compositions in more felsic lava samples.

Figure 6 shows that samples from the Recent Arc show no correlation between δ^{98}Mo values and MgO or SiO_2, indicating that their δ^{98}Mo compositions were not affected by fractional crystallization. However, samples from the Old Arc show a modest positive correlation between δ^{98}Mo and SiO_2 and negative correlation between δ^{98}Mo and MgO (Figure 6), which would be consistent with fractional crystallization leading to high δ^{98}Mo values. However, the isotopically heaviest samples also have the most radiogenic Sr and Pb isotopic compositions and the least radiogenic Nd and Hf isotopic compositions (Figure 7). Radiogenic isotopic compositions are unaffected by fractionation crystallization so it is likely that the isotopically heavy Mo in the more felsic samples is derived from the same multicomponent mixing process (i.e., source mixing, magma mixing, or assimilation) that also governed the radiogenic isotopes. Although previous workers

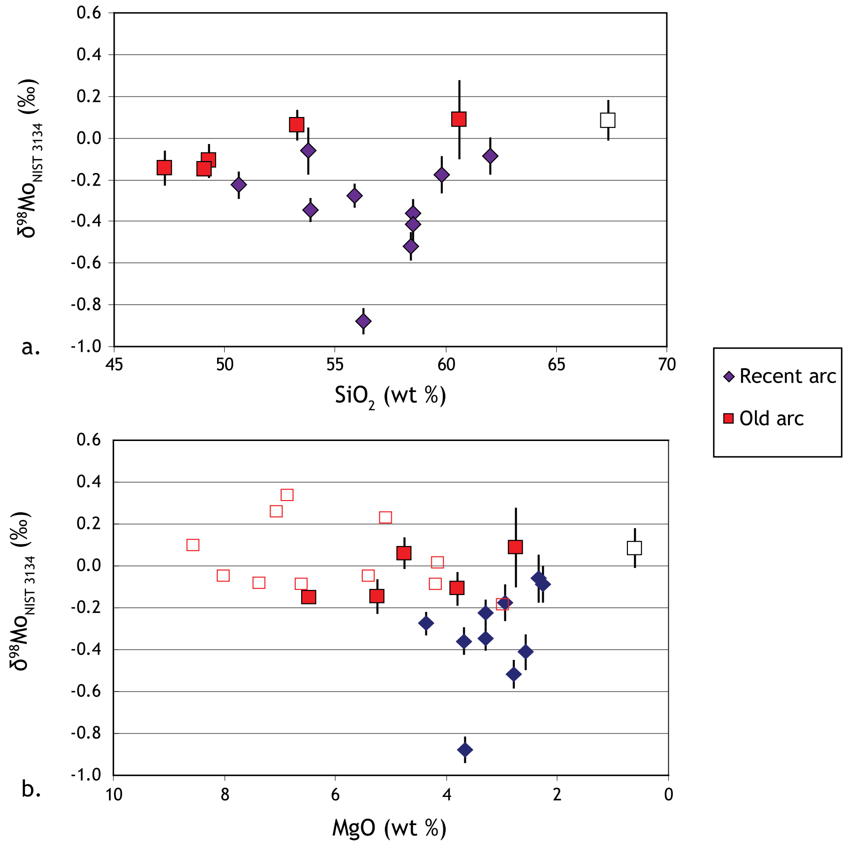

Figure 6. δ^{98}Mo versus (a) SiO_2 and (b) MgO for Martinique lavas. SiO_2 and MgO values (in weight percent) are from Labanieh et al. (2012). The Older Arc samples show a gentle increase in δ^{98}Mo with SiO_2 and decrease with MgO. While crystallization of amphibole and/or biotite has been shown to potentially remove lighter Mo isotopes from magma (König et al., 2016) and would explain the presence of higher δ^{98}Mo in the most evolved samples, differences in the radiogenic isotope compositions of the Older Arc samples argue against this. Red open boxes in Figure 6b are data for other Lesser Antilles islands from Freymuth et al. (2016). The unfilled box in this and Figure 3 is the Gros Islet dacite, which has previously singled out as having experienced significant crustal contamination.

using the same sample set have argued for the primacy of source mixing in the generation of geochemical diversity at Martinique, sample 06MT72, which has the second highest δ^{98}Mo value, may have been affected by upper plate assimilation. This sample is an unusually peraluminous dacite containing igneous garnets from Gros Islet, and this unit has previously been singled out as a likely example of crustal contamination (Davidson, 1986; Labanieh et al., 2012; Macdonald et al., 2000).

In summary, the effects of differentiation in crustal magma reservoirs on the Mo isotope compositional range seen in the Martinique lavas are at least secondary if not negligible. We make the case below that variability in Mo isotopic composition to be due to mixing between multiple Mo sources during lava formation.

5.3.2. Origin of δ^{98}Mo Variations in Lavas by Source Mixing Processes?

Labanieh et al. (2010) previously showed that Martinique lavas form well-defined mixing hyperbolas in radiogenic isotope space and that these hyperbolas for the Recent and Old Arc both project to enriched differing end-members that both overlap isotopically with parts of the sedimentary package at DSDP Site 144. Since the δ^{98}Mo compositions of the lavas are not strongly affected by fractional crystallization, the Mo isotope compositions probably reflect multicomponent mixing, and here we explore this hypothesis by considering how the Mo isotope compositions of the lavas and DSDP sediments covary with their published radiogenic isotope and stable isotope compositions (Bellot et al., 2015; Carpentier et al., 2008, 2009; Labanieh et al., 2010; Tang et al., 2014; Teng et al., 2016).

The relationships between δ^{98}Mo and other isotope systems for the lavas and sediments are shown in Figures 7 and 8. Samples of the Old Arc show a relatively limited range of δ^{98}Mo values but a significant range

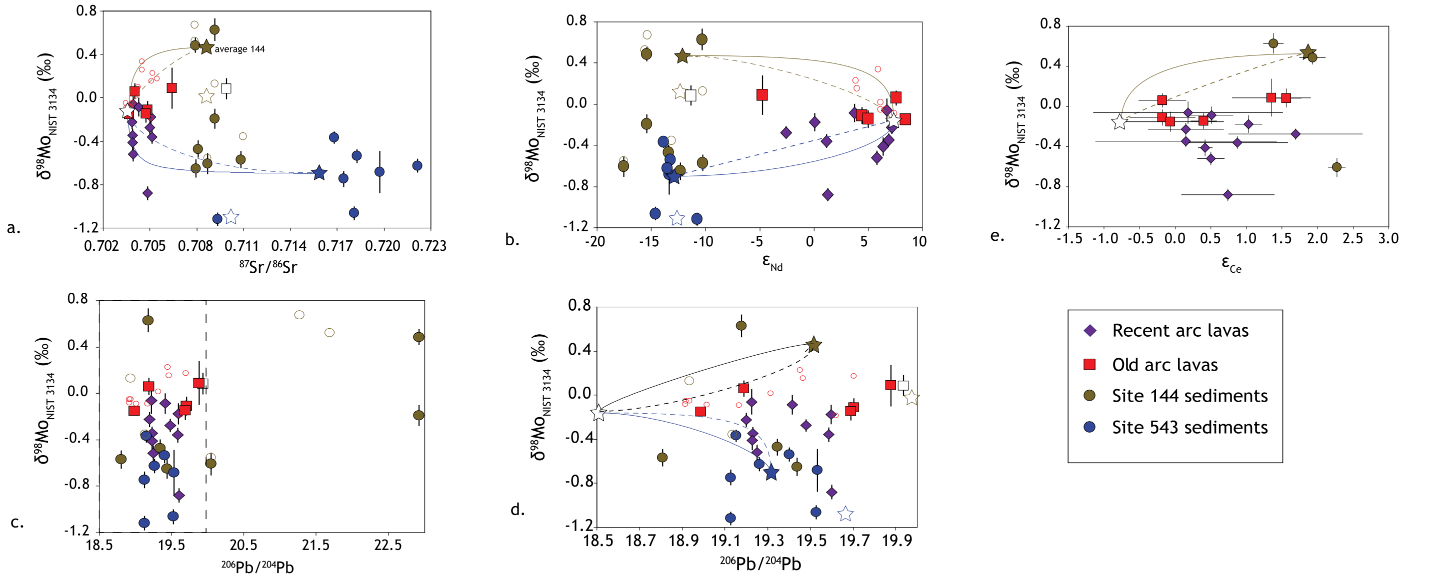

Figure 7. δ^{98}Mo versus published radiogenic isotope data for the same samples. Radiogenic data from Labanieh et al. (2010) for lavas and Carpentier et al. (2008, 2009) for sediments, with the exception of cerium isotope data in Figure 7e, which was reported by Bellot et al. (2015) for both lavas and sediments. Unfilled box is the Gros Islet dacite, which likely experienced crustal contamination. Unfilled circles are data from Freymuth et al. (2016) for Lesser Antilles lavas (red) and Site 144 sediments (brown). White stars with black outlines represent the mantle end-member in mixing calculations whereas the colored stars are the average compositions of the sediments from the two DSDP sites (accounting for sediment unit thickness and density). Stars with colored outlines are hypothetical sediment compositions needed to explain the data arrays. Solid mixing lines were calculated assuming a mantle end-member with 0.025 ppm Mo (after Salters & Stracke, 2004) whereas the dashed lines assume a high concentration of 0.17 ppm (after Liang et al., 2017). Plot (d) is an enlarged version of the dashed box in Figure 7c.

of Sr, Nd, Pb, and Ce isotope compositions (Figure 7). ^{87}Sr / ^{86}Sr and ε_{Nd} values are higher and lower, respectively, for higher δ^{98}Mo values but there is no comparable relationship with ^{206}Pb / ^{204}Pb and ε_{Ce}. Samples from the Recent Arc appear to form two separate curved arrays in δ^{98}Mo versus radiogenic isotope space. One group shows little radiogenic isotopic variability but large δ^{98}Mo variations whereas the another group shows large variation in radiogenic isotopes but more modest variation in δ^{98}Mo. The relationships between δ^{98}Mo and Li and Mg isotopes are shown in Figure 8. The range of Li and especially Mg isotopic variation relative to measurement uncertainty is small, and no strong correlation are observed when uncertainties are considered.

The incorporation of sediment into the arc mantle source can be modeled as bulk mixing between the grand averages (based on sediment unit thicknesses and densities, see above) of the sediments from Sites 144 and 543 and a mantle source, but choice of the composition of the mantle end-member is complicated by the differing results for both δ^{98}Mo and Mo concentration of the upper mantle in the literature. Bezard et al. (2016) reported Mo isotope data for MORB with a mean of $-0.16 \pm 0.09‰$ (2σ, excluding three anomalously high values), whereas Liang et al. (2017) reported Mo isotope data for MORB with a mean of $0.00 \pm 0.02‰$ and data for continental xenoliths and ultramafic rocks with a mean of $-0.19 \pm 0.06‰$. Willbold and Elliott (2017) recommended a δ^{98}Mo composition of the MORB mantle of $-0.21 \pm 0.02‰$ based on Hibbert et al. (2013), although those results were only presented in abstract form. The average concentration of Mo in the mantle is also subject to conflicting estimates. Estimates based on the ratio of Mo to light rare earth elements in basalts have yielded concentrations of 0.025 ppm for the depleted mantle (Salters & Stracke, 2004) and 0.047 ppm for the primitive mantle (Palme & O'Neill, 2014). A similarly low value of 0.023 ppm for the Archean primitive mantle was reported by Greber et al. (2014) based on data from komatiites. In contrast, recent direct measurement of Mo in ultramafic samples has yielded significantly high concentrations, with Liang et al. (2017) reporting values as high as 0.40 ppm and a mean of 0.17 ppm. Below, we consider mixing models that utilize mantle end-members with the Bezard et al. (2016) δ^{98}Mo average of $-0.16‰$ but with varying Mo concentrations, with a depleted end-member of 0.025 ppm and an enriched end-member of 0.17 ppm.

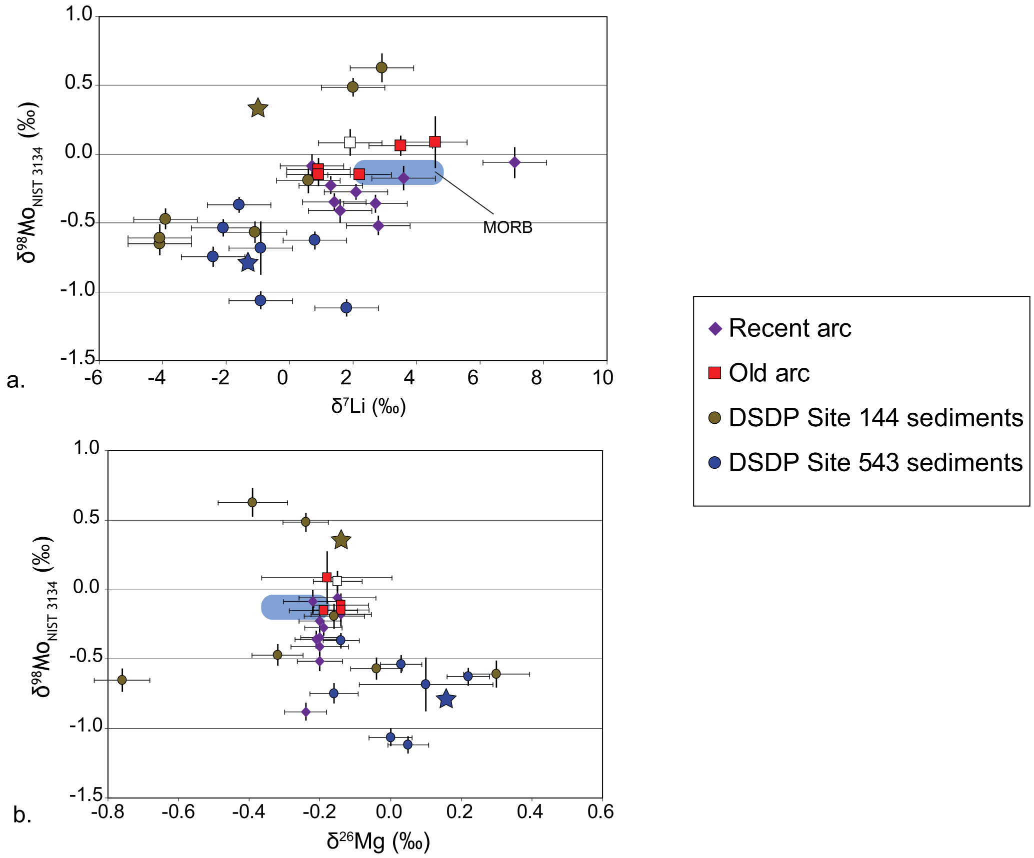

Figure 8. δ^{98}Mo versus Li and Mg stable isotope data for the same samples. Li isotope data is from Tang et al. (2014) and Mg isotope data is from Teng et al. (2016). Mantle field is from the data of Bezard et al. (2016) for δ^{98}Mo and average δ^{7}Li and δ^{26}Mg with uncertainties for the mantle from Tomascak et al. (2008) and Teng et al. (2010). Same symbols as in Figure 7.

Bulk mixing curves between mantle and the two sedimentary end-members are shown in Mo isotope versus radiogenic isotope space in Figure 7. In Mo isotope versus Sr and Nd isotope space (Figures 7a and 7b), many of the samples of the Old Arc do not fall on or near any of the mixing curves. Samples of the Recent arc trace out two curved arrays that the mixing lines partially overlap with. When considering the relationship between δ^{98}Mo and $^{206}Pb/^{204}Pb$ (Figures 7c and 7d), the Old Arc samples similarly do not fall along any of the mixing pathways, although some of the Recent Arc samples fall along the pathway between the mantle and Site 543. These mismatches are not surprising given the limited amount of sampling and data relative to the thickness of the sedimentary section and the relatively large compositional and isotopic heterogeneity that can be expected in natural sediments. Full quantitative evaluation of covariation between δ^{98}Mo and ε_{Ce} (Figure 7e) is hampered by the lack of data for Site 543 sediments and limited number of analyses of Site 144 sediments.

Although many lava samples do not track the mixing curves tied to average sediment compositions, the lavas do appear to form arcuate mixing arrays that lead to hypothetic end-members that lie within the *ranges* of sedimentary compositions. The Old Arc samples can be produced by mixing between the mantle end-member and sediment with a similar to slightly heavier Mo isotope signature and more enriched radiogenic isotope signatures. This is consistent with the range of sediment compositions seen at Site 144. The Recent Arc samples can be produced by mixing between the mantle end-member and sediments with isotopically light Mo similar to those at Site 543 (or the Cenozoic units from Site 144). While some of these samples fall on or plot near one of the mixing lines projecting to the Site 543 grand average, the other Recent Arc samples exhibit larger variations in radiogenic isotope compositions with smaller variations in Mo isotope composition. Given the huge variations seen in the various sediment samples, these other

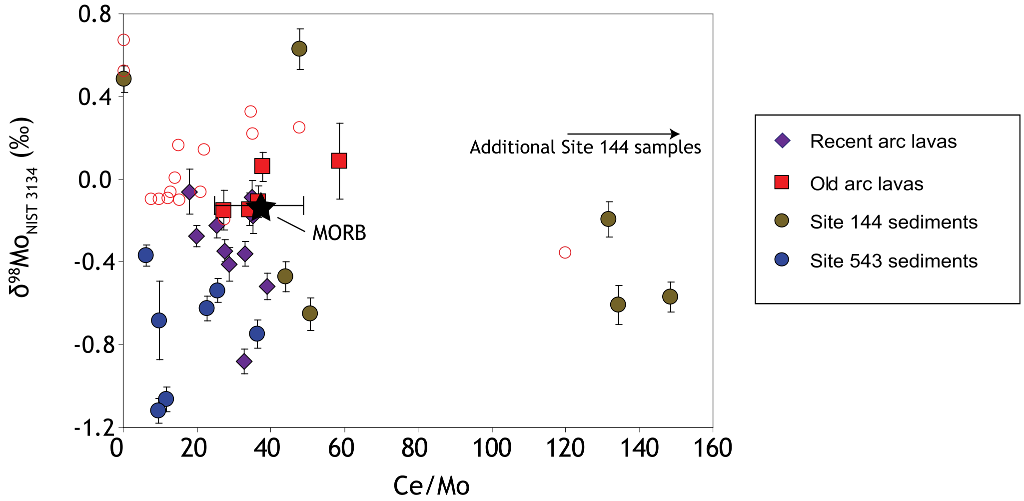

Figure 9. δ^{98}Mo versus Ce/Mo. Ce and Mo are thought to have similar compatibility in the mantle (Sims et al., 1990) and the Ce/Mo ratio is a frequently used as a proxy for selective retention of Mo in a residual slab mineral or selective removal in fluids. The Recent Arc lavas show Ce/Mo values that either overlap with MORB or are slightly less whereas the opposite is true of the Old Arc. Site 543 sediments are consistently enriched in Mo over Ce relative to MORB whereas Site 144 sediments exhibit a huge range from <1 to >100. MORB average δ^{98}Mo composition from Bezard et al. (2016), along with the range of Ce/Mo values observed. Open red circles are data for Site 144 sediments from Freymuth et al. (2016); two addition samples from that study plot at much higher Ce/Mo values than shown here.

Recent Arc samples could simply reflect greater dominance of another sedimentary lithology. Decoupling of Mo from the radiogenic carrier elements could explain the flatter pathway these following Mo versus radiogenic isotope space. This might be expected given the results of the melting experiments of Skora et al. (2017), which found that the Ce and Mo budgets are controlled by very different mineral assemblages during sediment melting and are therefore easily decoupled. This scenario can be explored by considering the covariation between δ^{98}Mo and Ce/Mo. Figure 9 shows that most of the Recent Arcs samples have Ce/Mo that fall within the range of MORB and fall on a pathway between MORB and the Site 543 sediment compositions, indicating little Ce/Mo fractionation. The Old Arc samples parallel the trend formed by the other Lesser Antilles samples described Freymuth et al. (2016). Skora et al. (2017) explained this trend in the Freymuth et al. (2016) by invoking the melting of a subducting sediment package that included both black shales and low-Ca marine clays and terrigenous sediments, where the residual mineralogy would not favor any retention of Ce but might (depending on redox conditions) favor the retention of Mo. The work of Canil and Fellows (2017) similarly supports the important role of Ca in determining residual slab mineralogy and determining whether Mo is retained or released. Retention of some Mo in the slab during genesis of the Old Arc therefore seems reasonable.

5.3.3. Why Are the Old and Recent Arcs so Different?

The Mo isotope compositions of the Old Arc volcanics are distinctly heavier than those of the Recent Arc. Labanieh et al. (2010) also noted that the radiogenic isotope systematics of Old and Recent Arcs varied and attributed this to differences in the composition of the input sediments at contrasting times. The Mo isotope results reported here and the previously reported Sr and Pb isotope results both suggest that subducting Cretaceous black shales, such as those related to Ocean Anoxic Event 2 (OAE-2), played a more important role in the production of the Old Arc volcanics on Martinique. The age of the ocean floor about to enter the Lesser Antilles subduction zone in front of Martinique (representing the minimum age of ocean crust beneath Martinique today) is Cenomanian-Turonian (Carpentier et al., 2008), meaning that sediments dating from OAE-2 (which occurred at the Cenomanian-Turonian boundary, ~93.9 Ma) should still be present beneath Martinique. However, given the close temporal distance between the age of the ocean crust and the age of the OAE-2, sediment deposition might have occurred in shallower water (i.e., closer to the ridge crest) above the carbonate compensation depth, limiting the presence of black shale and its isotopically heavy Mo. This model is consistent with the suggestion of Freymuth et al. (2016) that subducting black shales are the source of isotopically heavy Mo in lavas on islands south of Martinique, because the ocean crust subducting beneath these islands is older.

5.3.4. Does Mo Isotopically Fractionate When Leaving the Slab?

Molybdenum isotopic compositions heavier than MORB have been reported for arc lavas from the Marianas Islands (Freymuth et al., 2015) and Solomon Islands (König et al., 2016). Both of these systems are fluid-dominated (based on trace elements and other isotopic systematics) and the heavy Mo isotopic signature was attributed to incomplete removal of Mo from the slab with fluids being preferentially enriched in heavy isotopes. König et al. (2016) also observed that arc lavas with significant sediment contributions have isotopically lighter Mo and concluded that this might reflect the mobilization of the isotopically light Mo left behind after slab dehydration.

Our Mo isotope results show that it is possible to produce the combined Mo-radiogenic isotope systematics seen in lavas from Martinique without the need to invoke isotope fractionation during Mo removal from the slab package. While there is evidence in some samples of partial retention Mo relative to elements with similar geochemical properties, production of these arc lava compositions does not require isotope fractionation of Mo during its departure from the slab. The Mo isotope systematics of the Recent Arc lavas reflect the incorporation of isotopically light oxic to suboxic sediments similar to those at DSDP Site 543 and the upper portion of Site 144 into the ambient mantle wedge whereas the Old Arc reflects a greater contribution from Cretaceous black shales. In the case of the Lesser Antilles, as reported both here and by Freymuth et al. (2016) Mo isotopes appear to serve as a more straightforward tracer for the input of different kinds of sediments into subduction systems. This opens the possibility that the Mo isotope composition, through time, of well-preserved arcs can be used to track the Mo isotope composition of deep-sea (subducting) sediments. Given that the Mo isotope composition of sediments will vary with redox conditions (e.g., Scott & Lyons, 2012), this could provide a new means to track deep marine redox evolution. This approach could be particularly promising for tracking the oxygenation of deep marine environments through the Proterozoic and early Paleozoic, which is a topic that has been heavily debated and plagued by the lack of deep sea sediments from this interval.

6. Conclusions

Molybdenum isotopic data from mafic and intermediate lavas from the Lesser Antilles island of Martinique show a large range in compositions. Lavas older than ~7 Ma have Mo isotope compositions similar to or heavier than MORB whereas those younger than ~7 Ma have some of the lightest compositions yet observed for arc rocks. Covariation between Mo and previously published radiogenic isotope data indicate binary mixing between mantle wedge and subducting sediment can explain the observed isotope systematics, without invoking isotopic fractionation of Mo coming off of the slab. The heavier Mo isotopic composition of the Older Arc lavas is attributed to the greater involvement of subducted Cretaceous black shales. After 7 Ma, the input to the subduction zone was dominated by isotopically light oxic-suboxic sediments deposited in shallower water, and these sediments account for the isotopically light Mo compositions found in the Recent Arc rocks.

Acknowledgments
This work was supported by Alfred P. Sloan Foundation Research Fellowship FR-2015-65744 to CR and NSF EAR-1338290 and NASA NNA15BB03A to CR and NP. We thank Cin-Ty Lee for editorial handling and two anonymous reviewers for their suggestions. All new data are contained in Table 1.

References

Anbar, A. D., Duan, Y., Lyons, T. W., Arnold, G. L., Kendall, B., Creaser, R. A., . . . Buick, R. (2007). A whiff of oxygen before the great oxidation event? *Science*, *317*(5846), 1903–1906. https://doi.org/10.1126/science.1140325

Arnold, G. L., Anbar, A. D., Barling, J., & Lyons, T. W. (2004). Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science*, *304*(5667), 87–90. https://doi.org/10.1126/science.1091785

Asael, D., Tissot, F., Reinhard, C. T., Rouxel, O., Dauphas, N., Lyons, T. W., . . . Cheron, S. (2013). Coupled molybdenum, iron and uranium stable isotopes as oceanic paleoredox proxies during the Paleoproterozoic Shunga event. *Chemical Geology*, *362*, 193–210.

Barling, J., Arnold, G. L., & Anbar, A. D. (2001). Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth and Planetary Science Letters*, *193*(3–4), 447–457. https://doi.org/10.1016/S0012-821X(01)00514-3

Bellot, N., Boyet, M., Doucelance, R., Pin, C., Chauvel, C., & Auclair, D. (2015). Ce isotope systematics of island arc lavas from the Lesser Antilles. *Geochimica Et Cosmochimica Acta*, *168*, 261–279. https://doi.org/10.1016/j.gca.2015.07.002

Bezard, R., Fischer-Gödde, M., Hamelin, C., Brennecka, G. A., & Kleine, T. (2016). The effects of magmatic processes and crustal recycling on the molybdenum stable isotopic composition of mid-Ocean Ridge basalts. *Earth and Planetary Science Letters*, *453*, 171–181. https://doi.org/10.1016/j.epsl.2016.07.056

Bezard, R., Schaefer, B. F., Turner, S., Davidson, J. P., & Selby, D. (2015a). Lower crustal assimilation in oceanic arcs: Insights from an osmium isotopic study of the Lesser Antilles. *Geochimica Et Cosmochimica Acta*, *150*, 330–344. https://doi.org/10.1016/j.gca.2014.11.009

Bezard, R., Turner, S., Davidson, J. P., Macpherson, C. G., & Lindsay, J. M. (2015b). Seeing through the effects of crustal assimilation to assess the source composition beneath the southern Lesser Antilles Arc. *Journal of Petrology*, *56*(4), 815–844. https://doi.org/10.1093/petrology/egv018

Biju-Duval, B., & Moore, J. C. (Eds.). (1984). Site 543: Oceanic reference site east of the Barbados Ridge complex. In *Initial reports of the Deep Sea Drilling project* (Vol. LXXVIIIA, pp. 227–298). Washington, DC: U.S. Government Printing Office. https://doi.org/10.2973/dsdp.proc.78a.110.1984

Bouvier, A., Vervoort, J. D., & Patchett, P. J. (2008). The Lu-Hf and Sm-Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth and Planetary Science Letters*, *273*(1-2), 48–57.

Bouysse, P., & Westercamp, D. (1990). Subduction of Atlantic aseismic ridges and Late Cenozoic evolution of the Lesser Antilles island arc. *Tectonophysics*, *175*(4), 349–380. https://doi.org/10.1016/0040-1951(90)90180-G

Burkhardt, C., Hin, R. C., Kleine, T., & Bourdon, B. (2014). Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation. *Earth and Planetary Science Letters*, *391*, 201–211. https://doi.org/10.1016/j.epsl.2014.01.037

Canil, D., & Fellows, S. A. (2017). Sulphide-sulphate stability and melting in subducted sediment and its role in arc mantle redox and chalcophile cycling in space and time. *Earth and Planetary Science Letters*, *470*, 73–86.

Carpentier, M., Chauvel, C., & Mattielli, N. (2008). Pb-Nd isotopic constraints on sedimentary input into the Lesser Antilles arc system. *Earth and Planetary Science Letters*, *272*(1–2), 199–211. https://doi.org/10.1016/j.epsl.2008.04.036

Carpentier, M., Chauvel, C., Maury, R. C., & Mattielli, N. (2009). The ''zircon effect'' as recorded by the chemical and Hf isotopic compositions of Lesser Antilles forearc sediments. *Earth and Planetary Science Letters*, *287*(1–2), 86–99. https://doi.org/10.1016/j.epsl.2009.07.043

Davidson, J. P. (1986). Isotopic and trace element constraints on the petrogenesis of subduction-related lavas from Martinique, Lesser Antilles. *Journal of Geophysical Research*, *91*, 5943–5962. https://doi.org/10.1029/JB091iB06p05943

Davidson, J. P. (1987). Crustal contamination versus subduction zone enrichment: Examples from the Lesser Antilles and implications for mantle source compositions of island arc volcanic rocks. *Geochimica et Cosmochimica Acta*, *51*(8), 2185–2198. https://doi.org/10.1016/0016-7037(87)90268-7

Freymuth, H., Elliott, T., van Soest, M., & Skora, S. (2016). Tracing subducted black shales in the Lesser Antilles arc using molybdenum isotope ratios. *Geology*, *44*(12), 987–990. https://doi.org/10.1130/g38344.1

Freymuth, H., Vils, F., Willbold, M., Taylor, R. N., & Elliott, T. (2015). Molybdenum mobility and isotopic fractionation during subduction at the Mariana arc. *Earth and Planetary Science Letters*, *432*, 176–186. https://doi.org/10.1016/j.epsl.2015.10.006

Germa, A., Quidelleur, X., Labanieh, S., Chauvel, C., & Lahitte, P. (2011). The volcanic evolution of Martinique Island: Insights from K-Ar dating into the Lesser Antilles arc migration since the Oligocene. *Journal of Volcanology and Geothermal Research*, *208*(3–4), 122–135. https://doi.org/10.1016/j.jvolgeores.2011.09.007

Goldberg, T., Gordon, G., Izon, G., Archer, C., Pearce, C. R., McManus, J., . . . Rehkamper, M. (2013). Resolution of inter-laboratory discrepancies in Mo isotope data: An intercalibration. *Journal of Analytical Atomic Spectrometry*, *28*(5), 724–735. https://doi.org/10.1039/c3ja30375F

Goldberg, T., Poulton, S. W., Wagner, T., Kolonic, S. F., & Rehkämper, M. (2016). Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. *Earth and Planetary Science Letters*, *440*, 81–91. https://doi.org/10.1016/j.epsl.2016.02.006

Greber, N. D., Hofmann, B. A., Voegelin, A. R., Villa, I. M., & Nägler, T. F. (2011). Mo isotope composition in Mo-rich high- and low-T hydrothermal systems from the Swiss Alps. *Geochimica et Cosmochimica Acta*, *75*(21), 6600–6609. https://doi.org/10.1016/j.gca.2011.08.034

Greber, N. D., Pettke, T., & Nägler, T. F. (2014). Magmatic-hydrothermal molybdenum isotope fractionation and its relevance to the igneous crustal signature. *Lithos*, *190–191*, 104–110. https://doi.org/10.1016/j.lithos.2013.11.006

Greber, N. D., Puchtel, I. S., Nagler, T. F., & Mezger, K. (2015). Komatiites constrain molybdenum isotope composition of the Earth's mantle. *Earth and Planetary Science Letters*, *421*, 129–138.

Hayes, D. E., Pimm, A. C., Beckmann, J. P., Benson, W. E., Berger, W. H., Roth, P. H., . . . von Rad, U. (1972). Sites 143 and 144. In *Initial reports of the Deep Sea Drilling project* (Vol. XIV, pp. 283–338). Washington, DC: U.S. Government Printing Office. https://doi.org/10.2973/dsdp.proc.14.110.1972

Hibbert, K., Willbold, M., Andersen, M. B., & Elliot T. (2013). Searching for evidence for Mo isotope fractionation in the mantle. *Mineralogical Magazine*, *77*(5), 1296.

Hin, R. C., Burkhardt, C., Schmidt, M. W., Bourdon, B., & Kleine, T. (2013). Experimental evidence for Mo isotope fractionation between metal and silicate liquids. *Earth and Planetary Science Letters*, *379*, 38–48. https://doi.org/10.1016/j.epsl.2013.08.003

Kendall, B., Dahl, T. W., & Anbar, A. D. (2017). The stable isotope geochemistr of molybdenum. In F. Z. Teng, J. Watkins, & N. Dauphas (Eds.), *Non-traditional stable isotopes, Reviews in Mineralogy and Geochemistry* (Vol. 82, pp. 683–732). Chantilly, VA: Mineralogical Society of America.

König, S., Wille, M., Voegelin, A., & Schoenberg, R. (2016). Molybdenum isotope systematics in subduction zones. *Earth and Planetary Science Letters*, *447*, 95–102. https://doi.org/10.1016/j.epsl.2016.04.033

Labanieh, S., Chauvel, C., Germa, A., & Quidelleur, X. (2012). Martinique: A clear case for sediment melting and slab dehydration as a function of distance to the trench. *Journal of Petrology*, *53*(12), 2441–2464. https://doi.org/10.1093/petrology/egs055

Labanieh, S., Chauvel, C., Germa, A., Quidelleur, X., & Lewin, E. (2010). Isotopic hyperbolas constrain sources and processes under the Lesser Antilles arc. *Earth and Planetary Science Letters*, *298*(1–2), 35–46. https://doi.org/10.1016/j.epsl.2010.07.018

Leckie, R. M., Bralower, T. J., & Cashman, R. (2002). Oceanic anoxic events and plankton evolution: Biotic response to tectonic forcing during the mid-Cretaceous. *Paleoceanography*, *17*(3), 1041. https://doi.org/10.1029/2001PA000623

Li, J., Liang, X.-R., Zhong, L.-F., Wang, X.-C., Ren, Z.-Y., Sun, S.-L., Zhang, Z.-F., & Xu, J.-F. (2014). Measurement of the isotopic composition of molybdenum in geological samples by MC-ICP-MS using a novel chromatographic extraction technique. *Geostandards and Geoanalytical Research*, *38*(3), 345–354. https://doi.org/10.1111/j.1751-908X.2013.00279.x

Liang, Y.-H., Halliday, A. N., Siebert, C., Fitton, J. G., Burton, K. W., Wang, K.-L., & Harvey, J. (2017). Molybdenum isotope fractionation in the mantle. *Geochimica et Cosmochimica Acta*, *199*, 91–111. https://doi.org/10.1016/j.gca.2016.11.023

Macdonald, R., Hawkesworth, C. J., & Heath, E. (2000). The Lesser Antilles volcanic chain: A study in arc magmatism. *Earth-Science Reviews*, *49*(1–4), 1–76. https://doi.org/10.1016/S0012-8252(99)00069-0

Marschall, H. R., & Schumacher, J. C. (2012). Arc magmas sourced from melange diapirs in subduction zones. *Nature Geoscience*, *5*(12), 862–867.

McManus, J., Nägler, T. F., Siebert, C., Wheat, C. G., & Hammond, D. E. (2002). Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration. *Geochemistry, Geophysics, Geosystems*, *3*(12), 1078. https://doi.org/10.1029/2002GC000356

Nielsen, S. G., & Marschall, H. R. (2017). Geochemical evidence for mélange melting in global arcs. *Science Advances*, *3*(4), e1602402. https://doi.org/10.1126/sciadv.1602402

Palme, H., & O'Neill, H. S. C. (2014). 3.1-Cosmochemical estimates of mantle composition A2-Holland, Heinrich D. In K. K. Turekian (Ed.), *Treatise on geochemistry* (2nd ed., pp. 1–39). Oxford, UK: Elsevier.

Ryan, J. G., & Chauvel, C. (2014). The subduction-zone filter and the impact of recycled materials on the evolution of the mantle. In R. L. Rudnick (Ed.), *The crust* (pp. 479–508). Amsterdam, the Netherlands: Elsevier Science.

Salters, V. J. M., & Stracke, A. (2004). Composition of the depleted mantle. *Geochemistry, Geophysics, Geosystems*, *5*, Q05B07. https://doi.org/10.1029/2003GC000597

Scott, C., & Lyons, T. W. (2012). Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chemical Geology*, *324*, 19–27. https://doi.org/10.1016/j.chemgeo.2012.05.012

Scott, C., Lyons, T. W., Bekker, A., Shen, Y., Poulton, S. W., Chu, X., & Anbar, A. D. (2008). Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature*, *452*(7186), 456–459.

Siebert, C., Nägler, T. F., & Kramers, J. D. (2001). Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. *Geochemistry, Geophysics, Geosystems*, *2*(7), 1032.

Siebert, C., Nägler, T. F., von Blanckenburg, F., & Kramers, J. D. (2003). Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth and Planetary Science Letters*, *211*(1–2), 159–171. https://doi.org/10.1016/S0012-821X(03)00189-4

Sims, K. W. W., Newsom, H. E., & Gladney, E. S. (1990). Chemical fractionation during formation of the Earth's core and continental crust: Clues from As, Sb, W, and Mo. In J. Jones & H. E. Newsom (Eds.), *Origin of the earth* (pp. 291–318). Oxford, UK: Oxford University Press.

Skora, S., Freymuth, H., Blundy, J., Elliott, T., & Guillong, M. (2017). An experimental study of the behaviour of cerium/molybdenum ratios during subduction: Implications for tracing the slab component in the Lesser Antilles and Mariana Arc. *Geochimica et Cosmochimica Acta*, *212*, 133–155. https://doi.org/10.1016/j.gca.2017.05.025

Smith, H. J., Leeman, W. P., Davidson, J., & Spivack, A. J. (1997). The B isotopic composition of arc lavas from Martinique, Lesser Antilles. *Earth and Planetary Science Letters*, *146*(1–2), 303–314. https://doi.org/10.1016/S0012-821X(96)00209-9

Tang, M., Rudnick, R. L., & Chauvel, C. (2014). Sedimentary input to the source of Lesser Antilles lavas: A Li perspective. *Geochimica et Cosmochimica Acta*, *144*, 43–58. https://doi.org/10.1016/j.gca.2014.09.003

Teng, F.-Z., Li, W.-Y., Ke, S., Marty, B., Dauphas, N., Huang, S., . . . Pourmand, A. (2010). Magnesium isotopic composition of the Earth and chondrites. *Geochimica Et Cosmochimica Acta*, *74*(14), 4150–4166. https://doi.org/10.1016/j.gca.2010.04.019

Teng, F.-Z., Hu, Y., & Chauvel, C. (2016). Magnesium isotope geochemistry in arc volcanism. *Proceedings of the National Academy of Sciences of United States of America*, *113*(26), 7082–7087. https://doi.org/10.1073/pnas.1518456113

Tomascak, P. B., Langmuir, C. H., Le Roux, P. J., & Shirey, S. B. (2008). Lithium isotopes in global mid-ocean ridge basalts. *Geochimica et Cosmochimica Acta*, *72*(6), 1626–1637. https://doi.org/10.1016/j.gca.2007.12.021

Voegelin, A. R., Pettke, T., Greber, N. D., von Niederhäusern, B., & Nägler, T. F. (2014). Magma differentiation fractionates Mo isotope ratios: Evidence from the Kos Plateau Tuff (Aegean Arc). *Lithos*, *190–191*, 440–448. https://doi.org/10.1016/j.lithos.2013.12.016

White, W. M., & Dupré, B. (1986). Sediment subduction and magma genesis in the Lesser Antilles: Isotopic and trace element constraints. *Journal of Geophysical Research*, *91*, 5927–5941. https://doi.org/10.1029/JB091iB06p05927

Willbold, M., & Elliott, T. (2017). Molybdenum isotope variations in magmatic rocks. *Chemical Geology*, *449*, 253–268. https://doi.org/10.1016/j.chemgeo.2016.12.011

Yang, J., Siebert, C., Barling, J., Savage, P., Liang, Y.-H., & Halliday, A. N. (2015). Absence of molybdenum isotope fractionation during magmatic differentiation at Hekla volcano, Iceland. *Geochimica Et Cosmochimica Acta*, *162*, 126–136.

Zhao, P.-P., Li, J., Zhang, L., Wang, Z.-B., Kong, D.-X., Ma, J.-L., Wei, G.-J., & Xu, J.-F. (2016). Molybdenum mass fractions and isotopic compositions of international geological reference materials. *Geostandards and Geoanalytical Research*, *40*(2), 217–226. https://doi.org/10.1111/j.1751-908X.2015.00373.x