

Volatility of copper and zinc in a boiling hydrothermal solutions at temperatures between 350° and 450°C

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Abstract

High temperature hydrothermal experiments using specially designed apparatus have been completed. The starting solution containing 5 and 10 % NaCl, 85 - 850 ppm Cu and Zn was kept under the coexistence of vapor and liquid phases at temperatures between 350° and 450°C. After the attainment of physicochemical equilibrium, vapor samples were extracted from the apparatus for analysis. Vapor compositions were measured by atomic absorption spectrography and ion chromatography. The distribution quotient ($D = C_{\text{vapor}} / C_{\text{liquid}}$) of elements was in the order of $\text{Cu} > \text{Zn} > \text{Cl} > \text{Na}$. The logarithmic values of distribution coefficient of Cu were -2.33 (350°C), -2.34 (400°C), and -1.68 (450°C), respectively.

Comparison of experimental result of this study with metal concentration in natural fluid inclusions suggests that the order of metal fractionation between coexisting vapor and liquid phases agree with this study. The distribution quotients determined by the analyses of natural fluid inclusions (680°-700°C) are 1 to 2 orders of magnitude higher than those determined in this study (350°-450°C). Therefore, temperature, salinity of fluid, and possibly presence of sulfur has large effect for the distribution of metals between vapor and liquid phases.

Key words: vapor-liquid fractionation, metal, boiling, porphyry-type deposit, fluid inclusion

Introduction

Magmatic water that separated from hydrous magma during its ascent and crystallization (Burnham, 1997; Williams-Jones and Heinrich, 2005) moves upward through Earth's crust as a supercritical fluid. Subsequent ascent of fluid causes the drop of pressure and fluid phase separation ("boiling") will occur. Heavy metals and salts dissolved in high temperature hydrothermal fluid have been believed to remain in the liquid phase during boiling. Volatile components such as

gaseous SO_2 , HCl, CO_2 , selectively fractionate into the vapor phase, and pH of remaining liquid increases because of the decrease of acid components (Drummond and Ohmoto, 1985).

However, recent development of analytical techniques of single fluid inclusions clarified that significant amounts of metals such as copper and gold exist in the vapor phase rather than liquid phase (Heinrich et al., 1999; Ulrich et al., 1999; Audétat et al., 2000; Baker et al., 2004). Furthermore, chalcopyrite, CuFeS_2 , is often observed in vapor-rich inclusions as a daughter mineral (Heinrich et al., 1992). Concentrations of other heavy metals such as Pb, Zn, and Fe are higher in the liquid-rich inclusions (Audétat et al., 1998; Heinrich et al., 1999). Several examples of analysis of volcanic gas suggest that the amount of 100-1200 metric tons of copper is exhausted into the atmosphere every year (Hedenquist et al., 1993; Hedenquist and Lowenstern, 1994). Significant amount of molybdenum is also detected in volcanic gas (Symonds et al., 1992; Klemm et al., 2008). These examples suggest *unusual behavior* of metals at high temperature environments such as in the vicinity of granitic magma.

Porphyry type deposits are the major source of copper, gold, and molybdenum. However, base metals such as lead and zinc are not accompanied in the ore of this type. We know that brine and lower density vapor can coexist from the solidus conditions of mid-crustal plutons up to the Earth's surface. The analytical data of single fluid inclusion indicate that chemical segregation of ore-forming elements during fluid boiling is an ubiquitous process. Phase separation of hydrothermal fluid in the deeper parts of magmatic systems may play an important role in the segregation of Cu from hydrothermal fluid in the process of porphyry-type mineralization. This study reports the result of hydrothermal experiments on the fractionation of metals between coexisting vapor and liquid phases at temperatures between 350° and 450°C.

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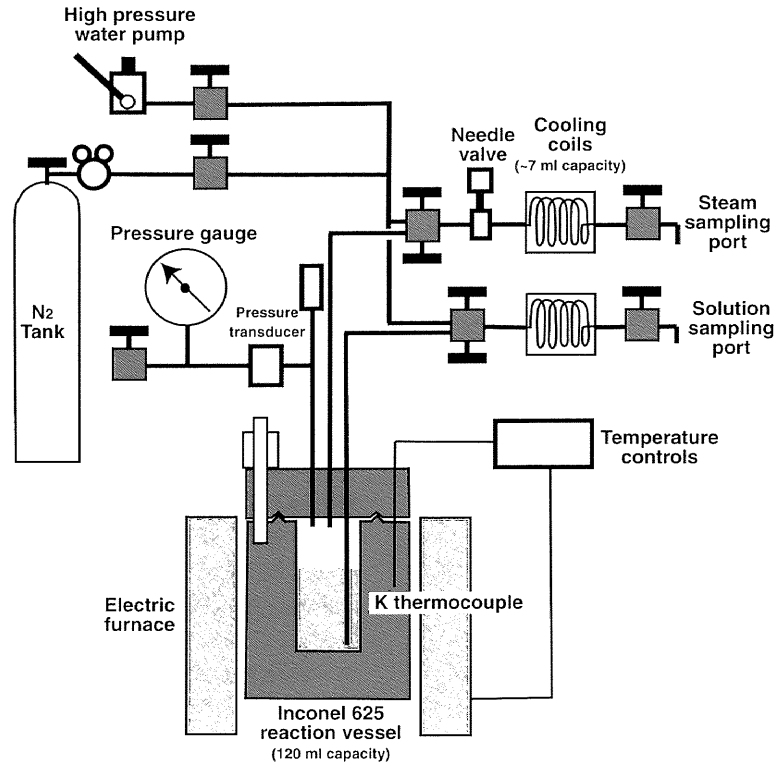


Fig. 1 Schematic drawing of an experimental apparatus used in this study for vapor-liquid partitioning measurements.

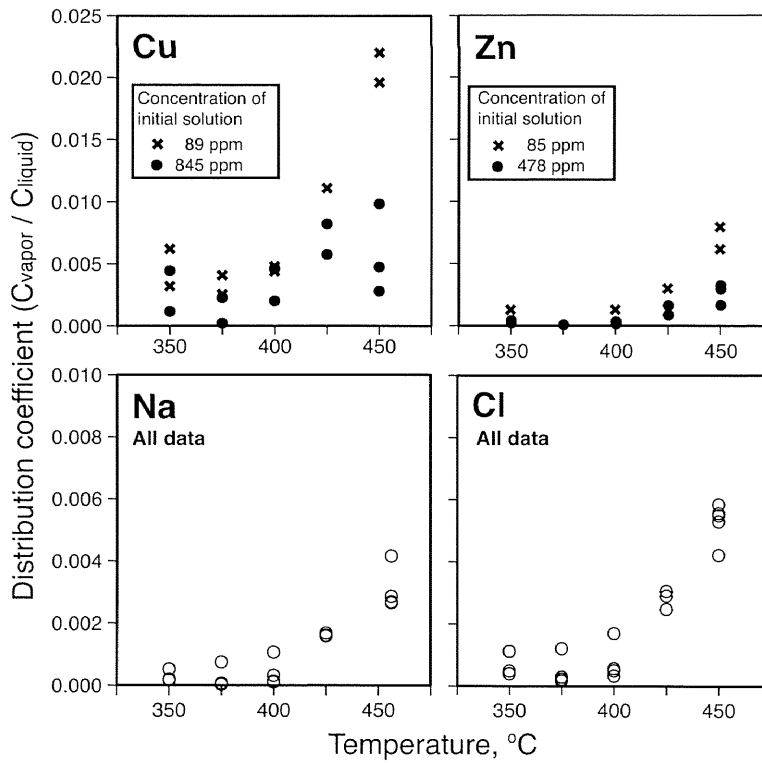


Fig. 2 Temperature dependence of vapor-liquid distribution coefficient of Cu, Zn, Na and Cl determined in 10 % NaCl solution.

Experiment

Apparatus

Newly designed apparatus shown in Fig. 1 was used for all experiments. An autoclave with 120 ml internal capacity made of Inconel 625 was used as a reaction vessel. Two capillary tubes, one is immersed into the solution and the other is not immersed, are inserted into the pressure vessel. Former was used to sample liquid phase, and the latter was used to sample vapor phase. During the extraction of liquid and vapor phases, vapor or liquid phase was condensed into the cooling coil of ~7 ml capacity which was cooled by water stream. A needle valve placed between the sampling valve of vapor phase and the cooling coil was used to control the rate of withdrawal of vapor phase. The temperature of the reaction vessel was controlled within $\pm 1^\circ\text{C}$ of experimental temperature by a digital temperature controller and temperature was measured by an alumel-chromel thermocouple inserted into the body of vessel.

Procedures

The 5 % and 10 % NaCl solutions were prepared from distilled and deionized water and the reagent grade NaCl. Stock solutions containing 85 - 850 ppm Cu and Zn were prepared to add reagent grade CuCl_2 and ZnCl_2 to the NaCl solutions. The stock solutions were kept in a plastic bottle under an N_2 atmosphere.

The 50 to 70 g of starting solution and ~2 mg of anthracene, $\text{C}_{14}\text{H}_{10}$, were placed in the reaction vessel. After assembling the apparatus, the vessel was pres-

surized with N_2 gas of ~500 kPa, then pressure was released by opening the valve to atmosphere. This procedure was repeated for several times in order to replace air in the reaction vessel with N_2 gas. Anthracene is known as a convenient material to keep the solution under a low $f\text{O}_2$ during hydrothermal experiments; the stable form of Cu in the experimental solutions of this study is cuprous.

Solution was kept under the coexistence of vapor and liquid phases at elevated temperatures. After the attainment of physicochemical equilibrium for ~10 hours, vapor samples were extracted from the reaction vessel. Because rapid extraction of vapor from the reaction vessel was particularly troublesome, sampling rate was controlled to adjust the needle valve. In most cases, it took ~5 minutes to condense 7 g of vapor phase. Since the weight of vapor sample with respect to initial amount of solution loaded in the reaction vessel is large (~20 %), experiment was terminated after the extraction of two vapor samples.

All experiments were carried out under the subcritical conditions at temperatures between 350° and 450°C with temperature interval of 25°C. Because critical temperature of 5 % NaCl solution is 420°C and that of 10 % NaCl solution is 458°C, experiments with 5 % NaCl solution was not conducted at temperatures >400°C. Concentrations of Cu, Zn, and Na in the vapor samples were measured by atomic absorption spectrography (AAS) and that of Cl was measured by ion chromatography.

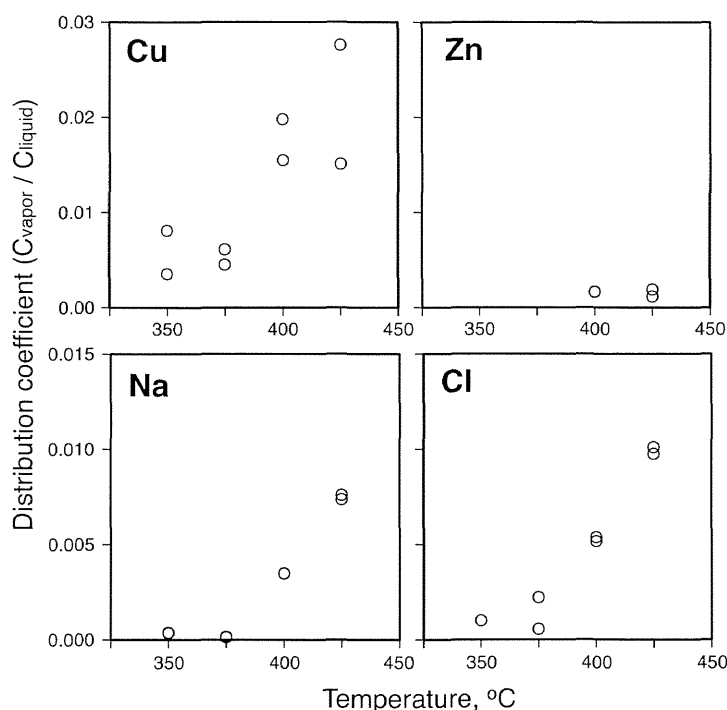


Fig. 3 Temperature dependence of vapor-liquid distribution coefficient of Cu, Zn, Na and Cl determined in 5 % NaCl solution.

Results and discussion

A total of 28 runs were completed, and the results are shown in Table 1. Two solutions of different Cu and Zn concentration, one that contains 89 ppm Cu and 85 ppm Zn (solution-A in Table 1) and the other that contains 845 ppm Cu and 478 ppm Zn (solution-B in Table 1), were used as starting solutions for the experiments conducted in 10 % NaCl solution. Concentrations of Cu in vapor were 0.2 to 8.3 ppm for experiments in 10 % NaCl solution, and 0.3 to 2.4 ppm for experiments in 5 % NaCl solution. Concentrations of Zn in the vapor phase were lower than those of Cu, they varied between less than the detection limit of AAS and 1.5 ppm for experiments conducted in 5 % and 10 % NaCl solutions.

Volatility of elements in our experiments is defined as following distribution coefficient (D).

$$D = C_{\text{vapor}} / C_{\text{liquid}},$$

where, C represents concentration of elements in vapor and liquid phases. Concentrations of Cu, Zn, Na and Cl in starting solution were used as C_{liquid} to calculate D-values. The values of D are shown in Table 1 and are plotted in Figs. 2 and 3. The D-values of Cu and Zn have a dependence on concentrations of Cu and Zn in starting solution. For example, D-value of Cu obtained at 450°C is 0.021 in the experiment with solution-A and 0.006 in the experiment with solution-B; D-values obtained from the experiments with solution-A are systematically larger by factor of 2 to 4 than the experiments with solution-B (Fig. 2). Similar results were obtained for Zn. This phenomenon probably suggests that vapor phase coexist with solution-B is saturated with respect to Cu and Zn. Therefore, D-values obtained from the experiments with solution-A are more accurate.

Table 1. Experimental results of volatility of Cu and Zn in 5 % and 10 % NaCl solutions

Run No.	Temp. °C	Starting solution*	Concentration in vapor (ppm)				Distribution coefficient (C vapor / C liquid)			
			Cu	Zn	Na	Cl	Cu	Zn	Na	Cl
024	350	A	0.55	<0.01	8.9	27.2	6.21×10^{-3}	-	2.04×10^{-4}	4.03×10^{-4}
029	350	A	0.29	0.11	7.5	33.2	3.21×10^{-3}	1.30×10^{-3}	1.72×10^{-4}	4.93×10^{-4}
023	375	A	0.36	<0.01	2.6	11.5	4.09×10^{-3}	-	5.95×10^{-5}	1.71×10^{-4}
028	375	A	0.23	<0.01	1.4	15.8	2.56×10^{-3}	-	3.21×10^{-5}	2.35×10^{-4}
020	400	A	0.39	<0.01	14.1	38.6	4.40×10^{-3}	-	3.22×10^{-4}	5.73×10^{-4}
027	400	A	0.43	0.11	4.7	22.5	4.81×10^{-3}	1.31×10^{-3}	1.07×10^{-4}	3.35×10^{-4}
026	425	A	0.99	0.26	74.0	167.4	1.11×10^{-2}	3.01×10^{-3}	1.69×10^{-3}	2.48×10^{-3}
022	450	A	1.96	0.52	192.5	375.3	2.20×10^{-2}	6.17×10^{-3}	4.40×10^{-3}	5.57×10^{-3}
025	450	A	1.75	0.68	126.2	284.3	1.96×10^{-2}	7.96×10^{-3}	2.89×10^{-3}	4.22×10^{-3}
047	350	B	3.77	0.19	22.9	76.1	4.46×10^{-3}	3.98×10^{-4}	5.24×10^{-4}	1.13×10^{-3}
048	350	B	1.00	0.10	23.1	75.4	1.18×10^{-3}	1.99×10^{-4}	5.28×10^{-4}	1.12×10^{-3}
045	375	B	0.19	0.03	32.8	81.5	2.29×10^{-4}	5.80×10^{-5}	7.51×10^{-4}	1.21×10^{-3}
046	375	B	1.92	<0.01	3.3	20.3	2.28×10^{-3}	-	7.61×10^{-5}	3.02×10^{-4}
043	400	B	1.71	0.06	6.3	33.9	2.03×10^{-3}	1.22×10^{-4}	1.44×10^{-4}	5.03×10^{-4}
044	400	B	3.91	0.15	46.8	114.8	4.62×10^{-3}	3.13×10^{-4}	1.07×10^{-3}	1.70×10^{-3}
040	425	B	4.87	0.77	69.7	196.2	5.76×10^{-3}	1.61×10^{-3}	1.59×10^{-3}	2.91×10^{-3}
042	425	B	6.94	0.40	71.0	206.5	8.22×10^{-3}	8.39×10^{-4}	1.62×10^{-3}	3.06×10^{-3}
039	450	B	4.01	0.78	2.7	394.1	4.75×10^{-3}	1.63×10^{-3}	6.16×10^{-5}	5.85×10^{-3}
041	450	B	8.32	1.54	128.1	370.5	9.84×10^{-3}	3.22×10^{-3}	2.93×10^{-3}	5.50×10^{-3}
049	450	B	2.37	1.40	135.6	357.5	2.81×10^{-3}	2.93×10^{-3}	3.10×10^{-3}	5.30×10^{-3}
037	350	C	0.71	<0.01	7.4	32.1	8.10×10^{-3}	-	3.58×10^{-4}	1.01×10^{-3}
038	350	C	0.31	<0.01	8.2	ND	3.55×10^{-3}	-	3.94×10^{-4}	-
035	375	C	0.40	<0.01	3.5	17.9	4.53×10^{-3}	-	1.67×10^{-4}	5.61×10^{-4}
036	375	C	0.54	<0.01	2.8	71.0	6.13×10^{-3}	-	1.36×10^{-4}	2.22×10^{-3}
033	400	C	1.74	0.16	71.9	171.3	1.98×10^{-2}	1.64×10^{-3}	3.48×10^{-3}	5.37×10^{-3}
034	400	C	1.36	0.17	72.3	164.7	1.55×10^{-2}	1.69×10^{-3}	3.50×10^{-3}	5.16×10^{-3}
031	425	C	1.33	0.12	157.3	322.5	1.51×10^{-2}	1.17×10^{-3}	7.60×10^{-3}	1.01×10^{-2}
032	425	C	2.43	0.19	152.5	311.1	2.76×10^{-2}	1.91×10^{-3}	7.37×10^{-3}	9.75×10^{-3}

*A: 10 % NaCl, 89 ppm Cu, and 85 ppm Zn

B: 10 % NaCl, 845 ppm Cu, and 478 ppm Zn

C: 5 % NaCl, 88 ppm Cu, and 100 ppm Zn

The distribution quotients of elements obtained in this study decrease in the order of $\text{Cu} > \text{Zn} > \text{Cl} > \text{Na}$. Generally, D-values calculated as above increase with temperature. However, D versus temperature plot suggests convex nature, the minimum D-value appears at $\sim 375^\circ\text{C}$. The logarithmic values of distribution coefficient of Cu were -2.33 (350°C), -2.48 (375°C), -2.34 (400°C), -1.95 (425°C), and -1.68 (450°C), respectively.

Concentrations of ore-forming metals in coexisting vapor and brine extracted from fluid inclusions by means of laser-ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) from several porphyry type deposits have been clarified (Audéat and Pettke, 2003; Ulrich et al., 2002). These data suggest that D-values of elements such as Cu, Au, and As are 1 to 2 orders of magnitude higher than those of non-volatile metals, Fe, Zn, Pb, Ag, Bi, Na, etc. This gap of D-values among metals corresponds to the result of this study; the D-value of Cu is larger than that of Zn and Na.

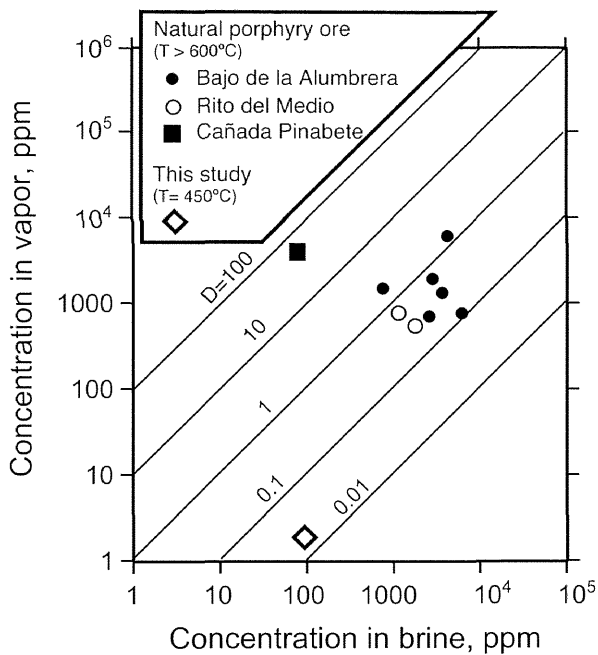


Fig. 4 Comparison of copper concentrations in vapor and brine obtained in this study with natural samples. Analytical data for coexisting vapor- and liquid-rich inclusions in hydrothermal ore deposits are from the Bajo de la Alumbrera (Ulrich et al., 2002), the Rito del Medio pluton (Audéat and Pettke, 2003) and the Cañada Pinabete pluton (Audéat and Pettke, 2003).

In Fig. 4, concentrations of Cu determined from coexisting vapor and brine inclusions at the porphyry copper deposits of the Bajo de la Alumbrera, Argentina, the Rito de Medio pluton and Cañada Pinabete pluton, New Mexico, USA are shown. The homogenization temperature of fluid inclusion obtained at these deposits suggests the formation temperature between 600° and 700°C (Audéat and Pettke, 2003; Ulrich et al., 2002). The experimental data obtained in this study at 450°C is also shown in Fig. 4. The distribution coefficient determined by the analyses of natural fluid inclusions are 1 to 2 orders of magnitude higher than that determined in this study at 450°C (Fig. 4). Clearly, temperature of fluid has large effect for the distribution of metals between coexisting vapor and liquid phases. Recently, Nagaseki and Hayashi (2008) conducted hydrothermal experiments to evaluate volatility of copper between coexisting vapor and brine phases at temperatures 500° - 600°C using combined synthetic fluid inclusion technique (Bodnar et al., 1989) and synchrotron X-ray fluorescence analysis (Nagaseki et al., 2006). They demonstrated that vapor-liquid distribution coefficient of Cu increases with sulfur concentration of the experimental solution. Some recent papers have also noted the effect of sulfur on vapor-liquid fractionation on metals (Pokrovski et al., 2008; Heinrich et al., 2004; Williams-Jones and Heinrich, 2005; Foustoukos and Seyfried, 2007). If sufficient amount of sulfur exists in the system, D-values of Cu increases to as high as those observed from natural fluid inclusions. These observations suggest that chemical factors, related to components other than $\text{NaCl-H}_2\text{O}$, control the degree of metal fractionation between the coexisting fluids. Among the geologically important ligand components, chloride has strong tendency to fractionate into the saline liquid, whereas sulfide preferentially fractionates into the vapor phase. If sufficient sulfur exists in the silicate magma, metals such as Cu^+ and possibly Au^+ may form stable complexes with hydrogen sulfide (Hayashi and Ohmoto, 1991), and may fractionate selectively into the vapor phase. Results of this study explain the vapor-liquid fractionation for copper as inferred in coexisting brine and vapor inclusions from porphyry-type deposits.

Conclusion

Volatility of Cu and Zn was measured in 5 % and 10 % NaCl solutions up to 450°C. Copper fractionates more preferentially into the vapor phase than Zn. However, distribution coefficient of Cu estimated from the analyses of coexisting brine and vapor inclusions from porphyry ore is 1 to 2 orders of magnitude larger than that determined in this study. Probably, HS⁻ complexation is responsible for the selective fractionation of Cu into the vapor phase in natural samples. Difference of volatility of each element is one of the major factors to separate metals during ore formation.

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