

Chemical bonds and formation process of actinide(IV) oligomers and colloids

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Tetravalent actinides show a strong tendency towards hydrolysis followed by the formation of oligomers and colloids. This formation process was investigated on Th (IV), U (IV) and Np (IV) species with EXAFS, LIBD, XPS, HEXS, UV-Vis, NMR and XRD. We investigated the involved chemical bonds, the local structure and structure development as well as the formation mechanism.

We observed that the oligomerization of tetravalent actinides was limited by the presence of chelating ligands. The presence of carboxylic acids, for example, resulted in hexanuclear complexes [1]. Such polynuclear species consist of a framework made of oxo and hydroxo bonds which is terminated by chelating carboxylic acids. In absence of such terminating ligands, the polymerization often continues until stable colloids are formed [2]. This formation process is kinetically hindered due to several reasons related with (a) the limited number of OH groups in the An (OH)_n⁴⁺ⁿ precursor and (b) terminating water molecules. The polymerization comprises of ololation and oxolation processes. At a later stage, the initially amorphous structure of the colloids undergoes an ordering process during which hydroxo groups are systematically replaced by oxo groups. Zeta potential measurements indicated that the colloidal particles carry positive charge at acidic pH and negative charge at alkaline pH. We found that silicate is able to stabilize such colloids at near-neutral pH through modification of the inner structure and by influencing the electrostatic repulsion caused by an enhanced negative surface charge.

UV/Vis, EXAFS spectroscopy and light scattering proved to be sensitive tools to differentiate between hydrolysis species, oligomers and colloids.

[1] Takao *et al.* (2009) *Eur. J. Inorg. Chem.* **32**, 4771-4775.

[2] Ikeda-Ohno *et al.* (2009) *Inorg. Chem.* **48**, 7201-7210.

Geochemistry and geochronology of a Precambrian active continental margin at the boundary between the Ossa Morena Zone and the Central Iberian Zone, Central Portugal

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Portugal has the important Tomar-Badajoz-Córdoba shear zone, between the Ossa-Morena Zone and the Central Iberian Zone (eg [1]), where the Mouriscas-Sardoal Granitic Gneiss Unit crops out. The Granitic Gneisses exhibit intensely deformed textural features and consist of quartz, oligoclase, orthoclase, microcline, biotite, muscovite, zircon, apatite, ilmenite and rutile. They range from calcic to alkali-calcic and are magnesian and peraluminous granites with A/CNK ratios ranging between 1.16 and 1.50. They contain 68.43-70.72 wt% SiO₂ and their Th/Ta ratio of 5.96-13.01 and Yb content of 1.76-2.85 ppm indicate an active continental margin setting. They show enrichments in trace elements relative to MORB and LILE compared to HFSE (Rb_N/Yb_N=70-107) and are depleted in Sr, Nb, P and Ti. The chondrite normalized REE patterns show enrichments in LREE relative to MREE (La_N/Sm_N)=6-8 and HREE (La_N/Yb_N=9-23) and have a negative Eu anomaly (Eu/Eu*=0.19-0.25). They are of S-type. The ID-TIMS U-Pb magmatic zircon age is 569 ± 3 Ma and the metamorphic monazite age is 540 ± 5 Ma, whereas inherited zircon ages are 1905 ± 85 and 2801 Ma. Therefore the granitic gneisses were derived by melting of metasedimentary materials that contain Paleoproterozoic and Neoproterozoic detritus. A biotite-muscovite S-type granite has a U-Pb age of 548 ± 4 Ma and intruded the Granitic Gneiss Unit. The geochemical data is consistent with a continental margin setting which was active during the Ediacaran period.

[1] Ribeiro *et al.* (2009) *C.R. Geoscience* **341**, 127-139.