U(VI)-Si colloids: metastable phases that should not be overlooked in the environment

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Actinides are present in the environment in many different ways, particularly due to activities related to the nuclear fuel cycle, military tests or severe accidents [1,2]. Several studies have demonstrated the existence of metastable polynuclear species incorporating actinides that can agglomerate under certain conditions to form nanometric-sized objects also called colloids [2–5]. Under this form, the mobility of actinides in soils, aquifers or surface waters can be strongly modified compared to soluble species, especially in presence of geological material [6]. These species could also act as reaction intermediaries between soluble species and crystalline phases in equilibrium with the solution. However, the conditions that favor the formation of actinide-based colloidal species remain only partially identified and their thermodynamic stability remains to be assessed.
In this study, we demonstrated the formation of metastable uranyl–silicate intrinsic colloids in model solutions having simplified compositions under air and at room temperature by centrifugation and ultrafiltration. The influence of the silicate ion concentration (between 10^{-4} and 10^{-2} M) and pH (from 7 to 13) on the quantity and nature of the formed species was investigated. The aqueous solutions were characterized by ICP-OES to determine the concentration of elements in solution and by *in situ* Small and Wide-Angle X-ray scattering (SWAXS) to characterize the formation of colloids. If precipitation occurred, High-Resolution Transmission Electron Microscopy (HR-TEM) has been used to determine the phase morphology. Using this methodology, we determined the formation and the evolution of the colloids in term of size, volume, concentration and stoichiometry under different conditions [5]. We also performed geochemical simulations with PHREEQC [7] to predict the phase precipitation and element speciation in our model solutions and compare these calculations with our experimental results. Taking into account all of these results, we demonstrated that pH and silicate concentration drive the nature of colloids and their lifetime, highlighting the need to integrate these intermediate species in geochemical calculations.

Keywords:
U(VI)-Si intrinsic colloids, actinide colloids, prenucleation cluster, Small and wide-angle X-ray scattering

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