Speciation of uranium: Compilation of a thermodynamic database and its experimental evaluation using different analytical techniques

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ABSTRACT

Environmental hazards are caused by uranium mining legacies and enhanced radioactivity in utilized groundwater and surface water resources. Knowledge of uranium speciation in these waters is essential for predicting radionuclide migration and for installing effective water purification technology.

The validity of the thermodynamic data for the environmental media affected by uranium mining legacies is of utmost importance. Therefore, a comprehensive and consistent database was established according to current knowledge. The uranium data included in the database is based on the NEA TDB (Guillaumont et al., 2003) and is modified or supplemented as necessary e.g. for calcium and magnesium uranyl carbonates. The specific ion interaction theory (Brönsted, 1922) is used to estimate activity constants, which is sufficient for the considered low ionic strengths. The success of this approach was evaluated by comparative experimental investigations and model calculations (PHREEQC (Parkhurst and Appelo, 1999)) for several model systems. The waters differ in pH (2.7–9.8), uranium concentration (10^{-9}-10^{-4} \text{ mol/L}) and ionic strength (0.002–0.2 \text{ mol/L}). We used chemical extraction experiments, ESI-Orbitrap-MS and time-resolved laser-induced fluorescence spectroscopy (TRLFS) to measure the uranium speciation. The latter method is nonintrusive and therefore does not change the chemical composition of the investigated waters. This is very important, because any change of the system under study may also change the speciation.

1. Introduction

The environmental hazard posed by geogenically increased radioactivity (NORM - Naturally Occurring Radioactive Material) in usable water resources is not limited to the remediation of contaminated sites of former uranium mining in Saxony and Thuringia or in Central Asia (Bernhard et al., 1998; Meinrath et al., 1999). Also in the exploration and utilization of new groundwater resources, for example in Burundi (Post et al., 2017), as well as in North Africa (Hakam et al., 2000, 2001a, 2001b) and the Middle East (Smith et al., 2000), NORM rather frequently poses a problem. The principle hazard associated with uranium is the potential for environmental migration through the soil, water, and air. Uranium uptake from these compartments by flora and fauna eventually leads to exposure of man. Isolation of uranium from the biosphere needs to be guaranteed on long time scales due to its long redox potential, and the type of available complexing agents, such as carbonates, phosphates, and sulfates, etc. (Langmuir, 1997; Silva and Nitsche, 1995).

The chemistry of the early actinides, of which uranium is a member, can be very complicated and is mainly controlled by the pH, redox potential and the type of available complexing agents, such as carbonates, phosphates, and sulfates, etc. (Langmuir, 1997; Silva and Nitsche, 1995).

The redox chemistry of uranium (dominated by U(IV) and U(VI) at environmental conditions) is especially significant with respect to the mobility of uranium in the environment. The reduced species (U(IV), U^{4+}) typically precipitates from natural waters near neutral pH due to its low solubility, and so is usually characterized as relatively immobile (Silva and Nitsche, 1995). In contrast, the oxidized species of uranium, uranyl (U(VI), UO_2^{2+}), typically forms more stable aqueous complexes and is much more mobile in natural waters (Silva and Nitsche, 1995), although there are many known minerals containing uranium in the VI oxidation state (Finch and Murakami, 1999). The pentavalent uranium species (UO_2^{3+}) also exists but it is less stable than the other two oxidation states and is of no relevance in the environment (Silva and Nitsche, 1995). Hydrogen ion concentration (pH) is a significant controlling factor in the speciation of uranium because solubility, sorption, complexation and colloid formation are all sensitive to solution pH (Brown and Ekberg, 2016). Natural waters vary in pH from about 2 to 10 (Silva and Nitsche, 1995), with groundwater typically ranging from 6 to 9. Equilibria are sensitive to pH, since [H^{+}] is a component of many reactions, and therefore pH plays an important role in the determination of equilibrium component concentrations.

Predictive modelling of uranium speciation in natural waters containing NORM are often developed on the basis of thermodynamic equilibrium modelling and adequate speciation software (e.g. PHREEQC). The thermodynamic data basis readily available are partly inconsistent and not always based on the current state of knowledge.
Careful attention should be payed when using such a database on the quality, up-to-datedness and range of applicability. The available thermodynamic datasets are very different in terms of completeness and consistency of uranium compounds. Furthermore, some specific databases for special applications such as in the management of radioactive waste or in geothermal systems have been developed. Generally, these are national projects selecting data restricted to use for targeted host rock, e.g. of a deep geological repository. The databases also differ in the model used to estimate activity coefficients and in the detail of the data selection documentation. The scope of ThermoChimie (Grive et al., 1991) and b) the database presented in this work.

This work attempts to optimize the thermodynamic database and confirm the calculation results by measuring the speciation of uranium in the different solutions representing a broad range of natural groundwaters with high dissolved uranium using time-resolved laser-induced fluorescence spectroscopy, ion extraction on a resin, and electrospray ionization mass spectrometry.

2. Selected thermodynamic data

The quality of geochemical speciation modelling strongly depends on the applied thermodynamic database. Table 1 lists the uranium related thermodynamic data in the selected dataset including the respective reference. The data selected for the database essentially follows the NEA TDB (Guillaumont et al., 2003) recommendations and has been modified or supplemented as necessary, with the additions mainly following the recommendations of THEREDA DB (Moog et al., 2015). Major improvements of the thermodynamic data from (Guillaumont et al., 2003) regarding uranium speciation comprise several alkaline-earth-metal uranium-carbonates, some U(IV) species as well as various mineral phases. The respective ion interaction coefficients are provided in the supporting information in Table S 1 for cations and in Table S 2 for anions.

3. Experimental

The optimized thermodynamic database has been evaluated by means of model calculations and comparative laboratory tests applying time-resolved laser fluorescence spectroscopy (TRLFS), mass spectrometry and extraction experiments using different waters as model systems.

3.1. Model systems

In all experiments, synthetic waters were used to reduce the complexity of the system, for example by the presence of unknown organics. The synthetic waters were prepared by dissolving or diluting corresponding amounts of CaCl₂·2H₂O (Merck, ACS, Reag. Ph Eur), CaCO₃ (Merck, Reag. Ph Eur), CaSO₄·2H₂O (Fluka, p.a.), FeSO₄·7H₂O (Fluka, p.a.), H₂SO₄ (Merck, 95-95%; %, Merck, 96%, suprapur), H₃PO₄ (Fluka, 85%, ACS), HCl (VWR Chemicals, 37%), HNO₃ (VWR Chemicals, 69%, Merck, 67% suprapur), K₂SO₄ (Merck, p.a.), KCl (Merck), KOH (Merck),...
Table 1
Selected thermodynamic data for reactions involving uranium compounds and complexes. All data refer to the reference temperature of 298.15 K and to the standard state, i.e., a pressure of 0.1 MPa and, for aqueous species, infinite dilution (\( I = 0 \)). All the values adapted from the NEA TDB (Guillaumont et al., 2003) are presented with three digits after the decimal point, regardless of the significance of these digits.

| Reaction | Log K° | Ref. |
|----------|--------|------|
| Aqueous species | | |
| \( U^{4+} + e^- = U^{3+} \) | -9.353 | a |
| \( 4H^+ + UO_2^{2+} + 2e^- = U^{4+} + 2H_2O \) | 9.038 | |
| \( UO_2^{2+} + e^- = UO_2^- \) | 1.484 | |
column. Phosphate concentration has been calculated based on the
determination of elemental phosphor (ICP-OES). The carbonate species
has been derived from sample alkalinity, which has been quantified by
titration (Mettler Toledo T90) with hydrochloric acid. The pH of the
samples was measured using an Orion™ Dual Star™ equipped with a
Orion™ PerpHecT™ combination pH micro electrode both from
Thermo Scientific™. Calibration was performed with technical buffer
solutions pH 4.01 and 7.0 from purchased from WTW and Thermo
Scientific Orion™ pH 9.18 and 12.46 buffer reference standard solution.
All water samples were filtered by a 0.2 μm mixed cellulose membrane
filter from Whatman prior to further treatment.

The uranium concentration in the model system 2_2 is too low for
TRLFS measurements, the typical uranyl fingerprint is not visible in the
spectra, strongly disturbed by scattered laser light. Therefore, a con-
centration series was prepared and used for further characterization of
the system. The composition of the water remained unchanged except
for increasing uranium concentrations of [U] = 10⁻⁵, 10⁻⁶, 10⁻⁷ and
10⁻⁸ mol/L.

3.2. Modelling

The measured composition of the synthesized waters (Table 2) were
used as data input for the speciation modelling using PhreeqC
(Parkhurst and Appelo, 1999). Because the filtered sample solutions
were clear, appeared homogeneous and did not show any precipitate,
undersaturation with respect to any minerals is assumed. The calcula-
tions were carried out for a temperature of 25 °C and oxygen and carbon
dioxide contents in equilibrium with the atmosphere. Thus, the dis-
solution of oxygen and carbon dioxide is considered and the carbonate
content of the solution in equilibrium is taken into account.

3.3. Time-resolved laser fluorescence spectroscopy (TRLFS)

In this work two different analysis modes of TRLFS are used. (1)
Fluorescence spectra are recorded after excitation at constant laser
wavelength. Band positions of the emission spectra intensity distribu-
tion depend on the chemical environments of the ions. (2) The fluor-
escence lifetimes of the uranyl species in solution are determined by
recording the decrease in fluorescence intensity after different delay
times after the (pulsed) excitation.

U(VI) luminescence spectra were measured using a Nd:YAG laser
system (PS6100 series, Ekspla, Vilnius, Lithuania) operated at 50 Hz
with a pulse duration of 7 ns. The excitation wavelength was 266 nm
with a measured laser power of 7 mW. The luminescence emission was
focused into a spectrograph (Shamrock 303i, Andor Technology Ltd.,
Belfast, UK) with a polychromatographic grating (150 or 300 lines/
mm) via fiber optics and detected using a CCD camera system (Andor
iStar 743, Andor Technology Ltd., Belfast, UK). For measuring the time
dependent emission decay, the delay time between laser pulse and
camera gating was varied between 0 and 10 000 μs. Time-resolved
spectra were recorded by measuring 80–100 spectra times. For im-
proved statistics, at each delay time, 80–100 fluorescence spectra were
measured and summed.

The evaluation of the measurement data to determine the fluores-
cence lifetime is carried out software-based on the computer, using an
in-house program. The fluorescence intensity is integrated over all ur-
anyl bands and plotted as a function of time. The fluorescence lifetime
is subsequently determined by a multi-exponential (usually mono- or
bi-exponential) fit (equation (1)) to these data

\[
I(t) = \sum_{i=1}^{N} A_i e^{-t/\tau_i}
\]

(1)

Where I is the number of fitted components, A_i is a pre-exponential
factor, which corresponds to the number of the emitted photons of the
respective component, and \( \tau_i \) is the corresponding fluorescence lifetime.

The details of lifetime fitting are described, e.g., in (Kimura and
Choppin, 1994) for differential lifetime measurements on uranyl in
(Geipel et al., 1996) and for the method of integrated lifetime emission
spectroscopy used in the present work in (Freyer et al., 2009).

Due to very strong dynamic quenching observed in measurements at
room temperature, which is caused by the in some cases very high
chloride contents, the measurements had to be carried out at low
temperatures. Previous work has shown that under cryogenic tem-
peratures, many of the fluorescence quenching and spectral broadening
effects can be suppressed, resulting in a significant increase in spectral
intensity and resolution (Wang et al., 2004, 2008). For cooling pur-
poses, a cryostat working at liquid helium temperature (4K) is used in
this work. In the present work, cooling was the only choice for ob-
taining spectra at all and was successfully applied to the speciation of
uranyl complexes in aqueous systems (Osman et al., 2013; Steudtner
et al., 2010). However, if fast kinetics are involved such as for instance
hydrolysis changes in species distributions might occur.

3.4. Extraction experiments

The ratio of ternary complexes (MUO₂(CO₃)₃)(H₂O)²⁻ and M₂UO₂(CO₃)₃
of uranyl and carbonate with alkaline earth metals (M²⁺ corresponds to
Mg²⁺ and Ca²⁺) to anionic uranyl carbonate complexes
(UO₂(CO₃)₃)⁶⁻ is determined by extraction experiments on an
anion exchange resin. Uranium sorption on the resin corresponds to
anion exchange between NO₃⁻ and anionic uranyl species
(UO₂(CO₃)₃)⁶⁻, UO₂(CO₃)₃²⁻, (UO₂)₂CO₃(OH)₂⁻. As described by
(Dong and Brooks, 2006, 2008) the uranium absorption on the ion
exchange resin in the absence of alkaline earth metals in the pH range
of 7–10 leads to a constant distribution coefficient D (equation (2))
of 25760 mg/L.

\[
D = \frac{[U(VI)]_{R}}{[U(VI)]_{aq}}
\]

(2)

M-UO₂(CO₃)₂-complexes are not or only weakly adsorbed on the
anion exchange resin (Dong and Brooks, 2006), allowing one to cal-
culate the proportion of these complexes in the solution from the de-
termined partition coefficient. Extraction experiments were carried out
for the model systems 1_1, 1_2, 2_1, and 3_1. For the remaining model
systems, corresponding investigations were not useful, because at the
corresponding pH no anionic uranyl species are expected for sample
2_2, the uranium concentration in sample 3_2 was below the detection
limit of the ICP-OES and samples 4_1 and 4_2 do not contain any car-
bonate. Gel Type Amberlite IRA-410 strong base anion exchange resin
was purchased from Sigma-Aldrich (St. Louis, MO) in the chloride form
and converted to the nitrate form prior to use as described in (Dong
and Brooks, 2006). Uranium batch adsorption experiments were carried out
at 25 °C and atmospheric CO₂ in 50 ml polyethylene bottles using 20 ml
solution and 0.05 g air-dry resin. The suspensions were equilibrated on
a shaker for 5 days. Thereafter, the solution was filtered and prepared
by acidification for U(VI) and metal quantification. The resin beads
were separated by filtration, rinsed rapidly with three 5 ml aliquots of
distilled water, and transferred to 2.5 ml of 1% HNO₃ in a 10 ml poly-
ethylene bottle. Desorbed metal were quantified after an extraction
period of three days either by ICP-MS or ICP-OES.

Aqueous Mg, Ca and U concentrations were measured using in-
ductively coupled plasma mass spectrometry (ICP-MS, iCAP Q from
ThermoFisher), autosampler Cetax ASX-520, concentric atomizer,
quadruartz cyclone spray chamber with inner tube, plasma power 1550 W
and inductively coupled plasma optical emission spectrometry (ICP-
OES) with an iCAP 6200 Duo from ThermoFisher (iTeva Software,
Cetax ASX-260 autosampler, Mira-Mist nebulizer, cyclone spray
chamber, 1150 W plasma power) or an ARCONS from Spectro Analytical
Instruments GmbH (Klieve, Germany).

The measured amount of desorbed metal was used to determine the
corrected U(VI) distribution coefficients, as described in (Dong and Brooks, 2006). This takes into account the possibility that MUO₂(CO₃)₂⁻ and M₂UO₂(CO₃) could be adsorbed to the resin according to the following exchange reactions

\[ 2\text{RNO}^+ + \text{MUO}_2(\text{CO}_3)_2^- = (\text{R}^+)\text{MUO}_2(\text{CO}_3)_2^- + 2\text{NO}_3^- \]  
(3)

\[ 2\text{RNO}^+ + 2\text{MUO}_2(\text{CO}_3)_2^- = (\text{R}^+)\text{MUO}_2(\text{CO}_3)_2^- + 2\text{NO}_3^- + M^{2+} \]  
(4)

Where \( R^+ \) is the functional group of the anion-exchange resin.

To address this issue (Dong and Brooks, 2006), developed a correction procedure. The total amount of \( M^{2+} \) on the resin phase, either was extracted and quantified in acidic solution (1% HNO₃) by the aforementioned desorption process. The amount of \( M^{2+} \), corresponding to \( (\text{R}^+)\text{MUO}_2(\text{CO}_3)_2^- \), \( M_R \) (μmol), was obtained from equation (5)

\[ M_R = C_d - V_d \frac{m_{W} \varepsilon}{\rho_W} \]  
(5)

With the total metal concentration in the desorption solution \( C_d \) (μmol/mL), the volume of desorption solution \( V_d \) (mL), the metal concentration in the equilibrated bulk solution \( C_b \) (μmol/mL) (here \( M^{2+} \) concentration in resin pore water is assumed to equal that in the bulk solution at equilibrium), the solution density \( \rho_N \) (g/cm³), the mass \( (g) \) of wet resin \( m_W \), and the fractional water content of wet resin \( \varepsilon \). According to the stoichiometric ratio, \( M_R \) (μmol) should correspond to the amount of U(VI) associated or entrained in the resin pore water, was extracted and quantified in acidic solution (1% HNO₃) by the aforementioned desorption process. The amount of \( M^{2+} \), corresponding to \( (\text{R}^+)\text{MUO}_2(\text{CO}_3)_2^- \), \( M_R \) (μmol), was obtained from equation (5) by subtracting \( M_R \) from the total absorbed [U(VI)]\(_{\text{aq.}}\) and adding \( M_R/V \) to the aqueous phase [U(VI)]\(_{\text{aq.}}\).

3.5. Orbitrap mass spectrometry

The mass spectrometric measurements were carried out on a hybrid mass spectrometer Orbitrap Elite (Thermo Fisher Scientific, Waltham, Massachusetts, USA) equipped with a Nanospray Flex Ion Source. Nanospray needles were purchased from New Objective Inc (Woburn, MA, Massachusetts, USA) equipped with a Nanospray Flex Ion Source. NanoESI needles were purchased from New Objective Inc (Woburn, MA, USA). The evaluation of the obtained spectra was carried out with the Xcalibur software (Thermo Fisher Scientific, Waltham, Massachusetts, USA). For each sample, a mass spectrum was recorded for 30 s and the intensities were then averaged over time.

4. Results and discussion

4.1. Modelling

Species distributions for the model systems are calculated by PhreeQ using the database equilibrium constants of Table 1. All uranium species with a relative abundance exceeding 0.01% are plotted in Fig. 2. The polymeric species are weighted with respect to their number of uranyl units.

The results for the model system 1_1 and 1_2 are very similar and dominated by alkaline-earth-metal uranium-carbonates. The same applies for sample 2_1, while 2_2 is dominated by UO₂CO₃. This system is characterized by a lower pH and a significantly lower concentration of uranium. Since the concentrations of calcium and magnesium are low, sample 3_1 is dominated by uranyl carbonate. Samples 4_1 and 4_2 are acidic waters with high sulfate content and are therefore dominated by uranyl sulfates.

Sample 3_2 was prepared from sample 3_1 by addition of phosphate ions. Uranium speciation is not shown in Fig. 1, since speciation modelling revealed the appearance of some supersaturated uranyl phosphate phases of low solubility, namely uranyl phosphate, autunite, and saleeite. A precipitate was not observed visually, due to the low U(VI) concentration and the resulting small amount of precipitate. The TRLFS measurement delivered no signal, regardless of the delay time, which also indicates precipitation of the U(VI) most likely phosphate compounds. The uranium concentration in sample 3_2 was below the detection limit of the ICP-OES. The modeled species distribution based on sample 3_1, and the addition of phosphate and pH change, taking the precipitation of supersaturated phases into account, predicted 4.10⁻⁶ mol/L of dissolved uranium, which is one order of magnitude less compared to sample 3_1.

The results for the dilution series of sample 2_2 are shown in Fig. 3 together with those for the actual system. The uranium speciation in the systems are relatively similar for uranium concentrations between 10⁻⁹ and 10⁻⁷ mol/L and change dramatically as the concentration is further increased. At a uranium concentration of 10⁻³ mol/L, uranylhydroxocarbonate is the dominant uranium species.

4.2. Cryogenic time resolved laser fluorescence spectroscopy

To evaluate the thermodynamic calculations, all water samples were measured by TRLFS. Uranium speciation can be obtained from the characteristic lifetimes and the fluorescence wavelengths of the different complexes. Fig. 4 displays the TRLFS spectra of sample 1_1 measured at low temperature (4 K) with delay times between 0.1 and 5 ms. A detailed comparison of the emission band positions of the model systems together with reference data from (Wang et al., 2004) is given in Table 3.

Calcium uranyl carbonate can be assigned as the dominant species for samples 1_1, 1_2, and 2_1, which is in agreement with the calculations. However, the two calcium uranitates (CaUO₂(CO₃)₃⁻ and Ca₂UO₂(CO₃)₃) cannot be distinguished by TRLFS. Additionally, fluorescence lifetimes were determined for the model systems as described above. They are also included in Table 3. For the samples 1_1, 1_2, and 2_1, the longer lifetime can be attributed to the calcium uranyl carbonate, which has already been identified as the dominant species by the band position. A second species cannot be unambiguously assigned.

A comparison of the emission maxima of sample 3_1 with literature data (Table 3) identifies UO₂(CO₃)₃⁻ as the most abundant uranium (VI) species. This finding corroborates the results of the speciation calculation. The calculated fluorescence lifetimes for sample 3_1 cannot be clearly assigned to any species. The longer calculated lifetime of 1045 μs agrees reasonably well with the literature value of the uranium (VI) species of the highest expected abundance UO₂(CO₃)₄⁻, whose lifetime may be overestimated as the lifetimes of UO₂(CO₃)₄⁻ (τ = 883 μs) and Ca₂UO₂(CO₃)₃ (τ = 1282 μs) cannot be resolved. The shorter lifetime (τ = 241 μs) most closely matches the one of MgUO₂(CO₃)₂⁻, although the lifetime is greater than expected. The reason might originate from the process of data fitting: A biexponential function is characterized by five parameters that are to some extent covariant limiting the robustness of each individual parameter of the fit.

The emission maxima of sample 4_1 are compared in Table 3 with literature data by (Wang et al., 2004) for different uranyl species. The emission band positions most closely match the calcium uranyl carbonate complex, but this is not consistent with its very long lifetime of 1282 μs. A comparison with the water analysis (Table 2) also excludes a calcium uranyl carbonate complex, since the water contains no carbonate. Unfortunately, for uranyl sulfate complexes, no comparative data is available at low temperatures. The time resolved spectroscopy of sample 4_1 gave two lifetimes. The shorter one matches the lifetime of the free uranyl cation of τ = 270 μs (Wang et al., 2004) at 4 K. While this assignment is rather plausible, spectral band positions do not match. The longer lifetime of τ = 747 μs cannot be assigned to any species expected based on the modelling. The band positions and fluorescence lifetime determined for sample 4_2 correspond most likely to the free uranyl ion.

According to the thermodynamic modelling (compare Fig. 2),
uranyl sulfate is expected to be the principal (most abundant) species in sample 4_2. As with sample 4_1, however, a comparison with the literature for the sulfate species is not possible. The free uranyl ion, which in band position and lifetime agrees well with the literature, has an expected relative abundance of 12.0% in this sample.

The band positions of the samples from the dilution series of system 2_2 with uranium concentrations of 10\(^{-5}\), 10\(^{-6}\), and 10\(^{-7}\) mol/L agree quite well. The matching bands are slightly shifted to shorter wavelengths compared to the UO\(_2\)CO\(_3\)(aq). The time resolved spectroscopy results in lifetimes around 600 μs for all three samples which can be assigned to UO\(_2\)CO\(_3\)(aq). For samples with higher uranium concentrations (10\(^{-5}\) and 10\(^{-6}\) mol/L) a second shorter lived species was detected and can be assigned as (UO\(_2\))\(_2\)CO\(_3\)(OH)\(_3\)^-, which is in good agreement with the modelling results. Table 4 summarizes the results of the cryo-TRLFS investigations.

### 4.3. Time resolved laser fluorescence spectroscopy at room temperature

Due to the lack of reference data for TRLFS measurements of uranyl sulfate at low temperature, additional investigations were performed for samples 4_1 and 4_2 at room temperature. Due to quenching effects, the signal to noise ratio was rather low as can be seen in Fig. 5 and the evaluation of the lifetimes was difficult. Nevertheless, two fluorescence lifetimes were determined for both samples.

In the case of sample 4_2 the shorter fluorescence lifetime agrees very well with UO\(_2\)(SO\(_4\))\(_2\)^{2-} (compare Table 5), while the positions of the emission bands are slightly shifted to higher wavelengths. While UO\(_2\)(SO\(_4\))\(_2\)^{2-} is identified as major species on the basis of the measurement, UO\(_2\)SO\(_4\)(aq) is expected as most abundant species in this sample as can be seen in Fig. 2. However, distinguishing the uranyl sulfate complexes based on the band position is difficult because the
The longer fluorescence lifetimes cannot be assigned to any species expected on the basis of the modelling results. For sample 4_1 an assignment is not possible on the basis of the TRLFS investigation at room temperature. The difficulties in the interpretation are caused by the rather low quality of the TRLFS measurements at room temperature, which is due to quenching effects as discussed above, and do not necessarily point to an inaccuracy in the thermodynamic data.

**Table 3**

A comparison of TRLFS measurements of the model systems with spectroscopic data for model complexes (Wang et al., 2004) and own spectroscopic data for MgUO₂(CO₃)₂⁻ (details are provided in the Supporting Information). All measurements were conducted at liquid helium temperature.

| Species/sample | Main emission wavelengths (nm) | τ (μs) |
|----------------|-------------------------------|-------|
| UO₂²⁺ | 492–514 – 538–564 – 592 | 270 |
| (UO₂)₂CO₃(OH)₃⁻ | 523–542 – 561 | 144 |
| UO₂CO₃ | 479–498 – 519–542 – 567 | 465 |
| UO₂(CO₃)₂⁻ | 477–496 – 517–540 – 564 | 962 |
| Ca₂(UO₂(CO₃)₃)₂⁻ | 480–499 – 520–542 – 566 | 883 |
| Mg₂(UO₂(CO₃)₆)₄⁻ | 481–501 – 523–546 – 572 | 1282 |
| 1,1 | 481–501 – 524–549 – 578 | 512 ± 44; 1237 ± 62 |
| 1,2 | 482–503 – 526–552 – 579 | 606 ± 128; 1404 ± 69 |
| 2,1 | 480–502 – 524–549 – 574 | 479 ± 27; 1155 ± 13 |
| 2,2 (U 10⁻⁵ mol/L) | 475–494 – 514–536 | 118 ± 32; 604 ± 100 |
| 2,2 (U 10⁻⁶ mol/L) | 470–493 – 514–530 | 129 ± 28; 666 ± 26 |
| 2,2 (U 10⁻⁷ mol/L) | 475–494 – 514–536 | 519 ± 281 |
| 3,1 | 480–499 – 520–541 – 565 | 241 ± 15; 1045 ± 9 |
| 3,2 | 481–501 – 522–544 | 230 ± 5; 747 ± 12 |
| 4,1 | 490–512 – 535–558 | 240 ± 90 |

**4.4. Extraction experiments**

From the uranium concentrations in the elution and desorption solutions, respectively, distribution coefficients $D_M$ are calculated and corrected according to Dong et al. (Dong and Brooks, 2006) They are given in Table 6 along with relative abundances of UO₂(CO₃)₃⁴⁻ and MgUO₂(CO₃)₃₂⁻ and calculated values. The proportion of anionic uranyl carbonates determined in the extraction experiments for the model systems 1_1, 1_2, and 3_1 is significantly lower than what is expected from the model calculations. The distribution coefficient for UO₂(CO₃)₃⁴⁻ $D_0$ is 25760 ml/g according to (Dong and Brooks, 2006). For sample 3_1, the distribution coefficient $D_M$ is 15363 mL/g, which corresponds to a proportion of UO₂(CO₃)₃⁴⁻ of 59.6%. The modelling gives an expected abundance of 90.7% (see Fig. 2). However, the experimental result and the calculation agree within the order of magnitude. Uncertainties in the extraction experiments lie in the quantitative transfer of the resin, the simplification that the only absorbed species was UO₂(CO₃)₃⁴⁻ and measurement uncertainties in the analysis. The overall trend is in line positions of the main emission bands are very similar (Vercouter et al., 2008). The longer fluorescence lifetimes cannot be assigned to any species expected on the basis of the modelling results. For sample 4_1 an assignment is not possible on the basis of the TRLFS investigation at room temperature. The difficulties in the interpretation are caused by the rather low quality of the TRLFS measurements at room temperature, which is due to quenching effects as discussed above, and do not necessarily point to an inaccuracy in the thermodynamic data.

**Table 4**

Summary of the cryo-TRLFS investigation. All identified species are denoted with X.

| Species/sample | 1_1 | 1_2 | 2_1 | 2_2 (10⁻⁵) | 2_2 (10⁻⁶) | 2_2 (10⁻⁷) | 3_1 | 4_1 | 4_2 |
|----------------|-----|-----|-----|------------|------------|------------|-----|-----|-----|
| UO₂²⁺ | X | X | X | X | X | X | X | X | X |
| (UO₂)₂CO₃(OH)₃⁻ | X | X | X | X | X | X | X | X | X |
| UO₂CO₃ | X | X | X | X | X | X | X | X | X |
| UO₂(CO₃)₂⁻ | X | X | X | X | X | X | X | X | X |
| Ca₂(UO₂(CO₃)₃)₂⁻ | X | X | X | X | X | X | X | X | X |
| Mg₂(UO₂(CO₃)₆)₄⁻ | X | X | X | X | X | X | X | X | X |
with expectations.

Between 0.007 and 0.024 μmol magnesium and up to 0.05 μmol calcium metal adsorb on the anion exchange resin in the extraction experiments. Adsorbed magnesium and calcium were found in all samples, except for calcium in sample 3_1 (Dong and Brooks, 2006). Reported no metal adsorption to the resin in uranium-free controls. Accordingly, the metals adsorbed in the present study can be assigned to the alkaline-earth-metal uranium-carbonates, and thus a qualitative detection of these species has taken place.

4.5. Orbitrap mass spectrometry

The samples from the dilution series of the model system 2_2 with uranium concentrations of 10⁻⁵-10⁻⁷ mol/L were further analyzed by an electrospray Orbitrap mass spectrometer. The source was operated in positive mode because the uranyl hydroxide (UO₂OH⁺) cation was expected to be the second most abundant species besides the uncharged uranyl carbonate (UO₂CO₃). In order to simplify spectra evaluation, high-purity chemicals were used. Nevertheless, the spectra are dominated by the background electrolyte. Only a few additional peaks in the solutions could be identified and attributed to uranium species.

The peaks at mass to charge ratios of 323.06 and 305.05 and 287.04 can be assigned to the uranyl hydroxide ion carrying different numbers of water molecules in the solvent shell. The water molecules are a remnant of the ESI process, where the evaporation of the solvent was not complete. While this effect increases the number of peaks it is nevertheless desirable because it demonstrates soft ionization by the ESI process. Furthermore, additional peaks in the spectra can be assigned to the uranyl ion (UO₂²⁺) carrying one or two water molecules. The uranyl ion (UO₂²⁺) appears as a singly-charged species, but it is known from previous ESI-MS studies that uranyl undergoes partial reduction after desolvation, resulting in a UO₂⁻ peak at 270.04 m/z and 288.05 and 306.06 respectively (Agnes and Horlick, 1992; Galindo and Del Nero, 2013; Moulin et al., 2000). Uranyl hydroxide, as just described, could be identified as the dominant positively charged species in all samples of the dilution series. Fig. 6 compares the intensities of the peaks of uranyl hydroxide with 0, 1 and 2 water molecules and free uranyl with one or two water molecules. The intensity of the peaks increases with increasing uranium concentration and the number of water molecules. As can be seen from the diagram, the intensity of the peaks increases with the uranium concentration and the number of water molecules, with no more than two water molecules in the solution shell. The stability of the measurements and the associated reproducibility do not allow absolute quantification, but only a comparison of the intensities with each other.

4.6. Comparison of modelling and experimental results

The results of the model calculations are summarized in Table 7, the calculated relative abundances are given as percentage and are printed in bold for all species confirmed experimentally. In addition, for all species with expected relative abundances greater than one percent, which could not be confirmed experimentally, the absolute concentrations in mol/L are given in parentheses. For species with relative abundances < 0.1% or equal to zero the value is omitted for the sake of clarity.

For all investigated neutral and alkaline systems, at least the two, in most cases the three, species with the highest expected relative abundances could be confirmed. All species with expected concentrations > 10⁻⁷ mol/L were detected. It should be noted that Ca₂UO₂(CO₃)₃ and Ca₂UO₂(CO₃)₂⁻ cannot be distinguished by the chosen methods. The same applies to the detection of UO₂(CO₃)₄⁻ and UO₂(CO₃)₂²⁻ in the extraction experiments. Low temperature spectroscopic data of MgUO₂(CO₃)₃⁻ has been obtained for the first time using TRLFS (Supplementary Information).

For the acidic waters of the mining area Königstein, however, there are contradictions to the model calculations. Based on the model calculation, UO₂SO₄(aq) is the dominating uranium species for both waters, while the emission bands of the two solutions are clearly shifted from each other both at low and room temperature. On the other hand, the

Table 6

| DM  | UO₂(CO₃)ₓ²⁻ (%) | MₓUO₂(CO₃)₂(x−1)⁻ (%) | Calc: UO₂(CO₃)ₓ²⁻ (%) |
|-----|----------------|------------------------|-----------------------|
| 1_1 | 2681           | 10.4                   | 89.6                  |
| 1_2 | 220            | 0.9                    | 99.1                  |
| 2_1 | 494            | 1.9                    | 98.1                  |
| 3_1 | 15364          | 59.6                   | 40.4                  |
evaluation of the fluorescence lifetimes gives comparable results for both samples. Due to the experimental difficulties described above, no clear statement can be made here.

5. Conclusions and outlook

It has been found that common thermodynamic databases for geochemical modelling software differ strongly in completeness, consistency and recent knowledge about uranium speciation in aquatic environments. This affects especially stable earth alkali uranyl carbonate and low dissolvable phosphate uranyl complexes that are highly relevant for migration behavior of uranium in neutral and alkaline systems. This paper not only strives to increase the sensitivity of geochemical modelers for this fundamental issue. Furthermore, it attempts to optimize the thermodynamic database and evaluate its validity for various natural high uranium aquatic systems.

The optimized database was evaluated using model calculations and comparative laboratory experiments applying time-resolved laser fluorescence spectroscopy (TRLFS), extraction experiments and orbitrap mass spectrometry. The results reflect the capabilities as well as limitations of these advanced analytical techniques to quantify uranyl speciation in natural water. In the case of model system 2,2, a concentration series with uranium concentrations of 10⁻⁵, 10⁻⁶ and 10⁻⁷ mol/L was prepared and used for evaluation because the concentration of uranium in the natural analogue was below the detection limits of TRLFS and Orbitrap-MS. While some contradictions remain for the acidic waters, in the cases of all neutral and alkaline systems, at least the two, in most cases the three, species with the highest expected relative abundances could be confirmed.

The presented database is inherently consistent. Keeping the above mentioned analytical capabilities in mind, it can be considered to meet the observed uranyl speciation distribution in the used neutral and alkaline model systems and comparable waters, such as shallow groundwater and pore water, reasonably well. Additional investigations are required for waters with significantly different compositions, such as acidic, sulfate dominated waters.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.10.006.

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