

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

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### **ABSTRACT**

Oxygen fugacity ( $f_{\text{O}_2}$ ) is typically controlled in high  $P$ - $T$  experiments by using solid-state redox buffer assemblages. However, these are restricted to impose discrete  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$  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  $f_{\text{H}_2}$ , 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  $f_{\text{O}_2}$  imposed by the fayalite-magnetite-quartz, Re-ReO<sub>2</sub>, and MnO-Mn<sub>2</sub>O<sub>3</sub> buffers and identical target  $f_{\text{O}_2}$  imposed by the hydrogen membrane confirmed consistency between the two methods within 0.25 log units  $f_{\text{O}_2}$  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 H<sub>2</sub>O-saturated calc-alkaline basalt and shoshonite melt compositions at five different  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$ , and the Fe<sup>3+</sup>/Fe<sub>total</sub> ratios in the silicate melt were determined based on Fe(II)-Mg exchange between olivine and melt. The Fe<sup>3+</sup>/Fe<sub>total</sub> ratios in the shoshonite melt were systematically higher by about  $0.06 \pm 0.01$  than those in the calc alkaline basalt melt at identical  $f_{\text{O}_2}$ . The values determined for the basaltic melt were consistent within 1  $\sigma$  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  $1.73 \pm 0.19$  (1  $\sigma$ ) at NNO -0.5 to  $+7.12 \pm 0.36$  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