

The special case of actinide(IV) complexation by the carboxylic function of small and large organic ligands

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Accidental release of radionuclides from mining activities, nuclear energy production, and radioactive waste storage sites requires research to predict the fate and mobility of these contaminants in the environment and more specific in organisms. To date, the interaction of actinides with biological systems is widely unknown, due to the lack of structural information on the molecular level. The aim of this presentation is to summarize recently explored coordination principles of tetravalent actinides with small carboxylic [1] and aminocarboxylic ligands as well as the interaction with proteins [2].

Tetravalent actinides form with carboxylate ligands in aqueous solutions at low pH values usually monomeric complexes. They show at the other hand a strong tendency toward hydrolysis already at low pH. As the pH reaches the onset of An(IV) hydrolysis, olation and oxolation occur as competing reactions to the carboxylate complexation. We observed under these circumstances the formation of several well-defined polynuclear species. The carboxylic group acts in such systems as a terminating ligand and stabilizes nanosized polynuclear clusters in solution and in the solid state [1]. It is important to note that this reaction prevents widely the formation of polynuclear hydrolysis species as well as the formation of An(IV) hydrous oxide colloids.

[1] Takao *et al.* (2009) *Eur. J. Inorg. Chem.* 4771-4775. [2] Jeanson *et al.* (2009) *New J. Chem.* **33**, 976-985.

Geochemistry of cold seeps - Fluid sources and systematics

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Emanation of fluids at cold seeps, mud volcanoes, and other types of submarine seepage structures is a typical phenomenon occurring at continental margins worldwide. They represent pathways along which volatiles and solutes are recycled from deeply buried sediments into the global ocean, and hence they may be considered as a potentially important link in global geochemical cycles.

In this contribution we present geochemical data from various geological and tectonic settings such as the Gulf of Cadiz, the convergent margin off Central America, and/or the Black Sea and provide approaches how to systemize available data sets. Clay-mineral dewatering plays a central role in terms of fluid-mobilization from greater depth, however, resulting cold seep fluids are typically very different from each other and cover a large range of geochemical signatures. This is due to variations in control parameters such as the type and thickness of the sediment cover, thermal conditions, extension of fluid pathways, and the potential for secondary overprinting. For example, freshened fluids emanating at cold seeps off Costa Rica indicate dewatering and related geochemical reactions in subducting sediments, while fluids sampled at mud volcanoes in the Gulf of Cadiz provide evidence for a high-temperature fluid source originating in the underlying oceanic basement. The latter finding provides evidence for a hydrological connection between buried oceanic crust and the water column even at old crustal ages.

Variou geochemical tracers were proposed in the past to decipher relevant processes in the subsurface. In a recent systematic study, Scholz *et al.* [1] demonstrated the general use of Li, reflecting the temperature-dependent isotope fractionation during early diagenetic Li uptake and burial diagenetic Li release from sediments. However, additional approaches are required in order to provide robust geochemical interpretations of cold seep fluids.

[1] Scholz *et al.*, (2010) *GCA*, **74**, 3459-3475.