Oxidation in CSPV experiments involving H₂O-bearing mafic magmas: Quantification and mitigation

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ABSTRACT

A difficulty in performing high-temperature (>900°C) experiments on near-liquidus hydrous mafic melts in gas-medium cold-seal pressure vessels (CSPV) is the tendency for H₂O in the fluid phase to dissociate and H₂ to diffuse through capsule material, leading to progressive oxidation of sample material. Negative consequences include premature stabilization of Fe-Ti oxide phases and commensurate deviation of the liquid line of descent toward silica enrichment. Moreover, time-variance of an intensive variable equal in importance to temperature or total pressure is an unwanted feature of any experimental study. Methodologies commonly employed to mitigate the oxidation problem, not without their own drawbacks, include incorporating CH₄ into the pressurizing gas, limiting run duration to 24 h, enclosing samples in Au-alloy capsules, and incorporating solid buffering assemblages to serve as indicators of fO₂ excursion. Using the Co-Pd-O system as a fO₂ sensor, we investigated progressive oxidation of basaltic andesite at 1010°C and P_H₂O = 150 MPa. Our time-series of 12, 24, 36, 48, and 60 h run durations reveals that oxidation occurs at a very high rate (~3–4 log unit change in fO₂ in 48 h). Both the variability of fO₂ and magnitude of dehydration-oxidation are considered unacceptable for phase equilibria work. Incorporation of additional CH₄ serves only to offset the progressive oxidation trend toward a lower absolute range in fO₂. Ultimately, rapid oxidation in CSPV hinders the chemical equilibration of experimental charges. To mitigate the issue, we propose the following solution: Incorporation of a substantial mass of Ni metal powder as an O₂ getter to the outer capsule successfully: (1) slows down oxidation; (2) stabilizes fO₂ at the nickel-nickel oxide (NNO) buffer after ~20 h; and (3) allows compositions to approach equilibrium. Runs much longer than 48 h may require one or more steps involving quenching and re-filling the pressure system with CH₄.

Keywords: Experimental petrology, oxygen fugacity, rates of oxidation, crystallization, chemical equilibrium

INTRODUCTION

Experimental petrology explores the effects of environmental conditions [e.g., temperature (T), pressure (P), time (t), oxygen fugacity (fO₂), volatile content (X_h₂o), chemical composition (X_melt)] on the chemical behavior of magmas (e.g., Holloway and Wood 1988). Particularly pertinent to the field of volcanology are experiments that investigate the melting, crystallization, mixing, or vesiculation of magmas and the transport of chemical constituents (e.g., Kouchi and Sunagawa 1983; Blundy and Cashman 2008; Hammer 2008; Zhang and Cherniak 2010). Experiments using magmas of intermediate-to-felsic compositions at crustal pressures (P > 1 atm) and moderate temperatures (T < 900 °C) have increased in frequency in the past few decades (e.g., Hammer 2008 and references therein). Similar studies involving hotter (T > 900–950 °C) hydrous mafic magmas at high pressures are sparse (e.g., Sisson and Grove 1993), mostly due to the technical challenges associated with volatile-rich melts at these temperatures. In many instances, high-T experiments involving mafic compositions are run using internally heated pressure vessels (IHPV; Holloway 1971; Muncill and Lasaga 1988; Moore et al. 1995; Moore and Carmichael 1998, Pichavant et al. 2002; Berndt et al. 2005; Di Carlo et al. 2006; Simakin et al. 2009), because they allow for large volumes of material and accommodate higher P and T conditions than cold-seal pressure vessels (CSPV; Holloway 1971). Despite their being used more often for colder, more silicic experiments (e.g., Hammer 2008 and references therein), CSPVs are increasingly used for hotter, hydrous experiments (e.g., Métrich and Rutherford 1998; Coombs et al. 2000; Hammer et al. 2002). IHPVs are relatively expensive, difficult to maintain and operate in comparison with CSPV apparatus (Lofgren 1987). Given the growing interest in explosive mafic volcanism (e.g., Houghton and Gonnerman 2008; Di Traglia et al. 2009), there is an opportunity for intensified use of CSPVs in laboratory experimentation involving hydrous mafic magmas. Thus, it is important to evaluate the practical limits of methods already in common use to impose and maintain desired thermodynamic conditions.

Oxygen fugacity (fO₂), along with P and T, is widely recognized as an important factor controlling magmatic crystallization sequences and liquid lines of descent (e.g., Muan 1958; Osborn 1959; Sisson and Grove 1993; Toplis and Carroll 1995; Berndt et al. 2005; Hammer 2006; Feig et al. 2010). Oxygen fugacity exerts a direct control on the valence state of metal elements (dominantly Fe²⁺/Fe³⁺ in natural magmas), which, in addition to controlling the appearance of iron-bearing oxides (Carmichael and Nicholls 1967; Toplis and Carroll 1995), dictates how Fe partitions into