

Stability of uranyl-carbonate complexes at 25-150 °C

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Aqueous speciation is one of the main factors that controls the ability of hydrothermal fluids to transport, disseminate, and concentrate uranium in natural systems. Uranyl-carbonate species have long been considered one of the main vehicles of uranium transport in such systems. This conclusion has been drawn primarily based on the observation of extremely high stability of uranyl-carbonate complexes at ambient conditions. However, our recent experiments [1] have demonstrated that the stability of these carbonate complexes is drastically decreased with increasing temperature – their role as a complexing ligand becomes almost insignificant at temperatures above 150°C. Thus, at temperatures between 25 – 150 °C, the uranyl-carbonate systems undergo large changes shifting from a state where these complexes predominate in solution to one where they effectively play no key role in the hydrothermal transport of uranium. These changes are still not quantified in the form of reaction stability parameters, precluding modeling of the speciation behavior of uranium in hydrothermal systems.

Here we report results of *in situ* spectroscopic studies of uranyl-carbonate systems at 25 - 150 °C. The experiments were performed using both Raman and UV-vis spectroscopic techniques. The Raman spectroscopy experiments were performed using sealed quartz tubes with NaHCO₃ solutions (pH (25 °C)= 7 to 8) containing 0.1 molal of dissolved U. These data were used to evaluate the stepwise formation constants for UO₂(CO₃)₂²⁻ → UO₂(CO₃)₃⁴⁻ transition. The UV-vis experiments were performed using the high-*T* flow-through cell with acidic solutions (pH(25 °C) = 1 to 3.8) with a U concentration of 0.05 molal and saturated with carbonate at pCO₂ up to 200 bars to induce the formation of uranyl-carbonate complexes. These data were used to derive the cumulative formation constants (β) for UO₂CO₃⁰ and UO₂(CO₃)₂²⁻ complexes. The experimental data permits evaluation of the decrease in the stability of uranyl-carbonate complexes with increasing temperature, and can be used for modeling of the behavior of U in carbonate-bearing hydrothermal systems.

[1] Kalintsev et al (2021) Uranium carbonate complexes demonstrate drastic decrease in stability at elevated temperatures. Commun. Chem. 4, 1–8.