**In situ redox control and Raman spectroscopic characterisation of solutions below 300 °C**

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**Abstract**

Redox reactions often occur and significantly affect many geological processes. To simulate redox reactions in low temperature (T < 400 °C) hydrothermal experiments, fused silica was used as a hydrogen membrane to impose an externally fixed H2 pressure (P<sub>H2</sub>) on a fused silica capillary capsule (FSCC; 150 μm inner diameter, 375 μm outer diameter and ~6 mm long) to define the redox state of the sample in the FSCC. At 300 °C, it required less than 7 hours to reach osmotic equilibrium. In this study, a constant P<sub>H2</sub> was imposed on an FSCC, which originally contained a 0.5 m (mole/kg H2O) SnCl<sub>4</sub> + 0.5 m HCl aqueous solution, at 300 °C and vapour saturation pressure. In situ Raman spectra of the sample solution collected at 300 °C show that the reduction rate of Sn<sup>IV</sup> to Sn<sup>II</sup> species increased substantially with an increase of 1.1 bar of P<sub>H2</sub>. We characterised precipitation and dissolution of cassiterite under various P-T-pH-P<sub>H2</sub> conditions and greatly increased our capabilities for performing rigorous hydrothermal experiments at temperatures below 400 °C, in which redox control is difficult to ensure without *in situ* approaches.

**Introduction**

Many geological processes are affected by the redox state of the system, particularly those involving multivalent elements. To simulate these processes in laboratories, several well-established redox control techniques have been applied in hydrothermal experiments, including the double capsule (or oxygen buffer) (Eugster, 1957) and Shaw membrane techniques (Shaw, 1963). However, even after considerable refinements in the past six decades (Chou, 1987; Taylor et al., 1992; Berndt et al., 2002; Matthews et al., 2003; Alex and Zajacz, 2020), these techniques cannot be applied at low temperatures (T < 400 °C) because the precious metal hydrogen membranes that are commonly used in these techniques, such as Pt or Ag-Pd alloys, are not effective at these Ts (Chou, 1986).

To overcome this difficulty, other experimental techniques that do not require precious metal hydrogen membranes were developed (see Supplementary Information, S1). However, these methods may suffer from leakage of H2 from the autoclave, contamination by the buffer materials and possibly slow reaction kinetics of the redox buffer at low Ts. On the other hand, due to its high permeability to H2, fused silica has been adopted as a hydrogen membrane for T < 400 °C hydrothermal experiments (Chou et al., 2008; Shang et al., 2009; Fang and Chou, 2021). A vacuumed FSCC has been employed as a hydrogen fugacity (fH2) sensor, which was sealed together with a redox buffer (either Ni-NiO or Co-CoO) in an Au capsule and pressurised externally in a cold seal pressure vessel (CSPV) at 100 MPa and equilibrated between 250 and 400 °C (Fang and Chou, 2021). The H2 pressures (P<sub>H2</sub>) equilibrated at elevated P-T conditions, calculated based on the ideal gas law from the P<sub>H2</sub> values measured from quenched FSCCs at room T<sub>r</sub>, were in good agreement with those predicted from available thermodynamic data. However, *in situ* Raman spectroscopic measurements are not possible because neither Au nor CSPV are transparent. Nevertheless, this technique opens perspectives for simultaneous *in situ* measurements that will be tackled in the present study.

Before the use of optical cells (e.g., hydrothermal diamond anvil cells [HDACs], HPOCs, FSCCs), the quench method was used in most hydrothermal experiments, and the interpretation of the observed quenched products was always a great challenge, especially when non-quenchable species were involved. For example, trisulfur ion (S<sub>3-</sub>) plays important role during the hydrothermal transport and mineralisation of gold, but it is stable only at elevated P-Ts (Pokrovski and Dubrovinsky, 2011; Pokrovski and Dubessy, 2015; Pokrovski et al., 2015).

Therefore, this study proposes a new design combining HPOC and FSCC optical cells with a quantitative Raman spectroscopic analysis technique to perform *in situ* redox control.
and spectroscopic analyses for hydrothermal experiments below 300 °C. The sample is loaded in an FSCC, which is exposed to and equilibrated with H₂ at two different fixed Pₛ in an HPOC. A case study on Sn-Cl complexes using this design is also reported.

**Experimental Procedure**

A schematic diagram of the experimental setup is shown in Figure 1. Detailed descriptions of optical cell setup, sample preparation, experimental procedures, collection and processing of Raman spectra are given in SI.

**Osmotic Equilibrium and In Situ Redox Control in an FSCC**

To achieve in situ redox control in an FSCC at elevated P-T conditions, we determined the experimental duration required to reach osmotic equilibrium between the sample in an FSCC and the externally imposed H₂ pressure (P_{H₂}) in an HPOC at a fixed T. The experimental setup shown in Figure 1 was modified by replacing the solution-containing FSCC with a vacuumed FSCC (inner tube 1 in Fig. 2a) and inserting a short fused silica capillary tube with the same ID and OD as the FSCC, but with two ends open (inner tube 2 in Fig. 2a). In situ Raman spectra were collected from inner tube 1 at 300 °C, first at a P_{H₂} of 1.2 bar (0 to 470 min) and then reduced to 0.5 bar (480 to 1050 min); the representative spectra collected at 0 to 900 min are shown in Figure 2b. The peak heights of Q₁(1) vibrations of H₂ (P_{H₂}) as a function of time are shown in Figure 2c. Results show that approximately 300 minutes were required for the vacuumed FSCC to reach the externally imposed P_{H₂} of 1.2 bar, and approximately 400 minutes to achieve osmotic equilibrium when the external P_{H₂} was reduced to 0.5 bar.

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**Figure 1** A schematic diagram showing the experimental setup. The sample solution was sealed in an FSCC, which was heated to a fixed T on a heating-cooling stage (Linkam CAP500) and exposed to a fixed external P_{H₂} either during heating or after reaching the target T (see SI for details).

**Figure 2** (a) A schematic diagram (modified from Fig. 1) showing the experimental setup for testing the osmotic equilibrium between P_{H₂} in an FSCC (inner tube 1) and externally imposed P_{H₂}. (b) Representative spectra collected from inner tube 1 under an externally imposed P_{H₂} of 1.2 bar (0 to 330 min) and 0.5 bar (480 to 900 min) with the four vibrational bands of H₂ marked. (c) Peak height of the Q₁(1) vibrational band of H₂ (P_{H₂}) measured in a vacuumed FSCC (inner tube 1) at various times after being externally imposed with a P_{H₂} of 1.2 bar (black dots) and then 0.5 bar (red triangles). The values of P_{H₂} measured from inner tube 2 are shown by squares at 1.2 and 0.5 bar.
Schmidt (2018, and references therein) showed that Sn-Cl complexes in hydrothermal solutions have characteristic Raman spectra for species with Sn in either the $^{\text{+2}}$ (SnII) or $^{\text{+4}}$ (SnIV) valence state. To demonstrate the current in situ redox control technique, a 0.5 m (mole/kg H$_2$O) SnCl$_4$ + 0.5 m HCl solution was sealed in an FSCC together with a vapour phase and exposed to a $P_{H_2}$ of 0.2 bar in an HPOC after being heated to 300 °C (Fig. 1). Raman spectra of the solution were collected in situ under vapour saturation conditions as time elapsed from 0 to 156 hr (Fig. 3a).

The results show that all of the Sn was in the SnIV state at the beginning, and the amount of SnII species increased slowly with time up to 156 hr; at least 276 hr is needed to reach the reaction equilibrium (Figs. S-3, S-7). However, when the external $P_{H_2}$ in the HPOC was increased to 1.3 bar, almost all of the SnIV were converted to SnII species within 48 hours (Fig. 3b); the tail around 321 cm$^{-1}$ in the 48 hr spectrum may indicate a minor amount of remaining SnIV. Figure 4 shows in situ Raman spectra collected at various $T$s (30 to 300 °C) from an aqueous solution under vapour saturated pressures and an external $P_{H_2}$ of 0.2 bar. For details see SI.

Deconvolution of Raman bands of SnII & IV-Cl complexes collected at 30 °C before and after heating and reduction. Due to uncertain $T$ effects on Raman shift for different SnII & IV-Cl complexes, two spectra collected from the second FSCC sample solution at a constant temperature of 30 °C after being exposed to (a) a $P_{H_2}$ of 0.2 bar and then (b) a $P_{H_2}$ of 1.3 bar for various durations (shown in hours). The spectrum taken at 0 hr in (b) is the same spectrum taken at 156 hr in (a). According to Schmidt (2018), the major SnIV species was [SnIVCl$_5$(H$_2$O)${}^-$], which was reduced slowly to the SnII species, [SnIICl$_3$], under a $P_{H_2}$ of 0.2 bar, as shown in (a), and then quickly under a $P_{H_2}$ of 1.3 bar, as shown in (b). Each spectrum was collected for 200 s with 3 accumulations. The vertical gray lines were taken from Schmidt (2018), showing Raman peak positions of various Sn-Cl species at ambient P-T conditions.

Figure 3  In situ Raman spectra of a 0.5 m SnCl$_4$ + 0.5 m HCl solution (300 °C) in an FSCC under vapour saturated pressure after being exposed to (a) a $P_{H_2}$ of 0.2 bar and then (b) 1.3 bar for various durations (shown in hours). The spectrum taken at 0 hr in (b) is the same spectrum taken at 156 hr in (a). According to Schmidt (2018), the major SnIV species was [SnIVCl$_5$(H$_2$O)${}^-$], which was reduced slowly to the SnII species, [SnIICl$_3$], under a $P_{H_2}$ of 0.2 bar, as shown in (a), and then quickly under a $P_{H_2}$ of 1.3 bar, as shown in (b). Each spectrum was collected for 200 s with 3 accumulations. The vertical gray lines were taken from Schmidt (2018), showing Raman peak positions of various Sn-Cl species at ambient P-T conditions.

### Advantages of In Situ Observation and Raman Spectroscopic Characterisation

In situ observations show that the initial sample solution (0.5 m SnCl$_4$ + 0.5 m HCl) was a homogeneous solution at 25 °C,
presumably consisting mainly of Sn-Cl complexes and other unknown species, and they were saturated with respect to cassiterite at 125 °C (Fig. S-1a). However, the cassiterite precipitate could not be detected after being heated at 300 °C under an external pressure of 0.2 bar for 72 hours (Fig. S-1h), indicating that the formation and stabilisation of SnII & IV-Cl complexes (and also the increase in acidity) increase the solubility of the cassiterite. These SnII & IV-Cl complexes are still present after quenching (Fig. S-4b), and no cassiterite precipitation occurred during or after quenching. Even though these SnII & IV-Cl complexes are quenchable, there is no guarantee that the proportions of these complexes remain the same. In contrast to the use of the conventional quench method for the study of cassiterite solubility, the coexistence of SnII and SnIV complexes and their quantities equilibrated at a specified P-T-pH-\(P_{H_2}\) experimental condition can be identified using our in situ method, when quantitative Raman spectroscopic analysis technique is eventually developed, such that the chemical equation for the dissolution of cassiterite in hydrothermal solutions can be correctly expressed.

### Conclusions

Here we present an experimental technique for in situ redox control and Raman spectroscopic characterisation of complexes (i.e. SnII & IV-Cl interactions) in vapour saturated aqueous solutions. We demonstrated that the (a) time required to reach osmotic equilibrium for \(H_2\) across the fused silica membrane is shorter than that for chemical equilibrium between SnII and SnIV, (b) a 0.5 m SnCl4 + 0.5 m HCl solution was saturated with respect to cassiterite (SnO2) between 125 and 300 °C, before the species in the solution were converted to stable SnII & IV-Cl complexes under an externally imposed \(P_{H_2}\) of 0.2 bar, and (c) the reduction rate from SnIV-Cl to SnII-Cl complexes at 300 °C under a \(P_{H_2}\) of 0.2 bar (equivalent to NNO buffer) was slow, but the rate increased substantially when \(P_{H_2}\) increased to 1.3 bar (equivalent to FMQ buffer). These findings are critical for the construction of a sound Sn mineralising mechanism. Furthermore, by using in situ Raman spectroscopic characterisation of the sample in an FSCC under a fixed P-T and redox state, we avoided the possible quench effects on the distribution of dissolved species and greatly increased our capabilities of performing rigorous hydrothermal experiments involving redox reactions at low temperatures, possibly even down to 200 °C (Fang and Chou, 2021).

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### Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2135.

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