Support Information

Effect of pH on aqueous Se(IV) reduction by pyrite

*Mingliang Kang [a,b], Fanrong Chen [a] *, Shijun Wu [a], Yongqiang Yang [a], C. Bruggeman [c], L. Charlet [d]*

a Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

c SCK.CEN, Research unit R&D Waste Disposal, Boeretang 200, B-2400 Mol, Belgium

d Environmental Geochemistry Group, LGIT-OSUG, Grenoble University, 38041 Grenoble Cedex 9, France

*Corresponding author phone: +86 2085290291; fax: +86 2085290130; e-mail: frchen@gig.ac.cn

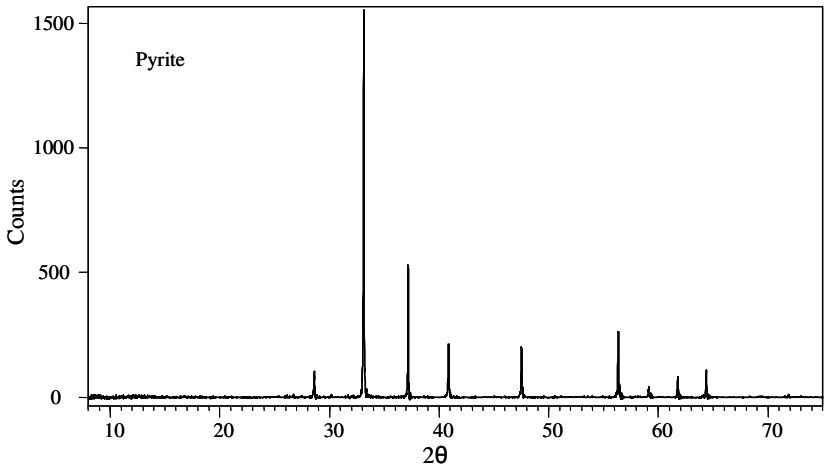

Figure S1. XRD pattern for the natural pyrite phase (ICSD PDF card No. [01-071-1680]).

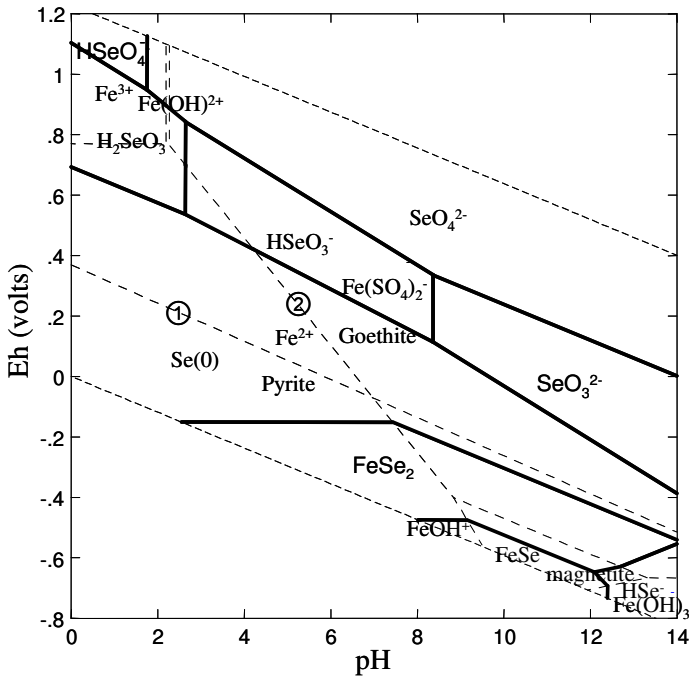

Figure S2. pH vs Eh predominance diagram for pyrite-Se system, T=25℃. [Se]tot = 5×10^{-4} M. $[Fe^{2+}]$ = 1×10^{-7} M. Calculation was performed by Geochemist's Workbench *(1)* with the thermodynamic data from NEA for Se *(2)* and ANDRA for iron chemicals *(3)*. Boundary lines:

① Pyrite + $8H_2O$ = $Fe(SO4)_2^-$ + $16H^+$ + $15e^-$; ② Fe^{2+} + $2H_2O$ = Goethite + $3H^+$ + e^-

Table S1. Selected thermodynamic data used in the present study. Data for selenium chemicals, H_2O, OH- and O2(aq) are from OECD/NEA *(2)*, data for iron and sulfur are from French ANDRA *(3)*.

Chemicals name	$\Delta_f G^\theta$ kJ/mol	Chemicals name	$\Delta_f G^\theta$ kJ/mol	Chemicals name	$\Delta_f G^\theta$ kJ/mol
Se(0)(cry)	0	FeSe	-70.1	$FeSe_2$	-101.3

Se^{2-}	128.6	HSe^-	43.471	$H_2Se(aq)$	21.495
SeO_3^{2-}	-362.392	$HSeO_3^-$	-410.112	$H_2SeO_3(aq)$	-425.181
SeO_4^{2-}	-439.485	$HSeO_4^-$	-449.474	H_2O	-237.14
OH^-	-157.22	O2(aq)	16.521		
FeS_2	-156.17	$Fe(OH)_{3(S)}$	-705.47	goethite	-492.1
Fe^{2+}	-90.53	Fe^{3+}	-16.28	SO_4^{2-}	-744
HSO_4^-	-755.3	HS^-	12.2	H2S(aq)	-27.6

Table S2. Dissolved iron and Se(IV) content in the FeS_2-SeO_3^{2-} system of the preliminary experiments

Time /h	I					II				
	pH	Se(IV) mmol/L	$HSeO_3^-$ mmol/L	Fe_{aq} $\times10^{-6}$ mol/L	Fe^{2+} $\times10^{-7}$mol/L	pH	Se(IV)m mol/L	$HSeO_3^-$ mmol/L	Fe_{aq} $\times10^{-5}$ mol/L	Fe^{2+} $\times10^{-5}$ mol/L
0	6.55	1.35	1.31	2.86	2.42	4.48	1.59	1.57	3.69	2.92
72	6.60	1.34	1.30	0.52	0.41	4.50	1.56	1.54	5.45	4.29
120	6.58	1.32	1.28	0.23	0.19	4.51	1.54	1.52	5.76	4.52
168	6.59	1.32	1.28	0.16	0.13	4.50	1.52	1.50	6.07	4.77

. Concentration of $HSeO_3^-$ and Fe^{2+} are calculated by PHREEQC (*4*) using the revised llnl.data based on the data from NEA for Se (*2*) and ANDRA for iron chemicals (3).

Table S3. Experimental data for selenite interaction with natural pyrite in the second series experiments.

Reactor A							
time /h	pH	Total Se(IV) $\times10^{-4}$ mol/L	$HSeO_3^-$ $\times10^{-4}$ mol/L	Measurement RSD/ %	Total Fe_{aq} $\times10^{-5}$ mol/L	Fe^{2+} $\times10^{-5}$ mol/L	Measurement RSD/ %
0	5.00	4.48	4.46		ND	ND	
120	5.03	ND	ND		ND	ND	
168	5.01	4.02	4.01		2.19	1.45	
216	5.03	3.97	3.95		2.32	1.53	
288	5.11	3.71	3.69	0.34	2.32	1.49	0.90
360	5.24	3.51	3.50	0.88	1.99	1.24	0.71
408	5.12	3.44	3.43	0.39	2.20	1.41	0.18
456	5.17	3.39	3.38	0.59	2.31	1.47	0.02

504	5.15	3.38	3.36	1.15	2.37	1.51	1.44
600	5.17	3.23	3.22	1.48	2.21	1.40	0.20
648	5.20	3.18	3.17	1.79	2.25	1.42	0.29

Reactor B

time /h	pH	Total Se(IV) $\times10^{-4}$ mol/L	$HSeO_3^-$ $\times10^{-4}$ mol/L	Measurement RSD/ %	Total Fe_{aq} $\times10^{-5}$ mol/L	Fe^{2+} $\times10^{-5}$ mol/L	Measurement RSD/ %
0	4.74	4.78	4.75		ND	ND	
120	4.75	ND	ND		ND	ND	
168	4.73	4.24	4.21		2.11	1.53	
216	4.74	4.13	4.10		2.26	1.64	
288	4.79	3.82	3.80	1.15	2.65	1.89	1.08
360	4.87	3.66	3.64	0.05	2.85	1.98	0.18
408	4.79	3.63	3.61	0.36	3.06	2.18	0.44
456	4.82	3.58	3.56	0.95	3.30	2.32	0.41
504	4.79	3.54	3.52	0.22	3.37	2.40	0.20
600	4.83	3.46	3.44	0.05	3.41	2.39	1.09
648	4.83	3.44	3.42	0.74	3.46	2.43	1.56
696	4.82	3.36	3.34	0.40	3.48	2.45	0.29
744	4.82	3.33	3.31	0.66	3.46	2.44	1.23
816	4.84	3.27	3.25	0.62	3.55	2.48	0.11

Reactor C

time /h	pH	Total Se(IV) $\times10^{-4}$ mol/L	$HSeO_3^-$ $\times10^{-4}$ mol/L	Measurement RSD/ %	Total Fe_{aq} $\times10^{-5}$ mol/L	Fe^{2+} $\times10^{-5}$ mol/L	Measurement RSD/ %
0	4.50	4.18	4.13		ND	ND	ND
120	4.50	ND	ND		ND	ND	ND
168	4.51	3.71	3.67		1.94	1.52	
216	4.51	3.64	3.60		2.13	1.67	
288	4.53	3.36	3.32	1.13	2.18	1.70	0.88

360	4.55	3.32	3.29	0.43	2.32	1.79	0.22
408	4.54	3.29	3.25	1.02	2.37	1.84	0.33
456	4.55	3.26	3.23	0.06	2.45	1.89	0.43
504	4.54	3.23	3.20	0.30	2.49	1.93	0.25
600	4.52	3.21	3.17	1.07	2.60	2.03	1.36
648	4.54	3.19	3.16	0.09	2.65	2.05	0.23
696	4.52	3.18	3.14	0.03	2.72	2.12	0.02
744	4.54	3.15	3.12	0.72	2.73	2.12	0.61
816	4.54	3.11	3.08	0.77	2.81	2.18	0.29

ND means not determined. Concentration of $HSeO_3^-$ and Fe^{2+} are calculated by PHREEQC *(4)* using the revised llnl.data based on the data from NEA for Se (*2*) and ANDRA for iron chemicals (3).

Table S4 Reaction parameters for batch experiments in which natural FeS_2 (10g/L, 90-120μm) reacted with 1 mmol/L Na_2SeO_3. NaH_2PO4-H_3PO4 and NaH_2PO_4-Na_2HPO_4 were used in pH 3.3 and pH 6.5 systems, respectively. Reaction time is 21 days. In sample 1 and 3, 1mmol/L $FeCl_2$ was added initially.

Sample	Initially added Fe^{2+} mmol/L	Initial pH	Final pH	Final Fe $\times10^{-4}$ mol/L	Final Se(IV) $\times10^{-4}$ mol/L
1	1	3.26	3.06	6.21	5.93
2	0	3.28	3.12	0.342	6.62
3	1	6.5	5.83	0.557	5.26
4	0	6.53	5.78	0.280	6.90

Text S1: Activity coefficient calculation.

Geochemical calculation was performed with GWB package (*1*) or PHREEQC (*4*) code, using the latest NEA thermodynamic data for Se (*2*) and ANDRA thermodynamic data for iron chemicals (*3*), implemented into the llnl.dat or the thermo V8.R6+.dat provided by Lawrence Livermore National Laboratories.

Given the ionic strength of the solution from the chemical analysis, the activity coefficient can be calculated using several approximation equations. All of them are inferred from the Debye-Hückel equation and apply for a certain range of the ion strength, respectively. WATEQ Debye-Hückel equation is expressed as follows:

$$\log \gamma = \frac{-A \cdot Z^2 \cdot \sqrt{I}}{1 + B \cdot a_i \cdot \sqrt{I}} + b_i \cdot I \quad \text{(I<1 mol/kg)}$$

Since only a_i is provided for every species in llnl.data and V8.R6+.dat, activity-coefficient parameters thus are calculated according to the extended Debye-Hückel equation (b_i=0):

$$\log \gamma = \frac{-A \cdot Z^2 \cdot \sqrt{I}}{1 + B \cdot a_i \cdot \sqrt{I}} \quad \text{(I<0.1 mol/kg)}$$

Actually, the ion-association databases (phreeqc.data, llnl.data, wateq.data, V8.R6+.dat and others) can be applicable when ionic strength is below 1 molal, hence the revised database is suitable for the calculation in the present study.

Literature cited

(1) Bethke, C. M.; Yeakel, S. *The Geochemist's Workbench released 7.0: GWB Essentials Guide.* Hydrogeology Program, University of Illinois: 2008.

(2) Olin, A.; Nolang, B.; Osadchii, E. G.; Ohman, L.-O.; Rosen, E. *Chemical Thermodynamics 7: Chemical Thermodynamics of Selenium*; OECD Nuclear Agency/Elsevier: Amsterdam, 2005.

(3) Chivot, J. *Thermodynamique des produits de corrosion*. Sciences et Techniques Series, ANDRA: 2004.

(4) Parkhurst, D. L.; 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*. Water-Resources Investigations Report 99-4259; U.S.Geological Survey, Denver, CO, 1999.