Alkaline earth uranyl compounds – from solution to mineral phases

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The uranyl tricarbonato complex is one of the most important uranyl species under environmental conditions. The tendency to form stable metal-uranyl tricarbonato complexes was found particularly for the interaction with alkaline earth elements. We studied chemical behavior of these compounds in aqueous solution by time-resolved laser-induced fluorescence spectroscopy (TRLFS). However, under comparable chemical conditions the formation of these complexes is very different. While magnesium tends mainly to the formation of a $MgUO_2(CO_3)_3^{2+}$ - complex, in the case of calcium the $Ca_2UO_2(CO_3)_3$(aq.) complex is the most stable. The stability constant for the $Ca_2UO_2(CO_3)_3$ – complex is derived to be log $\beta°_{213}$ = 30.90 ± 0.25 [1]. In the corresponding systems with strontium as well as for barium only the $MeUO_2(CO_3)_3^{2+}$ - complex is formed. The stability constants of the $MeUO_2(CO_3)_3^{2+}$ - complexes are determined to be log $\beta°_{113}$ = 26.13 ± 0.27 and 26.24 ± 0.31 for the alkaline earth elements Sr and Ba, respectively. The $Me_2UO_2(CO_3)_3$ – complexes for Mg and Ca form stable natural minerals as bayleyite and liebigite. However several other mineral modifications as zellerite, fontanite, sharpite and rabbittite underline the geochemical importance of this class of compounds.

Analogous phenomena can be expected in the alkaline earth uranyl phosphate systems. Therefore we studied the interaction of alklaine earth metal ione with $UO_2(PO_4)^-$ at pH 7.0. From the fluorescence data the formation of $MeUO_2(PO_4)^+$ complexes in solution can be concluded. The stability constants are derived to be $\beta°_{111}$ = 16.85 ± 0.16, 16.62 ± 0.15, 17.4 ± 0.4 and 16.9 ± 0.4 for Mg, Ca, Sr and Ba, respectively. The formation of complexes with the common formula $Me(UO_2)_2(PO_4)_2aq$ has not yet been obeserved due to the low solubility of these componds. In the case of Mg and Ca the fluorescence data will be compared to the correspondong minerals saleiite and autunite [2].

References

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