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Tracing subducted black shales in the Lesser Antilles arc using molybdenum isotope ratios

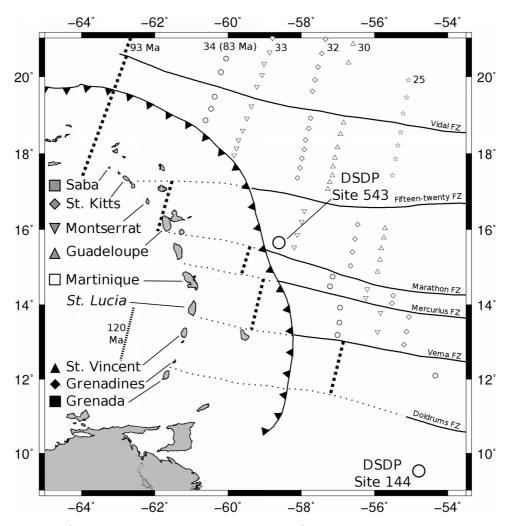


Figure DR1. Map of the Lesser Antilles arc. Oceanic fracture zones (FZ) and projections of the fracture zones into the subduction zone (from Schlaphorst et al., 2016) are shown by solid black lines and dotted black lines, respectively. Seafloor magnetic anomalies are plotted in circles (anomaly C34o, 83 Ma), inverted triangles (anomaly C33y, 79.075 Ma), diamonds (anomaly C32y, 73.004 Ma), triangles (anomaly C30y, 67.610 Ma) and stars (anomaly C25y, 56.391 Ma) (Müller et al., 1999, ages from Gee and Kent, 2007). Thick dotted lines indicate oceanic crust with an estimated age of 93 Ma. Oceanic crust older than 93 Ma should contain black shales deposited during OAE 2. The thin dotted line labeled '120 Ma' indicates a crustal age of 120 Ma (the age of OAE 1). The 93 Ma and 120 Ma crustal ages were derived by linear extrapolation from anomaly 34 assuming the same, constant spreading rate as between anomalies 34 and 33. A plate dip of 42.4 degrees (Syracuse et al. 2010) has been assumed for sections south of the Marathon FZ in order to extrapolate ages west of the trench. Plate dip was considered negligible for age extrapolation beneath the northern sections where the fracture zones are approximately parallel to the trench.

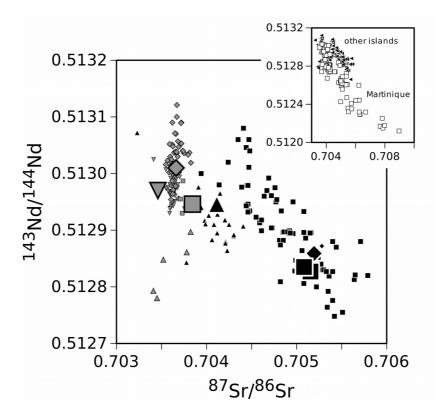


Figure DR2. Radiogenic isotope compositions of northern and southern Lesser Antilles arc lavas. Symbols indicate different islands as defined in Fig. DR1. Large symbols are from this study (Table DR1), small symbols are for previously published data (georoc.mpch-mainz.gwdg.de/). Open symbols in the inset are for samples from Martinique, closed symbols are for samples from other islands.

Table DR1: Mo, Pb, Sr and Nd isotope ratios in Lesser Antilles arc lavas and DSDP Site 144 sediments.

island / site	sample	lithology	Latitude	Longitude	phenocrysts present (a)	sediment unit; thickness (b)	Mo [µg/g]	Се [µg/g] (с, d)	MgO [wt.%] (c, d)	δ ^{98.95} Mo [‰]	2 SE (e)	²⁰⁶ Pb/ ²⁰⁴ Pb (d)	2 SE (e)	²⁰⁷ Pb/ ²⁰⁴ Pb (d)	2 SE (e)	²⁰⁸ Pb/ ²⁰⁴ Pb (d)	2 SE (e)	⁸⁷ Sr/ ⁸⁶ Sr (c)	¹⁴³ Nd/ ¹⁴⁴ Nd (c)
1	Lesser Antilles arc lava	S																	
Saba	LSS1	basaltic andesite	N 17°38.7'	W 63°12.8'	am, ol, pl		1.10	12.77	7.37	-0.082	0.017	18.913	0.0008	15.633	0.0007	38.621	0.0020	0.70371	-
Saba	LSS3 (g)	basalt	N 17°38.7'	W 63°12.8′	am, ol, pl		1.27	8.73	11.0	-0.087	0.021							0.70377	-
Saba	LAS1	basalt	N 17°38.8'	W 63°12.7'	cp, ol, pl		1.01	12.31	8.01	-0.051	0.016	18.935	0.0010	15.639	0.0007	38.656	0.0021	0.70384	0.512946
St. Kitts	LSK2	basaltic andesite	N 17°24.1'	W 62°46.6'	cp, ol, pl		1.04	9.55	4.20	-0.089	0.020	19.016	0.0005	15.660	0.0006	38.759	0.0017	0.70366	0.513010
Montserrat	LSM07	basaltic andesite	N 16°40.6'	W 62°10.5'	cp, ol, pl		1.13	23.12	5.39	-0.051	0.015	18.917	0.0014	15.615	0.0019	38.593	0.0069	0.70346	0.512970
Guadeloupe	GUAD511	basalt	-	-	NA		0.61	8.84	6.61	-0.090	0.020	19.166	0.0004	15.667	0.0005	38.835	0.0014	0.70350	-
Martinique	LSM2	andesite	N 14°43.6'	W 61°05.6'	NA		0.78	20.90	2.98	-0.186	0.016	19.620	0.0006	15.789	0.0008	39.441	0.0030	0.70506	-
St. Vincent	LAV2	basaltic andesite	N 13°19.6'	W 61°10.8'	cp, ol, pl		1.05	14.04	4.15	0.016	0.021	19.314	0.0009	15.720	0.0007	38.925	0.0022	0.70411	0.512946
Grenadines	WIC19	basalt	N 12°17.5'	W 61°35'	NA		1.12	16.09	10.4	0.174	0.018	19.703	0.0009	15.792	0.0011	39.254	0.0032	0.70546	-
Grenada	LSG5 (g)	basalt	N 12°13.7′	W 61°36.9′	cp, ol, pl		0.26	57.78	8.55	0.097	0.035							0.70424	-
Grenada	LSG8 (g)	basalt	N 12°08.1′	W 61°44.9′	cp, ol, pl		0.84	39.54	7.06	0.258	0.017							0.70448	-
Grenada	LAG2 (g)	basalt	N 12°08.1′	W 61°44.9′	cp, ol, pl		1.15	39.05	6.86	0.336	0.017							0.70448	0.512934
Grenada	LAG3	basaltic andesite	N 12°14.1'	W 61°39.7'	am, cp, pl		1.43	49.42	5.09	0.228	0.017	19.451	0.0010	15.745	0.0010	39.008	0.0031	0.70515	0.512827
Grenada	LAG4	basalt	N 12°03.7'	W 61°45.3'	ol, pl		0.85	18.11	17.3	0.153	0.016	19.465	0.0006	15.754	0.0006	39.080	0.0023	0.70508	0.512835
	rock standards																		
	JB-2	basaltic andesite					0.89			0.062	0.025 (n = 3) (f)								
	BHVO-2	basalt					4.16			-0.059	0.054 (n =5) (f)	18.646	0.0014	15.491	0.0014	38.207	0.0044		
	AGV-2	trachyandesite									(11 5)(1)	18.907	0.0018	15.615	0.0022	38.568	0.0073		
DSDP Site 144 sediments																			
DSDP Site 144	144B-2-2W-11.5-13		halk ooze			1; 120 m	0.51	61.2	1.8	-0.355	0.028	19.135	0.0019	15.743	0.0019	39.271	0.0040	0.71097	0.511959
DSDP Site 144	144-3-1W-120-121	slightly zeoliti	c calcereous m	udstone		2; 60 m	0.11	27.1	0.8	-0.555	0.047	20.042	0.0030	15.886	0.0028	39.862	0.0060	0.70869	0.511730
DSDP Site 144	144A-5-1W-119–124	zeolitic calcere shale	eous carbonace	ous black		3; 60 m	41.9	12.8	0.8	0.674	0.030	21.273	0.0041	15.882	0.0029	39.423	0.0070	0.70787	0.511843
DSDP Site 144	144A-6-1W-90-93	zeolitic calcere shale	eous carbonace	ous black		3; 60 m	51.0	13.7	0.7	0.522	0.019	21.691	0.0022	15.925	0.0016	39.422	0.0040	0.70788	0.511832
DSDP Site 144	144-7-1W-125-130	slightly quartz	ose carbonace	ous clay		5; 47 m	0.20	56.3	1.6	0.129	0.048	18.935	0.0015	15.691	0.0016	39.062	0.0040	0.70914	0.512105
DSDP Site 144	average sediment (h)					327 m	7.92	44.1		0.543		19.601		15.784		39.307		0.70851	0.511990

(a) am = amphibole, ol = olivine, pl = plagioclase, cp = clinopyroxene, NA = information not available.
(b) sediment units and thickness as described in Hayes et al. (1972).
(c) Ce and MgO concentrations, Sr and Nd isotope ratios in Lesser Antilles arc lavas are from van Soest (2000).

(d) Ce and MgO concentrations, Sr, Nd and Pb isotope ratios in DSDP Site 144 sediments are from Carpentier et al. (2009).

(e) $2 \text{ SE} = 2\sigma$ standard error (internal measurement error).

(f) n = number of individual analyses measured on separate dissolutions. The error represents the 2 σ standard deviation of the individual measurements.

(g) samples are considered contaminated and are not used in the figure or discussion. See analytical methods for detail.

(h) Bulk DSDP Site 144 sediment composition is the average for the different sediment units weighted by their sediment thickness. For this purpose, DSPD Site 144 Unit 3 (comprising OAE 2 and OAE 3) has been assumed to be made of 50% black shales and 50% sediments similar to those of unit 2, as indicated by the stratigraphic variation in total organic carbon content in this unit (Erbacher et al., 2004). Unit 4 has been assumed to be similar in δ^{9895} Mo to unit 2 because both are dominantly made of marl. Average isotope ratios were additionally weighted by the concentration of the respective element in the sediment unit.

Analytical methods

Mo isotope ratios and Mo concentrations were measured using a ⁹⁷Mo-¹⁰⁰Mo double spike following the methods decribed in Freymuth et al. (2015) and Willbold et al. (2016). Mo isotope ratios are reported relative to NIST 3134. The rock standards BHVO-2 and JB-2 were analysed together with the samples. BHVO-2 appears to be isotopically heterogeneous (see Willbold et al., 2016) and we therefore consider the replicate analyses of JB-2 more appropriate as a measure of external reproducibility.

Powders used for Pb isotope analyses were leached in 6 M HCl for 1 hour at 100°C prior to dissolution in HF/HNO₃. Pb was separated from the matrix on AG1-X8 resin using the approach of Strelow and Van der Walt (1981) further described by Galer (1986). Pb isotope ratios were measured using a Neptune MC-ICP-MS at the University of Bristol and corrected for instrumental mass bias by sample-standard bracketing with NBS 981. Ratios assumed for NBS 981 are ²⁰⁶Pb/²⁰⁴Pb = 16.9416, ²⁰⁷Pb/²⁰⁴Pb = 15.4998, ²⁰⁸Pb/²⁰⁴Pb = 36.7249 (Baker et al., 2004).

Pb contamination has previously been described for Lesser Antilles arc lava samples (Thirlwall et al., 1996). We therefore performed additional Pb isotope measurements on sample powders that were not previously leached. Pb isotope ratios measured on leached and unleached powders usually agreed within 1 %. For these samples we assume the Pb isotope ratios measured on leached powders to reflect magmatic values. Pb contamination of samples for which this was not the case was considered too severe for the leaching to fully remove the contaminant. These samples are reported in italics in Table DR1 and were not plotted in Fig. 2. Mo isotope ratios in these samples are similar to those of other samples from the same islands suggesting that Mo was likely unaffected by contamination. We nevertheless took a conservative approach and did not include these samples in plots and the discussion.

Additional References

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