A filler-rod technique for controlling redox conditions in cold-seal pressure vessels

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ABSTRACT

A new method has been developed to impose different redox conditions in high-temperature-pressure experiments in cold-seal pressure vessels, at 800 °C and 2000 bars. Experiments were conducted by loading a metallic filler rod into the autoclave together with H₂ sensor capsules, and pressuring the autoclave with H₂O. Rod materials tested successfully were Co, Ti, and C (graphite). The oxidation of these rods produces H₂, but because of diffusive H₂ loss through the walls of the autoclave, the system may not be buffered with respect to H₂. However, fO₂ quickly reaches a steady state value, and because fH₂ is easily measured by the hydrogen sensor method, the effect of the filler rods on the intrinsic fO₂ of the autoclave can be quantified. In order to produce oxidized conditions, Ar was used as the pressure medium and metal oxides, contained in Al₂O₃ tubes, were employed. By using either Ar or H₂O as a pressure medium, a log fO₂ range of NNO –3.9 to NNO +4.6 can be imposed by this method, where NNO is the log fO₂ value of the Ni-NiO buffer. The ability to conduct long-run-duration experiments at high temperature and high fO₂ conditions is not possible with the traditional double-capsule technique because the buffer assemblage is consumed too quickly. However, run durations of up to 4 weeks with constant fO₂ at reduced conditions have been conducted using the filler-rod technique. This technique has been shown to be an effective method in controlling redox conditions in cold-seal autoclaves, and thus can be applied to investigating redox-dependent reactions in a wide range of geochemical systems.

INTRODUCTION

Many geochemical reactions are dependent on oxygen fugacity (fO₂), e.g., Eugster (1957), Eugster and Skippen (1967). Some more recent experiments on the effects of fO₂ include mineral solubility (Linnen et al. 1996) trace-element partitioning (Canil 1999) and phase equilibria reactions (Scaillet and MacDonald 2001). Controlling the redox conditions of experiments therefore is of critical importance in studying a variety of different systems. One of the most versatile and widely used types of experimental apparatus is the cold-seal pressure vessel, which is used to investigate systems at crustal temperatures and pressures. Different techniques have been developed to control or measure redox conditions during experiments, but each of these techniques has shortcomings. The double-capsule technique is often limited by the length of time that experiments can be run at high temperature. Other techniques such as the Shaw membrane or graphite-methane buffer have the disadvantage of using dangerous gases at high pressure. To overcome these problems, a new technique has been developed that uses filler rods of different compositions to impose different hydrogen fugacities (fH₂) that are measured using the hydrogen sensor technique of Chou (1987a). We will show that experiments can be conducted over long duration (4 weeks), at high temperature (800 °C), and over a wide range of redox conditions. This method can be employed to determine the effect of oxygen fugacity on a great number of reactions, particularly those involving granitic melts.

Background on redox control in cold-seal pressure vessels

The redox state in most experiments conducted in cold-seal pressure vessels is not controlled. However, if water is used as the pressure medium, the intrinsic oxygen fugacity of the autoclave is typically close to that of the Ni-NiO buffer because the alloys used to construct the autoclaves are Ni-rich. The most common method to control the redox state of experiments in cold-seal pressure vessels is the double-capsule technique, (Eugster 1957; Chou 1987a). In this method, an oxygen buffer assemblage (such as Ni-NiO) is placed in a thick-walled outer capsule together with water. The buffer assemblage fixes fO₂ and at fixed T and P, the fH₂ can be calculated using available fugacity coefficients, and fH₂ can be calculated from the dissociation constant of water (at low fH₂ P H₂O = P total, but at high fH₂ the fH₂ is calculated using P H₂O + P H₂ = P total). The fH₂ of the inner capsule is the same as the fH₂ of the outer capsule because hydrogen diffuses across the inner capsule wall. If the fH₂ of the inner capsule is known, then the fO₂ of the experiment can be calculated. The problem with this technique is that at high temperature (>700 °C), the buffer assemblage is consumed quickly; hence, it is not possible to conduct redox-controlled experiments that are several weeks in duration, particularly when the redox conditions differ significantly from Ni-NiO. An additional problem is that if the fH₂ within the capsule is significantly different from that of the pressure medium, the equilibrium fH₂ of the buffer assemblage may not be reached (Chou and Cygan 1990). In this case, the high fH₂ gradient between the fluid in the capsules and the pressure medium will result in rapid diffusion of hydrogen across the capsule wall. If the rate of hydrogen loss (or gain) from the capsule exceeds the rate at which the buffer assemblage can react, redox conditions will not be fixed at the equilibrium value of the buffer assemblage. A final problem with the double-capsule technique is that the metals in assemblages such as Ni-NiO and Co-CoO can diffuse across the inner capsule wall and contaminate the experiment.

An alternate method of controlling the redox conditions of