

## **Oxidation of La Réunion lavas with MORB-like $fO_2$ by assimilation**

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### **Supplementary Information**

The Supplementary Information includes:

- LA-ICP-MS Analytical Method
- Calculation of Parental Magma Compositions
- Issues Regarding Olivine Equilibrium and Resetting
- Table S-1

### **LA-ICP-MS Analytical Method**

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses were conducted at the Scripps Isotope Geochemistry Laboratory (SIGL), Scripps Institution of Oceanography, University of California San Diego. The analyses were performed using a New Wave UP213 (213 nm) laser, coupled to a Thermo Scientific iCAPq Qc ICP-MS. The spot size for all analyses was 100  $\mu\text{m}$  and the laser operating conditions were 5 Hz, with a laser fluence controlled between 3.0 and 3.5  $\text{J}/\text{cm}^2$ . Measured isotopes were  $^{25}\text{Mg}$  and  $^{57}\text{Fe}$  (to verify mineral composition from electron microprobe analyses),  $^{29}\text{Si}$  (for internal normalisation), and  $^{27}\text{Al}$ ,  $^{43}\text{Ca}$ ,  $^{51}\text{V}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{71}\text{Ga}$ , and  $^{89}\text{Y}$  (trace elements of interest). The count time for all isotopes was 0.01 seconds per cycle, with the exceptions of  $^{29}\text{Si}$  and  $^{51}\text{V}$  at 0.02 and 0.05 seconds, respectively. The USGS standard reference glasses BHVO-2g and BCR-2g were used as external standards while the average Si concentration from the EPMA data of Peters *et al.* (2016) was used as an internal standard to normalise for ablation efficiency. Analysis of the natural olivine standard MongOL (Batanova *et al.*, 2019) using identical analytical methodology showed that this method can measure V concentrations in natural olivine with a

precision of 5.1 % (Nicklas *et al.*, 2021b). Due to the high abundance of Al in all other major phases relative to olivine, Al abundances were used to filter the data for accidental ablation of oxides and glass inclusions. All data showing Al abundances greater than two standard deviations (s.d.) above the mean for the sample were rejected as contaminated by other phases. This process was repeated until all Al abundances were within 2 s.d. of the mean.

## Calculation of Parental Magma Compositions

Parental magma compositions were determined assuming that bulk compositions were controlled by addition or subtraction of olivine, a good assumption for these olivine-rich (oceanite/picrite) lavas. Bulk lava compositions as well as olivine major-element data were taken from Peters *et al.* (2016). In general, La Réunion lavas have ranges in olivine major element compositions that are limited (<2 wt. %) and have negligible effect on calculated parental magma compositions. Using  $K_{\text{Fe-Mg}}^{\text{olivine/melt}} = 0.33$  (Toplis, 2005) the parental magma MgO composition was calculated by assuming that FeO in the bulk rock equalled that of the parental magma. The measured olivine composition was then added or subtracted from the bulk rock composition until its MgO content was equal to that of the parental magma. The amount of olivine added or subtracted varied between adding 28.8 % (RU0719) and subtracting 50.4 % (RU0705), with the samples from which olivine was subtracted (RU0702 and RU0705) having a high modal abundance of olivine (~44 % modal olivine in RU0702, ~49 % modal olivine in RU0705) consistent with accumulation of olivine. Parental magma compositions are reported in Table 1 and are all similar in composition owing to similar olivine compositions. The partition coefficient ( $D_V^{\text{olivine/melt}}$ ) was calculated for each lava by dividing the average olivine V content by the calculated parental magma V content. Uncertainty of the partition coefficients were propagated in quadrature using the 2 s.d. uncertainties of the average olivine concentrations and assuming 10 % uncertainty on parental magma V contents. The partition coefficient was converted into oxygen fugacity in log units relative to the FMQ buffer using equation (1) of Wang *et al.* (2019), a temperature calculated using the



equation of Nisbet *et al.* (1993), and the ratio of non-bridging oxygens to tetrahedrally coordinated cations (NBO/T) calculated from the parental magma composition using the algorithm of Mills (1993). The uncertainties of the concentrations of V in olivine have a first order effect on the uncertainties of the reported oxygen fugacity, and other factors such as temperature and NBO/T have a minor second-order effect. For instance, varying the temperature of the most reduced sample, RU0702 (+0.38  $\Delta$ FMQ) from 1100 to 1200 to 1300 °C leads to oxygen fugacity ranging from +0.74 to 0.06  $\Delta$ FMQ, these variations are insufficient to explain the range of data. Liquidus temperatures of the lavas should not vary by more than 100 °C given their similar major element compositions, as evidenced by the calculated parental magma liquidus temperatures ranging only from 1220–1250 °C. Similarly, varying the NBO/T ratio by  $\pm 0.25$  changes the calculated  $fO_2$  by +0.23 and  $-0.24$  log units, respectively, smaller than the reported uncertainties. Finally,  $K_{Fe-Mg}^{olivine/melt}$  has been found to vary with temperature and melt composition (Toplis, 2005) but varying this value from 0.30 to 0.35, the range reported for basaltic magmas, does not change the data outside of uncertainties, nor does accounting for the presence of  $Fe^{+3}$  (predicted to be <23 %; Kress and Carmichael, 1991) in the parental lavas. Similarly, the fitting uncertainties on the experimental regression of Wang (*et al.*, 2019), when propagated in quadrature are only  $\sim 0.35$  log units. As all the oxygen fugacity data, including the literature MORB data are calculated using the same regression, this 0.35 log unit uncertainty will at least partially cancel between datapoints. For all these reasons, the uncertainties reported in this paper therefore reflect the absolute uncertainties of the data as corrected. More discussion of the effect of NBO/T and temperature of oxygen fugacity using this method can be found in Nicklas *et al.* (2021a).

## Issues Regarding Olivine Equilibrium and Resetting

The method of V-in-olivine oxybarometry assumes that measured olivine crystals are either phenocrysts (crystallised from the magma that ultimately forms the bulk rock within which the olivine was found) or antecrysts (crystallised from an earlier, more primitive version of their bulk rock that then re-



entrained the olivine). If the analysed olivine crystals are xenocrysts (unrelated to their bulk rock compositions) then the oxybarometry method are likely to yield results without petrological meaning. All of the olivine grains found in the polished sections have V and Ca contents higher than mantle peridotites, and therefore cannot be mantle xenocrysts. This means that any xenocrystic olivine can only come from crystallisation of the relatively homogeneous Reunion lavas in the lithosphere or crust (*e.g.*, Peters *et al.*, 2016). Given that the calculated  $fO_2$  data show the effects of assimilation on the lavas, even if the data are erroneous due to any xenocrystic olivine, the conclusion that assimilation within the edifice affected the lavas remains robust.

Overall, it seems unlikely that the olivine was derived from more than one source, as the olivine populations in each sample shows unimodal and homogenous compositions (Table S-1). In two of the samples, RU0709 and RU0715, olivine crystals are close to Fe-Mg equilibrium with the bulk rock composition (Table 1) and are either best classified as phenocrysts or have experienced very rapid Fe-Mg equilibration (Couperthwaite *et al.*, 2021). The two equilibrium lavas do not show extreme  $fO_2$ , plotting in the middle of the sample set. The five other samples have olivine out of Fe-Mg equilibrium with their bulk rock compositions and have either accumulated (RU0702 and RU0705) or fractionated (RU0703, RU0707 and RU0719) olivine, making the olivine in those samples either antecrysts or xenocrysts. Given that olivine was entrained from a single source, it is likely that the entraining lavas are related to the olivine as the lava and olivine would be present in a single magma chamber during magma differentiation. Additionally, fractionated olivine would likely be presented as loose, non-lithified cumulates in the magma chamber making it relatively easy to entrain. It is difficult to conclude that the samples could have acquired such large amounts of olivine (~49 % modal olivine in RU0705; Peters *et al.*, 2016) from an unrelated source within the Réunion edifice and none from within the same magma chamber in which it differentiated. It is thermodynamically difficult to assimilate such a large amount of cooler, olivine xenocrysts and maintain a high enough temperature to allow the magma to erupt. For all these reasons, it is concluded that the measured olivine crystals are most



likely antecrysts and not xenocrysts and can be used to estimate the oxygen fugacity of the parental lavas to their bulk rock carriers.

It is also possible that olivine has been diffusively re-equilibrated leading to a decoupling between major element and V systematics. If both major element and V systematics diffusively re-equilibrated with carrier lavas, then the oxygen fugacity data are valid, but if only one of the two re-equilibrated then calculated  $fO_2$  would be erroneous. Although experimental data are scant, it is likely that V diffuses more quickly ( $D \approx 10^{-14} \text{ m}^2/\text{s}$ ) in solid olivine than Fe and Mg ( $D \approx 10^{-15}$  to  $10^{-18} \text{ m}^2/\text{s}$ ) (Chakraborty, 2010). It is therefore possible that V concentrations have been re-equilibrated while Fe and Mg concentrations were not changed. If all the olivine were hosted in a deep crystal mush, a homogenous olivine population could have been entrained by diverse unrelated lava compositions. Evidence for the existence of a large, relatively homogenous crystal mush have been presented for other OIB localities, such as Kilauea in Hawaii (Wieser *et al.*, 2019). Such a scenario would explain the relatively homogenous V concentrations in all the samples' olivine populations (Table S-1). However, the olivine compositions are not entirely homogenous between samples, with olivine from RU0709 being distinct from the other lavas at the 1 s.d. level (Table S-1). Additionally, it is unlikely that assimilation of crystal mush olivine would lead to two lavas (RU0709 and RU0715) in major element equilibrium with their bulk rock compositions without invoking especially fortuitous circumstances. Although the existence of a diffusively equilibrated crystal mush beneath Piton de la Fournaise cannot be ruled out, given the lack of additional evidence for such a scenario, it is not favoured here. If geochemical or geophysical evidence can be found for a diffusively equilibrated olivine crystal mush beneath Piton de la Fournaise, the  $fO_2$  values may not be accurate but the conclusion of assimilation being important for the sample set will still stand.



## Supplementary Table

**Table S-1** Average concentrations (ppm) of selected elements in primitive olivine cores in Réunion lavas, as well as from a single depleted Tonga forearc peridotite (NOVA-8801). 2 s.d., two standard deviation uncertainties on each average; *N*, number of olivine analyses included in each average.

Sample	<i>N</i>	Al	Ca	V	Co	Ni	Ga	Y
RU0702	20	236.2	1941	6.49	173.5	1969	0.19	0.14
2 s.d.		79.1	253	1.06	8.7	179	0.05	0.04
RU0703	21	253.3	1851	5.96	174.5	1788	0.19	0.15
2 s.d.		100.3	238	1.32	19.2	213	0.04	0.05
RU0705	21	252.0	1913	6.94	177.0	1985	0.18	0.15
2 s.d.		91.3	261	1.00	17.9	165	0.04	0.02
RU0707	19	194.5	1849	6.83	176.2	1395	0.17	0.14
2 s.d.		29.8	131	1.07	12.9	69	0.04	0.02
RU0709	36	317.3	1761	8.55	175.0	1866	0.19	0.19
2 s.d.		236.4	781	2.06	19.3	712	0.06	0.13
RU0715	21	511.5	2257	6.66	169.0	2149	0.19	0.16
2 s.d.		336.5	281	0.79	15.0	196	0.05	0.03
RU0719	21	437.8	1985	6.00	169.9	1829	0.17	0.13
2 s.d.		505.2	199	1.05	16.0	148	0.04	0.03
NOVA-88-1	10	5.48		0.67	128.5	2786		
2 s.d.		2.30		0.15	11.8	231		



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