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Estimation of Model VII humic binding constants for Pd^{2+}, Sn^{2+}, U^{4+}, NpO_2^{2+}, Pu^{4+} and PuO_2^{2+}

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Supporting information

Figure S1

Figure S2

Compilation of data for formation of inorganic species

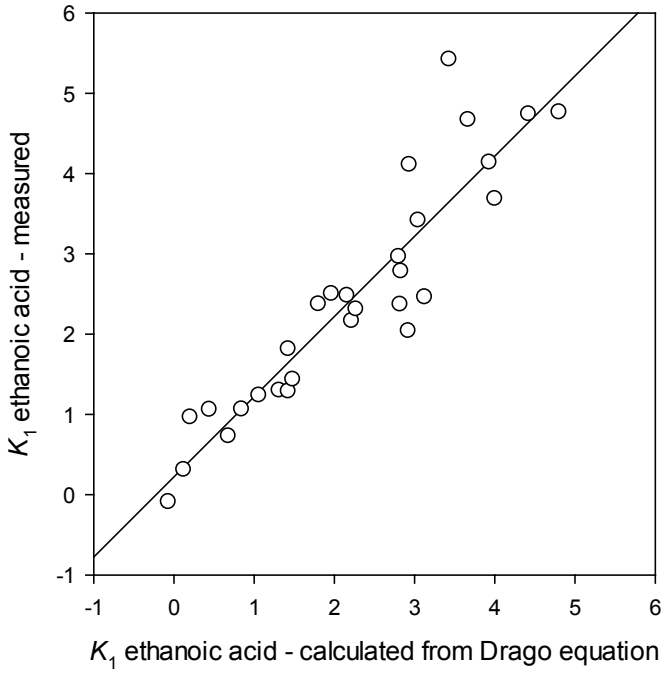

Figure S1. Plot showing the correlation between measured stability constants and those calculated from the Drago equation and variables as reported in reference 9.

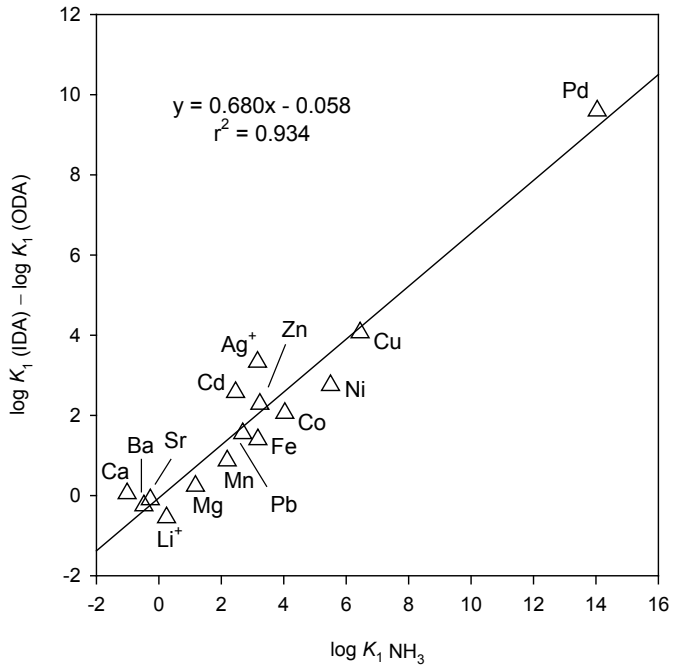

Figure S2. Liner free energy relationship between the ligand pair oxydiacetic acid/iminodiacetic acid and NH_3. All metals are divalent cations unless otherwise stated.

Compilation of data for formation of inorganic species

To model aqueous speciation fully in WHAM, a comprehensive dataset of important inorganic equilibrium constants is required. To achieve this we have compiled these data using a pragmatic procedure using the latest available data compilations (references 14-16 in the main manuscript). The NAGRA/PSI Chemical Thermodynamics compilation (2002; reference 15) is largely based on the compilations undertaken by the NEA thermodynamics database project, with some additional data. This was updated by the Swedish Nuclear Fuel and Waste Management Company (2006; reference 16) to expand the number of data for ΔH, to include data from more recent literature, and to estimate values where significant gaps existed. The latest volume in the Chemical Thermodynamics series for thorium (2007; reference 11) was printed after these compilations. Data for inorganic speciation with the ligands CO_3^{2-}, Cl^-, OH^- and SO_4^{2-} are shown in Table S1 (we refer readers to the cited references for error ranges associated with these data and further data for other ligands such as F^- and NO_3^-). Some data were already included in the WHAM default database for some cations. Table S2 shows these data and the values reported in the recent literature. The WHAM database is fully user definable so updates can be implemented by any user.

Table S1. Compilation of log β^0 and ΔH^0 values for species of CO_3^{2-}, Cl^-, OH^- and SO_4^{2-}. Included are full data for those cations not previously included in the WHAM database (Pd^{2+}, Sn^{2+}, NpO_2^{2+}) and additional data for those cations previously included in the default database (Th^{4+}, Pu^{4+}, PuO_2^{2+}, U^{4+}, UO_2^{2+}).

Species	Log β^0	ΔH^0	Source
$PdOH^+$	12.14	-44.006	Reference 16
$Pd(OH)_2$	24.21	-96.519	Reference 16
$Pd(OH)_3^-$	26.07	-112.855	Reference 16
$Pd(OH)_4^{2-}$	26.64	-105.061	Reference 16
$PdCO_3$	6.83	0	Reference 16
$Pd(CO_3)_2^{2-}$	12.53	0	Reference 16
$PdSO_4$	2.91	0	Reference 16
$Pd(SO_4)_2^{2-}$	4.17	0	Reference 16
$PdCl^+$	5.1	-24.542	Reference 15 (ΔH from Reference 16)
$Pd(Cl)_2$	8.3	-47.297	Reference 15 (ΔH from Reference 16)
$Pd(Cl)_3^-$	10.9	-77.344	Reference 15 (ΔH from Reference 16)
$Pd(Cl)_4^{2-}$	11.7	-112.469	Reference 15 (ΔH from Reference 16)
$SnOH^+$	10.2	-26.141	Reference 16
$Sn(OH)_2$	20.2	-70.091	Reference 16
$Sn(OH)_3^-$	24.5	-72.148	Reference 16
$SnSO_4$	2.91	0	Reference 16
$Sn(SO_4)_2^{2-}$	-0.85	0	Reference 16
$SnCl^+$	1.54	11.18	Reference 16
$Sn(Cl)_2$	2.3	13.36	Reference 16
$Sn(Cl)_3^-$	1.97	23.14	Reference 16
NpO_2OH^+	8.9	-12.9	Reference 15 (ΔH from Reference 16)
$NpO_2(OH)_2$	15.79	0	Reference 16
$NpO_2(OH)_3^-$	23	0	Reference 15
$NpO_2(OH)_4^{2-}$	23	0	Reference 15
NpO_2CO_3	9.32	0	Reference 15
$NpO_2(CO_3)_2^{2-}$	16.52	0	Reference 15
NpO_2SO_4	3.28	16.7	Reference 15
$NpO_2(SO_4)_2^{2-}$	4.7	26	Reference 15
NpO_2Cl^+	0.4	8.4	Reference 15 (ΔH from Reference 16)
Additional data for species of UO_2^{2+}, U^{4+}, Pu^{4+}, PuO_2^{2+} and Th^{4+} not included in the WHAM default database			
$ThSO_4^{2+}$	6.17	20.92	Reference 14 (Vol. 11)
$Th(SO_4)_2$	9.69	40.38	Reference 14 (Vol. 11)
$Th(SO_4)_3^{2-}$	10.748		Reference 14 (Vol. 11)
$Th(CO_3)_5^{6-}$	31		Reference 14 (Vol. 11)
$Th(OH)_3(CO_3)$	40.1		Reference 16
$Th(OH)_2(CO_3)_3$	38.2		Reference 16
$Pu(CO_3)_4^{4-}$	37		Reference 16
$Pu(CO_3)_5^{6-}$	35.65		Reference 16
$PuO_2(CO_3)_3^{4-}$	18		Reference 16
$PuO_2(SO_4)_2^{2-}$	4.4	43	Reference 15
PuO_2Cl_2	-1.15		Reference 14 (Vol. 5)
$UO_2(OH)_4$	23.6	-67.5	Reference 16
$UO_2(CO_3)_3^{2-}$	21.6	-39.2	Reference 15
$UO_2(SO_4)_2^{2-}$	4.14		Reference 14 (Vol. 5)
$UO_2(SO_4)_3^{4-}$	3.02		Reference 14 (Vol. 5)
UO_2Cl^-	0.17	8	Reference 15
$UO_2(Cl)_2$	-1.1	15	Reference 15
$U(SO_3)_2$	10.51	32.7	Reference 14 (Vol. 5)
$U(CO_3)_4^{2-}$	35.12		Reference 16
$U(CO_3)_5^{4-}$	34	-20	Reference 16

Table S2. Comparison of log β^0 values for species of CO_3^{2-}, Cl^-, OH^- and SO_4^{2-} included in the default WHAM database and those most recently reported in literature compilations.

	Species	WHAM default log β^0	Most recently reported log β^0	Source
UO_2^{2+}	UO_2OH^+	8.8	8.8	Reference 15
	$UO_2(OH)_2$	16.1	16	Reference 15
	$UO_2(OH)_3^-$	21	22.8	Reference 15
	UO_2SO_4	3	3.15	Reference 15
	UO_2CO_3	9.4	9.94	Reference 14/16
	$UO_2(CO_3)_2^{2-}$	16.4	16.61	Reference 14/16
U^{4+}	UOH^{3+}	13.3	13.46	Reference 16
	$U(OH)_2^{2+}$	24.7	26.9	Reference 16
	$U(OH)_3^+$	34.2	37.3	Reference 16
	$U(OH)_4$	41.7	46	Reference 16
	$U(OH)_5^-$	47.3		
	USO_4^{2+}	6.11	6.38	Reference 15
	UCl^{3+}	1.16	1.72	Reference 15
Pu^{4+}	$PuOH^{3+}$	13.3	14.6	Reference 16
	$Pu(OH)_2^{2+}$	28.14	28.6	Reference 16
	$Pu(OH)_3^+$	39.11	39.7	Reference 16
	$Pu(OH)_4$	46.81	47.5	Reference 16
	$PuSO_4^{2+}$	6.42	6.89	Reference 15
	$Pu(SO_4)_2$	10.78	11.14	Reference 15
	$PuCl^{3+}$	1.22	1.8	Reference 15
	$PuCO_3^{2+}$	19.14		
	$Pu(CO_3)_2$	33.12		
PuO_2^{2+}	PuO_2OH^+	8.3	8.5	Reference 15
	$PuO_2(OH)_2$	16.85	14.8	Reference 15
	$PuO_2(OH)_3^-$	20.88		
	PuO_2CO_3	12	9.5	Reference 16
	$PuO_2(CO_3)_2^{2-}$	14.9	14.7	Reference 16
	PuO_2Cl^+	0.63	0.23	Reference 16
	PuO_2SO_4	4.68	3.38	Reference 15
Th^{4+}	$ThOH^{3+}$	11.66	11.5	Reference 14 (Vol. 11)
	$Th(OH)_2^{2+}$	21.64	21.8	Reference 14 (Vol. 11)
	$Th(OH)_3^+$	30.3		
	$Th(OH)_4$	40.1	38.6	Reference 14 (Vol. 11)
	$ThCO_3^{2+}$	11.03		
	$ThCl^{3+}$	1.18	1.21	Reference 14 (Vol. 11)