

Quantitative Raman Spectroscopic Techniques for Monitoring Hydrogen Pressure and Oxygen Fugacity in Optical Cells

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Accurate control and measurement of oxygen fugacity are fundamental in experimental geochemistry and petrology simulating redox-sensitive geological processes. Traditional methods, including metal-metal oxide buffers and electrochemical techniques, have significantly advanced research in magma evolution, petrogenesis, ore formation, and hydrothermal processes. However, these methods face limitations such as restricted temperature ranges, slow equilibration, and the inability to provide real-time in situ observations.

This study integrates high pressure–temperature optical cells—such as fused silica capillaries and hydrothermal diamond anvil cells equipped with fused silica and diamond windows, respectively—with in situ Raman spectroscopy to enable real-time redox monitoring in hydrothermal experiments.

In these experiments, oxygen fugacity of the sample can be obtained through the quantitative measurement of hydrogen pressure, using a calibration line that correlates hydrogen pressure with Raman intensity of the hydrogen $Q_1(1)$ band (Fig. 1). By optimizing hydrogen pressure control and assessing redox buffer performance, we refine the accuracy of oxygen fugacity quantification under hydrothermal conditions [2]. Our findings demonstrate the feasibility of precise redox control in both low- (≤ 450 °C) and high-temperature hydrothermal experiments, enhancing simulations of natural fluid-rock interactions. These results provide new insights into redox-dependent mineral transformations, element mobility, and metal transport, with implications for ore deposition, hydrothermal alteration, and deep-sea vent geochemistry.

Fig. 1. Peak height of the $Q_1(1)$ Raman band for H_2 collected at room temperature ($PH_{hydrogen-rt}$) and different pressures through diamond (black dot) and fused silica (red dot) windows (modified after Fig. 2 of [2]). The dashed linear regression lines are calibration lines for quantitative determination of hydrogen pressures of samples in the optical cells from measured $PH_{hydrogen-rt}$. Similar calibration lines can be established for optical cells with fused silica window at elevated temperatures up to 500 °C. Notable, these calibration lines are system dependent, usually established right before and/or after each experiment to ensure accuracy.

References

- [1] Chou, I.M. et al. (2021). *Geochemical Perspectives Letters*, **20**, 1–5.
- [2] Wang, R.H. & Chou, I.M. (2023). *Chemical Geology*, **636**, 121649.

