

Quantitative *in situ* Raman spectroscopy investigation on HSO_4^- dissociation at high pressures (up to 420 MPa) and its geological implication

HAO CUI AND RICHEN ZHONG

University of Science and Technology Beijing

Sulfate-bearing hydrothermal fluids are widespread in crustal environments, and recent papers highlight a possible important role of sulfate as an agent for mass and electron transfers in subduction zone. The geochemical characters of sulfate-bearing fluids (e.g., ability of complexing with ore-forming elements) depend largely on the dissociation behavior of HSO_4^- . However, the dissociation of HSO_4^- was only investigated at vapor saturation pressures and the pressure dependence of the dissociation behavior is thus unclear. In this study, we modified the fused silica capillary capsule (FSCC) method to explore the dissociation behavior of HSO_4^- quantitatively via *in situ* Raman spectroscopy experiments. We designed a new heating stage that can accommodate a 7 cm-long FSCC, and we show that thick-walled FSCCs with high degrees of filling can withstand pressures up to 645 MPa at temperatures to 450 °C. The sulfate concentrations in $\text{Cs}_2\text{SO}_4\text{--H}_2\text{SO}_4$ solutions were measured using Raman spectroscopy with increasing pressures and temperatures ($P\text{--}T$). The sulfate concentrations were calibrated using Cs_2SO_4 solutions with known concentrations, and the concentrations of HSO_4^- were determined by mass balance. According to our experimental results, increasing pressure increases the dissociation of HSO_4^- into SO_4^{2-} and H^+ while increasing temperature promotes ion association, which means that HSO_4^- dissociation is favored in high-density fluids. Comparisons between our experimental results with those of thermodynamic predictions using currently available thermodynamic properties indicate that the dissociation of HSO_4^- is stronger than previously thought in high-density fluids, especially at high pressures. We then optimized the thermodynamic properties of HSO_4^- based on our experimental results, and used them to simulate the S(VI) speciation in slab-derived fluids. Similar with our experimental results, the simulations also predict that the HSO_4^- will largely dissociate into SO_4^{2-} and H^+ in fluids with high $P\text{--}T$ conditions, causing the SO_4^{2-} as the predominant S(VI) speciation in subduction zone.