Supplemental Table 1. Solution compositions for HDAC (APS) and large volume autoclave (ESRF) experiments

APS-HDAC experiments			Max *T*,*P*[a]	Calculated pH, Eh
Sol2 (RT cell)	0.12 g ZnBr2 in 1.16 m NaBr + 0.002 m HBr		Room temperature	$pH_{25°C}$ = 2.8
Sol5	Sphalerite in 1.03 m NaHS + 0.20 m HCl	Th = 211 °C, density ~ 0.85	500 °C, *P* ~ 4.5 kbar	$pH_{25°C}$ = 7.4 $pH_{500°C}$ = 6.7 $Eh_{500°C}$ = -1.08
Sol6	Sphalerite in 0.20 m HCl Th = 218 °C, density ~ 0.85		500 °C, *P* ~ 4.5 kbar	pH25°C = 0.8 $pH_{500°C}$ = 1.9 $Eh_{500°C}$ = -0.27
Sol10	Sphalerite in 1.84 m NaHS + excess S	Th = 229 °C, density ~ 0.91	400 °C, *P* ~ 2.95 kbar	$pH_{25°C}$ = 7.8 $pH_{400°C}$ = 4.4 $Eh_{400°C}$ = -0.50
ESRF - large volume autoclave (FAME cell) experiments[b]				
SolA	ZnBr2 in 0 m NaBr + 0.01 m HBr		600 °C, 1 kbar	$pH_{25°C}$ = 2.0 pH_600°C = 2.3
SolB	ZnCl2 in 0 m NaCl + 0.01 m HCl	Mei et al. 2015	500 °C, 1 kbar	$pH_{25°C}$ = 2.1 pH_500°C = 2.7
SolC	ZnCl2 in 0.5 m NaCl + 0.01 m HCl	Mei et al. 2015	600 °C, 1 kbar	$pH_{25°C}$ = 2.1 $pH_{600°C}$ = 5.4
SolD	ZnCl2 in 3.5 m NaCl + 0.01 m HCl	Mei et al. 2015	500 °C, 1 kbar	$pH_{25°C}$ = 2.2 $pH_{500°C}$ = 4.6
SolE[a]	ZnS in 2 m NaHS	Mei et al. 2016	500 °C, 1 kbar	$pH_{25°C}$ = 10.3 $Eh_{25°C}$ = –0.53 $pH_{500°C}$ = 10.0 $Eh_{500°C}$ = –1.58

Notes: Solubility was calculated following $\Delta u = \Delta\sigma \cdot l \cdot M \cdot m \cdot d$ (Pokrovski et al. 2005), where Δu is step height = 0.05(1); Δσ is the difference in X-ray cross section for Zn before (9600 eV) and after (9700 eV) the edge =215.3 cm^2/g; l is path length = 0.4 cm; M is atomic mass of Zn = 0.06538 kg/mol; m is the molal concentration of Zn in solution (mol/kg); and d is the density of fluid, estimated to be similar to that of a 2 m NaCl @ 500 °C, 1 kbar) = 0.66 g/cc (Driesner and Heinrich 2007).

[a] Zinc solubility at 500 °C, 1 kbar was estimated to be 13(3) mmolal (850 ppm), based on the step height in transmission. This compares to 70 mmolal predicted using the properties from Zn-bisulfide complexes of Mei et al. (2016), and 338 mmolal using those of Tagirov and Seward (2010). For all other conditions (ESRF data), solubility was below detection limit based on transmission (≤ 3 mmolal).

[b] Solutions A-D were acidified to prevent hydrolyzed complexes.

Supplemental Table S2. Simulation results of Zn(2)-Cl/HS complexes at high pressure

Job ID	*T* (°C)	*P* (kbar)	Total time (ps)	Initial configuration	Stabilization time (ps)	Stable species	Zn-S			Zn-Cl			Zn-O			CN_{tot}
							N	r	σ^2	N	r	σ^2	N	r	σ^2	
1a[a]	100	1.5	14.44	$Zn(H_2O)_5Cl^+$	2.32	$Zn(H_2O)_3Cl^+$	0	–	–	1	2.23	0.0046	3	2.00	0.0067	4
1b	100	1.5	14.32	$Zn(H_2O)_5(HS)^+$	1.45	$Zn(H_2O)_3(HS)^+$	1	2.25	0.0045	0	–	–	3	2.02	0.0078	4
1c	100	1.5	14.58	$Zn(H_2O)_6^{2+}$	5.08	$Zn(H_2O)_4^{2+}$	0	–	–	0	–	–	4	1.97	0.0054	4
2	500	1.5	14.43	$Zn(HS)_3^-$	1.45	$Zn(HS)_3^-$	3	2.28	0.0160	0	–	–	0.16	2.10	–	3.16
3	500	4.5	15.01	$Zn(HS)_3^-$	1.45	$Zn(HS)_3^-$	3	2.26	0.0125	0	–	–	0.17	2.33	–	3.17
4a	500	20	15.94	$Zn(HS)_3^-$	7.62	$Zn(HS)_4^{2-}$	4	2.32	0.0195	0	–	–	0	0	–	4
4b	500	20	15.86	$Zn(H_2O)_6^{2+}$	4.35	$Zn(HS)_2O_{1-2}$[b]	2	2.26	0.0126	0	–	–	1.68	1.97	–	3.68

[a] Elemental solution composition: 1 Zn^{2+}, 5 HS^-, 1 Cl^-, 4 Na, 111 H_2O.

[b] O = H_2O/OH^-.