Piston-cylinder experiments on H₂O undersaturated Fe-bearing systems: An experimental setup approaching fO₂ conditions of natural calc-alkaline magmas

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ABSTRACT

In this study, we present a modified double-capsule technique to perform experiments on H₂O undersaturated, Fe-bearing systems at elevated pressures and temperatures and oxygen fugacities (fO₂) relevant for natural calc-alkaline magmas. Welded shut, Fe-preconditioned Au₉₀Pd₁₀ capsules were placed in an outer Pt capsule that contains the same starting material. Experiments were performed at 1.0 GPa and 1200 °C using a synthetic, hydrous basalt and run with either boron nitride (BN) or MgO surrounding the welded capsules. Optimum results were obtained by using Fe-preconditioned Au₉₀Pd₁₀ inner capsules in combination with MgO assemblies. The application of the modified double-capsule technique with Fe-preconditioned inner AuPd capsules reduced Fe loss to less than 3% relative, conserved H₂O within the error of ion-microprobe analyses, and kept the fO₂(QFM+1.1) within 1 log unit of the initial value constrained by the Fe₂O₃/FeO ratio of the starting material (QFM+0.43). These conditions are similar to estimates of fO₂ during the crystallization of natural calc-alkaline magmas.

INTRODUCTION

Experimental studies on natural calc-alkaline, arc-related magmas (H₂O-undersaturated Fe-bearing systems) are hampered by Fe-loss to and H₂ loss through noble-metal capsules (Merrill and Wyllie 1973; Stern and Wyllie 1975; Johannes and Bode 1978; Grove 1981; Kawamoto and Hirose 1994; Gaetani and Grove 1998). Ratajeski and Sisson (1999) demonstrated that even Au, commonly regarded as an inert metal-container, alloys with Fe to some extent. The reduction of FeO from the experimental charge and thus the oxygen fugacity (fO₂) is significantly lower than that calculated for calc-alkaline magmas (i.e., QFM to QFM+4; Carmichael 1991; Ballhaus 1995; Brandon and Draper 1996; Parkinson and Arclus 1999) at conditions of less than 2 GPa and temperatures in excess of 1000 °C (e.g., Ulmer and Luth 1991; Frost and Wood 1995). Production of mixed-volatile C-O-H fluids/melts can cause additional problems when performing hydrous experiments in combination with graphite capsules. For hydrous systems applied to “wet” mantle melting, Gaetani and Grove (1998) suggested the use of Fe-preconditioned, inner Au-Pd capsules to overcome the problem of Fe loss. Ratajeski and Sisson (1999) also recommended preconditioning of Au capsules when performing experiments under lower fO₂(QFM-1) conditions.

The fO₂ of an experimental charge is linked to the fO₂ via the water dissociation constant. The ability of H₂ to diffuse through noble-metal capsules has successively been applied to control the fO₂ in fluid-saturated experiments (Eugster 1957; Sisson and Grove 1993) using a double-capsule technique: An outer capsule contains an oxidation/reduction couple (the buffer assemblage) such as mixtures of Ni + NiO or fayalite + SiO₂ + magnetite plus sufficient H₂O to allow complete oxidation of the oxidation/reduction couple through reaction with H₂O (e.g., Ni + H₂O = NiO + H₂). As long as all phases (including H₂O) are present, the fO₂ is determined by the fO₂ and the H₂O equilibrium constant, K₉O = (fO₂)²/fO₂. As H₂ diffuses through the noble-metal containers it maintains a constant fO₂ in the outer and inner, H₂O-saturated capsules. This principle, however, cannot be strictly applied to “control” fO₂ in fluid-undersaturated piston-cylinder experiments, irrespective of whether undersaturation is obtained through dilution of H₂O by another (inert?) fluid species such as CO₂ or by supplying less H₂O to the starting material than required to saturate the liquid phase with H₂O. In both cases, fH₂O is lower than for H₂O saturated systems and, consequently, the fO₂ in the inner capsule is less than the fO₂ in the outer capsule. In principle, fH₂O and hence fO₂ can be calculated for the initial conditions but, as discussed by Luth (1989), the fO₂ gradient across the inner capsule wall leads to a constant drain of H₂ from