DATA REPOSITORY ITEM

MATERIALS AND METHODS

Experiments at 350 and 400 °C were performed at the vapor-liquid equilibrium curve of the system H_2O-NaCl ± HCl using ~120 cm^3 titanium-alloy batch reactors (Pokrovski et al., 2002a) externally heated at a controlled temperature (±1 °C) and pressure (±0.2 MPa). An NaCl-HCl aqueous solution, together with weighted amounts of chlorides ($FeCl_2$, $ZnCl_2$, CuCl, AgCl) and oxides (As_2O_3, Sb_2O_3, SiO_2), were introduced under an argon or hydrogen flux into the autoclave. In some low-concentration runs, a few milligrams of metallic aluminum were also added into the autoclave to generate low levels of H_2 (~10^{-4} mol/kg) at the experimental temperature, and thus exclude any eventual oxidation of redox-sensitive metals like Cu(I), Fe(II), or As(III). Vapor condensate samples were periodically taken via titanium capillary tubing and valves and were analyzed for As, Sb, Fe, Zn, Ag, Au, Na, K, and Si using flame atomic absorption spectroscopy (AAS) and inductively-coupled-plasma atomic-emission spectroscopy (ICP-AES), and for Cl using liquid chromatography. Selected vapor condensates and solutions after experiments were also analyzed for both total As, As(III) + As(V), and arsenate, As(V), by the colorimetric molybdate blue method (Pokrovski et al., 2002b). No As(V) was detected in experimental samples in the limit of 2% of the total value. Hydrochloric acid vapor-phase concentrations were calculated from pH values measured in the condensates, assuming that the low concentrations of metals (a few parts per million) do not change these values significantly. Metal concentrations measured in condensates sampled at different flow rates, ranging from 1 g/s to 0.01 g/s, were similar, typically within 30% of the value, demonstrating that neither metal precipitation within the sampling device nor condensate

contamination by the liquid phase occurs during the sampling. In most runs, the quantities of introduced solid chlorides and oxides were low enough to ensure their complete dissolution at the experimental temperature. Liquid-phase metal contents were thus calculated via the mass balance from measured vapor-phase concentrations, volumetric properties of the NaCl-H_2O system (see below), and reactor volume. Some experiments contained excess of Sb_2O_3, AgCl and SiO_2 which yielded saturated aqueous solutions. In this case, Sb, Ag and Si liquid-phase concentrations were calculated assuming equilibrium with senarmontite (Sb_2O_3, cub), chlorargyrite (AgCl, cub.), and amorphous silica or quartz, respectively, and using available solubility data for these compounds (see tables DR1 and DR2). Solids precipitated on cooling after runs were examined using optical microscopy and X-ray diffraction. Only initially charged compounds poorly soluble at ambient temperature such as Sb_2O_3, AgCl, CuCl, and SiO_2 were detected; and there was no indication of redox changes (e.g., formation of Fe(III) oxy-hydroxides, metallic Ag, Sb_2O_4). Experiments at 450 °C were performed at the vapor-liquid equilibrium curve of the system H_2O-NaCl±KCl using a flexible-cell (~150 cm^3) Coretest hydrothermal reactor (Seyfried et al., 1987). Redox potential and pH were buffered using the magnetite-hematite and andalusite-muscovite-quartz assemblages, respectively. Gold was added in the system as a pure-metal foil. Vapor- and liquid-phase condensates were alternatively taken by inverting the reactor and were processed similarly to the lower-temperature experiments.

In both types of experiments, vapor-liquid equilibrium for all studied metals was attained within a few hours after the temperature-pressure stabilization, as demonstrated by the constancy of the vapor-liquid partition coefficients in subsequent samples vs. time. This agrees with the rapid vapor-liquid equilibration observed in previous studies using similar experimental configurations (e.g., Hovey et al., 1990; Bischoff, 1991; Pokrovski et al., 2002). In our

experiments, all dissolved metals were present in the fluid in their oxidation states occurring in natural hydrothermal systems—i.e., Fe(II), Cu(I), Ag(I), Au(I), As(III), and Sb(III)—as inferred from both chemical analyses of sampled solutions and solids precipitated on cooling after experiments (see above), and thermodynamic calculations using available data for aqueous metal complexes and solid phases (Pokrovski et al., 1996, 2002a,b; Wood and Samson, 1998). Apparent molal vapor-liquid equilibrium distribution coefficients for each element ($K_m = m_{vapor}/m_{liquid}$, where m denotes the total concentration of the metal in the corresponding phase expressed as number of moles per kilogram of vapor or liquid, respectively) were generated from the obtained equilibrium vapor- and liquid-phase metal concentrations. The validity of our measurements is also supported by close agreement, typically within ~30-50% of the partition coefficient value, with the extensive literature data for NaCl-H_2O and KCl-H_2O (Palmer et al., 2004, references therein), and available data on arsenic (Pokrovski et al., 2002), silica (Manning, 1994), HCl (Simonson and Palmer, 1993), silver (Migdisov et al., 1999), and copper (Archibald et al., 2002) vapor-aqueous solution and/or vapor-solid equilibria. Values of the vapor and liquid-phase densities in the system H_2O-NaCl ± KCl were taken from Bischoff (1991) and Hovey et al. (1990). It is assumed that small amounts of HCl (<0.5 mol/kg) and dissolved metals (<0.2 mol/kg) do not change these properties significantly. Raw data on vapor- and liquid-phase metal concentrations and vapor-liquid partition coefficients are reported in Tables DR1 to DR3 below.

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TABLE DR1. Element concentrations in coexisting vapor and liquid at 350°C in the system H_2O-NaCl-HCl at different pressures, and corresponding equilibrium vapor-liquid partition coefficients for metals

Run number	1	2-1	2-2	3-1	3-2	3-3
Pressure (bar)	151.9	137.8	126.6	143.9	140.9	135.8
Vapor						
Density (g/cm^3)	0.092	0.071	0.060	0.080	0.078	0.070
HCl	0.0065	0.0053	0.0053	0.084	0.082	0.082
Na	4.42e-4	1.04e-4	9.49e-5	1.17e-4	2.17e-4	6.09e-5
As	2.34e-3	8.08e-4	1.22e-3	1.07e-3	1.35e-3	1.46e-3
Sb	6.63e-4	4.96e-5	6.04e-5	1.67e-3	2.08e-3	2.17e-3
Fe	2.40e-5	3.40e-6	1.97e-6	1.56e-5	7.16e-6	1.79e-6
Zn	1.27e-5	2.14e-6	9.48e-7	1.50e-6	1.48e-6	9.48e-7
Cu	1.86e-5	6.45e-6	2.05e-6	6.29e-6	3.62e-6	2.48e-6
Ag	2.18e-6	4.64e-7	3.71e-7	5.10e-7	4.91e-7	2.87e-7
Liquid						
Density (g/cm^3)	0.76	0.90	0.97	0.84	0.87	0.91
Total Cl	1.58	3.59	4.97	2.90	3.28	3.74
Na	1.14	3.24	4.48	2.40	2.70	3.10
As	0.029	0.014	0.019	0.012	0.013	0.015
Sb	0.074**	0.026	0.036	0.049	0.055	0.063
Fe	0.055	0.041	0.057	0.064	0.073	0.083
Zn	0.062	0.062	0.085	0.060	0.069	0.079
Cu	0.091	0.067	0.093	0.074	0.084	0.096
Ag	0.097	0.070	0.096	0.070	0.080	0.091
$\log_{10} K_m$						
Na	-3.41	-4.49	-4.68	-4.31	-4.09	-4.71
As	-1.05	-1.24	-1.19	-1.05	-1.00	-1.01
Sb	-2.05	-2.72	-2.78	-1.47	-1.42	-1.47
Fe	-3.36	-4.08	-4.46	-3.61	-4.01	-4.67
Zn	-3.69	-4.46	-4.95	-4.61	-4.67	-4.92
Cu	-3.69	-4.02	-4.66	-4.07	-4.37	-4.59
Ag	-4.65	-5.18	-5.41	-5.14	-5.21	-5.50

TABLE DR1, CONTINUED

Run number	4-1/2	4-3	5-1	5-2	5-3	6
Pressure (bar)	155.1	146.0	155.0	151.2	146.0	163.0
Vapor						
Density (g/cm^3)	0.094	0.082	0.094	0.089	0.082	0.108
HCl	0.024	0.024	0.25	0.16	0.13	0.0050
Na	2.96e-4	2.17e-4	6.09e-4	2.09e-4	1.44e-4	1.08e-4
Si	N.A.	N.A.	N.A.	N.A.	N.A.	4.27e-4
As	5.64e-4	6.94e-4	8.97e-4	9.37e-4	9.71e-4	7.25e-4
Sb	1.84e-4	1.14e-4	1.64e-3	1.13e-3	1.52e-3	9.57e-4
Fe	5.77e-5	2.69e-5	6.98e-6	5.37e-6	3.22e-6	N.A.*
Zn	3.93e-5	2.20e-5	5.09e-6	2.45e-6	1.99e-6	2.54e-4
Cu	7.55e-6	4.88e-6	4.42e-5	8.18e-6	1.53e-5	2.72e-4
Ag	1.99e-6	1.48e-6	N.D.#	6.12e-6	5.93e-6	1.30e-6
Liquid						
Density (g/cm^3)	0.76	0.86	0.77	0.80	0.84	0.66
Total Cl	2.21	3.34	1.64	1.98	2.51	0.38
Na	1.32	2.00	1.15	1.40	1.80	0.12
Si	N.A.	N.A.	N.A.	N.A.	N.A.	0.027##
As	0.0067	0.0094	0.0063	0.0074	0.0096	0.0057
Sb	0.015	0.021	0.013	0.015	0.020	0.051**
Fe	0.205	0.300	0.018	0.022	0.028	N.A.
Zn	0.209	0.300	0.018	0.022	0.029	0.057
Cu	0.030	0.046	0.151	0.185	0.240	0.112
Ag	0.030	0.046	N.D.	0.210	0.270	0.020***
$\log_{10}K_m$						
Na	-3.65	-3.96	-3.28	-3.83	-4.10	-3.04
Si	N.A.	N.A.	N.A.	N.A.	N.A.	-1.80
As	-1.07	-1.13	-0.84	-0.90	-1.00	-0.89
Sb	-1.91	-2.27	-0.89	-1.13	-1.12	-1.73
Fe	-3.55	-4.05	-3.41	-3.61	-3.94	N.A.
Zn	-3.72	-4.13	-3.56	-3.96	-4.15	-2.36
Cu	-3.59	-3.97	-3.53	-4.35	-4.20	-2.58
Ag	-4.18	-4.49	N.D.	-4.53	-4.66	-4.18

Note: Concentrations of all constituents are expressed as number of moles per kilogram of vapor or liquid.
*N.A. = not available (i.e., the corresponding chemical element was not used in the given experiment).
#N.D. = not determined.
**Liquid is saturated with respect to Sb_2O_3 (cub.), Sb aqueous concentrations are taken from Zotov et al. (2003).
##Liquid is saturated with respect to amorphous silica, Si aqueous concentrations are taken from Gunnarsson and Arnórsson (2000).
***Liquid is saturated with respect to AgCl, Ag aqueous concentrations are calculated according to Akinfiev and Zotov (2001).

TABLE DR2. Element concentrations in coexisting vapor and liquid at 400°C in the system H_2O-NaCl-0.01mol HCl at different pressures, and corresponding equilibrium vapor-liquid partition coefficients for metals

Run number	**7-1**	**7-2**	**7-3**	**7-4**	**7-5**
Pressure (bar)	265	256	244	226	209
vapor					
Density (g/cm^3)	0.21	0.18	0.16	0.13	0.11
HCl	0.014	0.014	0.013	0.013	0.013
Na	2.27e-2	1.21e-2	6.54e-3	1.58e-3	8.54e-4
Si	1.87e-3	1.98e-3	1.84e-3	1.16e-3	6.94e-4
As	1.24e-3	1.27e-3	1.19e-3	1.26e-3	1.14e-3
Sb	5.22e-4	9.69e-4	1.02e-3	7.42e-4	3.09e-4
Zn	2.29e-5	2.22e-5	1.39e-5	3.98e-6	1.30e-6
Cu	2.44e-4	1.49e-4	8.32e-5	2.36e-5	1.16e-5
Ag	5.02e-5	4.98e-5	1.60e-5	2.32e-6	1.48e-6
liquid					
Density (g/cm^3)	0.68	0.75	0.81	0.89	0.96
Total Cl	1.78	2.31	2.95	4.00	5.02
Na	1.66	2.16	2.76	3.76	4.71
Si*	0.032	0.036	0.040	0.046	0.053
As	0.0043	0.0052	0.0063	0.0081	0.0098
Sb	0.016	0.020	0.026	0.035	0.043
Zn	0.021	0.027	0.034	0.046	0.058
Cu	0.017	0.022	0.029	0.039	0.049
Ag	0.017	0.022	0.028	0.039	0.049
$Log_{10}K_m$					
Na	-1.88	-2.27	-2.64	-3.39	-3.76
Si	-1.24	-1.26	-1.34	-1.60	-1.88
As	-0.54	-0.61	-0.72	-0.81	-0.93
Sb	-1.48	-1.32	-1.40	-1.67	-2.15
Zn	-2.95	-3.08	-3.39	-4.07	-4.65
Cu	-1.85	-2.18	-2.54	-3.22	-3.62
Ag	-2.53	-2.65	-3.25	-4.22	-4.51

Note: Concentrations of all constituents are expressed as number of moles per kilogram of vapor or liquid
*Liquid is saturated with respect to quartz; Si aqueous concentrations are calculated according to Xie and Walther (1993).

TABLE DR3. Element concentrations in coexisting vapor and liquid at 450°C in the system H_2O-NaCl-0.06m HCl (series #9) and H_2O-NaCl-KCl-quartz-andalusite-muscovite-hematite-magnetite (series #10) at different pressures, and corresponding equilibrium vapor-liquid partition coefficients for metals

Run number	9-2	9-3	9-4	9-5	9-6	9-7/9	10-5/6	10-10
Pressure (bar)	419	418	403	382	352	335	415	362
vapor								
Density (g/cm^3)	0.38	0.38	0.30	0.25	0.21	0.18	0.36	0.22
HCl	0.069	0.058	0.050	0.042	0.038	0.025	N.D.[#]	N.D.
Na	3.35e-1	2.50e-1	1.49e-1	7.53e-2	4.28e-2	2.48e-2	2.57e-1	5.13e-2
K	N.A.[*]	N.A	N.A	N.A	N.A	N.A	6.30e-2	1.07e-2
Si	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	5.80e-3	1.46e-3
As	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	9.77e-4	7.34e-4
Sb	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	3.65e-4	2.63e-4
Fe	9.15e-4	6.61e-4	3.10e-4	1.13e-4	6.55e-5	4.83e-5	9.50e-3	1.30e-3
Zn	7.18e-4	4.93e-4	2.07e-4	8.21e-5	5.14e-5	2.76e-5	4.50e-4	9.02e-5
Cu	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1.02e-4	5.51e-5
Ag	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	3.24e-5	2.22e-5
Au	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1.51e-7	6.09e-8
liquid								
Density (g/cm^3)	0.65	0.65	0.74	0.80	0.89	0.93	0.69	0.89
Total Cl	2.43	2.43	3.32	4.27	5.64	6.34	2.34	4.57
Na	2.40	2.40	3.27	4.21	5.56	6.25	1.95	3.83
K	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.38	0.74
Si	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.018	0.019
As	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.0023	0.0033
Sb	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.0050	0.013
Fe	0.0090	0.0092	0.013	0.016	0.022	0.024	0.275	0.400
Zn	0.0079	0.0080	0.011	0.014	0.019	0.021	0.0075	0.015
Cu	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.0070	0.015
Ag	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.0020	0.0030
Au	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1.38e-6	2.28e-6
$Log_{10}K_m$								
Na	-0.85	-0.98	-1.34	-1.75	-2.11	-2.40	-0.88	-1.87
K	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-0.78	-1.84
Si	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-0.49	-1.11
As	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-0.37	-0.65
Sb	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-1.14	-1.69
Fe	-0.99	-1.14	-1.61	-2.15	-2.52	-2.69	-1.46	-2.49
Zn	-1.04	-1.21	-1.72	-2.23	-2.56	-2.88	-1.22	-2.22
Cu	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-1.84	-2.44
Ag	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-1.80	-2.13
Au	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-0.96	-1.57

Note: Concentrations of all constituents are expressed as number of moles per kilogram of vapor or liquid
*N.A. = not available
[#]N.D. = not determined