High-Precision Determination of the Oxidation State of Komatiite Lavas using Vanadium Liquid-Mineral Partitioning

Robert W. Nicklas¹, Igor S. Puchtel¹, and Richard D. Ash¹

¹Department of Geology, University of Maryland, College Park, MD 20742, USA

Corresponding author:

Robert William Nicklas; e-mail: rnicklas@umd.edu

Revised for:

Chemical Geology

Version 2016/04/07

Abstract

Oxygen fugacity of the mantle (fO_2) is an important intensive variable in Earth sciences that is largely unconstrained throughout Earth history. Oxygen fugacity of modern basalts is determined by examining the Fe^{+3}/Fe^{+2} ratios of fresh volcanic glass, but this method cannot be applied to older lavas that have experienced post-magmatic alteration and/or metamorphism.

Here, we report the newly developed analytical techniques that, using the published experimental petrology data, have enabled us to determine the fO_2 of mantle-derived lavas with a precision of better than 0.10 log fO_2 units. This new method uses the partitioning behavior of the redox-sensitive transition metal vanadium between olivine and/or chromite and komatiitic melt as oxybarometers. In order to obtain accurate and precise results, a series of whole-rock samples was collected across differentiated komatiitic basalt Victoria's Lava Lake in Fennoscandia. Special attention was paid to ensure that the lava contained magmatic olivine and chromite that were in equilibrium with the emplaced melt composition, and that no re-equilibration has occurred during the lava differentiation. Vanadium and other transition metal abundances in the whole-rock samples were determined using standard addition solution ICP-MS technique with a precision of better than 5% (2SD), and in liquidus olivine and chromite by laser ablation ICP-MS, with a precision of better than 5% (2SE). The MgO and transition metal abundances in the emplaced komatiitic basalt lava were precisely calculated using several independent approaches; these approaches provided consistent results that agreed within the uncertainty of the method. The partition coefficients $D_V^{Ol, Chr-Liq}$ were then calculated and used to determine the fO_2 of the lava lake to be -0.24 ± 0.04 and -0.21 ± 0.03 ΔNNO log units, respectively (2SE). The two independent estimates are identical within the respective uncertainties and attest to the accuracy of the method; the average value of -0.22 ± 0.04 ΔNNO log units (2SD) represents our best estimate for the redox state of the lava lake. Corrected for 4% crustal contamination, the redox state of the original komatiite is calculated to be -0.29 ± 0.04 ΔNNO log units. The new method provides a high-resolution tool for constraining the evolution of the redox state of the mantle over Earth's history.

1. Introduction

Oxygen fugacity ($f\text{O}_2$) is an important intensive variable in igneous petrology that controls the behavior of redox-sensitive elements, such as Fe, V, and Cr, during igneous differentiation. Unlike many other important variables, oxygen fugacity of the mantle is not well constrained throughout Earth's history. Previous attempts to constrain the evolution of mantle oxygen fugacity have relied on variations in Cr and V contents (Canil, 1997, 1999, 2002; Delano, 2001) and V/Sc ratios (Li and Lee, 2004) of mantle-derived mafic and ultramafic rocks. These studies concluded that, within ~ 0.5 - 1.0 log units, oxygen fugacity of the mantle has remained essentially constant since at least the early Archean. The 1.0 log $f\text{O}_2$ unit is in itself a very large change in oxygen fugacity and a more precise method for determining the oxidation state of the Archean and post-Archean mantle is needed. Accurate and precise determination of the variations in oxygen fugacity of the mantle throughout Earth's history may also hold the answer to one of the most debated questions in the Earth sciences of why oxygen abundance suddenly rose in the atmosphere at the Archean-Proterozoic boundary (Holland, 2002).

The work of Canil (1997) and Canil and Fedortchouk (2001) demonstrated that the partitioning of V between liquidus olivine and ultramafic melt is a strong function of $f\text{O}_2$, with little to no dependence on temperature and melt composition. Further work (Canil, 1999; 2002) demonstrated that the partitioning of V between liquidus chromite and melt was also a strong function of $f\text{O}_2$, although this partitioning is significantly affected by the Cr/Al ratio of the system. However, no accurate and precise combined data for V and Cr partitioning between olivine, chromite and natural mafic and ultramafic liquids have been reported by far. This is partly due to the scarcity of well-preserved ultramafic lavas in the ancient geological record that would retain primary magmatic minerals suitable for this type of study, and partly due to the lack of appropriate analytical techniques at the time these studies took place, that would have

49 allowed precise and accurate determination of V abundances in liquidus olivine, chromite, and the
50 ultramafic magmas with which these mineral phases were in equilibrium.

51 Here, we report the newly developed analytical techniques that, using the experimental petrology
52 data of Canil (1997, 1999, 2002) and Canil and Fedortchouk (2001), enabled us to determine the fO_2 of
53 komatiite lavas with a precision of better than 0.10 log fO_2 units. It should be noted, however, that the
54 precision of this method is very case-specific. In addition to our ability to measure V and other transition
55 metal abundances in whole-rock samples and liquidus olivines and chromites with a sufficiently high
56 degree of precision, it depends heavily on the availability of sufficient amounts of fresh liquidus olivine
57 and/or chromite grains that were in equilibrium with the emplaced komatiite lava, and on the availability
58 and the degree of alteration of samples with a wide range of chemical compositions collected across a
59 single differentiated komatiitic lava flow. If these requirements are not met, it may become impossible
60 to determine fO_2 of a komatiite system with any reasonable degree of precision.

61 The lavas that this method has been developed for are komatiites, ultramafic volcanic rocks having
62 an MgO content of >18% (Arndt and Nisbet, 1982). Komatiites are thought to be the result of either
63 deep, hot, anhydrous melting in mantle plumes (Campbell et al., 1989), with degrees of melting of up to
64 60% (Arndt, 1976), or lower-temperature, hydrous melting in a subduction zone environment (Parman *et*
65 *al.*, 2004). The very high temperatures (up to 1600°C) and low viscosity of dry komatiitic melts enabled
66 them to reach the surface rapidly, with little or no fractionation *en route*. Once on the surface, komatiite
67 lava flows crystallized only olivine, and some minor chromite at the later stages of differentiation,
68 forming olivine cumulate layers overlain by a zone of olivine– and pyroxene spinifex–textured rocks.
69 Most komatiites are confined to Archean terrains, but Proterozoic and Phanerozoic komatiite
70 occurrences have also been reported (see review in Arndt *et al.*, 2008). Although all komatiites are
71 altered to some degree, in many instances they preserve original, magmatic mineralogy, and some have

even been characterized as “uniquely” (Nisbet *et al.*, 1987) and “remarkably” (Puchtel *et al.*, 1996) fresh, by Archean standards.

2. Geological background and samples

For this study, we chose the remarkably fresh komatiitic basalt lavas of the Victoria’s Lava Lake located within the *ca.* 2.4 Ga Vetreny Belt in SE Fennoscandia (Puchtel *et al.*, 1996, 1997). The 250 km long Vetreny Belt is considered to be part of the oldest known large igneous province that formed in a continental rift setting, during the interaction of a mantle plume with the Archean continental crust of the Karelian granite-greenstone terrain (Puchtel *et al.*, 1997). Modeling involving lithophile trace element and Nd isotopic data has shown that komatiitic magmas parental to the Victoria’s Lava Lake contained *ca.* 27% MgO, and were derived from a long-term LREE-depleted mantle source (Puchtel *et al.*, 1997, 2016). These authors concluded that the chemical evolution of the primary komatiite magmas *en route* to the surface was controlled by a combination of ~50% fractional crystallization and ~4.0±0.4% assimilation of tonalites from the adjacent ~3.2 Ga Vodla Block. Puchtel *et al.* (2016) reported Re-Os and Sm–Nd isochron ages for the lava lake of 2407±6 and 2403±32 Ma, respectively.

The lava lake is a ~110 m-deep sequence of komatiitic basalt, which filled a large topographic depression following eruption, and was estimated to have emplaced with *ca.* 15 wt.% MgO (Puchtel *et al.*, 1996, 2016). After emplacement, the lava lake underwent differentiation and developed a prominent internally layered structure comprised of three main units (from the top down): an upper chilled margin, a spinifex zone, and a cumulate zone (Fig. 1). The rocks are characterized by a superb state of preservation; the metamorphic grade did not exceed the prehnite-pumpellyite facies and most magmatic minerals are well preserved.

For this study, we used the same set of samples collected across several sections of the lava lake and studied by Puchtel *et al.* (2016). The locations of the samples are shown on the integrated section of the lava lake in Fig. 1.

3. Analytical techniques

3.1. Sample selection

3.1.1. Whole-rock samples. In order to obtain accurate estimates of emplaced lava composition for a given komatiite lava flow, and to monitor the behavior of petrogenetically important elements during post-magmatic alteration and metamorphism, we studied samples with the widest possible range of MgO contents. In differentiated komatiite lava units, the most MgO-poor horizons are located at the bottom of spinifex-textured zones, and the most MgO-rich parts are usually located in the lower half of cumulate zones. We also included an upper chilled margin sample, since these normally represent the composition of the emplaced lava from which liquidus olivine crystallized. We, therefore, included samples collected across the entire section of the lava lake, with the MgO contents ranging from 7.4% to 27% (Fig. 1).

3.1.2. Olivine and chromite. In order to determine V abundances in the liquidus olivine and chromite in equilibrium with the emplaced komatiite lava composition, solid, equant olivine and chromite grains from both the upper chilled margin and the cumulate zone of the lava lake were analyzed in this study (Fig. 2). Based on electron probe analyses, olivines from the chilled margin and the cumulate zone were shown to be in equilibrium with the emplaced lava composition (Puchtel *et al.*, 1996). Chips of the chilled margin sample 12110 and olivine cumulates 12001, 12105, and 12105/1 approximately 10 mm across were mounted in epoxy, and polished. Pure solid equant chromite grains were separated from the chilled margin sample 12110 and the olivine cumulate samples 12001 and 12105 using conventional magnetic and heavy liquid separation techniques and were also mounted in epoxy and polished.

3.2. Determination of the emplaced lava composition

Accurate determination of the composition of the emplaced komatiite lava is crucial for evaluating V partitioning behavior between liquidus olivine, chromite and the melt from which they crystallized. In order to calculate the MgO content of the emplaced lava, Puchtel *et al.* (1996, 2016) used several independent approaches.

The first approach used the composition of the upper chilled margin as a proxy for the parental liquid composition. This approach is based on the fact that upper chilled margins of komatiite lava flows likely crystallized rapidly. Consistent with this, they usually do not show evidence of differentiation after emplacement, although some may contain a small amount of olivine phenocrysts (Arndt, 1986).

The second approach is based on the well-established relationship between the composition of olivine and that of the liquid from which it crystallized (Roeder and Emslie, 1970; Beattie *et al.*, 1991). The maximum average MgO and minimum FeO contents of the cores of the cumulate olivine grains and olivine phenocrysts in the upper chilled margin of the Victoria's Lava Lake were determined and the composition of the komatiite liquid in equilibrium with these olivine compositions was

estimated using the partition coefficients from Beattie et al. (1991). Further, the compositions of the chilled margin derived from approach (1) and that of the emplaced lava derived from approach (2) were tested for consistency.

Finally, the third approach required calculation of the average MgO content of liquidus olivine in equilibrium with the emplaced lava by means of regressing the abundances of the elements that are incompatible with olivine, against the MgO contents; the intersections with the MgO axis corresponded to the average MgO content in the liquidus olivine. The average calculated MgO content of the liquidus olivine was then used to back-calculate the MgO content of the emplaced lava using approach (2). The MgO contents obtained using the three independent approaches were then averaged to yield the MgO content of the emplaced komatiite lava.

3.3. Analysis of major and minor elements in whole-rock samples

Major-element analyses of whole rock komatiite samples were carried out at Franklin & Marshall College on fused glass discs using a Phillips 2404 XRF spectrometer, following the procedure of Mertzman (2000). Typical accuracy of the analyses was ~1% relative for major elements with concentrations >0.5% and ~5% relative for the other major elements. In this study, we used the major element data obtained by Puchtel *et al.* (2016) for the set of samples studied here.

3.4. Electron microprobe analysis of olivine and chromite

Major element analyses of olivines were performed on polished thin sections using the JEOL JXA 8900 R electron probe microanalyzer at the Center for Microanalysis, University of Maryland. Special attention was paid to select and analyze only early-crystallized, solid equant grains that were likely in equilibrium with the emplaced Victoria's Lava Lake lava. Operating conditions were 15 KeV accelerating potential, a 20 nA focused electron beam current, and a 10 μ m spot size. Major element analyses of epoxy-mounted chromite separates were performed under the same conditions. These electron probe data were then used for data normalization purposes for the laser ablation analysis, as specified below.

3.5. Analysis of transition metal abundances in whole-rock samples

The abundances of the transition metals in whole-rock samples were determined using the standard addition solution inductively-coupled plasma mass-spectrometry technique (SA ICP-MS). Between 25 and 35 mg of sample powder, 0.5 mL double-distilled conc. HNO₃ and 3 mL double-distilled conc. HF were weighed out in 15 mL screw-cap Savillex Teflon vials, sealed using Teflon tape, and kept on a hotplate at 200°C for 48 hours. The vials were then opened, the sample solutions evaporated to dryness, 0.5 mL of distilled SeaStar HClO₄ was added to the dry residue to convert fluorides into perchlorides. The vials were sealed again and kept on the hotplate at 200°C for 48 hours. The vials were then opened and the sample solutions dried down on the hotplate at 230°C. This step was followed by re-dissolution of the residue in 2-3 mL of 6M HCl to convert it into the chloride form, and dried down. This step was repeated twice. The dry residue was then taken up in ~10 grams of 0.8M HNO₃ and this stock solution was used for preparing spiked aliquots used for the ICP-MS measurements. A standard addition spike was prepared, containing concentrated mixed solutions of Sc, V, Cu, Co, Ga, Y, and Zr. Three aliquots of each sample, each containing 0.5-1.0 mL of sample stock solution, were prepared, one containing no spike, one with the amount of spike 2× the estimated amount of element present in the sample aliquot, and one with the amount of spike 4× the estimated amount of element present in the sample aliquot. One total analytical blank (TAB) was also prepared and

measured with every batch of 6 samples. Approximately 100 mg of 500 ppb In solution was added to each sample aliquot and the TAB solutions to monitor and correct for the signal drift during the analysis, and the three mixed solutions for each sample were diluted to 10 grams using 0.8N HNO₃.

The sample solutions were analyzed on a *ThermoFinnigan Element2* sector field inductively-coupled plasma mass-spectrometer (ICP-MS) at the *Plasma Laboratory*, Department of Geology, University of Maryland. Prior to analysis, the instrument was thoroughly tuned to maximize sensitivity and minimize oxide production, and mass-calibrated. The intensities of selected isotopes of each element were measured in both low- and medium resolution modes. The raw data were reduced using an in-house Excel macro. The in-run uncertainties on the concentrations were typically better than 2% for all elements (2SE). The external precision of the analysis was determined via the analysis of USGS standard reference materials (SRM) BIR-1, BHVO-1, and BCR-1; for most elements, including V, it was between 2 and 5% (2SD) and included the uncertainty introduced by sample powder heterogeneity (Tables 1-3, Fig. 3). The largest of the 2SD uncertainties (5%) obtained for the three USGS SRM was used as a measure of uncertainty on the transition metal abundances for the individual whole-rock samples. These 2SD uncertainties were further used for the ISOPLOT regression calculations.

3.6. Laser ablation analysis of liquidus olivine and chromite

Several chips (~1 cm across) of the chilled margin sample 12110 and of olivine cumulates 12001, 12105, and 12105/1, as well as pure chromite separates from these samples, were selected for analysis. A total of 133 olivine grains and 139 chromite grains were analyzed using a *UP213 New Wave* laser-ablation system coupled to the *ThermoFinnigan Element2* ICP-MS at the *Plasma Laboratory*, Department of Geology, University of Maryland. The quintupled Nd-YAG laser operated at ~60% power and 7 Hz with fluence controlled between 2-4 J/cm² (~60% laser power). The spot size of each analysis varied between 55 and 100 μm for the olivines and 25-40 μm for the chromites, depending on the size of the grains being analyzed. Only solid, equant olivine and chromite grains containing no visible inclusions were selected for analysis (Fig. 2). Replicate analyses of the USGS SRM BHVO-2G and BCR-2G were performed with each set of 12-16 spots analyzed. The raw data were reduced using the in-house *LAMTRACE* software, using either the FeO abundances for liquidus olivine in equilibrium with the emplaced komatiite lava or average FeO for the population of chromite grains for each particular sample obtained from the electron microprobe analyses, as normalizing values.

Based on the available major and minor element abundance data for the studied olivine and chromite (e.g., Puchtel et al., 1996, and this study), variations in the abundances of these elements within individual samples are estimated to not exceed 5% relative, implying rather homogenous compositions of the solid equant olivine and chromite grains selected for analysis. Based on this observation, it is assumed that all the variations in V and other transition metal abundances in the studied populations of olivine and chromite grains within the same samples reflect the analytical uncertainty of the LA-ICP-MS analysis. As such, the 2SE was used as the measure of the uncertainty on the calculated average concentrations of transition metals in either olivine or chromite for the individual samples (Figs. 4 and 5). For V concentrations, these uncertainties were

~5% for the olivine, and between 2 and 3% for the chromite. For the ISOPLOT regression calculations, the 2SD uncertainty on the average transition metal abundances in the studied olivine and chromite samples was used.

4. Results

4.1. Compositions of the emplaced komatiitic basalt lava and of the liquidus olivine and chromite

Transition metal abundance data for the whole-rock samples analyzed in this study are presented in **Table 4**, and for the liquidus olivines and chromites in **Table 5**. The V abundances in the individual olivine and chromite grains analyzed in this study are also plotted in **Figs. 4 and 5**, respectively.

The average V abundances in the liquidus olivines are 7.82 ± 0.39 ppm in the chilled margin sample 12110 and 7.31 ± 0.39 , 7.21 ± 0.36 , and 7.18 ± 0.36 ppm in the olivine cumulate samples 12001, 12105, and 12105/1, respectively (2SE). The average V abundances in the liquidus chromites are 1378 ± 40 ppm in the chilled margin sample 12110, and 1395 ± 28 and 1394 ± 25 ppm in the olivine cumulate samples 12001 and 12105, respectively (2SE). It is important to note that the average V abundances for both olivines and chromites are identical between different cumulate samples collected across the lava lake. Even more importantly, the average V abundances in both olivine and chromite grains from the chilled margin and the cumulate zone samples are also identical, within their respective uncertainties.

Plotted in **Fig. 6** are variations in lithophile trace element and transition metal abundances (ppm) vs. MgO contents (wt. %) in the whole-rock samples and liquidus olivines in equilibrium with the emplaced komatiite lava. The data form tight linear correlations for all elements analyzed; these linear correlations coincide with olivine control lines for the corresponding elements, indicating that olivine was the only major liquidus phase controlling variations of these elements over the entire range of the lava lake compositions. These correlations also attest to immobile behavior during secondary alteration and metamorphism of the lava lake, of all the transition metals analyzed in this study. This conclusion is

consistent with the findings of Puchtel et al. (1996, 2016) regarding immobile behavior of lithophile trace and highly siderophile elements that those authors studied.

In order to estimate the composition of the emplaced komatiitic basalt lava, several independent approaches were used, as outlined in the section on Analytical Techniques. Samples 91110, 01110/1, and 12110/1 collected from the upper chilled margin of the lava lake (Puchtel et al., 1996; 2016) are glassy rocks composed of ~15% euhedral olivine phenocrysts in a quenched groundmass of olivine microphenocrysts, cruciform and euhedral chromite grains, and devitrified glass. This part of the lava lake must have crystallized very quickly. It did not undergo any post-eruption differentiation and is interpreted to have a bulk composition very similar to that of the komatiitic basalt liquid from which the lava lake formed. The average MgO content of the three samples is 14.65 ± 0.04 wt. % MgO (2SD).

The second approach to estimate the composition of the emplaced komatiitic basalt lava was based on the relationship between the composition of olivine and that of the liquid from which it crystallized (Beattie et al., 1991). The most magnesian olivines ($\text{Fo}_{88.7-88.9}$) were documented in the upper and lower chilled margins of the lava lake (Puchtel et al., 1996). Using a $D^{\text{Mg-Fe}}_{\text{Ol-Liq}} = 0.31$ (Beattie et al., 1991) and the Mg/Fe ratio in the emplaced komatiite lava from Puchtel et al. (1996; 2016), these olivines were calculated to have been in equilibrium with a liquid containing 15.0 ± 0.4 wt. % MgO (2SD).

Finally, the liquidus olivine composition was inferred using an indirect approach based on the general differentiation trends established for the lava lake. In the plots of MgO versus an element that is excluded from the olivine crystal lattice, the analytical data for samples containing different proportions of olivine crystallized from the emplaced komatiitic basalt lava must plot on the mixing lines, a.k.a. olivine control lines. The intercepts of these regression lines with the MgO axis correspond directly to the average composition of liquidus olivine. Using regressions for the incompatible lithophile trace element data from Puchtel et al. (1996; 2016), the average MgO content of the liquidus olivine has been

calculated to be $47.8 \pm 0.5\%$ MgO. Recalculating for the olivine stoichiometry, this gives an olivine composition of Fo_{88.7}, in excellent agreement with the results of the olivine microprobe studies. This result also implies equilibrium between liquidus olivine and the emplaced lava in terms of the Mg-Fe relationship. Thus, the three independent approaches yield an average MgO content of the emplaced komatiitic basalt lava of 14.8 ± 0.3 wt. % (2SD).

Using the estimated MgO content of the emplaced komatiitic basalt lava of 14.8 ± 0.3 wt. % and ISOPLLOT regression analysis, we calculated abundances of the transition metals in the emplaced komatiitic basalt lava; these data are reported in **Table 4**. These calculations gave the V content of 192 ± 4 ppm. The average V contents of the liquidus olivines and chromites from the lava lake are calculated to be 7.38 ± 0.30 and 1389 ± 11 ppm, respectively, and the average Sc abundances are calculated to be 5.66 ± 0.67 and 7.6 ± 1.1 ppm, respectively. These data, thus, yielded the following liquidus mineral/komatiitic basalt melt partition coefficients for V and Sc: $D_V^{Ol-Liq} = 0.0385 \pm 0.0009$ and $D_V^{Chr-Liq} = 7.25 \pm 0.16$; $D_{Sc}^{Ol-Liq} = 0.174 \pm 0.006$ and $D_{Sc}^{Chr-Liq} = 0.236 \pm 0.007$. It is noteworthy that there are substantial differences in V and Sc partitioning behavior between olivine, chromite, and komatiitic melt. As a result, fractionation of chromite and olivine may have appreciable effect on the V/Sc ratio in the komatiitic and basaltic systems. In this study, we did not use the V/Sc systematics of the Victoria's Lava Lake to evaluate its redox state.

4.2. Evaluation of the redox state of the Victoria's Lava Lake system

Having determined the V partition coefficients between the liquidus olivine, chromite and the komatiitic basalt melt of the Victoria's Lava Lake, we used the experimental calibrations of Canil (1997, 1999; 2002) and Canil and Fedortchouk (2001) to evaluate the oxidation state of the komatiite system. Regressions of the experimental data yielded $\log(D_V^{Ol-Liq}) = -0.2416 \times \Delta NNO - 1.4796$ ($r^2 = 0.94$) for the olivines (Canil, 1997; Canil and Fedortchouk, 2001), and $D_V^{Chr-Liq} = -5.442 * (\Delta NNO) + 6.1143$ ($r^2 = 0.97$)

for the chromites (Canil, 1999). Though partitioning behavior of V has been shown to have little to no dependence on temperature, pressure, or melt composition, $D_V^{\text{Chr-Liq}}$ is known to depend strongly on the Cr/Al ratio of the system (Canil, 2002). For our calculations, we used the experimental calibration curve for komatiitic composition “komv” of Canil (1999). This composition was selected due to the fact that, among all experimental compositions studied by Canil (1999, 2002), it had the Cr/Al ratio that was most similar to that of the emplaced komatiitic basalt of the lava lake.

The fO_2 value calculated from the V partitioning data for the olivines is, thus, $-0.24 \pm 0.04 \Delta\text{NNO}$ log units, and the fO_2 value calculated from the V partitioning data for the chromite is $-0.21 \pm 0.03 \Delta\text{NNO}$ log units. The two independently obtained fO_2 values overlap within the respective uncertainties; the average fO_2 value of -0.22 ± 0.04 (2SD) represents our best estimate for the redox state of the Victoria’s Lava Lake.

5. Discussion

5.1. Effects of secondary alteration, re-equilibration, and crustal contamination

5.1.1. Secondary alteration

All komatiite lavas are altered to a greater or lesser degree as a result of interaction with seawater, as almost all were erupted subaqueously including the Victoria’s Lava Lake, and also by subsequent metamorphism. Secondary alteration may result in post-magmatic re-distribution of petrogenetically important elements, including V, which, in turn, may have affected the estimates for V (and other transition metal) abundances in the emplaced komatiite lava. One way to test whether an element has been affected by postmagmatic processes is to plot its abundances against indices of magmatic differentiation, such as the MgO content (Arndt, 1986). Since the only liquidus phase present in komatiite lavas over a large range of temperatures and compositions is olivine, accompanied by minor chromite in lavas with less than 20-24% MgO depending on the oxidation state of the system (Barnes,

1998), samples with primary, magmatic distribution of the elements of interest should plot on olivine control lines. In case of the Victoria's Lava Lake, immobile behavior of most major, minor, and trace elements has been well documented (*e.g.*, Puchtel *et al.*, 1996, 2016). In this study, abundances of all transition metals are strongly inversely correlated with MgO content and follow olivine control lines (Fig. 6), providing evidence for immobile behavior of these elements during alteration.

5.1.2. Mineral re-equilibration

The method to determine the redox state of a komatiite system used in this study requires liquidus olivine and chromite to be in equilibrium with the emplaced komatiite lava. Although olivine and chromite phenocrysts found in the upper chilled margins of komatiite lava flows likely preserve their original V partitioning characteristics due to the very quick solidification of this part of the lava flows (*e.g.*, Arndt, 1986), olivine and chromite from cumulate parts, which take longer to crystallize, may experience re-equilibration with the residual liquid (Barnes, 1998). In this study, several lines of evidence indicate that V re-equilibration between the olivine, chromite, and the komatiitic liquid played a very minor role during differentiation and crystallization of the Victoria's Lava Lake.

First, we analyzed only cores of solid, equant grains that were shown to be in equilibrium with the emplaced komatiite lava for major elements (Puchtel *et al.*, 1996). These cores of olivine and chromite grains, analyzed in samples collected across the lava lake, have similar V abundances between the samples, and little variations among the grains from the same samples, reflected in rather small uncertainties on the averages for individual samples.

Second, both olivine and chromite grains in the chilled margin sample 12110 have average V abundances identical to those of olivine and chromite grains in samples from the cumulate portion of the lava lake. Since the upper chilled margin of the lava lake most likely crystallized almost instantaneously as a result of intensive heat dissipation caused by turbulent flow and interaction with seawater (Huppert

et al., 1984; Huppert and Sparks, 1985b), as also evidenced by its essentially glassy texture (Puchtel *et al.*, 1996), it is very unlikely that the olivine and chromite grains from the cumulate zone of the lava lake would have retained the same V abundances as the olivine and chromite phenocrysts from the upper chilled margin, should any re-equilibration have taken place.

Finally, the consistency of the independent estimates of the redox state of the Victoria's Lava Lake system calculated on the basis of the olivine and chromite oxybarometers strongly argue against any late re-equilibration.

5.1.3. Crustal contamination

Due to their extremely high liquidus temperatures, in many instances exceeding 1600°C, and low viscosities, komatiitic magmas are known to be able to assimilate up to 40% of country rocks on their way to the surface (Huppert and Sparks, 1985a) and up to 10% *via* thermal erosion after emplacement (Huppert and Sparks, 1985b). Due to one- to two orders of magnitude lower concentrations of lithophile trace elements in komatiitic magmas compared to upper crustal materials, crustal contamination may result in substantial changes in lithophile trace element and isotopic parameters of original komatiite magmas. Based on lithophile trace element data, Puchtel *et al.* (1996, 2016) calculated that the emplaced lava of the Victoria's Lava Lake was derived from a komatiite magma containing ca. 27% MgO *via* the combination of ca. 50% fractional crystallization and assimilation of $4.0 \pm 0.4\%$ felsic crustal material of the adjacent Vodla Block tonalites. Although fractionation of olivine and minor chromite is not expected to cause any changes in the redox state of the original komatiite magma, the effects of assimilation of the tonalites must be evaluated and accounted for.

For the purpose of modeling, we assumed simple mixing between a tonalite endmember and the original komatiite magma parental to the Victoria's Lava Lake komatiitic basalt. As an estimate for the redox state of the tonalite endmember, we used an average fO_2 (+0.5 ΔNNO log units) of the andesitic

continental crust produced at modern island arcs (Carmichael, 1991). Using the fO_2 of the contaminated Victoria's Lava Lake komatiite of -0.22 ± 0.04 ΔNNO log units, addition of 4.0 wt. % of the tonalitic endmember is calculated to result in an increase in the oxygen fugacity of the original komatiite lava by 0.07 ΔNNO log units. Even though the redox state of the Archean continental crust is currently not very well constrained and may slightly differ from the redox state of the modern continental crust, it was likely less oxidized due to the more reducing atmosphere in the Archean compared to the present. As such, this shift in the redox state of the original komatiite magma of 0.07 ΔNNO log units represents the maximum estimate. Assuming a rather conservative 50% uncertainty on this estimate from the range in crustal fO_2 , crustal contamination is calculated to increase the oxidation state of the Victoria's Lava Lake system by 0.07 ± 0.04 ΔNNO log units. Corrected for the effects of crustal contamination, the estimated redox state of the komatiite system is, thus, calculated to be -0.29 ± 0.04 ΔNNO log units.

5.2. The significance of the redox data for the Victoria's Lava Lake

Based on the argument presented above, we conclude that the redox state of the Victoria's Lava Lake komatiite system of -0.29 ± 0.04 ΔNNO log units, calculated on the basis of the combined olivine and chromite oxybarometers and corrected for crustal contamination, represents our best estimate for the redox state of the Victoria's Lava Lake primary komatiite magma. The uncertainty on this estimate is at least a factor of 10 smaller than those reported in the previous studies (Canil, 1997; Delano, 2001; Li and Lee, 2004).

Even though the absolute uncertainty on the estimate for the redox state of a komatiite system reached in this study is ca. 0.04 ΔNNO log units, it still can be affected by the absolute uncertainties on the experimental calibrations of both the olivine and chromite oxybarometers, which can be as large as 0.20 ΔNNO log units (Canil, 1999; Canil and Fedortchouk, 2001). However, since uncertainties on the relative estimates for redox states of different komatiite systems are insensitive to the uncertainties in the

experimental calibrations, this method provides a high-resolution, accurate tool for constraining the evolution of mantle oxygen fugacity over Earth's history.

6. Concluding remarks

Komatiites represent a valuable tool for studying Earth's interior, especially during the first 2 billion years of Earth's history. This study reports details of a newly developed high-resolution method for determining redox state of komatiite lavas with a precision of better than 0.10 Δ NNO log units.

The new method uses the partitioning behavior of the redox-sensitive transition metal vanadium between olivine, chromite and komatiitic melt as oxybarometers, and the experimental calibrations of Canil (1997), Canil and Fedortchouk (2001) and Canil (1999, 2002). In order for this methodology to produce accurate and precise results, several important conditions must be met.

First, V must be shown to be immobile during secondary alteration and metamorphism of the selected komatiite lava. This is accomplished via systematic collection of a series of samples across differentiated komatiite lava flow(s), obtaining high-precision whole-rock major element and V (and other transition metal) concentration data using standard addition ICP-MS, and regressing these data against indices of magmatic differentiation (e.g., MgO content) to establish the magmatic nature of the variations in V abundances across the lava flows. Second, MgO, V, and other transition metal abundances in the emplaced komatiite lava must be precisely calculated using several independent approaches; these approaches should provide consistent results that must agree within the uncertainty of the method. Third, the komatiite lavas of interest must contain sufficient amounts of liquidus olivine and/or chromite and these must be shown to be in equilibrium with the emplaced komatiite lava. A special attention must be paid to ensure that no re-equilibration has occurred during differentiation of the komatiite lava units, which can be achieved via analyzing only cores of solid, equant olivine and/or

chromite grains from both upper chilled margins and cumulate layers of lava flows and closely monitoring the consistency between their chemical compositions. Finally, laser ablation ICP-MS analyses of the olivine and/or chromite grains must be performed to determine V (and other transition metal) concentrations with the highest possible precision and accuracy, which is achieved via analyzing sufficiently large number of inclusion-free grains.

The independent olivine and chromite oxybarometers studied here yielded results that overlapped within the respective uncertainties, attesting to the accuracy of the redox data obtained for the lava lake.

Even though the uncertainty on the oxygen fugacity of a komatiite system reached in this study is ca. 0.04 Δ NNO log units, it still can be affected by the absolute uncertainty on the experimental calibrations of the olivine and chromite oxybarometers, which can be as large as 0.20 Δ NNO log units (Canil, 1999; Canil and Fedortchouk, 2001). However, since uncertainties on the relative estimates for redox states of different komatiite systems are insensitive to the uncertainties in the experimental calibrations, this method provides a high-resolution tool for constraining evolution of the redox state of the mantle over Earth's history.

Acknowledgments

This study was supported by NSF FESD Type I Grant #1338810 "The Dynamics of Earth System Oxygenation" (lead PI is A.D. Anbar, I.S. Puchtel is a co-PI). This source of support is gratefully acknowledged. We thank Cin Ty Lee, Dante Canil, and Fabrice Gaillard for constructive reviews that helped improve the original version of the manuscript, and Catherine Chauvel for editorial handling. We also thank Valentina Puchtel for help with sample preparation for the ICP-MS analyses.

References

Arndt, N.T., 1976. Melting relations of ultramafic lavas (komatiites) at one atmosphere and high pressure. *Yearbook of Carnegie Inst. Wash.* **75**: 555-562.

- Arndt, N.T., 1986. Differentiation of komatiite flows. *Journal of Petrology* **27**(2): 279-301.
- Arndt, N.T., Lesher, C.M., and Barnes, S.J. (2008). *Komatiite*. Cambridge, UK, Cambridge University Press.
- Arndt, N.T., and Nisbet, E.G. (1982). What is a komatiite? *Komatiites*. Arndt, N.T. and Nisbet, E.G. London, George Allen and Unwin: 19-28.
- Barnes, S.J., 1998. Chromite in komatiites, I. Magmatic controls on crystallization and composition. *Journal of Petrology* **39**(10): 1689-1720.
- Barnes, S.J., Hill, R.E.T., and Gole, M.J., 1988. The Perseverance ultramafic complex, Western Australia: the product of a komatiite lava river. *Journal of Petrology* **29**(2): 305-331.
- Beattie, P., Ford, C., and Russell, D., 1991. Partition coefficients for olivine-melt and orthopyroxene-melt systems. *Contributions to Mineralogy and Petrology* **109**(2): 212-224.
- Campbell, I.H., Griffiths, R.W., Hill, R.I. (1989). Melting in an Archean Mantle Plume: heads it's basalts, tails it's komatiites. *Nature* **339**: 697-699.
- Canil, D., 1997. Vanadium partitioning and the oxidation state of Archean komatiite magmas. *Nature* **389**(6653): 842-845.
- Canil, D., 1999. Vanadium partitioning between orthopyroxene, spinel and silicate melt and the redox states of mantle source regions for primary magmas. *Geochimica et Cosmochimica Acta* **63**(3-4): 557-572.
- Canil, D., and Fedortchouk, Y., 2001. Olivine-liquid partitioning of vanadium and other trace elements, with applications to modern and ancient picrites. *Canadian Mineralogist* **39**: 319-330.
- Canil, D., 2002. Vanadium in peridotites, mantle redox and tectonic environments: Archean to present. *Earth and Planetary Science Letters* **195**(1-2): 75-90.
- Carmichael, I.S.E., 1991. The redox states of basic and silicic magmas: a reflection of their source regions? *Contributions to Mineralogy and Petrology* **106**(2): 129-141.
- Cottrell, E., and Kelley, K.A., 2011. The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth and Planetary Science Letters* **305**(3-4): 270-282.
- Cottrell, E., Kelley, K.A., Lanzirotti, A., and Fischer, R.A., 2009. High-precision determination of iron oxidation state in silicate glasses using XANES. *Chemical Geology* **268**(3-4): 167-179.
- Delano, J.W., 2001. Redox History of the Earth's Interior since ~3900 Ma: Implications for Prebiotic Molecules. *Origins of life and evolution of the biosphere* **31**(4-5): 311-341.
- Farquhar, J., Bao, H., and Thieme, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**(5480): 756-758.
- Huppert, H.E., and Sparks, R.S.J., 1985a. Cooling and contamination of mafic and ultramafic magmas during ascent through continental crust. *Earth and Planetary Science Letters* **74**(4): 371-386.
- Huppert, H.E., and Sparks, R.S.J., 1985b. Komatiites I: Eruption and flow. *Journal of Petrology* **26**(3): 694-725.
- Huppert, H.E., Sparks, R.S.J., Turner, J.S., and Arndt, N.T., 1984. Emplacement and cooling of komatiite lavas. *Nature* **309**(5963): 19-22.
- Li, Z.X.A., and Lee, C.T.A., 2004. The constancy of upper mantle fO_2 through time inferred from V/Sc ratios in basalts. *Earth and Planetary Science Letters* **228**(3-4): 483-493.
- Lyons, T.W., Reinhard, C.T., and Planavsky, N.J., 2014. The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**(7488): 307-315.
- Mertzman, S.A., 2000. K-Ar results from the southern Oregon - northern California Cascade range. *Oregon Geology* **62**(4): 99-122.

- 442 Nisbet, E.G., Arndt, N.T., Bickle, M.J., Cameron, W.E., Chauvel, C., Cheadle, M., Hegner, E., Kyser,
443 T.K., Martin, A., Renner, R., and Roedder, E., 1987. Uniquely fresh 2.7 Ga komatiites from the
444 Belingwe greenstone belt, Zimbabwe. *Geology* **15**(12): 1147-1150.
- 445 Parman, S.W., Grove, T.L., Dann, J.C., and de Wit, M.J., 2004. A subduction origin for komatiites and
446 cratonic lithospheric mantle. *South African Journal of Geology* **107**(1-2): 107-118.
- 447 Puchtel, I.S., Haase, K.M., Hofmann, A.W., Chauvel, C., Kulikov, V.S., Garbe-Schönberg, C.D., and
448 Nemchin, A.A., 1997. Petrology and geochemistry of crustally contaminated komatiitic basalts
449 from the Vetreny Belt, southeastern Baltic Shield: Evidence for an early Proterozoic mantle
450 plume beneath rifted Archean continental lithosphere. *Geochimica et Cosmochimica Acta* **61**(6):
451 1205-1222.
- 452 Puchtel, I.S., Hofmann, A.W., Mezger, K., Shchipansky, A.A., Kulikov, V.S., and Kulikova, V.V.,
453 1996. Petrology of a 2.41 Ga remarkably fresh komatiitic basalt lava lake in Lion Hills, central
454 Vetreny Belt, Baltic Shield. *Contributions to Mineralogy and Petrology* **124**: 273-290.
- 455 Puchtel, I.S., Touboul, M., Blichert-Toft, J., Walker, R.J., Brandon, A.D., Nicklas, R.W., Kulikov, V.S.,
456 and Samsonov, A.V., 2016. Lithophile and siderophile element systematics of the mantle at the
457 Archean-Proterozoic boundary: Evidence from 2.4 Ga komatiites. *Geochimica et Cosmochimica*
458 *Acta* **180**: 227-255.
- 459 Roeder, P.L., and Emslie, R.F., 1970. Olivine-liquid equilibrium. *Contributions to Mineralogy and*
460 *Petrology* **29**(4): 275-282.
- 461

Figure captions

- Fig. 1.** Schematic integrated section through the Victoria's Lava Lake showing textural variations within the lake and location of the samples analyzed in this study. The MgO contents of the individual samples (wt.%) are shown in parentheses.
- Fig. 2.** Photomicrographs of the upper chilled margin sample 12110 (*a*) and the olivine cumulate sample 12105 (*b*) showing the type of solid equant olivine grains analyzed in this study. Clearly visible are rounded laser ablation pits within the grains analyzed. The fields of view are 3.0×2.5 mm; cross-polarized light.
- Fig. 3.** Vanadium, Sc, and Ga abundances in replicate digestions of the USGS standards BIR-1, BHVO-1, and BCR-1 determined using standard addition solution ICP-MS. The external reproducibility (2SD) is listed for each element. The GEOREM preferred values for each standard are provided for reference.
- Fig. 4.** Laser ablation ICP-MS data for cores of solid, equant olivine grains from the chilled margin sample 12110 and olivine cumulate samples 12001, 12105, and 12105/1. The uncertainty on the concentrations is 2SE. Note the consistency of the average V abundances between samples collected from different parts of the lava lake.
- Fig. 5.** Laser ablation ICP-MS data for solid, equant chromite grains from the chilled margin sample 12110 and olivine cumulate samples 12001 and 12105. The uncertainty on the concentrations is 2SE. Note that, similarly to the olivine grains analyzed, chromite grains from the different parts of the lava lake have average V concentrations that are identical within the uncertainty.
- Fig. 6.** Concentrations of selected lithophile trace elements and transition metals (ppm) plotted against MgO contents (wt.%) for the whole rock samples and liquidus olivines of the Victoria's Lava Lake. All data plot on the tight, well constrained trends corresponding to olivine control lines, indicating that olivine was the only major fractionating phase controlling variations of these elements during differentiation of the lava lake, and that the samples fully retained their primary, igneous signatures with respect to concentrations of these elements.

Table 1. Transition metal abundances (ppm) in USGS SRM BIR-1 obtained via the SA ICP-MS analysis technique. The GEOREM preferred values and the uncertainties ($\pm 2SD$) are listed at the bottom.

SRM	Sc	V	Cu	Ga	Y	Zr
BIR1-01	44.2	323	125	16.0	15.2	16.9
BIR1-02	42.8	310	122	15.7	14.5	16.0
BIR1-03	43.9	316	126	16.1	14.8	15.5
BIR1-04	44.8	322	126	16.2	15.0	15.9
BIR1-05	43.1	313	123	15.5	14.6	17.0
BIR1-06	43.3	317	122	15.5	14.7	16.7
BIR1-07	45.3	331	131	15.6	14.7	16.1
BIR1-08	42.7	326	130	15.6	15.2	16.0
BIR1-09	43.0	310	126	15.5	14.6	16.3
BIR1-10	44.8	333	135	17.1	15.1	17.0
BIR1-11	42.5	307	119	14.9	14.6	15.5
BIR1-12	44.8	335	132	17.0	15.5	16.1
BIR1-13	43.7	315	131	16.1	15.2	16.0
BIR1-14	46.1	319	133	17.0	15.5	16.2
BIR1-15	46.4	322	144	16.9	15.9	16.6
BIR1-16	46.3	323	121	16.8	15.5	19.9
BIR1-17	44.6	319	113	16.3	14.9	15.7
BIR1-18	45.0	333	127	16.1	15.4	16.5
BIR1-19	45.1	335	130	16.5	15.1	16.1
BIR1-20	44.7	331	130	16.6	15.3	16.7
BIR1-21	44.9	326	125	16.3	14.8	17.2
BIR1-22	43.5	320	125	15.8	14.9	15.7
Average ($\pm 2SD$)	44.3 $\pm$ 2.3	322 $\pm$ 17	127 $\pm$ 13	16.1 $\pm$ 1.2	15.0 $\pm$ 0.8	16.4 $\pm$ 1.9
$\pm 2SD$ (%)	5.2	5.3	10	7.3	5.0	11
GEOREM ($\pm 2SD$)	43$\pm$4	319$\pm$36	119$\pm$16	15.3$\pm$1.6	15.6$\pm$1.8	14.0$\pm$0.2

Table 2. Transition metal abundances (ppm) in USGS SRM BCR-1 obtained via the SA ICP-MS analysis technique. The GEOREM preferred values and the uncertainties ($\pm 2SD$) are listed at the bottom.

SRM	Sc	V	Cu	Ga	Y	Zr
BCR1-01	32.07		16.1	21.9	32.7	182
BCR1-02	33.37	396	16.0	22.6	34.8	197
BCR1-03	33.45	397	15.7	22.5	34.4	188
BCR1-04	31.93	404		22.5	33.9	186
BCR1-05	32.84	394	15.8	22.4	34.5	193
BCR1-06	33.22	401	15.7	22.6	34.2	195
BCR1-07	32.71	399	16.2	22.5	34.1	187
BCR1-08	33.09	396	15.9	22.3	35.0	196
BCR1-09	33.06	402	15.9	22.6	35.3	198
BCR1-10	32.46	401	16.3	22.3	34.0	185
BCR1-11	32.64	392	15.8	22.0	33.3	187
BCR1-12	32.82	399	15.8	22.6	33.6	192
BCR1-13	31.83	389	15.8	21.9	33.1	184
BCR1-14	33.04	398	16.1	22.5	34.2	191
BCR1-15	32.89	398	16.0	22.5	34.3	192
BCR1-16	32.43	408	16.9	22.4	34.1	190
BCR1-17	32.98	393	15.6	22.0	33.1	183
Average ($\pm 2SD$)	32.8 $\pm$ 1.0	398 $\pm$ 10	16.0 $\pm$ 0.6	22.3 $\pm$ 0.5	34.0 $\pm$ 1.4	190 $\pm$ 10
2SD (%)	2.9	2.4	3.9	2.4	4.1	5.3
GEOREM ($\pm 2SD$)	32$\pm$4	410$\pm$40	21$\pm$6	23$\pm$4	36$\pm$4	189$\pm$18

Table 3. Transition metal abundances (ppm) in USGS SRM BHVO-1 obtained via the SA ICP-MS analysis technique. The GEOREM preferred values and the uncertainties ($\pm 2SD$) are listed at the bottom.

SRM	Sc	V	Cu	Ga	Y	Zr
BHVO1-01	33.1	315	153	22.0	25.2	189
BHVO1-02	32.3	309	152	22.2	25.1	177
BHVO1-03	32.8	311	143	22.5	26.2	185
BHVO1-04	32.0	301	147	21.1	25.2	165
BHVO1-05	31.9	306	155	21.6	25.0	166
BHVO1-06	31.5	303	142	21.6	24.5	169
Average ($\pm 2SD$)	32.3 $\pm$ 1.1	306 $\pm$ 9	149 $\pm$ 11	21.8 $\pm$ 1.0	25.2 $\pm$ 1.1	175 $\pm$ 20
2SD (%)	3.5	2.8	7.2	4.7	4.3	12
GEOREM ($\pm 2SD$)	31$\pm$4	318$\pm$30	137$\pm$18	21$\pm$4	26$\pm$4	174$\pm$18

465

Table 4. MgO (wt. %) and transition metal (ppm) abundances in whole rock samples from the Victoria's Lava Lake and in the calculated emplaced lava composition.

Sample	Sc	V	Cu	Ga	Y	Zr	MgO	LOI
12110	32.6	189	90.3	12.5	12.6	53.7	13.7	2.25
12116	35.9	212	97.3	13.6	13.6	54.9	11.1	0.75
12117	35.5	208	98.3	13.4	13.7	55.0	11.2	0.58
12124	39.3	228	107	15.1	15.2	61.7	7.42	0.25
01001_B	22.6	131	59.6	8.10	7.98	31.2	25.4	2.78
12001	22.4	135	60.0	8.15	7.80	31.7	26.4	2.99
01103_B	28.2	161	71.4	10.0	10.4	37.4	20.2	1.49
01104_B	26.7	155	73.4	9.86	10.0	40.0	21.6	1.27
01105_B	23.2	138	58.9	8.40	8.33	37.0	25.6	2.80
12105	22.6	133	57.8	7.92	7.70	30.6	26.6	3.21
01106_B	27.7	155	68.2	9.40	9.77	36.4	21.4	1.42
12106	27.3	153	68.7	9.71	9.32	36.4	21.5	1.06
Slope	-1.232±30	-0.1815±41	-0.3953±90	-2.778±62	-2.755±62			
Intercept	54.77±0.98	49.59±0.48	49.31±0.49	48.51±0.47	48.27±0.46			
MSWD	3.4	1.2	0.82	0.45	0.67			
Emplaced lava	32.4±1.0	192±4	87.3±1.9	12.1±0.3	12.1±0.3	*	14.8±0.3	

Note. Analyses were re-calculated on an anhydrous basis using the loss on ignition (LOI) data from Puchtel et al. (2016). The transition metal abundances in the emplaced lava were calculated using ISOPLLOT regressions for each element versus the calculated MgO content of the emplaced lava from this study. The uncertainties used in the regression analyses were as follows: for the transition metals, 5% (2SD) as derived from the external reproducibility of analyses of USGS SRM BIR-1, BCR-1, and BHVO-1; for MgO, 1% (2SD) as derived from the long-term reproducibility of analyses of USGS SRM BIR-1 and BCR-1 (Puchtel et al., 2016).

Table 5. Transition metal abundances in liquidus olivines and chromites from the Victoria's Lava Lake.

Sample	Sc	V	Cu	Ga	Y
12110 Olivine (N = 14)	5.84±0.18	7.82±0.39	4.25±0.19	0.239±0.067	0.122±0.025
12001 Olivine (N = 24)	6.02±0.45	7.31±0.39	2.62±0.67	0.115±0.043	0.093±0.010
12105 Olivine (N = 48)	6.12±0.21	7.21±0.36	2.87±0.42	0.097±0.017	0.093±0.009
12105/1 Olivine (N = 47)	4.66±0.14	7.18±0.36	2.72±0.43	0.149±0.048	0.079±0.010
12110 Chromite (N = 11)	10.1±4.8	1378±40	12.1±3.9	37.4±8.8	1.76±1.05
12001 Chromite (N = 64)	7.10±0.97	1395±28	9.47±3.15	19.6±0.8	0.407±0.554
12105 Chromite (N = 64)	7.12±0.67	1394±25	9.26±2.04	17.3± 0.5	0.092±0.060

Note. The data were obtained using the laser ablation ICP-MS technique. Each datum represents averages of multiple analyses performed on several mounts, as specified in the text. The uncertainties are 2SE.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5

Fig. 6