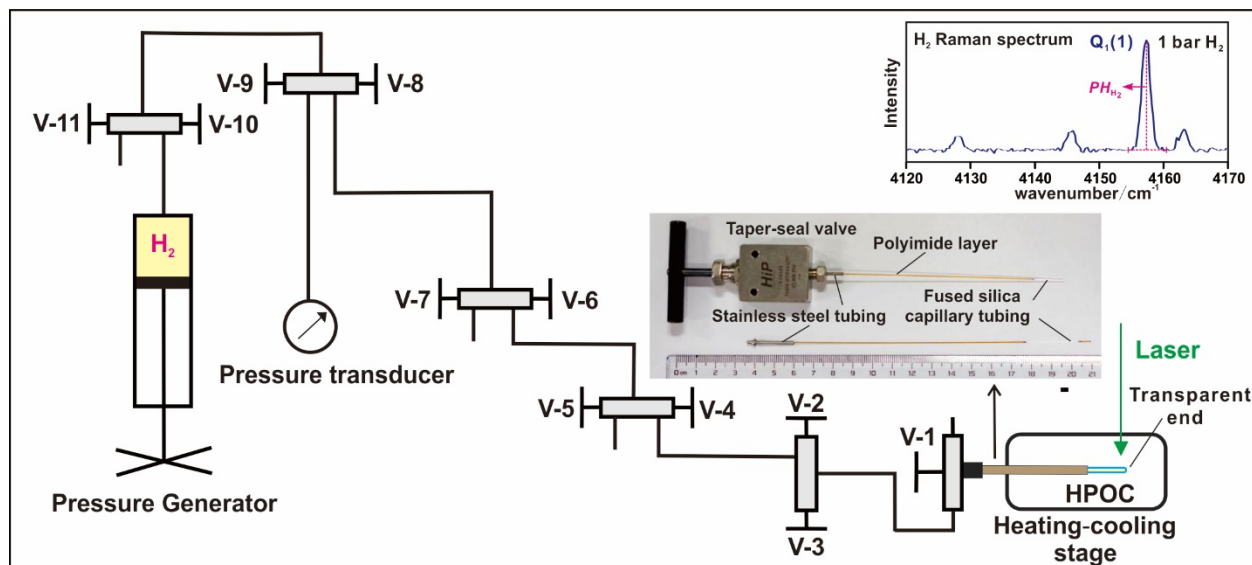# Appendix

## Appendix A. Measurement of $(P_{H_2})_{RT}$ in vacuumed FSCCs

By using a high-pressure optical cell (HPOC; Chou et al. 2005; Appendix Fig. 1), Raman spectra of vibrational bands of $H_2$ (4100–4200 cm$^{-1}$) at different pressures ($P_{H_2}$) were collected at room $T$, and the peak heights of the $Q_1(1)$ band of $H_2$ ($PH_{H_2}$) were acquired. The quantitative relationship between $PH_{H_2}$ and the corresponding $P_{H_2}$ was subsequently established through regression fitting:

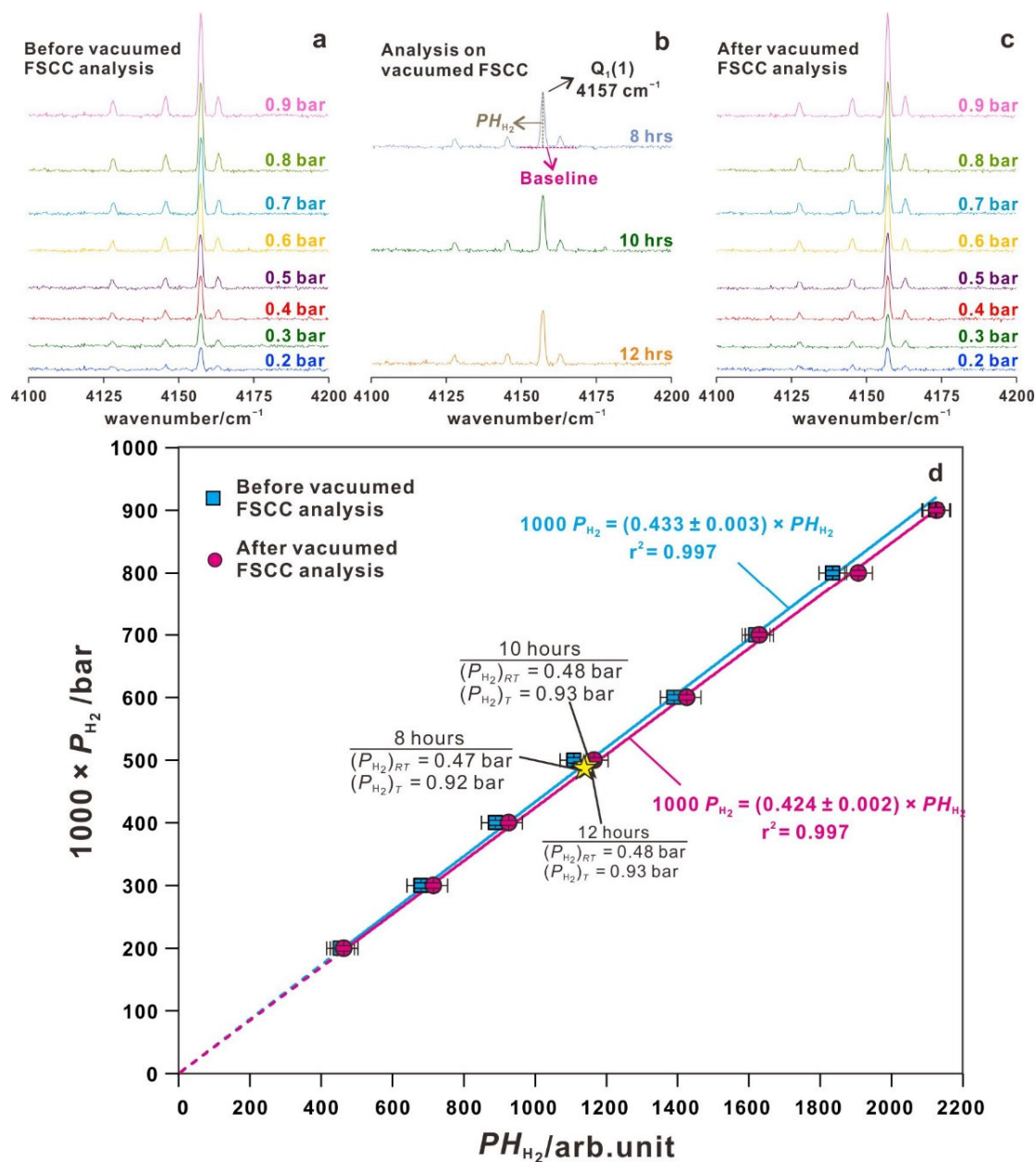$$P_{H_2} = k \times PH_{H_2} \tag{A1}$$

where $k$ is the fitting constant. The calibrated Eq. (A1) was then used to obtain the pressure of $H_2$ in a vacuumed FSCC at room $T$, $(P_{H_2})_{RT}$, from the their measured peak height, $(PH_{H_2})_{RT}$.

The HPOC (Chou et al. 2005) is a one-end sealed capillary cell, ~15 cm long, and was constructed from fused silica capillary tubing which has the same ID (100 μm) and OD (375 μm) as those in FSCC (Appendix Fig. 1). The sealed end was inserted into the sample chamber of a Linkam heating-cooling stage and the other open end was epoxied inside a stainless steel tubing through which the HPOC was connected to a pressure line (Appendix Fig. 1). Pure $H_2$ gas (>99.99 %, Jiateng Air Production Inc.) at different pressures can be introduced to the HPOC through the pressure line and their Raman spectra can be collected at the sealed, transparent end (Appendix Fig. 1). Pressures of $H_2$ were monitored by a Setra 225 digital pressure transducer (1.7 bar Full Scale, accurate to ±0.25 % FS (±0.004 bar)). Immediately before and after the analyses of a group of vacuumed FSCCs (normally eight to twelve vacuumed FSCCs), the $P_{H_2}$-$PH_{H_2}$ relationship were quantitatively calibrated.

**Appendix Figure 1**. A schematic diagram of the experimental setup for $(P_{H_2})_{RT}$ measurement. The two insets show the physical photograph of HPOC (lower) and a Raman spectrum of 1 bar $H_2$ (upper), respectively. All the valves (V) are tree-way/two-stem combination taper-seal valves from High-Pressure Equipment Co. (Cat. No. 15-15AF1).

Appendix Fig. 2 shows a case of $(P_{H_2})_{RT}$ measurements for three quenched vacuumed FSCCs after being heated at 300 °C, under 1 bar external $H_2$ pressure. Before measurements of vacuumed FSCCs, $1000P_{H_2} = (0.433 \pm 0.003) \times PH_{H_2}$ (1σ), which became $1000P_{H_2} = (0.424 \pm 0.002) \times PH_{H_2}$ after the measurements. The results show that after 8, 10 and 12 hours of $H_2$ diffusion, the $(P_{H_2})_{RT}$ values in the quenched vacuumed FSCCs are 0.47, 0.48 and 0.48 bar, and the corresponding $H_2$ pressures at the experimental $T$ of 300 °C $((P_{H_2})_T)$ are calculated to be 0.92, 0.93 and 0.93 bar, respectively, and they are very close to the externally imposed $H_2$ pressure (1 bar).
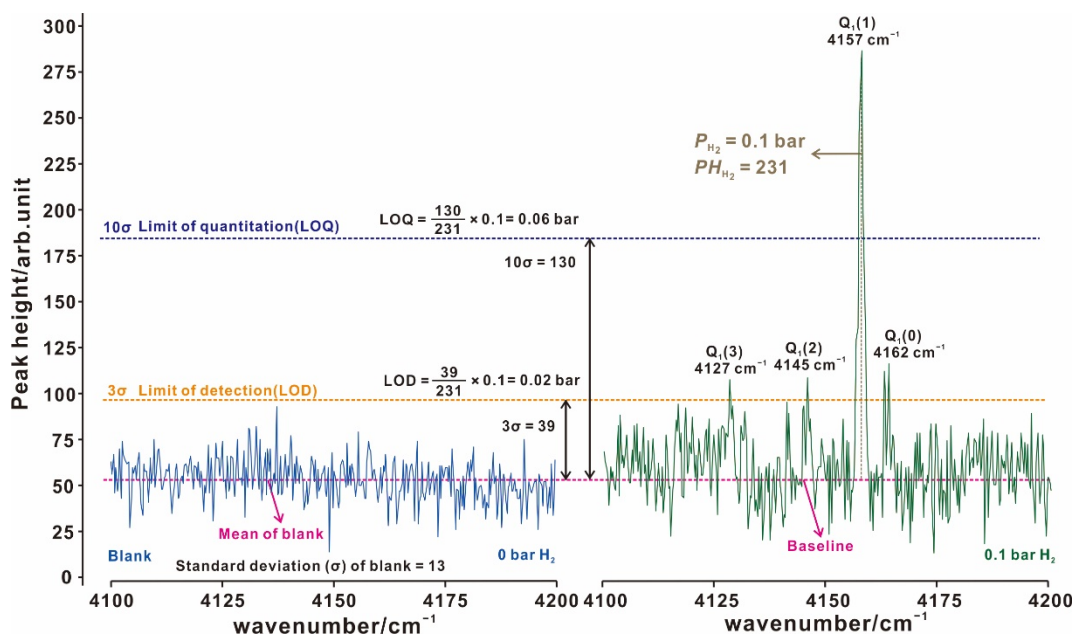
**Appendix Figure 2.** A diagram showing the results of the $(P_{H_2})_{RT}$ and $(P_{H_2})_T$ determinations of three vacuumed FSCCs after they were heated at 300 °C under 1 bar $H_2$ external pressure for 8, 10 and 12 hours. Raman spectra of vibrational bands of $H_2$ at pressures from 0.2 to 0.9 bar were collected by using a HPOC before (a) and after (c) the analyses of quenched vacuumed FSCCs (b). Based on the established quantitative relationships between $PH_{H_2}$ and $P_{H_2}$ (blue and red lines), $(P_{H_2})_{RT}$ of in quenched vacuumed FSCCs were calculated (d). Three measured $(P_{H_2})_{RT}$ values in the FSCCs (stars) are close to each other (~0.48 bar), and the calculated $H_2$ pressures at experimental $T$ of 300 ºC $((P_{H_2})_T)$ are ~0.93 bar, close to the externally imposed $H_2$ pressure of 1

bar in the CSPVs ($(P_{H_2})_{CSPV}$). The errors in $PH_{H_2}$ and $P_{H_2}$ are ±39 and ±0.004 bar, respectively (see Appendix C).

## Appendix B. Limit of detection and limit of quantitation

For a given Raman spectrometer, the limit of detection (LOD) and the limit of quantitation (LOQ) for $H_2$ in vacuumed FSCCs depend mainly on the acquisition time and the wall thickness of the FSCC, and less on the size of pinhole; longer acquisition time and thinner tube wall give lower LOD and LOQ values. FSCCs and the HPOC used in present study have the same OD (375 μm), ID (100 μm) and wall thickness (~90 μm) and 100s or 200s acquisition time were used in Raman spectra collection. Appendix Fig. 3 shows Raman spectra of 0 bar $H_2$ (blank signal) and 0.1 bar $H_2$ collected from an HPOC with 200s acquisition time. The baseline of 0.1 bar $H_2$ spectrum overlaps the mean of blank signal, and the $PH_{H_2}$ was calculated to be 231. The standard deviation (σ) of the blank signal is 13. We take "Mean + 3σ" and "Mean + 10σ" of the blank signal as the LOD and LOQ, respectively, which correspond to 0.02 bar (LOD) and 0.06 bar (LOQ).



**Appendix Figure 3.** Raman spectra of 0 bar $H_2$ (blank signal) and 0.1 bar $H_2$ (200s with two accumulation). The baseline of 0.1 bar $H_2$ spectrum was chosen to overlap the mean of the blank

signal. The standard deviation ($\sigma$) of blank signal is calculated to be 13 which gives the LOD and LOQ of 0.02 bar and 0.06 bar, respectively.

## Appendix C. Error analysis

As $(P_{H_2})_{RT}$ of vacuumed FSCCs is determined through Eq. (A1), its uncertainty is mainly determined by $k$ and $PH_{H_2}$. Based on Eq. (A1), the relative uncertainty of $P_{H_2}$, $\dfrac{\Delta P_{H_2}}{P_{H_2}}$, can be represented by

$$\frac{\Delta P_{H_2}}{P_{H_2}} = \sqrt{(\frac{\Delta k}{k})^2 + (\frac{\Delta PH_{H_2}}{PH_{H_2}})^2} \tag{A2}$$

where $\Delta k$ and $\Delta PH_{H_2}$ are the uncertainty in $k$ and $PH_{H_2}$. In present study, $\Delta PH_{H_2}$ is taken as $3\sigma$ of blank signal, *i.e.,* $\pm 39$, for all acquired $PH_{H_2}$, whereas $\Delta k$ is taken as $3\sigma$ of $k$ obtained in regression fitting ($\pm 0.009$ and $\pm 0.006$, for example, in the case shown in Appendix Fig. 2).

Combine Eqs. (1)–(4) in the main text, $\log f_{O_2}$ is related to $P_{H_2}$ through

$$\log f_{O_2} = 2\log f_{H_2O} - 2\log K_w - 2\log \frac{T}{T_{room}} P_{H_2} \tag{A3}$$

At a given $T$, $\log f_{H_2O}$, $\log K_w$ and $\dfrac{T}{T_{room}}$ are constants and uncertainty of $\log f_{O_2}$ ($\Delta \log f_{O_2}$) can be obtained through error propagation as

$$\Delta \log f_{O_2} = \frac{2}{\text{Ln}(10)} \times \frac{\Delta P_{H_2}}{P_{H_2}} = 0.869 \times \frac{\Delta P_{H_2}}{P_{H_2}} \tag{A4}$$

# Reference cited

Chou, I.M., Burruss, R. C. and Lu, W. (2005) A new optical capillary cell for spectroscopic studies of geologic fluids at pressure up to 100 MPa. In Jiuhua Chen et al., Eds., Advances in High-Pressure Technology for Geophysical Applications, p. 475–485. Elsevier, Amsterdam.