Oxidation of Réunion Island Lavas with MORB-like fO_2 by Crustal Assimilation

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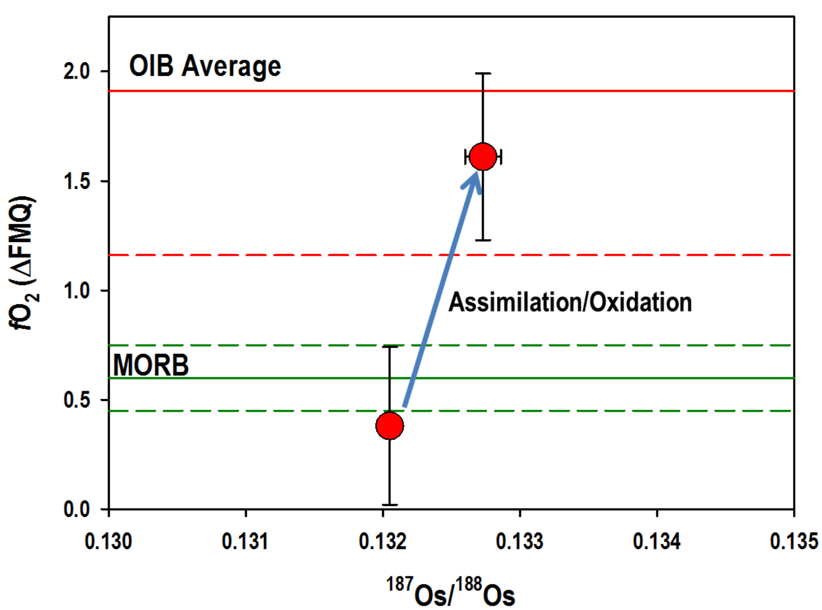
Abstract:

Oxygen fugacity (fO_2) is poorly constrained in mantle reservoirs, especially those sampled by ocean island basalts (OIB). This is partially due to complications from the effects of secondary processes after partial melt generation on fO_2 in OIB parental magmas. To investigate these issues new *in situ* trace element data of olivine in lavas from La Réunion are reported. Réunion is a useful location to examine post-melting modification due to the limited range in radiogenic isotope compositions of its lavas, indicating a homogenous source. Vanadium abundances in olivine were used to constrain the lava fO_2 to between +0.4 and +1.6 ΔFMQ, intermediate between that of ridge basalts and other OIB. The variable fO_2 of Réunion lavas likely results from assimilation during transit through the crust, and not source heterogeneity, indicating that their mantle source is similar in fO_2 to that of MORB. This reveals that a deep, early formed mantle source has fO_2 similar to that of the depleted upper mantle. Assimilation can have a pronounced effect on lava fO_2 and must be accounted for when constraining mantle redox.

Graphical Abstract



Introduction:

Oxygen fugacity (fO_2) of primitive lavas is a proxy for the fO_2 of their mantle sources and is useful for constraining redox variability within the mantle (Carmichael, 1991; Moussallam et al. 2019; Nicklas et al. 2021a). Redox constraints are important for testing models of recycling into the deep Earth, as well as for tracking planetary differentiation and mixing processes (Carmichael, 1991; Frost et al. 2008; Brounce et al. 2017). While fO_2 in primitive melts can potentially be modified by processes such as fractional crystallization (Kelley and Cottrell, 2012), crustal contamination (Grocke et al. 2016) and degassing (Moussallam et al. 2019), the fO_2 of erupted basalts is, to a first order, controlled by their mantle source fO_2 (Birner et al. 2018). Oxygen fugacity varies strongly in primitive melts according to tectonic environment (Carmichael, 1991), with arc basalts ($\Delta FMQ \geq +2$) having elevated fO_2 relative to mid ocean ridge basalts (MORB; $\Delta FMQ \sim 0$), possibly by metasomatism of the mantle wedge by oxidized recycled materials (Kelley and Cottrell, 2012), or by distinct differentiation processes (Tang et al. 2018). Global mass balance calculations show, however, that ~90% of oxidants are not returned in arcs and are, instead, taken into the deep mantle (Evans, 2012). Ocean island basalts (OIB) are the result of melting in deep-seated plumes that contain a variety of recycled crustal lithologies (e.g., Hofmann, 1997), and so are expected to contain some of these recycled oxidants, of which Fe^{+3} is the most important (Evans, 2012).

Compared to arc lavas and MORB, OIB fO_2 is not comprehensively documented. This is partly due to the absence of sufficient quenched glassy materials for x-ray near-edge absorption spectroscopy (XANES) measurements meaning that alternative methods for determining fO_2 are required. It has recently been suggested that OIB could be as oxidized, or even more oxidized, than arc lavas (Moussallam et al. 2019), possibly as the result of sampling oxidized altered oceanic crust (AOC). It has also been shown that sulfur degassing of OIB melts can have a variable and large (~2 log units) effect on the fO_2 measured in glasses and glassy melt inclusions (Moussallam et al. 2019), making some OIB appear to be as reduced as MORB. In contrast with XANES, the V-in-olivine oxybarometry method records fO_2 as a melt crystallizes olivine, which in most systems occurs prior to significant degassing of sulfur and is relatively difficult to reset (Nicklas et al. 2021a).

In this study, the OIB fO_2 database is extended to lavas from the Réunion hotspot. La Réunion is an island in the south Indian Ocean composed of two major shield volcanos that have been active within the past two million years including the currently active Piton de la Fournaise (Albarede et al. 1997). Lavas from Réunion are remarkable for their uniform He, Nd, Os and Pb isotope signatures, with elevated $^3He/^4He$ and primitive mantle like Pb isotopes that suggest an ancient deep mantle source (Vlastelic et al. 2006; Furi et al. 2011; Peters et al. 2016; 2018). La Réunion has one of the highest-$^3He/^4He$ and is least influenced by crustal recycling, and therefore represents a key locality to characterize for OIB fO_2.

Methods and Results

The sample set includes seven olivine-rich lavas Réunion island, all of which have been characterized for their bulk geochemical characteristics previously (Peters et al. 2016; 2018). Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of cores of olivine were performed for 24-36 grains for each sample. The details of these analyses are described in the Online Supplement. Average olivine trace element concentrations are reported in **Table S1**. The V content of a calculated parental melt coupled with the V content in olivine, an assumed liquidus temperature of 1200 °C, and the empirical equation of Wang et al. (2019) yielded fO_2 for each lava. Details on modeling parental magma compositions are in the Online Supplement. Parental magma major element and V concentrations and oxygen fugacities are listed in **Table 1**. Reported uncertainties of fO_2 values are based on the uncertainties of V concentrations in olivine and parental lavas, as temperature and parental magma major element composition have only a second-order effect on the reported fO_2. Vanadium concentrations in olivine vary between 6.0 ± 1.3 and 8.6 ± 2.1 ppm in the lavas. Also analyzed for comparison was olivine from a highly depleted harzburgite dredged from the Tonga trench, showing olivine containing 0.7 ± 0.2 ppm V. Réunion olivine show a broader range in V content than other OIB olivine (**Figure 1**). The fO_2 of the lavas show wide variation, between $+0.38^{+0.36}_{-0.29}$ and $+1.61^{+0.38}_{-0.31}$ ΔFMQ and show no correlation with parental magma composition. The fO_2 of the lavas range between MORB values of +0.60 ± 0.15 (Nicklas et al. 2019) and the global OIB average of +1.91 ± 0.75 ΔFMQ measured using the same oxybarometry method (Nicklas et al 2021a). The Réunion lavas also overlap with MORB fO_2 estimates by other oxybarometry methods (Li and Lee, 2004; Berry et al. 2018; Zhang et al. 2018; Wang et al. 2019; Novella et al. 2020).

Oxygen Fugacity of Réunion Lavas

The calculated fO_2 of Réunion lavas is highly variable compared to other OIB and overlaps with them only for its most oxidized samples (**Figure 2**). The more reduced Réunion lavas overlap with the MORB range, unlike any other OIB studied to date. The variability of the data is unanticipated given the highly limited range of isotopic compositions and formation by partial melting from a homogenous mantle source region (Albarede et al. 1997; Vlastelic et al. 2006; Peters et al., 2016; 2018).

A possibility that can be precluded to explain the wide variation in fO_2 is that it results from variable amounts of old altered oceanic crust (AOC) in the plume, due to the uniform and unradiogenic Pb and Os isotopic signatures of lavas (Vlastelic et al. 2006; Peters et al. 2016). Alternatively, the most oxidized Réunion lava (RU0719 at +1.6 ΔFMQ) may be representative of the plume with the other lavas being reduced by degassing of SO_2. Sulfur degassing can lead to marked reduction of a melt (Moussallam et al. 2019), with loss of ~4000 ppm S in the near surface from Canary and Cape Verde OIB leading to a ~2.5 log unit fO_2 reduction. Primitive Réunion lavas are tholeiitic and higher degree (~10%) melt fractions compared to more alkaline (~3%) Canary lavas and so are unlikely to be as S-rich. La Réunion lavas may have degassed at most 1510 ppm S, but likely only 100 ppm (Bureau et al. 1998; Collins et al. 2012). If S degassing has a similar redox effect in Réunion lavas as it does in other OIB, even maximum loss of 1510 ppm S would cause only a 1.05 log unit reduction in fO_2, smaller than the range of the data even in this most extreme case. For this reason, S-degassing can only explain part of the fO_2 variations in Réunion lavas, assuming that such degassing took place during olivine crystallization.

Assimilation of material from within the volcanic edifice is well-known in OIB. For Réunion, if the lavas were to assimilate altered and oxidized basaltic material, then radiogenic isotope modification from such assimilation would be minimal due to the young age of Réunion. The whole rock dataset of Peters et al. (2016) includes concentrations of both ferrous and ferric iron, with $Fe^{+3}/\Sigma Fe$ ratios varying between 0.03 and 0.90, ranging significantly higher than mantle derived basalts at <0.3 (Moussallam et al. 2019), indicating that many of the basalts have suffered oxidative alteration of glassy groundmass. Starting from the lowest fO_2 Réunion sample (+0.4 ΔFMQ) and crustal $Fe^{+3}/\Sigma Fe$ ratios of 0.14, 0.21, and 0.90, mixing calculations were performed to determine the amount of assimilation needed to oxidize RU0702 to +1.6 ΔFMQ (**Figure 3**). This modeling shows that 8% to 55% crustal assimilation would be required to explain the range in data if assimilated materials had $Fe^{+3}/\Sigma Fe = 0.21$ and 0.90, respectively. Although 8% assimilation is reasonable for a picritic magma, 55% assimilation will spur extensive fractional crystallization from cooling and could not plausibly produce primitive lavas (~12.5 wt.% MgO), suggesting that assimilation of highly oxidized crustal materials would be necessary. The presence of such materials in the volcanic edifice indicates that assimilation is a plausible mechanism for explaining the range in measured fO_2. An issue is that it either requires magmas to cross the olivine liquidus in crustal magma chambers or for altered material to be present at depth. Better constraints on the depth of olivine crystallization beneath Réunion are required.

Another process potentially operative in Réunion is the inheritance of olivine by lavas. This is evident from the presence of 'oceanite' lavas containing up to 45 modal% olivine, which are not realistic parental melt compositions. Accumulation of low-V olivine antecrysts would have a profound effect on V-in-olivine oxybarometry if not properly accounted for. Antecrystic olivine with low V would artificially drive the calculated fO_2 to higher values if included in the sampled olivine data. For a lava at +0.4 ΔFMQ (RU0702), ~62% antecrystic olivine with a V content of ~1 ppm, similar to the Tonga trench olivine, must be added to sufficiently lower the average olivine content so that the calculated fO_2 is equal to that of RU0719. None of the ~30 vanadium measurements for olivine cores in RU0702 reach 1 ppm, with a minimum of 4.9 ppm (Supplemental Datasets). Even if antecrystic olivine were to re-equilibrate with the magma, 62% is a high proportion of olivine to be xenocrystic.

Implications for V-in-olivine Oxybarometry and fO_2 in OIB

Vanadium-in-olivine oxybarometry measures the fO_2 of a melt early in its evolution and is assumed to record fO_2 prior to secondary processes (Nicklas et al. 2019). La Réunion data presented here suggest that this may not always be the case. In this setting, assimilation of AOC (~1.2 log unit oxidation with 8% assimilation of highly oxidized material) as well as reduction from SO_2 degassing likely both affected the measured fO_2. A possible complicating factor with the oxybarometry method is xenocrystic/antecrystic olivine, yielding results without geological meaning. Such xenocrysts and antecrysts appear to be relatively common in OIB lavas (Wieser et al. 2019). Olivine populations should be examined for both high Ca concentrations (indicating non-Mantle origin) as well as for showing a unimodal trace element concentration distribution. None of the sampled lavas contain mantle xenocrysts, as mantle olivine has much lower V contents (0.7 ± 0.2 ppm, **Figure 1**) than any olivine analyzed. This cautionary tale shows that special attention to secondary processes is required during oxybarometry studies of olivines.

Other OIB have been measured using V-in-olivine oxybarometry (**Figure 2**) but these data are unlikely to be compromised as all those samples show consistent fO_2 regardless of bulk composition, isotopic signatures or location. Given that secondary processes affected the lavas, the fO_2 of Réunion plume is likely to be within the range of contemporary MORB (ΔFMQ ~ 0), and the scatter is probably due to crustal assimilation. This is dissimilar to other OIB (**Figure 2**) and may indicate that the Réunion plume entrains significant MORB-source mantle. Isotopic work, however, has shown a minimal contribution from the MORB-source mantle and that Réunion lavas instead come from a primitive source with elevated $^{3}He/^{4}He$, variable $^{142}Nd/^{144}Nd$, low $^{182}W/^{184}W$ and low highly siderophile element abundances (Vlastelic et al. 2006; Furi et al. 2011; Peters et al. 2016; 2018; 2021; Rizo et al. 2019). This would infer that upwelling deep mantle material has fO_2 similar to that of the depleted upper mantle source of MORB despite being isolated from the MORB source mantle for much of Earth history.

Acknowledgements:

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Figures Captions:

Figure 1: Average V concentrations in olivine cores in Réunion lavas, plotted against forsterite number (from Peters et al. 2016), along with olivine from a Tonga Trench forearc peridotite, MORB olivine (Nicklas et al. 2019), and olivine from other OIB (Nicklas et al. 2021a).

Figure 2 Oxygen fugacity plotted against the bulk rock $^{187}Os/^{188}Os$ ratio. Literature OIB data from (Nicklas et al. 2019; 2021a). Also plotted is the range of MORB oxygen fugacity estimates using other oxybarometry methods (Li and Lee 2004; Berry et al. 2018; Zhang et al. 2018; Wang et al. 2019; Novella et al. 2020).

Figure 3: Results of mixing calculations between a parental magma composition of RU0702 and an $Fe^{+3}/\Sigma Fe$ of 0.099 and an altered basalt with the same composition but an $Fe^{+3}/\Sigma Fe$ of 0.14, 0.21 and 0.90. Oxygen fugacity was calculated assuming bulk mixing, the calibration of Kress and Carmichael (1991), and a temperature of 1200°C. Horizontal dashed line represents the maximum measured Réunion lava fO_2.

Table 1 - Parental magma compositions, oxides are in weight %, V is in ppm (~10% uncertainty). Average V in olivine is also listed. NBO/T – non-bonding oxygens divided by tetrahedrally bonded oxygens in each parental melt. ΔFMQ – oxygen fugacity relative to FMQ buffer. Up – positive uncertainty, down – negative uncertainty. $^{187}Os/^{188}Os$ are bulk rock values for lavas (Peters et al. 2016). Ol add/subtract: the amount of olivine added or subtracted from the bulk rock composition to calculate the parental magma composition. Positive percentages are added olivine, and negative percentages are subtracted.

Sample Name	RU0702	RU0703	RU0705	RU0707	RU0709	RU0715	RU0719
SiO_2	46.3	48.6	46.3	49.1	47.2	48.3	46.4
TiO_2	2.35	2.46	2.42	2.35	2.48	2.13	2.40
Al_2O_3	12.4	12.9	12.3	12.8	12.5	12.4	12.4
FeO	13.1	11.4	13.1	11.2	11.9	12.0	12.8
MnO	0.19	0.17	0.20	0.17	0.18	0.19	0.18
MgO	12.7	11.1	13.2	11.0	11.6	11.7	12.5
CaO	10.0	10.0	9.7	10.1	10.8	10.0	10.2
Na_2O	2.03	2.39	2.10	2.37	2.23	2.37	2.15
K_2O	0.59	0.66	0.52	0.60	0.72	0.68	0.65
P_2O_5	0.27	0.29	0.28	0.28	0.29	0.29	0.28
V (ppm)	163	139	294	263	315	283	313
NBO/T	1.14	0.97	1.16	0.96	1.07	1.04	1.13
Olivine V (ppm)	6.49	5.96	6.94	6.83	8.55	6.66	6.00
2SD	1.06	1.32	1.00	1.07	2.06	0.79	1.05
ΔFMQ	0.38	0.40	1.24	1.26	1.09	1.35	1.61
Up	0.36	0.47	0.32	0.35	0.51	0.28	0.38
Down	0.29	0.37	0.27	0.29	0.39	0.24	0.31
$^{187}Os/^{188}Os$	0.13205	0.13110	0.13194	0.13179	0.13328		0.13273
2SE	0.00007	0.00024	0.00006	0.00028	0.00013		0.00013
Ol add/subtract	-37.7%	+10.7%	-50.4%	+11.3%	+1.4%	+2.0%	+28.1%

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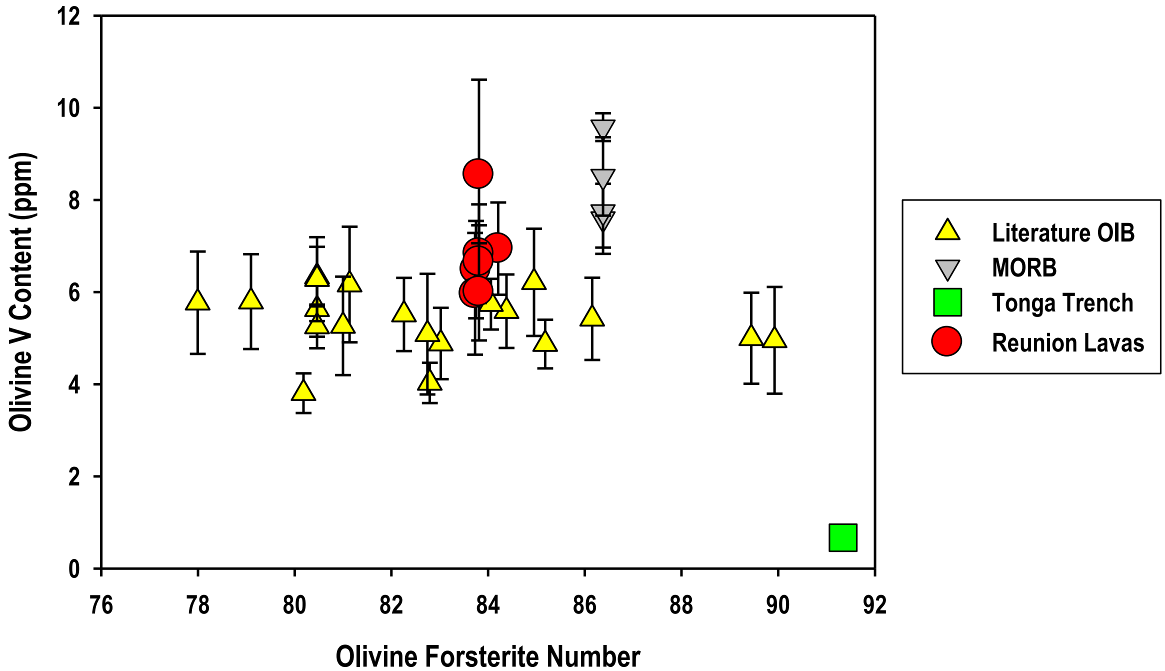
Figure 1:



Olivine V Content (ppm)
Olivine Forsterite Number
0
2
4
6
8
10
12
76
78
80
82
84
86
88
90
92
Literature OIB
MORB
Tonga Trench
Reunion Lavas

Figure 2:

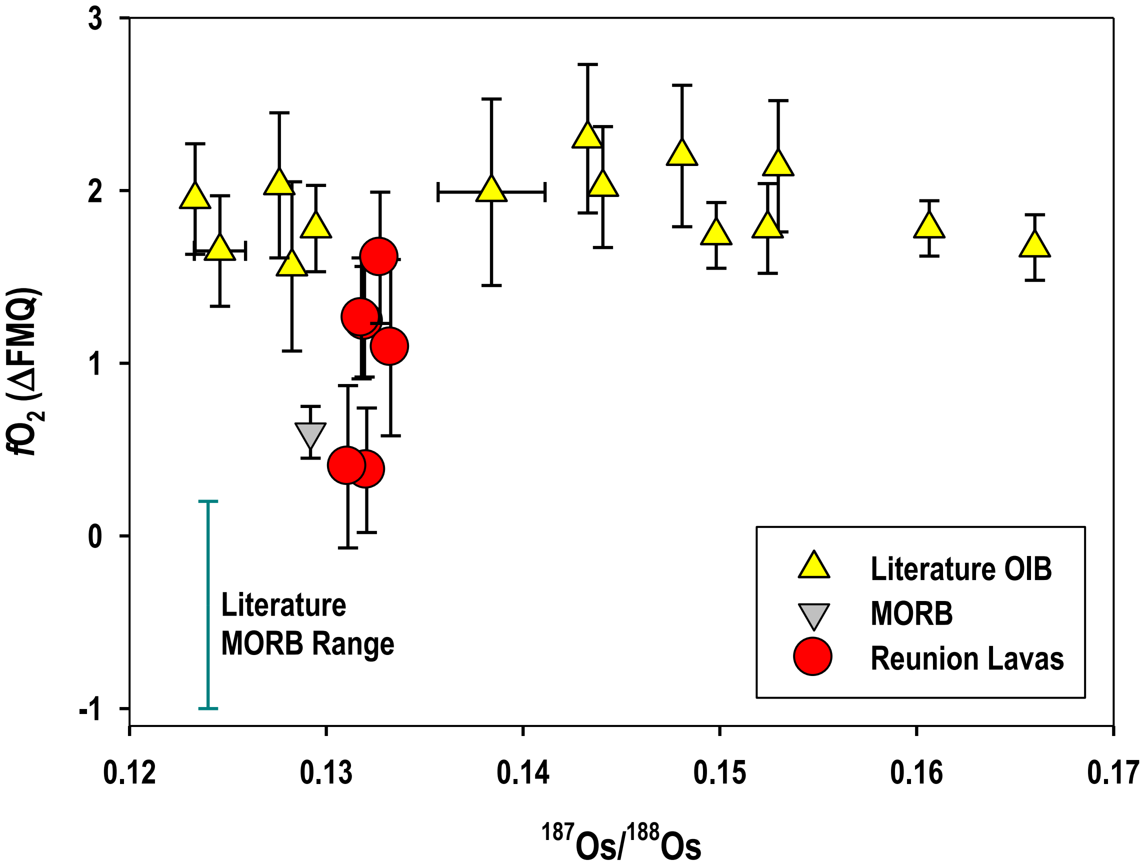
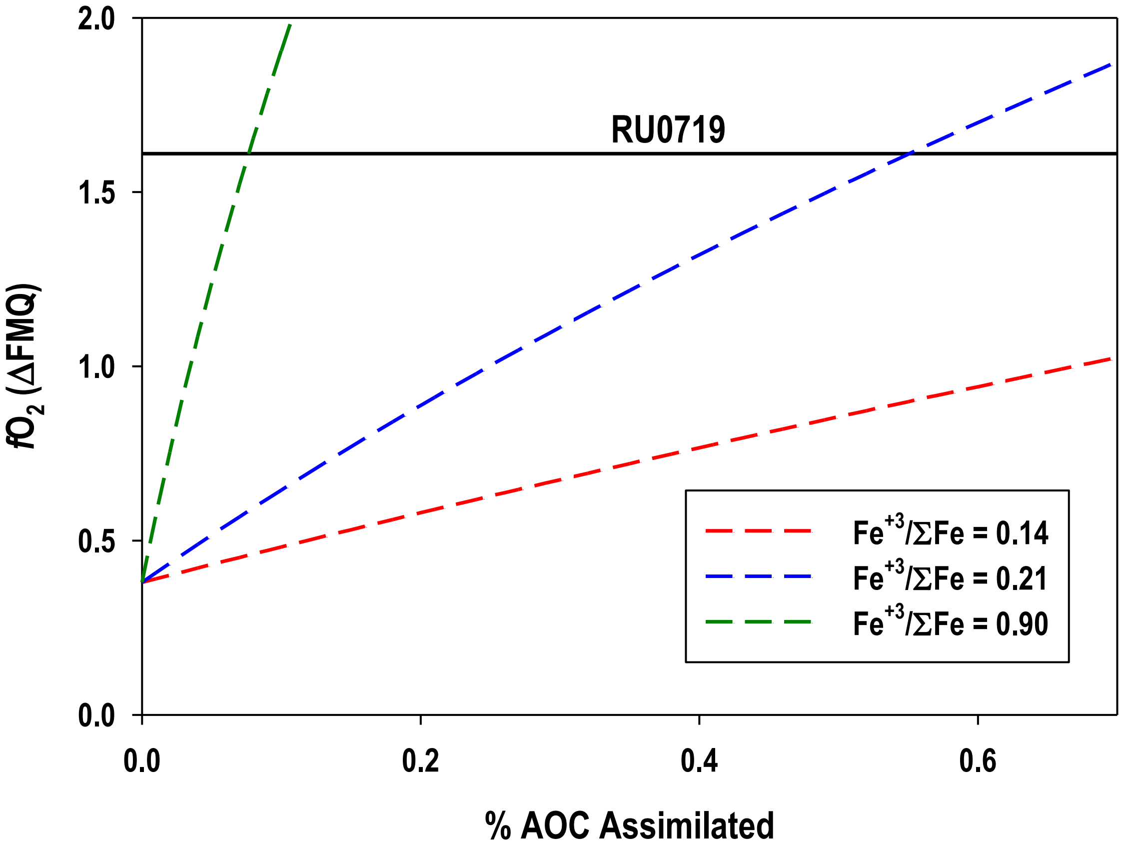

3
2
1
0
-1
fO_2 (ΔFMQ)
0.12
0.13
0.14
0.15
0.16
0.17
$^{187}Os/^{188}Os$
Literature
MORB Range
Literature OIB
MORB
Reunion Lavas

Figure 3:


2.0
1.5
1.0
0.5
0.0
fO_2 (ΔFMQ)
RU0719
$Fe^{+3}/\Sigma Fe$ = 0.14
$Fe^{+3}/\Sigma Fe$ = 0.21
$Fe^{+3}/\Sigma Fe$ = 0.90
0.0
0.2
0.4
0.6
% AOC Assimilated