

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, f_{H_2} quickly reaches a steady state value, and because f_{H_2} is easily measured by the hydrogen sensor method, the effect of the filler rods on the intrinsic f_{O_2} 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 f_{O_2} range of NNO –3.9 to NNO +4.6 can be imposed by this method, where NNO is the log f_{O_2} value of the Ni-NiO buffer. The ability to conduct long-run-duration experiments at high temperature and high f_{H_2} 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 f_{H_2} 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 (f_{O_2}), e.g., Eugster (1957), Eugster and Skippen (1967). Some more recent experiments on the effects of f_{O_2} include mineral solubility (Linnen et al. 1996) trace-element partitioning (Canil 1999) and phase equilibria reactions (Scailliet 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 (f_{H_2}) 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 f_{O_2} and at fixed T and P , the $f_{\text{H}_2\text{O}}$ can be calculated using available fugacity coefficients, and f_{H_2} can be calculated from the dissociation constant of water (at low f_{H_2} , $P_{\text{H}_2\text{O}} \approx P_{\text{total}}$, but at high f_{H_2} the $f_{\text{H}_2\text{O}}$ is calculated using $P_{\text{H}_2\text{O}} + P_{\text{H}_2} = P_{\text{total}}$). The f_{H_2} of the inner capsule is the same as the f_{H_2} of the outer capsule because hydrogen diffuses across the inner capsule wall. If the $f_{\text{H}_2\text{O}}$ of the inner capsule is known, then the f_{O_2} 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 f_{H_2} within the capsule is significantly different from that of the pressure medium, the equilibrium f_{H_2} of the buffer assemblage may not be reached (Chou and Cygan 1990). In this case, the high f_{H_2} 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

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experiments in cold-seal pressure vessels is the Shaw membrane technique (Shaw 1963; Hewitt 1977; Gunter et al. 1987; Schmidt et al. 1995). In this technique hydrogen is introduced into the autoclave through a permeable platinum or silver-palladium membrane that is welded to the end of a capillary tube, and hydrogen pressure is measured by a gauge or a pressure transducer. The diffusion of hydrogen across the membrane allows the pressure of hydrogen inside the autoclave to equilibrate with the pressure inside the membrane. As f_{H_2} is equal on both sides of the membrane (at equilibrium) and pure H_2 is present inside the membrane, the partial pressure of H_2 in the membrane is the same as the f_{H_2} of the autoclave. This technique provides an excellent redox control, but at high T and high f_{H_2} , the H_2 reservoir may need to be replenished frequently; however, if the ratio of the volume of the reservoir to volume of the autoclave is high, this problem is greatly reduced (Schmidt et al. 1995). An additional advantage of this technique is that redox conditions can be changed during an experiment. The main disadvantage of this technique is that it involves the use of a dangerous gas, H_2 . The use of graphite filler rods and methane as the pressure medium imposes very reduced conditions (Eugster and Skippen 1967; Chou 1987b), similarly involves the use of a hazardous gas, CH_4 . For laboratories where many students are conducting experiments, it may not be feasible to use these gases.

EXPERIMENTAL METHOD

The object of this study was to determine whether redox conditions in an autoclave reach a steady state when a reactive filler rod is introduced into the system. This approach is different from trying to buffer an experiment to a fixed f_{O_2} or f_{H_2} value. For example, if Co filler rods are used, the redox conditions of an experiment may not be buffered to the Co-CoO value because H_2 will continually diffuse out of the autoclave. However, the f_{H_2} in the autoclave may reach a steady state value, depending on the rate of H_2 diffusion, the rate of oxidation of the Co rod, and other factors such as whether or not armoring of CoO on Co occurs (i.e., whether the rate of oxidation of Co is time-dependent). If, in fact, a steady state is reached, and the f_{H_2} value of the autoclave and experiments can be quantified, then this technique can be applied to any series of experiments where redox conditions are one of the variables.

Equipment

The autoclaves are constructed of Udimet 720[®], a Ni-rich alloy that contains Cr, Co, Ti, and Mo as well as several other elements at trace levels. All the autoclaves in this study are new, so there is no prior history of them being used at oxidized or reduced conditions. The cold-seal pressure vessels used in this study are rapid-quench autoclaves that are operated vertically. The autoclave is the only portion of the system that is placed inside a furnace and is separated from an extension tube by a coupling and a double cone (Fig. 1). Water circulates inside the coupling, outside of the double cone, and the experiment is quenched by dropping capsules into this cold zone. This is accomplished by having the capsules held at the end of the autoclave during an experiment by a support rod. The support rod remains in place because a small stainless steel sleeve

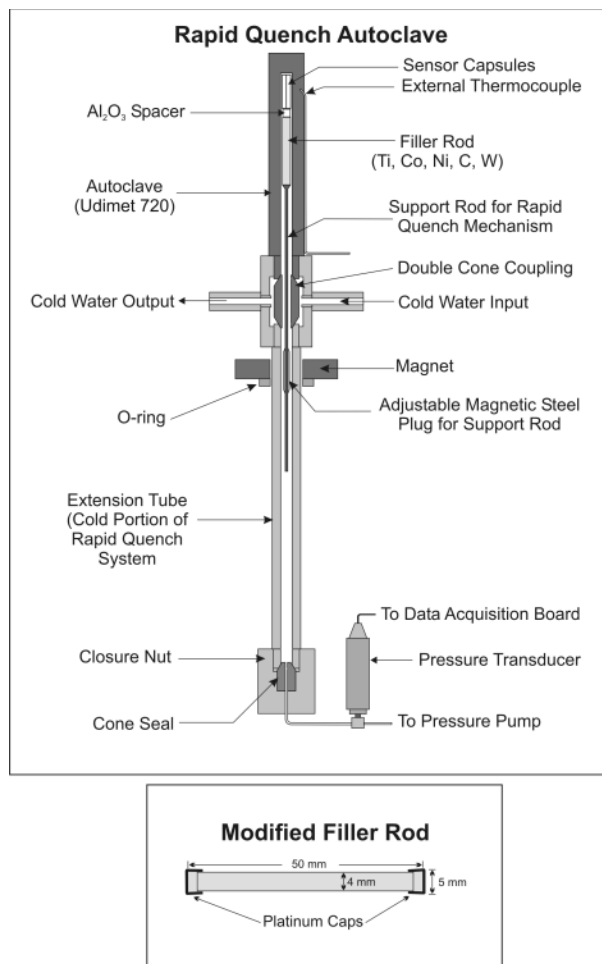


FIGURE 1. Schematic diagram of the rapid-quench, cold-seal autoclave and the modified filler rod. The autoclaves were constructed of UDIMET 720 alloy, which has an approximate composition of 56.0% Ni, 16.0% Cr, 14.7% Co, 5.0% Ti, 3.0% Mo, 2.5% Al, and 1.25% W (see www.specialmetals.com/products/data_720.htm).

is fixed to the support rod by setscrews. The sleeve + rod assembly is held in place by a donut-shaped magnet, outside the extension tube, fixed in place by an O-ring with a setscrew. In order to quench an experiment, the setscrew is loosened, both the O-ring and the magnet fall, and the capsule also falls into the cold zone such that the quench is near instantaneous. This experimental design was adapted from that of Hans Keppler at the Bayerisches Geoinstitut, which in turn is similar to a design previously developed by Phil Ihinger at the California Institute of Technology.

Temperature was measured using an external Ni-CrNi thermocouple that was calibrated both against the melting temperature of pure NaCl as well as an internal multi-point thermocouple. The internal multi-point thermocouple had 4 measurement points, over a distance of 4 cm, and the thermocouple point at the tip was also calibrated against the melting temperature of pure NaCl. The internal thermocouples established that the temperature gradient in these autoclaves at 700–800 °C and 2000 bars (H_2O pressure medium) was typically less than 5 °C over the top 3 cm where capsules are placed.

The external thermocouple has an error of approximately ± 1 °C, so the total error in measuring the temperature of the experiments is ± 5 °C at 800 °C and 2000 bars. Pressure was measured by transducers and results were checked against a pressure gauge. The transducers and gauge are factory calibrated and have an accuracy of better than ± 100 bars. Several experiments were also conducted using Ar as the pressure medium, because the use of Ar instead of water should produce more oxidized conditions. In these cases the pressure of the experiments was 1500 bars, the maximum pressure attainable with the current pump. Although the Ar pressure is slightly lower than the H₂O pressure, we do not believe that the small pressure difference has any significant effect on the redox conditions of the experiments [see Chou (1987a) for pressure effect on f_{O_2}].

Experimental configuration

The experimental configuration for working at reduced conditions is shown on Figure 1. During an experiment, the autoclave is inserted into a vertical furnace. Two hydrogen sensor capsules are placed at the top end of the autoclave. The capsules were made from 2 mm o.d., 1.8 mm i.d., 20 mm length Pt tubing after the method of Chou (1987a). In the "A" sensor, approximately 20 μ L of distilled water was loaded into a capsule together with a mixture of ~ 20 mg Ag and 20 mg AgCl, and the capsule was welded shut. The "B" sensor consists of the same solid mixture together with ~ 20 μ L of 3 or 5 *m* HCl. The sensors were placed inside a container constructed of 5 mm o.d. Pt tube with a flat-bottom cap to prevent the sensors from catching on the sides of the autoclave during quenching. An Al₂O₃ spacer, a filler rod, and the support rod for the rapid-quench mechanism are placed below the Pt container with the sensors. The spacer greatly reduces contamination of an experiment by diffusion of metals (e.g., Co) from the filler rod across the Pt capsule. The spacer also prevents the filler rod from sticking to the Pt container during an experiment. Filler rods were constructed of materials that will change the intrinsic f_{O_2} of the autoclave. The filler rods were all 5 cm in length and 3–5 mm in diameter; the materials tested in this study are Ni, Co, Ti, W, and C (graphite). Contamination of the autoclave will cause a change in the strength of the alloy and thus is a major concern. We were first alerted to this potential problem during the initial experiment with Ti rods, where the rod stuck to the inside of the autoclave after an experiment. Pre-oxidation of the Ti did not prevent this problem, and the solution found was to make an I-shaped rod on a lathe (Fig. 1), then place Pt caps over the ends of the rod to prevent any contact between the rod and the inside walls of the autoclave. Finally, the support rod for the quench mechanism is beneath the filler rod.

The filler-rod technique is well suited to produce reduced conditions, by generating H₂ through oxidation of a metal and dissociation of water, e.g.:



For producing oxidized (low f_{H_2}) conditions, Ar is used as the pressure medium. The reactions are opposite to the ones that produced reduced conditions. H₂ is consumed to produce H₂O and a metal oxide is reduced to a metal, e.g.:

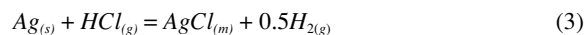


There is sufficient H₂ for reactions such as Reaction 2 to proceed because, during long duration experiments, the buffer material has been completely consumed (discussed below). There are trace amounts of H₂O in the Ar from the gas bottle, and trace H₂ will diffuse from the atmosphere into the autoclave during an experiment, but the H₂ in both of these sources are negligible. Another potential source of H₂ is the water that is contained in the sensor capsules; however, no weight loss was observed in any of the sensor capsules. The most likely source of H₂ is from absorbed H₂O. The buffer powders were not dried in an oven and thus will contain some absorbed H₂O. In addition, the pressure release from the preceding experiment results in adiabatic cooling that causes condensation of H₂O inside the autoclave (particularly the extension tube) after the closure nut is opened. Although we have not quantified this, enough H₂O is apparently absorbed to be a sufficient source of H₂ for reactions such as 2.

Rods of most metal oxides are not readily available, so for oxidized experiments a 5 cm long Al₂O₃ tube filled with a metal oxide powder replaces the filler rod of the above experiments. The Al₂O₃ tube was sealed at the lower end with high temperature cement, and filled with an oxide powder, Fe₂O₃ or Cu₂O. The upper end of the tube was stuffed with SiO₂ wool, to prevent the metal oxide from spilling out of the container.

Analytical method

The hydrogen sensor technique is based on the Ag-AgCl reaction, which was first used as a buffer for HCl fugacity by Frantz and Eugster (1973), then applied later as a hydrogen sensor by Chou and Eugster (1976):



where the superscripts (s), (m), and (g) are abbreviations for solid, melt, and gas, respectively. The reaction constant for Equation 3 is:

$$K_r = \frac{a_{\text{AgCl}} \cdot f_{\text{H}_2}^{0.5}}{a_{\text{Ag}} \cdot f_{\text{HCl}}} \quad (4)$$

At high temperature, hydrogen diffusion through the capsule walls allows the f_{H_2} of the capsule to equilibrate with the f_{H_2} of the pressure medium. Because the activity of Ag_(s) is one and that of AgCl_(m) is close to one, and f_{H_2} is imposed by redox conditions in the autoclave, the f_{HCl} is proportional to the f_{H_2} of the pressure medium. The capsules are quenched from the temperature of the experiment to 25 °C in a few seconds, quenching the Ag-AgCl reaction and ensuring that the capsules do not re-equilibrate at a lower temperature. At the temperature and pressure of the experiments of this study, HCl is completely associated [note that this is not necessarily true at higher pressures or lower temperatures (Chou 1987a)], and at 25 °C HCl is fully dissociated. By measuring the chloride concentration within the capsule after quenching the experiment, the f_{H_2} of the pressure medium at temperature and pressure can be determined, and then related to f_{O_2} by the dissociation constant of water. Using the equation from Chou (1987a) the f_{O_2} of the ex-

periment can be calculated by:

$$(f_{O_2}^{\text{sample}})_{P,T} = (f_{O_2}^{\text{std}})_{P,T} \cdot \left(\frac{m_{\text{Cl}^-}^{\text{std}}}{m_{\text{Cl}^-}^{\text{sample}}} \right)_{1 \text{ atm}, 25 \text{ }^\circ\text{C}}^4 \quad (5)$$

where $\log f_{O_2}^{\text{std}} = -13.788$ and $m_{\text{Cl}^-}^{\text{std}} = 0.9251$, the values for the oxygen fugacity and molality of the NNO buffer assemblage, respectively, at 800 °C and 2000 bars pressure reported by Chou (1987a). The measurement of f_{H_2} by the hydrogen sensor technique is dependent upon the capsule reaching osmotic equilibrium with the pressure medium. Therefore, two sensors, with initial chloride concentrations above and below the anticipated equilibrium value, are used to bracket the equilibrium chloride concentration. A similar chloride concentration from both capsules is interpreted to indicate that osmotic equilibrium was reached. The calculated oxygen fugacities of the “A” and “B” capsules were averaged to determine the oxygen fugacity of the experiment.

After experiments the “A” and “B” capsules were cleaned, punctured, and fluids extracted with a capillary. These fluids were then diluted with nanopure water, and chloride concentrations were determined by the mercuric thiocyanate spectrophotometric method (Vogel and Jeffery 1989), using a *Pharmacia Novaspec II* visible spectrophotometer to measure absorbencies at a wavelength of 460 nm. The chloride concentration of the aliquot was calculated using the second-order equation of the best-fit line to a set of standards ($R^2 > 0.997$). Chloride concentrations for at least two aliquots were averaged and the concentration of the fluid in the capsule was then back calculated. The accuracy of this technique was determined using a chloride standard solution. Five samples weighing between 6.21 and 13.25 mg of a ~1 M HCl solution were collected using a 20 µL capillary tube, transferred to vials, and diluted to 9 ml using nanopure water. The relative error on the spectrophotometric analysis was determined to be ±6.2%. This translates to an error of approximately ±0.1 for a $\log f_{O_2}$ determination. In some cases the variation of the “A” and “B” sensors was greater than 6.2%, and this value was assigned as the error on the measurements (Table 1).

It also should be noted that for high f_{H_2} conditions the errors for determining Cl concentrations are higher. Chou (1987a) recommended using the Ag-AgBr-HBr buffer, although in this study, Cl concentrations are consistent even for the most reduced experiments. For the 1500 bar experiments, the $m_{\text{Cl}^-}^{\text{std}}$ was unknown; therefore, an additional experiment at 800 °C was performed to determine this value. In this experiment, a mixture of Ni and NiO was placed in a 5.0 mm gold capsule together with 40 µg of H₂O and two (“A” and “B”) sensor capsules. The chlorine molalities were 1.337 and 1.492, for an average of 1.415 moles/kg. The latter value, and the 1500 bar value (−13.80) for $\log f_{O_2}^{\text{std}}$ of Ni-NiO at 800 °C were used to calculate oxygen fugacities for the experiments conducted at 1500 bars. The additional uncertainty of the $\log f_{O_2}^{\text{std}}$ adds an error of ±0.1 log units to the experiments at 1500 bars. Lastly, there is a more recent equation for f_{O_2} values of Ni-NiO (O'Neill and Pownceby 1993), but this equation yields a value is nearly identical to that of Chou (1987a) at 1 bar and 800 °C. The values from Chou (1987a) were preferred because the latter equation has a pressure-dependent term.

TABLE 1. Experimental results; intrinsic f_{O_2} of autoclaves

No.	Pressure medium	Run time (hrs)	$m_{\text{Cl}^-}^{\text{A}}$	$m_{\text{Cl}^-}^{\text{B}}$	$\log f_{O_2}$	error	Δ NNO
1	H ₂ O	24	1.28	1.29	−14.4	0.1	−0.6
1	H ₂ O	48	1.04	1.13	−14.1	0.1	−0.3
2	H ₂ O	24	0.98	0.91	−13.8	0.1	0.0
3	H ₂ O	24	0.64	0.75	−13.3	0.1	+0.5
3	H ₂ O	48	0.31	0.34	−12.0	0.1	+1.8
3	H ₂ O	96	0.14	0.15	−10.6	0.1	+3.2
3	H ₂ O	72	0.19	0.20	−11.1	0.1	+2.7
4	H ₂ O	24	0.23	0.26	−11.5	0.1	+2.3
4	H ₂ O	72	0.14	0.12	−10.4	0.1	+3.4
4	H ₂ O	120	0.26	—	−11.6	—	+2.2
5	H ₂ O	24	1.53	1.38	−14.6	0.1	−0.8
5	H ₂ O	48	1.09	1.12	−14.1	0.1	−0.3
6	H ₂ O	24	1.02	1.07	−14.0	0.1	−0.2
7	Ar	24	2.71	0.69	−14.9	1.2	+0.1
7	Ar	48	0.52	0.52	−12.1	0.1	+1.7
8	Ar	48	0.52	0.52	−12.1	0.1	+1.7
Tungsten Rod							
2	H ₂ O	12	3.86	4.11	−16.3	0.1	−2.5
2	H ₂ O	24	2.86	2.73	−15.7	0.1	−1.9
Nickel Rod							
5	H ₂ O	24	1.08	1.06	−14.0	0.1	−0.3
Titanium Rod							
6	H ₂ O	12	5.37	6.10	−17.0	0.1	−3.2
6	H ₂ O	12	5.36	4.40	−16.7	0.2	−2.9
6	H ₂ O	12	6.00	5.36	−16.9	0.1	−3.2
6	H ₂ O	24	2.63	2.96	−15.7	0.1	−1.9
6	H ₂ O	72	5.79	6.15	−17.0	0.1	−3.2
6	H ₂ O	240	5.32	5.33	−16.8	0.1	−3.0
6	H ₂ O	384	7.04	7.27	−17.3	0.1	−3.6
6	H ₂ O	504	6.04	6.76	−17.1	0.1	−3.4
6	H ₂ O	P-336	0.75	0.74	−13.4	0.1	+0.3
Graphite Rod							
2	H ₂ O	12	3.40	3.39	−16.1	0.1	−2.3
2	H ₂ O	24	3.30	3.61	−16.1	0.1	−2.3
2	H ₂ O	72	3.61	3.74	−16.2	0.1	−2.4
2	H ₂ O	240	5.53	6.51	−17.0	0.1	−3.3
2	H ₂ O	504	—	3.60	−16.2	—	−2.4
2	H ₂ O	P-24	1.32	—	−14.4	—	−0.6
Cobalt Rod							
1	H ₂ O	12	1.73	1.74	−14.9	0.1	−1.1
1	H ₂ O	24	1.86	2.12	−15.1	0.1	−1.3
1	H ₂ O	72	1.83	1.93	−15.1	0.1	−1.2
1*	H ₂ O	240	1.94	4.80	−15.1	—	−1.3
1	H ₂ O	780	1.91	1.98	−15.1	0.1	−1.3
1	H ₂ O	P-42	0.86	0.93	−13.7	0.1	+0.1
1	H ₂ O	P-96	0.59	0.63	−13.1	0.1	+0.7
1	H ₂ O	P-144	0.35	0.15	−11.4	0.8	+2.4
Hematite Powder							
7	Ar	24	0.29	0.31	−11.1	0.2	+2.7
7	Ar	48	0.22	0.23	−10.6	0.2	+3.2
7	Ar	168	0.09	0.10	−9.1	0.2	+4.7
7	Ar	336	0.09	0.10	−9.2	0.2	+4.6
7	Ar	504	0.12	0.13	−9.6	0.2	+4.2
7	Ar	48	0.08	0.09	−8.9	0.2	+4.9
7	Ar	120	0.10	0.13	−9.4	0.2	+4.4
7	Ar	240	—	0.09	−8.9	—	+5.4
7	Ar	504†	0.06	0.06	−8.4	0.2	+5.4
Copper Oxide Powder							
7	Ar	24	0.22	0.25	−10.7	0.2	+3.1
7	Ar	48	0.25	0.28	−10.9	0.2	+2.9

Notes: All experiments were conducted at 800 °C. Pressures were 2000 and 1500 bars with H₂O and Ar as pressure media, respectively; no. = the autoclave number. Time is measured as cumulative time and ‘P’ denotes post-experiment intrinsic f_{O_2} (without filler rod) of autoclave. $m_{\text{Cl}^-}^{\text{A}}$ and $m_{\text{Cl}^-}^{\text{B}}$ are the Cl molalities of the “A” and “B” sensors, respectively, the error is the difference in $\log f_{O_2}$ values calculated from average Cl molalities and the range of Cl molalities. DNN0 is $\log f_{O_2}$ of the experiment minus the $\log f_{O_2}$ value of Ni-NiO (−13.78) from Chou (1987a).

* For this experiment only the “A” sensor was used (see text for details).
† The experiment was quenched after 11 days, the buffer material was replenished then the experiment was run for a further 10 days, for a total of 21 days.

EXPERIMENTAL RESULTS

Intrinsic oxygen fugacity

The intrinsic f_{O_2} of six autoclaves were measured at 800 °C and 2000 bars pressure, with H₂O as the pressure medium (Table 1). Autoclaves 1, 2, 5, and 6 have an average intrinsic $\log f_{O_2}$ of -14.1 ± 0.3 , which we believe to be representative of the f_{O_2} of these autoclaves with a H₂O pressure medium. This value is, as expected, close to the $\log f_{O_2}$ value for the Ni-NiO buffer (NNO - 0.3). Analyses from autoclaves 3 and 4 have higher intrinsic f_{O_2} values. It is not clear why these values are higher, but this finding illustrates that the intrinsic f_{O_2} of all autoclaves need to be determined. The intrinsic f_{O_2} values for autoclaves pressurized with Ar are more oxidized. Autoclaves 7 and 8 at 800 °C and 1500 bars had a $\log f_{O_2} = -12.1$, or $\log f_{O_2} = \text{NNO} + 1.7$.

Tungsten rod

Two experiments were performed using a tungsten filler rod (Table 1, Fig. 2). This material was chosen because the oxidation of tungsten should produce relatively high H₂ fugacities (Cygan and Chou 1990). After 12 hours at 800 °C and 2000 bars (H₂O pressure), a thick layer of purplish-blue, gelatinous material (presumably a tungsten oxide) had coated both the filler rod and the top four centimeters of the support rod. After the 24 hour experiment, this coating had thickened to ~2 mm and was beginning to inhibit the operation of the rapid-quench mechanism, making vertical movements of the filler rod difficult. The $\log f_{O_2}$ measured after 12 and 24 hours was -16.3 ± 0.05 (NNO - 2.5) and -15.7 ± 0.04 (NNO - 1.9), respectively. The rise in f_{O_2} between the two experiments may be the result of armoring of the filler rod by tungsten oxide. Experiments using the tungsten filler rod were discontinued due to concerns about the possible contamination of the autoclave by tungsten oxide and the apparent armoring of the filler rod.

Cobalt rod

Oxygen fugacities using the cobalt rod and H₂O pressure medium are shown in Table 1 and Figure 2. In the case of the

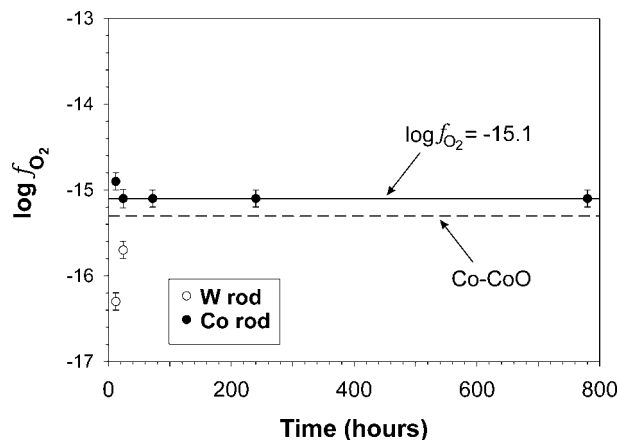


FIGURE 2. Log f_{O_2} vs. cumulative time of experiments using tungsten and cobalt filler rods. All experiments were conducted at 800 °C and 2000 bars with H₂O as the pressure medium.

240-hour experiment the “B” sensor had anomalously high chlorine and this data point was excluded from the f_{O_2} value calculated on Figure 2. After 12 and 24 hours at temperature, a thin layer of shiny-black material (presumably cobalt oxide) had developed over the top ~4 cm of the rod. The oxidized material formed thin sheets, which separated easily from the rod. Upon removing the oxidized material, the exposed surface was unchanged from its initial appearance. After 780 hours (~4 weeks) cumulative time, the thickness of the oxide layer had increased and now coated the full length of the rod. The thickness varied vertically, with the oxide layer being thickest near the top of the rod or closest to the hot zone.

Figure 2 shows that a $\log f_{O_2}$ value of roughly -15.1 (NNO - 1.3) was maintained for 780 hours. The intrinsic $\log f_{O_2}$ of the first (12 hour) experiment is -14.9 ± 0.1 , which is nearly the same as the subsequent experiments. We interpret these results to indicate that a steady state was reached at 24 hours, and possibly in less than 12 hours. The consistency of the data also indicates that armoring of cobalt was not a problem, which is likely because CoO sheets continuously spalled off the Co rod during experiments. The intrinsic value is only 0.2 log units more oxidized than the value of Co-CoO at 800 °C and 2000 bars (Chou 1987a), implying that a steady state intrinsic f_{O_2} was achieved, rather than f_{O_2} being buffered by Co-CoO.

Three post-cobalt filler-rod experiments were conducted to determine how quickly the autoclave returned to its intrinsic f_{O_2} value. Post filler-rod experiments P-42, P-96, and P-144 (42, 96, and 144 hours, respectively) indicate intrinsic $\log f_{O_2}$ values of -13.73 (NNO + 0.1), -13.06 (NNO + 0.7), and -11.36 (NNO + 2.5), respectively. These values are increasingly more oxidized with time and are more oxidized than the initial intrinsic values. This result is surprising because it was expected that H₂ dissolved into the autoclave, and would have dissolved out of the autoclave in the absence of a filler rod. This unusual result may be related to the fact that the autoclave was new, but it is beyond the scope of this study to determine whether hydrogen has dissolved into the alloy, or whether there have been other changes to the alloy. However, the variability of redox conditions in a single autoclave demonstrates that the intrinsic f_{O_2} can change, and that H₂ sensors are needed in all experiments where knowledge of the redox conditions may be important. Thus, it cannot be assumed that the f_{O_2} of an autoclave or autoclave + filler-rod assemblage has been calibrated based on a single series of hydrogen sensor experiments.

Nickel rod

One experiment of 24 hours duration was performed using the nickel filler rod and H₂O pressure medium (Table 1, Fig.3). The log oxygen fugacity within the autoclave was found to be -14.0 (NNO - 0.3), the same as the intrinsic value. In hindsight, this result was predictable, as the intrinsic f_{O_2} of the autoclave is less than Ni-NiO. Thus the nickel rod should not oxidize and therefore should not change the f_{O_2} of an experiment.

Graphite rod

The results of experiments using a graphite rod and H₂O pressure medium are shown in Table 1 and Figure 3. The graphite rod did not show visible signs of reaction, but it was noted that the

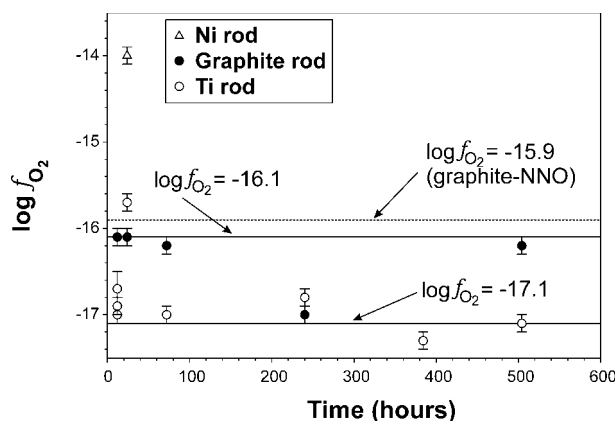


FIGURE 3. $\log f_{O_2}$ vs. cumulative time of experiments using nickel, graphite, and titanium filler rods. All experiments were conducted at 800 °C and 2000 bars with H_2O as the pressure medium.

pressure increased during experiments (and was periodically bled off) indicating that CO_2 and CH_4 were produced by the reaction of water and graphite. The $\log f_{O_2}$ values for the experiments at 12, 24, 72, and 504 hours have an average of -16.1 ± 0.1 (NNO -2.3), and the redox conditions appear to have reached a steady state. Only one data point, at 240 hours cumulative time and a $\log f_{O_2}$ of -17.0 , deviates from the steady state trend. We consider that this point is anomalously low and the experiment probably did not quench properly. One post-experiment intrinsic f_{O_2} also was determined (Table 1). In this case, after 24 hours the intrinsic oxygen fugacity had returned to a $\log f_{O_2}$ value of -14.40 (NNO -0.6), similar to the intrinsic value before the graphite rod was introduced. Also shown in Figure 3 is the $\log f_{O_2}$ value for graphite coexisting with a C-O-H fluid where the f_{O_2} is buffered by the Ni-NiO reaction. This value is -15.9 (Eugster and Skippen 1967), which is very close to the average of -16.1 observed in this study. The similarity of these two values indicates that the steady state value is in fact close to being an equilibrium one.

Titanium rod

The results for experiments with a titanium rod are shown in Table 1 and Figure 3. After the 24-hour experiment, the titanium rod appeared heavily oxidized. A dull black oxide was present over the entire length of the rod. A powder X-ray diffraction pattern of the oxide indicates that it is rutile. After the 240-hour experiment using the filler rod with platinum caps, the rod was accidentally broken. The fragility of the rod suggests that oxidation had occurred throughout its thickness, although black oxides, such as those found on the rods surface, were not visible within the rod and the core appeared to be metallic. Calculated oxygen fugacities using the titanium filler rod did not vary significantly between experiments and yielded an average $\log f_{O_2}$ value of -17.1 ± 0.2 (excluding the anomalous value at -15.7). This finding indicates that armoring is not a problem and that titanium filler rods can be used to impose reduced conditions in an experiment. The $\log f_{O_2}$ of the Ti-TiO₂ buffer is much lower than -17.1 at this temperature and pressure, which contrasts with the graphite rod experiments. However, the time invariance of $\log f_{O_2}$ indicates that a steady state had been reached.

Cu₂O powder

Two experiments were conducted using Cu_2O that was loaded into an Al_2O_3 tube, together with a trace amount of copper metal to act as seeds (Table 1, Fig. 4). The experiments did, as intended, produce more oxidized conditions, with $\log f_{O_2}$ values of approximately -11.5 (NNO $+2.3$). However, it was observed that metallic copper had precipitated on the bottom of the Al_2O_3 spacer, indicating that copper is volatile at these conditions. Because autoclave contamination is potentially a serious problem, the Cu_2O experiments were halted.

Fe₂O₃ powder

Fe_2O_3 powder was mixed with a trace amount of magnetite powder and loaded into an Al_2O_3 tube, as above. The data from two series of experiments using this material are listed in Table 1 and shown on Figure 4. In the first series experiments, the first 2 points define an increasing f_{O_2} trend, which differs from other experimental series. This result could reflect a longer time to reach a steady state (likely related to a more sluggish hematite-magnetite reaction); however, this effect was not observed in the second series. The third and fourth data points of the first series have nearly identical $\log f_{O_2}$ values, which is interpreted to reflect the system having reached a steady state at a $\log f_{O_2}$ of -9.2 (NNO $+4.6$). This value is the same as the $\log f_{O_2}$ for the hematite-magnetite buffer, suggesting that the f_{O_2} was buffered in these experiments rather than f_{H_2} simply reaching a steady state value. The last data point of this series is at a slightly lower value but after this experiment, the Al_2O_3 tube was emptied, and it was observed that all of the Fe_2O_3 had been converted to magnetite. The drop in f_{O_2} is interpreted to reflect total consumption of the f_{O_2} buffer. Because of this problem, a second series of experiments was conducted. The first data point, after 48 hours, is more oxidized ($\log f_{O_2}$ of -8.9) than after the same period of time for the first series of experiments. This difference may reflect the fact that the autoclaves were new and oxidation/armoring of the autoclaves during the first few experiments affected their intrinsic f_{O_2} . In the case of the second series, the three-week experiment was quenched after ten days, the buffer material was replenished and the experiment continued for another eleven days. The average f_{O_2} for the second series is -8.9 ± 0.5 (NNO $+4.9$). This value is slightly higher than the $\log f_{O_2}$ value for the hematite-magnetite buffer at 800 °C and 1500 bars (-9.2 ; Chou 1987a). However, the last data point appears to be anomalously high and, if this point is excluded, the average is -9.1 . Thus, the f_{O_2} of the second series also appears to be buffered to hematite-magnetite.

The facts that in the first series of experiments the buffer was totally consumed and in the second series of experiments a steady state f_{O_2} value was maintained, indicates that the hematite-magnetite oxide buffer changed the intrinsic f_{O_2} of the autoclave as desired. The reduction of hematite to magnetite produces oxygen:



The f_{H_2} at the hematite-magnetite f_{O_2} buffer is very low in the presence of pure H_2O , approximately 0.03 bars at 800 °C and 1500 bars. However, because Ar was the pressure medium, the activity of H_2O in the pressure medium was $\ll 1$. If the f_{O_2}

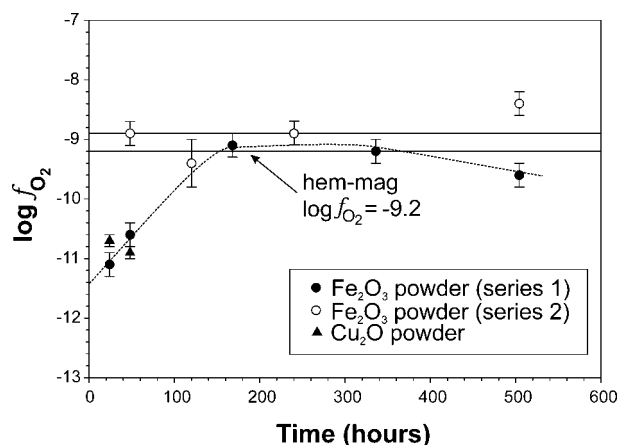


FIGURE 4. $\log f_{\text{O}_2}$ vs. cumulative time of experiments using Fe_2O_3 and Cu_2O powders packed in an Al_2O_3 tube. All experiments were conducted at 800°C and approximately 1500 bars with Ar as the pressure medium.

is controlled by the hematite-magnetite buffer, the f_{H_2} required to maintain this buffer is substantially lower. For example if the fugacity of H_2O was 10 bars, instead of 1221 bars (the fugacity of pure H_2O at 800°C and 1500 bars; Kerrick and Jacobs 1981), the f_{H_2} would be two orders of magnitude lower. Thus, an alternative explanation for why the second series of experiments produced a higher f_{O_2} is because the amount of absorbed H_2O in that series was lower, thus the hematite-magnetite buffer produced a lower f_{H_2} . In addition, part of the explanation of why the hematite powder produces oxidized conditions is that very low H_2 fugacities are required, and the small amount of absorbed water is sufficient to produce the required f_{H_2} (which isn't possible if the Ar pressure medium is completely H_2O - and H_2 -free).

CONCLUDING REMARKS

The filler-rod technique, developed here, is a cost-effective and simple method of imposing redox conditions during experiments at high temperature and moderate pressure. It has been shown that experiments of up to four weeks duration, and possibly longer, can be conducted at a steady state f_{O_2} value and that the $\log f_{\text{O}_2}$ values imposed by the materials tested here range over more than seven orders of magnitude, from approximately -17.1 to -9.2 (NNO -3.4 to NNO $+4.6$). This technique thus has great promise for the determination of the effect of redox conditions for a wide variety of reactions. However, caution should be exercised in employing this technique. It is not yet known whether the use of filler rods can contaminate the alloy of the autoclave. This problem is currently under investigation by conducting experiments using filler rods and a small cylinder of autoclave alloy. Contamination is not expected to be significant because Pt caps are placed over the ends of the filler rods; thus, metal transport will only occur via the pressure medium. However, if contamination does occur, it poses a serious problem because it could weaken the alloy and cause autoclave failure, which is particularly dangerous in the Ar pres-

surized experiments. In addition, high H_2 pressures are produced at reduced conditions, e.g., at a $\log f_{\text{O}_2}$ of -17.1 recorded for the titanium filler-rod experiments, the f_{H_2} was greater than 300 bars. Hydrogen weakens the autoclave alloy, but hydrogen also diffuses back out of the alloy at oxidized conditions (evident by the post-filler-rod intrinsic f_{O_2} determinations). However, periodic re-annealing of the autoclaves should also prolong autoclave life. Any potential user of this or any other technique involving high f_{H_2} should be aware of the risks beforehand.

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