

Supporting Information

Thermodynamic constants of $\text{MgUO}_2(\text{CO}_3)_3^{2-}$ complex in NaClO_4 and NaCl media using time-resolved luminescence spectroscopy, and applications to different geochemical contexts.

*Chengming Shang and Pascal E. Reiller**.

Université Paris-Saclay, CEA, Service d'Études Analytiques et de Réactivité des Surfaces (SEARS), F-91191 Gif-sur-Yvette CEDEX, France.

Uranium; Carbonate; Ternary magnesium-uranyl-carbonate complexes; Luminescence.

*Email pascal.reiller@cea.fr

Number of tables: 10

Number of figures: 6

Table S1. Potential values E_{mes} read on pH-meter for NaCl solutions of $I_m = 0.01$ m to 3.19 m at $\text{pH} = 2$ using the combined-glass electrode with the filling solution of saturated KCl: liquid junction potentials ΔE_{mes} calculated to estimate the potential differences between the solution of $I_m = 3.19$ m and those of different I_m ; ΔE_{mes} then used in the four-point calibration with commercial buffer solution of $\text{pH} 1.64, 4.01, 6.87, 9.18$, assumed as diluted solutions of $I_m \approx 0.01$ m.

Solution	Conversion factor (from molarity M to molality m)	I_m (mol kg_w^{-1})	E_{mes} (mV)	$\Delta E_{\text{mes}} = E_{\text{mes}} (I_m = 3.19 \text{ m}) - E_{\text{mes}}$
HCl 0.01 M + NaCl 2.99 M	1.0668 ^a	3.19	299.5	0.0
HCl 0.01 M + NaCl 1.49 M	1.0319 ^a	1.56	286	13.5
HCl 0.01 M + NaCl 0.99 M	1.0215 ^a	1.04	280.8	18.7
HCl 0.01M + NaCl 0.74 M	1.0165 ^a	0.76	279.7	19.8
HCl 0.01 M + NaCl 0.59 M	1.0135 ^b	0.61	277.9	21.6
HCl 0.01 M + NaCl 0.49 M	1.0118 ^a	0.51	277.8	21.7
HCl 0.01 M + NaCl 0.41 M	1.0092 ^b	0.42	276.7	22.8
HCl 0.01M + NaCl 0.29M	1.0064 ^b	0.30	276.5	23.0
HCl 0.01M + NaCl 0.19M	1.0040 ^b	0.20	276.4	23.1
HCl 0.01M + NaCl 0.11M	1.0020 ^b	0.12	275.4	24.1
HCl 0.01M	1.0000	0.01	275.0	24.5

The conversion factor was taken as 1 for the solution of $I_m = 0.01$ M,. The factor values for the solutions of $I_m \geq 0.1$ M were either ^ataken from Guillaumont et al.¹ or ^bextrapolated from these known values.

Table S2. Experimental sample information – pH values, calculated Ringböm coefficients α , $[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$) and deduced F_0 and τ ; the sample solutions giving the slope of 1 are set in *italics*.

I_m NaClO_4 ($\text{mol}\cdot\text{kg}_w^{-1}$)	0.10					0.51				
Sample	pH value	α	$[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$)	F_0 (counts)	τ (ns)	pH value	α	$[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$)	F_0 (counts)	τ (ns)
1	9.00	1.00	0	1.60E+07	8.59	9.00	1.00	0	2.23E+07	10.42
2	8.45	1.02	1.76E-04	1.83E+07	13.28	8.23	1.05	9.46E-03	3.68E+07	11.46
3	8.30	1.06	4.50E-04	2.29E+07	12.21	8.16	1.07	1.93E-02	3.17E+07	12.65
4	8.23	1.12	1.57E-03	1.58E+07	16.71	8.09	1.03	2.14E-02	2.04E+07	14.74
5	8.20	1.17	2.12E-03	1.59E+07	16.24	7.89	1.15	2.69E-02	3.16E+07	13.79
6	8.09	1.45	4.45E-03	1.61E+07	23.44	7.82	1.34	3.61E-02	3.12E+07	15.75
7	8.06	1.62	6.82E-03	2.07E+07	27.92	7.71	2.11	4.69E-02	2.08E+07	19.50
8	8.01	3.71	1.35E-02	2.36E+07	28.39	7.66	2.82	6.45E-02	2.58E+07	20.56
9	7.84	6.17	2.36E-02	2.43E+07	31.61	7.62	3.65	1.13E-01	2.61E+07	23.21
10	7.76	10.78	4.18E-02	2.79E+07	33.48	7.58	4.81	1.16E-01	2.99E+07	25.55
11	7.73	14.18	6.41E-02	3.45E+07	34.83	7.53	6.91	1.87E-01	3.35E+07	26.53
I_m NaClO_4 ($\text{mol}\cdot\text{kg}_w^{-1}$)	1.05					1.62				
Sample	pH value	α	$[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$)	F_0 (counts)	τ (ns)	pH value	α	$[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$)	F_0 (counts)	τ (ns)
1	9.00	1	0	3.33E+07	10.28	9.00	1.00	0	5.44E+07	8.19
2	8.45	1.01	1.00E-03	2.49E+07	12.43	8.70	1.01	9.38E-04	3.56E+07	11.35
3	8.30	1.02	5.12E-03	2.57E+07	13.38	8.22	1.02	2.37E-02	4.32E+07	15.04
4	8.23	1.05	1.60E-02	2.57E+07	13.38	8.18	1.05	5.52E-02	4.49E+07	17.32
5	8.16	1.06	2.02E-02	1.88E+07	16.22	8.09	1.06	1.43E-02	4.23E+07	14.30
6	7.70	1.27	2.68E-02	2.65E+07	15.07	7.98	1.02	2.32E-02	4.20E+07	15.54
7	7.67	1.38	3.44E-02	2.36E+07	17.83	7.89	1.02	2.60E-02	3.74E+07	17.42
8	7.64	1.54	4.50E-02	2.51E+07	18.62	7.78	1.06	3.36E-02	4.13E+07	18.62
9	7.61	1.74	6.30E-02	2.75E+07	19.86	7.69	1.11	4.55E-02	4.11E+07	20.13
10	7.58	2.02	7.43E-02	2.52E+07	22.79	7.64	1.21	6.19E-02	4.67E+07	23.50
11	7.54	2.53	9.44E-02	3.18E+07	22.99	7.56	1.54	8.60E-02	4.67E+07	22.17
12	7.51	3.05	1.20E-01	3.27E+07	26.04	7.50	2.06	1.08E-01	5.05E+07	23.72
13	7.48	3.73	1.46E-01	3.54E+07	27.08	7.47	2.53	1.39E-01	5.80E+07	24.88
I_m NaClO_4 ($\text{mol}\cdot\text{kg}_w^{-1}$)	2.21									
Sample	pH value	α	$[\text{Mg}^{2+}]$ ($\text{mol}\cdot\text{kg}_w^{-1}$)	F_0 (counts)	τ (ns)					
1	9.00	1.00	0	3.86E+07	9.27					
2	8.30	1.02	3.11E-03	3.19E+07	10.77					
3	8.23	1.05	1.53E-02	3.80E+07	10.40					
4	8.16	1.06	4.31E-02	3.19E+07	12.31					
5	7.85	1.02	5.86E-02	3.27E+07	13.60					
6	7.70	1.07	6.50E-02	3.32E+07	15.74					
7	7.59	1.23	7.89E-02	3.47E+07	16.70					
8	7.54	1.40	9.80E-02	3.23E+07	19.15					
9	7.51	1.57	1.31E-01	3.71E+07	20.27					
10	7.49	1.71	1.59E-01	3.64E+07	27.86					
11	7.46	1.98	1.80E-01	4.38E+07	25.32					
12	7.43	2.34	2.11E-01	4.45E+07	28.66					

Table S2 (continued)

I_m NaCl (mol·kg _w ⁻¹)	0.10					0.25				
Sample	pH value	α	[Mg ²⁺] (mol·kg _w ⁻¹)	F ₀ (counts)	τ (ns)	pH value	α	[Mg ²⁺] (mol·kg _w ⁻¹)	F ₀ (counts)	τ (ns)
1	9.17	1.00	0	2.61E+07	9.16	9.00	1.00	0	4.82E+07	9.93
2	8.26	1.09	3.48E-04	2.82E+07	13.15	8.30	1.05	8.23E-04	4.52E+07	9.72
3	8.22	1.12	7.32E-04	2.37E+07	14.38	8.23	1.04	1.72E-03	2.49E+07	13.59
4	8.07	1.49	1.25E-03	2.23E+07	18.58	8.00	1.20	2.79E-03	2.54E+07	15.33
5	8.05	1.64	1.49E-03	2.49E+07	19.11	7.95	1.31	3.66E-03	2.76E+07	15.61
6	8.00	2.08	2.38E-03	2.62E+07	20.35	7.88	1.70	4.08E-03	2.97E+07	15.79
7	7.90	3.80	4.16E-03	2.90E+07	23.99	7.81	2.42	6.10E-03	3.23E+07	15.60
8	7.87	4.80	6.36E-03	3.30E+07	25.72	7.79	2.73	8.46E-03	3.22E+07	18.31
9	7.78	8.90	1.56E-02	3.51E+07	28.22	7.77	3.16	1.02E-02	3.42E+07	20.05
10	7.74	12.13	2.50E-02	4.59E+07	28.30	7.75	3.50	1.27E-02	3.85E+07	20.36
11						7.73	4.03	1.65E-02	3.83E+07	22.22
12						7.70	5.01	2.10E-02	4.05E+07	23.07
I_m NaCl (mol·kg _w ⁻¹)	0.50					0.75				
Sample	pH value	α	[Mg ²⁺] (mol·kg _w ⁻¹)	F ₀ (counts)	τ (ns)	pH value	α	[Mg ²⁺] (mol·kg _w ⁻¹)	F ₀ (counts)	τ (ns)
1	9.00	1.00	0	7.96E+07	7.91	9.00	1.00	0	5.03E+07	9.48
2	8.45	1.01	8.50E-04	8.48E+07	8.97	8.45	1.01	8.19E-04	6.70E+07	9.59
3	7.95	1.09	5.91E-03	3.88E+07	11.65	8.30	1.02	3.17E-03	6.21E+07	9.63
4	7.87	1.19	6.34E-03	2.97E+07	13.09	7.90	1.08	6.39E-03	5.82E+07	9.93
5	7.75	1.70	7.37E-03	3.60E+07	13.09	7.82	1.14	2.87E-02	4.83E+07	11.22
6	7.70	2.20	9.57E-03	3.22E+07	14.37	7.73	1.38	3.61E-02	5.51E+07	10.75
7	7.68	2.45	1.50E-02	3.25E+07	15.11	7.68	1.68	5.03E-02	5.64E+07	11.11
8	7.63	3.35	1.93E-02	2.86E+07	17.26	7.65	1.94	6.23E-02	5.74E+07	11.65
9	7.60	4.17	2.32E-02	3.58E+07	16.70	7.62	2.29	7.72E-02	5.83E+07	12.28
10	7.59	4.36	3.07E-02	3.44E+07	17.94	7.59	2.73	8.44E-02	5.23E+07	13.18
11	7.57	5.05	4.07E-02	4.85E+07	19.69	7.57	3.12	9.54E-02	5.12E+07	14.26
12	7.55	5.89	6.08E-02	5.98E+07	18.11	7.55	3.57	1.10E-01	6.07E+07	13.48
I_m NaCl (mol·kg _w ⁻¹)	1.00									
Sample	pH value	α	[Mg ²⁺] (mol·kg _w ⁻¹)	F ₀ (counts)	τ (ns)					
1	9.00	1.00	0	1.16E+08	7.44					
2	8.45	1.01	7.92E-04	7.43E+07	8.58					
3	8.30	1.03	3.00E-03	6.40E+07	8.84					
4	8.23	1.03	1.18E-02	6.22E+07	9.36					
5	8.16	1.03	1.71E-02	4.17E+07	10.73					
6	7.71	1.14	2.85E-02	6.38E+07	10.16					
7	7.68	1.24	3.21E-02	7.95E+07	9.40					
8	7.65	1.38	4.22E-02	7.53E+07	10.44					
9	7.61	1.64	5.67E-02	8.12E+07	10.20					
10	7.53	2.59	6.65E-02	5.81E+07	12.89					
11	7.52	2.78	7.83E-02	6.96E+07	12.48					
12	7.50	3.20	1.05E-01	7.25E+07	12.65					

Table S3 .Characteristic decomposition parameters of the luminescence spectrum in Fig 4 of the main text.

Peak Index	Area Fit	Center Max	Max Height	FWHM
1	8.94E+06	464.62	6.43E+04	13.06
2	2.19E+06	484.37	1.34E+05	15.50
3	2.02E+06	504.75	1.21E+05	15.74
4	1.16E+06	525.76	6.27E+04	17.29
5	4.68E+05	547.63	2.06E+04	21.32
6	3.25E+05	569.17	6.81E+03	44.75

Table S4. Formation constants $\log_{10}K^0$ used in Fig. S1.

$\log_{10}K^0$	Mg	Ca
MCO ₃ (aq)	2.98 ^a	3.22 ^b
MOH ⁺	2.32 ^c	1.17 ^d
MF ⁺	1.35 ^a	0.68 ^a
MSO ₄ (aq)	2.26 ^e	2.02 ^f
MPO ₄ ⁻	4.85 ^g	6.46 ^g
MHPO ₄ (aq)	2.88 ^g	2.55 ^g
MH ₂ PO ₄ ⁺	1.17 ^g	1.40 ^g
MSeO ₄ (aq)	2.2 ^h	2 ^h

^a Sverjensky, *et al.*²; ^b Plummer and Busenberg³; ^c Palmer and Wesolowski⁴; ^d Shock, *et al.*⁵; ^e Wagman, *et al.*⁶; ^f Yeatts and Marshall⁷; ^g Turner, *et al.*⁸; ^h Olin, *et al.*⁹

Table S5. Evolutions of $\log_{10}K^\circ$ values from Mg^{2+} to Ba^{2+} with different ligands, used in Fig. S2.

$\log_{10}K^\circ_{1.1.3}$	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
F^-	1.35 ^a	0.68 ^a	0.14 ^a	-0.18 ^a
OH^-	2.32 ^b	1.17 ^c	0.69 ^c	0.49 ^d
CO_3^{2-}	2.98 ^a	3.22 ^e	2.81 ^f	2.71 ^g
Ox^{2-}	3.43 ^h	3.19 ^h	2.92 ^h	2.93 ^h
SO_4^{2-}	2.26 ^d	2.02 ⁱ	2.30 ^j	2.70 ^k
$\text{S}_2\text{O}_3^{2-}$	1.84 ^l	2.02 ^l	2.04 ^l	2.3 ^l
$\text{UO}_2(\text{CO}_3)_3^{4-}$	4.27 ^m 4.73 p.w. in NaCl 4.43 p.w. in NaClO ₄	5.34 ^m 5.36 in NaCl ⁿ 5.42 in NaClO ₄ ⁿ	5.02 ⁿ	4.84 ⁿ

^a Sverjensky, *et al.*²; ^b Palmer and Wesolowski⁴; ^c Shock, *et al.*⁵; ^d Wagman, *et al.*⁶; ^e Plummer and Busenberg³; ^f Busenberg, *et al.*¹⁰; ^g Busenberg and Plummer¹¹; ^h Prapaipong, *et al.*¹²; ⁱ Yeatts and Marshall⁷; ^j Reardon and Armstrong¹³; ^k Reardon and Armstrong¹³; ^l Davies¹⁴; ^m Dong and Brooks¹⁵; ⁿ Shang and Reiller¹⁶

Table S6. Seawater composition from Millero, *et al.*¹⁷

Temp	25°C
pH	8.1
pe	4
Density (g/cm ³)	1.023
Units	mol kg _w ⁻¹
Na	0.4861
Mg	0.0547
Ca	0.0106
K	0.0106
Sr	0.0001
Cl	0.5658
S(6)	0.0293
Br	0.0018
F	0.0001
U	1.386E-08

Table S7. Thermodynamic constants used in theoretical speciation of seawater case in Fig 8 of the main text and in Fig. S4.

		$\text{CaUO}_2(\text{CO}_3)_3^{2-}$	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	$\text{MgUO}_2(\text{CO}_3)_3^{2-}$	$\text{Mg}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$
Fig 8	$\log_{10}\beta^\circ$	27.20 ^a	30.49 ^a	26.57 p.w.	/
	ϵ	0.29 ± 0.11^a	0.66 ± 0.12^a	0.31 ± 0.02 p.w.	/
Fig S4a	$\log_{10}\beta^\circ$	27.27 ^b	29.81 ^b	25.8 ^c	27.1 ^c
	ϵ	-0.02 ^b	0 ^b	-0.02 ^c	0 ^c
Fig S4b	$\log_{10}\beta^\circ$	27.18 ^d	30.70 ^d	25.02 ^e	/
	ϵ	-3 ^d	0 ^d	-3 ^e	/

^a Shang and Reiller¹⁶; ^b Lee and Yun¹⁸; ^c Lee, *et al.*¹⁹; ^d Dong and Brooks¹⁵; ^e Dong and Brooks²⁰

Table S8 Thermodynamic constants used in theoretical speciation of Canadian aquitard case in Fig 9 of the main text and in Fig. S6.

		CaUO ₂ (CO ₃) ₃ ²⁻	Ca ₂ UO ₂ (CO ₃) ₃ (aq)	MgUO ₂ (CO ₃) ₃ ²⁻
Fig 9a and Fig. S6	log ₁₀ K ^o	5.36 ^a	8.65 ^a	4.73 p.w.
	ε	0.29 ± 0.11 ^a	0.66 ± 0.12 ^a	0.31 ± 0.02 p.w.
	Δ _r H _m (KJ mol ⁻¹)	-8 ± 6 ^b	-8 ± 7 ^b	/
		-1.2 ± 0.3 ^c	-3.1 ± 3.0 ^c	4.3 ± 1.5 ^c
	-4.6 (average)	-5.55 (average)	4.3 (average)	
Fig 9b	log ₁₀ β ^o	27.18 ^d	30.70 ^d	25.02 ^e
	ε	0	0	-3.2
	Δ _r H _m (KJ mol ⁻¹)	-47 ^b	-47 ^b	/

^a Shang and Reiller¹⁶, ^b Endrizzi and Rao²¹; ^c Jo *et al.*^{22,23}; ^d Dong and Brooks¹⁵; ^e Dong and Brooks²⁰

Table S9. Compositions of selected Indian drinking water samples, collected from the work of Coyte, *et al.*²⁴

Description	Units	Jai-112	Tonk-110	Bundi-104	Tonk-104	Jai-24
Temperature	°C	29.6	29.7	27.1	29.1	30.5
pH		7.4	7.15	7.68	7.55	6.83
F	mg/L	1.83	2.68	5.15	5.25	0
Cl	mg/L	293	314	388	1050	545
Br	mg/L	0.58	1.6	1.18	2.11	1.15
I	mg/L	0	0	1.512	0	0
N(5) as NO ₃ ⁻	mg/L	23.1	207	31.6	28.6	252
S(6) as SO ₄ ²⁻	mg/L	166	119	337	400	90.3
C(4) as HCO ₃ ⁻	mg/L	1530	737	970	1030	832
Ca	mg/L	13.9	38.9	20.5	14.9	212
Mg	mg/L	23	38	39.3	21.5	119
Sr	mg/L	0.99	1.45	0.92	1.58	2.89
Na	mg/L	800	484	700	1320	372
Fe	mg/L	0	0	0	0	0.53
Ba	mg/L	0.27	0.24	0.11	0.02	0.38
Mn	mg/L	0	0	0	0	0.45
Si	mg/L	10.5	26.8	12.4	6.31	23
Li	µg/L	0	11.26	30.35	31.33	13.28
B	µg/L	2310	754	2180	4140	893
V	µg/L	0	0	0	0	0
Cr	µg/L	0	0	0	0	0
Ni	µg/L	0	0	0	0	3.79
Cu	µg/L	0	0	0	0	20.69
Zn	µg/L	392.15	10.8	13.1	22.13	0
As	µg/L	0	0	0	0	0
Se	µg/L	0	0	0	0	0
Mo	µg/L	52.31	6.64	29.19	15.25	2.63
Pb	µg/L	0.69	0.52	0.63	1.06	0.34
U	µg/L	181.28	32.71	50.45	319.67	31.23

Table S10. Modeling of uranium speciation for selected Indian underground water samples.

(a) Using Ilnl.dat ^{25,26} with $\log_{10}K^{\circ}_{n.1.3}$ from Dong and Brooks ^{15,20} as follows:					
$\log_{10}K^{\circ}_{1.1.3}(\text{CaUO}_2(\text{CO}_3)_3^{2-}) = 5.34$		$\log_{10}K^{\circ}_{1.1.3}(\text{MgUO}_2(\text{CO}_3)_3^{2-}) = 4.27$			
$\log_{10}K^{\circ}_{2.1.3}(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})) = 8.86$		$\log_{10}K^{\circ}_{1.1.3}(\text{SrUO}_2(\text{CO}_3)_3^{2-}) = 5.02$			
Sample	$\text{CaUO}_2(\text{CO}_3)_3^{2-}$	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	$\text{MgUO}_2(\text{CO}_3)_3^{2-}$	$\text{UO}_2(\text{CO}_3)_3^{4-}$	Other
Jai-112	54.9%	12.8%	13.0%	16.0%	3.4%
Tonk-110	47.9%	39.2%	6.6%	3.3%	2.9%
Bundi-104	54.6%	18.8%	14.4%	10.6%	1.7%
Tonk-104	51.6%	10.2%	10.3%	24.2%	3.7%
Jai-24	20.6%	76.7%	1.7%	0.4%	0.5%
(b) Using Thermochemie.dat (http://www.thermochemie-tdb.com) with $\log_{10}\beta^{\circ}_{n.1.3}$ from Dong and Brooks ^{15,20} as follows:					
$\log_{10}\beta^{\circ}_{1.1.3}(\text{CaUO}_2(\text{CO}_3)_3^{2-}) = 27.18$		$\log_{10}\beta^{\circ}_{1.1.3}(\text{MgUO}_2(\text{CO}_3)_3^{2-}) = 26.11$			
$\log_{10}\beta^{\circ}_{2.1.3}(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})) = 30.7$		$\log_{10}\beta^{\circ}_{1.1.3}(\text{SrUO}_2(\text{CO}_3)_3^{2-}) = 26.86$			
Sample	$\text{CaUO}_2(\text{CO}_3)_3^{2-}$	$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$	$\text{MgUO}_2(\text{CO}_3)_3^{2-}$	$\text{UO}_2(\text{CO}_3)_3^{4-}$	Other
Jai-112	58.5%	12.9%	13.9%	13.3%	1.4%
Tonk-110	50.0%	39.5%	6.9%	2.7%	0.9%
Bundi-104	56.0%	17.8%	15.4%	10.0%	0.8%
Tonk-104	55.7%	10.0%	11.4%	21.2%	1.8%
Jai-24	21.3%	76.5%	1.7%	0.3%	0.2%

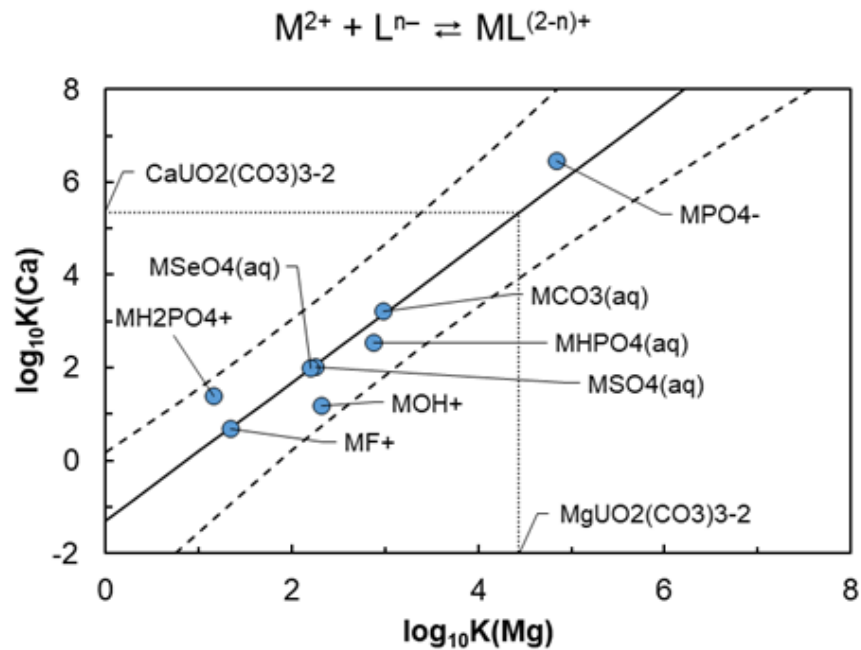


Fig. S1 Linear relationship between the formation constants $\log_{10}K^\circ$ for Mg and Ca with different ligands. The values of $\log_{10}K^\circ$ are listed in Table S4.

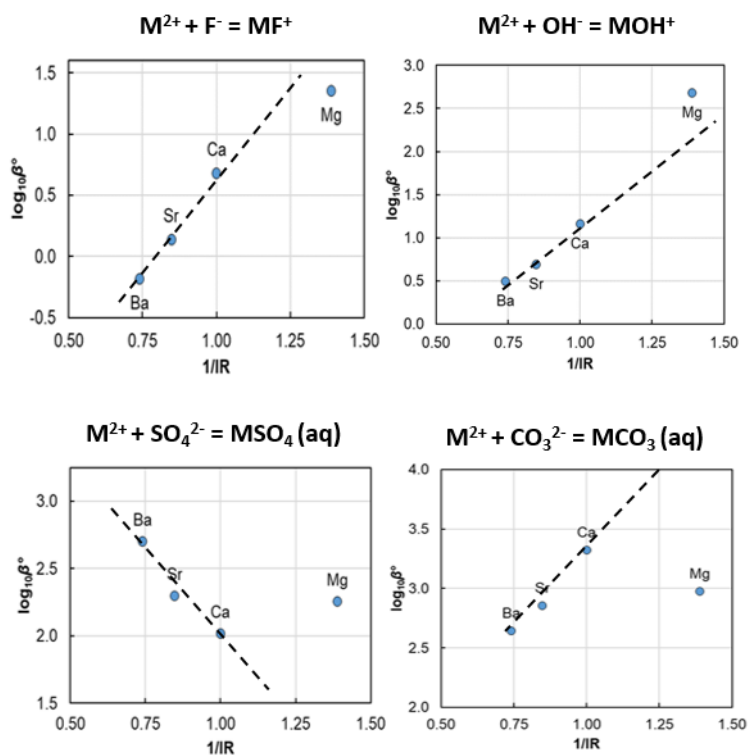


Fig. S2 Stability constants of alkali earth metal ions and different ligands – F^- , OH^- , SO_4^{2-} , CO_3^{2-} – as a function of $1/R$ with R being the size of the ionic radius. The values of $\log_{10}K^\circ$ are listed in Table S5.

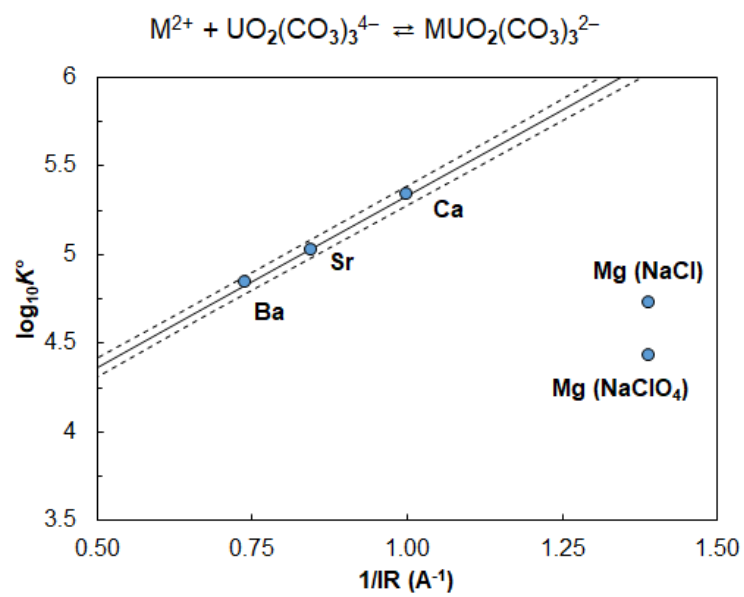


Fig. S3. Stability constants of alkaline earth metal ions and $UO_2(CO_3)_3^{4-}$ as a function of $1/R$ with R being the size of the ionic radius. The values of $\log_{10}K^\ominus$ are listed in Table S5.

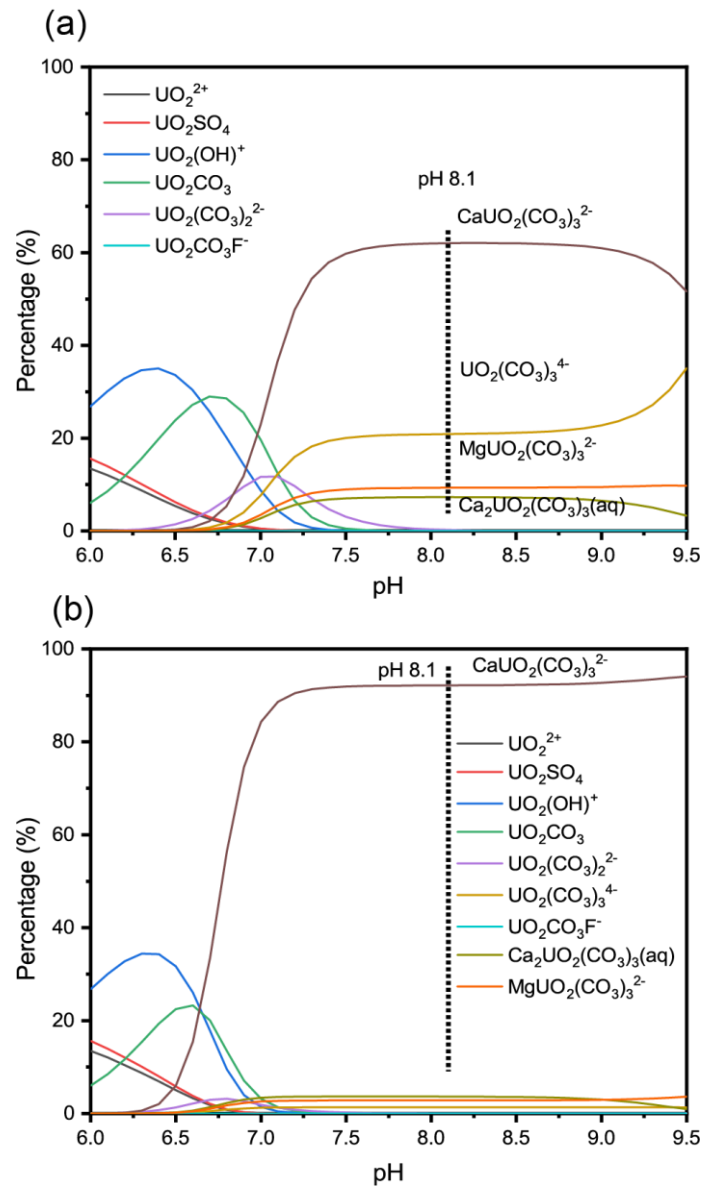


Fig. S4 Theoretical speciation of uranium in standard seawater (composition listed in Table S6) at $P(\text{CO}_2) = 10^{-3.5}$ atm. Thermochemie 10a database was used in calculations by implementing the thermodynamic constants of $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, $\text{Ca}_n\text{UO}_2(\text{CO}_3)_3^{(4-2n)-}$ listed in Table S7.

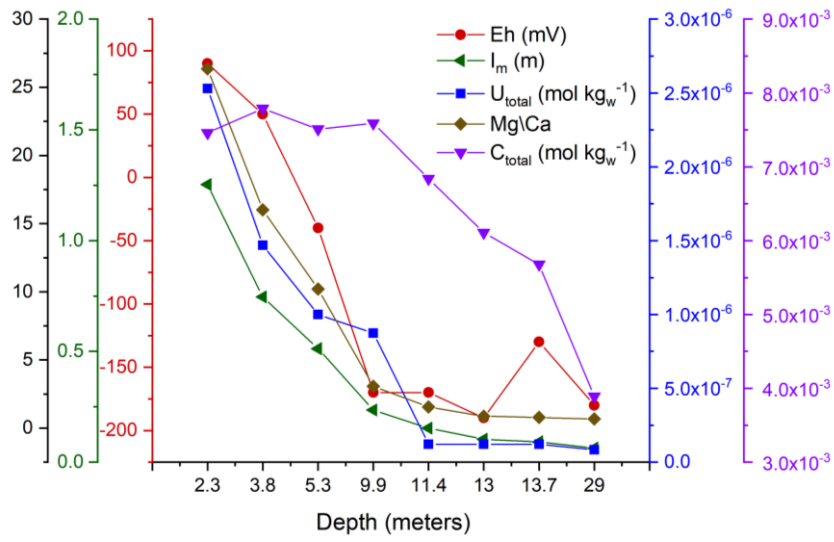


Fig. S5 Evolutions of principal parameters in the selected Canadian aquitard waters.^{27,28}

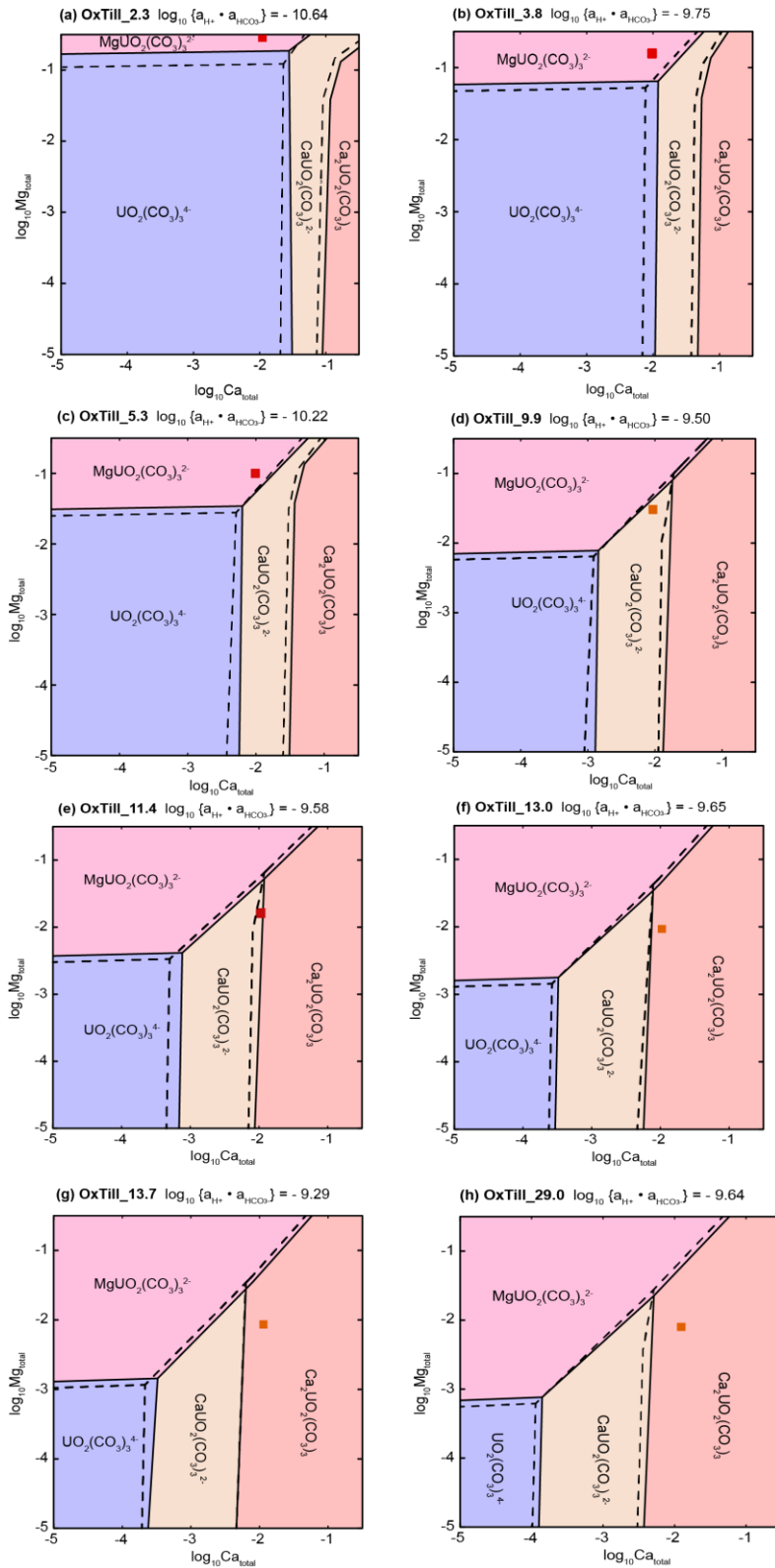


Fig. S6 Predominance plots of uranium species at the fixed values of $\log_{10} \{a_{H^+} \cdot a_{HCO_3^-}\}$ corresponding to the aqueous conditions of the collected samples in Canadian aquitard site. Thermochemie 10a database file²⁹ and SIT ionic strength correction were used in calculations with implemented thermodynamic constants of $MgUO_2(CO_3)_3^{2-}$, $Ca_nUO_2(CO_3)_3^{(4-2n)-}$ listed in Table S8. The boundaries plotted in dashed lines represent the simulation results at 5°C and the solid lines at 25°C. The ionic strength varies from 1.38 mol kg_w^{-1} at 29 m to 0.06 mol kg_w^{-1} to at 2.3 m.

References

1. R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D. A. Palmer, I. Grenthe and M. H. Rand, *Update of the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, 2003.
2. D. A. Sverjensky, E. L. Shock and H. C. Helgeson, *Geochimica et Cosmochimica Acta*, 1997, **61**, 1359-1412.
3. L. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta*, 1982, **46**, 1011-1040.
4. D. A. Palmer and D. J. Wesolowski, *J. Solution Chem.*, 1997, **26**, 217-232.
5. E. L. Shock, D. C. Sassani, M. Willis and D. A. Sverjensky, *Geochimica et cosmochimica acta*, 1997, **61**, 907-950.
6. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm and I. Halow, *J. Chem. Ref. Data*, 1982, **11**, 392.
7. L. B. Yeatts and W. L. Marshall, *J. Phys. Chem.*, 1969, **73**, 81-90.
8. D. R. Turner, M. Whitfield and A. Dickson, *Geochim. Cosmochim. Acta*, 1981, **45**, 855-881.
9. Å. Olin, B. Noläng, E. Osadchii, L.-O. Öhman and E. Rosén, *Chemical Thermodynamics of Selenium*, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, 2005.
10. E. Busenberg, L. N. Plummer and V. B. Parker, *Geochim. Cosmochim. Acta*, 1984, **48**, 2021-2035.
11. E. Busenberg and L. N. Plummer, *Geochim. Cosmochim. Acta*, 1986, **50**, 2225-2233.
12. P. Prapaipong, E. L. Shock and C. M. Koretsky, *Geochimica et Cosmochimica Acta*, 1999, **63**, 2547-2577.
13. E. J. Reardon and D. K. Armstrong, *Geochimica et Cosmochimica Acta*, 1987, **51**, 63-72.
14. C. W. Davies, in *The Structure of Electrolytic Solutions*, John Wiley and Sons, New York, 1959, pp. 19-34.
15. W. M. Dong and S. C. Brooks, *Environ. Sci. Technol.*, 2006, **40**, 4689-4695.
16. C. Shang and P. E. Reiller, *Dalton. Trans*, 2020, **49**, 466-481.
17. F. J. Millero, R. Feistel, D. G. Wright and T. J. McDougall, *Deep-Sea Res. Pt. I*, 2008, **55**, 50-72.
18. J. Y. Lee and J. I. Yun, *Dalton Trans.*, 2013, **42**, 9862-9869.
19. J. Y. Lee, M. Vespa, X. Gaona, K. Dardenne, J. Rothe, T. Rabung, M. Altmaier and J.-I. Yun, *Radiochim. Acta*, 2017, **105**.
20. W. Dong and S. C. Brooks, *Environ. Sci. Technol.*, 2008, **42**, 1979-1983.
21. F. Endrizzi and L. F. Rao, *Chem.-Eur. J.*, 2014, **20**, 14499-14506.
22. Y. Jo, A. Kirishima, S. Kimuro, H.-K. Kim and J.-I. Yun, *Dalton Trans.*, 2019, **48**, 6942-6950.
23. Y. Jo, H.-K. Kim and J.-I. Yun, *Dalton. Trans*, 2019, **48**, 14769-14776.
24. R. M. Coyte, R. C. Jain, S. K. Srivastava, K. C. Sharma, A. Khalil, L. Ma and A. Vengosh, *Environmental Science & Technology Letters*, 2018, **5**, 341-347.
25. D. L. Parkhurst and C. A. J. Appelo, *Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. Chapter 43 of Section A, Groundwater Book 6, Modeling Techniques*, U.S. Geological Survey, Denver, Colorado, USA, 2013. <http://pubs.usgs.gov/tm/06/a43/pdf/tm6-A43.pdf>

26. D. L. Parkhurst and C. A. J. Appelo, *User's Guide to PHREEQC (Version 2) — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*, Report 99-4259, U.S. Geological Survey, Water-Resources Investigations, Lakewood, Colorado, USA, 1999.
http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/
27. M. J. Hendry and L. I. Wassenaar, *Water Resour. Res.*, 2000, **36**, 503-513.
28. J. F. Ranville, M. J. Hendry, T. N. Reszat, Q. L. Xie and B. D. Honeyman, *J. Contam. Hydrol.*, 2007, **91**, 233-246.
29. Thermochimie, <http://www.thermochimie-tdb.com/>.