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Hydrothermal aqueous speciation: studies at LANL

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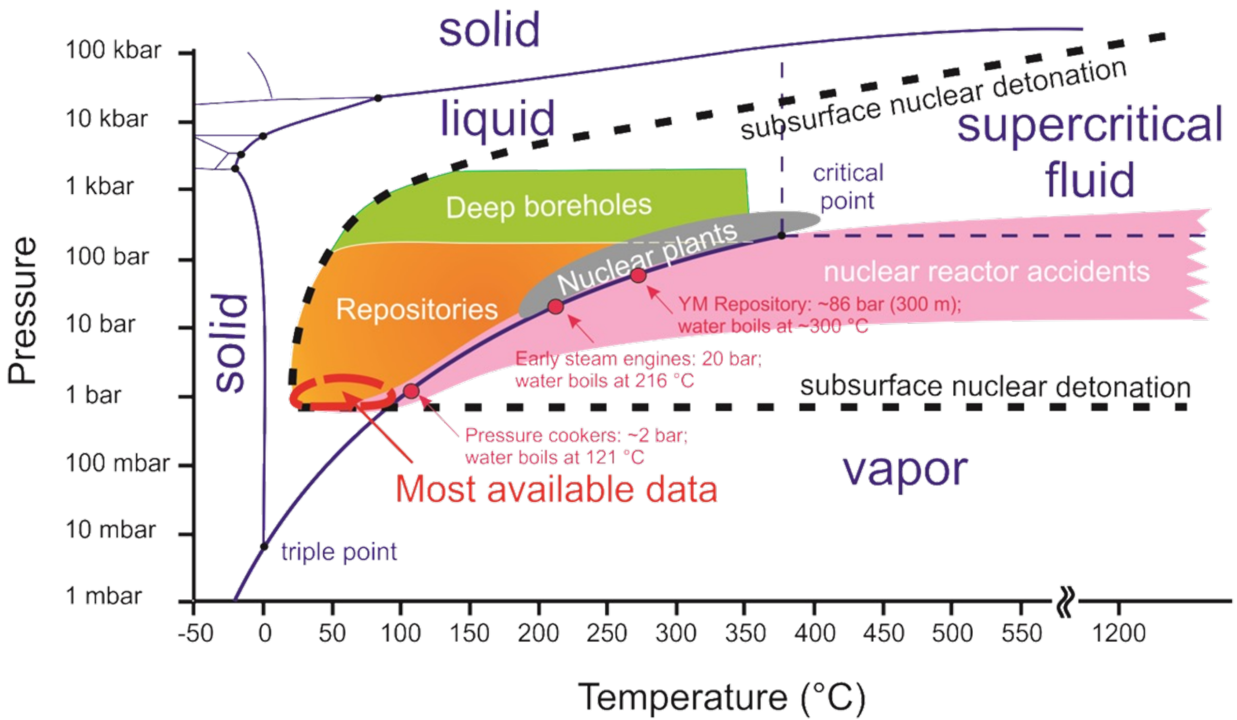
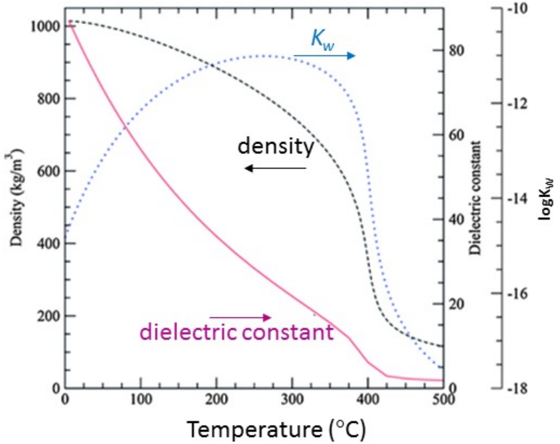


Actinides: speciation is well mapped at T<100 C, but is poorly known at high T

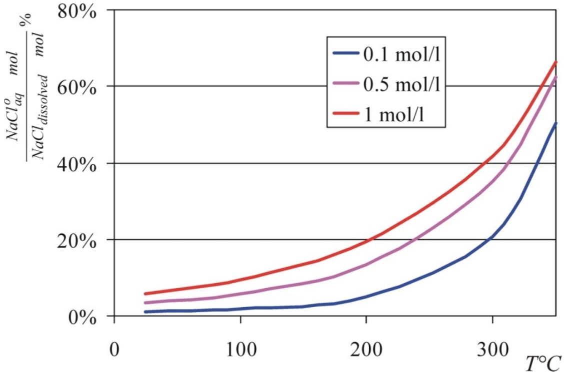
General considerations - what to expect at high T

3D hydrogen bonding network ➔ shielding ➔ stabilizes dissolved charged species

Effect of temperature → disruption of H-bonding network → shielding efficiency decreases

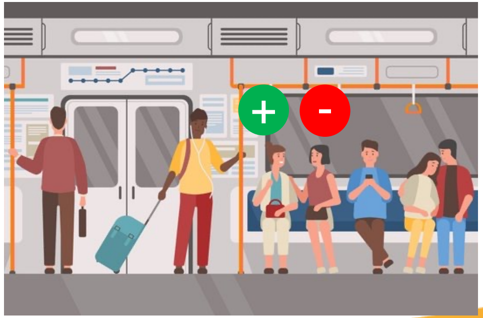


$NaCl^o_{aq} = Na^+ + Cl^-$



low T

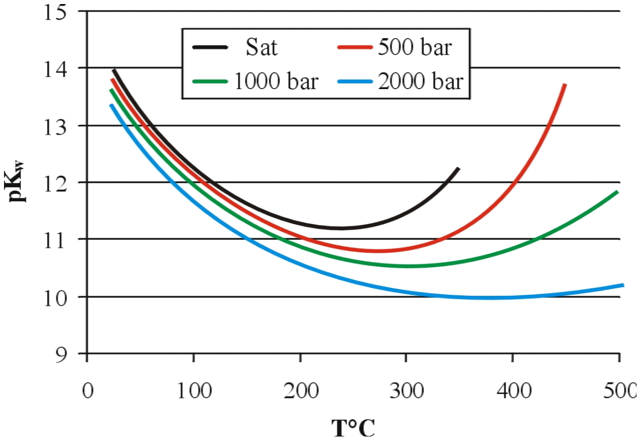
Charged species getting less stable



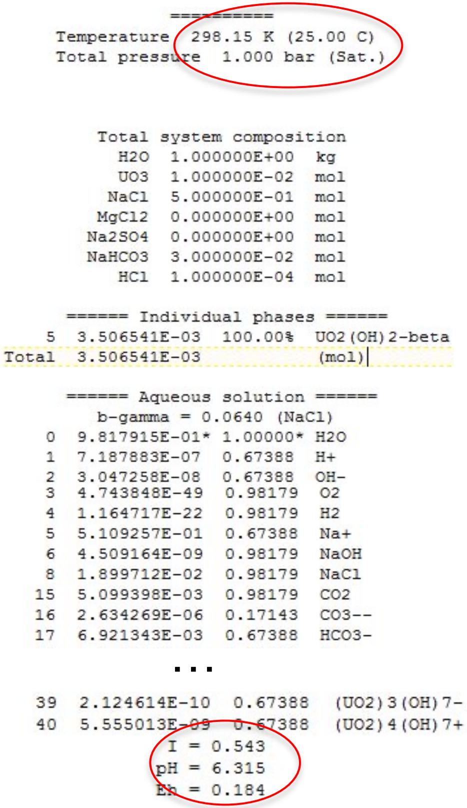
high T

General considerations - what to expect at high T

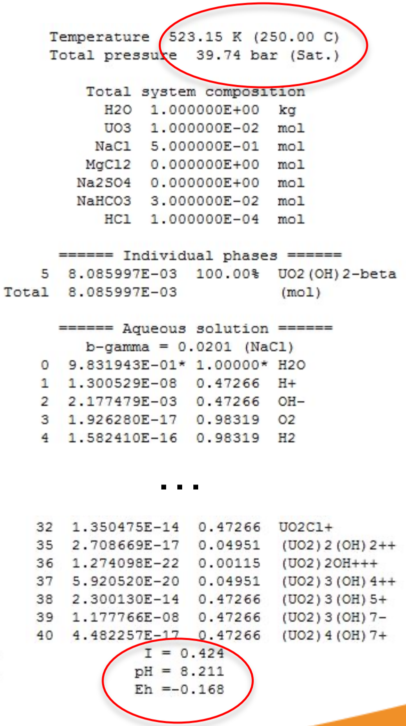
Marshall W.L., and Franck E.U. (1981) Ion product of water substance, 0-1000°C, 1-10,000 bars new international formulation and its background. *J. Phys. Chem. Ref. Data*, 10(2), 295-304



- pH(25 C) ≠ pH(T)
- We cannot use pH as the indicator of the solution acidity if temperature and/or pressure changes. It has to be normalized to the corresponding values of pK_w.



```
           ===========
  Temperature  298.15 K (25.00 C)
  Total pressure  1.000 bar (Sat.)


    Total system composition
       H2O  1.000000E+00  kg
       UO3  1.000000E-02  mol
      NaCl  5.000000E-01  mol
     MgCl2  0.000000E+00  mol
    Na2SO4  0.000000E+00  mol
    NaHCO3  3.000000E-02  mol
       HCl  1.000000E-04  mol

   ====== Individual phases ======
     5  3.506541E-03  100.00%  UO2(OH)2-beta
Total   3.506541E-03            (mol)

   ====== Aqueous solution ======
      b-gamma = 0.0640 (NaCl)
   0  9.817915E-01* 1.00000* H2O
   1  7.187883E-07  0.67388  H+
   2  3.047258E-08  0.67388  OH-
   3  4.743848E-49  0.98179  O2
   4  1.164717E-22  0.98179  H2
   5  5.109257E-01  0.67388  Na+
   6  4.509164E-09  0.98179  NaOH
   8  1.899712E-02  0.98179  NaCl
  15  5.099398E-03  0.98179  CO2
  16  2.634269E-06  0.17143  CO3--
  17  6.921343E-03  0.67388  HCO3-

             ...

  39  2.124614E-10  0.67388  (UO2)3(OH)7-
  40  5.555013E-09  0.67388  (UO2)4(OH)7+
          I = 0.543
         pH = 6.315
         Eh = 0.184
```



```
  Temperature  523.15 K (250.00 C)
  Total pressure  39.74 bar (Sat.)

      Total system composition
         H2O  1.000000E+00  kg
         UO3  1.000000E-02  mol
        NaCl  5.000000E-01  mol
       MgCl2  0.000000E+00  mol
      Na2SO4  0.000000E+00  mol
      NaHCO3  3.000000E-02  mol
         HCl  1.000000E-04  mol

     ====== Individual phases ======
        5  8.085997E-03  100.00%  UO2(OH)2-beta
  Total  8.085997E-03             (mol)

     ====== Aqueous solution ======
        b-gamma = 0.0201 (NaCl)
    0  9.831943E-01* 1.00000* H2O
    1  1.300529E-08  0.47266  H+
    2  2.177479E-03  0.47266  OH-
    3  1.926280E-17  0.98319  O2
    4  1.582410E-16  0.98319  H2

               ...

   32  1.350475E-14  0.47266  UO2Cl+
   35  2.708669E-17  0.04951  (UO2)2(OH)2++
   36  1.274098E-22  0.00115  (UO2)2OH+++
   37  5.920520E-20  0.04951  (UO2)3(OH)4++
   38  2.300130E-14  0.47266  (UO2)3(OH)5+
   39  1.177766E-08  0.47266  (UO2)3(OH)7-
   40  4.482257E-17  0.47266  (UO2)4(OH)7+
            I = 0.424
           pH = 8.211
           Eh =-0.168
```

General considerations - what to expect at high T

Extrapolation to infinite dilution

In order to derive thermodynamic properties of species at elevated temperature we need to use reliable ***activity models*** ($M = a*\gamma$)

Ambient conditions

SIT, Pitzer, etc.

A variety of developed EoS is available; model's coefficients are derived for solutions of very different compositions

Elevated temperatures

HKF- based models only

Have been developed for only solutions with predominance of 1:1 electrolytes; data are available for only **NaCl**, KCl, NaOH, KOH background electrolytes

We had to start from chloride speciation and to continue working with NaCl-predominated solutions

Solution's densities

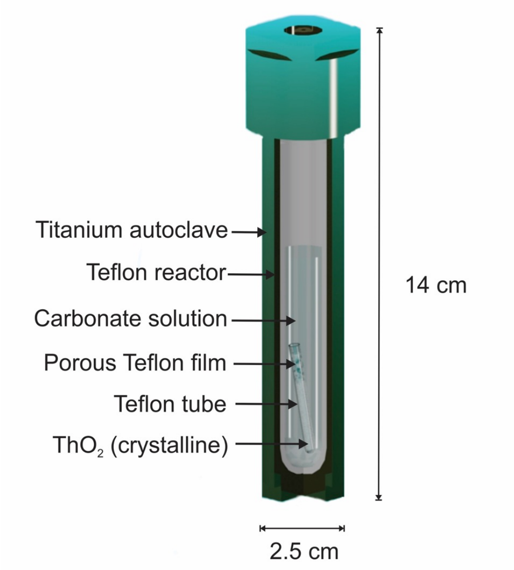
Solution's densities change with temperature ➔ all thermodynamic calculations at high T are performed in molality (mol/kg), not in molarity (mol/dm^3) scale.

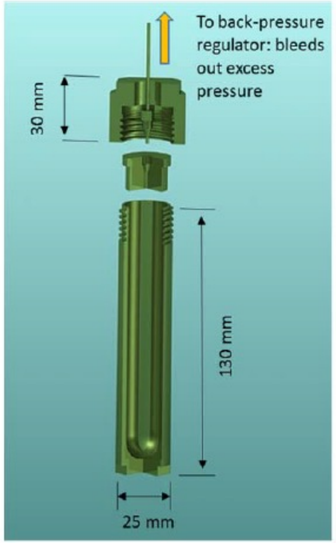
However, Lamber-Beer law requires volumetric concentrations ⇨

EoS for NaCl-predominant solutions:

Bodnar R. J. (1983) A method of calculating fluid inclusion volumes based on vapor bubble diameters and P–V–T–properties of inclusion fluids. Econ. Geol. 78, 535–542.

Autoclave solubility (saturation) technique





Ti light-weight test-tube size autoclaves

With Teflon liners:	up to 250 ºC, saturated water pressure
Without liners:	tested up to 440 C, 175 bar (180 bar – upper limit)

Retrograde solubility → can ruin experiments during the quenching cycle (false excess solubility)

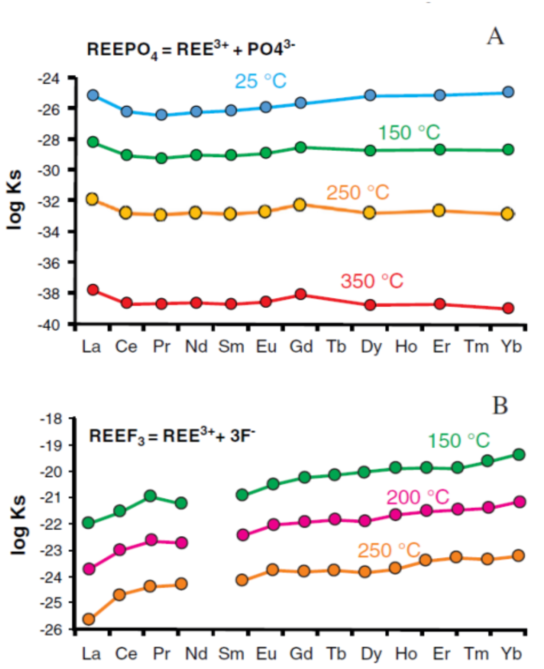
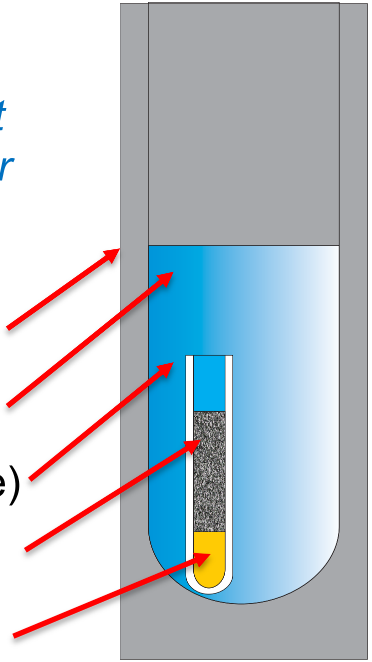


Fig. 26. The distribution of values for the solubility products of REE phosphates (A) and fluorides (B) at different temperatures.

Phase separation technique

Artificially slowing down interaction between the phase and the solution: to ensure that quenching time is much shorter than the saturation time



autoclave

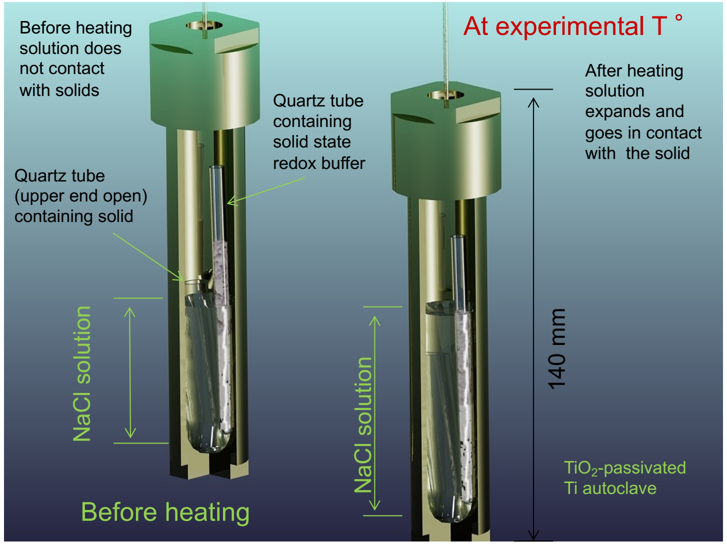
experimental solution

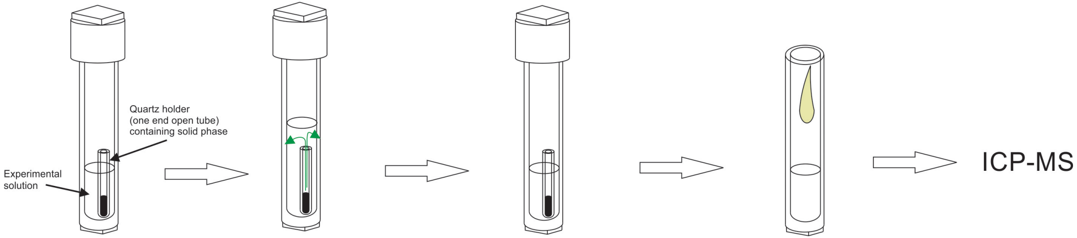
sample holder (one end open tube)

porous membrane

dissolving reference phase

Thermal expansion technique





Stage 1: Ambient conditions; solution does not contact solid

Stage 2: Experimental temperature; solution expands and flushes the holder; solid saturates the solution

Stage 3: Quenching and termination of the experiment; ambient conditions; solution loses contact solid; solution load and precipitates on the walls correspond to the saturation at experimental temperature

Stage 4: Holder removed; acid added to dissolve precipitates;

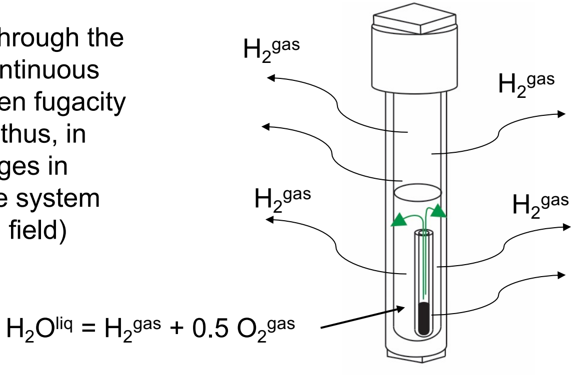
Next step: to ensure that the solution interacts with the phase only at/around the temperature of interest (phase separation technique is still in use)

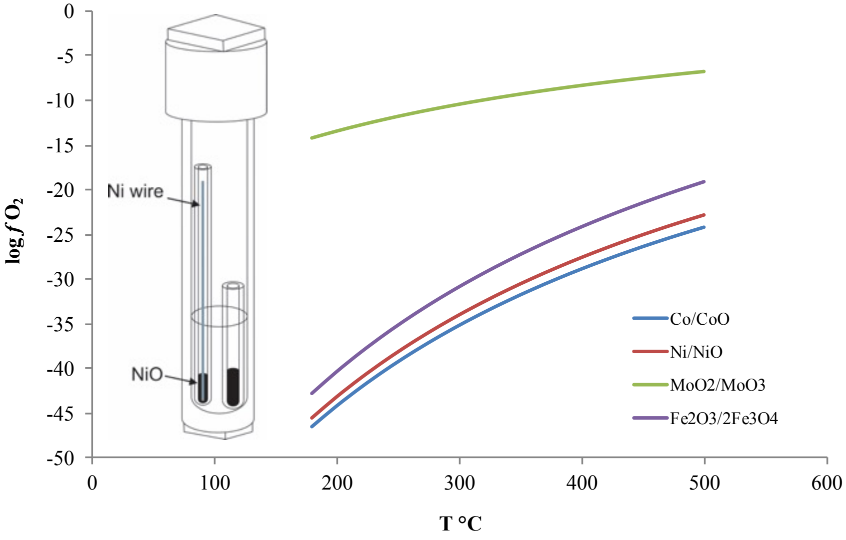
More precise, but applicable to only temperatures at which temperature expansion of the solution is sufficient enough to appreciably change the solution level.
Typically, above 150-175 C

Redox control T>175-200 C

- **At high temperature ALL materials are transparent for H_2^{gas}, but not for O_2^{gas}**

Losses of H_2^{gas} through the walls result in continuous increase of oxygen fugacity in the system → thus, in continuous changes in redox state of the system (shift to oxidizing field)





$$Ni^{metal} + 0.5\ O_2^{gas} = NiO^{solid}$$

$$\log K(T) = -0.5 \log f(O_2)$$

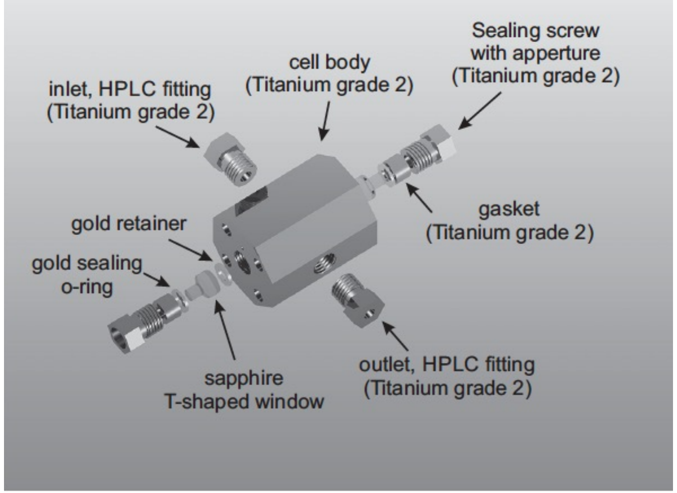
Thus, until both Ni and NiO present in the system, redox conditions are set precisely

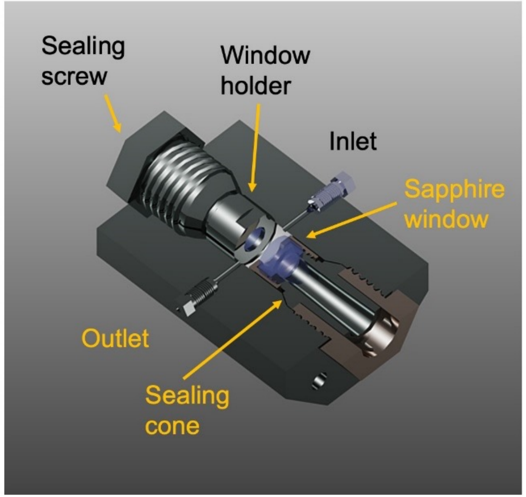
Kinetic restrictions!!! Redox re-equilibration of solid state buffers is too slow at T<200-175 C

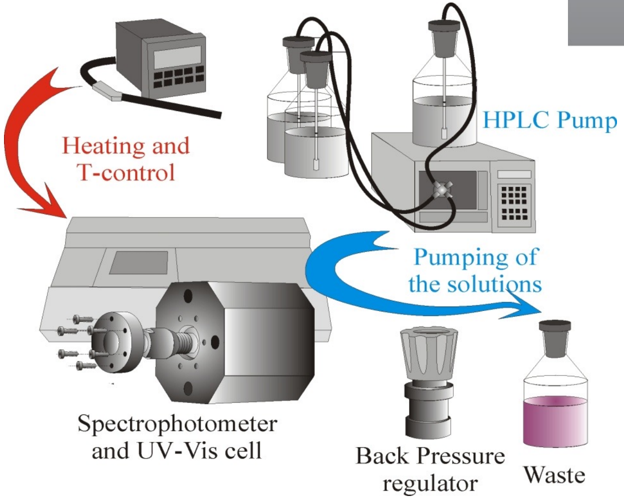
In situ solution spectroscopy

UV-Vis:

Ti flow-through cell
Now up to 350 ºC, 200 bar
Building up to 500 ºC, 1 kBar

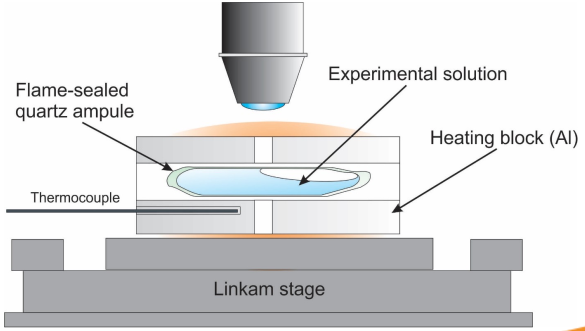




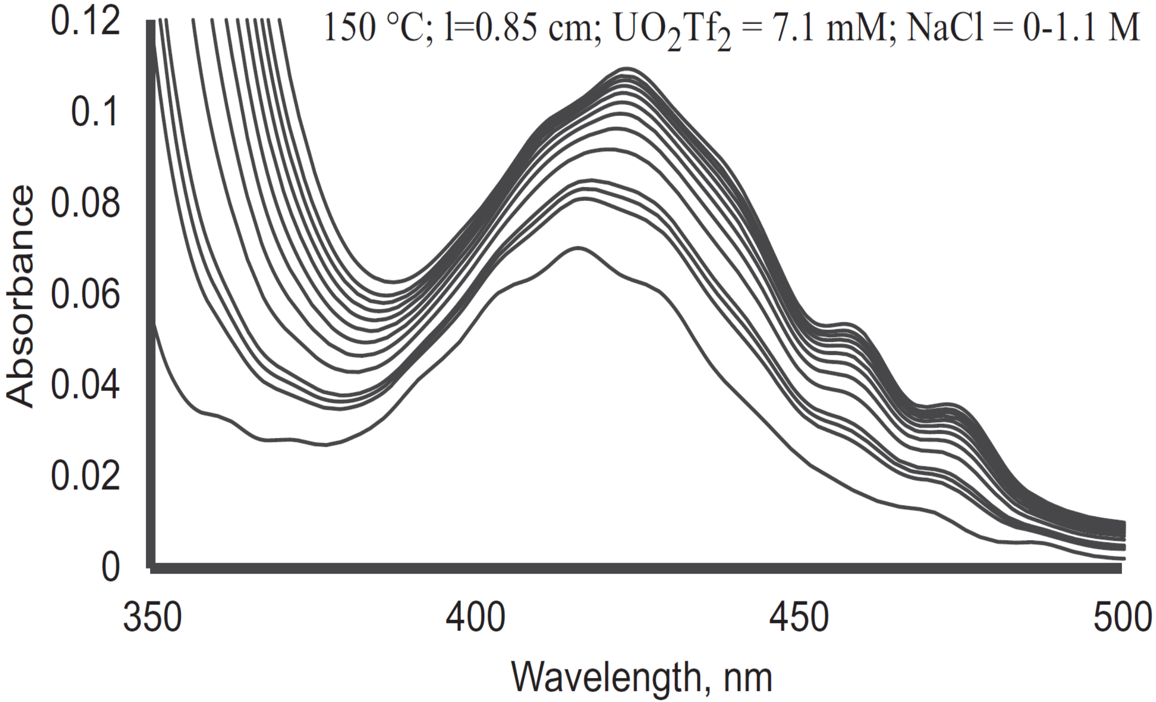


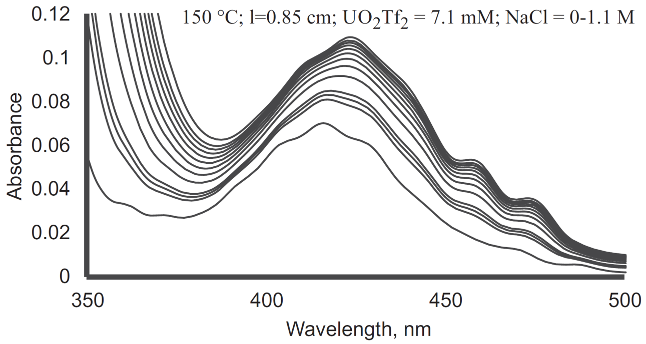
Raman:

Fused quartz capillary
Up to 500 ºC, 500 bar



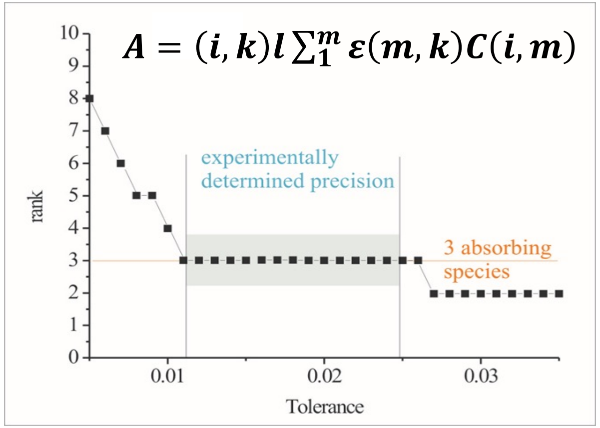
Recording isothermal spectra of solutions having systematically changing Me/L ratios





		380 nm	381 nm	382 nm	
Solution 1	…	$A_{1,380}$	$A_{1,381}$	$A_{1,382}$	…
Solution 2	…	$A_{2,380}$	$A_{2,381}$	$A_{2,382}$	…
Solution 3	…	$A_{3,380}$	$A_{3,381}$	$A_{3,382}$	…
Solution 4	…	$A_{4,380}$	$A_{4,381}$	$A_{4,382}$	…
Solution 5	…	$A_{5,380}$	$A_{5,381}$	$A_{5,382}$	…

The number of absorbing species can be determined from the dimensionality of the matrix



$$A = (i,k)\, l \sum_1^m \varepsilon(m,k)\, C(i,m)$$

Speciation model (list of absorbing species)

Iterative derivation of stability constants and molar absorbances coefficients

Numerical search for stability constants and spectra deconvolution – iterative minimization of the misfit

$$A = (i,k) l \sum_1^m \varepsilon(m,k) C(i,m)$$

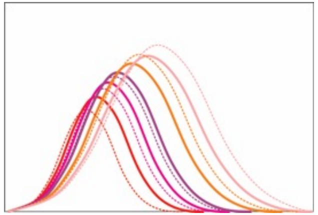
Speciation model

Determination of the matrix dimensionality

Initial guesses for formation constants

Based on the formation constants, adopted activity model, total concentrations in the solutions → derivation of **C** (matrix of concentrations) and **E** (matrix of molar absorbances)

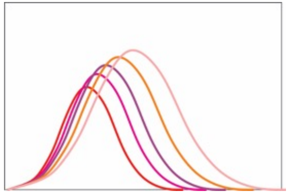
Typically use a Gibbs free energy minimization code, which re-calculates composition of the solutions at each iterative cycle based on starting compositions and NEW (changing from iteration to iteration) thermodynamics

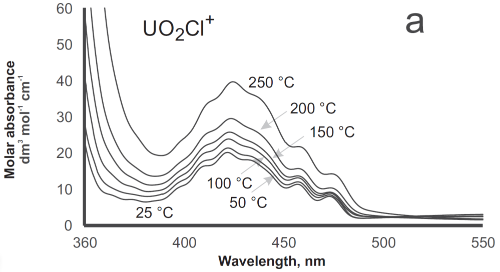


Based on **C** and **E** derivation of “theoretical” absorption matrix $\mathbf{A}^{calc}$ and calculation of the misfit

$$U = \sqrt{\sum_{i=1}^{I}\left[\sum_{j=1}^{J}\left(\frac{A_{ij}^{exp} - A_{ij}^{calc}}{A_{ij}^{exp}}\right)^2\right]}$$

Change of the formation constants to iteratively minimize U





U

U(VI)

UO_2Cl^+, $UO_2Cl_2^{o}$	UV-vis, up to 250 ºC
$UO_2SO_4^{o}$, $UO_2(SO_4)_2^{2-}$	UV-vis, up to 250 ºC
$UO_2CO_3^{o}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$	UV-vis, Raman up to 125 ºC (destabilization at higher T)
UO_2OH^+	UV-vis + solubility up to 250 ºC
$UO_2(OH)_2^{o}$, $UO_2(OH)_3^-$	solubility up to 250 ºC

U(IV)

UCl_4^{o}	solubility 200-350 ºC
$USO_4(OH)_2^{o}$, $U(SO_4)_2^{o}$	solubility 200-350 ºC

- No contribution of carbonate complexes was observed to U(VI) aqueous transport at T>125-150 ºC and $\Sigma(CO_3) < 0.8$ m
- At T≥250 ºC **U(IV)** can be **as mobile as U(VI)** in sulfate-bearing solutions

Th

$Th(OH)_2^{2+}$ $Th(OH)_4^{o}$ $Th(OH)_5^-$	solubility 175-250 ºC
$Th(SO4)_2^{o}$	solubility 175-250 ºC

- No contribution of carbonate or chloride complexes was observed to Th aqueous transport
- At T≥200 ºC Th is **extremely** mobile in sulfate-bearing solutions.

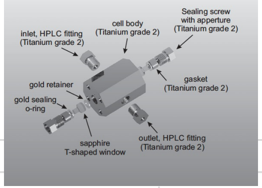
Nd

Chloride, fluoride, sulphate complexes	UV-vis + solubility up to 250 ºC – completed in 2002-2013
$NdCO_3^{+}$ $Nd(CO_3)_2^-$, $NdCO_3OH^{o}$	solubility up to 450 ºC – in progress

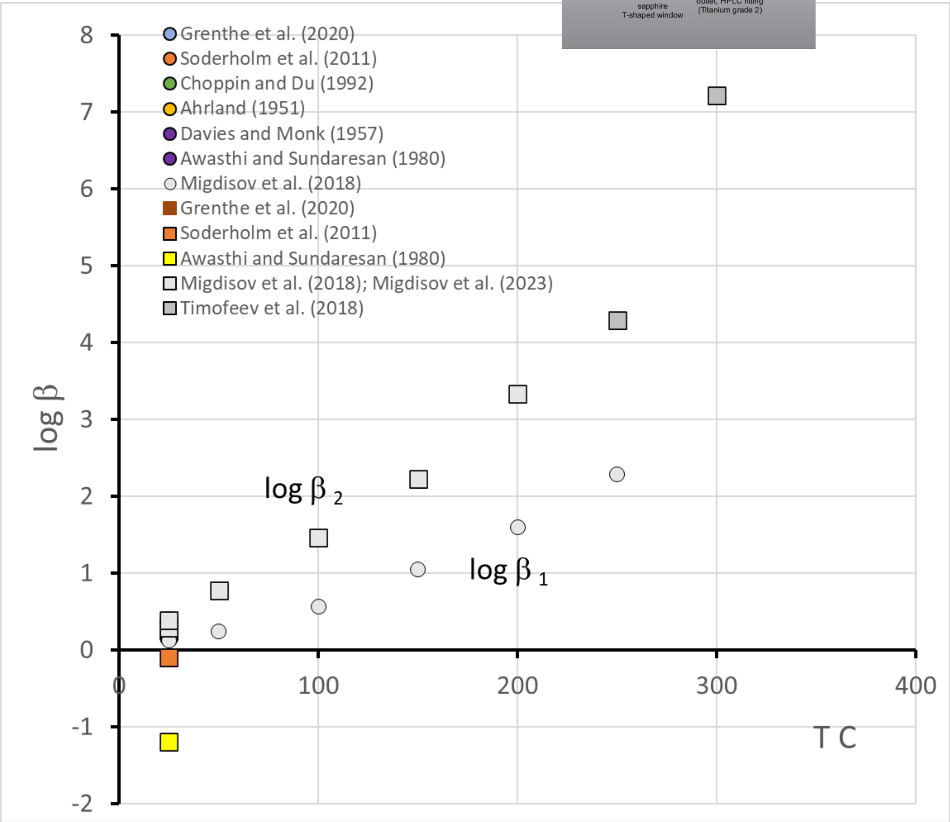
- High stability of sulfate and carbonate complexes.

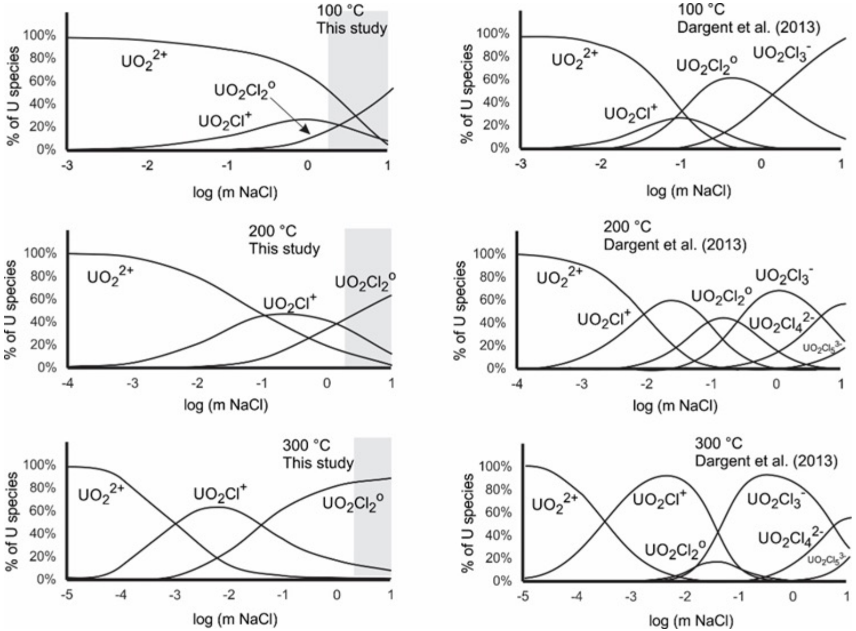
Neutrally charged species indeed expand their predominance fields at elevated temperatures

Chloride complexation
Uranyl-chloride



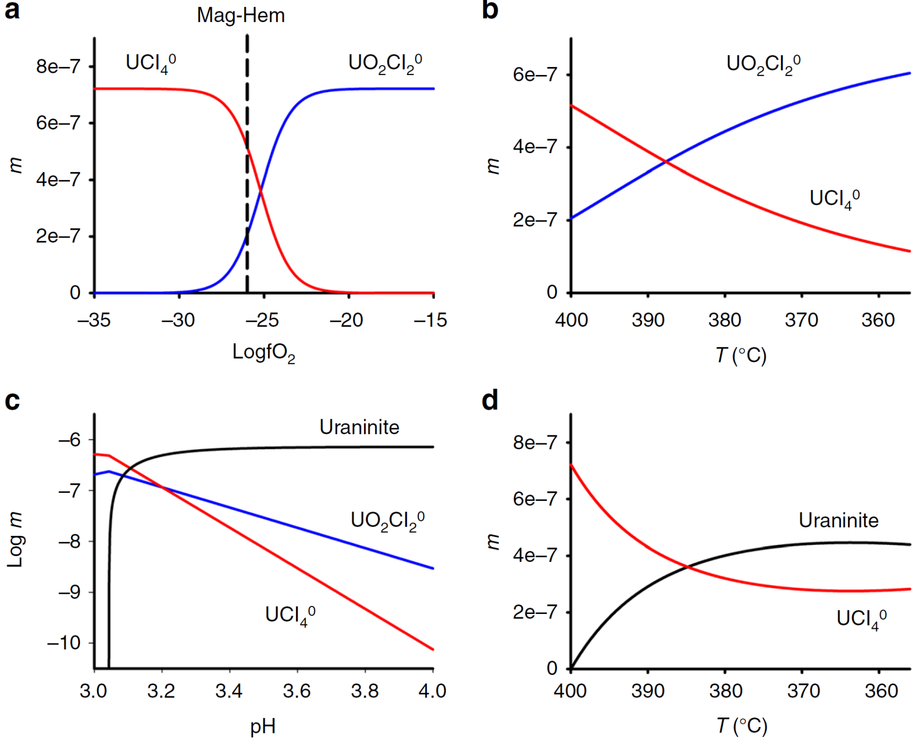
Migdisov et al. (2018) A spectroscopic study of uranyl speciation in chloride-bearing solutions at temperatures up to 250 °C. *Geochim. Cosmochim. Acta* **222**, 130–145.

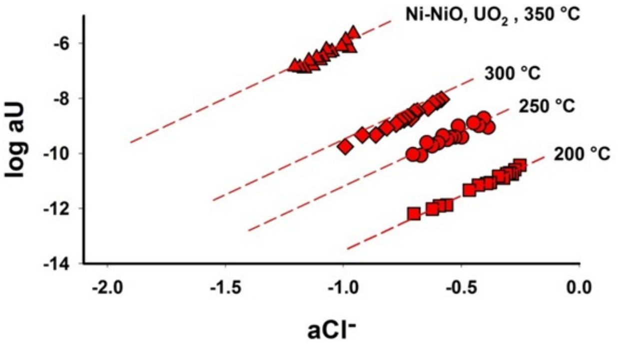


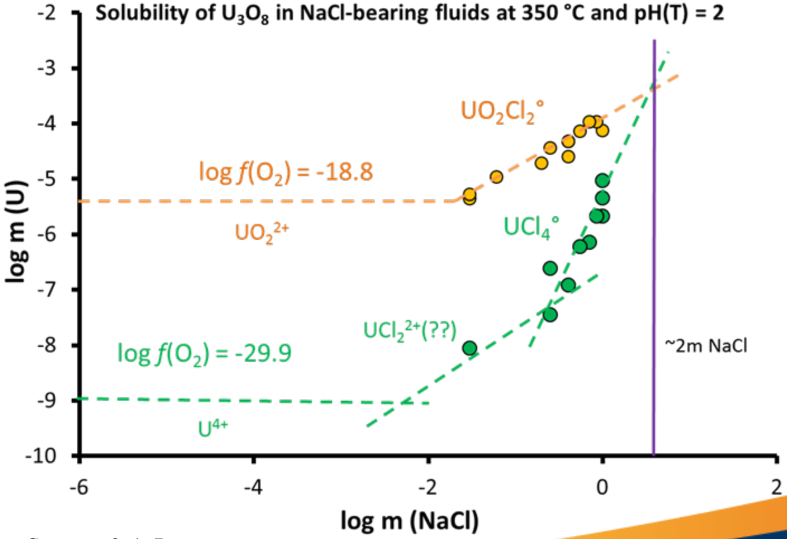


Our data: predominance of neutrally charged $UO_2Cl_2^\circ$ Disagreement with Dargent et al. (2013)

Chloride complexation
U(IV)-chloride

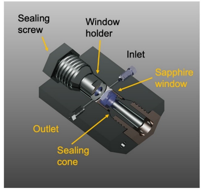


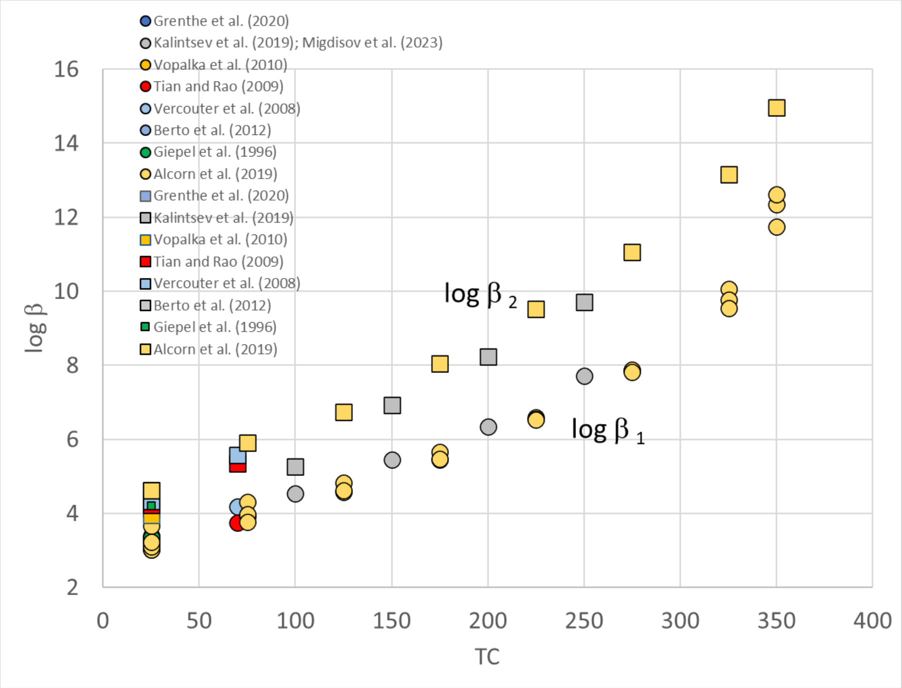


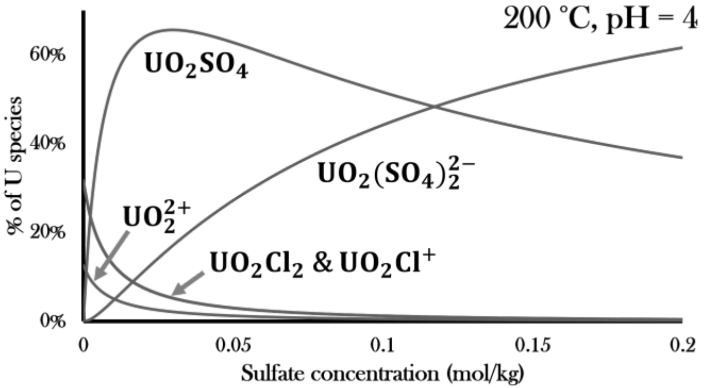


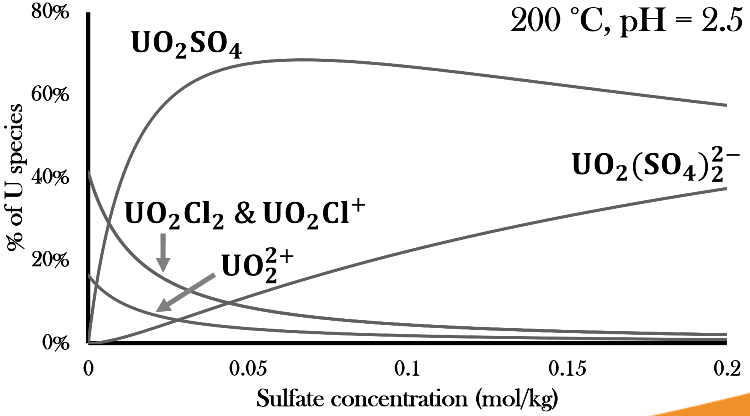
Timofeev et al. (2018) Uranium transport in acidic brines under reducing conditions. *Nat. Commun.* **9**, 1–7.

Sulphate complexation
Uranyl-sulphate



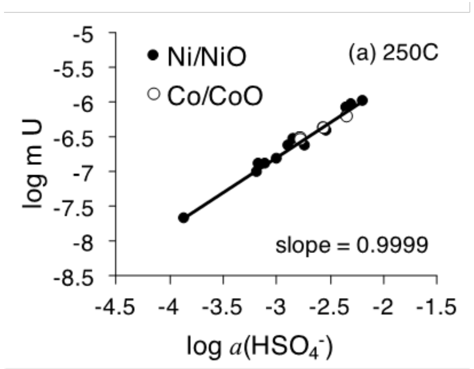


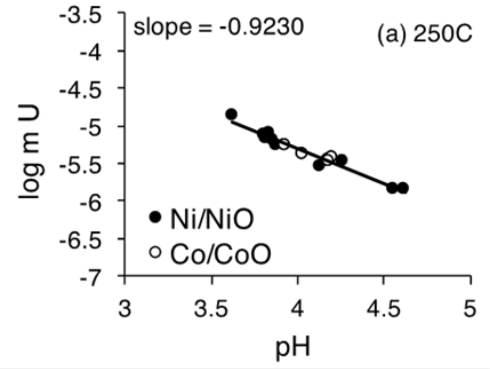


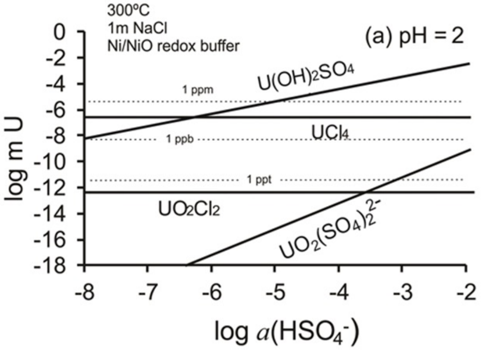


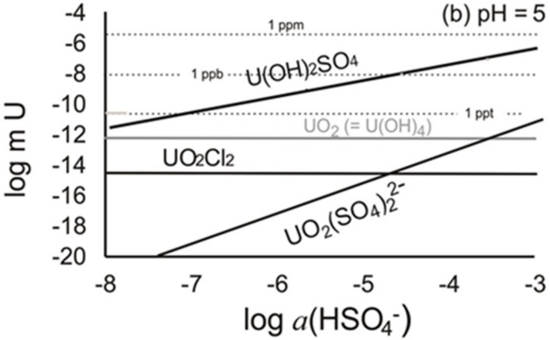
Kalintsev et al. (2019) Uranyl speciation in sulfate-bearing hydrothermal solutions up to 250 °C. *Geochim. Cosmochim. Acta* **267**, 75–91.

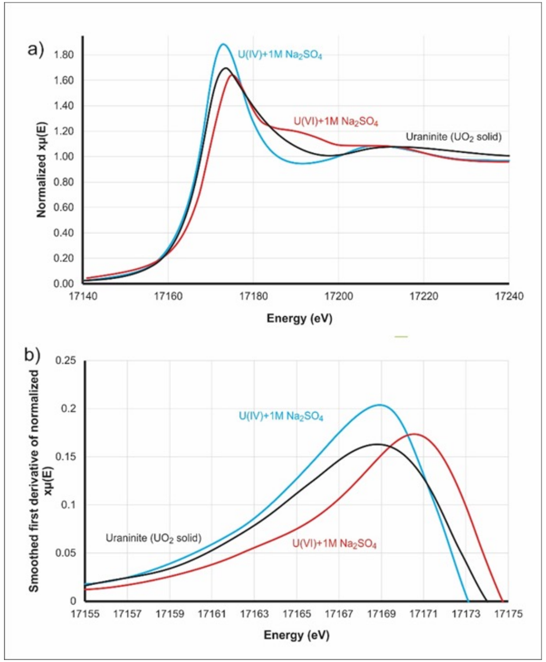
Sulphate complexation
U(IV)-sulphate







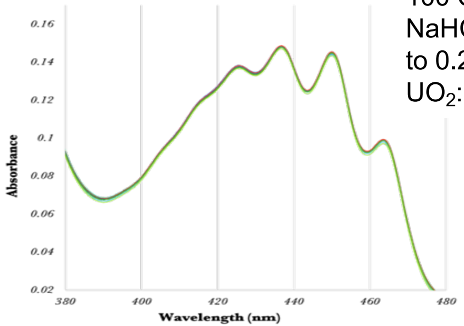




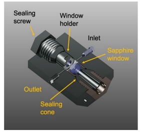
$$UO_2^{crys} + HSO_4^- + H^+ \leftrightarrow U(OH)_2SO_4^{\circ}$$

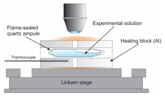
Migdisov et al. - in prep.

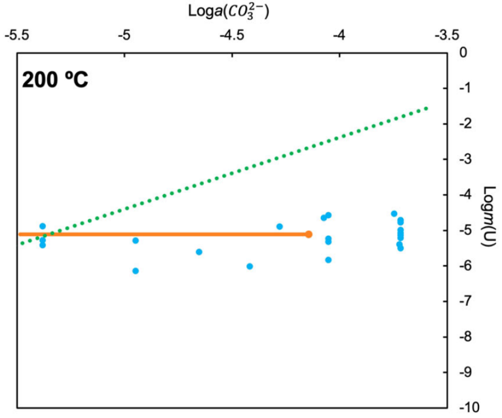
Carbonate complexation Uranyl-carbonate

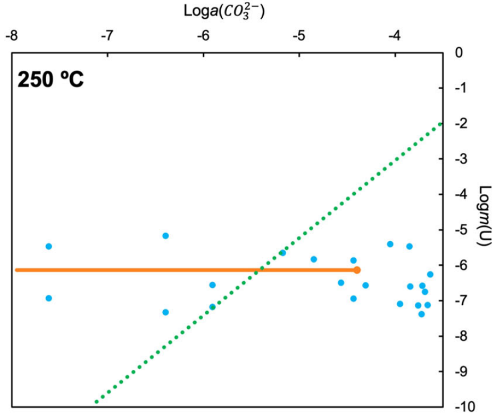


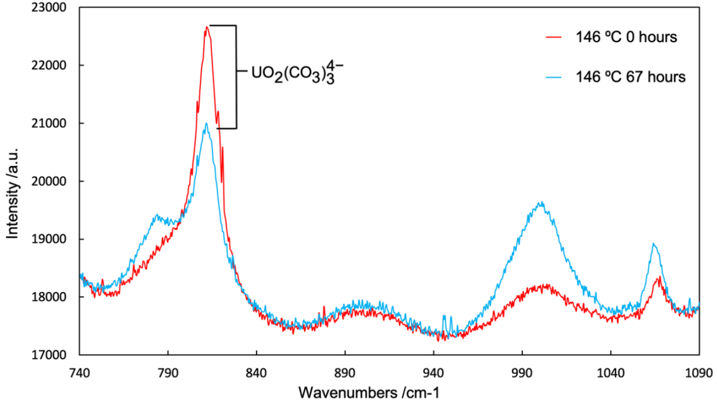
100 C,
$NaHCO_3$:.0.08 to 0.2 m,
UO_2: 0.02 m

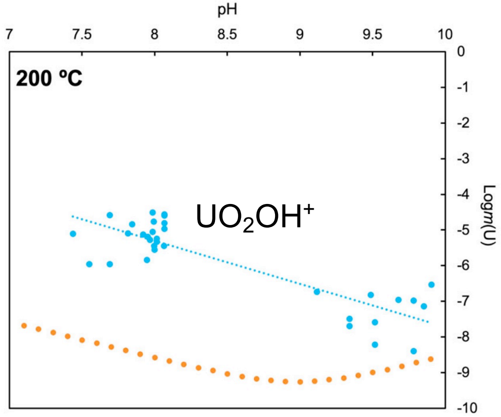


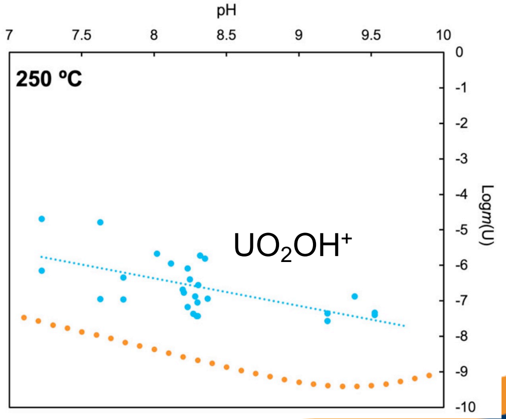






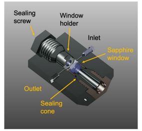


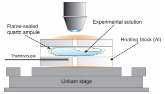




Kalintsev et al. (2021) Uranium carbonate complexes demonstrate drastic decrease in stability at elevated temperatures. *Commun. Chem.* **4**, 1–8.

Carbonate complexation
Uranyl-carbonate





$NaHCO_3 + HCl = NaCl + H_2CO_3$

1 m HCl solution

1 m $NaHCO_3$ solution

0.05m UO_2Cl_2, 1m NaCl, pH(HCl)=2.5

Mixing block

Pressure in the system = 200 bar → all carbonate remains in dissolved form

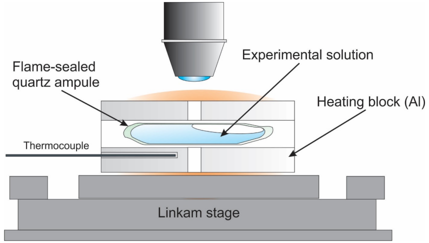
Ratios of U/CO_3 and pH is set by flow rates

To the UV-vis cell

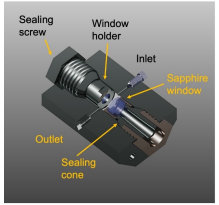
Back pressure

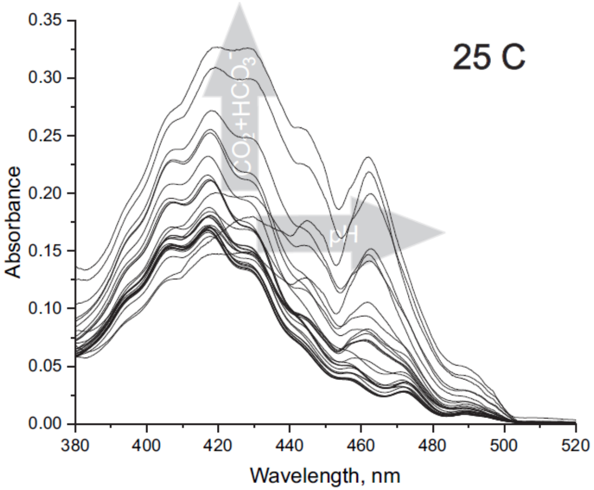
Recording pH

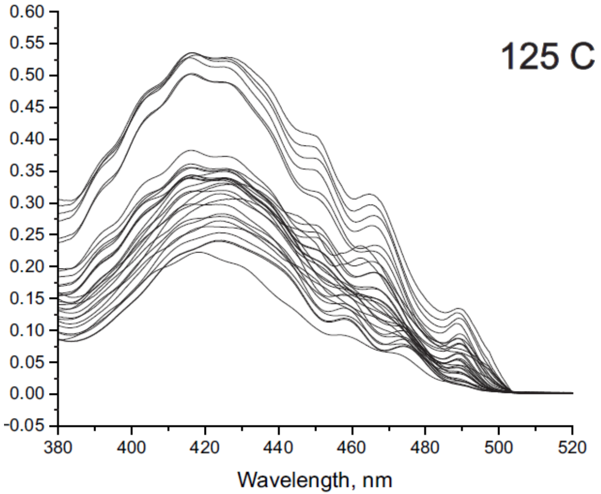
+



Carbonate complexation
Uranyl-carbonate







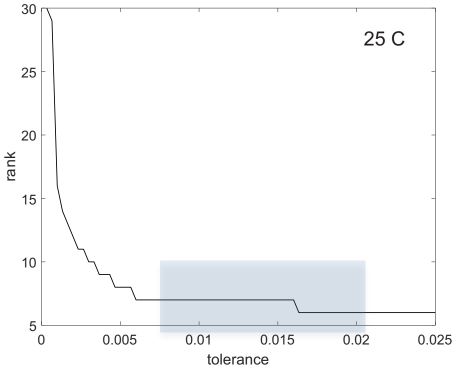
UV-vis: pH 0.75 to 3.6

Large number of species contributing:

UO_2^{2+}, UO_2Cl^+, UO_2Cl_2, UO_2OH^+, UO_2CO_3, $UO_2(CO_3)_2^{2-}$

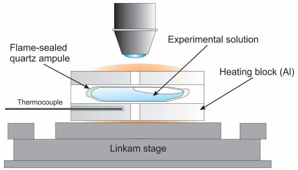
Migdisov et al. (2018) A spectroscopic study of uranyl speciation in chloride-bearing solutions at temperatures up to 250 °C. *Geochim. Cosmochim. Acta* **222**, 130–145.

optimized

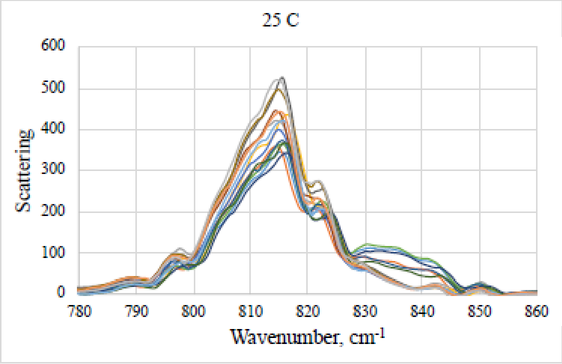


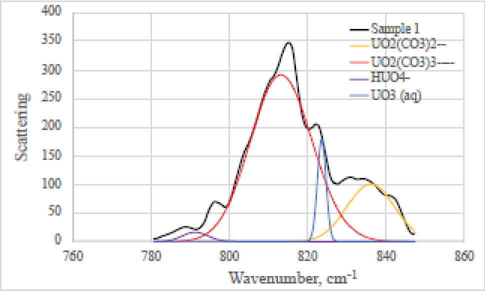
U crushes out at ~130-140 C

Migdisov et al. - in prep.



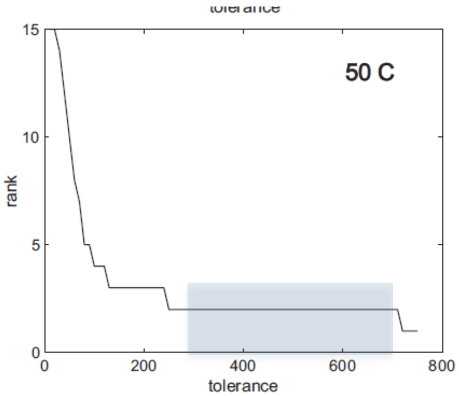
Raman: carbonate solutions
pH 6.8-8.2

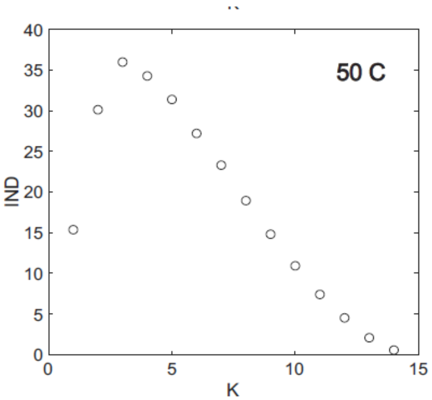




Much poorer specs quality, 2-3 contributing species, reliable derivation only for $UO_2(CO_3)_2^{2-}$, $UO_3(CO_3)_3^{4-}$

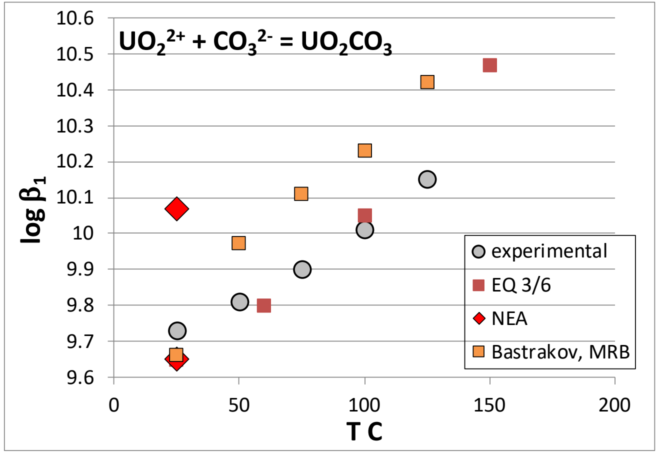
U crushes out
at ~152-156 C

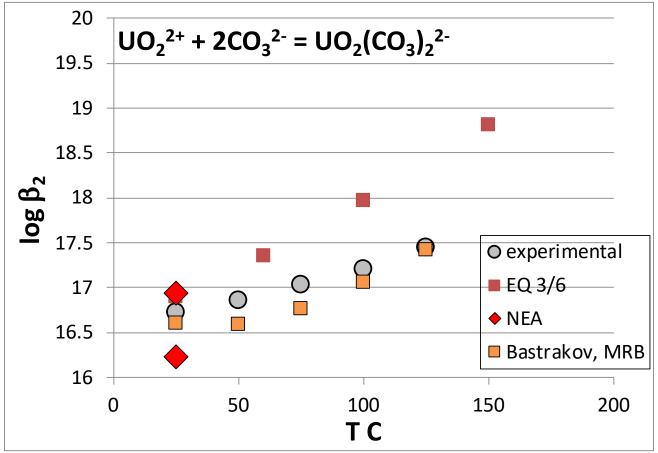


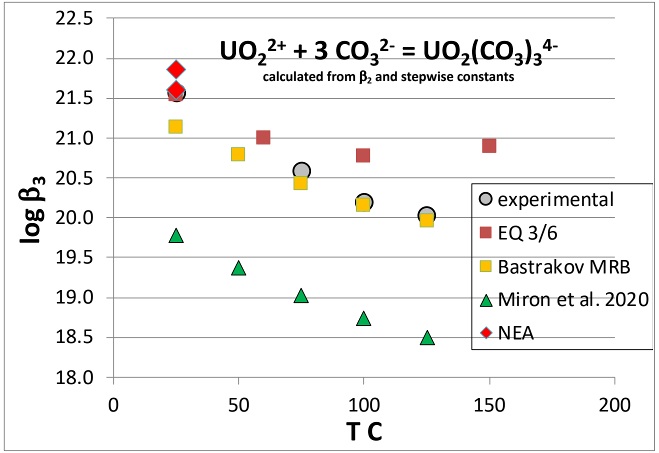


Migdisov et al. - in prep.

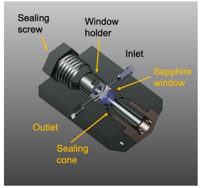
Carbonate complexation
Uranyl-carbonate





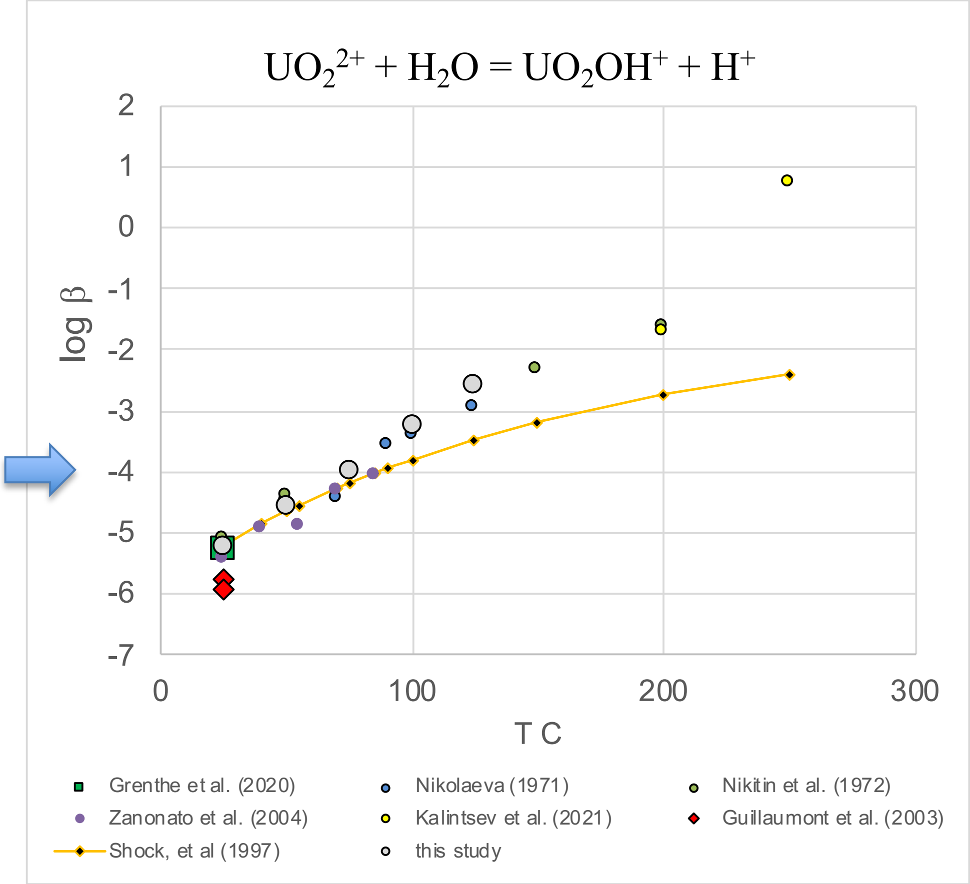


Hydroxyl complexation Uranyl-hydroxide



UO_2OH^+

Outcome from the UV-vis (carb) study



Migdisov et al. - in prep.

$UO_2(OH)_2^o$, $UO_2(OH)_3^-$

Solubility experiments at 200 and 250 C → in progress

Main outcome by now:

- Neutrally charged species are getting relatively more stable at elevated temperatures. Up to complete disappearance of highly charged species predominance fields.
  - Predominance field diagrams – to be published later this year

- Carbonate-mediated transport of U(VI) is likely insignificant at T>125 C

- U(IV) can be significantly mobile in aqueous solutions at T>200 C

Spent Fuel and Waste Disposition