The influence of Perchlorate (ClO_4^-) on the sorption behavior of Th(IV) on the Muscovite (001) basal plane

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In many sorption as well as other geochemical studies the perchlorate anion (ClO_4^-) is used as a constituent of the background electrolyte for its non-coordinating behavior. It is assumed that by restricting the competitive coordination reaction in solution it is possible to study the unperturbed sorption reaction. The adsorption of tetravalent thorium to the muscovite (001) basal plane gives a cautionary example, where the change from a weakly coordinating anion (Cl^-) to a non-coordinating anion (ClO_4^-) has a drastic and unexpected effect on the sorption behavior of the cation.

Results from surface x-ray diffraction techniques in combination with alpha-spectrometry measurements will be presented. On the basis of these results we will demonstrate that Th(IV) exhibits a straightforward sorption behavior driven by electrostatic attraction and, to a lesser degree solution complexation and hydrolysis, when the reaction is studied in NaCl background electrolyte media (Schmidt *et al.*, 2012). Thorium adsorbs up to a slightly higher than charge compensating coverage of 0.4 Th/A_{UC} predominantly as an extended outer sphere complex with two intact hydration spheres.

By the same method and under the same solution conditions – but with $NaClO_4$ instead of NaCl – the adsorption behavior changes drastically: no interaction of Th with the interface can be detected under these conditions. The changes in solution chemistry are comparably minor, and it appears unlikely that changes in the complexation behavior can explain this observation. Potential interfacial reaction mechanisms underlying this unanticipated behavior will be discussed.

[1] Schmidt, M., Lee, S.S., Wilson, R.E., Soderholm, L. and Fenter, P. (2012) Sorption of tetravalent thorium on muscovite. *Geochimica et Cosmochimica Acta*, **88**, 66-76.

Distribution and enrichment processes of lithium and other solutes in the Salar de Uyuni brine

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The world's largest salt pan, the Salar de Uyuni, is located in the Bolivian Altiplano, at 3650 masl between the eastern and western cordilleras of the Andes. Although it hosts one of the world's most promising lithium deposits, accumulation and horizontal distribution of lithium and other solutes in the brine are not satisfactorily understood.

During various drilling and sampling campaigns (2009-2012) numerous brine samples were taken from boreholes down to 12 m all over the salt lake. Further brine samples were gained from one meter deep drilling holes along three transects from the center to the border in the northeastern part of the Salar. All samples were investigated by IC and ICP-MS as well as for stable isotopes.

Li concentrations in the brine vary between 200 and 1500 mg/L, whereby a vertical gradient could not be observed in the upper 12 m. Li is peaking near the northeastern and southeastern shore, with concentration gradients of 100 mg/L/km (own data) and 40 mg/L/km [1], respectively. Li peaks match with the delta areas of former and recent inflowing rivers. Hence, more than one major tributary as a source of lithium exist, which is in contradiction to results of former investigations supposing the Rio Grande to be the only feeder of lithium to the salt lake basin [2].

The surface in areas where increased Li concentrations occur is characterized by muddy sediments interspersed with crystals of halite and other evaporites. Because clay is decreasing in direction from the shore a temporary fixation and release of Li on clay is assumed as controlling factor leading to an effective enrichment in the brine.

[1] F. Risacher & B. Fritz (2000) *Chemical Geology 167*: 373-392. [2] S.L. Rettig, B.F. Jones, F. Risacher (1980) *Chemical Geology 30*: 57-79

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