Studies on incorporation of radionuclides into the crystal structures of phosphate minerals strongly indicate that uranium and its mobile fission products can be efficiently immobilized through uptake from aqueous solution by formation of phosphate and carbonate minerals. Aiming at development of a new engineered backfill material, we have investigated uptake of uranium at a range of temperatures similar to those expected at waste repository sites, where thermal peak of the waste package (heated by radioactive decay) is ~300°C (Greenburg and Wen 2013). The available literature data on uranium uptake by phosphates are limited to ambient temperatures (e.g. Arey et al. 1999), and to our best knowledge no experimental studies on uranium uptake by phosphates and carbonate at hydrothermal conditions have been performed.

Experiments were conducted in the autoclaves at saturated water pressure and 200-350°C, where metastable phosphate (brushite) and carbonate (aragonite) were transformed to apatite/monetite and calcite in NaCl solutions. Uranium was introduced into autoclave in separate tubes in the forms of U₃O₈ and UO₃ in experiments at reduced and oxidized conditions. Oxidation state of dissolved uranium (U⁴⁺ or U⁶⁺) was controlled by addition of solid redox buffers into autoclaves.

X-ray diffraction (XRD) and backscattered electron diffraction (EBSD) of crystalline products allowed estimation of mineral transformation rate. Inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS allowed obtaining uranium content in crystals and its concentration in co-existed solution. Partition coefficient (D) of uranium was calculated as the ratio of uranium content in the solid to uranium concentration in the solution. Selected solids were examined with synchrotron-based X-ray absorption spectroscopy (XAS).

Overall, our results showed: 1) brushite transforms to monetite and apatite mixture during 6 days, but up to 1 month is required for complete transformation to apatite; 2) mineralogy of the final phase (monetite or hydroxyapatite) depends on ionic strength of the solution (confirmed by thermodynamic calculations); 3) uranium is compatible with phosphate and carbonate minerals, where D could be as high as 1000; 4) uptake of U⁴⁺ by calcite is higher than that of U⁶⁺ by up to a
factor of 100; 5) uranium incorporates into calcite structure as $\text{U}^{6+}$ at oxidized conditions. Additional analyses are pending and results will be presented at EGU meeting.

References
