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Flávia M.S. Maia, Solange Ribet, Céline Bailly, Mireia Grivé, Benoît Madé, et al.. Evaluation of thermodynamic data for aqueous Ca-U(VI)-CO₃ species under conditions characteristic of geological clay formation. Applied Geochemistry, 2021, 124, pp.104844. 10.1016/j.apgeochem.2020.104844 . hal-03137943

HAL Id: hal-03137943

<https://hal.science/hal-03137943>

Submitted on 2 Jan 2023

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Evaluation of thermodynamic data for aqueous Ca-U(VI)-CO₃ species under conditions characteristic of geological clay formation

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Keywords : Uranium, speciation, complexation, clay formation

Highlights:

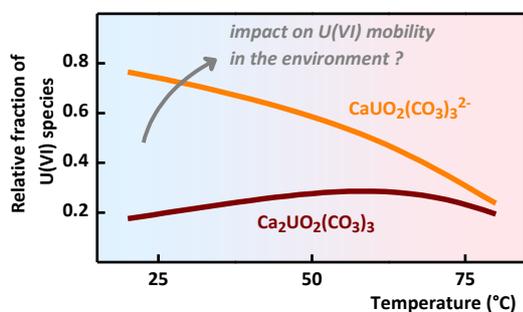
A specific experimental set-up has been designed in order to work in a biphasic solid/liquid system at various temperatures by means of controlling the temperature and $p\text{CO}_2$.

The Van't Hoff Equation can be applied to explain the variation in stability constant values as a function of temperature (20-80°C)

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The temperature does not facilitate the formation of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ ($\Delta_r H_m^\circ = -24.4 \pm 2.2$ kJ mol^{-1}), whereas it has very little effect on the stability of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ ($\Delta_r H_m^\circ = -3 \pm 10$ kJ mol^{-1}).

TOC



Abstract

Uranium(VI) forms stable Ca-U(VI)-CO₃ ternary complexes, which are highly mobile in the environment. This characteristic can be critical as regards radioactive waste disposal in deep geological formations. While the formation of aqueous ternary Ca-U(VI)-CO₃ complexes has been clearly established and identified under room temperature conditions, the effect of temperature on their formation has barely been investigated. An experimental study was thus designed to evaluate the stability of these complexes with temperature (20-80 °C) under well-controlled physicochemical conditions typical of clay rock formation (especially CO₂ pressure). This method is based on a study of the competition between the processes of

complex formation and uranium retention on an anion-exchange resin. A modelling approach with PhreeqC was carried out to derive the thermodynamic data for the formation of these complexes. The Van't Hoff Equation can be applied to explain the variation in stability constant values as a function of temperature. This work suggests: $\log_{10}K_{113}^0 = 27.27 \pm 0.04$ and $\log_{10}K_{213}^0 = 29.8 \pm 0.2$ for $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complexes, respectively, hence in good agreement with the literature data. The enthalpy of reaction determined here from experiments suggests that temperature does not facilitate the formation of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ ($\Delta_r H_m^0 = -24.4 \pm 2.2 \text{ kJ mol}^{-1}$), whereas it has very little effect on the stability of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ ($\Delta_r H_m^0 = -3 \pm 10 \text{ kJ mol}^{-1}$).

1. Introduction

Potential uranium contamination in nature, due to increased nuclear power generation and mining activities, raises distinct environmental concerns. Understanding the chemical behaviour of uranium is therefore essential to reliably predicting its migration (Runde, 2000). This understanding becomes crucial in the context of deep geological radioactive waste disposal, where uranium is a ubiquitous component. In France, the Callovo-Oxfordian clay rock formation (COx) was chosen as a potential host rock for such a disposal site. According to the disposal concept, the formation plays an important role in preventing radionuclide migration to the natural environment. One consequence of disposing long-lived, high-level radioactive waste is the transient increase in temperature due to the exothermic nature of this waste (ANDRA, 2005). The thermal evolution may modify pore water chemical composition (pH, redox potential, gas pressure) and therefore speciation, solubility or even radionuclide migration.

In the past, geochemical models applied to radioactive waste disposal typically predicted that the most relevant redox state of uranium in pore water was U(IV), through use of available

thermodynamic datasets, e.g. NEA-TDB (Guillaumont et al., 2003). However, several data publications have confirmed the formation of aqueous Ca-U(VI)-CO₃ ternary complexes even under reducing conditions (Bernhard et al., 1996; Bernhard et al., 2001; Dong and Brooks, 2006; Geipel et al., 2008; Kalmykov and Choppin, 2000; Lee and Yun, 2013; Shang and Reiller, 2020), which increases the solubility of uranium in pore water (Joseph, 2013; Tullborg et al., 2017; Vercouter et al., 2015) and influences its mobility and sorption properties (Dangelmayr et al., 2017; Kautenburger et al., 2019; Mühr-Ebert et al., 2019).

The formation conditions of aqueous Ca-U(VI)-CO₃ complexes are clearly established at room temperature, while only scarce information is available to predict the behaviour of uranium as temperature increases. To the best of our knowledge, just two studies address the effect of temperature on such species (Endrizzi and Rao, 2014; Jo et al., 2019). Both these studies used calorimetric titration and showed an exothermal reaction driven by entropy. Jo et al. (2019) also determined the stability constants of Ca-U(VI)-CO₃ complexes at various temperatures (10-70°C) in aqueous solution by applying spectroscopic techniques. However, the conclusions of this work indicate that an approximation of the constant enthalpy cannot explain the change in temperature of the thermodynamic constants. From an operational perspective, the formation of ternary complexes tends to be favoured by increasing the temperature and, depending on the conditions (pH, *p*CO₂, Ca concentration), this may then lead to an increase in uranium(VI) mobility. The significance of this finding requires further validation under more realistic physicochemical conditions, such as those within the CO_x clay rock.

The aim of this study was to investigate in greater detail the temperature effect on the formation of Ca-U(VI)-CO₃ species under the clay geochemical conditions applicable to the French concept of radioactive waste disposal (Gailhanou et al., 2017), whereby Ca/*p*CO₂/pH parameters are controlled by calcite dissolution/precipitation reactions (Figure 1). In this

study, the Schubert-type method (Schubert et al., 1988), which was also used by others (Dong and Brooks, 2006; Mühr-Ebert et al., 2019), has been chosen to directly evaluate the competition between ternary complex formation and uranium retention. A specific experimental set-up has been designed in order to work in a biphasic solid/liquid system at various temperatures by means of controlling the temperature and $p\text{CO}_2$.

2. Materials and Methods

2.1 Chemicals

All chemicals used herein were of analytical reagent grade or higher. Uranium solutions were prepared from $^{238}\text{U(VI)}$ -depleted ICP-MS standard solution (SCP Science, France). The anionic exchange resin used in the experiments was of the gel type Dowex-1x2 (Sigma-Aldrich, Merck), stable up to 99°C. This strong resin initially in chloride form was converted to nitrate form after overnight equilibration at least three times with 1 M NaNO_3 at a solid-to-liquid ratio of 10 g/L.

2.2 Analytical methods

The aqueous uranium concentration was analysed after filtration at 0.2 μm by Quadripole ICP-MS (Induced Coupled Plasma-Mass Spectrometry, ThermoScientific XSERIES 2), using an internal standard signal (^{205}Tl) to control any drift from the matrix effect. The organic carbon released by the tubes was measured by a Total Organic Carbon Analyser TOC V-CSH series (Shimadzu, Standalone, highly-sensitive method). The alkalinity was evaluated by colorimetric analysis using a Bromocresol green-methyl red indicator power pillow as a colour indicator and a digital titrator (Hach method 803), with a cartridge containing 0.16 N H_2SO_4 . pH was measured at the target temperature with a dual dry bath system (Fisher Scientific) and a pH-meter combined with a red-rod pH electrode and thermometer detector (pHC285, Hach Lange) of hydrogen ion activity. The pH-meter was automatically calibrated

by PHM220 Lab (Radiometer Analytical) using two standard buffer solutions produced according to Radiometer Analytical specifications (pH 4.0 and pH 7.0). All standard solutions were stable within a temperature range of 0° to 90°C. The pH calibration was verified by ensuring that the measured pH values of HCl/NaOH solutions corresponded to the recalculated values from known H⁺ concentrations.

2.2 Batch-type experiments

Sorption experiments were performed at 20, 40, 60 and 80 °C (±1 °C) in a glove box under conditions typical of CO_x clay rock (with calcite at equilibrium) by setting *p*CO₂ (to 1%, 1%, 3% and 5% at 20, 40, 60 and 80 °C, respectively) to control the carbonate content in aqueous solution (see Figure 1 and Table 1).

The indirect Schubert-type method (Schubert et al., 1988) allows working at trace concentrations in order to limit potential mineral precipitation. All experiments were conducted at a controlled atmosphere and temperature in an electrolyte background of 0.1 M NaNO₃ and initial 5·10⁻⁷ M of U(VI) (i.e. below the solubility of different U(VI)-bearing minerals so as to avoid any possible precipitation).

Two types of batch experiments were carried out:

- (i) in the absence of calcium, as a function of the solid-to-liquid ratio (1 to 25 g/L). The objective of these experiments was to establish the model describing sorption of U(VI) on the resin;
- (ii) and, as a function of the calcium concentration (0 to 5 mM) at a fixed solid-to-liquid ratio of 2.5 g/L. The objective of these experiments was to study the stability and temperature effect on Ca-U(VI)-CO₃ complex formation. The upper calcium concentration limit was calculated to avoid oversaturation of calcite in the experiments.

For each experimental set, two series of blank samples (no resin present) served to ensure that no precipitation of uranyl or sorption on the tube and filter surfaces occurred. Results indicated that these processes can be neglected under the studied experimental conditions. The resin was weighed under room conditions in 35 mL PPCO (Polypropylene Copolymer, Nalgen®) tubes (pre-washed at 20, 40, 60 or 80 °C with ultrapure water three times to limit the release of organic carbon during the experiments, i.e. < 1 ppm); next, the tubes were transferred into the Ar(g)/CO₂(g) glovebox (with the % of CO₂(g) dependent on the target temperature) and filled with the solution prepared from stock solutions of NaNO₃, Ca(NO₃)₂, NaHCO₃ and ²³⁸U(VI). The tubes were sealed with Teflon tape, closed and transferred outside the glovebox, for confinement in aluminium foil bags under vacuum (20 mbar). Afterwards, the tubes were transferred into an incubator coupled to a reciprocate shaker (Thermotron InforsHT) and left in contact at the target temperature. After 5 days of contact, sufficient to reach a steady state (as proven by preliminary experiments), the aluminium foil bag was opened and the tubes introduced into an insulated Teflon/aluminium box, specially designed to maintain the temperature of the tubes, followed by rapid transfer into the glovebox. Once again inside the glovebox, an aliquot was sampled and preserved for subsequent analysis; moreover, pH was measured at the target temperature. After cooling the samples to room temperature, the alkalinity of the blank samples (without resin) was measured, assuming the same values for the whole series. Note that in considering the uncertainty of the analysis, pH measured after equilibrium was in the same range as that calculated, thus indicating that the *p*CO₂/pH/temperature equilibrium was being relatively well controlled (see the "Modelling Approach" section for additional information).

The U concentration in solution was analysed in order to obtain the distribution coefficient (K_D , in mL/g) (eq 1) characterising the distribution of uranium between the solid (in mol/g) and the aqueous solution (in mol/mL) at equilibrium:

$$K_D = \frac{[U(VI)]_{\text{resin}}}{[U(VI)]_{\text{aq}}} = \frac{[U(VI)]_0 - [U(VI)]_{\text{aq}}}{[U(VI)]_{\text{aq}}} \quad (1)$$

The amount of uranium retained on the resin ($[U(VI)]_{\text{resin}}$) was determined by subtracting the initial concentration of uranium added to the system ($[U(VI)]_0$) and the concentration measured in the aqueous phase ($[U(VI)]_{\text{aq}}$).

2.4 Modelling approach

The modelling approach was defined so as to simulate the anionic exchange processes occurring between the resin and anionic species of U(VI) at different temperatures. A stepwise procedure was followed, with the first step quantifying uranium retention, as described by the following reaction



where X is an ion-exchanger resin functional group and K_{ex} corresponds to the exchange constant. In the presence of calcium (Ca), two additional reactions occur in solution



A change in the K_D value with respect to the conditions without Ca (eq 2) provides an indirect evidence of ternary complex formation in the aqueous phase (eqs 3 and 4). Since the exchange constant describing U(VI) retention is fixed, it then becomes possible to obtain the constants describing the formation of ternary complexes by fitting the experimental data.

All simulations were performed using the PhreeqC code, version 3.1.4 (Parkhurst and Appelo, 2013), and the ThermoChimie database (Giffaut et al., 2014; www.thermochimie-tdb.com) with the Davies Equation for ionic strength corrections. The chemical thermodynamic data ($\text{Log}_{10}K$) of pertinent aqueous complexation reaction at 20 °C, 40 °C, 60 °C, and 80 °C used

in our modelling approaches are provided in Table S1. The reaction constants K_{ex} , K_{113} and K_{213} from eqs 2–4 were fitted by implementing the PEST (Parameter ESTimation) code (Doherty, 2004) coupled with the batch version of PhreeqC. The PEST code is a public domain, open-source software suite that allows estimating both the model-independent parameters and the associated uncertainties. The first set of experiment (without calcium) allowed the determination of K_{ex} , whereas K_{113} and K_{213} are the fitting parameters of the second set of experiments (in the presence of calcium). Please note that in the geochemical calculations, the system $p\text{CO}_2$ was allowed to vary freely and instead the measured alkalinity, pH and Ca concentration were set as the fixed parameters (see Table 1).

2.5 Temperature dependence

The Van't Hoff Equation (eq 5) was applied to account for the dependence of stability constants on temperature (T), assuming a constant enthalpy of reaction and so that the standard heat capacity change $\Delta c_p^\circ=0$ (Puigdomenech et al., 1997) :

$$\log_{10}K^\circ(T) = \log_{10}K^\circ(T_0) - \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (5)$$

When temperature dependence follows a straight line, the slope is directly correlated with the enthalpy of reaction $\Delta_r H_m^\circ(T_0)$ (J mol^{-1}) at the reference temperature (298.15 K). $\log_{10}K^\circ(T_0)$ is the intersection of this line with the vertical axis. R is the gas constant ($8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$). Knowing both the standard stability constant and enthalpy of reaction from eq 5, the entropy can be determined from eq 6 and Gibbs free energy from eq 7

$$\Delta_r S_m^\circ(T_0) = \frac{\Delta_r H_m^\circ(T_0)}{T_0} + \ln(10) R \cdot \log_{10}K^\circ(T_0) \quad (6)$$

$$\Delta_r G_m^\circ(T_0) = \Delta_r H_m^\circ - T_0 \Delta_r S_m^\circ = -RT \log_{10}K^\circ(T_0) \cdot \ln(10) \quad (7)$$

3. Results and Discussion

3.1 Application of the modelling approach to Dong and Brooks' (2006) experimental data

The model was used to explain the experimental data obtained by Dong and Brooks (2006) (results given in Supporting Information, Figure S1). Results of the fitting approach yielded values of 27.26 ± 0.07 and 30.2 ± 0.5 for the stability constants, corresponding to reactions 3 and 4, respectively. These results differ very slightly from those proposed by Dong and Brooks (2006), in which $\log_{10}K_{113}^0 = 27.18 \pm 0.07$ and $\log_{10}K_{213}^0 = 30.7 \pm 0.06$, although they lie in the same range. Emphasis must be focused on the uncertainty of the derived stability constant. This uncertainty is correlated with the predominant range of species relative to the concentration range of calcium in aqueous solution (limited by calcite precipitation). While the $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ complex is predominant over the full range of calcium concentrations studied, the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complex is only formed for $[\text{Ca}^{2+}] > 1 \text{ mM}$ and never as a major species (see an example in Figure S2). The error associated with the formation constant of the 1:1:3 complex is therefore smaller than that associated with the 2:1:3 complex. Special attention should then be paid to calculating the uncertainty of $\log_{10}K_{213}^0$, which seems to be very low in the case of the work completed by Dong and Brooks (2006).

3.2 Quantification of the sorption process

The speciation of U(VI) in the presence of carbonates and the absence of calcium is mainly controlled by the $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ species in the temperature range from 20 °C to 80 °C (Figure S3). At 80 °C, hydrolysed species $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_2(\text{aq})$ are expected yet can be considered negligible. The experimental set-up and corresponding conceptual model proposed herein do not distinguish which aqueous species will control U(VI) sorption onto the resin. In fact, a description of the true ion exchange mechanism occurring on the anionic exchanger in the absence of calcium is not a priori necessary; considering a simple K_D approach is sufficient to apply the Schubert-type method (Schubert et al., 1988). For purposes of completeness however, a mechanistic approach has been

considered, assuming that $\text{UO}_2(\text{CO}_3)_3^{4-}$ present in all cases and displaying the highest anionic charge was the only species likely to be adsorbed onto the anionic exchange resin. This conclusion was also drawn from work conducted by Dong and Brooks (2006) at room temperature.

The proposed model explains the sorption data in absence of calcium (see the lines in Figure S3). Agreement between the experimental data and calculated values at 20 °, 40 ° and 60 °C is excellent. In contrast, the fit between the estimated and experimental observations at 80 °C and 5% $\text{CO}_2(\text{g})$ is less satisfactory, as the calculated uranium concentrations underestimate the values measured for the ratio $\text{S/L} > 10$ g/L. However, even at 80 °C, for an S/L ratio equal to 2.5 g/L (which will be the ratio subsequently used in experiments in the presence of calcium), the agreement between model and experiments is good. Note that at 80 °C, the $\text{UO}_2(\text{CO}_3)_2^{2-}$ complex is predominant in solution (Figure S3). Modelling tests were carried out in order to take into account the adsorption of the two complexes on the resin. In the end, the results were not modified: the experimental data were well described by the adsorption of the complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ and the addition of the second one did not improve the results. This confirms the reliability of our initial hypothesis. This is also validated by the fact that the dependence of reaction constants K_{ex} on temperature follows the Van't Hoff Equation (Figure 2A). This finding means that only one major species is interacting with the resin over the explored temperature range. If several U(VI) species were adsorbed, a linear relation would not be expected. Furthermore, these results show that the exchange of $\text{UO}_2(\text{CO}_3)_3^{4-}$ on the anionic-exchange resin is enhanced by a temperature increase. The resultant $\log_{10} K_{\text{ex}}^0$ ($\pm 1 \sigma$) equals 1.0 ± 0.1 , and the $\Delta_r H_{\text{m,ex}}^0$ ($\pm 1 \sigma$) is 26 ± 4 kJ mol⁻¹.

In conclusion, our simplified model serves to explain the sorption data and can thus be used as a reference state for describing uranium behaviour when calcium is present and the formation of Ca-U(VI)- CO_3 ternary complexes is being facilitated.

3.3 Sorption experiments in the presence of calcium

According to Dong and Brooks (2006), in the presence of calcium, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ sorption onto the resin at room temperature may be neglected; this observation also constituted a fundamental assumption of our conceptual model. Sorption of the uncharged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ species was considered negligible. Results of the sorption experiments performed as a function of calcium concentration at different temperatures are given in Figure 3 (symbols). As expected, regardless of experimental temperature, the concentration of U(VI) in the solution increases with calcium concentration in the system due to the formation of Ca-U(VI)- CO_3 complexes, which are not retained by the exchanger. The solid lines in Figure 3 account for the fitting results of the experimental data obtained from PEST on the two parameters: $\log_{10}K_{113}$ and $\log_{10}K_{213}$. The level of agreement between model and experimental data proves to be excellent for each experimental set; results follow a non-linear model since two ternary aqueous species $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ are formed. Nonetheless, a qualitative comparison of the data is not straightforward since the equilibrium conditions (pH, alkalinity) of each experimental set differ from one temperature to the next.

The $\log_{10}K_{113}$ and $\log_{10}K_{213}$ values obtained for the ternary complexes at each temperature from the fitting step are provided in Table S2. The temperature dependence on stability constants is shown as a function of $\left(\frac{1}{T_0} - \frac{1}{T}\right)$ in Figure 2B and 2C. For the 1:1:3 complex the Van't Hoff Equation appears to be applicable since a linear relationship has been obtained ($R^2 = 0.98$). For the 2:1:3 complex, the coefficient of determination is low ($R^2 = 0.04$), showing no true dependence on temperature. However, fitting the data with the approximation of a constant heat capacity change (Puigdomenech et al., 1997) show also a non-statistically significant values for Δc_p° and ΔH_r° . These results indicate that aqueous species formation does not exhibit the same behaviour. Formation of the $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ species is not promoted

with an increase in temperature, whereas $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ formation is only slightly affected by temperature changes.

The enthalpy of reaction (assumed to be constant over the temperature range explored) and standard stability constants (at 298.15 K) were therefore calculated from eq 5. The standard stability constants ($\pm 1\sigma$) for ternary species $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ are: $\log_{10}K_{113}^0 = 27.27 \pm 0.04$ and $\log_{10}K_{213}^0 = 29.8 \pm 0.2$, respectively. These values are consistent with those found in the literature (see Figure S5), thus providing confidence in the proposed methodology and conceptual model.

The aqueous speciation results indicate that the ternary complex $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ is the main aqueous species of U(VI) at all temperatures studied for calcium concentrations below 1 mM (see Figure S2). The fraction of ternary complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ increases with both calcium concentration and temperature yet is by no means the main species under the experimental conditions studied herein. As previously discussed for the fitting results of the published data reported in Dong and Brooks (2006), the weak proportion of 2:1:3 complex explains the high degree of uncertainty related to $\log_{10}K_{213}$, especially at the lowest temperatures where the contribution is smallest.

The standard enthalpy of reaction ($\pm 1\sigma$) of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ equal -24.4 ± 2.2 and $-3 \pm 10 \text{ kJ mol}^{-1}$, respectively. Based on the standard stability constant and enthalpy of reaction, both entropy (eq 6) and Gibbs free energy (eq 7) could also be determined (Table 2).

3.4 Comparison with data from the literature

For all three studies (i.e. the present work, Endrizzi and Rao (2014) and Jo et al. (2019)), the enthalpy values remain negative and low ($> -50 \text{ kJ/mol}$) as compared to the entropy values. Drawing the conclusion of an entropy-driven complexation therefore remains valid.

Furthermore, the exothermic reaction deduced from micro-calorimetry measurements, by studying the transition from $\text{UO}_2(\text{CO}_3)_3^{4-}$ to ternary complexes ($\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$) (Endrizzi and Rao, 2014; Jo et al., 2019), has been recovered by values deduced from the Van't Hoff Equation directly targeting the formation of ternary complexes from UO_2^{2+} as a function of temperature (eqs 3 and 4). For the 1:1:3 anionic complex, the enthalpy of reaction obtained in this study ($-24.4 \pm 2.2 \text{ kJ mol}^{-1}$) is similar to previous published values (-47 ± 6 (Endrizzi and Rao, 2014) or -40.4 ± 4.1 (Jo et al., 2019)) although higher. For the 2:1:3 neutral species, this agreement is less satisfactory, (i.e. $-3 \pm 10 \text{ kJ mol}^{-1}$ vs. -47 ± 7 (Endrizzi and Rao, 2014) or -42.3 ± 5.1 (Jo et al., 2019)). However, the low enthalpy value remains consistent with the fact that temperature does not exert a strong impact on formation (Figure 3).

The thermodynamic dataset proposed by Jo et al. (2019) was tested to determine whether it could explain our experimental results. The modelling results are shown as dashed lines in Figure 3; reasonable results are obtained at low temperatures, yet a greater deviation can be observed as temperature increases, particularly at 80 °C. The possibility that 1:1:3 anionic complex could in fact be adsorbed onto the resin at temperature higher than 50°C could explain this discrepancy. However, this hypothesis is not trustworthy since it would lead to disagreement for temperatures below 40 °C.

It is important to recall that in this work, we describe the formation of 1:1:3 and 2:1:3 complexes from UO_2^{2+} whereas in the previous work, the transition from species $\text{UO}_2(\text{CO}_3)_3^{4-}$ to 1:1:3 and 2:1:3 species is studied. In a last part, our data and those of Jo et al. (2019) were compared using their formalism of reaction ($x \text{ Ca}^{2+} + \text{UO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{Ca}_x\text{UO}_2(\text{CO}_3)_3^{(2x-4)}, K_{aq}^x$). The results are presented in Figure 4. Overall, taking into account the dispersion of the points, similar trends are observed with the possibility of using Van't Hoff Equation. The fitting values derived for 2:1:3 complex ($8.9 \pm$

0.1 for $\log_{10}K_{\text{aq}}^2$ and $+23 \pm 7 \text{ kJ mol}^{-1}$ for enthalpy) remain consistent with those obtained from our experiments (filled symbols; 7.96 ± 0.1 for $\log_{10}K_{\text{aq}}^2$ and $36.5 \pm 10 \text{ kJ mol}^{-1}$ for enthalpy). The conclusion is also valid for the 1:1:3 complex if we compare the data from our work (5.42 ± 0.09 and $14.9 \pm 5.1 \text{ kJ mol}^{-1}$ for $\log_{10}K_{\text{aq}}^1$ and the enthalpy, respectively) and those of Jo et al. (2019) (5.22 ± 0.15 and $10.5 \pm 9.5 \text{ kJ mol}^{-1}$ for $\log_{10}K_{\text{aq}}^1$ and the enthalpy, respectively). This illustrates the very high sensitivity of the parameters.

Moreover, all the values described in this work are dependent on the thermodynamic database used to perform the modelling analysis. It should be noted that the data in Thermochemie database for the HCO_3^- and CO_2 species deviate slightly at $60 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ from the one of Patterson and coll. (Patterson et al., 1984; Patterson et al., 1982) (See Table S1). Nevertheless, changing the values of the most pertinent reactions leads to almost the same conclusions on the enthalpy of reaction for the ternary complexes.

4. Conclusions

The present work focuses on the temperature effect on the formation of aqueous ternary “Ca-U(VI)- CO_3 ” species under the clay geochemical conditions applicable to the French concept of radioactive waste disposal (COx clayrock), whereby $\text{Ca}/p\text{CO}_2/\text{pH}$ parameters are controlled by calcite dissolution/precipitation reactions. The anionic exchange method has been chosen to directly evaluate the competition between ternary complex formation and uranium retention. A specific experimental set-up has been designed in order to work in a biphasic solid/liquid system at various temperatures by means of controlling the temperature and $p\text{CO}_2$. The Van't Hoff Equation can be applied to explain the variation in stability constant values as a function of temperature ($20\text{-}80 \text{ }^\circ\text{C}$). Increasing temperature does not facilitate the formation of $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, whereas it has very little effect on the stability of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$. Although similarities are found, it does not unfortunately seem possible to

explain all the experimental data obtained as a function of temperature with regard to literature data. At this stage, it is difficult to explain these differences, given the very high sensitivity of the parameters, but the study does reveal the importance of testing various approaches, whether direct or indirect, under different experimental conditions. From an application point of view, under radioactive waste disposal conditions where temperatures around 80 °C are expected, experimental results indicate that the increase in temperature is not to promote the formation of ternary complexes. This could obviously have a potential impact on the prediction of U(VI) mobility near a radioactive waste disposal site. Additional work seems therefore necessary to further investigate/consolidate the effects of temperature increase on uranium behaviour.

Acknowledgments

This research was funded by ANDRA (France's National Radioactive Waste Management Agency) within the framework of the GL-CTEC Project.

Available Supporting Information

Additional details on experimental methods and modelling results are provided in the supporting information file.

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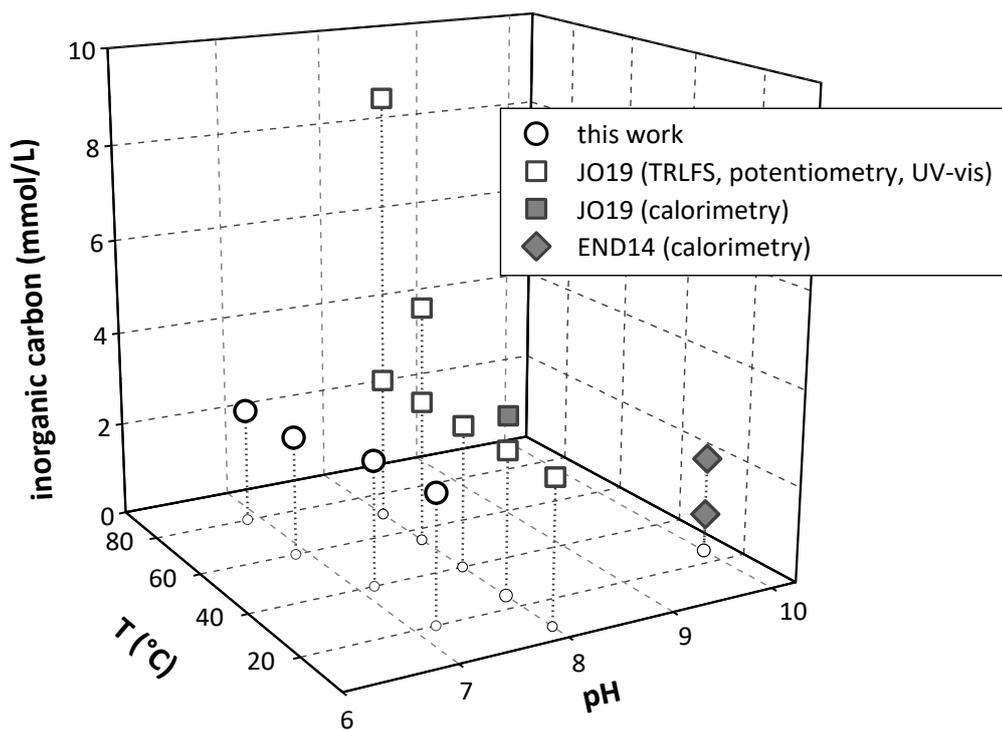


Figure 1: Experimental conditions for this work (additional information can be found in Table S1) and in previous studies: END14: (Endrizzi and Rao, 2014); JO19: (Jo et al., 2019). Calcium concentration range is controlled by calcite dissolution / precipitation. For all studies, an ionic strength of near 0.1 M was set with NaCl, NaClO₄ or NaNO₃.

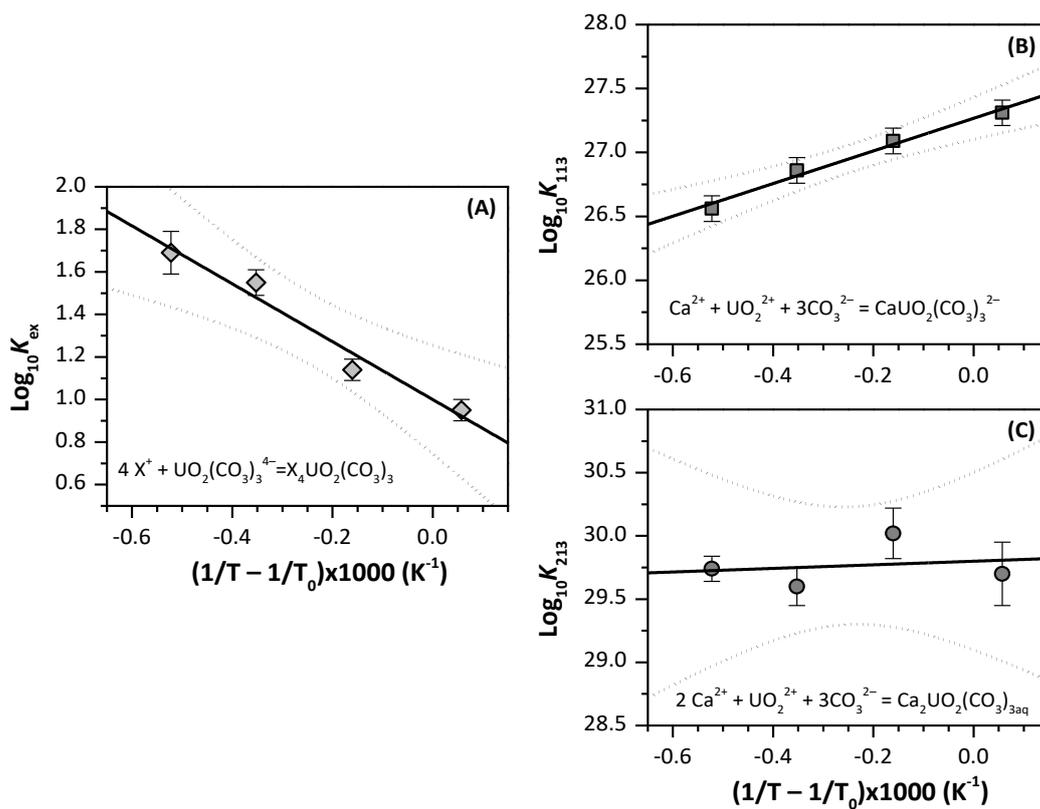


Figure 2 : Dependence on Temperature of the thermodynamic constant for (A) sorption of U(VI) on resin ($R^2=0.97$), (B) 1:1:3 ternary complex ($R^2=0.98$), (C) 2:1:3 ternary complex ($R^2=0.04$). Solid lines represent fitted curves based on the Van't Hoff Equation (eq 5), dotted lines are the confidence interval (95%). (See parameters in Table 2 and Table S1).

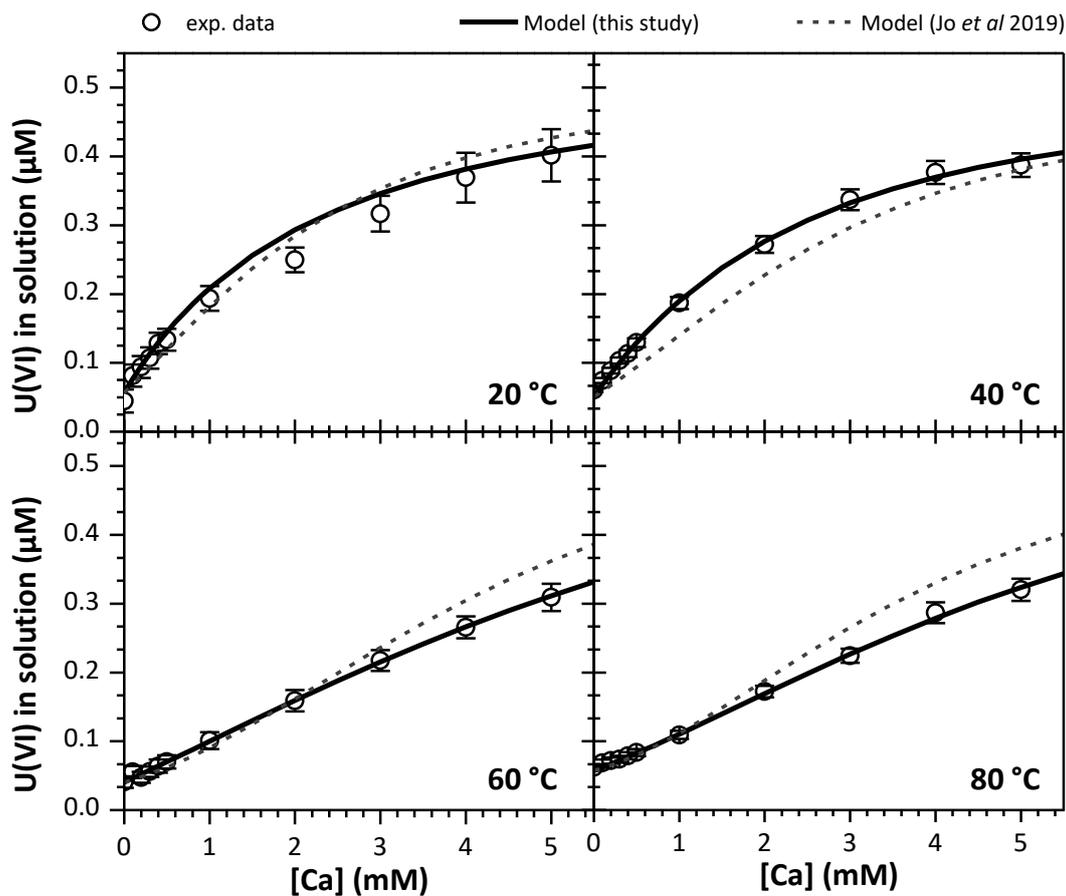


Figure 3 Uranium concentration (U(VI)) vs. calcium concentration in aqueous solution at $I = 0.1$ M NaNO_3 , total $[\text{U(VI)}_{\text{aq}}] \approx 0.5 \mu\text{M}$, with: $p\text{CO}_2 = 10^{-2.1}$ at 20°C , $p\text{CO}_2 = 10^{-2.0}$ at 40°C , $p\text{CO}_2 = 10^{-1.6}$ at 60°C , and $p\text{CO}_2 = 10^{-1.5}$ at 80°C . The lines represent the calculation performed using our model (solid lines) (see the parameters in Tables 2 and S1) and the calculation proposed by Jo et al. (dashed lines) (Jo et al., 2019)

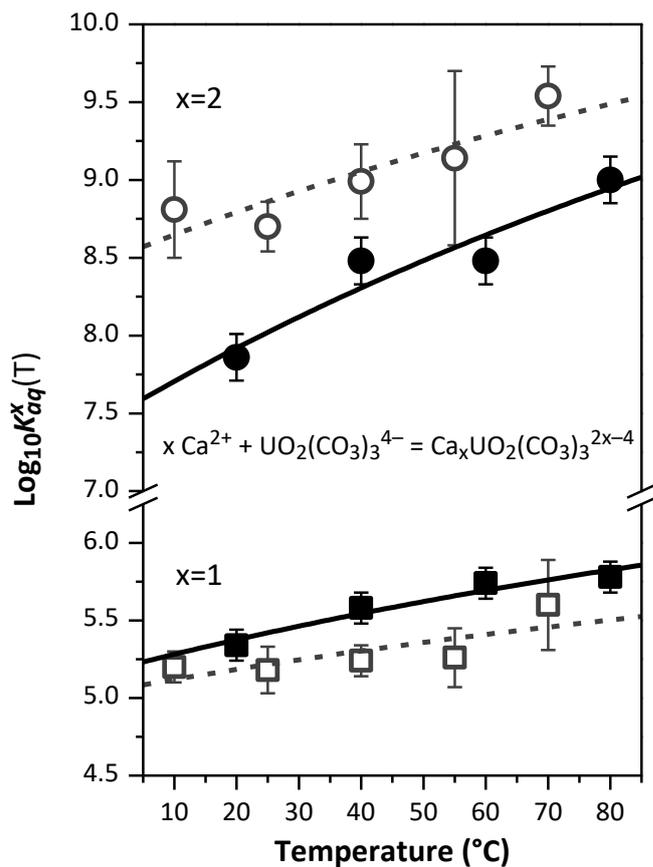


Figure 4 Comparison with literature data for temperature dependence of complexation constants; open symbols and dashed lines (Jo et al., 2019), filled symbols and solid lines (this study); x=1 (squares), x=2 (circles). The lines represent fitted curves based on the Van't Hoff Equation (eq 5). Fitting parameters can be found in the text.

Table 1: Summary of the batch experiments performed as part of the present work..

Type	NaNO ₃	S/L	[Ca]	[U(VI)] _{initial}	Temp.	pH	Alk	CO ₂ (g)
	M	g/L	mM	μM	°C		meq/L	%
I	0.1	1 – 25	0	0.46	20	7.5	2.25	1
				0.50	40	7.2	2.15	1
				0.48	60	6.9	2.2	3
				0.49	80	6.9	2.2	5
II	0.1	2.5	0 – 5	0.50	20	7.2	2.4	1
	0.1			0.48	40	7.2	2.4	1
	0.1			0.58	60	6.9	2.2	3
	0.087 ^(*)			0.54	80	6.9	2.2	5

(*) concentration set at 0.087 due to an experimental error. This situation has been taken into account in the modelling calculations.

Table 2. Comparison of the thermodynamic parameters of the Ca-U(VI)-CO₃ ternary complex reactions (p.w.: present work) with data reported in END14 (Endrizzi and Rao, 2014) and JO19 (Jo et al., 2019).

Reaction	$\log_{10} K^\circ \pm \sigma$	$\Delta_r G_m^\circ \pm \sigma$ (kJ/mol)	$\Delta_r H_m^\circ \pm \sigma$ (kJ/mol)	$T_0 \Delta_r S_m^\circ \pm \sigma$ (kJ/mol)	Reference
$\text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{CaUO}_2(\text{CO}_3)_3^{2-}$	27.27 ± 0.04	-155.6 ± 0.2	-24.4 ± 2.2	131 ± 5	p.w.
	27.00 ± 0.04	-154.1 ± 0.2	-47 ± 6	107 ± 6	END14
	$27.02 \pm 0.16^*$	$-154.2 \pm 0.9^*$	$-40.4 \pm 4.1^*$	$114 \pm 4^*$	JO19
$2 \text{Ca}^{2+} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} = \text{Ca}_2\text{UO}_2(\text{CO}_3)_3$	29.8 ± 0.2	-170.1 ± 0.9	-3 ± 10	167 ± 10	p.w.
	30.84 ± 0.04	-176.0 ± 0.2	-47 ± 7	129 ± 7	END14
	$30.55 \pm 0.16^*$	$-174.4 \pm 0.9^*$	$-42.3 \pm 5.1^*$	$132 \pm 5^*$	JO19

p.w.: present work. $\log_{10} K_{113}^\circ = \log_{10} K_{113} + \log_{10} K_{013}^\circ$ and $\log_{10} K_{213}^\circ = \log_{10} K_{213} + \log_{10} K_{013}^\circ$.

*Corrected data considering the thermodynamic data obtained from NEA-TDB. (Guillaumont et al., 2003) $\log_{10} K_{013}^\circ = 21.84 \pm 0.04$; $\Delta_r H_m^\circ = -39.2 \pm 4.1$