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Tungsten solubility and speciation in hydrothermal solutions revealed by in situ X-ray absorption spectroscopy

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Supplement. Additional information about thermodynamic modeling of tungsten speciation at hydrothermal conditions.

Table S1. Optimization results for experiments in water (WO_3), NaCl ($WO_{2.7}$ +/ – quartz) and HCl solutions (WO_3 and $WO_{2.7}$).

Reaction	Pressure [bar]	Temperature [°C]	$\Delta G^o_{i,T,P}$ for aq. species ($H_3WO_4^+$, HWO_4^-, $NaWO_4^-$), [kJ/mol]	Error for $\Delta G^o_{i,T,P}$, [kJ/mol]	OptimA program		OptimC program	
					$\log_{10}K$	$\log_{10}$ K error	$\log_{10}$ K	$\log_{10}K$ error*
$WO_4^{2-} + 3H^+ = H_3WO_4^+$	400	100	–989.2	1.0	10.43	0.14	10.18	0.24
		200	–1000.5	1.3	9.61	0.14	10.29	0.67
		300	–1030.0	0.6	11.39	0.05	11.17	0.22
		350	–1045.4	0.5	12.65	0.04	12.12	0.53
		400	–1057.9	0.3	13.85	0.02	14.16	0.38
$WO_4^{2-} + H^+ = HWO_4^-$	500	100	–948.6	1.8	5.04	0.01	4.78	0.26
		150	–955.5	0.4	5.11	0.01	5.07	0.04
		200	–962.4	2.2	5.65	0.01	5.41	0.24
		250	–969.1	1.2	5.95	0.01	5.83	0.12
		300	–975.7	0.3	6.34	0.01	6.37	0.03
$WO_4^{2-} + Na^+ = NaWO_4^-$	400	100	–1210.665	3.0	4.16	0.01	4.10	0.06
		200	–1225.431	3.8	3.92	0.01	4.17	0.25
		300	–1237.679	4.7	4.97	0.01	4.56	0.41
		350	–1240.357	9.2	4.74	0.01	4.96	0.22

* errors for equilibrium constants were calculated with OptimA; and as a difference between values of $\log_{10}K$ optimized with OptimA and OptimC.

Table S2. Thermodynamic data for solid phases used in this study and corresponding Maier-Kelly and Holland-Powell equations.

Source	Solid phase	T range, [°C]	$\Delta_f G^0_{298}$ [kJ mol^{-1}]	$\Delta_f H^0_{298}$ [kJ mol^{-1}]	S^0_{298} [J K^{-1}mol^{-1}]	C_p [J K^{-1}mol^{-1}]
Zhidikova & Khodakovskiy, 1984	$CaWO_{4\ scheelite}$	25 – 799.85	–1533.762	–1623.0	126.4	$123.1 + (37.7 \times 10^{-3}\ T) - ((17.87 \times 10^5)/T^2)$
Zhidikova & Khodakovskiy, 1984	$FeWO_{4\ ferberite}$	25 – 1100	–1072.161		132.26	$29.40966 + (11.9001 \times 10^{-3}\ T) - ((4.710803 \times 10^5)/T^2)$
Barin, 1995	$WO_{2.72}$	25 – 926.85	–708.627	–781.153	68.408	$84.5025 + (12.179 \times 10^{-3} T) - ((18.08661 \times 10^5)/T^2) - ((5.5807 \times 10^{-2})/\sqrt[2]{T})$
Han et al., 2020	$WO_{3\ monoclinic(\gamma)}$	25 – 326.4	–764.057	–842.909	75.910	$87.54 + (16.35 \times 10^{-3}\ T) - ((17.46 \times 10^5)/T^2)$
	$WO_{3\ orthorhombic}$	326.4 – 779.2				$87.59 + (15.92 \times 10^{-3}\ T) - ((17.64 \times 10^5)/T^2)$
SUPCRT, 2007	$C_{\ graphite}$	25 – 2226.85	0	0	5.740	$1.686152 + (4.76976 \times 10^{-3}\ T) - ((8.53536 \times 10^5)/T^2)$
Robie & Hemingway, 1995	$SiO_{2\ trigonal\ quartz}$	25 – 573.85	–856.3	–910.857	41.5	$81.145 + (18.28 \times 10^{-3}\ T) - ((1.81 \times 10^5)/T^2) - ((6.985 \times 10^2)/\sqrt[2]{T}) + (5.406 \times 10^{-6}\ T^2)$

Table S3. Association constants ($\log_{10}$ K) for tungsten species under ambient conditions (25 °C, P_{sat}) defined in previous studies.

Equation/ Reference	Yatsimirskii and Romanov, 1965 Yatsimirskii and Prik, 1964	Perrin, 1969	Shock et al., 1997	Bychkov and Zuykov, 2005	Wang et al., 2019	BR model, this study
$WO_4^{2-} + 2H^+ = H_2WO_4^0$ (aq)	5.851	8.1		11.14 +/– 0.55	6.570	8.140
$HWO_4^- + H^+ = H_2WO_4^0$ (aq)	2.194	3.5		4.76 +/– 0.15	3.157	3.403
$WO_4^{2-} + H^+ = HWO_4^-$	3.658	4.6	3.592	6.38 +/– 0.40	3.413	4.737
$HWO_4^- + Na^+ = NaHWO_4^0$ (aq)				–5.11 +/– 0.55		– 3.480
$WO_4^{2-} + H^+ + Na^+ = NaHWO_4^0$ (aq)				1.27 +/– 0.15		1.257

Table S4. Association constants (log_{10} K) for tungsten species at hydrothermal *TP* derived from this and previous studies.

	T [°C]	100	200	250	300	350	400	500	600	P [MPa]	Method	Reference
$log_{10}K_{III}$	$H_2WO_4^0 + H^+ =$	2.15	1.52	1.27	1.02	0.74				Sat.	BR model	this study
	$H_3WO_4^+$	2.17	1.55	1.30	1.08	0.87	0.63			50	BR model	this study
		2.19	1.57	1.33	1.12	0.93	0.75	0.39	0.11	100	BR model	this study
$log_{10}K_{II}$	$HWO_4^- + H^+ =$	2.80	2.63	2.63	2.71	2.96				Sat.	BR model	Wang et al., 2019
	$H_2WO_4^0$		4.20	4.10	3.90	3.90				Sat.	Calculation	Heinrich, 1990
					4.30					Sat.	Calculation	Gibert et al., 1992
			3.85	3.68	3.70	4.25				Sat.	BR model	Wood and Samson, 2000
		3.26	3.39	3.56	3.84	4.44				Sat.	BR model	this study
			3.56		3.39		3.96			50	Calculation	Wood and Samson, 2000
		2.76	2.57	2.55	2.57	2.66	2.87			50	BR model	Wang et al., 2019
		3.18	3.26	3.39	3.57	3.86	4.36			50	BR model	this study
								5.50		100	Calculation	Gibert et al., 1992
			3.37		3.08		3.14	3.57	4.16	100	Calculation	Wood and Samson, 2000
		2.72	2.52	2.48	2.48	2.51	2.59	2.88	3.31	100	BR model	Wang et al., 2019
		3.11	3.17	3.26	3.39	3.57	3.81	4.54	5.50	100	BR model	this study
$log_{10}K_{I}$	$WO_4^{2-} + H^+ =$	3.96	4.96	5.60	6.47	8.00				Sat.	BR model	Wang et al., 2019
	HWO_4^-		5.34	6.07	6.89					Sat.	Potentiometric study	Wesolowski et al., 1984
			6.31	6.79						Sat.	UV–vis spectroscopy	Minubaeva, 2007
			5.40	6.10	6.90	7.70				Sat.	Calculation	Heinrich, 1990
					6.90					Sat	Calculation	Gibert et al., 1992
		4.15	5.29	6.00	6.85	8.04				Sat.	HKF model	Shock et al., 1997
		4.96	5.67	6.20	6.95	8.36				Sat.	BR model	this study
			5.15		6.48		8.10			50	HKF model	Wood and Samson, 2000
		4.05	5.14	5.78	6.48	7.31	8.10			50	HKF model	Shock et al., 1997
		4.78	5.41	5.83	6.37	7.11	8.28			50	BR model	this study
								8.10		100	Calculation	Gibert et al., 1992
			5.03		6.23		7.58	9.17	11.10	100	HKF model	Wood and Samson, 2000
		3.98	5.02	5.61	6.23	6.88	7.58	9.17	11.09	100	HKF model	Shock et al., 1997
		3.61	4.47	4.93	5.44	6.03	6.73	8.63	10.98	100	BR model	Wang et al., 2019
		4.63	5.20	5.56	5.97	6.47	7.09	8.82	11.01	100	BR model	this study

Table S5. Association constants for ion pairs of tungsten species with sodium derived from this and previous studies.

	T [°C]	100	200	250	300	350	400	500	600	P [MPa]	Method	Reference
$\log_{10}K_a$	$Na^+ + HWO_4^- =$	–2.60	–1.41	–0.83	–0.22	0.47	1.26			50	Approximated	Wood and
	$NaHWO_4^0$	–2.66	–1.49	–0.94	–0.40	0.15	0.73	2.15	4.03	100	by the logK's	Samson,
$\log_{10}K_b$	$Na^+ + WO_4^{2-} =$		1.82		2.72		3.90			50	for K^+–HSO_4^{2-}	2000
	$NaWO_4^-$		1.77		2.50		3.41	4.59	6.11	100	/SO_4^{2-}reactions	
		4.18	4.29	4.49	4.83	5.55				Sat.		this study
		4.08	4.14	4.28	4.50	4.84	5.45			50		
		3.99	4.03	4.12	4.27	4.48	4.77	5.65	7.61	100		

Table S6. Solubility products for tungsten species derived from this and previous studies (pK= $-\log_{10}$K), exp. = experiment.

	T [°C]	100	200	250	300	350	400	500	600	P [MPa]	Method	Reference
pK_1	$WO_3^{cryst} + H_2O = H_2WO_4^0$	6.90	5.63	5.26	4.98	4.62				Sat.	BR model, exp.	Wang et al., 2019
				3.81	3.61	3.29				Sat.	BR model	Wood and Samson, 2000
		5.43	4.16	3.74	3.36	2.79				Sat.	BR model	this study
								2.55		100	Solubility exp.	Wood and Vlassopoulos, 1989
					4.00		3.40	3.10	2.70	100	Solubility exp.	Wood, 1992
								2.55		100	Calculation	Gibert et al., 1992
		7.02	5.77	5.42	5.17	4.97	4.80	4.50	4.60	100	BR model	Wang et al., 2019
		5.61	4.38	4.01	3.73	3.47	3.20	2.55	2.18	100	BR model	this study
pK_2	$WO_3^{cryst} + H_2O = HWO_4^- + H^+$	9.51	7.93	7.50	7.31	7.54				Sat.	HKF model	Shock et al., 1997
		9.70	8.26	7.89	7.69	7.58				Sat.	BR model, exp.	Wang et al., 2019
		8.70	7.55	7.30	7.21	7.23				Sat.	BR model	this study
		9.38	7.73	7.22	6.86	6.63	6.54	6.83	7.81	100	HKF model	Shock et al., 1997
		9.74	8.29	7.90	7.65	7.49	7.39	7.38	7.92	100	BR model	Wang et al., 2019
		8.72	7.55	7.27	7.12	7.05	7.01	7.09	7.67	100	BR model	this study

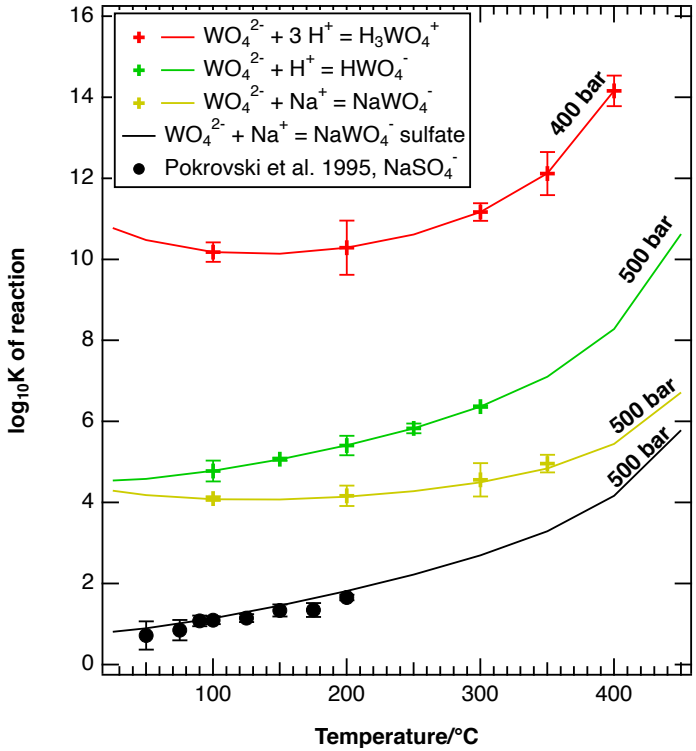

Figure S1: Equilibrium constants optimized using the OptimC program. Data points represent the values optimized on the experimental data of this study from Table S1. Lines were calculated using the Bryzgalin-Ryzhenko model (Eq. 4) using the parameters listed in Table 4. The model for the reaction $SO_4^{2-} + Na^+ = NaSO_4^-$ by Pokrovski et al. (1995) is provided for comparison together with data points.

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All other references see main text.