Electronic Supplementary Information

Spectroscopy of uranium and neptunium in seawater

Melody MALOUBIER[a,b], Pier Lorenzo SOLARI[c], Philippe MOISY[d], Marguerite MONFORT[b], Christophe DEN AUWER[a], Christophe MOULIN[b]***

Content: 8 pages including cover sheet

Table S1: Equilibrium constants for UO_2^{2+} at I=0 used for the speciation calculation

*Guidance but value not retained by the NEA-TDB

Equilibrium	$Log_{10}K°$	Reference
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3(aq)$	9.94	Guillaumont (19)
$UO_2^{2+} + 2\ CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.61	Guillaumont (19)
$UO_2^{2+}+3CO_3^{2-}=UO_2(CO_3)_3^{4-}$	21.84	Guillaumont (19)
$3UO_2^{2+}+6CO_3^{2-}=(UO_2)_3(CO_3)_3^{2-}$	54	Guillaumont (19)
$UO_2^{2+}+3CO_3^{2-}+Ca^{2+}=CaUO_2(CO_3)_3^{2-}$	27.18 25.4 *	Dong (20) Bernhard (21)
$UO_2^{2+}+3CO_3^{2-}+2Ca^{2+}=Ca_2UO_2(CO_3)_3(aq)$	30.70 30.6*	Dong (20) Guillaumont (19), Bernhard (21)
$UO_2^{2+}+3CO_3^{2-}+Mg^{2+}=MgUO_2(CO_3)_3^{2-}$	26.11	Dong (20)
$UO_2^{2+}+3CO_3^{2-}+Sr^{2+}=SrUO_2(CO_3)_3^{2-}$	26.86	Dong (20)
$2UO_2^{2+}+CO_3^{2-}+3H_2O=(UO_2)_2(OH)_3CO_3^{-}+3H^+$	-0.85	Guillaumont (19)
$3UO_2^{2+}+CO_3^{2-}+3H_2O=(UO_2)_3(OH)_3CO_3^{+}+3H^+$	0.65	Guillaumont (19)
$11UO_2^{2+}+6CO_3^{2-}+12H_2O=(UO_2)_{11}(OH)_{12}(CO_3)_6^{2-}+12H^+$	36.49	Guillaumont (19)
$2F^-+UO_2^{2+}=UO_2F_2(aq)$	8.83	Guillaumont (19)
$3F^-+UO_2^{2+}=UO_2F_3^-$	10.90	Guillaumont (19)
$4F^-+UO_2^{2+}=UO_2F_4^{2-}$	11.84	Guillaumont (19)
$Cl^-+UO_2^{2+}=UO_2Cl^+$	0.17	Guillaumont (19)
$Br^-+UO_2^{2+}=UO_2Br^+$	0.22	Guillaumont (19)
$SO_4^{2-}+UO_2^{2+}=UO_2SO_4(aq)$	3.15	Guillaumont (19)
$2SO_4^{2-}+UO_2^{2+}=UO_2(SO_4)_2^{2-}$	4.14	Guillaumont (19)
$NO_3^-+UO_2^{2+}=UO_2NO_3^+$	0.30	Guillaumont (19)
$PO_4^{3-}+UO_2^{2+}=UO_2PO_4^-$	13.23	Guillaumont (19)
$UO_2^{2+} + HPO_4^{2-}= UO_2HPO_4(aq)$	7.24	Guillaumont (19)

Table S2: Equilibrium constants for NpO_2^+ at I=0 used for the speciation calculation

Equilibrium	$Log_{10}K°$	Reference
$NpO_2^+ + CO_3^{2-} = NpO_2CO_3^-$	4.962	Guillaumont (19)
$NpO_2^+ + 2\ CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	6.534	Guillaumont (19)
$NpO_2^+ + 3CO_3^{2-} = NpO_2(CO_3)_3^{5-}$	5.500	Guillaumont (19)
$NpO_2^{2+} + 2CO_3^{2-} + H_2O = NpO_2(CO_3)_2OH^{4-} + H^+$	-5.305	Guillaumont (19)
$F^- + NpO_2^+ = NpO_2F(aq)$	1.2	Guillaumont (19)
$SO_4^{2-} + NpO_2^+ = NpO_2SO_4^-$	0.44	Guillaumont (19)
$HPO_4^{2-} + NpO_2^+ = NpO_2PO_4^{2-} + H^+$	-5.38	Morgenstern (22)
$HPO_4^{2-} + NpO_2^+ = NpO_2HPO_4^-$	2.95	Guillaumont (19)

Table S3: Average concentration for co-existing metal and other species in sweater

Metal	Concentration (nM)	Reference
Zn	8.1	Nolting (24) Saager (25)
Cu	3.3	Nolting (23,24) Saager (25)
Fe	2.7	Nolting (23)
Co	0.11	Robertson (27)
Pb	0.17	Schaule (28)
Cd	1.0	Quinby-Hunt (30) Nolting (23,24)
Ni	11	Quinby-Hunt (30) Nolting (24)
Hg	$8.5\ 10^{-3}$	Mason (31) , Ólafsson (32)
Al	38	Measures (33)
I	500	Wong (29)
B	0.4 mM	Noakes (26)

Figure S4: Uranium theoretical speciation diagram at 10^{-8} M in seawater

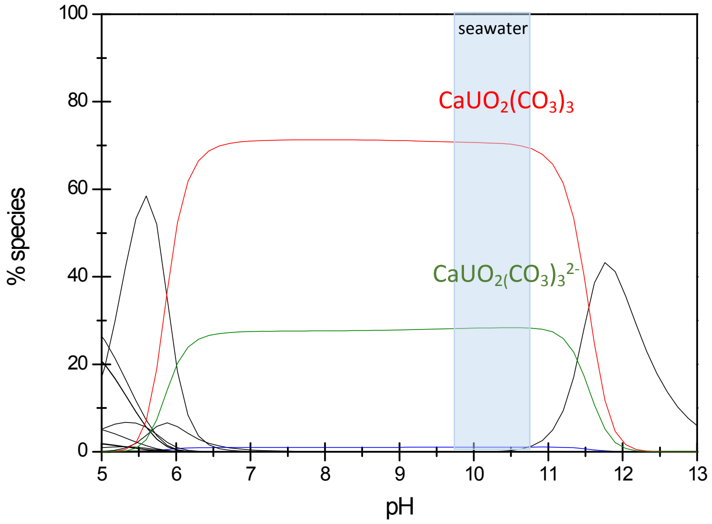

Figure S5: Neptunium theoretical speciation diagram at 10^{-14} M in seawater

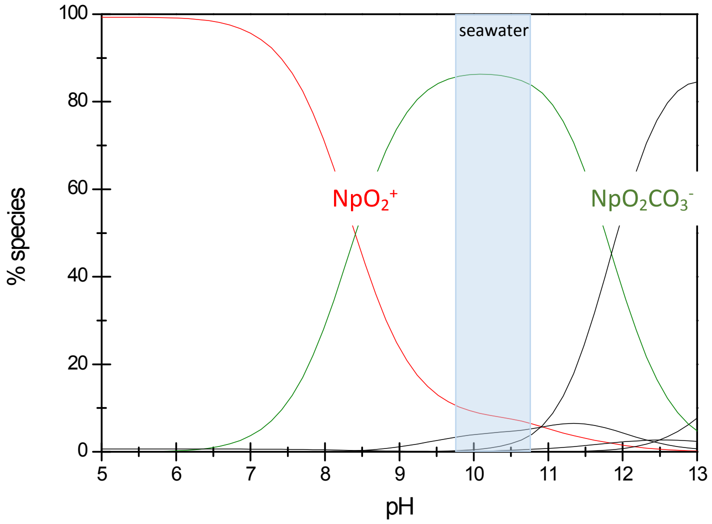

Figure S6: TRLIF spectra of uranium doped seawater at 5.10^{-5} M and 10^{-5} M, pH 8. Time delay 5 ns, aperture time 1 µs, number of accumulations 500.

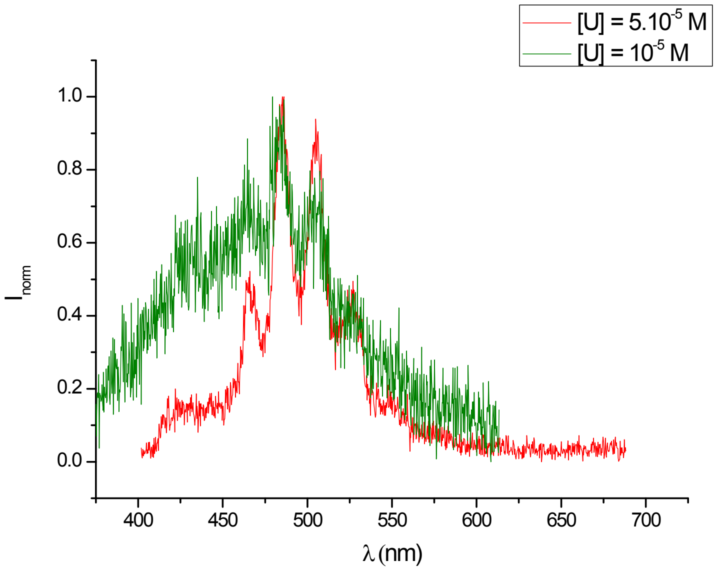

Figure S7: Experimental Np L_{II} edge XANES spectrum of the doped seawater solution at 5.10^{-5} M