

# The solubility, speciation, and transport of the high field strength elements (HFSE) niobium, tantalum, and uranium

A Timofeev<sup>1</sup>, AA Migdisov<sup>2</sup>, AE Williams-Jones<sup>1</sup>, R Roback<sup>2</sup>, A Nelson<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, McGill University, Montréal, Quebec; <sup>2</sup>Earth and Environmental Division, Los Alamos National Laboratory, Los Alamos, New Mexico, U.S.A.;

<sup>3</sup>Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico, U.S.A.;

The high field strength elements (HFSE) are considered to be immobile in many geochemical, hydrothermal fluid-bearing environments. Niobium is often used as a reference element, against which the mobility of other elements is compared, tantalum, the geochemical "twin" of niobium, is assumed to be equally difficult to transport, and uranium, known to be highly mobile in oxidizing environments, is deemed to be immobile in reducing systems. Through the use of field-based and experimental studies we have evaluated the actual mobility of these metals. The behaviours of niobium and tantalum in a pervasively hydrothermally altered setting were first described in the Nechalacho rare metal deposit situated in the Northwest Territories of Canada. Niobium and tantalum were found to be hosted in zircon, columbite-(Fe), fergusonite-(Y), uranopyrochlore and samarskite-(Y) with a genetic model incorporating the magmatic crystallization of these minerals followed by a hydrothermal overprint proposed to explain their occurrence. Local remobilization of the two metals was observed, but was limited to a sub-meter scale. Further experimental work on acidic, fluoride-bearing solutions at 150-250 °C identified the presence of the species  $\text{Nb}(\text{OH})_4^+$  at low HF concentration and  $\text{NbF}_2(\text{OH})_3^\circ$  at high HF concentration. Experiments with tantalum identified  $\text{Ta}(\text{OH})_5^0$  at low HF concentration, whereas at high HF concentration  $\text{TaF}_5$  at  $\leq 150$  °C and more commonly  $\text{TaF}_3(\text{OH})_3^-$  result in rapid increases in tantalum solubility. However, in an equivalent fluid, tantalum is almost invariably less soluble than niobium. Geochemical modeling of hydrothermal alteration demonstrated that Nb/Ta ratios may decrease in hydrothermally altered crystals and that removing HF from the fluid or increasing its pH result in niobium and tantalum deposition. These experimental data, together with the above observations from the Nechalacho deposit, indicate that hydrothermal mobilization of niobium and tantalum is indeed possible. Whereas niobium and tantalum are prevailingly found in the 5+ valence state, redox conditions have been considered to play a major role in uranium's geochemical behaviour. As such, we evaluated the solubility and speciation of uranium at 250-350 °C and identified the species  $\text{UO}_2\text{Cl}_2^\circ$  at oxidizing conditions and  $\text{UCl}_4^\circ$  at reducing conditions. While both species rapidly increase in abundance at higher chloride activities,  $\text{UCl}_4^\circ$  does so at a more rapid rate than  $\text{UO}_2\text{Cl}_2^\circ$ . As a result, further geochemical modelling of an irox-oxide copper gold (IOCG) system demonstrated that reducing fluids could lead to the formation of uranium ore deposits, thereby negating the assumption that uranium is immobile under reducing conditions.