## Redox control and measurement in low-temperature (<450 °C) hydrothermal experiments

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## ABSTRACT

Redox control in hydrothermal experiments is routinely achieved through double-capsule and Shaw membrane techniques. These techniques control oxygen fugacity  $(f_{0_2})$  by imposing a defined hydrogen fugacity ( $f_{H_2}$ ) on a studied sample enclosed, together with H<sub>2</sub>O, in a hydrogen membrane capsule made of Pt or Ag-Pd alloys. However, due to the low permeability of these membranes to  $H_2$ at low temperatures (T), these techniques do not work efficiently below 450 °C. Here, we tested fused silica as a new hydrogen membrane and successfully applied it to monitor and control the redox states of studied samples at T down to 200 °C in hydrothermal experiments. Our results showed that 3, 8, 16, 36, 96, and 216 h are sufficient for a fused silica capillary capsule (FSCC) to reach osmotic equilibrium with the externally imposed 1 bar of H<sub>2</sub> at 350, 300, 250, 200, 150, and 100 °C, respectively, and H<sub>2</sub> pressures inside a FSCC was very close to the externally imposed values after osmotic equilibrium. By using FSCC as a hydrogen fugacity sensor, equilibrium H<sub>2</sub> pressures for Ni-NiO-H<sub>2</sub>O and Co-CoO-H<sub>2</sub>O redox buffer assemblages at 250-400 °C and 1000 bar total pressure were measured. The equilibrated  $f_{02}$  calculated are consistent with those derived from previous literature. Besides, FSCC can be used as a sample container, where  $f_{H_2}$  and  $f_{O_2}$  of enclosed samples can be continuously controlled. Furthermore, FSCC is an ideal container for sulfur-bearing samples, and its transparency allows spectroscopic analyses of the sample. Our work extended the low-T limit of previously well-developed redox control techniques and may open up a new research avenue in low-T hydrothermal experiments.

**Keywords:** Redox buffer and control techniques, hydrothermal experiments, redox reactions, hydrogen fugacity sensor, fused silica capillary

## INTRODUCTION

Double-capsule (or oxygen buffer; Eugster 1957) and Shaw membrane (Shaw 1963) techniques are commonly applied to control  $f_{O_2}$  in hydrothermal experiments at elevated pressuretemperature (*P-T*) conditions (normally >50 MPa and 600 °C). The success of these two techniques relies on the effective diffusion of hydrogen across hydrogen membranes (e.g., Pt or Ag-Pd alloys), which are commonly used as the sample container. The oxygen buffer technique defines  $f_{O_2}$  by the equilibrium reaction between solid buffer assemblages (e.g., Ni-NiO) and H<sub>2</sub>O, while the Shaw membrane technique defines  $f_{O_2}$  by a hydrogen reservoir with known H<sub>2</sub> partial pressure. Over approximately the last 60 years, these two techniques have been greatly refined and widely used in hydrothermal experiments (Chou 1987; Scaillet et al. 1992; Taylor et al. 1992; Schmidt et al. 1995; Berndt et al. 2002; Matthews et al. 2003; Alex and Zajacz 2020).

However, double-capsule and Shaw membrane techniques do not work efficiently at T below 450 °C, as the permeability of commonly used precious metal hydrogen membranes to H<sub>2</sub> may become too low to achieve osmotic equilibrium between the sample system and the buffer/reservoir system in a reasonable duration (Chou 1986). Pd-rich Ag-Pd and Au-Pd alloys were tested to have high permeability to H<sub>2</sub> at low-T (e.g., Gunter et al. 1987; Sonwane et al. 2006). Nevertheless, a relatively long experimental duration is still needed for Pd-rich alloys to achieve  $H_2$  osmotic equilibrium at low-T (e.g., five days at 300 °C; Chou 1989), and they cannot be employed in sulfur-bearing studies. As a consequence,  $f_{02}$  conditions in hydrothermal experiments performed at T below 450 °C has normally been defined through: (1) mixing a solid oxygen buffer together with studied samples without a hydrogen membrane separating them (e.g., Gibert et al. 1998; Seewald 2001; Tagirov et al. 2005; Kokh et al. 2017); (2) loading a solid oxygen buffer into a quartz tube holder that is immersed in the sample solution in an autoclave with the open end exposed to the vapor phase of the sample (e.g., Archibald et al. 2001; Timofeev et al. 2018); and (3) redox equilibrium of aqueous multivalent-element species (e.g., sulfur; Pokrovski et al. 2015; Kokh et al. 2020). However, above-mentioned methods may suffer from leakage of H2 from the autoclave and possibly slow reaction kinetics of the redox buffer at low T. Therefore, it is necessary to develop a hydrogen fugacity sensor for directly monitoring the actual sample  $f_{\rm H_2}$  (or  $f_{\rm O_2}$ ) in low-T (<450 °C) hydrothermal experiments.

Diffusion coefficient measurements (Shang et al. 2009) demonstrated that fused silica is highly permeable to H<sub>2</sub> even at *T* below 400 °C. For example, the diffusion coefficient of H<sub>2</sub> in fused silica at 200 °C ( $10^{-12.9}$  m<sup>2</sup>/s) is two orders of magnitude higher than that in Pt at 600 °C ( $10^{-14.9}$  m<sup>2</sup>/s; Chou 1986). In addition, the transparency of fused silica enables phase observations and spectroscopic analyses for samples in a fused silica

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capillary capsule (FSCC). The composition and internal pressure (density) of fluid samples inside an FSCC can be determined by non-destructive spectroscopic methods (e.g., Raman spectroscopy; Chou et al. 2008). These characteristics make fused silica a potential hydrogen membrane and FSCC a suitable hydrogen fugacity senor and reactor for low-T hydrothermal experiments.

In this study, we first evaluated the viability of using fused silica as a low-*T* hydrogen membrane and then demonstrated that redox conditions in low-*T* hydrothermal experiments can be monitored and controlled by using FSCC as a hydrogen fugacity sensor and reactor.

## Methods

## **Experimental apparatus**

Fused silica capillary capsule (FSCC). FSCC was constructed from a fused silica capillary tubing with two ends sealed (Fig. 1; Chou et al. 2008). A FSCC can be loaded with solid, liquid, or gaseous samples and also can be vacuumed (Chou et al. 2008). Two types of FSCC, i.e.,  $CO_2$ -FSCC and vacuumed FSCC, were used in the present study.  $CO_2$ -FSCC contains a certain amount of  $CO_2$ , whereas vacuumed FSCC is internally vacuumed. Both  $CO_2$ - and vacuumed FSCC are normally ~10 mm long and have round cross sections with 0.1 mm inner diameter (ID) and 0.375 mm outer diameter (OD). Details about construction and sample-loading methods for FSCC are given in Chou et al. (2008).

**Cold-sealed pressure vessel (CSPV).** All experiments were carried out in horizontal CSPVs. Samples were normally loaded in a gold capsule (4.0 mm ID, 4.4 mm OD, and ~3 cm long) and then placed into a CSPV, followed by a stainless-steel filler rod (~20 cm long). The sample in the CSPV was heated by a horizontal electric furnace, and the sample *T* was monitored by using a K-type thermocouple, which was inserted into an external borehole of the CSPV near the sample. The accuracy of the reported temperature is within  $\pm 3$  °C, and the maximum temperature difference along the ~3 cm long sample is <3 °C. At the conclusion of heating, the CSPV was quenched in a compressed air jet, and the temperature of the sample decreased to near room *T* within 5 min.

### **Experimental design**

The experimental design of the present study was summarized in Table 1, and details about experimental runs were given in Online Material<sup>1</sup> Table OM1. Three sets of experiments were conducted. The first set of experiments (Set-I) determined the experimental durations required for the sample fluid in a FSCC to reach osmotic equilibrium with externally imposed 1 bar of H<sub>2</sub> at *T* between 100 and 350 °C. We used two CO<sub>2</sub>-FSCCs for each test: one contained ~1 bar of CO<sub>2</sub> (CO<sub>2</sub>-FSCC-A), and the other contained ~0.5 bar (CO<sub>2</sub>-FSCC-B). CO<sub>2</sub> was used as an internal reference in Raman analyses of H<sub>2</sub> and, due to the strong kinetic barriers, chemical reactions between H<sub>2</sub> and CO<sub>2</sub> are negligible in our experimental *P*-*T* conditions (<400 °C; McCollom 2016). The CO<sub>2</sub>-FSCCs were heated in a coldsealed pressure vessel (CSPV) at a desired *T* under 1 bar of external H<sub>2</sub> *P* (Fig. 1) for a certain period of duration before quenching. Raman spectra of CO<sub>2</sub> and H<sub>2</sub> in the quenched CO<sub>2</sub>-FSCCs were then collected, and the peak height ratios (HR) of H<sub>2</sub> and CO<sub>2</sub> of specific Raman bands were calculated.

The second set of experiments (Set-II) quantitatively determined the actual  $H_2$  pressures in FSCCs after they reached osmotic equilibrium with externally imposed 1.5, 1.0, and 0.5 bar of  $H_2$  at 200–350 °C. For each run, three vacumed FSCCs were loaded into a CSPV and imposed with pure  $H_2$  at a fixed  $P[(P_{H_2})_{CSPV} = 1.5, 1.0 \text{ or } 0.5 \text{ bar}]$  before being heated at a fixed T (350, 300, 250, or 200 °C; Fig. 1). After the vacuumed FSCCs were heated for durations that are enough for reaching hydrogen osmotic equilibria (based on results in Set-I), they were then quenched, and the hydrogen P in each of them was determined at room  $T[(P_{H_2})_{RT}]$ ; see "Analysis and calculation methods" below]. The hydrogen P at an experimental T,  $(P_{H_2})_{TT}$ , was calculated from the measured  $(P_{H_2})_{RT}$  based on the ideal gas law (see "Analysis and calculation methods" below).

In the third set of experiments (Set-III), we determined equilibrated hydrogen fugacity  $[(f_{H_2})_{P,T}]$  and oxygen fugacity  $[(f_{O_2})_{P,T}]$  defined by Co-CoO-H<sub>2</sub>O and Ni-NiO-H2O buffer assemblages at 1000 bar and 250-400 °C. In these experiments, three or four vacuumed FSCCs, together with a solid oxygen buffer and H2O, were sealed in a gold capsule (Fig. 2) and then pressurized with Ar in a CSPV before being heated to a desired P-T condition. During the experiments, H<sub>2</sub> produced by the reaction between the oxygen buffer and H2O diffused into the vacuumed FSCCs (Fig. 2). After osmotic and chemical equilibria were reached,  $(f_{H_2})_{P,T}$  defined by the redox buffer at the experimental P-T is equal to those in the vacuumed FSCCs, and can be calculated from the measured  $(P_{H_2})_{RT}$  in the quenched vacuumed FSCCs (see "Analysis and calculation methods" below). Chemical reagents used consist of Ni (99.99%, Aladdin Reagent), NiO (99.9%, Aladdin Reagent), Co (99.99%, Aladdin Reagent), CoO (99.5%, Aladdin Reagent), and deionized H<sub>2</sub>O. In runs with Ni-NiO-H2O or Co-CoO-H2O as the starting material, 40 mg H2O and ~400 mg Ni-NiO or Co-CoO mixtures (mass ratio = 1:1) were used while for runs with Ni-H<sub>2</sub>O or Co-H<sub>2</sub>O as the starting material, 40 mg H<sub>2</sub>O and ~200 mg Ni or Co were used.

#### Raman spectra collection and treatment

Raman spectra were acquired with a JY/Horiba LabRAM HR Evolution Raman spectrometer using a 532.06 nm (Nd: YAG) laser, an SLWD 50× Olympus objective with 0.35 numerical aperture. 1800 groove/mm grating and 150  $\mu$ m pinhole were used. The spectral resolution is ~0.2 cm<sup>-1</sup>. The output laser power is 100 mW, while ~14 mW of laser light was focused near the center of the sample cell to generate Raman signals during measurements.

In Set-I experiments, Raman spectra of the two quenched CO2-FSCCs between



**FIGURE 1.** Experimental setup and procedures for Set-I and Set-II experiments. (a) Schematic diagram showing the experimental setup. (b) A one-end sealed gold capsule and five fused silica capillary capsules (FSCCs). (c) Two CO<sub>2</sub>-FSCCs and three vacuumed FSCCs. CO<sub>2</sub>-FSCCs contain ~0.5 or ~1.0 bar CO<sub>2</sub> while vacuumed FSCCs are internally vacuumed (c). In Set-I experiments, two CO<sub>2</sub>-FSCCs were loaded in a gold capsule with one end open, which was in turn sealed and heated in a horizontal cold-sealed pressure vessel (CSPV), whereas, in Set-II experiments, three vacuumed FSCCs were used and loaded in the gold capsule. The CSPV was then evacuated and loaded with H<sub>2</sub>, the pressure of which can be adjusted and monitored. H<sub>2</sub> at the set pressure was allowed to diffuse into the FSCCs at a fixed *T*. (Color online.)

Run type	T (℃)	P (bar)	Duration (h)	Imposed H <sub>2</sub> /	FSCC	Raman quantitative
				Oxygen buffer	used	method
Set-l <sup>a</sup>	350	1	1, 2, 3, 4, 5	1 bar H₂	2 CO <sub>2</sub> -FSCCs	Raman spectra between
	300	1	2, 4, 6, 8, 10, 12	1 bar H₂	2 CO <sub>2</sub> -FSCCs	300 and 1500 cm <sup>-1</sup> were
	250	1	4, 8, 12, 16, 20, 24	1 bar H <sub>2</sub>	2 CO <sub>2</sub> -FSCCs	collected from quenched
	200	1	6, 12, 18, 24, 30, 36, 48, 60	1 bar H₂	2 CO <sub>2</sub> -FSCCs	CO <sub>2</sub> -FSCCs, and peak
Set-IIª	150	1	12, 24, 36, 48, 60, 72, 96, 120	1 bar H <sub>2</sub>	2 CO <sub>2</sub> -FSCCs	height ratios between H <sub>2</sub>
	100	1	48, 72, 96, 120, 168, 192, 216, 264	1 bar H <sub>2</sub>	2 CO <sub>2</sub> -FSCCs	and $CO_2$ were calculated.
Set-II <sup>a</sup>	350	Equal to imposed H <sub>2</sub> P	3, 4, 5	0.5, 1, 1.5 bar H₂	3 vacuumed FSCCs	Raman spectra of H <sub>2</sub>
Set-II <sup>a</sup>	300	Equal to imposed H <sub>2</sub> P	8, 10, 12	0.5, 1, 1.5 bar H <sub>2</sub>	3 vacuumed FSCCs	(4100–4200 cm <sup>-1</sup> ) were
	250	Equal to imposed H <sub>2</sub> P	16, 20, 24	0.5, 1, 1.5 bar H <sub>2</sub>	3 vacuumed FSCCs	collected from quenched
	200	Equal to imposed H <sub>2</sub> P	36, 48, 60	0.5, 1, 1.5 bar H <sub>2</sub>	3 vacuumed FSCCs	vacuumed FSCCs and <i>P</i> of H <sub>2</sub> in them at room <i>T</i> , $(P_{H_2})_{RT}$ , and experimental <i>T</i> , $(P_{H_2})_{T}$ , were determined.
Set-III <sup>b</sup>	400	1000	6, 12, 36, 48	Ni-NiO	4 vacuumed FSCC	Raman spectra of H₂
	350	1000	6, 12, 36, 48, 96	Ni-NiO	4 vacuumed FSCC	(4100–4200 cm <sup>-1</sup> ) were
	300	1000	6, 12, 24, 8, 72, 96	Ni-NiO	4 vacuumed FSCC	collected from quenched
	250	1000	24, 72, 120, 168	Ni-NiO	4 vacuumed FSCC	vacuumed FSCCs and $(P_{H2})_{RT}$ in
	400	1000	6, 12, 24, 36, 48	Co-CoO	4 vacuumed FSCC	them were calculated from
	350	1000	6, 12, 24, 48, 72	Co-CoO	4 vacuumed FSCC	H₂ peak height; based on
	300	1000	6, 12, 24, 8, 72	Co-CoO	3 vacuumed FSCC	$(P_{H_2})_{RT}$ , $f_{H_2}$ , and $f_{O_2}$ defined by
	250	1000	24, 72, 120, 168	Co-CoO	4 vacuumed FSCC	Ni-NiO and Co-CoO buffers at
						experimental P-T were derived.

**TABLE 1.** Summary of experimental design



**FIGURE 2.** A schematic diagram showing the capsule configuration for Set-III experiments.  $H_2$ , generated by the reaction of an oxygen buffer and  $H_2O$  in an enclosed gold capsule at a fixed *P*-*T* condition, diffused into vacuumed FSCCs. The ceramic tube is used to protect the FSCC when the external pressure is applied to the gold capsule. Modified from Figure 14 of Chou et al. 2008. (Color online.)

300 and 1500 cm<sup>-1</sup>, which covers four rational bands of  $H_2$  and two Fermi diad of  $CO_2$ , were collected with 100 s acquisition time, twice accumulations. For recovered vacuumed FSCCs from Set-II and Set-III experiments, Raman spectra in the range of 4100–4200 cm<sup>-1</sup>, which covers the four vibrational bands of  $H_2$ , were collected. The acquisition time is 100 s or 200 s with twice accumulations.

Raman peak heights of S<sub>0</sub>(1) band (~588 cm<sup>-1</sup>) of H<sub>2</sub>, upper band of Fermi diad of CO<sub>2</sub> (~1388 cm<sup>-1</sup>), and Q<sub>1</sub>(1) band of H<sub>2</sub> (~4157 cm<sup>-1</sup>) were calculated from acquired spectra by using GRAM32/AI software. No smoothing or baseline correction was applied to the spectra and a linear baseline, which is close to the mean of background (noise) signals, was manually defined during peak height acquisition (Fig. 3). It is worth noting that peak height, instead of peak area, was employed in quantitative analysis in the present study. This is because the pressure of H<sub>2</sub> in FSCCs is generally low (<1.5 bar), so that the acquired H<sub>2</sub> spectra are normally not of good quality for conducting precise peak area calculations, while peak height can be calculated more easily and accurately.

#### Analysis and calculation methods

**Determination of**  $(P_{H_2})_{RT}$  and  $(P_{H_2})_T$  in vacuumed FSCCs. The pressure of  $H_2$  in a quenched vacuumed FSCC at room *T*,  $(P_{H_2})_{RT}$ , was determined through a

quantitative Raman spectroscopic analysis method. In this method, the quantitative relationships between the peak height of  $H_2$  and its pressure were experimentally established. ( $P_{H_2}$ )<sub>RT</sub> was then calculated from the acquired  $H_2$  peak height, ( $PH_{H_2}$ )<sub>RT</sub>, based on the established quantitative relationships (details see Online Material<sup>1</sup> Appendix A).

Because of the low pressures (<1.5 bar) of  $H_2$  in vacuumed FSCCs,  $H_2$  gas in an individual vacuumed FSCC can be treated as an ideal gas both at room *T* and experimental *T*. Considering the low thermal expansion coefficient of fused silica ( $5.5 \times 10^{-7}$  K<sup>-1</sup>; Deng et al. 2020), the volume of each vacuumed FSCC can be treated as a constant during experiments and assume no  $H_2$  loss from the equilibrated FSCCs during and after quenching. We obtain:

$$(P_{\rm H_2})_{\rm T} = (P_{\rm H_2})_{\rm RT} (T/T_{\rm room})$$
(1)

where  $(P_{\rm H_2})_{\rm RT}$  and  $(P_{\rm H_2})_{\rm T}$  are the pressures of H<sub>2</sub> in a vacuumed FSCC at room *T* and experimental *T*, respectively. *T* is in K, and  $T_{\rm room}$  is equal to 298.15 K.

 $(f_{\text{H}_2})_{\text{P,T}}$ ,  $(f_{0_2})_{\text{P,T}}$ , and  $(f_{0_2})_{1,\text{T}}$  calculation. As an ideal gas, the fugacity of the H<sub>2</sub> in a vacuumed FSCC at an experimental *P*-*T* [ $(f_{\text{H}_2})_{\text{P,T}}$ ] is equal to its H<sub>2</sub> pressure  $(P_{\text{H}_2})_{\text{T}}$ :

$$(f_{\rm H2})_{\rm P,T} = (P_{\rm H2})_{\rm T} \tag{2}$$

For the formation reaction of H<sub>2</sub>O,

$$H_{2(g)} = 0.5 O_{2(g)} = H_2 O_{(g)}$$
(3)

$$\log K_{\rm w} = \log f_{\rm H_2O} - \log f_{\rm H_2} - 0.5 \log f_{\rm O_2} \tag{4}$$

where  $K_w$  is the formation constant of H<sub>2</sub>O at *T* and  $f_{\rm H_2O}$  is the fugacity of H<sub>2</sub>O at *P* and *T*. Because both  $K_w$  and  $f_{\rm H_2O}$  at *P* and *T* are well known (Burnham et al. 1969),  $\log f_{O_2}$  at *P* and *T*  $[\log (f_{O_2})_{\rm P,T}]$  can be calculated from Equations 1 and 2. The obtained  $(f_{O_2})_{\rm P,T}$  value is related to  $f_{O_2}$  at one bar and *T*  $[(f_{O_2})_{\rm I,T}]$  as:

$$\log(f_{O_2})_{1,T} = \log(f_{O_2})_{P,T} + \frac{\Delta V(P-1)}{2.303 \text{R}T}$$
(5)

where T is in K, P is in bar, R is the gas constant [8.314 J/(mol×K)], and  $\Delta V$  is the volume change for the solid phases in the buffer reaction and was calculated using molar volume data from Robie and Hemingway (1995).

The limit of detection (LOD) and limit of quantitation (LOQ) for the H<sub>2</sub> in vacuumed FSCCs at room *T* are estimated to be 0.02 and 0.06 bar, respectively (details see Online Material<sup>1</sup> Appendix B). The uncertainties in  $(P_{\rm H_2})_{\rm RT}$ ,  $(f_{\rm 0_2})_{\rm RT}$ , and  $(f_{\rm 0_2})_{\rm LT}$  were calculated based on the method described in Online Material<sup>1</sup> Appendix C.



**FIGURE 3.** Raman spectra collected from a quenched CO<sub>2</sub>-FSCC after it was heated at 250 °C, under 1 bar H<sub>2</sub> external pressure for various experimental durations. Peak heights of H<sub>2</sub> (near 588 cm<sup>-1</sup>) and CO<sub>2</sub> (near 1388 cm<sup>-1</sup>) were acquired (showing in two insets), and their ratios, HR values, were calculated and noted for each spectrum. (Color online.)

## **RESULTS AND DISCUSSION**

## Fused silica as a low-T (<450 °C) hydrogen membrane

Figure 3 shows Raman spectra collected from a quenched CO2-FSCC after it was heated at 250 °C, under 1 bar external H2 for various experimental durations (Set-I experiments). The peak height ratios between H2 and CO2 (HR) were derived from S0(1) Raman band (near 588 cm<sup>-1</sup>) of H<sub>2</sub> and the upper band of CO<sub>2</sub> Fermi diad (near 1388 cm<sup>-1</sup>). As shown in Figure 3, HR value increases with experimental duration at first (from 4 to12 h) and then remains almost unchanged (from 16 to 24 h), indicating the initial flux of H<sub>2</sub> into the CO<sub>2</sub>-FSCC until it reached osmotic equilibrium with the externally imposed 1 bar H<sub>2</sub>. This HR vs. experimental duration trend was observed for all CO2-FSCCs used in Set-I experiments (Fig. 4; Online Material<sup>1</sup> Table OM2). The experimental duration at which HR begins to level off represents the minimum duration required for a FSCC to achieve osmotic equilibrium with 1 bar H<sub>2</sub> at a specific T. Results show that 3, 8, 16, 36, 96, and 216 h are required for a FSCC to attain such equilibrium at 350, 300, 250, 200, 150, and 100 °C, respectively (Fig. 4).

Results of Set-II experiments were shown in Figure 5 and tabulated in Online Material<sup>1</sup> Table OM3. Each  $(P_{H_2})_{RT}$  value given is the average of three data derived from three Raman spectra collected at three different locations of a single quenched vacuumed FSCC. The hydrogen *P* at experimental *T*,  $(P_{H_2})_{T}$ , was calculated from the measured  $(P_{H_2})_{RT}$  based on Equation 1.  $\Delta P_{H_2}$  is the difference between  $(P_{H_2})_{T}$  and  $(P_{H_2})_{CSPV}$  [ $\Delta P_{H_2} = (P_{H_2})_{T} - (P_{H_2})_{CSPV}$ ]. The results show that  $(P_{H_2})_{T}$  is near the externally imposed  $(P_{H_2})_{CSPV}$  (Fig. 5).

These two sets (I and II) of experiments verified that fused silica can serve effectively as a low-T hydrogen membrane at least down to 200 °C: it reaches H<sub>2</sub> osmotic equilibrium very quickly at these low T values, and the H<sub>2</sub> pressure determined in V-FSCCs were very close to the externally imposed value, without hydrogen pressure lag existing (Hewitt 1977).

# Redox measurement or monitoring in low-T hydrothermal experiments

Redox measurement or monitoring in low-*T* hydrothermal experiments can be achieved by using a vacuumed FSCC as a hydrogen fugacity sensor. As an example, the  $f_{H_2}$  and  $f_{O_2}$  defined by Co-CoO and Ni-NiO buffers at 1000 bar and 250–400 °C were determined. The results show that equilibria between the studied solid oxygen buffers and H<sub>2</sub>O can be reached within 24 h at *T* between 250–400 °C, and steady ( $f_{O_2}$ )<sub>RT</sub> values were always present at each experimental *T* after reaching equilibrium (Figs. 6 and 7; Online Material<sup>1</sup> Tables OM4 and OM5). The log ( $f_{O_2}$ )<sub>LT</sub> values derived from measured ( $P_{H_2}$ )<sub>RT</sub> agree well with those retrieved from thermochemical data and previous literature (Fig. 8; Table 2).

The thermochemical and kinetic properties of solid oxygen buffers at elevated P-T conditions (>600 °C) have been extensively studied. However, these properties have rarely been experimentally measured at low temperatures (<450 °C); Burkhard and Ulmer (1995) evaluated the thermodynamic properties of several solid oxygen buffers at temperatures down to 300 °C at 1 atm in a dry system using a ZrO<sub>2</sub> oxygen sensor, and Kishima and Sakai (1984) and Lemke et al. (2008) measured  $f_{02}$ -T relationships of several solid buffers at a low-T range (300-500 °C) in a Dickson-type autoclave. Our experiments mimicked a realistic oxygen-buffering scenario and confirmed that equilibrium between solid buffers and H<sub>2</sub>O can be reached quickly at low T, with steady and reproducible equilibrated  $f_{02}$  values achieved at each experimental T. Therefore, we verified that the solid buffers can also be used to control  $f_{02}$  in relatively low-T hydrothermal experiments. However, considering that the leakage of H2 through the autoclave and the exhaustion of the redox buffer may happen during hydrothermal experiments, it is advisable to use a low-T redox sensor (a vacuumed FSCC, for instance) to directly measure the actual redox state of an experiment.

## Redox control in low-T hydrothermal experiments

FSCC can be used as a sample container for low-*T* hydrothermal experiments, where  $f_{\rm H_2}$  and  $f_{\rm O_2}$  can be continuously

TABLE 2.	Comparison of log $(f_{O_2})_{1,T}$ values for Ni-NiO and Co-CoO
	buffers derived from measured $H_2$ pressures at room T in
	present study and those reported previously

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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	f <sub>02</sub> ) <sub>1,T</sub>
350         -30.83 (±0.07)         -30.51         -30.65         -30           300         -34.15 (±0.13)         -33.98         -34.14         -33	.52
300 -34.15 (±0.13) -33.98 -34.14 -33	.46
	.92
250 -38.32 (±0.24) -38.12 -38.29 -38	.05
<b>Co-CoO</b> <sup>e</sup> log ( <i>f</i> <sub>O,</sub> ) <sub>1,T</sub>	
400 -28.71 (±0.03) -28.86 -28.8 <sup>3</sup> -28	.81
350 -31.89 (±0.03) -31.80 -31.74 -31	.70
300 -35.21 (±0.05) -35.25 -35.18 -35	.09
250 -39.14 (±0.10) -39.37 -39.27 -39	.13

<sup>a</sup> An average value derived from measured H<sub>2</sub> pressures at room *T* in quenched vacuumed FSCCs equilibrated with the buffer at 1000 bar and *T*. All H<sub>2</sub> pressures in vacuumed FSCCs measured at room *T* are listed in Online Material<sup>1</sup> Tables OM4 and OM5, and only those equilibrated values were used. Uncertainty is shown in parentheses and was calculated based on the method described in Online Material<sup>1</sup> Appendix C. Note that ( $f_{0_2}$ )<sub>1,T</sub> values listed are in bar.

<sup>b</sup> Calculated based on the thermodynamic data of Robie and Hemingway (1995).

<sup>c</sup> Calculated from the log  $f_{0_2}$ -*T* relationship of Huebner and Sato (1970).

<sup>d</sup> Calculated from the  $f_{0_2}$ -*T* relationship of O'Neill and Pownceby (1993).

<sup>e</sup> Calculated from the log  $f_{0_2}$ -*T* relationship of Chou (1987).



**FIGURE 4.** Diagrams showing the Raman peak height ratios between  $H_2$  and  $CO_2$  (HR) measured in quenched  $CO_2$ -FSCCs (-A and -B) after they were exposed to 1 bar of  $H_2$  external pressure at 350 °C (**a**), 300 °C (**b**), 250 °C (**c**), 200 °C (**d**), 150 °C (**e**), and 100 °C (**f**) for various durations. The error bars represent the standard deviations, and the horizontal dashed lines mark the leveling off trends of HR. (Color online.)

controlled. The  $f_{\rm H2}$  of samples sealed in FSCCs can be easily controlled by letting the FSCCs equilibrate with an externally imposed H<sub>2</sub> pressure in a CSPV at a given experimental *T* (Fig. 1). However, unlike a flexible Pt or Ag-Pd alloy capsule, FSCC is rigid, such that pressure cannot be transmitted from the external pressure medium into the sealed samples, and thus,  $f_{\rm H2O}$ , as well as  $f_{\rm O2}$ , of the samples cannot be easily controlled. Nonetheless, provided that there is always a coexisting vapor phase during an experiment, the studied sample will always be under vaporsaturated water pressures during the experiment. In this case,  $f_{\rm H2O}$  will be fixed at the specific experimental *T* (in K) by the following equation (Giggenbach 1980):

$$\log f_{\rm H_{20}} = 5.510 - 2048/T \tag{6}$$

Therefore, the  $f_{O_2}$  of the studied sample sealed in an FSCC can be defined by the externally imposed H<sub>2</sub> *P* through the formation constant of H<sub>2</sub>O.

## IMPLICATIONS

The new redox control and measurement technique presented here effectively extends the conventional double-capsule (or oxygen buffer) and Shaw membrane techniques down to 200 °C and the new technique also has its own advantages. (1) The volumes of FSCCs ( $n \times 10^{-3} \text{ mm}^3$ ) are much smaller than those of Pt or Ag-Pd alloy capsules ( $n \times 10^2$  mm<sup>3</sup>) and therefore a much shorter time is required to reach osmotic equilibrium. (2) The composition of studied samples before and after experiments can be directly measured by using Raman spectroscopic method.(3)The experimental setup is relatively simple without complex welding and soldering work. (4) Dozens of FSCCs loaded with various samples can be heated to the desired T and  $P_{\rm H_2}$  conditions at the same time. And (5) FSCCs can be used to study geologically important sulfur-bearing systems because they are inert to sulfur. This new technique has broad prospects for hydrothermal experiments conducted in the low-T regime.



**FIGURE 5.** Diagrams showing the results of Set-II experiments at 350 °C (**a**), 300 °C (**b**), 250 °C (**c**), and 200 °C (**d**). Each solid circle represents a  $(P_{H_2})_T$  value derived from measured  $(P_{H_2})_{RT}$  in a single vacuumed FSCC, and there were three vacuumed FSCCs in each experiment. Data for  $(P_{H_2})_{CSPV} = 1.5, 1.0$  and 0.5 bar experiments are marked in blue, red, and yellow, respectively. The shaded areas represent ±0.1, ±0.1, and ±0.05 bar, respectively. (Color online.)



**FIGURE 6.** Values of  $(P_{H_2})_{RT}$  measured as a function of experimental duration for Ni-NiO buffer at 400 °C (**a**), 350 °C (**b**), 300 °C (**c**), and 250 °C (**d**). Plotted are the data listed in Online Material<sup>1</sup> Table OM4. Dashed lines mark the average  $(P_{H_2})_{RT}$  values after equilibrium. Under each symbol, the log  $(f_{O_2})_{LT}$  value calculated from the corresponding  $(P_{H_2})_{RT}$  is shown. The starting materials were Ni-H<sub>2</sub>O (circles) and Ni-NiO-H<sub>2</sub>O (squares). (Color online.)



**FIGURE 7.** Values of  $(P_{H_2})_{RT}$  measured as a function of experimental duration for Co-CoO buffer at 400 °C (**a**), 350 °C (**b**), 300 °C (**c**), and 250 °C (**d**). Plotted are the data listed in Online Material<sup>1</sup> Table OM4. Dashed lines mark the average  $(P_{H_2})_{RT}$  values after equilibrium. Under each symbol, the log  $(f_{O_2})_{1,T}$  value calculated from the corresponding  $(P_{H_2})_{RT}$  is shown. The starting materials were Co-H<sub>2</sub>O (circles) and Co-CoO-H<sub>2</sub>O (squares). (Color online.)



**FIGURE 8.** Comparison of log  $(f_{O_2})_{1,T}$  values obtained in this study at various temperatures with previous data for Ni-NiO (**a**) and Co-CoO (**b**) buffers. The linear regression lines shown were derived from the data listed in Table 2. (Color online.)

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## Endnote:

<sup>1</sup>Deposit item AM-21-87687, Online Material. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2021/Aug2021\_data/ Aug2021\_data.html).