Oxygen fugacity, temperature reproducibility, and H_{2}O contents of nominally anhydrous piston-cylinder experiments using graphite capsules

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ABSTRACT

The Pt-graphite double-capsule technique is a very commonly used method in high-temperature, high-pressure experimental petrology, particularly for anhydrous experiments relevant to primitive basaltic magmas and mantle melting. We have performed a series of experiments that place better constraints on the range of oxygen fugacity imposed by this capsule material, on the Fe^{3+}/Fe^{2+} ratios in experimentally produced melts and minerals, and on the temperature reproducibility in Pt-graphite capsules. Oxygen fugacity in our piston-cylinder experiments using Pt-graphite capsules is CCO-0.7 (IW+1.5, QFM-2.2) at 1.5 GPa and 1360 °C. Comparison with other estimates and thermodynamic calculations indicate that a value of CCO-0.8 ± 0.3 can be used as a first approximation at least over the P-T range relevant for MORB and OIB magma generation (0.5–3.0 GPa, 1100–1500 °C). Under those conditions, the amount of Fe^{3+} in silicate phases (pyroxenes, olivine, glass) and spinel is negligible (Fe^{3+}/ΣFe < 0.05) and would not significantly affect thermodynamic properties. Significantly higher values of f_{O2} cannot be achieved using Pt-graphite or graphite only capsules, but f_{O2} can be tuned to lower values by using small pieces of PtFe alloys. The potential range of f_{O2} that can be reached in graphite or Pt-graphite capsules is CCO to CCO-4. Temperature reproducibility in piston-cylinder experiments has been examined and can be as low as ±10 °C. Finally, unless capsules are dried overnight at 400 °C before the experiment, small amounts of H_{2}O are always present in nominally dry experiments. These small amounts of H_{2}O should not, however, significantly change phase relations.

Keywords: Experimental petrology, oxygen fugacity, piston-cylinder, graphite, phase equilibria, reproducibility, Mössbauer spectroscopy, pyroxenes

INTRODUCTION

High-pressure, high-temperature experiments have been extensively used to characterize phase relations and melting properties in the Earth’s mantle. However, some natural processes like fractional crystallization, adiabatic decompression melting, fluxed melting, etc. cannot be reproduced by simple experiments and require the use of thermodynamic models (e.g., Ghiorso and Sack 1995). The quality and accuracy of these models rely on the quality and accuracy of the experimental database used for calibration. Most thermodynamic models of melting, as well as mineral/melts and mineral/mineral thermometers and barometers (olivine-melt, clinopyroxene-garnet, two pyroxenes, etc.), are based on large databases including published data from different sources (e.g., Hirschmann et al. 2008). Systematic differences in pressure, temperature, and oxygen fugacity between data sets can be a large factor in the uncertainties that need to be assessed when constructing thermodynamic models. The objective of our study is to characterize oxygen fugacity and temperature reproducibility in experiments relevant to mantle-melting models to assess systematic errors in experimental databases used for thermodynamic modeling.

One of the main goals of this paper is to experimentally determine the oxygen fugacity and the oxidation state of Fe in high-pressure, high-temperature experiments in equilibrium with graphite. We focus on experiments performed in the piston-cylinder device (Boyd and England 1960) using Pt-graphite (or graphite only) containers because such containers have been used since the 1960s in hundreds of studies (see Basaltic Volcanism Survey Program 1981, Tables 3.3.1, 3.4.2, and Appendix 3.1 for a summary of work done up until 1980, and Hirschmann et al. 2008 for later work) and have become the standard technique for anhydrous high-pressure experiments on Fe-bearing compositions. However, despite their common use, there have been only a few experimental studies that have attempted to systematically investigate the f_{O2} imposed by graphite containers (e.g., Ulmer and Luth 1991; Yasuda and Fujii 1993). Furthermore, these studies used COH fluids or solid-electrolyte sensors inside the graphite capsule, and do not take into account the variations in f_{O2} induced by interactions between the graphite capsule and the experimental sample (Holloway et al. 1992). We thus performed a systematic experimental study to determine f_{O2} and Fe^{3+}/Fe^{2+} in