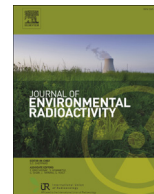




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## New insight into the ternary complexes of uranyl carbonate in seawater

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## ABSTRACT:

Uranium is naturally present in seawater at trace levels and may in some cases be present at higher concentrations, due to anthropogenic nuclear activities. Understanding uranium speciation in seawater is thus essential for predicting and controlling its behavior in this specific environmental compartment and consequently, its possible impact on living organisms. The carbonate calcic complex  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  was previously identified as the main uranium species in natural seawater, together with  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ . In this work, we further investigate the role of the alkaline earth cation in the structure of the ternary uranyl-carbonate complexes. For this purpose, artificial seawater, free of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , using  $\text{Sr}^{2+}$  as a spectroscopic probe was prepared. Combining TRLIF and EXAFS spectroscopy, together with DFT and theoretical thermodynamic calculations, evidence for the presence of Sr alkaline earth counter ion in the complex structure can be asserted. Furthermore, data suggest that when  $\text{Ca}^{2+}$  is replaced by  $\text{Sr}^{2+}$ ,  $\text{SrUO}_2(\text{CO}_3)_3^{2-}$  is the main complex in solution and it occurs with the presence of at least one monodentate carbonate in the uranyl coordination sphere.

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### 1. Introduction

Uranium is a radioactive element naturally occurring in the earth crust and in seawater. In addition, anthropogenic uranium may also be present in the environment as a legacy of past mining activities (Carvalho et al., 2009; Pereira et al., 2014), past nuclear weapon testing (Child and Hotchkis, 2013; Wendel et al., 2013), accidental or controlled discharges from nuclear facilities (Abe et al., 2014). Besides its radiotoxic effects that are considered as negligible (natural uranium has a very low specific activity), uranium is also considered as a chemical toxic for living organisms and human, making its impact on natural compartments and biota an environmental concern and in some cases a political issue. However, the solubility, migration behavior and bioavailability of

uranium strongly depend on its speciation (physico-chemical forms depending on different oxidation states or complex formation). Hence, understanding this speciation is essential for predicting and controlling uranium behavior in the environment. In particular, assessing the uranyl speciation in seawater is a fundamental question of societal - political interest, as oceans often represent the final repository for contaminated waters. In seawater uranium occurs mostly under its hexavalent oxidation state, in the form of the di-oxo uranyl cation,  $\{\text{UO}_2^{2+}\}$ . Its average concentration is close to  $10^{-8}$  M. Because of this low concentration and the complexity of marine environment, uranium speciation and its interaction with the marine biota is still understudied and largely unknown.

Carbonate anions are present in high concentration in seawater (2.2 mM (Maloubier et al., 2015)) and are extremely strong ligands of actinyls in general. Therefore, it is not surprising to find that they play an important role in actinide speciation and reactivity in this specific environmental compartment. In fact, in seawater, uranyl ion forms very stable ternary complexes with carbonates and alkaline earth cations. In a previous work we have identified the

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neutral carbonate calcic complex  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  as the main uranium species in natural seawater, together with  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  (Maloubier et al., 2015). Such information on uranyl speciation is fundamental in terms of environmental and biological impact, because  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  and  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  are considered as non-toxic or non-bioavailable species (Prat et al., 2009). Several studies have been performed on these uranyl ternary complexes and have investigated the uranyl coordination by carbonates (Choppin, 1989; Kelly et al., 2007). It was shown that uranyl ion is coordinated by three carbonate groups in a bidentate way, resulting in six equatorial oxygen atoms coming from 3 ligands. In contrast, confirming the presence of calcium in such carbonate complexes and its role in the molecular structure is more difficult. In particular, EXAFS spectroscopy, which is a powerful technique for revealing the atomic coordination of actinides in complex medium, does not give information on the presence of calcium in these complexes because the calcium signal overlaps the distant oxygen signal of the carbonate groups (Bernhard et al., 2001). A recent quantum mechanical investigation revealed that both calcium ions are necessary for the stability of the uranyl tricarbonate complex in aqueous solution (Tirler and Hofer, 2016). However, no experimental evidence of the presence and structural role of  $\text{Ca}^{2+}$  ion has been reported in literature to date. Moreover, uranyl tricarbonate complexes involving other alkaline earth counter ions ( $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ), have been identified in aqueous solution (Dong and Brooks, 2006; Geipel et al., 2008), but their molecular structures have not been characterized experimentally in solution.

Knowing the nature and the number of the alkaline earth counter ions within the uranyl tricarbonate family is essential: the counter ions may affect the total molecular charge and, therefore, may have an impact on the uranyl complex stability and migration behavior. For instance, it was previously shown that the presence of an alkaline earth counter ion ( $\text{M}^{2+}$ ) and the subsequent formation of a  $\text{M-UO}_2\text{-CO}_3$  ternary complex have an important role in the inhibition of U(VI) bioreduction (Brooks et al., 2003) and sorption onto sediments (Dong et al., 2005).

This work further explores the role of the alkaline earth metal ion in uranyl speciation in seawater because it is to date an open question. We have selected strontium that is structurally and chemically similar to calcium. But unlike calcium it is a detectable backscatter with EXAFS because of its larger atomic number ( $Z = 38$ ). Therefore, we investigated the speciation of uranyl in artificial seawater, replacing  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  by  $\text{Sr}^{2+}$ . Such a methodology allowed us to experimentally detect the presence or not of the alkaline earth ion within the uranyl complex. Moreover, the influence of the nature of the alkaline earth itself on the uranyl-carbonate coordination has been assessed by comparing the uranyl environment when exchanging  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  ions.

## 2. Materials and methods

### 2.1. Sample preparation

The artificial seawater was prepared in our laboratory by dissolving the appropriate amounts of salts in MQ water. The composition of the artificial seawater is reported in Table 1.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, whose concentrations in natural seawater are significant, were not included in our preparation.  $\text{Sr}^{2+}$  concentration is higher than the average  $\text{Sr}^{2+}$  concentration in natural seawater (5.0 mM instead of 0.1 mM), being of the same order of magnitude as  $\text{Ca}^{2+}$  concentration in natural seawater (11 mM) (although less because precipitation occurs above 6 mM). Solid  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  was then directly dissolved in the artificial seawater, to obtain a final concentration of  $[\text{U}] = 5 \times 10^{-5} \text{ M}$ . Final pH was adjusted to 7.8.

**Table 1**

Artificial seawater composition, used for both experimental analysis of uranium speciation and speciation modeling with JCHESS®.

ion	concentration
$\text{Cl}^-$	603 mM
$\text{HCO}_3^-$	2.2 mM
$\text{Br}^-$	0.88 mM
$\text{Na}^+$	560 mM
$\text{K}^+$	11.1 mM
$\text{Sr}^{2+}$	5 mM
$\text{NO}_3^-$	0.1 mM
$\text{ClO}_4^-$	62.4 mM
$\text{UO}_2^{2+}$	0.05 mM
pH	7.8

### 2.2. Speciation modeling

Speciation modeling for uranium in seawater was performed by using the JCHESS® package (van der Lee, 2003). Thermodynamic data from the database BASSIST (Base Applied to Speciation in Solution and at Interfaces and Solubility Thermodynamic database) (Bion, 2003) were used for calculations. All thermodynamic data of this database were collected from the NEA-OECD (Guillaumont et al., 2003) and from the literature.

### 2.3. TRLIF analysis

A Nd-YAG laser (Model Surelite Quantel) operating at 355 nm (tripled) and delivering about 5 mJ of energy in a 10 ns pulse with a repetition rate of 10 Hz, was used as the excitation source. The laser output energy was monitored by using a laser power meter (Scientech). The focused output beam was directed into the 4 mL quartz cell positioned within the cell holder (with temperature regulation) of the spectrofluorimeter (F900-Edinburgh). The detection was performed by using an intensified charge coupled device (Andor Technology) cooled by Peltier effect ( $-5 \text{ }^\circ\text{C}$ ) and positioned at the polychromator exit for the emission spectra measurement and by using a photomultiplier tube (PMT) to measure fluorescence decay time. Logic circuits, synchronized with the laser shot beam, allowed the intensifier to be activated with a determined time delay (from 0.005 to 1000  $\mu\text{s}$ ) and during a determined aperture time (from 0.005 to 1000  $\mu\text{s}$ ). From a spectroscopic point of view, various gate delays and durations were used to certify the presence of only one complex by the measurement of a single fluorescence lifetime and spectrum. Since lifetimes observed were very short, gate delay of 5 ns and gate durations between 20 and 100 ns were mainly used.

### 2.4. DFT calculations

All molecular structures were optimized by using the density-functional theory (DFT) approach as implemented in the Gaussian09 package (Frisch et al., 2009). For these calculations the hybrid B3LYP functional was used (Becke, 1993). MWB60 Stuttgart relativistic effective core potentials (Küchle et al., 1994) were used to describe the uranium atom, MWB28 for strontium, MWB10 for calcium, MWB2 for oxygen and carbon atoms. To take into account part of the solvent effect, solvation was introduced by using a dielectric continuum model of permittivity  $\epsilon_0 = 80$ . The conductor, like the polarizable continuum model (CPCM) implemented in Gaussian09, was used as well (Barone and Cossi, 1998).

### 2.5. EXAFS analysis

The EXAFS experiment was performed on the MARS beamline of the SOLEIL synchrotron facility. Energy calibration was performed

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