Plutonium environmental chemistry: Mechanisms for the surface-mediated reduction of Pu(V/VI)

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Electronic Supplementary Information:

Figure S1 - Aqueous speciation of Pu(IV) and Pu(V) in a carbonate-free environment.

Figure S2 - Aqueous speciation of Pu(IV) and Pu(V) in a solution containing 0.1 M carbonate.

Table S1 – Calculated log $\beta^{\circ}_{1,i}$ values for Pu(VI), Pu(V), and Pu(IV) complexation with carbonate at zero ionic strength.

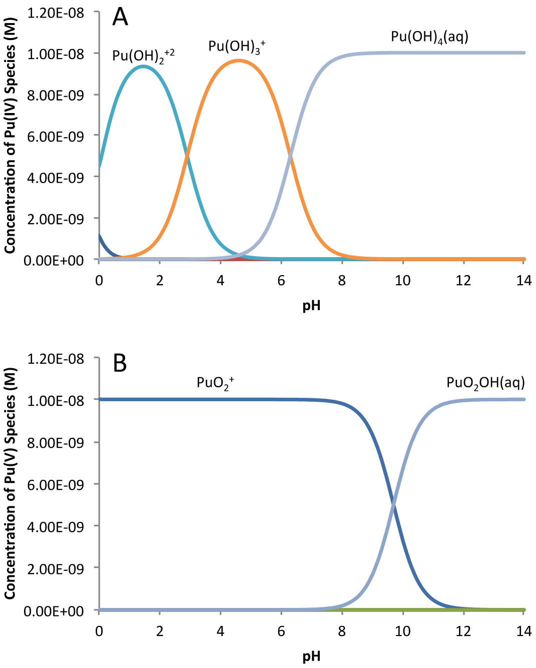

Figure S1 - Aqueous speciation of (A) Pu(IV) and (B) Pu(V) in a carbonate-free environment. [Pu] = 10^{-8} M. Modeling performed using HySS 2009. Hydrolysis constants obtained from Clark et al.[1]

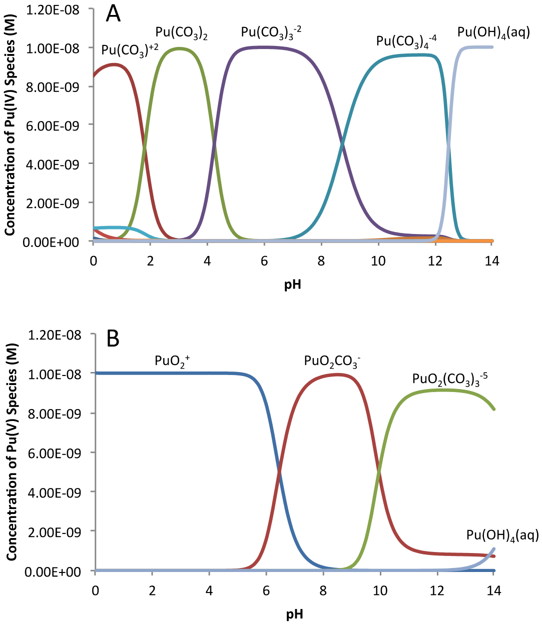

Figure S2 - Aqueous speciation of (A) Pu(IV) and (B) Pu(V) in a solution containing 0.1 M carbonate. [Pu] = 10^{-8} M. Modeling performed using HySS 2009. Hydrolysis constants obtained from Clark et al.[1] pK$_a$ and log $\beta^{\circ}_{1,i}$ values for carbonate complexes taken from Stumm and Morgan[2] and Table S1, respectively.

Table S1 – Calculated log $\beta^{\circ}_{1,i}$ values for Pu(VI), Pu(V), and Pu(IV) complexation with carbonate at zero ionic strength. Adapted from Clark et al.[3]

Species	Formation Reaction	Log $\beta^{\circ}_{1,i}$
$PuO_2(CO_3)$	$PuO_2^{+2} + CO_3^{-2} \rightleftharpoons PuO_2(CO_3)$	8.4 ± 0.3
$PuO_2(CO_3)_2^{-2}$	$PuO_2^{+2} + 2CO_3^{-2} \rightleftharpoons PuO_2(CO_3)_2^{-2}$	15.1
$PuO_2(CO_3)_3^{-4}$	$PuO_2^{+2} + 3CO_3^{-2} \rightleftharpoons PuO_2(CO_3)_3^{-4}$	18.5
$PuO_2(CO_3)^{-}$	$PuO_2^{+} + CO_3^{-2} \rightleftharpoons PuO_2(CO_3)^{-}$	5.1 ± 0.1
$PuO_2(CO_3)_3^{-5}$	$PuO_2^{+} + 3CO_3^{-2} \rightleftharpoons PuO_2(CO_3)_3^{-5}$	8.2 ± 2.1
$Pu(CO_3)^{+2}$	$Pu^{+4} + CO_3^{-2} \rightleftharpoons Pu(CO_3)^{+2}$	19.4 ± 0.7
$Pu(CO_3)_2$	$Pu^{+4} + 2CO_3^{-2} \rightleftharpoons Pu(CO_3)_2$	33.5 ± 1.0
$Pu(CO_3)_3^{-2}$	$Pu^{+4} + 3CO_3^{-2} \rightleftharpoons Pu(CO_3)_3^{-2}$	42.7 ± 0.8
$Pu(CO_3)_4^{-4}$	$Pu^{+4} + 4CO_3^{-2} \rightleftharpoons Pu(CO_3)_4^{-4}$	45.3 ± 0.8
$Pu(CO_3)_5^{-6}$	$Pu^{+4} + 5CO_3^{-2} \rightleftharpoons Pu(CO_3)_5^{-6}$	44.5 ± 0.8

Calculation supporting hypothesis 5, *Stabilization of Pu(IV) on the mineral surface due to increased concentration gradient within the EDL*

Assumptions based on the work of Romanchuk et al.[4]:

- $[Pu]_T = 10^{-10}$ M
- 99% sorption
- hematite surface area is 35 m^2/g and based on 1 g of material
- hematite particles are 50 nm in diameter and spherical

To calculate the surface area of each individual hematite particle:

$$A = 4\pi r^2 = 4\pi(25nm)^2 = 31415\ nm^2 = 3.14 \times 10^{-14}\ m^2$$

The total surface area is 35 m^2, therefore there are 10^{15} particles present.

The control volume can be calculated by subtracting the volume of a sphere with a radius equal to that of a hematite particle (r_h; in nm) from the volume of a sphere with radius equal to $r_h + 1$.

$$V_{r_h} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(25\ nm)^3 = 65450\ nm^3$$

$$V_{r_h+1} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(26\ nm)^3 = 73622\ nm^3$$

$$73622\ nm^3 - 65450\ nm^3 = 8172\ nm^3 \times \frac{10^{-24}\ L}{nm^3} = 8.172 \times 10^{-21}\ L$$

Therefore, the total control volume is (10^{15} particles)*(8.172×10^{-21} L) = 9×10^{-6} L. Depending upon the initial volume of solution (10 mL to 1 L), the concentration of plutonium in the control volume is $10^{-7} – 10^{-5}$ M.

References

1 D. L. Clark, S. S. Hecker, G. D. Jarvinen and M. P. Neu, in *The Chemistry of the Actinide and Transactinide Elements*, Springer, Dordrecht, The Netherlands, 2006, vol. 2, pp. 813–1264.
2 W. Stumm and J. J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, John Wiley & Sons, Inc., New York, NY, 1996, vol. 3rd.
3 D. L. Clark, D. E. Hobart and M. P. Neu, *Chem Rev*, 1995, **95**, 25–48.
4 A. Y. Romanchuk, S. N. Kalmykov and R. A. Aliev, *Radiochim. Acta*, 2011, **99**, 137–144.