Chemical Speciation of U(VI) in Marine Environments: Complexation of Ca^{2+} and Mg^{2+} with $(UO_2)(CO_3)_3^{4-}$ and the Effect on the Extraction of Uranium from Seawater

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ACRONYMS

EXAFS	Extended X-ray absorption fine structure
TRLFS	Time-resolved laser fluorescence spectroscopy
SIT	Specific Ion Interaction Theory

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Abstract

The interactions of Ca^{2+} and Mg^{2+} with $UO_2(CO_3)_3^{4-}$ were studied by Ca^{2+}-ion selective electrode potentiometry and spectrophotometry. The stability constants of ternary Ca-UO_2-CO_3 and Mg-UO_2-CO_3 complexes were determined, respectively, with Ca^{2+}-ion selective electrode potentiometry and optical absorption spectrophotometry. The enthalpies of complexation for two successive complexes, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3$(aq), were determined for the first time by microcalorimetry. The data help to revise the speciation of U(VI) under seawater conditions. On the contrary to the previously accepted assumption that the highly negatively charged $UO_2(CO_3)_3^{4-}$ is the dominant species, the revised speciation indicates that the dominant aqueous U(VI) species under seawater conditions is the neutral $Ca_2UO_2(CO_3)_3$(aq). The results have a significant impact on the strategies for developing efficient sorption processes to extract uranium from seawater.

KEYWORDS: Uranyl carbonate; Calcium; Magnesium; Complexation; Uranium speciation in seawater.

1. Introduction

In recent years, the recovery of uranium from seawater has become a topic of substantial interest, due to an increased demand for nuclear fuel and the seeking of sustainable alternatives to terrestrial mining for uranium.[1] The concentration of uranium in seawater is very low (3.3 ppb), nevertheless, the total amount of uranium in the ocean is estimated to be 4.5 billion metric tons,[1] more than one thousand times the quantity of uranium in the terrestrial ores. Therefore, a feasible and economically convenient process for the extraction of uranium from marine environments would provide a substantially larger supply of uranium than the terrestrial mining. Among the

technologies that have been studied, including solvent extraction, ion exchange, membrane separation, flotation, and sorption,[2–8] sorption of uranium on fiber-based materials functionalized with amidoxime-related ligands has proven to be promising.[9,10] In the course of a 30-day marine test conducted in Japan, kilograms of uranium were recovered.[9] Following this preliminary encouraging success, a number of laboratory studies have been conducted to understand the mechanisms of uranium sorption by the amidoxime-based sorbents, with the objectives of improving the sorption efficiency.[9,11–14] Results have indicated that amidoxime-related ligands can form strong complexes with U(VI)[12] and transition metal ions such as Fe(III),[13] and moderately strong complexes with Pb(II), Cu(II) and Ni(II).[13]

One fundamental question remains to be answered, i.e., what are the dominant species of uranium in seawater? The answer to this question is extremely important to the development of efficient sorbents because the efficiency of the sorption process depends on how the dominant uranium species interacts with the amidoxime ligands and the sorbents. Because the seawater pH is about 8.2 and the total concentration of carbonate is about 0.0023 M, uranium in seawater was generally believed to be in the triscarbonato ($UO_2(CO_3)_3^{4-}$, ~97%) and bicarbonato ($UO_2(CO_3)_2^{2-}$, ~3%) species.[10] Therefore, strategies for the development of ligands and sorbents have been based on the assumption that the sorbents would predominantly interact with $UO_2(CO_3)_3^{4-}$, a highly negatively charged species. However, the validity of this assumption was questioned recently while reviewing the data in the literature and taking into account the high concentrations of Ca(II) and Mg(II) in seawater. Literature data[15–20] have suggested the presence of a series of successive ternary complexes, with general formula $M_nUO_2(CO_3)_3^{2(2-n)-}$ where M = Ca or Mg and n = 1 – 2, in aqueous environments. In particular, the formation of the Ca-UO_2-CO_3 complexes was reported to effectively stabilize the triscarbonato uranyl anion, inhibiting U(VI) microbial reduction in underground waters.[21] Because the concentrations of Ca(II) and Mg(II) in seawater, 0.01 M and 0.053 M, respectively, are overwhelmingly high in comparison with that of U(VI) (1.4×10^{-8} M), we hypothesize that U(VI) may exist predominantly as the ternary Ca-UO_2-CO_3 and/or Mg-UO_2-CO_3 complexes in seawater, instead of the anionic $UO_2(CO_3)_3^{4-}$ species as previously believed. Neglecting the formation of Ca/Mg complexes with $UO_2(CO_3)_3^{4-}$ could probably lead to erroneous speciation of U(VI) under seawater conditions and, consequently, mislead the efforts in the development of efficient systems for extracting uranium from seawater. If the hypothesis is proven true, strategies for the development of efficient sorbents for the extraction of uranium must be accordingly modified.

To quantitatively evaluate the formation of the ternary Ca-UO_2-CO_3 and/or Mg-UO_2-CO_3 complexes, thermodynamic data are needed. However, such data are currently very scarce and, in some cases, highly uncertain. The interest in understanding the aqueous chemistry of calcium complexes with $UO_2(CO_3)_3^{4-}$ was originally raised in the study of the formation of minerals such as liebigite $Ca_2[UO_2(CO_3)_3]\cdot 6H_2O$ and andersonite $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$, obtained by slow precipitation from aqueous saline solutions with $[Ca^{2+}] > 0.05$ M.[22,23] The crystalline structure and the properties of these minerals are well-known, but the actual knowledge on the solution chemistry and the formation equilibria of the Ca^{2+} complexes with $UO_2(CO_3)_3^{4-}$ shows gaps and

disagreements. The available data are limited and untested by independent techniques. In addition, very few data are available on the formation of the analogous Mg-UO_2-CO_3 complexes and the uncertainty of the data on the Mg(II) complexes is higher than those on the Ca(II) complexes.

Until most recently, only a few studies have been reported on the determination of the formation constants of Ca-UO_2-CO_3 and/or Mg-UO_2-CO_3 complexes.[15–20,24,25] Time-resolved laser fluorescence spectroscopy (TRLFS) is exclusively the method used in all the studies except for one where anion exchange was used.[18] By TRLFS, the stability constants of Ca-UO_2-CO_3 and/or Mg-UO_2-CO_3 complexes were calculated based on the increase of the fluorescence intensity as Ca(II) or Mg(II) was added into the solution of $UO_2(CO_3)_3^{4-}$: the ternary Ca-UO_2-CO_3 complexes were characterized by a noticeable emission spectrum whereas the UO_2-CO_3 complexes did not show any emission. In addition to the stability constants, efforts were made to reveal the structures of the ternary Ca-UO_2-CO_3 complexes with very limited success. For example, EXAFS spectra of solutions of uranyl carbonate in the absence and presence of Ca(II) were collected, but did not distinctively illustrate the structure of $Ca_2UO_2(CO_3)_3$(aq).[17] The EXAFS data seemed to suggest that the structure of $Ca_2UO_2(CO_3)_3$(aq) consists of the same $UO_2(CO_3)_3^{4-}$ unit as in the solid liebigite. In the crystallographic analysis of liebigite, the detection of Ca was hindered by the nearly identical distances of U-Ca and U-$O_{\text{terminal carboxylate}}$. Presumably, the calcium atoms in $Ca_2UO_2(CO_3)_3$(aq) assume similar positions to those in the liebigite mineral.

In this work, the formation of ternary Ca-UO_2-CO_3 and Mg-UO_2-CO_3 complexes was studied with two methods, i.e., Ca^{2+} ion selective electrode potentiometry and optical absorption spectrophotometry. The stability constants of Ca-UO_2-CO_3 and Mg-UO_2-CO_3 complexes were determined in 0.1 M NaCl, and converted to the values in 0.5 NaCl (similar to the NaCl salinity in seawater) using the Specific Ion Interaction Theory (SIT). Using the data from this work in conjunction with relevant thermodynamic parameters from critically reviewed database in the literature,[26] the speciation of U(VI) under seawater conditions was re-evaluated. The speciation reveals that the dominant U(VI) species in seawater is the neutral $Ca_2UO_2(CO_3)_3$(aq). Additionally, the enthalpies of complexation for the two successive complexes, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3$(aq), were determined for the first time by microcalorimetry.

2. Experimental Section

2.1 Chemicals

NaCl was used as the inert background electrolyte to maintain a constant ionic strength (0.1 M) in all the solutions. It was obtained from Aldrich (purity > 99.0 %), and recrystallized twice from MilliQ water prior to use. All solutions in this work were prepared with MilliQ water, freshly boiled and degassed under an argon stream, and stored in a CO_2-free dry box.

A working solution of $CaCl_2$ (10 mM) was prepared by diluting a stock solution (1.0 M $CaCl_2$, from Fluka) and adjusting the ionic strength to 0.1 M by addition of NaCl. The calcium concentration in the working solution was determined by titration with a standard solution of EDTA using procedures modified from the literature.[27] A concentrated NH_4OH/NH_4Cl solution was used as a buffer to maintain the pH at 10. A Ca^{2+} ion selective electrode, instead of a complexometric indicator, was used to determine the equivalent point of the titration.

A working solution of $MgCl_2$ (10 mM) was prepared by diluting a stock solution (1.0 M $MgCl_2$, from Fluka) and adjusting the ionic strength to 0.1 M by addition of NaCl. The magnesium concentration was determined by a complexometric titration, in which a solution of Mg^{2+}/EDTA (EDTA in excess) was titrated with a standard Ca^{2+} solution (10 mM). The Ca^{2+} ion-selective electrode was used to determine the equivalent point of the titration.

A working solution of 30 mM Na_2CO_3/10 mM NaOH was prepared in a dry box with an inert atmosphere, by dissolution of anhydrous Na_2CO_3 (purity 99.999 %, Aldrich) and addition of a known volume of 1.000 M NaOH (Fluka analytical standard). Again, the ionic strength of the working solution was adjusted to 0.1 M by adding NaCl. This solution was standardized by a potentiometric titration with a standard hydrochloric acid solution.

The stock solution of U(VI) in perchloric acid was prepared and standardized as described elsewhere.[28] A working solution (31.3 mM UO_2^{2+}/35.4 mM $HClO_4$) was prepared by dilution of a weighed volume of the stock in MilliQ water.

2.2 Ca^{2+} ion selective electrode potentiometry

All experiments were carried out at 25.0 °C. A series of four potentiometric titrations were designed to study the formation of the Ca^{2+} complexes with $UO_2(CO_3)_3^{4-}$. Usually, the potentiometric cell contained a 6.0 mL solution with 0.2 – 1.0 mM UO_2^{2+} and a 4-fold excess of CO_3^{2-} (0.8 – 4.0 mM). The pH of the starting solution was about 10.0 – 10.3 (see the analytical data in Appendix). Under these conditions, U(VI) existed in solutions quantitatively as triscarbonato anionic complex and the formation of hydrolyzed U(VI) species is negligible. The titrant, 10 mM $CaCl_2$, was delivered into the cell by a Metrohm dosimat (prec. ± 0.001 mL).

A combined Ca^{2+} selective polymer membrane electrode (Metrohm) was used to determine the concentration of free Ca^{2+} in the solution during the titration. The Ca^{2+} selective electrode is sensitive to variations of Ca^{2+} concentrations in the ranges 10^{-6} – 1.0 M (pH = 2 – 12), but its performance is affected by the presence of interfering ions including Mg^{2+}, divalent transition metal cations, and Na^+ in high concentrations (> 0.25 M). As a result, experiments in this study were carried out in an ionic medium of 0.1 M NaCl. Because the concentration was significantly lower than that in seawater ([NaCl] ~ 0.5 M), the stability constants obtained at 0.1 M NaCl were converted to those at 0.5 M NaCl for discussions through the empirical equations of the Specific Ion Interaction Theory.[26,29] A series of preliminary experiments were carried out to verify the behavior of the electrode according to the manufacturer's specifications. In particular, the

stability of the electrode and the absence of interference by Na^+ in the concentration range of 0 – 0.1 M were checked and confirmed.

The electrode potential (E, mV), related to the concentration of free Ca^{2+} as shown in equation 1, was measured with a Metrohm potentiometer (prec. ± 0.1 mV).

$$E = E^0 + S \times \log[Ca^{2+}] \qquad (1)$$

where E^0 is the electrode standard potential (mV) and S is the slope of the electrode response (mV). Ideally, $S = 2.303 \times RT/nF$, where $R = 8.314$ J mol^{-1}K^{-1}, $T = 298.15$ K, $F = 9.649 \times 10^4$ C·mol^{-1}, and $n = 2$ for a bi-electronic process such as the case for Ca^{2+}. The theoretical value of S, called the Nernst slope, is therefore 29.58 mV at 25 ^{o}C. Immediately prior to each complexation titration, a calibration titration was carried out in order to determine the electrode parameters E^0 and S. These parameters were then used to calculate the concentration of the free $[Ca^{2+}]$ in solution from the measured E during the subsequent complexation titration. In the calibration titration, the cell solutions of 10 mL 0.1 M NaCl were prepared and degassed in advance with a stream of argon, to remove the carbon dioxide possibly dissolved. Increasing volumes of the standardized 10.0 mM $CaCl_2$ solution were added and the electrode potential E (mV) was measured. Calibration titrations in this study have indicated that a reliable slope value for this type of electrode is about 28.0 – 29.3 mV, in agreement with the observations in other studies.[30]

2.3 UV-Vis spectrophotometry

A series of four UV-Vis spectrophotometric titrations were designed to study the formation of magnesium complexes with $UO_2(CO_3)_3^{4-}$. A Varian Cary 6000i spectrophotometer was used to collect the spectra. The instrument is equipped with a thermostatic system to control the temperature of the solutions in both the sample and reference cells. An inert atmosphere was maintained in the sample chamber during the experiments by a stream of argon. Solutions were loaded in quartz cells (1.00 cm path length, Starna). Spectra were collected in the wavelength region 215 - 400 nm, where intensive absorption of the triscarbonato U(VI) complex occurs. Other authors reported that the most characteristic absorption bands of the uranyl-carbonate complexes were in the region 380 - 600 nm,[24] but we found that the absorption of carbonate complexes in this region was not sensitive to the formation of successive complexes with magnesium.

Prior to each experiment, a baseline spectrum was collected using 0.1 M NaCl in both the sample and reference cells. Then, cell solutions of U(VI) (0.0199 – 0.0799 mM) with a 5-fold molar excess of carbonate (0.10 – 0.40 mM) were prepared directly in the spectrophotometric cell by dilution of weighed quantities of the stock solutions. Weighed aliquots of 10.22 mM Mg^{2+} solution were added and the spectrum was collected after each addition.

2.4 Microcalorimetry

Microcalorimetry was used to determine the enthalpies of complexation for the two successive complexes, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$. An isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp.) was used to carry out these experiments. Details of the calorimeter and its calibration were described previously.[31] Multiple titrations were carried out, with the titration cell containing 0.90 mL UO_2^{2+} (0.199 – 0.481 mM) and a 4:1 excess of CO_3^{2-} (0.816 – 2.04 mM) at pH 10, titrated with 10.05 mM $CaCl_2$ (0.010 mL/addition). The measured heat after the jth addition, $Q_{ex,j}$, was corrected by the heat of titrant dilution ($Q_{dil,j}$) that was measured in separate runs, to obtain the net reaction heat at the jth point, $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_U, $C_{carbonate}$, C_H, and C_{Ca}), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. The reaction heats measured by microcalorimetry were used, in conjunction with the complex stability constants for $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$, to calculate the enthalpies of complexation.

3. Results and Discussion

3.1 Stability constants of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ in 0.1 M NaCl

Figure 1 shows an example of potentiometric titrations carried out to study the formation of the successive complexes of Ca^{2+} with $UO_2(CO_3)_3^{4-}$. The data were processed with the minimization software *Hyperquad 2008*.[32,33] The best fit was obtained with a model consistent with the formation of two successive complexes, described by equations (2) and (3), with the stability constants in 0.1 M NaCl: $\log\beta_{113}$ = (25.26 ± 0.04) for $CaUO_2(CO_3)_3^{2-}$, and $\log\beta_{213}$ = (28.26 ± 0.04) for $Ca_2UO_2(CO_3)_3(aq)$ (see Table 1, the third column). As shown in Figure 1, the agreement between the experimental and calculated values is excellent.

$$Ca^{2+} + UO_2(CO_3)_3^{4-} = CaUO_2(CO_3)_3^{2-} \quad (2)$$

$$2\,Ca^{2+} + UO_2(CO_3)_3^{4-} = Ca_2UO_2(CO_3)_3(aq) \quad (3)$$

Stepwise, the formation of the 1:2 complex can be described by equation (4):

$$Ca^{2+} + CaUO_2(CO_3)_3^{2-} = Ca_2UO_2(CO_3)_3(aq) \quad (4)$$

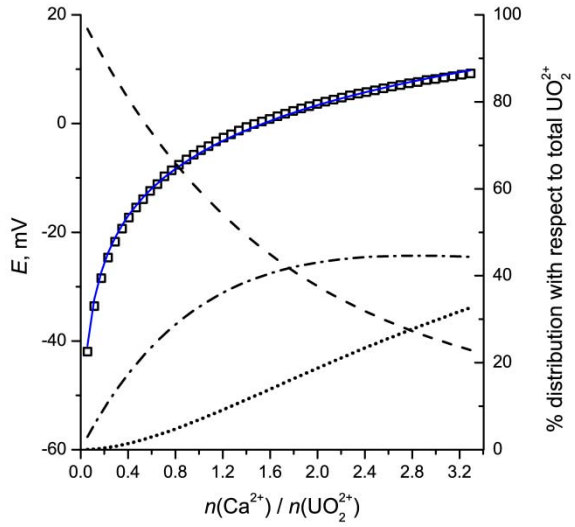

Figure 1 A representative Ca^{2+} ion selective electrode potentiometric titration. : $[UO_2^{2+}]_{initial}$ = 0.469 mM; $[CO_3^{2-}]_{initial}$ = 1.85 mM; $[Ca^{2+}]_{titrant}$ = 10.05 mM; pH = 10.3–10.0. Symbols: (left y-axis, *E* in mV) □ observed *E*; solid line - calculated *E*; (right y-axis, percentage of U(VI) species) -- $UO_2(CO_3)_3^{4-}$, -·- $CaUO_2(CO_3)_3^{2-}$, ··· $Ca_2UO_2(CO_3)_3(aq)$.

3.2 Stability constant of $MgUO_2(CO_3)_3^{2-}$ in 0.1 M NaCl

Figure 2 shows a representative spectrophotometric titration for the complexation of Mg^{2+} with the triscarbonato uranyl species. As $MgCl_2$ was added into the solution of $UO_2(CO_3)_3^{4-}$, subtle changes in the spectra were observed in the wavelength region of 220 – 400 nm (Figure 2, upper left diagram). The data were processed with the minimization software *HypSpec*.[32,33] Factor analysis of the data indicated that there were two absorbing species, $UO_2(CO_3)_3^{4-}$ and an $Mg^{2+}/UO_2(CO_3)_3^{4-}$ complex. The best fit was obtained with the model consistent with the formation of the 1:1 complex, described by equation (5). The stability constant and molar absorptivity (Figure 2, upper right diagram) of $MgUO_2(CO_3)_3^{2-}$ were calculated. As shown in the lower diagrams of Figure 2, the agreement between the experimental and calculated spectra (lower left diagram) and absorbance (lower right diagram) is very good. The stability constant of $MgUO_2(CO_3)_3^{2-}$ in 0.1 M NaCl, $\log\beta_{113}$ = (24.53 ± 0.01), is slightly lower than that of $CaUO_2(CO_3)_3^{2-}$, indicating that the former complex is weaker than the latter (see Table 1, the third column).

$$Mg^{2+} + UO_2(CO_3)_3^{4-} = MgUO_2(CO_3)_3^{2-} \qquad (5)$$

In fitting the spectra, a model including the formation of both the 1:1 and 1:2 $Mg^{2+}/UO_2(CO_3)_3^{4-}$ complexes, $MgUO_2(CO_3)_3^{2-}$ and $Mg_2UO_2(CO_3)_3(aq)$, was also tested. However, the refinement of the data was not satisfactory. We believe that, though the formation of the 1:2 $Mg^{2+}/UO_2(CO_3)_3^{4-}$ complex (to some extent) cannot be completely excluded, it is a very weak complex and its concentration was too low under the experimental conditions in this work.

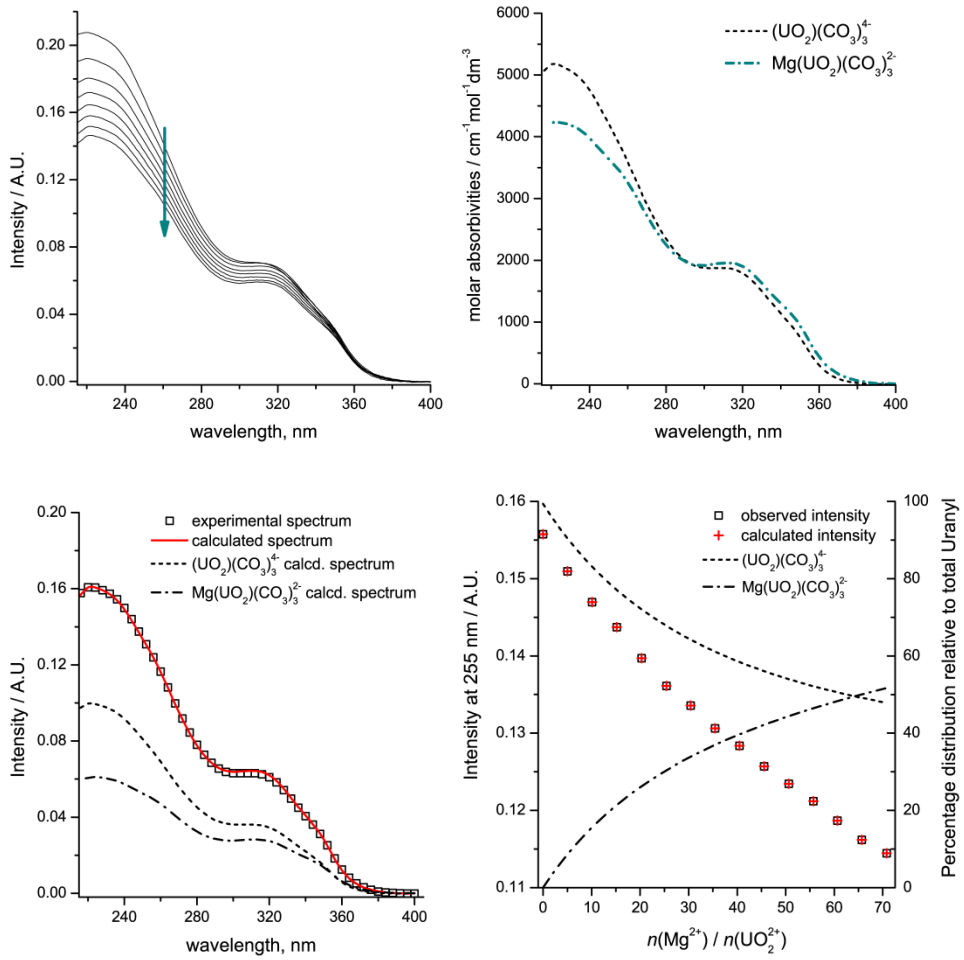

Figure 2 Spectrophotometric titration of $Mg^{2+}/UO_2(CO_3)_3^{4-}$. $[UO_2^{2+}]_{initial}$ = 0.040 mM; $[CO_3^{2-}]_{initial}$ = 0.200 mM; $[Mg^{2+}]_{titrant}$ = 10.22 mM (final $n(Mg)/n(UO_2^{2+})$ = 70.8); pH = 9.75–9.68. Upper left: un-normalized spectra (the number of spectra was reduced for clarity). Upper right: Calculated molar absorptivities of $UO_2(CO_3)_3^{4-}$ and $MgUO_2(CO_3)_3^{2-}$. Lower left: Experimental and calculated spectra at $n(Mg)/n(UO_2^{2+})$ = 45.5 (some experimental points omitted for clarity). Lower right: experimental and calculated absorbance at 255 nm as a function of $n(Mg)/n(UO_2^{2+})$ and the percentage distribution relative to total uranyl on the right axis of the diagram.

3.3 Effect of Ca/Mg complexation with $(UO_2)(CO_3)_3^{4-}$ on the speciation of U(VI) in seawater

To evaluate the effect of the complexation between Ca/Mg and $UO_2(CO_3)_3^{4-}$ on the speciation of U(VI) in seawater, the stability constants obtained in this work (for 0.1 M NaCl) should be converted to those for 0.5 M NaCl (close to seawater salt concentrations). Therefore, empirical equations of the *Specific Ion Interaction Theory*[26,29] were used to first convert the values for 0.1 M NaCl to those in infinite dilution (I = 0), and then calculate the values for 0.5 M NaCl. The ion interaction parameters used in the calculation, mostly from the OECD-NEA Database,[26] are listed in Table 2. Because no specific interaction parameters for (Na^+, $CaUO_2(CO_3)_3^{2-}$) or (Na^+, $MgUO_2(CO_3)_3^{2-}$) are available in the literature, we assume they are equal to -(0.02 ± 0.09) $mol^{-1}kg^{-1}$, identical to ε (Na^+, $UO_2(CO_3)_2^{2-}$), owing to the same charge and a

similar structure, as already suggested in the literature.[20] The ion interactions involving neutral species, including $UO_2(CO_3)_2$(aq) and $Ca_2UO_2(CO_3)_3$(aq), are neglected.

Table 1 shows a comparison of the stability constants obtained by ion-selective potentiometry (for $Ca^{2+}/UO_2(CO_3)_3^{4-}$) and spectrophotometry (for $Mg^{2+}/UO_2(CO_3)_3^{4-}$) in this work, with those obtained by other techniques in the literature. Conversion of experimental values at different ionic strengths to those at infinite dilution (I = 0 M) allows such comparison on the same basis (Table 1). For $CaUO_2(CO_3)_3^{2-}$, the value from this work ($\log\beta^0_{113}$ = (27.00 ± 0.04)) is in good agreement with those by an anion exchange method[18] and by TRLIFS.[20] For $Ca_2UO_2(CO_3)_3$(aq), the value from this work ($\log\beta^0_{213}$ = (30.84 ± 0.04)) is in good agreement with those by the anion exchange method[18] and by TRLIFS using competitive EDTA titrations,[17] but slightly higher than those[16,20] obtained by direct TRLIFS measurements. For the system of $Mg^{2+}/UO_2(CO_3)_3^{4-}$, only one complex, $MgUO_2(CO_3)_3^{2-}$, has been observed in this and previous studies.[18,25] The stability constant obtained by spectrophotometry in this work ($\log\beta^0_{113}$ = (26.25 ± 0.04)) agrees with the values obtained by different techniques.[18,25] As Table 1 shows, the results obtained by Ca^{2+}-ion selective potentiometry and spectrophotometry in this work have improved the accuracy of the stability constants and provided independent validation of the previous results obtained by different methods.

Though the complexation between Ca/Mg and $UO_2(CO_3)_3^{4-}$ is fairly weak, the speciation of U(VI) in seawater could be affected due to the high concentrations of Ca and Mg relative to U(VI) in seawater ([Ca(II)] = 0.01 M, [Mg(II)] = 0.053 M, and [U(VI)] = 1.4×10^{-8} M). Consequently, neglecting the formation of Ca/Mg complexes with $UO_2(CO_3)_3^{4-}$ could probably lead to erroneous speciation of U(VI) under seawater conditions. As shown in the lower diagram of Figure 3, when pH is above 6, the aqueous chemistry of U(VI) in the presence of Ca(II) (0.01 M) and Mg(II) (0.053 M) is dominated by the formation of the $M_nUO_2(CO_3)_3^{2(2-n)-}$ (M = Ca or Mg, and n = 1 or 2) complexes. In particular, at the seawater pH (8.2), $Ca_2UO_2(CO_3)_3$(aq) accounts for 58% of the total uranium in solution, $CaUO_2(CO_3)_3^{2-}$ and $MgUO_2(CO_3)_3^{2-}$ 18% each, and $UO_2(CO_3)_3^{4-}$ only 6%. In contrast, more than 97% of U(VI) would exist as $UO_2(CO_3)_3^{4-}$ if the formation of Ca/Mg complexes with $UO_2(CO_3)_3^{4-}$ was neglected, as shown in the upper speciation diagram of Figure 3.

Understanding the speciation of U(VI) under seawater conditions is of great significance in the development of strategies for the extraction of uranium from seawater. Since the dominant species of U(VI) is the neutral complex, $Ca_2UO_2(CO_3)_3$(aq), instead of the highly negatively charged $UO_2(CO_3)_3^{4-}$ as previously believed, the sorbents must be able to interact with $Ca_2UO_2(CO_3)_3$(aq) effectively to achieve efficient collection.

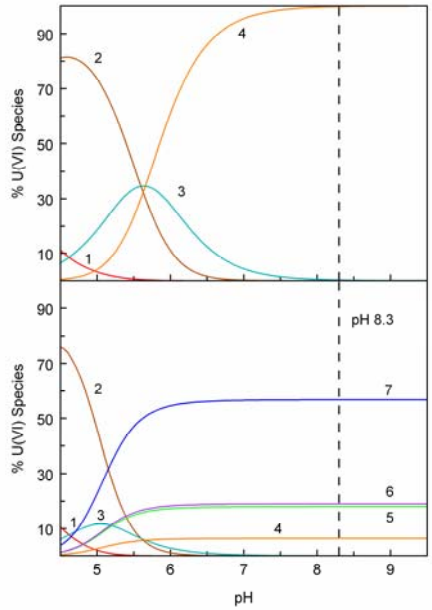

Figure 3 U(VI) speciation under seawater conditions in the absence (upper figure) and presence of 0.01 M Ca(II) and 0.053 M Mg(II) (lower figure). $C_U = 1.4 \times 10^{-8}$ M, $C_{carbonate} = 0.0023$ M. 1 – UO_2^{2+}, 2 - $UO_2(CO_3)(aq)$, 3 - $UO_2(CO_3)_2^{2-}$, 4 - $UO_2(CO_3)_3^{4-}$, 5 - $CaUO_2(CO_3)_3^{2-}$, 6 - $MgUO_2(CO_3)_3^{2-}$, 7 – $Ca_2UO_2(CO_3)_3(aq)$.

3.4 Enthalpy of complexation for $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$.

Figure 4 shows the thermogram of a representative calorimetric titration (heat rate *vs* time, left diagram), and the experimental/fitted heat as a function of the titrant volume (right diagram). As the thermogram shows, small positive heat was observed as Ca(II) was added into the solution containing $UO_2(CO_3)_3^{4-}$, indicating that the formation of the calcium complexes is slightly exothermic. The reaction heat, in conjunction with the stability constants of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ obtained by potentiometry, was fitted with the minimization software *HypDeltaH*[32] to calculate the enthalpies of complexation for the two complexes. As shown in Figure 4 (right diagram), the fitting of the data is reasonably good considering the very small amounts of reaction heat developed during the titrations (50 - 200 μJ/addition). The calculated enthalpies of complexation are shown in Table 3. For the stepwise reactions described by equations (2) and (4), ΔH_r = -(7.6 ± 5.8) kJ/mol and (0 ± 7) kJ/mol, respectively. The uncertainties of the ΔH_r data are relatively high due to the propagation of errors in the calculation involving: (1) the use of the literature value of the enthalpy of formation of $UO_2(CO_3)_3^{4-}$ that has high uncertainty, -(39.2 ± 4.1) kJ/mol;[26] (2) the subtraction of the dilution heat of 10.0 mM Ca^{2+} in 0.1 M NaCl, -(0.28 ± 0.1) kJ/mol; and (3) the measurement of small reaction heats (as small as 50 μJ per addition of titrant).

Table 3 summarizes the values of the Gibbs free energy, enthalpies and corresponding entropies of complexation (ΔG, Δ*H*, and *T*Δ*S*) determined in 0.1 M NaCl in this study. Corresponding values for infinite dilution (*I* = 0 M) were obtained by correcting the Δ*G* values using the SIT method. The enthalpies of complexation at *I* = 0.1 M were not corrected because the dependence of the enthalpies on the ionic strength in the range 0.0 - 0.1 M has been reported to be negligible.[28]

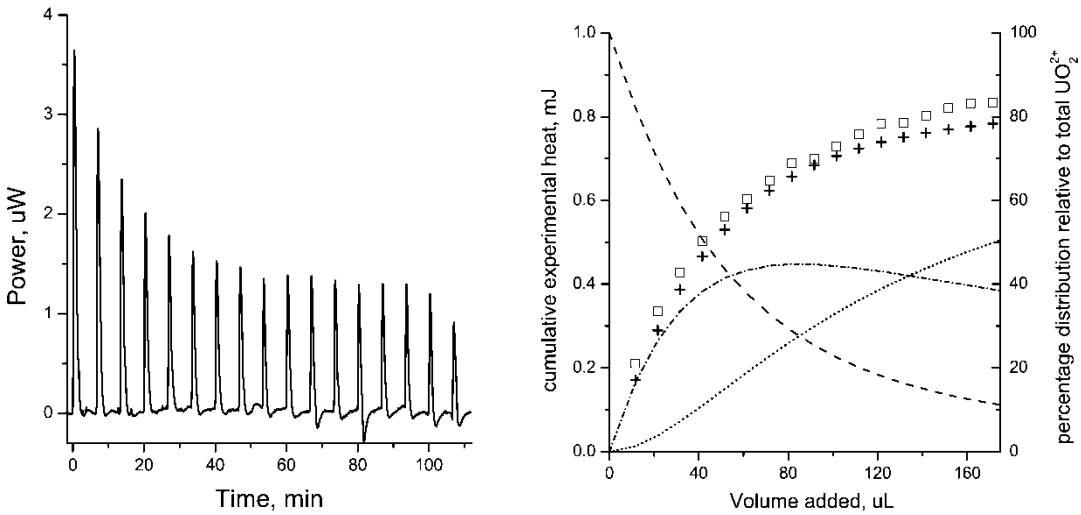

Figure 4 Microcalorimetric titrations on the complexation of Ca^{2+} with $UO_2(CO_3)_3^{4-}$ (0.1 M NaCl, 25.0°C) (a): $[UO_2^{2+}]_{initial}$ = 0.20 mM; $[CO_3^{2-}]_{initial}$ = 0.80 mM; $[Ca^{2+}]_{titrant}$ = 10.05 mM; pH=10.3–10.0. Left: thermogram (Power, μW *vs* time, min). Each peak corresponds to an addition of titrant. Right: cumulative experimental and calculated heats (mJ) on the left axis, percentage distribution of the complexes with respect to total uranyl on the right axis. Symbols: -- $UO_2(CO_3)_3^{4-}$; -·-$CaUO_2(CO_3)_3^{2-}$; ··· $Ca_2UO_2(CO_3)_3(aq)$; □ experimental cumulative heat (mJ); + Calculated cumulative heat (mJ).

Figure 5 shows the stepwise thermodynamic parameters of $Ca^{2+}/UO_2(CO_3)_3^{4-}$ complexation from this work and those of UO_2^{2+}/CO_3^{2-} from the literature[26] at *I* = 0 M. The trends of the thermodynamic parameters, Δ*H* and *T*Δ*S* in particular, provide interesting insight into the relationship between the energetics of complexation and the associated charge neutralization. For a complexation reaction with complete or partial charge neutralization (i.e., the absolute charge of the complex is zero or less than the total absolute charges of the reactants), the entropy term is usually the driving force of the complexation because the solvation sphere of the complex is much less ordered than those of the reacting species. The formation of successive $Ca^{2+}/UO_2(CO_3)_3^{4-}$ complexes, as described by equations (2) and (4), is such processes where the charges are partially (for equation (2)) or completely (for equation (4)) neutralized. As shown in Figure 5, indeed, the spontaneity of the formation of $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ results predominantly from the entropy term (*T*Δ*S* = 22 kJ/mol for both equation (2) and (4)), while the enthalpy of complexation does not contribute significantly to the complexation (Δ*H* = -8 kJ/mol and 0 kJ/mol, respectively, for equation (2) and (4)).

Similar discussions are applicable to the stepwise formation of UO_2^{2+}/CO_3^{2-} complexes, particularly the formation of $UO_2CO_3^0(aq)$ and $UO_2(CO_3)_3^{4-}$. Figure 5 shows that the formation of $UO_2CO_3^0(aq)$, accompanied by the neutralization of four net charges, is solely entropy driven, which can be attributed to

the increase of the degree of disorder upon complexation. The neutral $UO_2CO_3^0$(aq) species is expected to have a much less ordered solvation sphere than the reacting charged UO_2^{2+} and CO_3^{2-} species. On the contrary, the formation of the third complex, $UO_2(CO_3)_3^{4-}$, is accompanied by large exothermicity (ΔH = -58 kJ/mol) favoring the complexation and negative entropy ($T\Delta S$ = -28 kJ/mol) opposing the complexation. This observation can be explained by the argument that a highly charged species such as $UO_2(CO_3)_3^{4-}$ is expected to exert a significant ordering effect in the solvent that results in the decrease of the degree of disorder in the complexation system.

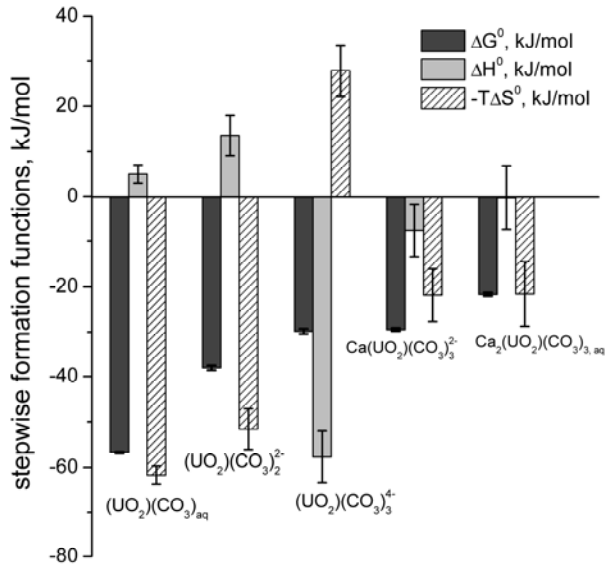

Figure 5 Stepwise equilibrium functions (I = 0 M) for uranyl carbonato complexes and calcium complexes with uranyl triscarbonato species. Error bars indicate the uncertainties (see values in Table 3).

4. Conclusion

The formation of Ca(II) and Mg(II) complexes with $UO_2(CO_3)_3^{4-}$ was studied with two independent methods, Ca^{2+} ion-selective electrode potentiometry for the Ca-UO_2-CO_3 system and optical absorption spectrophotometry for the Mg-UO_2-CO_3 system. In particular, the use of potentiometry with a Ca^{2+} ion-selective electrode proved to be an original and reliable technique for studying the solution equilibria of Ca-UO_2-CO_3 complexes. The speciation of U(VI) under seawater conditions was revised using the data from this work. It shows that the aqueous chemistry of U(VI) in seawater is dominated by the ternary Ca-UO_2-CO_3 and Mg-UO_2-CO_3 complexes. In particular, the neutral complex $Ca_2UO_2(CO_3)_3$(aq) accounts for nearly 60% of total U(VI).

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Table 1. Equilibrium constants of Ca/Mg complexation with $UO_2(CO_3)_3^{4-}$ and related reactions, p.w.= present work.

Reaction	$\log\beta \pm \sigma$			Ref.
	I = 0 M	I = 0.1 M NaCl	I = 0.5 M NaCl	
$UO_2^{2+} + CO_3^{2-} = UO_2(CO_3)(aq)$	9.94 ± 0.03	9.08 ± 0.03	8.61 ± 0.04	[26]
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.61 ± 0.09	15.75 ± 0.09	15.26 ± 0.10	[26]
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.84 ± 0.04	21.84 ± 0.04	21.85 ± 0.07	[26]
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-}$	**27.00 ± 0.04**	**25.26 ± 0.04**	**24.28 ± 0.07**	**p.w.**
	27.18 ± 0.06			[18]
	27.27 ± 0.14			[20]
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3(aq)$	**30.84 ± 0.04**	**28.26 ± 0.04**	**26.81 ± 0.07**	**p.w.**
	29.8 ± 0.7			[16]
	30.77 ± 0.25			[17]
	30.70 ± 0.05			[18]
	29.81 ± 0.19			[20]
$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} = MgUO_2(CO_3)_3^{2-}$	**26.25 ± 0.04**	**24.53 ± 0.04**	**23.62 ± 0.07**	**p.w.**
	26.11 ± 0.04			[18]
	26.24 ± 0.13			[25]
$Ca^{2+} + UO_2(CO_3)_3^{4-} = CaUO_2(CO_3)_3^{2-}$	**5.15 ± 0.06**	**3.42 ± 0.06**	**2.43 ± 0.10**	**p.w**
$2Ca^{2+} + UO_2(CO_3)_3^{4-} = Ca_2UO_2(CO_3)_3(aq)$	**9.00 ± 0.06**	**6.42 ± 0.06**	**4.96 ± 0.10**	**p.w.**
$Mg^{2+} + UO_2(CO_3)_3^{4-} = MgUO_2(CO_3)_3^{2-}$	**4.41 ± 0.06**	**2.69 ± 0.06**	**1.77 ± 0.10**	**p.w.**

Table 2. SIT ion interaction parameters, p.w.= present work

Interacting ions		Interaction parameter, $mol^{-1}kg^{-1}$	Ref.
UO_2^{2+}	Cl^-	0.21 ± 0.02	[26]
Ca^{2+}	Cl^-	0.14 ± 0.01	[26]
Mg^{2+}	Cl^-	0.19 ± 0.02	[26]
Na^+	CO_3^{2-}	-0.08 ± 0.03	[26]
Na^+	$UO_2(CO_3)_2^{2-}$	-0.02 ± 0.09	[26]
Na^+	$UO_2(CO_3)_3^{4-}$	-0.01 ± 0.11	[26]
Na^+	$CaUO_2(CO_3)_3^{2-}$	-0.02 ± 0.09	[20], p.w.
Na^+	$MgUO_2(CO_3)_3^{2-}$	-0.02 ± 0.09	[20], p.w.

Table 3. Thermodynamic parameters of Ca(II) complexation with $UO_2(CO_3)_3^{4-}$ and related reactions, p.w. = present work.

Reaction	***I*, M**	**log β ± σ**	**ΔG ± σ kJ/mol**	**ΔH ± σ kJ/mol**	**$T\Delta S$ ± σ kJ/mol**	**Ref.**
$UO_2^{2+} + CO_3^{2-} = UO_2(CO_3)(aq)$	0.1	9.08 ± 0.03	−51.8 ± 0.2	5 ± 2	57 ± 2	
	0	9.94 ± 0.03	−56.8 ± 0.2	5 ± 2	62 ± 2	[26]
$UO_2(CO_3)(aq) + CO_3^{2-} = UO_2(CO_3)_2^{2-}$	0.1	6.67 ± 0.09	−38.1 ± 0.5	14 ± 4	52 ± 5	
	0	6.67 ± 0.09	−38.1 ± 0.5	14 ± 4	52 ± 5	[26]
$UO_2(CO_3)_2^{2-} + CO_3^{2-} = UO_2(CO_3)_3^{4-}$	0.1	6.09 ± 0.10	−34.8 ± 0.6	−58 ± 6	−23 ± 6	
	0	5.23 ± 0.10	−29.9 ± 0.6	−58 ± 6	−28 ± 6	[26]
$Ca^{2+} + UO_2(CO_3)_3^{4-} = CaUO_2(CO_3)_3^{2-}$	0.1	3.42 ± 0.06	−19.5 ± 0.3	−8 ± 6	12 ± 6	p.w.
	0	5.16 ± 0.06	−29.5 ± 0.3	−8 ± 6	22 ± 6	
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-}$	0.1	25.26 ± 0.04	−144.1 ± 0.2	−47 ± 6	326 ± 6	p.w.
	0	27.00 ± 0.04	−154.1 ± 0.2	−47 ± 6	359 ± 6	
$Ca^{2+} + CaUO_2(CO_3)_3^{2-} = Ca_2UO_2(CO_3)_3(aq)$	0.1	3.00 ± 0.07	−17.1 ± 0.4	0 ± 7	17 ± 7	p.w.
	0	3.84 ± 0.07	−21.9 ± 0.4	0 ± 7	22 ± 7	
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3(aq)$	0.1	28.26 ± 0.04	−161.2 ± 0.2	-47 ± 7	383 ± 7	p.w.
	0	30.84 ± 0.04	−176.0 ± 0.2	-47 ± 7	432 ± 7	