



High-precision determination of the oxidation state of komatiite lavas using vanadium liquid–mineral partitioning



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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 Δ NNO 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 Δ NNO 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 Δ NNO 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.

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1. Introduction

Oxygen fugacity (fO_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 fO_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 fO_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 fO_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

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

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

The lavas that this method has been developed for are komatiites, ultramafic volcanic rocks having an MgO content of > 18% (Arndt and Nisbet, 1982). Komatiites are thought to be the result of either deep, hot, anhydrous melting in mantle plumes (Campbell et al., 1989), with degrees of melting of up to 60% (Arndt, 1976), or lower-temperature, hydrous melting in a subduction zone environment (Parman et al., 2004). The very high temperatures (up to 1600 °C) and low viscosity of dry komatiitic melts enabled them to reach the surface rapidly, with little or no fractionation *en route*. Once on the surface, komatiite lava flows crystallized only olivine, and some minor chromite at the later stages of differentiation, forming olivine cumulate layers overlain by a zone of olivine- and pyroxene spinifex-textured rocks. Most komatiites are confined to Archean terrains, but Proterozoic and Phanerozoic komatiite occurrences have also been reported (see review in Arndt et al., 2008). Although all komatiites are 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 $4.0 \pm 0.4\%$ 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

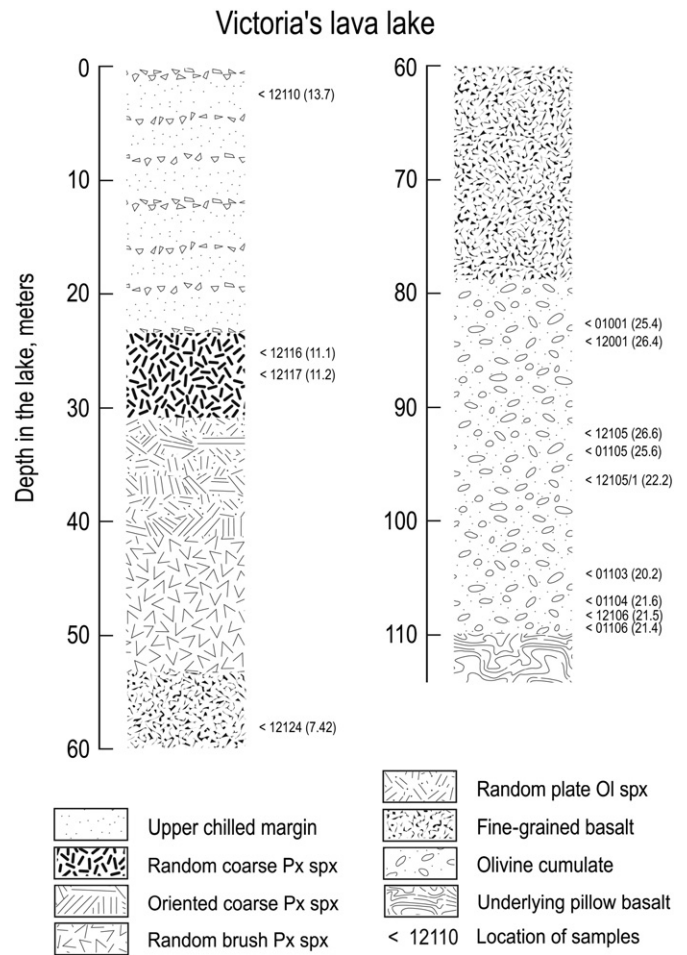


Fig. 1. Schematic integrated section through the Victoria's Lava Lake showing textural variations within the lake and location of the samples analyzed in this study. The MgO contents of the individual samples (wt.%) are shown in parentheses.

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).

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