Lower crustal assimilation in oceanic arcs: insights from an osmium isotopic study of the Lesser Antilles

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Abstract

We present whole rock $^{187}Os/^{188}Os$ data for the most mafic lavas along the Lesser Antilles arc (MgO = 5-17 wt. %) and for the subducting basalt and sediments. $^{187}Os/^{188}Os$ ratios vary from 0.127-0.202 in the arc lavas. Inverse correlations between $^{187}Os/^{188}Os$ and Os concentrations and between $^{187}Os/^{188}Os$ and indices of differentiation such as MgO suggests that assimilation, rather than source variation, is responsible for the range of Os isotopic variation observed. $^{87}Sr/^{86}Sr$, La/Sm and Sr/Th are also modified by assimilation since they all correlate with $^{187}Os/^{188}Os$. The assimilant is inferred to have a MORB-like $^{87}Sr/^{86}Sr$ with high Sr (>700 ppm), low light on middle and heavy rare earth elements (L/M-HREE; La/Sm ~2.5) and $^{187}Os/^{188}Os$ > 0.2. Such compositional features are likely to correspond to a plagioclase-rich early-arc cumulate. Given that assimilation affects lavas that were last stored at more than 5 kbar, assimilation must occur in the middle-lower crust.

Only a high MgO picrite from Grenada escaped obvious assimilation (MgO = 17% wt. %) and could reflect mantle source composition. It has a very radiogenic $^{87}Sr/^{86}Sr$ (0.705) but a $^{187}Os/^{188}Os$ ratio that overlaps the mantle range (0.127). $^{187}Os/^{188}Os$ and $^{87}Sr/^{88}Sr$ ratios of the sediments and an altered basalt from the subducting slab vary from 0.18-3.52 and 0.708-0.714. We therefore suggest that, unlike Sr, no Os from the slab was transferred to the parental magmas. Os may be either retained in the mantle wedge or even returned to the deep mantle in the subducting slab.

1. INTRODUCTION

Understanding the behaviour of siderophile elements such as Os in subduction zones is important for both scientific and economic reasons. Whether Os stays in the subducting slab, is transferred to residual phases of the upper mantle, or is recycled back to the crust via the magma needs to be constrained in order to (1) better estimate the crust-mantle fluxes of siderophile elements throughout Earth evolution; (2) constrain their application as a powerful isotope tracer to understand subduction processes; and (3) understand the formation of precious metal ore-bodies.

In this context, the origin of radiogenic $^{187}Os/^{188}Os$ ratios within arc lavas, compared to the depleted upper mantle (DMM), has been debated for more than a decade (Borg et al., 2000; Alves et al., 2002; Chesley et al., 2002; Righter et al., 2002). While the enrichment in radiogenic Os could be due to contamination of the mantle wedge by slab derived fluids/melts (e.g. Borg et al., 2000; Alves et al., 2002), it could also be caused by assimilation of arc crust during the magmatic ascent (Righter et al., 2002), or both (Suzuki et al., 2011). Arguments for crustal assimilation include (1) a negative correlation between $^{187}Os/^{188}Os$ and Os that is observed in most arcs lavas (Chesley et al., 2002; Righter et al., 2002); (2) the very low Re concentrations in primitive arc lavas coupled with the results of experimental studies predicting that slab derived-fluids capable of carrying Os would carry several order of magnitude more Re than Os (Righter et al., 2002; Xiong and Wood, 1999; 2000). Since both Re and Os were shown to be similarly volatile (Finnegan et al., 1990), the absence of high Re concentrations in primitive lavas suggests that Re from the slab is not efficiently transported into primitive magmas, in which case Os is very unlikely to be transported too; and (3) the very unradiogenic $^{187}Os/^{188}Os$ of some mantle xenoliths from the Japan and Izu Bonin arcs (Parkinson et al., 1998; Senda et al., 2007) which suggest the absence of enrichment in radiogenic Os of the mantle wedge. On the other hand, a slab origin for radiogenic Os in arc lavas is supported by (1) the radiogenic signature of some mantle xenoliths from the Cascades, Japan, New Ireland and Kamchatka arcs (Brandon et al., 1996; McInnes et al., 1999; Widom et al., 2003); (2) the trend to more radiogenic $^{187}Os/^{188}Os$ with decreasing Cr# and increasing Fe^{3+} in Cr-spinels from the Izu Bonin arc which suggests an increase in mobility of slab derived Os during an arc lifetime due to a progressive change in oxidation state of the mantle (Suzuki et al., 2011); and (3) the existence, in high-pressure melange zones, of 'hybrid' rocks between crustal and mantle materials which display similar inverse correlation between Os and $^{187}Os/^{188}Os$ to that observed in most arc lavas (Penniston-Dorland et al., 2012; 2014)

The Lesser Antilles arc (Fig. 1) is an excellent natural laboratory to investigate the mobility of Os in subduction zones since: (1) very primitive lavas such as picrites with MgO = 17.4 (wt. %) can be sampled; (2) very radiogenic Os should be subducted in the southern part of the subduction zone where the slab contains organic-rich sediments (black shales); and (3) the arc lavas and the subducting slab sediment/basalts are both very well constrained in terms of major, trace elements and radiogenic isotopes. Accordingly, we have analysed the most mafic and well constrained lavas from along the arc, as well as representative sediments and altered basalt from the subducting slab.

2. SAMPLES AND ANALYTICAL METHODS

2.1 Samples

We selected the most mafic lava samples (MgO=5-17 wt. %) available from 7 different islands along the Lesser Antilles arc (n=8), as well as an altered basalt (n=1; DSDP site 543), an organic-poor sediment (n=1; DSDP site 543) and organic-rich sediments including black shales (n=11; Unit 3-5 DSDP site 144) from the subducting American Plate (Tables 1 and 2).

The sediments were selected to characterize a key north-south difference in the nature of the subducting sediments, likely to be reflected in their Os isotopic signature. The nature and composition of the sediments present at the front of the arc was investigated by Hayes et al. (1972), Pudsey and Reading (1982) and Biju-Duval et al. (1984; 1985) using cored sediments from the DSDP site 543 for the northern sequences and DSDP site 144 and Barbados sediments for the southern sequences. These studies showed that the northern subducting pile (north of Martinique) was dominated by clays and radiolarites while the southern subducting pile (Martinique and southward) was mainly composed of clay and carbonate with the occurrence of significant amounts of organics (up to 30%), biogenic silica (up to 30%) and detrital quartz (up to 40%) in some units. In terms of Os isotopes, the most important difference between the northern and the southern sequences is the presence of (Late Cretaceous) organic-rich layers at the base of the southern sedimentary pile (the absence of such organic-rich units in the north is due to the younger age of the subducting plate, as supported by the magnetic map of the Atlantic Ocean floor at the front of the arc). This is because organic-rich sediments typically concentrate Re during deposition and are expected to present higher $^{187}Os/^{188}Os$ than organic-poor sediments, due to Re decay. The presence of more radiogenic Os in the southern subducting pile could in turn be reflected in the lava compositions. Therefore, analysing both organic-rich and organic-poor sediments is important to understand if, as predicted, they have different isotopic composition.

The organic-poor sediment analysed consists of early Miocene clay with minor ash (Biju-Duval et al., 1984). The organic-bearing sediments selected record sedimentation preceding (Unit-5-4; up to 5% organics; Late-Aptian to lower Cenomanian; Carpentier et al., 2008) and contemporaneous (Unit-3; up to 30% organics; Lower Turonian to Santonian) with the oceanic anoxic event 2 (OAE2; 93.5 My e.g. Turgeon and Creaser, 2008). Samples from Unit 5 consist of quartzose carbonaceous clay or mudstone while Unit 4 sample is marl. Finally samples from Unit 3 are zeolitic calcareous carbonaceous black shale (Hayes et al., 1972).

By selecting the most mafic lavas, we attempted to minimise the effects of assimilation of continent-derived sediment present in the arc crust. Such sediment is responsible for the extreme isotopic compositions observed in the central-southern parts of the arc (e.g. Davidson, 1987; Bezard et al., 2014). All lavas (Fig. 2) and sediments have previously been analysed for major, trace elements and Sr-Nd isotopes (Davidson, 1984; Davidson, 1986; Heat et al., 1998; Van Soest, 2000; Dufrane et al., 2009; see Table 2). The most primitive lava sampled, which is also the most primitive lava in the arc, is an olivine and plagioclase phyric picrite from Grenada (LAG4) with both high MgO (17.4 wt. %) and Mg# (77.4) (Van Soest, 2000). It belongs to the abundant M-series suite of picrites found on the island. Previous studies on M-series picrites with MgO as high as 15.5 wt. % suggested that these were primary mantle melts by precluding olivine phenocrysts accumulation, or incorporation of mantle xenocrysts, as the cause of their high MgO. LAG 4 olivine crystals have similar Mg# in cores (90-82) and rims (89-82) which does not support a xenocrystic origin of the crystals. Furthermore, the D_{Ni} calculated from the picrite MgO (D_{Ni} = 6.27; using Hart and Davis (1978) equation) is similar to the D_{Ni} calculated using the whole rock and the mean olivine Ni concentrations (D_{Ni} = 6.67; using probe data from Van Soest (2000)). This suggest that the Ni content in the olivine crystals is consistent with that expected from crystals growing in a magma with an MgO similar to that of LAG4 and that no significant olivine accumulation or mantle xenocryst incorporation should have occurred. Out of the samples selected, it displays the highest Light on Middle Rare Earth Element ratio (L/M-HREE), the lowest Sr/Th and the most radiogenic Sr isotopic composition (Sr/Th = 123; $^{87}Sr/^{86}Sr$ = 0.7051; Fig. 2). Such features characterise all Grenada primitive lavas when compared to basaltic lavas from other islands of the arc (Macdonald et al., 2000). St Vincent contains very mafic lavas (MgO = 12.6 wt. %) with phenocryst assemblages dominated by olivine (traces of Cpx and Ti-magnetite). A less primitive basalt from the same island (MgO = 5.12 wt. %) mainly presenting plagioclase, olivine and clinopyroxene phenocrysts was also analysed. The most primitive lavas from the remaining islands (Saba, Redonda, Guadeloupe, Martinique and St Lucia) have MgO contents that range from 5.1 to 8.7 (wt. %). Their phenocryst assemblage comprise olivine crystals and variable amount of clinopyroxene and plagioclase. All of the lavas selected are 1 Ma old or younger with the exception of the St Lucia lava flow which is dated at 11 Ma (Table 1).

2.2. Analytical methods

All samples, except the organic-rich sediments, were analysed for Os and $^{187}Os/^{188}Os$ at the Geochemical Analysis Unit (GAU) at Macquarie University. The organic-rich sediments were analysed for Re, Os and isotope compositions ($^{187}Re/^{188}Os$;

$^{187}Os/^{188}Os$) at the TOTAL Laboratory for Source Rock Geochronology and Geochemistry which is part of the Durham Geochemistry Centre (DGC) at Durham University.

At Macquarie, whole rock powders (2-5g) (produced in agate ball mills) were spiked for Os and digested using large carius tubes (60 cm^3) in inverse *aqua-regia* using double Teflon distilled reagents at 220°C for 3 days. Given the young age of the samples, no age correction on the $^{187}Os/^{188}Os$ ratio was necessary and Re was not analysed. Os was separated by solvent extraction following the method of Cohen and Waters (1996) and was analysed by negative thermal ion mass spectrometry (N-TIMS) on the electron multiplier (SEM) of the Thermo-Finnigan Triton mass spectrometer at Macquarie University in dynamic mode. All data were blank corrected using the total procedural blank (TPB) processed with the samples analysed. TPB was 6.30 pg Os with an $^{187}Os/^{188}Os$ ratio of 0.1821 (n=1). This corresponds to corrections of 0-12% except for the two lavas with the lowest abundances where these corrections amounted to 21 and 25%. During the analytical session, instrument performance was monitored by analysis of Os in-house solution standard JMC-2. $^{187}Os/^{188}Os$ for 5 ng loads in dynamic collection mode was 0.18311 ± 0.00016 (2SD; n=4) which is in good agreement with the long term running means of 5ng JMC-2 in dynamic mode of 0.18294 ± 0.00070 (2SD; n=17 since 2006). The performance of the instrument when running small loads similar to the lavas was verified by the analysis of ~1.7ng loads of WPR-1 (0.1g digested). The average $^{187}Os/^{188}Os$ ratio of the WPR-1 international rock standard was 0.1451 ± 0.0013 (2SD; n=4) with concentrations of 17.19 ppb ± 0.71 (2SD; n=4) which is in good agreement with the accepted values (Cohen and Waters, 1996; $^{187}Os/^{188}Os = 0.14543 \pm 0.00018$ (2SD) and Os = 16.06 ppb ± 0.8 (2SD)).

At Durham, the organic-rich whole rock powders were also analysed by isotope-dilution negative thermal ionization mass spectrometry. Prior to being powdered, all the samples were cleaned to remove any minor drill marks using a diamond polish cloth with no polishing agent, except water. Samples were pre crushed without metal contact and then powdered in a Zr dish. A dried sample weight of ≥ 30 g was powdered in order to homogenise the Re and Os within the sample (Kendall et al., 2009). The Re-Os isotopic analysis was conducted using Carius tube digestion in a 0.25 g/g CrO_3 4N H_2SO_4 reagent at 220°C for 48hrs with the Re and Os isolated from the acid medium using solvent extraction, micro-distillation and anion chromatography methodology (Selby and Creaser, 2003). This method preferentially liberates hydrogenous Re-Os (Selby and Creaser, 2003; Kendall et al. 2009 and references therein). In brief, ~0.5 g of sample powder was loaded in a Carius tube with a known amount of mixed tracer solution. $^{190}Os + ^{185}Re$, with 8 ml of CrO_3-H_2SO_4 solution. The sealed Carius tubes were then placed in an oven at 220 ˚C for 48 hrs. Osmium was isolated and purified using solvent extraction ($CHCl_3$) and microdistillation methods. Anion chromatography was used to purify the Re from 1 ml of the CrO_3-H_2SO_4 solution (Selby and Creaser, 2003). The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively (Selby and Creaser, 2003) with the addition of ~0.5 µl $BaNO_3$ and BaOH activator solutions, respectively. Isotope compositions were measured using N-TIMS (Creaser et al., 1991; Volkening et al., 1991) via faraday cups for Re and electron multiplier in peak hopping mode for Os. All samples were analysed as one batch. For this batch the total procedural blank for Re and Os during this study is 13.3 ± 1.8 pg and 0.32 ± 0.17 pg, respectively, with $^{187}Os/^{188}Os$ value of 0.19 ± 0.05. Uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ are determined through full propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values. In-house standard solutions (DROsS and Re Std) are 0.16094 ± 0.00030 and 0.5980 ± 0.0032 (2 S.D.), which are consistent within uncertainty to those published by Nowell et al. (2008). Additionally at Durham, sample Re-Os data reproducibility is monitored using the USGS rock reference material SDO-1 (Devonian Ohio Shale). Average (2 S.D.) Re-Os data for SDO-1 are: 75.5 ppb ± 11.3 Re, and 626.1 ppt ± 101.8 Os, and 1166.0 ± 88.1 $^{187}Re/^{188}Os$ and 7.831 ± 0.568 $^{187}Os/^{188}Os$ (Du Vivier et al., 2014).

3. RESULTS

All $^{187}Os/^{188}Os$ and Os concentrations as well as $^{187}Re/^{188}Os$ and Re for the organic-rich sediments are presented in Table 1 and corresponding lithophile element concentrations and isotopic ratios from the literature are presented in Table 2. All lavas apart from the most mafic sample, (Grenada picrite; MgO = 17 wt. %), have more radiogenic $^{187}Os/^{188}Os$ than the depleted mantle range (DMM; $^{187}Os/^{188}Os$ = 0.1238 ± 0.0042; Rudnick and Walker (2009)) and variable $^{187}Os/^{188}Os$ ratios and Os concentrations ranging between 0.127-0.202 and 0.005-0.362 ppb respectively (Fig. 3). The $^{187}Os/^{188}Os$ ratio of the altered basalt is 0.466 and this sample has a very low Os abundance (0.0095 ppb). The organic-poor claystone from DSDP site 543 is enriched in Os (11.15 ppb) and possesses moderately radiogenic $^{187}Os/^{188}Os$ (0.185). The most organic-rich sedimentary units from DSDP 144 (Unit 3) have highly radiogenic

$^{187}Os/^{188}Os$ (1.33-3.25) and moderate Os concentrations (0.10-0.94 ppb), while the older units (4 and 5), which are characterized by lower organic matter content, have moderately radiogenic $^{187}Os/^{188}Os$ (0.32-0.72) and variable Os concentrations from 0.09 to 34.48 ppb. (Fig. 3). The abundances of Os in all sediments analysed is above that of average continental crust (<50 ppt; Peuker-Ehrenbrink and Ravizza, 2000). The isotopic variations observed between Unit 3 and Units 4 and 5 are also observed in the calculated initial $^{187}Os/^{188}Os$ ratio (using sediment ages from Hayes et al. (1972) and Carpentier et al. (2008); Table 1) which indicates that part of the isotopic variations observed in site 144 sediment are not due to variations in Re content. Given that the analytical method used for these sedimentary units preferentially liberates hydrogenous Re and Os and not detrital associated Re-Os, the variations of the initial isotopic ratios need to be inherited from sea water compositional variations during sediment deposition.

4. DISCUSSION

4.1 Crustal assimilation control on $^{187}Os/^{188}Os$

In the Lesser Antilles arc, all studies addressing the quantification of the subducting slab derived components in the magma source, using the isotopic (Sr, Nd, Pb, Hf, U-series) and trace element composition of the lavas, suggested either a similar (e.g. Davidson and Wilson (2011); Dufrane et al. (2009)) or increasing amount of sediment in the mantle source along the arc (e.g. Carpentier et al., 2008). Therefore, if transfer of slab-derived Os into the mantle wedge was to be reflected in the isotopic variations observed in the lavas, a north-south trend to more radiogenic $^{187}Os/^{188}Os$ in the lavas should be observed. This is because the dominantly organic-poor sediment sequences subducted in the north have markedly less radiogenic $^{187}Os/^{188}Os$ than the sequences subducted in the south which comprise organic-rich sediments. However, no such geographic variation is observed. Indeed the least radiogenic compositions are observed in lavas from the south of the arc, in Grenada and St Vincent. These observations argue against the direct control of lava isotopic variations by slab-derived Os. Instead, the samples form inverse correlations between $^{187}Os/^{188}Os$ and both Os (0.005-0.36) (Fig. 4a) and MgO (Fig. 4b) with compositions of the southern lavas plotting on a steeper trend than the northern islands (from Martinique northward). These negative correlations between an index of differentiation and $^{187}Os/^{188}Os$ cannot easily be produced in the mantle source since it would either need to be explained by (1) a mantle source with homogeneous MgO, affected by a process able to enrich it in ^{187}Os and additionally control the future extent of magmatic differentiation; or (2) a heterogeneous source characterized by coupled variations in MgO and $^{187}Os/^{188}Os$ (e.g. in sources with a different mineralogy due to metasomatism, such as a peridotitic mantle comprising pyroxenites) that would be transmitted to the magma and conserved until eruption. Both scenario seem very unlikely since the degree of lava differentiation is known to be influenced by the structure and thickness of the crust, both thought to be heterogeneous along the arc (e.g. Boynton et al., 1979). Therefore, the $^{187}Os/^{188}Os$ variations in the Lesser Antilles arc lavas is more likely accounted for by a process, or processes, which postdate mantle melting. Since both trends formed by lavas from the southern and northern islands back project toward the composition of the Grenada picrite (Fig. 4), they could be explained by evolution from a common parental magma. The differences in subsequent magmatic evolution may reflect either different phases fractionated during assimilation with different partitioning for MgO and Os, different rates of assimilation or slightly different $^{187}Os/^{188}Os$ ratios of the putative assimilants.

Control of the osmium isotopic composition by assimilation rather than by slab contributions is emphasized when the $^{187}Os/^{188}Os$ ratios of both lavas and sediments are plotted against Sr isotope ratios (Fig. 5a). Once again, a negative correlation is observed for the lavas with a decrease in $^{87}Sr/^{86}Sr$ with increasing $^{187}Os/^{188}Os$. This negative correlation precludes the simple mixing of sediment-derived Os in the lavas sources since the sediments display both radiogenic Sr and Os and a mixing line between the mantle and the sediments would therefore have a positive slope which is the opposite of that observed (Fig. 5a). Although the altered basalt from the slab has a lower Sr isotopic composition than the sediment, mixing of fluids derived from this component with the mantle wedge would also result in a positive trend.

A source process capable of increasing slab-derived Os while decreasing slab derived Sr in the mantle is inconsistent with the decrease in Os concentrations observed with increasing $^{187}Os/^{188}Os$ (Fig. 4a). So too, stabilisation of an Os-bearing phase in the mantle wedge due to fluid fluxing from the slab (Borg et al., 2000) is inconsistent with the covariant decrease in both MgO and Os (Fig. 4a,b).

An increase in slab derived Os mobility in response to increasing the oxidation state of the mantle through time (Suzuki et al., 2011) is inconsistent with the decrease in $^{87}Sr/^{86}Sr$ observed with the increasing $^{187}Os/^{188}Os$ (Fig. 5a). Indeed slab derived Sr mobility is very unlikely to be sensitive to variation in oxygen fugacity given that, unlike Os, Sr displays only one valence state (bivalent) under normal geological conditions.

Instead, the contents of slab-derived Sr in the mantle are likely to be controlled by the extent of slab-derived fluid fluxing through the wedge, the latter fluid being also responsible for the increase in mantle oxygen fugacity through time (Brandon and Draper, 1996). Therefore, an increase rather than a decrease in slab derived Sr with increasing mantle oxygen fugacity would be expected. For example, such positive correlation between Sr concentration and oxygen fugacity was observed in melt inclusions from primitive lavas in the Cascades (Rowe et al., 2009). Furthermore, because the increase in $^{187}Os/^{188}Os$ ratios correlates inversely with MgO, any postulated increase in oxygen fugacity of the mantle would need to have a tight control on the future degree of differentiation of the magma, which seems very unlikely.

Finally, a complex case occurring at the slab-mantle interface and involving (1) a mechanical mixing of ultramafic and mafic material from the subducing slab around blocks of subducted basalts and (2) the metasomatism of the resulting hybrid rocks by sediment-derived fluids, was shown to produce a suite of rocks with similar negative correlation between Os, MgO and $^{187}Os/^{188}Os$ to that observed in the Lesser Antilles lavas (Penniston-Dorland et al., 2012; 2014). A negative correlation between $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$ in these hybrid rocks would also be predicted. It has been suggested that, if these rocks from the slab-mantle interface ascended within diapirs to the base of the arc lithosphere (e.f. Marschall and Schumacher, 2012), these heterogeneities could be directly reflected in the arc lavas (Penniston-Dorland et al., 2012; 2014). However, as mentioned in the previous section, if the correlation observed in the lava compositions resulted from a direct reflection of these source heterogeneities, then no, or similar amounts of differentiation would need to have occurred for all lavas analysed, which seems unlikely. Furthermore, rocks in the melange having $^{187}Os/^{186}Os$ out of the mantle range are dominantly made of altered basalt and should therefore have high $\delta^{18}O$ signatures which would be transferred to the related magma. This scenario is inconsistent with the mantle like $\delta^{18}O$ of the olivine and pyroxene crystals analysed in the Lesser Antilles lavas with the highest $^{187}Os/^{188}Os$ ratios. Therefore, although source contamination cannot be completely ruled out, it is considered highly unlikely, and the trends defined by the lavas seem more plausibly explained by a process occurring after melting in the source, .i.e. crustal assimilation.

4.2 Source $^{187}Os/^{188}Os$

Since crustal assimilation appears to have affected lava $^{187}Os/^{188}Os$ during differentiation in the Lesser Antilles, the only sample suitable for constraining source characteristics is the sample with the highest MgO and highest Os concentrations, which is the picrite from Grenada (LAG4). This picrite $^{187}Os/^{188}Os$ (0.1267) plots within the mantle range (DMM = 0.1238 ± 0.0042) (Fig. 4a, b) which indicates that assimilation had no, or very limited (in the case where the ambient mantle lies in the lower hand of the DMM range), effect on its composition and that it therefore represent the lava with the closest composition to that of the mantle source region. The apparent absence, or very limited amount, of radiogenic Os from either the subducting altered basalt or sediments in the Grenada picrite indicates either that (1) Os from the subducting slab is not, or not efficiently, transported into the magma source regions or (2) that it was retained in a residual mantle phase before the primitive Grenada melts were generated.

Conversely, the Grenada picrite has very radiogenic $^{87}Sr/^{88}Sr$ (0.70508; Fig 5a) which indicates that, as expected, Sr was mobilised from the slab into the wedge. As mentioned earlier, the more radiogenic Sr isotopic ratio of the Grenada picrite analysed, compared to other islands of the arc, is a general feature of Grenada mafic lavas, which has often been interpreted to reflect a greater contribution of sediment to the mantle source (Thirlwall et al., 1996). However, we show that Sr isotopes correlate inversely with Os isotopes which appear to be controlled by assimilation. Therefore, the negative trend in $^{87}Sr/^{86}Sr$ observed in the Lesser Antilles lavas would need to be accounted for by the same process. Hence $^{87}Sr/^{88}Sr$ in the Grenada picrite may not be more radiogenic than primary magmas of the other islands along the arc but instead provide the only true representative indication of source $^{87}Sr/^{86}Sr$ prior to crustal assimilation. In this case, estimations of slab contributions to the magma source based on Sr isotopes in mafic lavas would have historically been misestimated for most islands.

4.3 Characteristics and nature of the assimilant

4.3.1 Trace element and isotopic characteristics

As described in section 4.1, the lavas show an inverse correlation between $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$ (Fig. 5a). However, unlike MgO and Os vs. $^{187}Os/^{188}Os$, where two trends are observed, no north-south separation of the data exists. Given that isotopic ratios are not affected by crystal fractionation, we suggest that the same assimilant is present in both the north and the south of the arc and that the north-south trends observed on plots of MgO and Os vs. $^{187}Os/^{188}Os$ can be accounted for by different fractionated assemblages during assimilation (i.e. different bulk partition coefficients). For example, fractionation of olivine during assimilation will produce a steeper decrease in MgO and Os compared with clinopyroxene fractionation.

Given that $^{87}Sr/^{86}Sr$ decreases down to ~0.703, the assimilant must have $^{87}Sr/^{86}Sr$ close to the DMM (Salters and Stracke, 2004), which precludes any sedimentary origin and is in agreement with the mantle-like clinopyroxene and olivine $\delta^{18}O$ data available for some of the high $^{187}Os/^{188}Os$ lavas, which are similar to those of Grenada picrites (Saba: $\delta^{18}O_{ol}$ = 5.13 and $\delta^{18}O_{cpx}$ = 5.74 for LAS1; Guadeloupe: $\delta^{18}O_{Ol}$ = 5.00-5.12 and $\delta^{18}O_{cpx}$ = 5.51 for GUAD510; Grenada: $\delta^{18}O_{ol}$ = 5.18 for LAG4; Van Soest et al., 2002). No clear correlation between Pb isotopes and $^{187}Os/^{188}Os$ can be observed and no correlation between $^{143}Nd/^{144}Nd$ and $^{187}Os/^{188}Os$ exist (not shown). This could either indicate that the isotopic composition of the assimilant is similar to that of the primitive magma, or that the concentrations in Pb and Nd in the assimilant are not high enough to buffer existing source variations between islands.

When La/Sm or La/Yb are plotted against $^{187}Os/^{188}Os$ (Fig. 5b), the same negative correlation observed on plots of MgO and Os vs. $^{187}Os/^{188}Os$ exists. Such correlations suggest that the REE were affected during assimilation. As with MgO and Os, we propose that the separation of the samples into two similar trends is due to different phases being fractionated during assimilation. The decrease in L/M-HREE in itself (observed in both trends) could therefore reflect the interplay of the progressive incorporation of a low La/Sm assimilant and of fractional crystallization of minerals that fractionate L/M-HREE (such as clinopyroxene or amphibole).

Finally, Sr/Th seems also affected by crustal assimilation since it correlates negatively with $^{187}Os/^{188}Os$ (Fig. 5c). The correlation is clearly due to increasing Sr since Th does not decrease with $^{187}Os/^{188}Os$. As for $^{87}Sr/^{88}Sr$ vs. $^{187}Os/^{188}Os$, no distinction between the north-south sections of the arc can be observed, consistent with a common assimilant composition along the arc. The assimilant must also have very high Sr content with a minimum Sr/Th of 624 (the highest ratio found in the lavas).

In summary, the isotopic and trace element composition of the lavas suggest that one of the assimilants present in the basement of Lesser Antilles islands (the other being continent-derived sediment, not discussed here) displays a mantle-like $^{87}Sr/^{88}Sr$ ratio, a $^{187}Os/^{188}Os$ higher than 0.2, a high Sr/Th (> 620), and a low La/Sm and La/Yb. Significantly, thermobarometric estimations performed on St Vincent picrite (STV301) indicate that it was last stored at depths corresponding to the arc middle-lower crust (Heat et al., 1998; Pichavant et al., 2007). This would imply that assimilation would need to have occurred at depths equivalent to or greater than these.

4.3.2 Nature of the assimilant

Recent (~ late Cretaceous to Paleogene) altered Mid-Ocean Ridge Basalts (MORB) or Fore-arc Basalts (FAB; Reagan et al. (2010)) could have a DMM-like $^{87}Sr/^{86}Sr$ with $^{187}Os/^{188}Os$ higher than 0.2 and low L/M-HREE (typically <1), but their Sr concentration is typically far too low (typically ≤ 90 ppm) to be able to modify the primitive magma concentrations. Bulk mafic MORB or FAB cumulates would also be too depleted in Sr to represent an appropriate assimilant. Instead, we suggest that the assimilant could be MORB or FAB plagioclase-rich cumulates present in the lower crust. Given that the Lesser Antilles arc is thought to be built on the Aves ridge (extinct arc) forearc after a slab rollback that displaced the activity eastward, FAB cumulates are more likely to be present at the base of the Lesser Antilles arc than MORB cumulates. Such rocks would likely occur under every island and meet the geochemical requirements of the assimilant described above. They could comprise mafic layers, but the more felsic sections would be preferentially assimilated by primitive magmas. While the mafic layers of cumulates tend to concentrate the iridium platinum group element (IPGE) because these elements are removed from the melt early during differentiation and concentrate in cumulus phases such as olivine or chromite, plagioclase-rich layers tend to concentrate more Re (and palladium platinum group elements: PPGE) since it remain longer in the melt and is more likely to be present as interstitial sulfides. Radiogenic Os, produced by Re decay, is therefore more likely to be present in such layers. Since the Lesser Antilles arc started accreting during the Oligocene (Germa et al., 2011), it would be predicted that the early-arc FAB lavas and cumulates would have a moderately radiogenic $^{187}Os/^{188}Os$, consistent with the signature of the assimilant. The mantle-like Sr isotopic composition of the cumulate would also be consistent with their production early in the arc existence, prior to significant fluids fluxing through the mantle.

Finally, none of the lavas analysed have a europium positive anomaly, the latter being expected in the case of assimilation of large amounts of plagioclase. However, all but one lava (STV301) contain plagioclase phenocrysts which indicate that plagioclase fractionation may have erased any such positive anomaly. The absence of any Eu anomaly in the plagioclase-free high-MgO basalt from St Vincent could be explained by the low amount of assimilation involved in that lava (~ 7%; Fig. 6) or if the assimilated plagioclase cumulates did not have a significant positive Eu anomaly. A low Eu anomaly in plagioclase can only occur in highly oxidised magmas. Since the plagioclase cumulates are likely to have crystallised at the initiation of the subduction zone, their oxygen fugacity is likely to be similar to that of FAB erupted at the onset of the Mariana subduction, which have been shown to present high oxygen fugacity (QFM +0.4; Brounce et al., 2013), and are likely to crystallise plagioclase with small Eu anomalies.

4.3.3 Assimilation and fractional crystallisation (AFC) modelling

The AFC equation (DePaolo, 1981) can be used to model the $^{187}Os/^{188}Os$, $^{87}Sr/^{88}Sr$, La/Sm and Sr/Th relationships using reasonable parameters (Figs. 6a, b, c). We used the Grenada picrite (LAG4) for the initial magma composition, since it plots within the mantle range in terms of $^{187}Os/^{188}Os$ and its Os concentration (360 ppt Os) is consistent with that expected with a melt in equilibrium with sulfide-bearing mantle. The range of Os, Sr, Th, La and Sm bulk partition coefficients (D) (Table 3) were estimated by dividing the concentration of these elements in the Grenada picrite by their concentration in the most differentiated samples. Sr, Th, La and Sm bulk D's obtained are consistent with fractionation of the observed phenocryst assemblages (olivine ± pyroxene ± plagioclase). The Os bulk partition coefficients used (D = 12-16) are in agreement with that expected for ~0.5% of chromian-spinel fractionation (Chesley et al., 2002; Righter et al., 2002). The $^{187}Os/^{188}Os$ ratio of the assimilant ($^{187}Os/^{188}Os$ = 0.245) can be easily produced by radiogenic ingrowth of a DMM composition with an initial ratio of $^{187}Os/^{188}Os$ (0.127). This could occur within the 25 My since magmatism was initiated in the Lesser Antilles (Germa et al., 2011), even if the initial $^{187}Re/^{188}Os$ is lower than MORB (~600). The Os concentration of the assimilant used in the model (20 ppt) is consistent with that expected from a plagioclase-rich cumulate grown from the residual melt of a MORB/FAB primitive magma (with ~ 350-200 ppt Os; derived from a sulfide-bearing mantle) after fractionation of important amounts of olivine and spinel. Indeed 20 ppb Os is within the range of concentrations observed in the basalts with the lowest MgO analysed in this study (5-44 ppt for MgO 5.1-8.7 wt.%), some of the latter presenting phenocryst assemblages with up to 70% plagioclase and less than 20% olivine (e.g. STV324; Heath et al. (1998)).

All data could be modeled using the same starting (LAG-4) and assimilant composition (Table 3) and with F > 0.8. In $^{87}Sr/^{86}Sr$ vs. $^{187}Os/^{188}Os$ space, the lavas fall on two trends produced by different rates of assimilation and small variations in D_{Sr} (r = 0.56 vs. 0.70; D_{Sr} = 1.4-1.8). On trace element ratio vs. isotope diagrams (Fig.6b, c), the effect of variations in the fractionating assemblage during assimilation on different islands (= variation in D) is reflected by small displacement of the samples on these trends compared to isotope-isotope space (Fig. 6a). The north-south difference observed in La/Sm vs. $^{187}Os/^{188}Os$ can be easily produced by increasing $D_{La/Sm}$. We suggest that such north-south variations in $D_{La/Sm}$ could be related to the depth at which AFC occurs. In this case, the assemblage fractionated during assimilation in the north of the arc depleted La less than the assemblage fractionated in the south for a constant D_{Sm}. For example, it would be the case if, during assimilation, the fractionated assemblage is dominated by olivine ($D_{La/Sm}$ ~1) in the south of the arc and by clinopyroxene ($D_{La/Sm}$ < 1) in the north of the arc. Such variations in the fractionating assemblage composition would have negligible effect on the isotopic composition of the lavas, consistent with the single trend observed in Sr vs Os isotopes from north to south.

4.4 Implications

4.4.1 The Lesser Antilles

Although assimilation of sediment (high $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $^{208-207-206}Pb/^{204}Pb$ and low $^{176}Hf/^{177}Hf$ and $^{143}Nd/^{144}Nd$ ratios) had been shown to modify some lava compositions in the central-southern part of the arc (Thirlwall and Graham, 1984; Davidson, 1987; Davidson and Harmon, 1989; Smith et al., 1996; Thirlwall et al., 1996; Van Soest et al., 2002; Bezard et al., 2014), assimilation of another component in the deep crust of the Lesser Antilles arc (Fig. 7) was not anticipated and differences between the Grenada picrite compositions and the rest of the arc lavas have traditionally been attributed to differences in source composition. This work suggests that the Grenada picrites might provide the only close estimates of the source composition in terms of $^{87}Sr/^{86}Sr$, $^{187}Os/^{188}Os$, Sr and REE. Thus, the use of such proxies in less primitive lavas to constrain the relative contributions of fluids versus sediment in the arc source may need reappraisal. All the arc data seem to back-project toward a primitive magma with the Grenada picrite composition (Fig. 4) although small variations in the source from north to south can't be precluded. The investigation of such variations is, however, hampered by the absence of very mafic lavas, such as those found in St Vincent and Grenada, in the northern arc. Since the Grenada picrite is the only silica undersaturated lavas, this suggests that primitive magma along the arc in general could be of a similar alkaline nature before AFC, as suggested by Macdonald et al. (2000). The absence of cumulate assimilation by Grenada picrites could be either due to a lack of significant amount of cumulate at the base of the arc crust, or to the presence of crustal structures allowing the magma to reach the surface with minimal stalling at the base of the crust. The latter hypothesis could be supported by the presence of a transform fault in Grenada, which has been suggested to control the emplacement of the most recent products (Arculus, 1976).

4.4.2 Other arcs

The correlation between Os (or 1/Os) and $^{187}Os/^{188}Os$ observed in the Lesser Antilles arc is not unique and has been noted in most continental and oceanic arc lavas (Fig. 8a; Alves et al., 1999; 2002; Borg et al., 2000; Chesley et al. 2002; Woodland et al., 2002; Woodhead et al., 2004; Turner et al., 2009; Righter et al., 2012). However, clear correlations between Os isotopes and both Os concentrations and indices of differentiation (MgO, SiO_2) have only been noted in continental arcs (Lassiter and Luhr, 2001; Chesley et al., 2002). The absence of clear MgO-SiO_2 correlations with $^{187}Os/^{188}Os$ in oceanic arc lavas (Fig. 8b) led previous studies to suggest source control of the inverse correlation between Os concentration and $^{187}Os/^{188}Os$ (Alves et al., 1999). Our Lesser Antilles study suggests that the correlations between $^{187}Os/^{188}Os$ and Os content and the "radiogenic $^{187}Os/^{188}Os$ ratios observed in oceanic arcs could reflect crustal assimilation and that slab-derived Os may not be transferred into the magma source regions, as proposed by Righter et al. (2012). It also suggests, based on the radiogenic $^{187}Os/^{188}Os$ ratio in the St Vincent high-MgO lavas (MgO = 12.6 wt. %), that the process can affect very primitive magmas. Although the conditions of assimilation may be different in every arc, early assimilation during differentiation could explain the radiogenic $^{187}Os/^{188}Os$ observed in early crystallizing phases such as Cr-spinel in Bonin Islands tholeiites (Suzuki et al, 2011).

Unlike the correlation between Os isotopes and Os concentrations, the covariation of Os isotopes with lithophile isotope or trace element ratios observed in the Lesser Antilles (e.g. Sr isotopes, Sr/Th and La/Sm) is not ubiquitous in other arcs (e.g. Fig. 8c, d), with only the Cascades lavas showing similarly clear correlations between $^{187}Os/^{188}Os$

and $^{87}Sr/^{86}Sr$ ratios and Sr concentrations (Borg et al., 2000; Fig. 8c, d). This lack of obvious co-variation could be explained by more limited compositional differences between the primary magma and the assimilant which would rend the impact of assimilation harder to observe. Indeed, in the Lesser Antilles, the $^{87}Sr/^{86}Sr$, Sr/Th and La/Sm ratios of the primitive magmas differs significantly from those of the assimilant, which results in obvious mixing lines. However, the $^{87}Sr/^{86}Sr$, Sr/Th and La/Sm ratios of primitive magmas are likely to vary with the composition of the subducted sediment and as demonstrated in Fig. 8c and 8d, the very 'continental' isotopic and trace element signature of the Lesser Antilles primitive magma is not commonly observed in other oceanic arcs, the latter presenting composition closer to MORB (e.g. picrites from the Vanuatu or Salomon islands have $^{87}Sr/^{86}Sr$ ~0.703-0.7045 contrasting with the $^{87}Sr/^{86}Sr$ of ~ 0.7051 of the most primitive picrite in Grenada; Peate et al., 1997; Schuth et al., 2004). Therefore, assimilation of a recent FAB like cumulate by primitive magmas would be much harder to detect in most oceanic arcs than in the Lesser Antilles. In addition, the rocks assimilated in other arcs might have lower Sr concentrations, rending the impact of the process on Sr/Th and $^{87}Sr/^{86}Sr$ hard to fingerprint. Alternatively, along-arc primitive magma compositional variations may exist, interfering with the variations produced by assimilation.

5. CONCLUSIONS

Our observations suggest that no significant slab derived Os is present in the primitive magmas of the Lesser Antilles arc. We interpret the increase in Os isotopic ratios observed in the lavas as caused by crustal assimilation in the deep crust of the arc. The assimilant would be similar all along the arc and display lower $^{87}Sr/^{86}Sr$ (MORB-like), La/Sm and higher $^{187}Os/^{188}Os$, Sr and Sr/Th than the primitive magma. We suggest that it could be a plagioclase-rich cumulate present at the base of the arc. Such cumulate could have been produced during the early-arc stage, prior to significant amount of fluids/sediments fluxing in the mantle.

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Figure captions:

Fig. 1: Map of the Lesser Antilles arc with the location of selected lava samples (in black). One sample from each island (except St. Vincent, n=2) was analysed. See Table 1 for sample identification. The latitude of DSDP sites 543/543A and 144 are also indicated.

Fig. 2: $^{87}Sr/^{86}Sr$ vs. (a) $^{143}Nd/^{144}Nd$, (b) MgO (wt. %), (c) La/Sm and (d) Sr/Th of the lavas selected. Data presented in Table 2.

Fig. 3: Os (ppb) vs. $^{187}Os/^{188}Os$ of the arc lavas and the subducting slab. DMM = Depleted MORB mantle from Rudnick and Walker (2009). Note logarithmic scales. Data presented in Table 1.

Fig. 4: Lavas Os (ppb) and MgO (wt. %) against $^{187}Os/^{188}Os$. Same legend as in figure 3. The same negative correlation is also observed between $^{187}Os/^{188}Os$ and Mg#. Woodland et al. (2002) data on different Grenada lavas are shown for comparison. Arrows shows potential differentiation trends for the northern and southern islands, starting with the most primitive lava of the arc.

Fig. 5: (a) $^{87}Sr/^{86}Sr$, (b) La/Sm and (c) Sr/Th vs $^{187}Os/^{188}Os$ composition of the lavas. Subducting slab composition are also indicated. Data for arc lavas and sediment and altered basalt from the slab are presented in Tables 1 and 3. DMM = depleted mantle from Rudnick and Walker (2009) for Os isotopes and Salters and Stracke (2004) for Sr. isotopes; Lower continental crust composition is from Saal et al. (1999), N-MORB trace element composition is from Sun and McDonough (1989). Arrows highlight the negative trends drawn by the data.

Fig. 6: Assimilation during Fractional Crystallization (AFC) models of (a,b) $^{87}Sr/^{86}Sr$, (a,c) $^{187}Os/^{188}Os$, (b) Sr/Th and (c) La/Sm ratios of the Lesser Antilles primitive lavas using DePaolo (1981) equation. Parameters for Models 1 and 2 are shown in Table 3. Dots represent the fraction of melt remaining (F). In (b) and (c), samples with compositions displaced from their position on the trends defined in the isotope-isotope space (a) (likely due to the impact of mineral fractionation) are circled. The arrows show the inferred compositions before displacements.

Fig. 7: Schematic model for the Lesser Antilles plumbing system to explain the main factors influencing the compositional variations of the arc lavas. The figure illustrates both the locus (cartoon) and the impact (diagrams) of cumulate assimilation on the lava's $^{187}Os/^{188}Os$, $^{87}Sr/^{86}Sr$, La/Sm and $\delta^{18}O$ compositions (evolution of Sr/Th ratio is not shown). The impact of subsequent assimilation of sediment (Bezard et al., 2014), which is not discussed in this contribution, is also shown for a full illustration of the arc processes. The arc primary magmas would come from a source strongly influence by the subducted sediment. Grenada picrite (A) would have avoided any storage in the arc crust and retained the primitive magma composition. All the less primitive lavas (B) would

have spent variable amounts of time in contact with a plagioclase-rich cumulate in the lower parts of the crust. The resulting magmas would have either ascended directly to the surface (B) or assimilated some sediment during the ascent (C). M = mantle composition.

Fig. 8: Comparison of the Lesser Antilles arc lava compositions with those of other arcs (continental and oceanic). The negative correlation observed between Os isotopes and Os concentrations is ubiquitous in arcs (a). On the other hand, negative correlations between Os isotopes and MgO (b) or Sr isotopes (c) as well as a positive correlation between Sr/Th and Os isotopes (d) are not observed in every arcs. Lava compositions are from Borg et al., (2000) for the Cascades, Chesley et al. (2002) for the Trans-Mexican arc, Turner et al. (2009) for the Tonga-Kermadec, Alves et al. (1999) for Java, Woodhead and Brauns (2004) for New Britain and Woodland et al. (2002) for the additional Lesser Antilles arc data.

Fig. 1

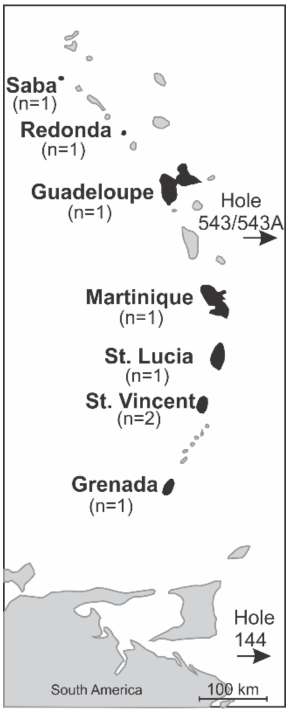


Fig. 2

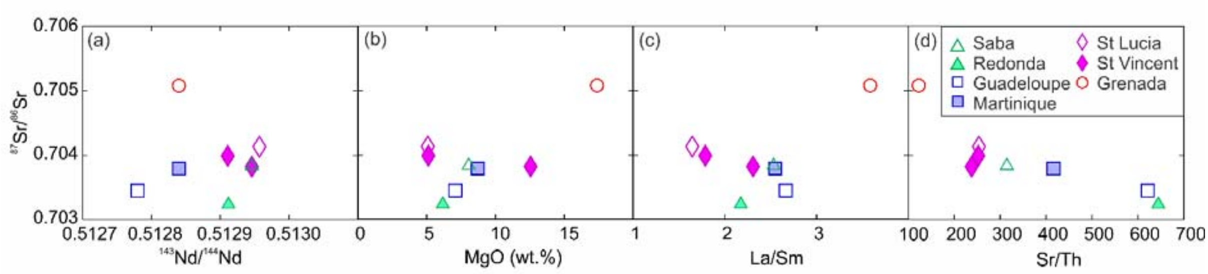


Fig. 3

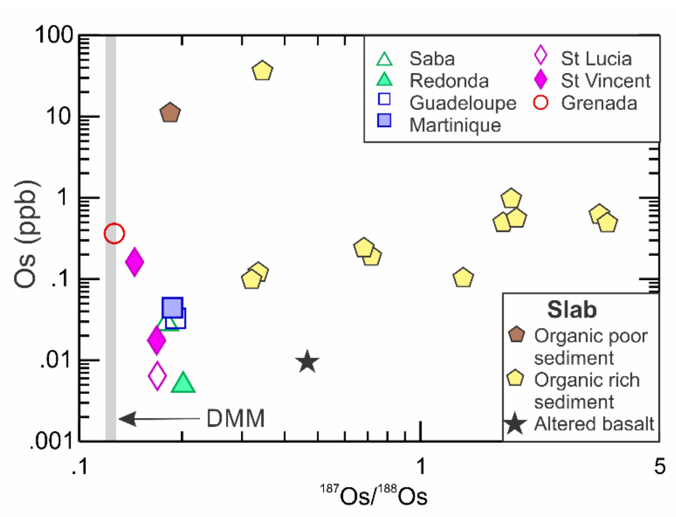
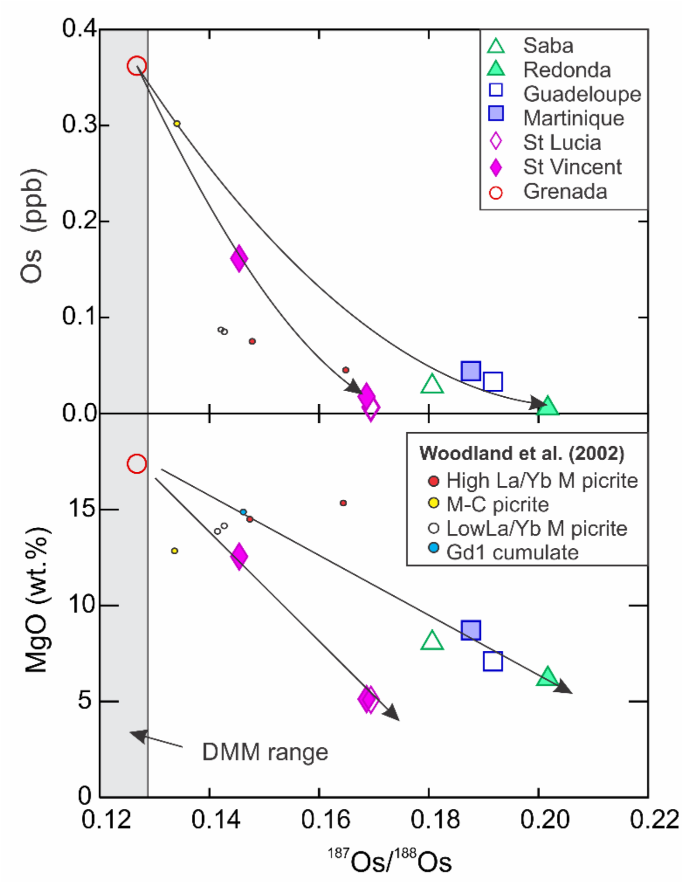


Fig. 4



0.4
0.3
0.2
0.1
0.0
Os (ppb)
Saba
Redonda
Guadeloupe
Martinique
St Lucia
St Vincent
Grenada
Woodland et al. (2002)
High La/Yb M picrite
M-C picrite
LowLa/Yb M picrite
Gd1 cumulate
15
10
5
0
MgO (wt.%)
DMM range
0.12
0.14
0.16
0.18
0.20
0.22
187Os/188Os

Fig. 5

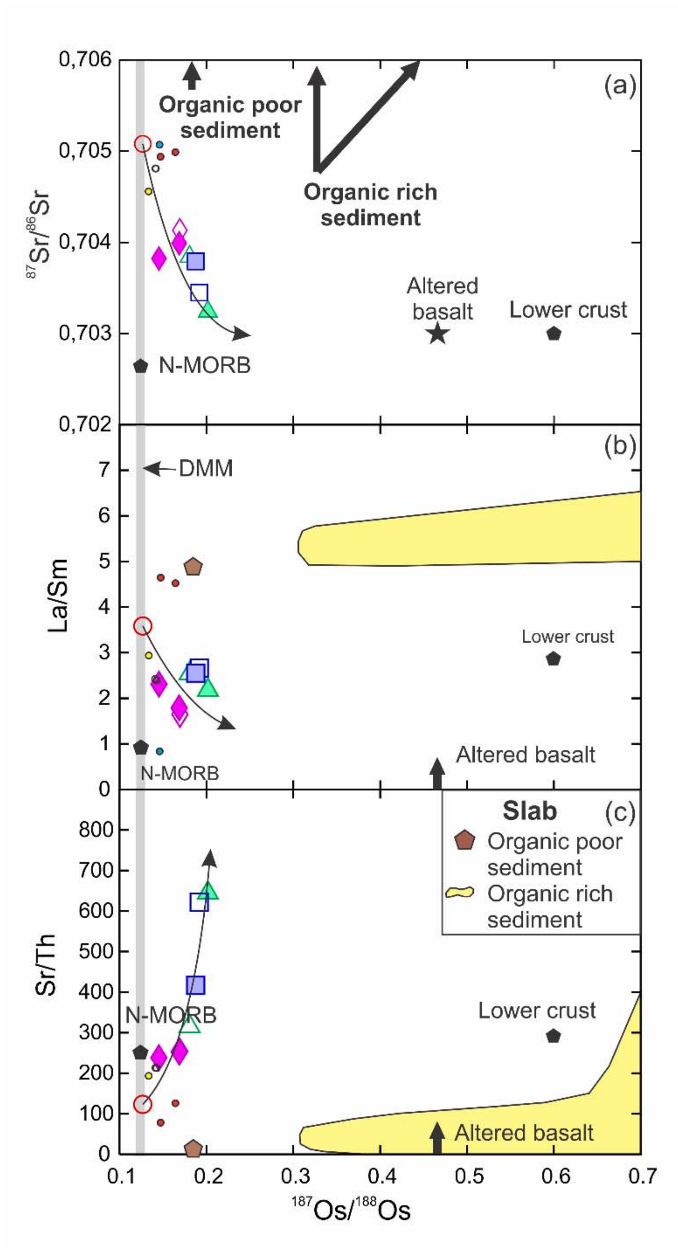

(a)
Organic poor
sediment
Organic rich
sediment
Altered
basalt
Lower crust
N-MORB
(b)
DMM
Lower crust
Altered basalt
N-MORB
(c)
Slab
Organic poor
sediment
Organic rich
sediment
N-MORB
Lower crust
Altered basalt
87Sr/86Sr
La/Sm
Sr/Th
187Os/188Os

Fig. 6

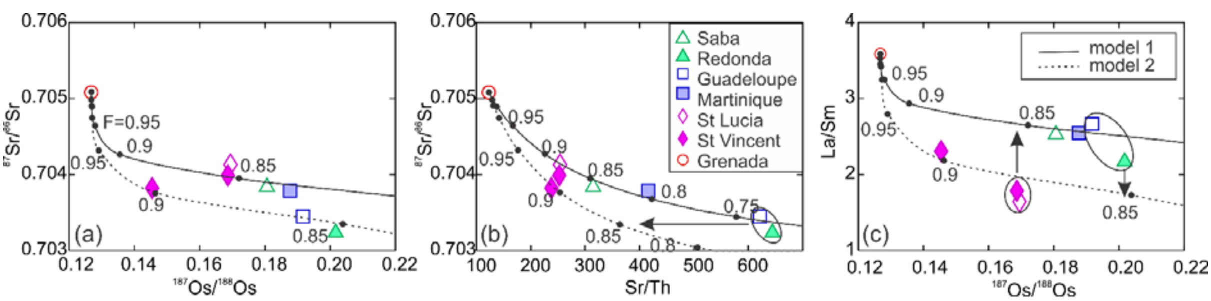
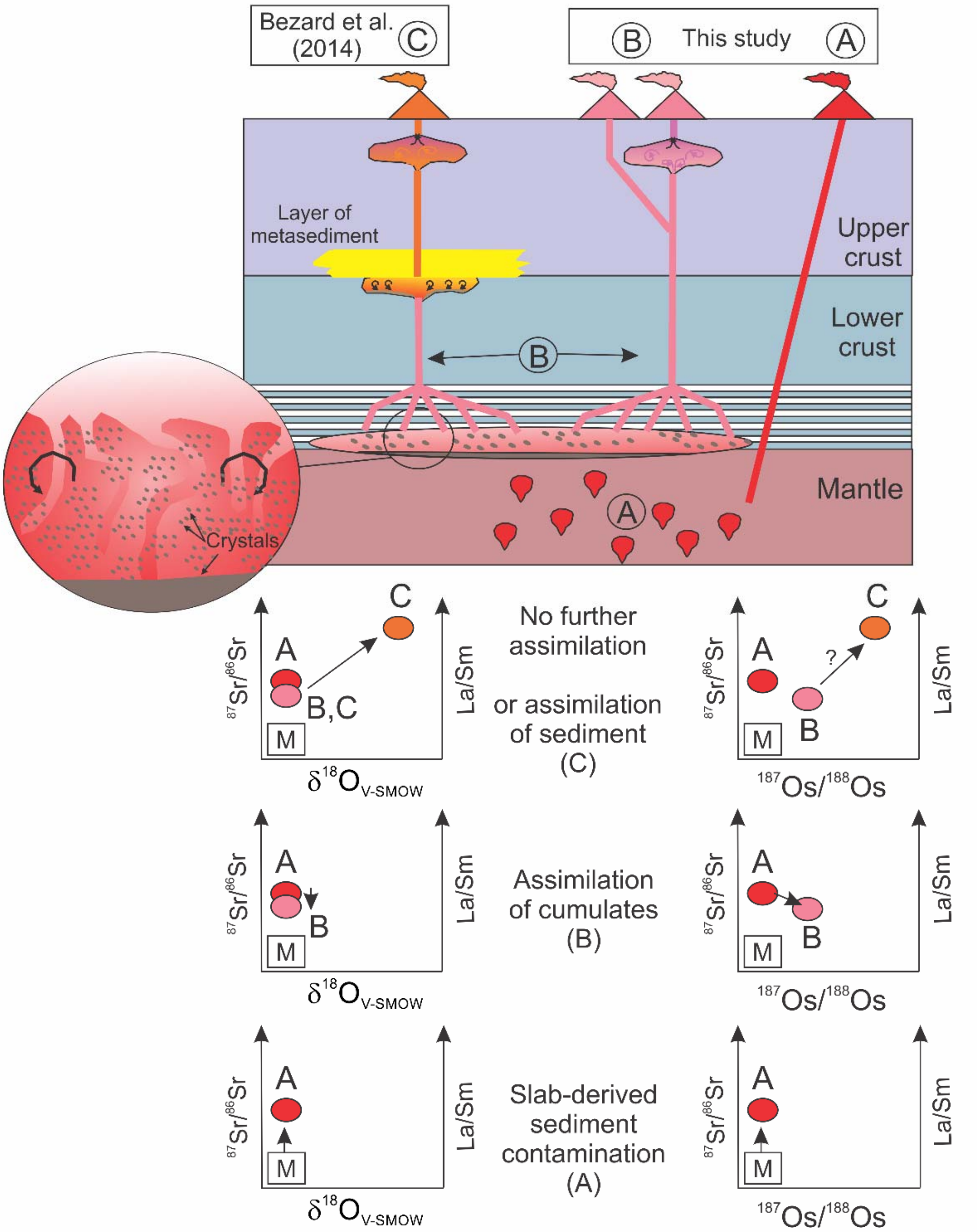
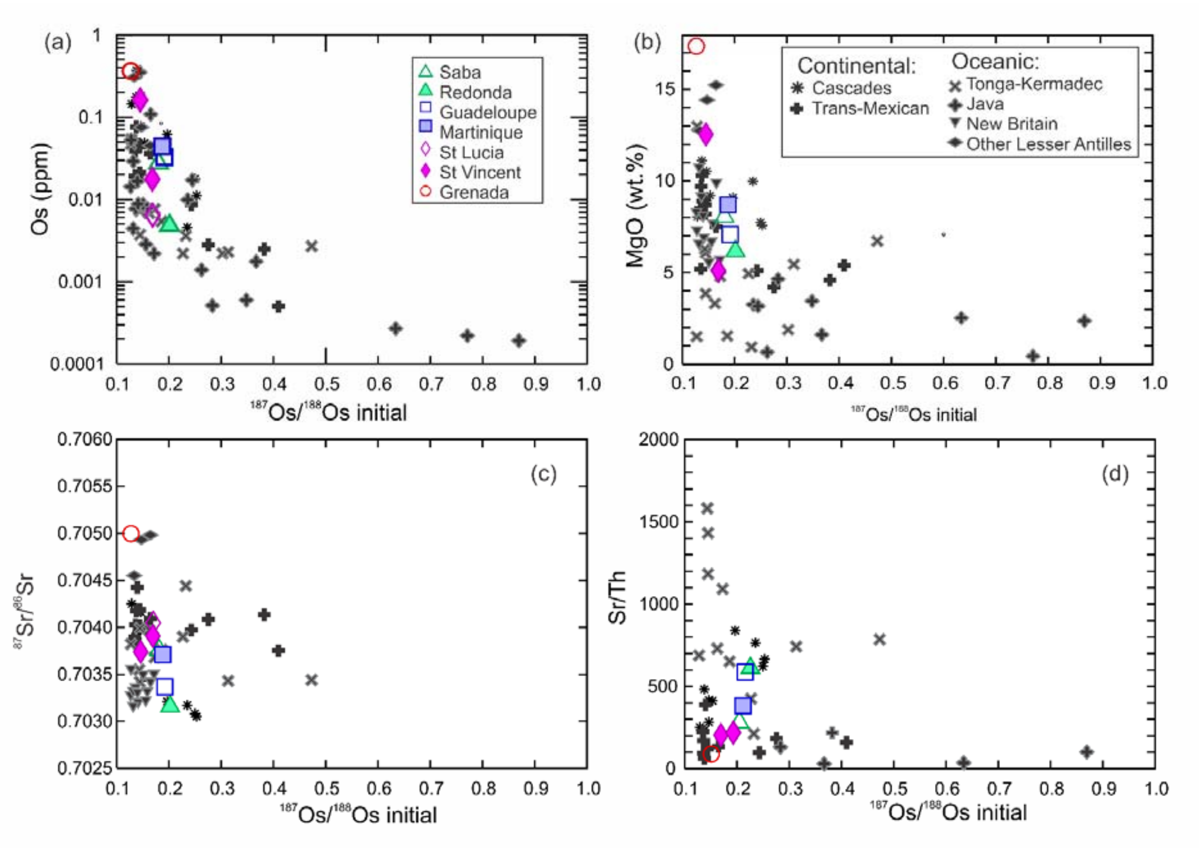

(a)
F=0.95
0.9
0.85
87Sr/86Sr
187Os/188Os
(b)
Saba
Redonda
Guadeloupe
Martinique
St Lucia
St Vincent
Grenada
Sr/Th
(c)
model 1
model 2
La/Sm
187Os/188Os

Fig. 7



Bezard et al. (2014) C
B This study A
Layer of metasediment
Upper crust
Lower crust
B
Mantle
A
Crystals
C
A
B,C
M
$^{87}Sr/^{86}Sr$
La/Sm
$\delta^{18}O_{V\text{-}SMOW}$
No further assimilation
or assimilation of sediment (C)
C
A
?
B
M
$^{87}Sr/^{86}Sr$
La/Sm
$^{187}Os/^{188}Os$
A
B
M
$^{87}Sr/^{86}Sr$
La/Sm
$\delta^{18}O_{V\text{-}SMOW}$
Assimilation of cumulates (B)
A
B
M
$^{87}Sr/^{86}Sr$
La/Sm
$^{187}Os/^{188}Os$
A
M
$^{87}Sr/^{86}Sr$
La/Sm
$\delta^{18}O_{V\text{-}SMOW}$
Slab-derived sediment contamination (A)
A
M
$^{87}Sr/^{86}Sr$
La/Sm
$^{187}Os/^{188}Os$

Fig. 8



(a)
(b)
(c)
(d)
Saba
Redonda
Guadeloupe
Martinique
St Lucia
St Vincent
Grenada
Continental:
Cascades
Trans-Mexican
Oceanic:
Tonga-Kermadec
Java
New Britain
Other Lesser Antilles
Os (ppm)
MgO (wt.%)
87Sr/86Sr
Sr/Th
187Os/188Os initial

Table 1: Os data for the arc lavas and altered basalt and sediments from the subducting slab.

	Subbottom depth (m)	Lithology Unit #	Os (ppb)	±	^{187}Os/^{188}Os	±	^{187}Re/^{188}Os	±	Re (ppb)	±	Age (ka)[d]	^{187}Os/^{188}Os initial
Lavas (from N to S):												
Saba-LAS1[a]	–	–	0.0281	0.0001	0.181	0.001	–		–		<10	–
Redonda-R8204 [a]	–	–	0.0049	0.0001	0.202	0.002	–		–		1000	–
Guadeloupe-GUAD510 [a]	–	–	0.0328	0.0004	0.192	0.001	–		–		500	–
Martinique-M8328 [a]	–	–	0.0441	0.0002	0.188	0.001	–		–		<1000	–
St Lucia-SL8344 [a]	–	–	0.0064	0.0001	0.170	0.005	–		–		11400	–
St Vincent-STV301 [a]	–	–	0.161	0.001	0.1451	0.0007	–		–		180	–
St Vincent-STV324 [a]	–	–	0.0175	0.0001	0.169	0.002	–		–		<3.6	–
Grenada-LAG4 [a]	–	–	0.362	0.001	0.1268	0.0004	–		–		<10	–
Altered basalt 543 16 5 20-24 [a]	–	–	0.0096	0.0002	0.466	0.003	–		–		–	–
Sediments (increasing depth):												
Site DSDP 543												
78A-543-17-3-120-124 [b]	166	3	11.2	0.4	0.185	0.007	–		–	–	16000	–
Site DSDP 144/144A												
14-144A-5-1 interval 123-124 [c]	181	3	0.1009	0.0008	1.33	0.02	389	5	7.03	0.03	85000	0.78
14-144A-6-1 interval 70-110 [c]	189	3	0.941	0.003	1.844	0.005	721	3	115.0	0.4	89000	0.77
14-144Z-4-2 interval 60-64 [c]	215	3	0.478	0.003	3.52	0.02	1494	8	102.8	0.3	93000	1.21
14-144Z-4-2 interval 143-146 [c]	216	3	0.602	0.003	3.34	0.01	1425	6	125.4	0.4	93000	1.13
14-144Z-4-3 interval 31-33 [c]	216	3	0.534	0.002	1.913	0.006	755	3	67.8	0.2	93000	0.74
14-144Z-4-3 interval 100-103 [c]	217	3	0.484	0.002	1.746	0.007	580	3	48.1	0.2	93000	0.85
14-144Z-5-1 interval 5-6 [c]	264	4	0.231	0.001	0.682	0.008	178	2	7.93	0.03	98000	0.39
14-144Z-5-1 interval 143-143 [c]	265	4	0.186	0.002	0.72	0.02	164	3	5.89	0.02	98000	0.45
14-144Z-7-1 interval 136-137 [c]	299	5	0.116	0.001	0.34	0.01	32.3	0.7	0.757	0.007	106000	0.28
14-144Z-7-1 interval 123-124 [c]	299	5	34.5	0.3	0.34	0.01	122	3	847	3	106000	0.13
14-144Z-8-3 interval 136-137 [c]	328	5	0.0934	0.0005	0.321	0.005	16.7	0.7	0.32	0.01	113000	0.29

[a] Os, ^{187}Os/^{188}Os analysed at Macquarie University.
[b] Organic poor sediment: Os, ^{187}Os/^{188}Os analysed at Macquarie University.
[c] Organic rich sediment: Os, ^{187}Os/^{188}Os, Re analysed at Durham University
[d] Ages of Lava flows were taken from the following sources: Saba (Dufrane et al. 2009); Redonda (Baker, 1984); Guadeloupe (Dufrane et al., 2009); Martinique, Carbet Complex (Germa et al. (2011); St Lucia, Anse Galet (Le Guen de Kerneizon et al. (1983); St Vincent (Heath et al. (1998); Grenada (Dufrane, 2009). Ages indicated for the sediments, also used to calculate the initial ^{187}Os/^{188}Os ratios, correspond to that of the samples analysed by Carpentier et al. (2008; 2009) named in Table 2.

Note: Uncertainties are given as 2 sigma. For the latter the uncertainty includes the 2SE uncertainty for mass spectrometer analysis plus uncertainties for Os blank abundance and isotopic composition. The external reproducibility for ^{187}Os/^{188}Os and Os in lavas and organic-poor sediment, based on replicate analyses of WPR-1, is 1% and 4%, respectively. The external reproducibility for ^{187}Os/^{188}Os, ^{187}Re/^{188}Os, Os and Re in organic rich sediments, based on replicate analyses of SDO-1, is 7%, 7%, 16% and 15% respectively (see section 2.2).

Table 2: Lithophile major and trace element concentrations and isotopes of the arc lavas and altered basalt and sediments from the subducting slab analysed.

	Sample used for sediment lithophile element compositions (Carpentier et al., 2008;2009)	Subbotom Depth	MgO (wt. %)	Mg#	Sr (ppm)	La (ppm)	Sm (ppm)	Th (ppm)	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$
Lavas (from N to S):										
Saba-LAS1[a]	–	–	8.05	0.82	321	5.8	2.29	1.02	0.70384	0.51295
Redonda-R8204 [a]	–	–	6.17	0.74	493	4	1.84	0.77	0.70324	0.51291
Guadeloupe-GUAD510 [a]	–	–	7.08	0.76	261	3.7	1.4	0.42	0.70345	0.51278
Martinique-M8328 [a]	–	–	8.71	0.83	358	5.2	2.04	0.86	0.70379	0.51284
St Lucia-SL8344 [a]	–	–	5.08	0.69	177	3.3	2.03	0.70	0.70413	0.51296
St Vincent-STV301 [a]	–	–	12.55	0.86	202	5.7	2.47	0.85	0.70382	0.51295
St Vincent-STV324 [a]	–	–	5.12	0.74	236	4.9	2.72	0.94	0.70399	0.51291
Grenada-LAG4 [a]	–	–	17.38	0.89	296	9.3	2.6	2.41	0.70508	0.51284
Altered basalt 543 16 5 20-24 [a]	–	–	–	–	–	–	3.36	–	0.70304	0.51312
Sediment (increasing depth):										
Site DSDP 543:										
78A-543-17-3-120-124[b]	543 18 4W 15-17	174	2.91	–	83	23.5	4.83	8.69	0.714076	0.51207
Site DSDP 144/144A:										
14-144A-5-1 interval 123-124 [b]	144A 5 1W 119-124	181	0.78	–	750	10.4	1.46	2.31	0.707871	0.51184
14-144A-6-1 interval 70-110 [b]	144A 6 1W 90-93	190	0.77	–	681	11.5	1.56	2.16	0.707884	0.51183
14-144Z-4-2 interval 60-64 [b]	144 4 2W 60-64	215	1.21	–	570	6.5	0.97	1.45	0.707806	0.51188
14-144Z-4-2 interval 143-146 [b]	144 4 2W 60-64	215	1.13	–	570	6.5	0.97	1.45	0.707806	0.51188
14-144Z-4-3 interval 31-33 [b]	144 4 2W 60-64	215	0.74	–	570	6.5	0.97	1.45	0.707806	0.51188
14-144Z-4-3 interval 100-103 [b]	144 4 2W 60-64	215	0.85	–	570	6.5	0.97	1.45	0.707806	0.51188
14-144Z-5-1 interval 5-6 [b]	144 5 1W 123-125	265	0.39	–	446	22.5	4.2	6.39	0.708556	0.51211
14-144Z-5-1 interval 143-143 [b]	144 5 1W 123-125	265	0.45	–	446	22.5	4.2	6.39	0.708556	0.51211
14-144Z-7-1 interval 136-137 [b]	144 7 1W 80-82	299	0.28	–	270	28.8	5.4	8.42	0.710830	0.51211
14-144Z-7-1 interval 123-124 [b]	144 7 1W 80-82	299	0.13	–	270	28.8	5.4	8.42	0.710830	0.51211
14-144Z-8-3 interval 136-137 [b]	144 8 3W 130-135	328	0.29	–	349	29.4	5.5	8.19	0.710293	0.51210

[a] Data from from Van Soest (2000) (LAS1; LAG4), Davidson (1984;1986) (R8204; M8328; Altered basalt); Bezard et al. (2014; under review) (SL8344); Dufrane et al. (2009) (GUAD510) and Heat et al. (1998) (STV301; STV 324).

[b] Data indicated correspond to the samples analysed by Carpentier et al. (2008; 2009) named in the table.

Table 3 : AFC model parameters

Endmember compositions[a]		
	Initial Magma[b]	**Assimilant**[c]
Sr (ppm)	296	790
Os (ppb)	0.36	0.02
La (ppm	9.32	4.00
Sm (ppm)	2.60	1.84
Th (ppm)	2.41	0.50
$^{87}Sr/^{86}Sr$	0.7051	0.7023
$^{187}Os/^{188}Os$	0.1268	0.2450

Bulk partition coefficients		
	Model 1	**Model 2**
DSr	1.4	1.8
DOs	16	12
DTh	2.7	2.3
DLa	2	2.6
DSm	1.3	1.3
r =Ma/Mc[c]	0.56	0.70

[a]used in both models 1 and 2

[b] composition of LAG 4 picrite

[c] determined iteratively