U distribution and speciation in Fe-bearing alteration minerals at the McArthur River U-deposit

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The unconformity-related U-deposits of the Athabasca Basin represent an increasingly important energy resource (18% world's U-reserves) [1] and have been used as natural analogues for the deep geological disposal of radioactive waste products [2]. Since these deposits serve as large-scale natural records of U redox reactions, understanding their formation will contribute to reducing U mobility around contaminated environments. Multiple alteration and uranium mineralization events occurred throughout the basin's history [3] however the role of authigenic, diagenetic and hydrothermal alteration minerals in the reduction of uranium and subsequent precipitation of uraninite is not well understood. Graphite and various other organic compounds have been proposed as possible solid phase reductants [4] but more recent studies suggest the oxidation of Fe in alteration minerals may have played a role in the reduction of U in the Athabasca Basin [5]. In order to better understand the relationship between Fe and U, synchrotron based µXRF and µXAS experiments were conducted on altered and relatively unaltered samples from the McArthur River deposit using the VESPERS beamline at the Canadian Light Source. The distribution of Fe and U as well as other trace elements were determined by collecting µXRF element distribution maps on specific Fe-bearing alteration minerals. XANES and EXAFS spectra were measured on Fe-bearing clay and sulfide minerals, which were selected on the basis of their paragenesis, U concentrations and their proximity to the ore zone. The oxidation states of Fe and U were determined by measuring U LIII and Fe Kα absorption edges and in some cases EXAFS was used to further determine the speciation of U. Results indicate the distribution of U is closely related to that of Fe in proximity to the ore zone but become inversely related with increasing distance away from the ore zone. Variations in the shape of the Fe Kα pre-edge as well as the edge location, measured on similar phases, were attributed to changes in oxidation states. Least altered samples contained abundant reduced Fe and negligible U whereas higher uranium concentrations, and mixed Fe and U oxidation states were observed in altered samples. This study further suggests that Fe-bearing minerals played an important role in the redox processes involved in the formation of the McArthur River U deposit.

[1] Thomas *et al.* (2000) *Geol.Soc.Nevada Symp Proc.*, **1,** 103-126 [2] Burns (1999) *Rev.in Min.*, **38**, 23-90 [3] Alexandre *et al.* (2009) *Mineral. Dep.*, **44**, 41-59 & ref. therein. [4] Kyser *et al.* (1989) *Can.Jour.Earth Sci.,* **26**, 490-498 [5] Alexandre *et al.* (2004) *Tectonics,* **23(5)**

Proton and metal adsorption onto oxidized graphene

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Oxidized graphene is produced from the chemical or mechanical exfoliation of oxidized graphite, and the resulting particles exhibit distinct physical, electrical, and thermal properties ideal for use in advanced materials, sensors, and transistors. The increasing utility of these materials suggests a strong likelihood for current and future environmental releases, and it will be important to understand the interactions between these particles and other environmental constituents. For example, due to a relatively high surface area to mass ratio and the presence of a variety of proton-active function groups, oxidized graphene may significantly influence the partitioning of metals via adsorption in environments where they exist. However, the surface chemistry and reactivity of oxidized graphene are poorly characterized. In order to construct quantitative surface complexation models of the effects of oxidized graphene adsorption on the distribution of metals in geologic systems, stability constants for the important oxidized graphene surface complexes must be determined. Hence, the objective of this study was to evaluate the capacity of oxidized graphene to adsorb protons and metals via potentiometric titrations and batch adsorption studies, respectively. Target metals included Cd, Pb, Ca, and U, and all adsorption studies were conducted over a wide pH range of approximately 2 to 10 in 0.1 M $NaClO_4$ solutions to buffer ionic strength. The potentiometric titration data indicate that oxidized graphene exhibits proton adsorption over a wide range of pH, and the data constrain the pKa values and site concentrations of the binding sites on the oxidized graphene surface. The batch metal adsorption measurements indicated extensive and strong adsorption of metals by oxidized graphene particles, with increasing adsorption with increasing pH. The pH dependence is consistent with measurements of electrochemical surface properties that indicate a more negative ζ-potential at higher pH values. Using the proton-active site concentrations determined from the potentiometric titrations, the metal adsorption data enable us to determine the thermodynamic stability constants for each of the important surface complexes. Through comparison of these stability constants to those for other environmental surfaces, we consider the propensity of oxidized graphene to influence the distribution of metals in natural and engineered systems.