A new high-pressure experimental apparatus to study magmatic processes at precisely controlled redox conditions

**ALICE ALEX**1,* and ZOLTÁN ZAJACZ2

1Department of Earth Sciences, University of Toronto, 22 Russell Street, Toronto, Ontario M5S 3B1, Canada
2Department of Earth Sciences, University of Geneva, 13, Rue des Maraîchers, Geneva 1205, Switzerland

**ABSTRACT**

Oxygen fugacity ($f_{O2}$) is typically controlled in high $P$-$T$ experiments by using solid-state redox buffer assemblages. However, these are restricted to impose discrete $f_{O2}$ values, often with significant gaps between neighboring assemblages. Semi-permeable hydrogen membranes (Shaw 1963) are often used in internally heated pressure vessels for more flexible $f_{O2}$ control in hydrous experiments; however, their implementation in more widely available externally heated pressure vessels has not yet gained space. We propose a prototype molybdenum-hafnium carbide (MHC) pressure vessel apparatus that simultaneously allows rapid quenching and flexible, precise, and accurate redox control via a custom-designed hydrogen membrane. Test runs with two membranes at a time, one imposing and another one monitoring $f_{O2}$, demonstrated that 95% of the imposed hydrogen pressure was attained inside the pressure vessel within 2 h at 800–1000 °C, after which a steady state equilibrium was established. Furthermore, experiments comparing redox-dependent Cu solubility in silicate melts at $f_{O2}$ imposed by the fayalite-magnetite-quartz, Re-ReO2, and MnO-Mn2O3 buffers and identical target $f_{O2}$ imposed by the hydrogen membrane confirmed consistency between the two methods within 0.25 log units $f_{O2}$ deviation at $T=900$ °C and $P=2000$ bar. This powerful yet cost-effective and low-maintenance apparatus may open up new pathways for studying redox reactions in hydrous magmas and magmatic fluids. As a proof of concept, we conducted near-liquidus phase-equilibrium experiments with H2O-saturated calc-alkaline basalt and shoshonite melt compositions at five different $f_{O2}$ values equally distributed between half log unit below the Ni-NiO buffer (NNO-0.5) and NNO+2.7. Most experiments crystallized olivine, clinopyroxene, and Ti-magnetite. The Mg$#$ of the olivine increased with $f_{O2}$, and the Fe$^{3+}$/Fe$^{total}$ ratios in the silicate melt were determined based on Fe(II)-Mg exchange between olivine and melt. The Fe$^{3+}$/Fe$^{total}$ ratios in the shoshonite melt were systematically higher by about 0.06 than those in the calc-alkaline basalt melt at identical $f_{O2}$. The values determined for the basaltic melt were consistent within 1σ error (<0.033 deviation) from those predicted by the equation of Kress and Carmichael (1991). The Fe-Ti exchange coefficient between magnetite and silicate melt increases from 1.73 ± 0.19 (1σ) at NNO -0.5 to +7.12 ± 0.36 at NNO+2.7 for shoshonite and has a similar range for the calc-alkaline basalt.

**Keywords:** Redox, externally heated pressure vessels (EHPV), hydrogen membrane, sulfur, MHC pressure vessels, experimental geochemistry, oxygen fugacity, heterovalent element

**INTRODUCTION**

Because of the abundance of heterovalent elements such as Fe and S in magmatic and hydrothermal systems, accurate control of $f_{O2}$ is essential in high-pressure ($P$) and high-temperature ($T$) experiments for the of study phase equilibria, element partitioning, and the solubilities of ore minerals and ore metals in silicate melts and hydrothermal fluids. Several techniques have been developed to control $f_{O2}$ in high $P$-$T$ experiments. Most take advantage of the high permeability of metals to hydrogen at magmatic temperatures and impose $f_{O2}$ in the experimental capsule by controlling $f_{O2}$ in its external environment. In hydrous experimental charges, $f_{O2}$ is defined in turn through the water decomposition reaction. The following are the methods used currently to control the oxygen fugacity in high $P$-$T$ experiments.

1 Redox buffers: Developed by Eugster (1957), solid oxygen buffers control the $f_{O2}$ in an experimental charge. This technique allows imposing well-constrained $f_{O2}$ either directly or by regulating $f_{O2}$ when using the double capsule technique (Eugster 1959; Chou 1986) with water added to the buffer assemblage. The direct use of redox buffers is, however, limited by unwanted chemical reactions between the buffer assemblage and the experimental phase assemblage and/or the experimental assembly itself. An important general limitation of the technique is that it can only be used to impose discrete $f_{O2}$ values using the available buffer assemblages, often with 1–2 log unit gaps between the $f_{O2}$ of neighboring buffers. Most importantly, there is a nearly two log unit gap between the neighboring Ni-NiO and the Re-ReO2 buffers, and a major part of the characteristic $f_{O2}$ range of convergent plate magmatism on Earth falls within this gap. An additional drawback of the redox buffer technique is the limited lifetime of the buffer assemblages, which limits the maximum time that can be provided for the attainment of equilibrium in the experimental phase assemblage.

* E-mail: alice.alex@mail.utoronto.ca