Effect of Temperature on the Complexation of Triscarbonatouranyl(VI) with Calcium and Magnesium in NaCl Aqueous Solution.

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Table S1. Composition and properties of standard buffer solutions.

pH value at 25°	1.68	4.01	6.87	9.18
Composition[1]	0.05m potassium tetraoxalate ($KH_3C_4O_8$)	0.05 m potassium hydrogen phthalate ($KHC_8H_4O_4$)	0.025 m KH_2PO_4 and 0.025 m (Na_2HPO_4)	0.01 m $Na_2B_4O_7$:$10H_2O$
Temperature range	0-95	0-95	0-95	0-50
Temperature coefficient dpH/dt	--	+0.0012	-0.0028	-0.0028

Table S2. Recalculated pH values of buffer solutions at investigated temperatures and potential values E_{mes} read on pH-meter.

Temp	pH	E_{mes}(mV)	pH	E_{mes}(mV)	pH	E_{mes}(mV)	pH	E_{mes}(mV)	Slope	Intercept
5°	1.67	299.1	4.00	166.9	6.95	1.8	9.39	-133.4	-56.01	391.81
10°	1.67	299.5	4.00	166.2	6.92	0.8	9.33	-135.1	-56.72	393.69
15°	1.67	302.2	4.00	165.5	6.90	-0.5	9.28	-135.2	-57.45	396.79
22°	1.68	304.2	4.00	164.9	6.88	-1.4	9.23	-136.1	-58.24	400.18
30°	1.68	308.2	4.01	165.6	6.85	-3.3	9.14	-138.8	-59.86	407.39
35°	1.69	311.2	4.02	167.1	6.84	-3.2	9.11	-139.5	-60.70	412.58
40°	1.69	314	4.03	168.7	6.84	-3	9.07	-140.2	-61.49	417.38
45°	1.70	318.2	4.04	171.4	6.83	-3.1	9.04	-140	-62.44	423.97
50°	1.71	321.2	4.06	171.9	6.83	-3.3	9.02	-140.4	-63.16	428.74

Table S3 Stability constants of the U(VI) complexes at 25°C and I_m = 0, used in this work.

Reaction	$\log_{10}K^\circ$	$\Delta_r H_m^\circ$ (kJ mol^{-1})	References
$CO_2(g) + H_2O \rightleftarrows CO_3^{2-} + 2H^+$	-18.15 ± 0.06	4.11 ± 0.28	Guillaumont *et al.*[2]
$CO_3^{2-} + 2H^+ \rightleftarrows CO_2(aq) + H_2O$	16.68 ± 0.05	-23.86 ± 0.14	Guillaumont *et al.*[2]
$CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$	10.33 ± 0.05	-14.70 ± 0.15	Guillaumont *et al.*[2]
$UO_2^{2+} + H_2O \rightleftarrows UO_2(OH)^+ + H^+$	-5.25 ± 0.24	43.46 ± 5.55	Guillaumont *et al.*[2]
$UO_2^{2+} + 2H_2O \rightleftarrows UO_2(OH)_2(aq) + 2H^+$	-12.15 ± 0.07	111.16 [3]	Guillaumont *et al.*[2]
$3UO_2^{2+} + 5H_2O \rightleftarrows (UO_2)_3(OH)_5^+ + 5H^+$	-15.55 ± 0.12	123.70 ± 0.60	Guillaumont *et al.*[2]
$UO_2^{2+} + CO_3^{2-} \rightleftarrows UO_2(CO_3)(aq)$	9.94 ± 0.03	5.0 ± 2.0	Guillaumont *et al.*[2]
$UO_2^{2+} + 2CO_3^{2-} \rightleftarrows UO_2(CO_3)_2^{2-}$	16.61 ± 0.09	18.50 ± 4.0	Guillaumont *et al.*[2]
$UO_2^{2+} + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-}$	21.84 ± 0.04	-39.20 ± 4.10	Guillaumont *et al.*[2]
$2UO_2^{2+} + CO_2(g) + 4H_2O \rightleftarrows (UO_2)_2CO_3(OH)_3^- + 5H^+$	-19.01 ± 0.50	–	Guillaumont *et al.*[2]
$2UO_2^{2+} + CO_3^{2-} + 3H_2O \rightleftarrows (UO_2)_2CO_3(OH)_3^- + 3H^+$	-0.86 ± 0.50		Recalculated from Guillaumont *et al.*[2]
$UO_2(CO_3)_3^{4-} + 4H^+ \rightleftarrows UO_2(CO_3)(aq) + 2CO_2(g) + 2H_2O$	24.40 ± 0.19	35.98 ± 3.64	Recalculated from Guillaumont *et al.*[2]
$UO_2(CO_3)_3^{4-} + 2H^+ \rightleftarrows UO_2(CO_3)_2^{2-} + CO_2(g) + H_2O$	12.92 ± 0.13	53.59 ± 1.05	Recalculated from Guillaumont *et al.*[2]
$2UO_2(CO_3)_3^{4-} + 7H^+ \rightleftarrows (UO_2)_2CO_3(OH)_3^- + 5CO_2(g) + 2H_2O$	46.22 ± 0.30	–	Recalculated from Guillaumont *et al.*[2]

Table S4 Main specific ion interaction coefficients used in this work.

Specific ion interaction coefficient	Value (± 1σ)	Ref.
$\varepsilon(H^+, Cl^-)$	0.12 ± 0.01	Guillaumont *et al.*[2]
$\varepsilon(Na^+, CO_3^{2-})$	-0.08 ± 0.03	Guillaumont *et al.*[2]
$\varepsilon(UO_2^{2+}, Cl^-)$	0.46 ± 0.03	Guillaumont *et al.*[2]
$\varepsilon(Mg^{2+}, Cl^-)$	0.19 ± 0.02	Guillaumont *et al.*[2]
$\varepsilon(UO_2(CO_3)_2^{2-}, Na^+)$	-0.02 ± 0.09	Guillaumont *et al.*[2]
$\varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$	-0.01 ± 0.11	Guillaumont *et al.*[2]
$\varepsilon(MgUO_2(CO_3)_3^{2-}, Na^+)$ (in NaCl)	0.31 ± 0.02	Shang *et al.*[4]
$\varepsilon(CaUO_2(CO_3)_3^{2-}, Na^+)$ (in NaCl)	0.29 ± 0.11	Shang *et al.*[5]
$\varepsilon(Ca_2UO_2(CO_3)_3, NaCl)$	0.66 ± 0.22	Shang *et al.*[5]

Table S5(a). Experimental sample information: pH values, calculated Ringböm coefficients α — see Shang *et al.*[4-6] for details —, $[Mg^{2+}]$ (mol kg_w^{-1}) and deduced F_0; the sample solutions giving the slope of 1 are set in *italics*.

T (°C)	5				10			
Sample	pH value	α	$[Mg^{2+}]$ (mol·kg_w^{-1})	F_0 (counts)	pH value	α	$[Mg^{2+}]$ (mol·kg_w^{-1})	F_0 (counts)
1	8.92	1.00	0	1.46E+08	8.99	1.00	1.00E-05	1.26E+08
2	8.59	1.00	1.57E-04	1.16E+08	8.61	1.00	1.57E-04	1.45E+08
3	8.29	1.01	2.37E-04	1.23E+08	8.30	1.01	2.37E-04	1.29E+08
4	8.24	1.02	5.31E-04	1.16E+08	8.26	1.01	5.31E-04	1.66E+08
5	*8.13*	*1.08*	*7.50E-04*	*1.11E+08*	8.18	1.03	1.18E-03	1.35E+08
6	*7.99*	*1.48*	*1.18E-03*	*1.13E+08*	8.05	1.19	1.18E-03	1.24E+08
7	*7.88*	*2.57*	*1.82E-03*	*6.41E+07*	*7.89*	*1.31*	*1.82E-03*	*1.06E+08*
8	*7.82*	*3.78*	*2.21E-03*	*1.11E+08*	*7.82*	*2.63*	*2.21E-03*	*1.42E+08*
9	*7.79*	*4.65*	*3.38E-03*	*1.23E+08*	*7.79*	*5.13*	*3.38E-03*	*1.04E+08*
10	*7.72*	*7.74*	*4.58E-03*	*1.14E+08*	*7.72*	*7.96*	*4.58E-03*	*1.16E+08*
11	*7.69*	*9.70*	*8.89E-03*	*1.37E+08*	*7.69*	*12.55*	*8.89E-03*	*1.77E+08*
12	*7.64*	*14.25*	*1.34E-02*	*1.32E+08*	*7.64*	*16.95*	*1.34E-02*	*2.06E+08*
13	*7.61*	*17.99*	*1.51E-02*	*1.28E+08*	*7.61*	*25.30*	*1.51E-02*	*2.39E+08*
14	*7.54*	*31.21*	*3.02E-02*	*1.29E+08*	*7.54*	*34.37*	*3.02E-02*	*2.26E+08*
T (°C)	15				22[4]			
Sample	pH value	α	$[Mg^{2+}]$ (mol·kg_w^{-1})	F_0 (counts)	pH value	α	$[Mg^{2+}]$ (mol·kg_w^{-1})	F_0 (counts)
1	8.97	1.00	1.00E-05	7.97E+07	9.17	1.00	0	2.61E+07
2	8.80	1.00	1.57E-04	6.20E+07	8.26	1.09	3.48E-04	2.82E+07
3	8.42	1.01	2.37E-04	6.38E+07	8.22	1.12	7.32E-04	2.37E+07
4	8.38	1.01	5.31E-04	5.52E+07	*8.07*	*1.49*	*1.25E-03*	*2.23E+07*
5	*8.26*	*1.04*	*1.18E-03*	*5.04E+07*	*8.05*	*1.64*	*1.49E-03*	*2.49E+07*
6	*8.10*	*1.22*	*1.18E-03*	*5.38E+07*	*8.00*	*2.08*	*2.38E-03*	*2.62E+07*
7	*8.05*	*1.41*	*1.82E-03*	*5.74E+07*	*7.90*	*3.80*	*4.16E-03*	*2.90E+07*
8	*7.90*	*3.00*	*2.21E-03*	*6.08E+07*	*7.87*	*4.80*	*6.36E-03*	*3.30E+07*
9	*7.86*	*3.90*	*3.38E-03*	*5.95E+07*	*7.78*	*8.90*	*1.56E-02*	*3.51E+07*
10	*7.78*	*6.88*	*4.58E-03*	*6.21E+07*	*7.74*	*12.13*	*2.50E-02*	*4.59E+07*
11	*7.72*	*10.80*	*8.89E-03*	*7.20E+07*				
T (°C)	30							
Sample	pH value	α	$[Mg^{2+}]$ (mol·kg_w^{-1})	F_0 (counts)				
1	8.97	1.00	1.00E-05	9.65E+07				
2	8.80	1.00	1.57E-04	4.32E+07				
3	8.42	1.03	2.37E-04	8.18E+07				
4	8.38	1.04	5.31E-04	3.85E+07				
5	*8.25*	*1.10*	*1.18E-03*	*5.23E+07*				
6	*8.09*	*1.55*	*1.18E-03*	*5.59E+07*				
7	*8.05*	*1.84*	*2.21E-03*	*4.96E+07*				
8	*7.90*	*4.49*	*3.38E-03*	*4.24E+07*				
9	*7.81*	*8.56*	*4.58E-03*	*6.01E+07*				
10	*7.78*	*10.72*	*1.34E-02*	*1.04E+08*				
11	*7.75*	*13.48*	*1.51E-02*	*1.23E+08*				
12	*7.72*	*16.98*	*3.02E-02*	*1.95E+08*				

Table S5(b). Experimental sample information – pH values, calculated Ringböm coefficients α, [Ca^{2+}] (mol kg_w^{-1}) and deduced F_0; the sample solutions giving the slope of 1 are set in *italics*; the sample solutions giving the slope of 2 are set in **bold**.

T (°C)	10				15			
Sample	pH value	α	[Ca^{2+}] (mol·kg_w^{-1})	F_0 (counts)	pH value	α	[Ca^{2+}] (mol·kg_w^{-1})	F_0 (counts)
1	8.97	1.00	0	3.42E+08	8.97	1.00	0	5.22E+08
2	8.50	1.00	5.72E-05	2.92E+08	8.50	1.01	5.72E-05	3.75E+08
3	8.48	1.00	6.18E-05	3.10E+08	8.48	1.01	6.18E-05	3.65E+08
4	8.36	1.01	6.48E-05	3.15E+08	8.36	1.02	6.46E-05	3.91E+08
5	8.30	1.01	8.06E-05	3.42E+08	*8.20*	*1.07*	*8.72E-05*	*4.21E+08*
6	*8.22*	*1.03*	*9.87E-05*	*3.50E+08*	*8.16*	*1.11*	*1.19E-04*	*4.43E+08*
7	*8.18*	*1.05*	*1.23E-04*	*3.66E+08*	*8.12*	*1.18*	*1.56E-04*	*4.44E+08*
8	*8.08*	*1.18*	*1.57E-04*	*3.80E+08*	*8.05*	*1.41*	*1.74E-04*	*4.92E+08*
9	*7.99*	*1.55*	*2.31E-04*	*4.29E+08*	*8.00*	*1.72*	*2.45E-04*	*5.19E+08*
10	*7.92*	*2.17*	*4.80E-04*	*4.51E+08*	*7.93*	*2.49*	*4.34E-04*	*5.30E+08*
11	*7.82*	*4.08*	*7.41E-04*	*5.25E+08*	*7.87*	*3.64*	*6.65E-04*	*5.35E+08*
12	**7.78**	**5.43**	**1.12E-03**	**5.28E+08**	**7.83**	**4.80**	**1.15E-03**	**5.42E+08**
13	**7.75**	**6.75**	**1.33E-03**	**5.68E+08**	**7.76**	**7.98**	**1.76E-03**	**5.78E+08**
14	**7.70**	**9.82**	**2.00E-03**	**6.02E+08**	**7.70**	**12.59**	**1.96E-03**	**5.94E+08**
15	**7.62**	**18.17**	**2.63E-03**	**6.13E+08**	**7.62**	**23.45**	**2.26E-03**	**6.58E+08**
16	**7.56**	**29.13**	**3.34E-03**	**6.84E+08**	**7.57**	**34.79**	**3.86E-03**	**6.74E+08**
17	**7.51**	**43.34**	**4.40E-03**	**7.77E+08**	**7.50**	**60.70**	**4.28E-03**	**7.12E+08**
T (°C)	22[5]				25			
Sample	pH value	α	[Ca^{2+}] (mol·kg_w^{-1})	F_0 (counts)	pH value	α	[Ca^{2+}] (mol·kg_w^{-1})	F_0 (counts)
1	9.90	1.00	0	1.70E+08	8.97	1.00	0	3.77E+08
2	8.66	1.06	2.78E-05	1.66E+08	8.36	1.03	6.48E-05	3.04E+08
3	8.42	1.04	9.09E-05	1.29E+08	8.16	1.19	1.39E-04	3.27E+08
4	8.26	1.10	1.76E-04	1.75E+08	*8.12*	*1.30*	*1.96E-04*	*3.44E+08*
5	8.23	1.12	2.22E-04	2.25E+08	*8.05*	*1.65*	*2.87E-04*	*3.70E+08*
6	8.15	1.24	3.06E-04	2.40E+08	*8.00*	*2.10*	*4.71E-04*	*4.10E+08*
7	8.11	1.37	4.04E-04	2.27E+08	*7.93*	*3.19*	*8.44E-04*	*3.91E+08*
8	*8.10*	*1.34*	*4.93E-04*	*2.18E+08*	*7.87*	*4.76*	*1.09E-03*	*3.84E+08*
9	*8.08*	*1.51*	*6.00E-04*	*2.74E+08*	**7.83**	**6.33**	**1.87E-03**	**3.69E+08**
10	*8.00*	*2.06*	*9.03E-04*	*2.47E+08*	**7.76**	**10.64**	**2.69E-03**	**3.88E+08**
11	*7.97*	*2.52*	*1.22E-03*	*3.08E+08*	**7.70**	**16.88**	**3.02E-03**	**4.00E+08**
12	*7.92*	*3.30*	*1.72E-03*	*3.12E+08*	**7.62**	**31.61**	**4.07E-03**	**4.19E+08**
13	*7.87*	*4.79*	*2.08E-03*	*3.32E+08*	**7.57**	**46.99**	**5.72E-03**	**3.92E+08**
14	*7.85*	*5.51*	*2.64E-03*	*3.55E+08*	**7.50**	**82.02**	**8.23E-03**	**4.33E+08**
15	**7.81**	**7.07**	**3.42E-03**	**3.08E+08**				
16	**7.75**	**11.55**	**4.70E-03**	**3.53E+08**				
17	**7.63**	**28.25**	**6.25E-03**	**3.43E+08**				
18	**7.60**	**37.08**	**8.55E-03**	**3.74E+08**				
19	**7.55**	**53.34**	**1.04E-02**	**3.84E+08**				
20	**7.52**	**70.02**	**1.53E-02**	**4.25E+08**				
21	**7.50**	**79.91**	**1.74E-02**	**4.30E+08**				
22	**7.48**	**96.30**	**2.49E-02**	**5.85E+08**				

Table S5(b). continued

T (°C)	35				40			
Sample	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)
1	8.97	1.00	0	3.86E+08	8.97	1.00	0	2.85E+07
2	8.58	1.01	2.69E-05	1.71E+08	8.36	1.08	1.94E-04	5.43E+07
3	8.55	1.02	4.67E-05	1.04E+08	*8.16*	*1.42*	*2.98E-04*	*5.78E+07*
4	8.50	1.02	5.72E-05	3.66E+08	*8.12*	*1.62*	*4.19E-04*	*5.89E+07*
5	8.48	1.03	6.18E-05	3.49E+08	*8.05*	*2.23*	*6.13E-04*	*6.24E+07*
6	*8.36*	*1.06*	*6.48E-05*	*2.07E+08*	*8.00*	*2.96*	*1.01E-03*	*6.27E+07*
7	*8.16*	*1.33*	*1.39E-04*	*2.90E+08*	*7.93*	*4.66*	*1.80E-03*	*7.83E+07*
8	*8.12*	*1.50*	*1.96E-04*	*2.98E+08*	*7.87*	*7.11*	*2.56E-03*	*7.96E+07*
9	*8.05*	*2.02*	*2.87E-04*	*3.20E+08*	**7.81**	**11.09**	**3.30E-03**	**8.15E+07**
10	*8.00*	*2.65*	*4.71E-04*	*3.03E+08*	**7.78**	**13.93**	**4.25E-03**	**9.20E+07**
11	*7.93*	*4.13*	*8.44E-04*	*3.19E+08*	**7.75**	**17.53**	**5.59E-03**	**1.29E+08**
12	*7.87*	*6.28*	*1.09E-03*	*3.09E+08*	**7.71**	**23.90**	**7.04E-03**	**1.43E+08**
13	**7.78**	**12.24**	**1.80E-03**	**3.11E+08**	**7.68**	**30.21**	**7.77E-03**	**1.58E+08**
14	**7.70**	**22.69**	**2.15E-03**	**3.73E+08**				
15	**7.62**	**42.54**	**3.25E-03**	**3.37E+08**				
16	**7.57**	**80.28**	**4.50E-03**	**3.41E+08**				
17	**7.49**	**119.6**	**7.20E-03**	**3.79E+08**				
T (°C)	*45*				50			
Sample	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)	pH value	α	$[Ca^{2+}]$ ($mol \cdot kg_w^{-1}$)	F_0 (counts)
1	8.97	1.00	0	2.64E+07	8.97	1.00	0	2.76E+07
2	8.48	1.05	1.10E-04	3.20E+07	*8.16*	*1.64*	*2.98E-04*	*2.79E+07*
3	8.36	1.10	1.94E-04	4.81E+07	*8.12*	*1.92*	*4.19E-04*	*3.01E+07*
4	*8.16*	*1.52*	*2.98E-04*	*3.08E+07*	*7.98*	*4.20*	*6.13E-04*	*3.02E+07*
5	*8.12*	*1.76*	*4.19E-04*	*3.82E+07*	*7.95*	*5.14*	*1.01E-03*	*3.99E+07*
6	*8.05*	*2.47*	*6.13E-04*	*4.30E+07*	*7.92*	*6.33*	*1.80E-03*	*5.58E+07*
7	*8.00*	*3.31*	*1.01E-03*	*4.34E+07*	*7.88*	*8.42*	*2.56E-03*	*5.14E+07*
8	*7.93*	*5.24*	*1.80E-03*	*5.57E+07*	**7.85**	**10.50**	**3.30E-03**	**5.58E+07**
9	**7.82**	**8.04**	**2.56E-03**	**5.64E+07**	**7.80**	**15.29**	**4.25E-03**	**6.60E+07**
10	**7.78**	**15.78**	**3.30E-03**	**7.19E+07**	**7.75**	**22.42**	**5.59E-03**	**7.22E+07**
11	**7.72**	**19.87**	**4.25E-03**	**7.94E+07**	**7.73**	**26.18**	**7.70E-03**	**8.28E+07**
12	**7.69**	**27.09**	**5.59E-03**	**1.00E+08**	**7.70**	**33.06**	**9.09E-03**	**9.48E+07**
13	**7.65**	**34.25**	**7.70E-03**	**1.00E+08**				
14	**7.62**	**43.35**	**9.09E-03**	**1.20E+08**				

Table S6. Values of the Debye-Hückel parameters A(T) at different temperatures, taken from the NEA-TDB reviews.[7]

t/°C (p = 1bar)	A(T) / $kg^{1/2}$ $mol^{-1/2}$
5	0.494
10	0.497
15	0.501
20	0.505
25	0.509
30	0.513
35	0.518
40	0.523
50	0.533
75	0.564

Table S7 The formation constants of $\log_{10}K_{013}°$, $\log_{10}Q_1$ and $\log_{10}Q_2$ in the temperature range of 5-90°C, calculated using the exiting general formula; the global formation constants of $\log_{10}\beta_{113}°$(Ca), $\log_{10}\beta_{213}°$(Ca) and $\log_{10}\beta°_{113}$ (Mg) were estimated with the Van't Hoff Equation; the formation constants of $\log_{10}K°_{113}$ (Ca), $\log_{10}K°_{213}$(Ca), $\log_{10}K°_{113}$ (Mg) were finally determined by subtracting the sum of $\log_{10}K°_{013}$, $\log_{10}Q_1$ and $\log_{10}Q_2$ from the global equilibrium constants $\log_{10}\beta°_{113}$ (Ca), $\log_{10}\beta°_{213}$ (Ca) and $\log_{10}\beta°_{113}$ (Mg).

T (°C)	$\log_{10}K°_{013}$ Götz *et al.*[8]	$\log_{10}Q_1$ Patterson *et al.*[9]	$\log_{10}Q_2$ Patterson *et al.*[10]	$\log_{10}\beta°_{113}$(Ca)	$\log_{10}\beta°_{213}$(Ca)	$\log_{10}\beta°_{113}$(Mg)	$\log_{10}K°_{113}$(Ca)	$\log_{10}K°_{213}$(Ca)	$\log_{10}K°_{113}°$(Mg)
5	22.48	-6.51	-10.56	-6.06	-19.35	-6.93	5.60	9.37	4.72
10	22.28	-6.46	-10.49	-6.04	-19.29	-6.95	5.57	9.27	4.67
15	22.11	-6.41	-10.43	-6.03	-19.23	-6.96	5.55	9.20	4.63
20	21.95	-6.38	-10.38	-6.02	-19.18	-6.97	5.55	9.15	4.60
22	21.93	-6.37	-10.36	-6.02	-19.16	-6.97	5.51	9.10	4.55
25	21.81	-6.35	-10.34	-6.01	-19.13	-6.98	5.55	9.12	4.58
35	21.58	-6.31	-10.26	-5.99	-19.08	-6.99	5.56	9.18	4.57
40	21.48	-6.29	-10.23	-5.98	-18.98	-7.00	5.58	9.11	4.56
45	21.40	-6.28	-10.20	-5.98	-18.94	-7.01	5.60	9.13	4.55
50	21.33	-6.28	-10.18	-5.97	-18.89	-7.02	5.62	9.16	4.56
55	21.27	-6.28	-10.16	-5.96	-18.85	-7.03	5.65	9.20	4.56
60	21.22	-6.28	-10.15	-5.95	-18.80	-7.04	5.68	9.25	4.57
65	21.18	-6.29	-10.13	-5.94	-18.76	-7.05	5.71	9.31	4.58
70	21.15	-6.29	-10.12	-5.94	-18.72	-7.05	5.75	9.38	4.60
75	20.96	-6.30	-10.12	-5.93	-18.69	-7.06	5.96	9.62	4.62
80	20.88	-6.32	-10.11	-5.92	-18.65	-7.07	6.06	9.77	4.82
85	20.81	-6.33	-10.11	-5.91	-18.61	-7.08	6.17	9.92	4.90
90	20.73	-6.35	-10.11	-5.91	-18.58	-7.09	6.29	10.09	5.00

K_{013}: $UO_2^{2+} + 3CO_3^{2-} \rightleftarrows UO_2(CO_3)_3^{4-}$ (Eq. 14 in the manuscript)

Q_1: $CO_2(aq) + H_2O \rightleftarrows H^+ + HCO_3^-$

Q_2: $HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$ ($Q_1 + Q_2$ = Eq. 14 in the manuscript)

$\beta_{113}°$(Ca): $Ca^{2+} + UO_2^{2+} + 2CO_2(aq) + CO_3^{2-} + 2H_2O(l) \rightleftarrows CaUO_2(CO_3)_3^{2-} + 4H^+$ (Eq. 15 in the manuscript)

$\beta_{213}°$(Ca): $2Ca^{2+} + UO_2^{2+} + 3CO_2(aq) + 3H_2O(l) \rightleftarrows Ca_2UO_2(CO_3)_3(aq) + 6H^+$ (Eq. 16 in the manuscript)

$\beta_{113}°$(Mg): $Mg^{2+} + UO_2^{2+} + 2CO_2(aq) + CO_3^{2-} + 2H_2O(l) \rightleftarrows MgUO_2(CO_3)_3^{2-} + 4H^+$ (Eq. 15 in the manuscript)

$K_{113}°$(Ca): $Ca^{2+} + UO_2(CO_3)_3^{4-} \rightleftarrows CaUO_2(CO_3)_3^{2-}$ (Eq. 2 in the manuscript)

$K_{213}°$(Ca): $2Ca^{2+} + UO_2(CO_3)_3^{4-} \rightleftarrows Ca_2UO_2(CO_3)_3$ (Eq. 2 in the manuscript)

$K_{113}°$(Mg): $Mg^{2+} + UO_2(CO_3)_3^{4-} \rightleftarrows MgUO_2(CO_3)_3^{2-}$ (Eq. 2 in the manuscript)

Table S8 Decay-times of $Mg/Ca_nUO_2(CO_3)_3^{2n-4}$ in 0.10 mol kg_w^{-1} NaCl at variable temperatures: 5-30°C for Mg^{2+} and 10-50°C for Ca^{2+}. The values were deduced by averaging the measured decay-times of correspondent sample solutions that gave the slope of 1 or 2 in slope analysis (shown in Fig. 6 for $Ca_nUO_2(CO_3)_3^{2n-4}$ and in Fig. 7 for $MgUO_2(CO_3)_3^{2-}$). The values at 22°C were obtained in our previous studies.

T(°C)	$MgUO_2(CO_3)_3^{2-}$ (ns)	$CaUO_2(CO_3)_3^{2-}$(ns)	$Ca_2UO_2(CO_3)_3$ (ns)
5	33.80 ± 2.07	/	/
10	25.80 ± 0.85	48.52 ± 2.84	64.13 ± 1.89
15	22.98 ± 0.80	36.70 ± 2.60	53.84 ± 1.47
22	23.47 ± 1.57[4]	28.30 ± 0.57[5]	46.68 ± 2.70[5]
25	/	22.19 ± 1.01	31.97 ± 1.14
30	18.49 ± 0.53	/	/
35	/	16.18 ± 0.70	22.06 ± 0.82
40	/	16.02 ± 0.38	20.07 ± 0.89
45	/	16.60 ± 0.70	17.70 ± 0.71
50	/	17.17 ± 1.16	16.73 ± 1.10

Table S9 Characteristic decomposition parameters of the pure spectral components of $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ and $MgUO_2(CO_3)_3^{2-}$ shown in Fig. S2 and Fig. S3.

Peak index $CaUO_2(CO_3)_3^{2-}$	Peak Type	FWHM	Center	Area IntgP
1	Gaussian	23.10	479.58	14.98
2	Gaussian	17.97241	496.618	28.22
3	Gaussian	17.17688	514.51	24.26
4	Gaussian	23.7694	533.45	16.11
5	Gaussian	52.32048	552.16	16.42
Peak index $Ca_2UO_2(CO_3)_3(aq)$	Peak Type	FWHM	Center	Area IntgP
1	Gaussian	13.65	465.01	14.54
2	Gaussian	13.69	484.14	27.03
3	Gaussian	15.97	504.62	28.42
4	Gaussian	17.37	525.98	17.13
5	Gaussian	23.51	548.13	9.13
6	Gaussian	34.64	576.52	3.76
Peak index $MgUO_2(CO_3)_3^{2-}$	Peak Type	FWHM	Center	Area IntgP
1	Gaussian	24.15	465.60	21.44
2	Gaussian	15.45	484.98	21.17
3	Gaussian	17.89	502.85	22.221
4	Gaussian	26.34	523	16.81
5	Gaussian	59.05	545.93	18.38

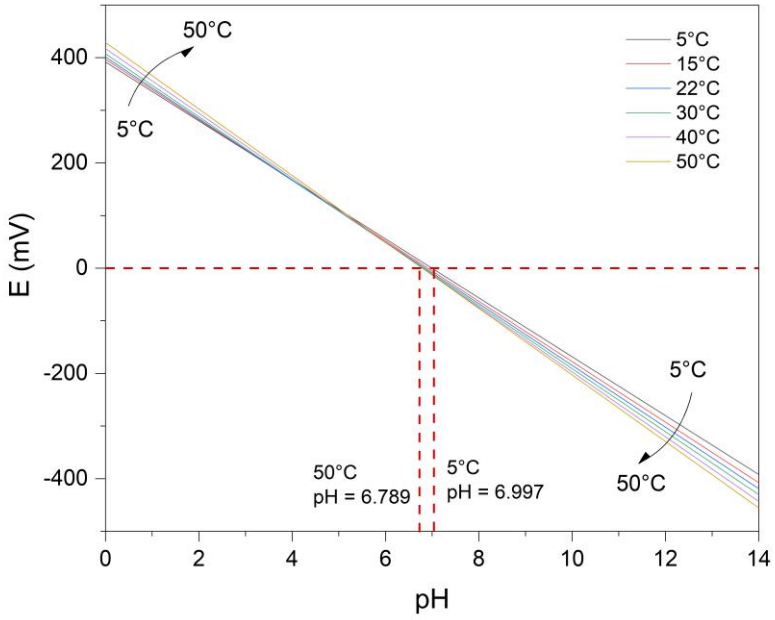

Fig. S1. Calibration lines in the temperature range of 5-50°C and the pH values corresponding to the zero point of electrode at 5°C and 50°C.

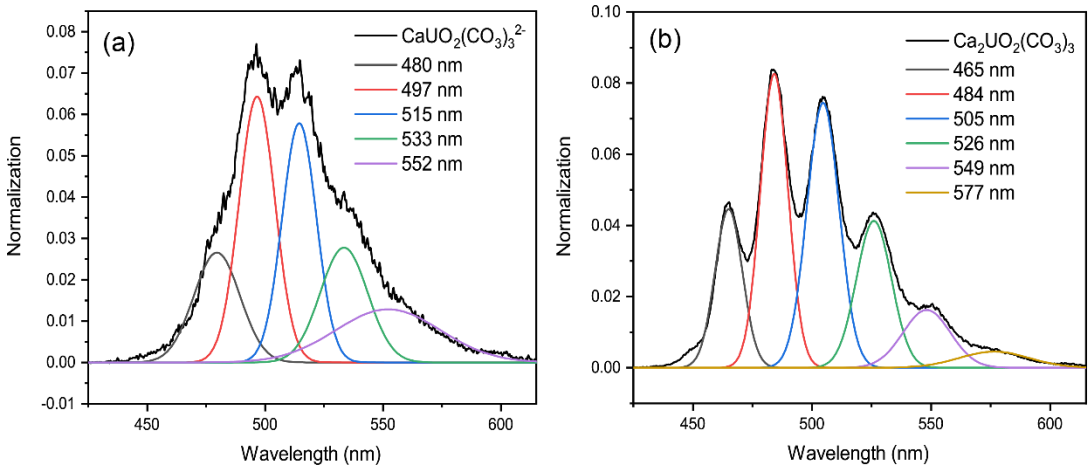

Fig. S2. Gaussian decomposition of the luminescence spectrum of the pure spectral components of (a) $CaUO_2(CO_3)_3^{2-}$ and (b) $Ca_2UO_2(CO_3)_3$(aq) normalized to the same area by the MCR-ALS analysis.

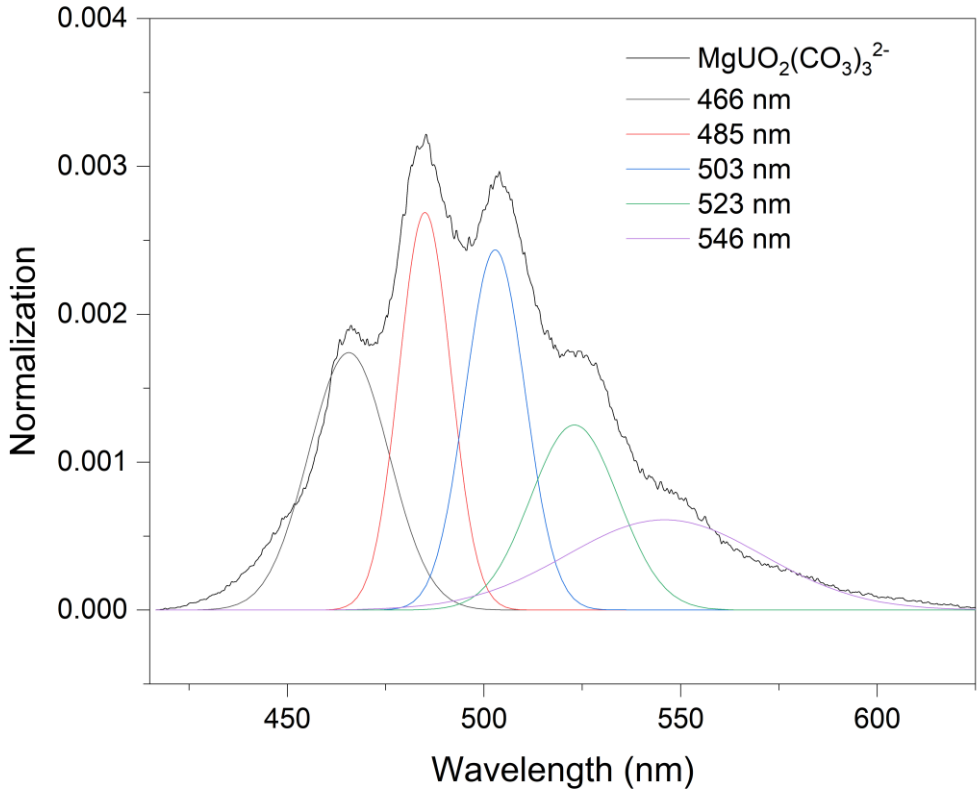

Fig. S3. Gaussian decomposition of the luminescence spectrum of the pure spectral components of $MgUO_2(CO_3)_3^{2-}$ normalized to the same area by the MCR-ALS analysis.

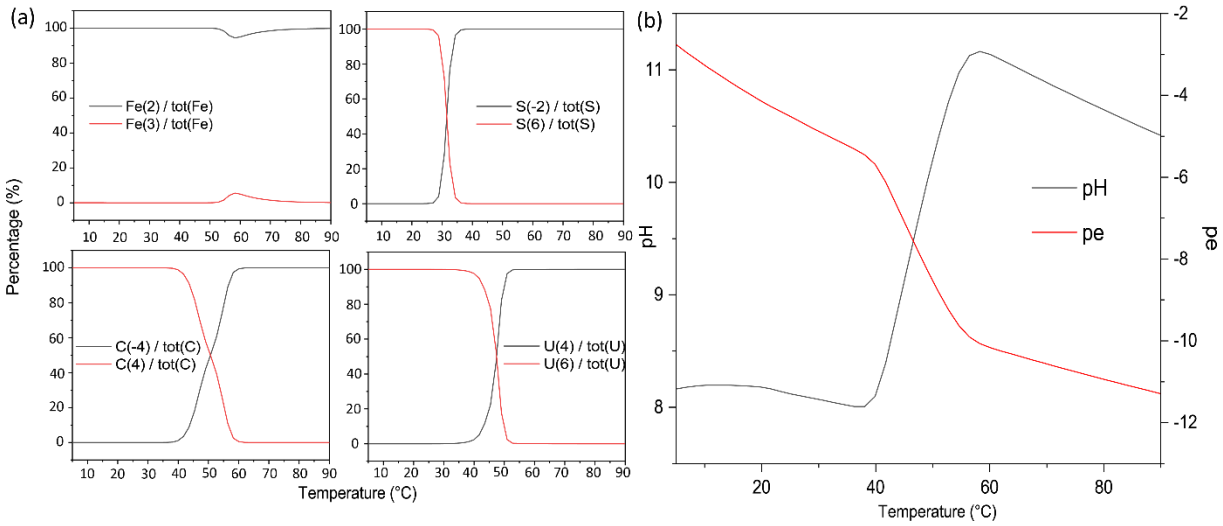

Fig. S4. Change in main oxidation states of Fe, S, C, U (a) and variation of pH and pe (b) as a function of temperature for Boom clay equilibrium waters,[11] $P(O_2) = 10^{-68.67}$ atm using thermodynamic data from the Thermochimie 10a database,[12] implementing $SrUO_2(CO_3)_3^{2-}$,[13] specific ion interaction coefficients of $Mg_nCa_nUO_2(CO_3)_3^{(4-2n)-,4-6}$ and their $\Delta_r H°_m$ values determined in this work based on the isoelectric reaction approximation.

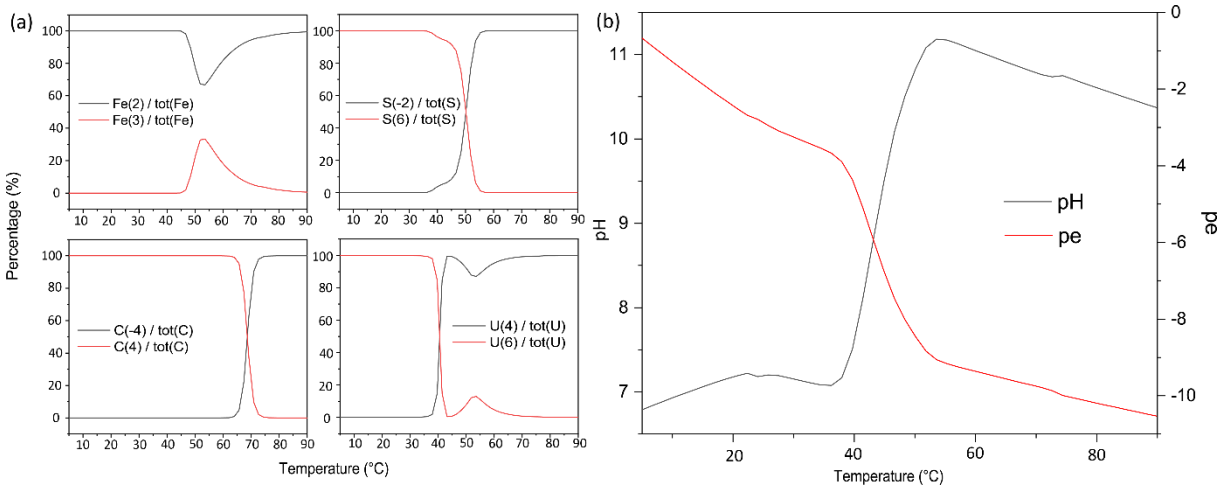

Fig. S5. Change in main oxidation states of Fe, S, C, U (a) and variation of pH and pe (b) as a function of temperature for Callovo-Oxfordian clay equilibrium water,[14] $P(O_2) = 10^{-65.83}$ atm using thermodynamic data from the Thermochimie 10a database,[12] implementing $SrUO_2(CO_3)_3^{2-}$,[13] specific ion interaction coefficients of $Mg_nCa_nUO_2(CO_3)_3^{(4-2n)-}$,4-6 and their $\Delta_r H°_m$ values determined in this work based on the isoelectric reaction approximation.

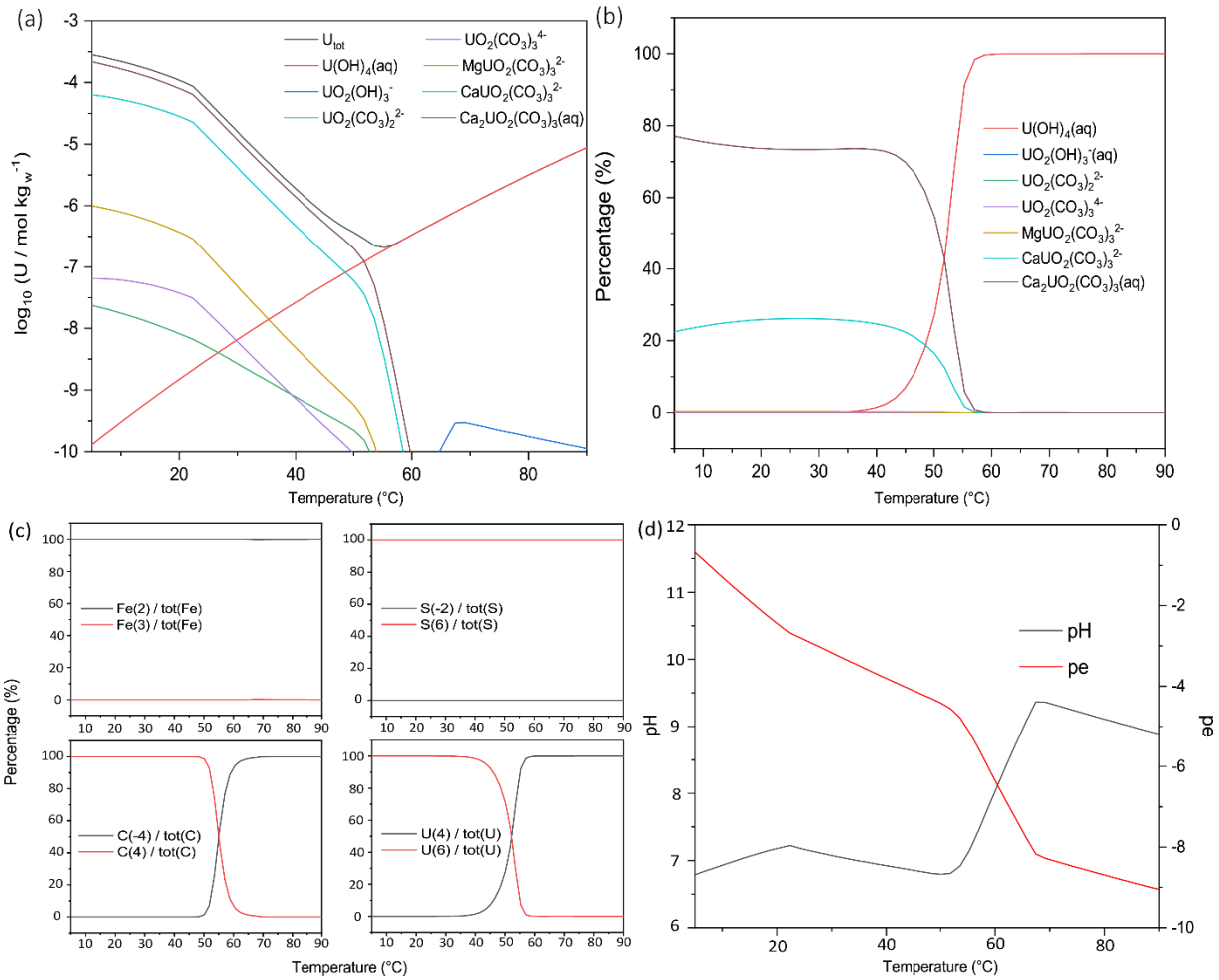

Fig. S6 Solubility of UO_2:$2H_2O$(am) (a) and aqueous uranium speciation (b) change in main oxidation states of Fe, S, C, U (c) and variation of pH, pe (d), as a function of temperature for Callovo-Oxfordian clay equilibrium waters,[14] $P(O_2) = 10^{-65.83}$ atm using thermodynamic data from the Thermochimie 10a database,[12] implementing $SrUO_2(CO_3)_3^{2-}$,[13] specific ion interaction coefficients of $Mg_nCa_nUO_2(CO_3)_3^{(4-2n)-}$ [4-6] and their $\Delta_r H°_m$ values determined in this work based on the isoelectric reaction approximation. The reduction reactions of S(+VI) to lower oxidations states were prevented in the input PhreeqC file.

(a) (b)

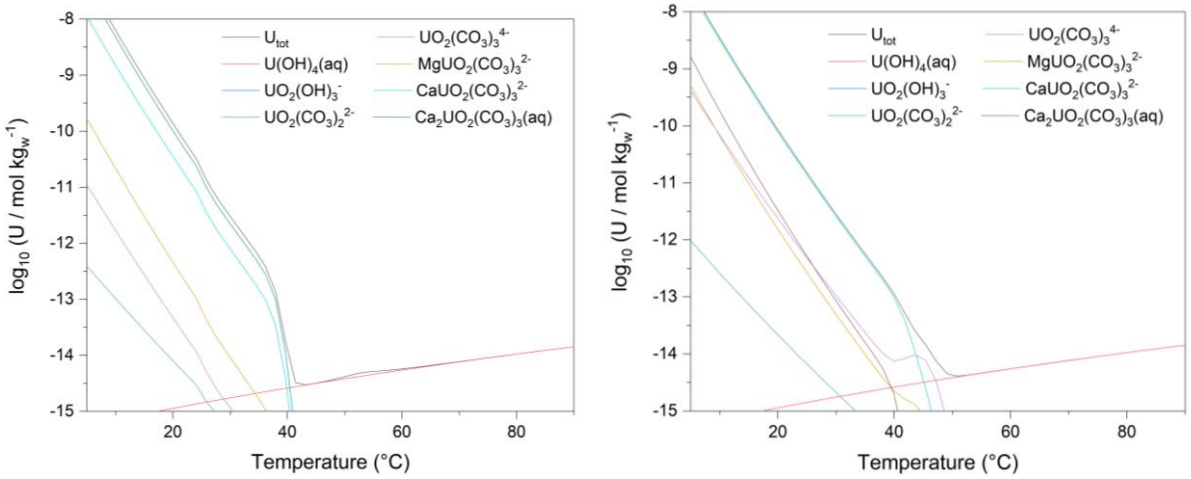

Fig. S7 Solubility of UO_2(cr) as a function of temperature (a) for Boom clay equilibrium waters,[11] $P(O_2) = 10^{-68.67}$ atm and (b) for Callovo-Oxfordian clay equilibrium waters,[14] $P(O_2) = 10^{-65.83}$ atm using thermodynamic data from the Thermochimie 10a database,[12] implementing $SrUO_2(CO_3)_3^{2-}$,[13] specific ion interaction coefficients of $Mg_nCa_nUO_2(CO_3)_3^{(4-2n)-}$ [4-6] and their $\Delta_r H°_m$ values determined in this work based on the isoelectric reaction approximation.

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