Uranyl speciation up to 250 ºC in near-neutral to basic solutions: The carbonate – hydroxy interplay

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In hydrothermal systems, be they ore deposits or radiogenically heated groundwaters around nuclear waste repositories, uranium is typically most mobile in its hexavalent oxidation state. In this state, it invariably manifests as the uranyl (UO_2^{2+}) ion which in turn readily complexes with a range of inorganic ligands (e.g. Cl^-, SO_4^{2-}, OH^-, CO_3^{2-}, F^-). The formation of these complexes is a first order control on the mobility of uranium in these hydrothermal systems.

Until very recently, the determination of formation constants for uranyl complexes at elevated temperatures has had to rely upon extrapolations of room temperature data. Given the typically poor accuracy of these extrapolations, any thermodynamic models hoping to describe the movement of uranium through hydrothermal systems are likely to be dubious at best. Recent efforts have ameliorated this somewhat by experimentally determining the formation constants for uranyl chloride and sulfate complexes, however these complexes are only relevant under acidic (pH <4) conditions.

Under near-neutral to basic pH conditions which are relevant for some hydrothermal uranium-bearing ore deposits[1] and carbonate buffered groundwaters (such as might be found around geological nuclear waste repositories) uranyl mobility is controlled by hydroxy and carbonate complexes - for which (until now) no experimental data existed at high temperatures.

Here, we will present the results of high temperature solubility and X-ray absorption spectroscopy (XAS) experiments performed to determine the structures, stoichiometries and formation constants of the most geologically relevant uranyl hydroxy and carbonate complexes.

[1] Ondruš, P., Veselovsky, F., Gabašová, A., Drábek, M., Dobeš, P., Malý, K., Hloušek, J., Sejkora, J. (2003) *Journal of the Czech Geological Society* **48**, 157-192