

In-situ Raman spectroscopic investigation of nitrogen speciation in hydrothermal fluids

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Nitrogen has multiple valence states and is the most abundant volatile component in the atmosphere. Nitrogen speciation in hydrothermal fluids is crucial for understanding the evolution of the atmosphere and global nitrogen cycling. A recent study quantified the proportions of NH_3 and N_2 in fluid inclusions quenched from 600–1400°C, 0.2–3.5 GPa, and a range of redox states [1]. However, it is questionable whether the measured speciation faithfully reflects the equilibrium speciation at experimental conditions. We hence carried out in situ Raman spectroscopic investigation of nitrogen speciation in N-H-O fluids in a hydrothermal diamond anvil cell. Hydroxylamine (NH_2OH) solutions (12 to 50 wt%) were used as the starting material. In the absence of a catalyst, upon heating the solution decomposed stoichiometrically to produce equivalent amount of NH_3 and N_2 . But when Pt powder was added as a catalyst, we observed a marked increase in N_2 band intensity and a decrease in NH_3 band intensity above 600°C (Fig. 1). The obtained data series of $\text{N}_2/\text{H}_2\text{O}$ ratio vs. $\text{NH}_3/\text{H}_2\text{O}$ at $T > 600^\circ\text{C}$ yield a slope of about -0.5, further confirming the conversion of NH_3 to N_2 . The inferred $\text{H}_2/\text{H}_2\text{O}$ ratio was used to constrain the intrinsic oxygen fugacity of the system and the equilibrium constant of the reaction $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$. Our preliminary results appear to be consistent with the equilibrium constant obtained from the quench method [1].

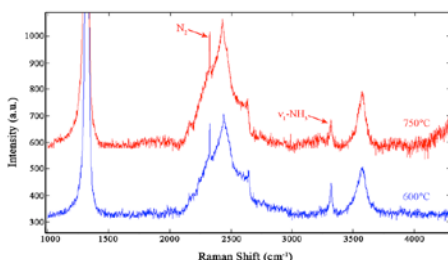


Figure 1: Raman spectra of N-H-O fluid (normalized to the same H_2O band intensity).

[1] Li Y & Keppler H (2014), *Geochimica et Cosmochimica Acta* **129**, 13-32.