

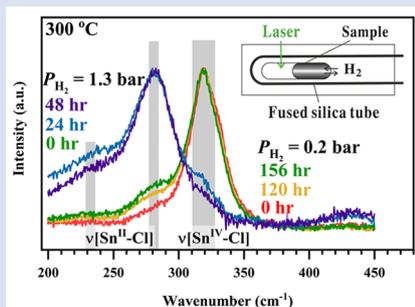
In situ redox control and Raman spectroscopic characterisation of solutions below 300 °C

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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 H_2 pressure (P_{H_2}) 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_{H_2} was imposed on an FSCC, which originally contained a 0.5 m (mole/kg H_2O) $SnCl_4 + 0.5 m$ 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^{IV} to Sn^{II} species increased substantially with an increase of 1.1 bar of P_{H_2} . We characterised precipitation and dissolution of cassiterite under various P - T - pH - P_{H_2} 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.

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Introduction

Many geological processes are affected by the redox state of the system, particularly those involving multivalence 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 T s (Chou, 1986).

To overcome this difficulty, other experimental techniques that do not require precious metal hydrogen membranes were developed (see Supplementary Information, SI). However, these methods may suffer from leakage of H_2 from the autoclave, contamination by the buffer materials and possibly slow reaction kinetics of the redox buffer at low T s. On the other hand, due to its high permeability to H_2 , 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 (f_{H_2}) 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 H_2 pressures (P_{H_2}) equilibrated at elevated P - T conditions, calculated based on the ideal gas law from the P_{H_2} values measured from quenched FSCCs at room T , 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_3^{2-}) plays important role during the hydrothermal transport and mineralisation of gold, but it is stable only at elevated P - T s (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

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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 P_s 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_{H_2}) 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_{H_2} 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 (PH_{H_2}) 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_{H_2} of 1.2 bar, and approximately 400 minutes to achieve osmotic equilibrium when the external P_{H_2} was reduced to 0.5 bar.

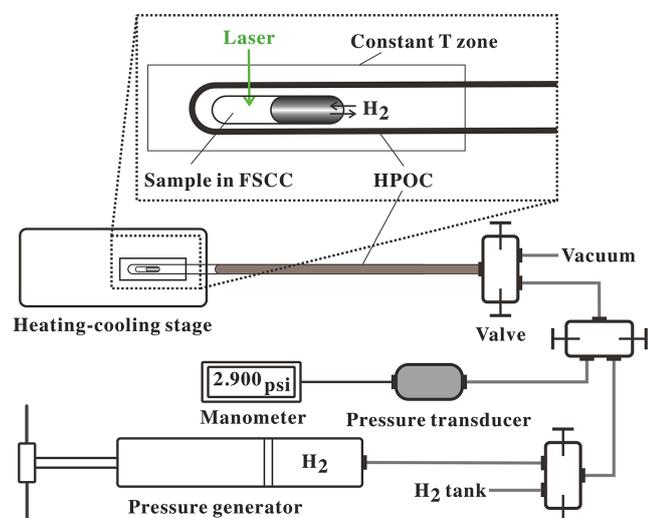


Figure 1 A schematic diagram showing the experimental setup. The sample solution was sealed in an FSCC, which was heated to a fixed T on a heating-cooling stage (Linkam CAP500) and exposed to a fixed external P_{H_2} either during heating or after reaching the target T (see SI for details).

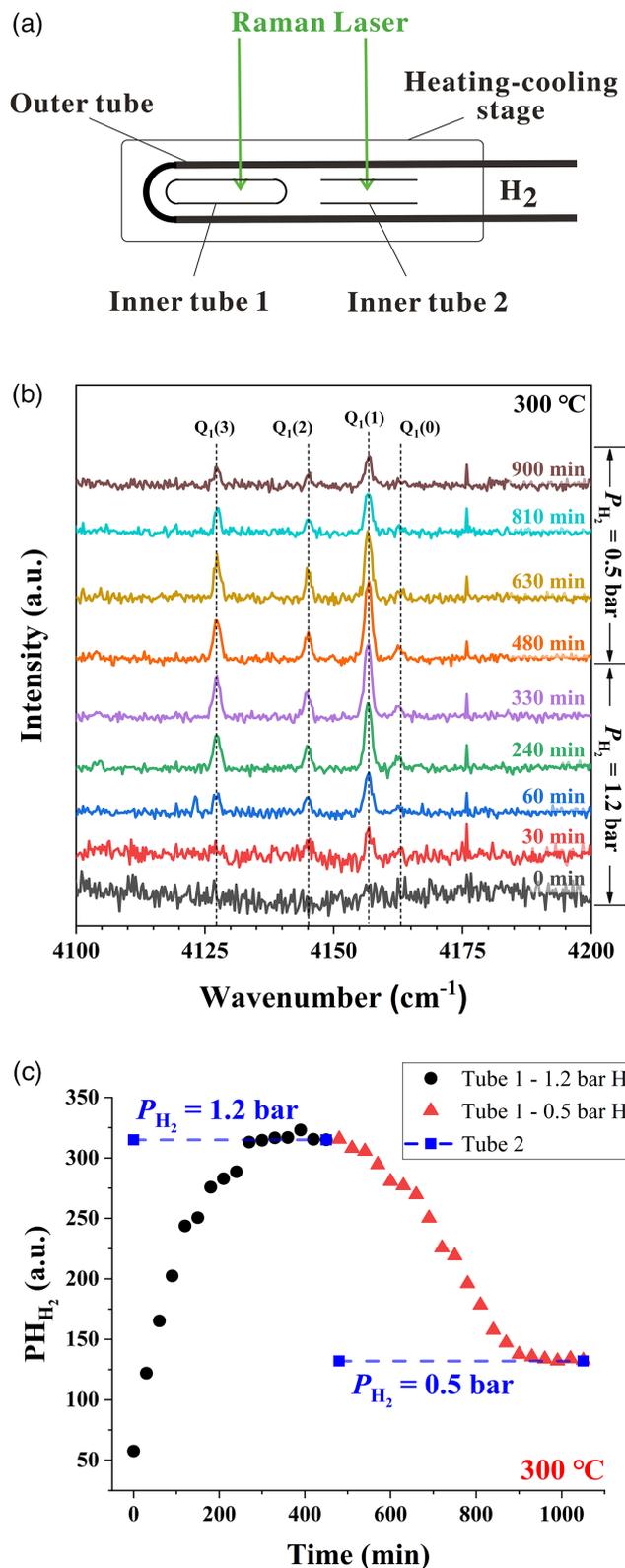


Figure 2 (a) A schematic diagram (modified from Fig. 1) showing the experimental setup for testing the osmotic equilibrium between P_{H_2} in an FSCC (inner tube 1) and externally imposed P_{H_2} . (b) Representative spectra collected from inner tube 1 under an externally imposed P_{H_2} of 1.2 bar (0 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 (PH_{H_2}) measured in a vacuumed FSCC (inner tube 1) at various times after being externally imposed with a P_{H_2} of 1.2 bar (black dots) and then 0.5 bar (red triangles). The values of PH_{H_2} measured from inner tube 2 are shown by squares at 1.2 and 0.5 bar.

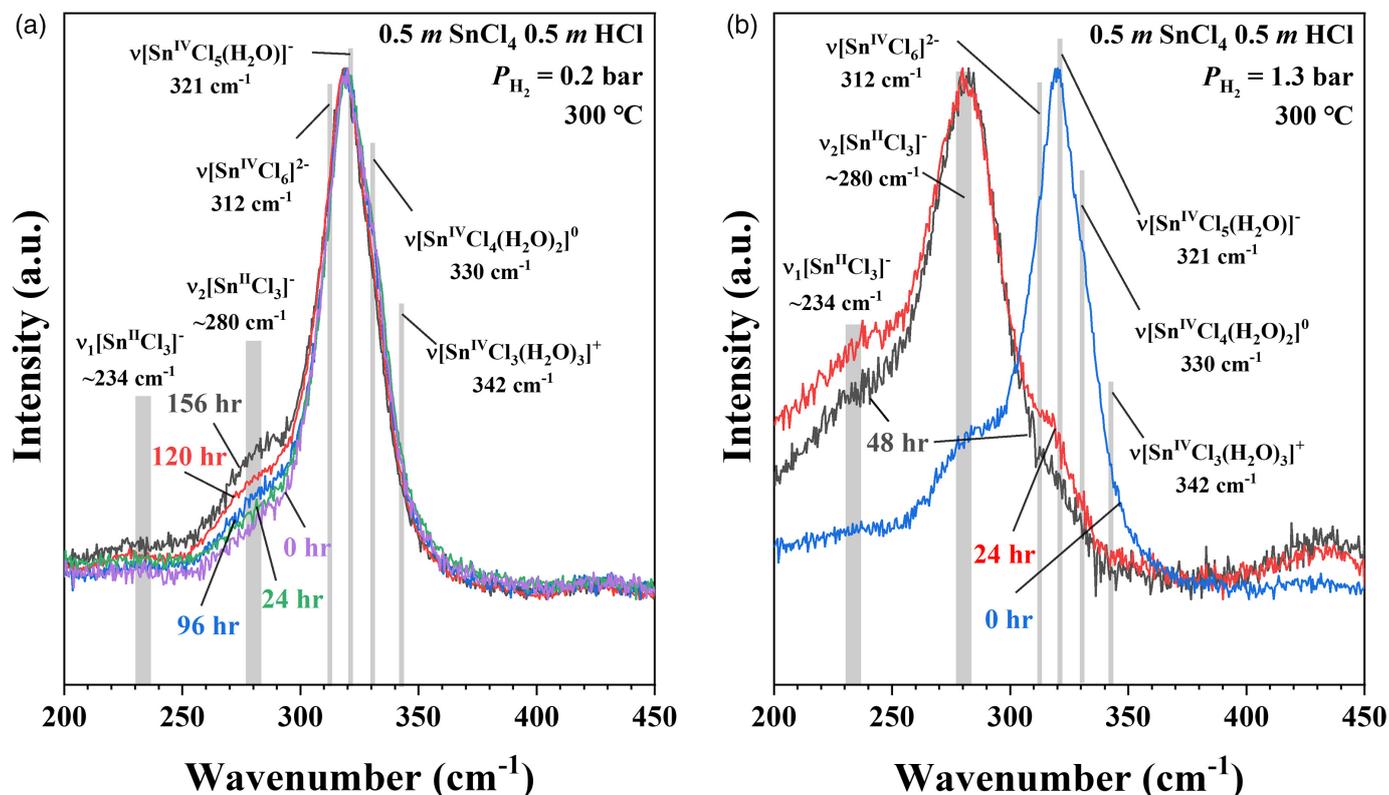


Figure 3 *In situ* Raman spectra of 0.5 m SnCl₄ + 0.5 m HCl solution (300 °C) in an FSCC under vapour saturated pressure after being exposed to (a) a P_{H_2} of 0.2 bar and then (b) 1.3 bar for various durations (shown in hours). The spectrum taken at 0 hr in (b) is the same spectrum taken at 156 hr in (a). According to Schmidt (2018), the major Sn^{IV} species was [Sn^{IV}Cl₅(H₂O)]⁻, which was reduced slowly to the Sn^{II} species, [Sn^{II}Cl₃]⁻, 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.

Application to the Investigation of Hydrothermal Sn Species

Schmidt (2018, and references therein) showed that Sn-Cl complexes in hydrothermal solutions have characteristic Raman spectra for species with Sn in either the +2 (Sn^{II}) or +4 (Sn^{IV}) valence state. To demonstrate the current *in situ* redox control technique, a 0.5 m (mole/kg H₂O) SnCl₄ + 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 Sn^{IV} state at the beginning, and the amount of Sn^{II} 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 Sn^{IV} were converted to Sn^{II} species within 48 hours (Fig. 3b); the tail around 321 cm⁻¹ in the 48 hr spectrum may indicate a minor amount of remaining Sn^{IV}. 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 Sn^{II}&IV-Cl complexes collected at 30 °C before and after heating and reduction. Due to uncertain T effects on Raman shift for different Sn^{II}&IV-Cl complexes, two spectra collected from the second FSCC sample solution at a constant temperature of 30 °C were selected for processing, in order to evaluate the contributions of different Sn-Cl complex

species to the Raman bands before and after heating and reduction. Results were shown in Figure S-4; for details see SI.

Chemical vs. osmotic equilibrium. Our experimental results at 300 °C indicate that reaching chemical equilibrium in the Sn-H-Cl system requires a much longer time than that for the osmotic equilibrium for H₂ across the fused silica membrane (Figs. 2, 3). However, this conclusion is system specific and may not be valid for (a) other chemical systems, (b) the use of FSCC with different dimensions (*i.e.* OD, ID and length), or (c) other P - T experimental conditions. Therefore, more testing is required when applying this method.

The presence of unknown Sn^{IV} species between 30 and 75 °C. Figure S-5 shows that, at a constant T between 30 and 75 °C, the intensities of Raman spectroscopic band of Sn^{IV}-Cl species collected from an aqueous solution in an FSCC-containing 0.8 m SnCl₄ + 0.5 m HCl + 0.8 m NaCl during heating (blue) are lower than those collected during cooling (red). This may result from the presence of unknown Sn^{IV} species. For details, see SI.

Reduction kinetics of Sn^{IV}-Cl to Sn^{II}-Cl complexes at 300 °C. The reduction reaction of Sn^{IV}-Cl to Sn^{II}-Cl complexes at 300 °C under externally imposed P_{H_2} of 0.2 bar can be described by Eq. S-1, and the details on the derivation of reaction rate constant are given in SI.

Advantages of *In Situ* Observation and Raman Spectroscopic Characterisation

In situ observations show that the initial sample solution (0.5 m SnCl₄ + 0.5 m HCl) was a homogeneous solution at 25 °C,

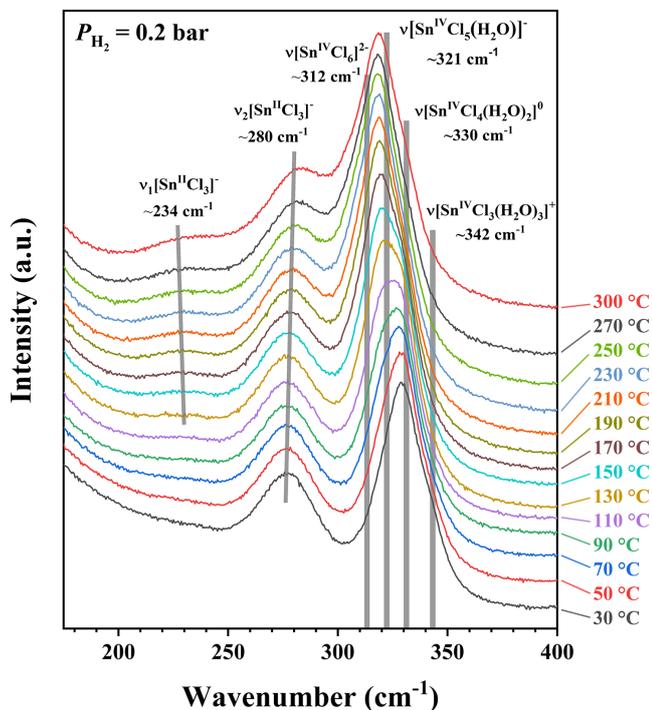


Figure 4 *In situ* Raman spectra collected at various T s (30 to 300 °C) from an aqueous solution under vapour saturated pressures and an externally imposed P_{H_2} of 0.2 bar. The sample initially contained 0.5 *m* SnCl_4 and 0.5 *m* HCl in an FSCC and was quenched from 300 °C after being kept at that T for 311 hr. Each spectrum was collected after the sample was kept at the specified T for at least 10 minutes, which were long enough for reaching equilibrium. The vertical gray lines were taken from Schmidt (2018), showing Raman peak positions of various Sn-bearing species at ambient P - T conditions.

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 P_{H_2} of 0.2 bar for 72 hours (Fig. S-1h), indicating that the formation and stabilisation of $\text{Sn}^{\text{II}} \& \text{IV}$ -Cl complexes (and also the increase in acidity) increase the solubility of the cassiterite. These $\text{Sn}^{\text{II}} \& \text{IV}$ -Cl complexes are still present after quenching (Fig. S-4b), and no cassiterite precipitation occurred during or after quenching. Even though these $\text{Sn}^{\text{II}} \& \text{IV}$ -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 Sn^{II} and Sn^{IV} 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.* $\text{Sn}^{\text{II}} \& \text{IV}$ -Cl interactions) in vapour saturated aqueous solutions. We demonstrated that (a) the time required to reach osmotic equilibrium for H_2 across the fused silica membrane is shorter than that for chemical equilibrium between Sn^{II} and Sn^{IV} , (b) a 0.5 *m* SnCl_4 + 0.5 *m* HCl solution was saturated with

respect to cassiterite (SnO_2) between 125 and 300 °C, before the species in the solution were converted to stable $\text{Sn}^{\text{II}} \& \text{IV}$ -Cl complexes under an externally imposed P_{H_2} of 0.2 bar, and (c) the reduction rate from Sn^{IV} -Cl to Sn^{II} -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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