



An experimental study on the solubility of copper bichloride in water vapor

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Using the solubility method, the solubility of CuCl_2 in liquid-undersaturated HCl-bearing water vapor was investigated experimentally at temperatures of 330–370°C and pressures of 4.2–10 MPa. The results have shown that hydration could significantly enhance copper solubility and the concentrations of copper were positively correlated with $P_{\text{H}_2\text{O}}$. The solubility of copper in vapor phase increased with increasing $P_{\text{H}_2\text{O}}$ at the constant temperature. CuCl_2 was transported as hydrated species $\text{CuCl}_2(\text{H}_2\text{O})_n^{\text{gas}}$ in water vapor. The formation of complexes is proposed to be the result of the following reaction:



The hydration number n decreased slightly with increasing temperature. Statistical hydration numbers are 4.0, 3.6 and 3.3 at 330, 350 and 370°C, respectively.

CuCl_2 , water vapor, solubility, experimental study

The vapor transport of metals is an important geochemical process. For example, the condensates of volcanic gases commonly contain appreciable concentrations of metals^[1–7]; the high concentrations of metals have been detected in vapor-rich fluid inclusions^[8–12], and the condensates of metal compounds usually exist in the dash of flue in the process of metallurgy^[13]. Previous experimental research on metals in vapor focused on the volatility of metals or their compounds, and it was considered that only highly volatile metals could be transported in vapor.

But more and more weakly volatile metals (Cu, Au, Zn, Pb, Fe and so on) have been detected in vapor, which makes researchers have to think about whether or not the metal transport in vapor is solely related with the volatility of metals. In addition to the volatility of metals, which factors enhance the solubility of metals in vapor? How significant are the metallic elements transported in vapor? In recent years, the vapor transport of metals has attracted ever increasing attention, and results of experimental research have shown that solvents such as H_2O , HCl and H_2S could enhance the

solubility of metals in vapor^[14–21]. The high concentrations of the transition metal copper in vapor can be taken as a typical example. The highest concentration of copper reported is 8.4×10^{-6} in the condensates of volcanic gases^[1], and recent LA-ICP-MS analyses have revealed that its concentrations are as high as 3.3wt% in vapor-rich fluid inclusions^[10]. The available copper volatility data can not explain the high concentrations of copper in vapor-rich fluid inclusions^[17,19]. In order to shed light on the mechanisms of the dissolution and transport of copper in vapor, more experiments need to be done. Up to now, only Archibald et al.^[17] described the behavior of copper in water vapor at 280 to 320°C. The results showed that water vapor could enhance the solubility of copper in vapor. But at higher temperatures, little is known about the behavior of copper differing in valence in vapor. This paper presents the results of experiments

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for the solubility of CuCl_2 in HCl-bearing water vapor at 330 to 370°C.

1 Experimental method

The experimental method used in this study is identical to that employed by Migdisov et al.^[14] and Archibald et al.^[17]. The experiments were conducted in titanium autoclaves at temperatures between 330°C and 370°C and pressures up to 10 MPa. Each of the autoclaves was conditioned with nitric acid to produce a protective layer of TiO_2 on the inner surface. Autoclave volumes were determined by filling the autoclaves with 25°C distilled water from a Teflon flask, and this flask was weighed before and after filling. This pressure was calculated in terms of the autoclave volume and the equation of state for water of Kestin et al.^[22]. The autoclaves were heated in a forced draft oven (Sx2-6-6). The temperature gradient in the furnace was less than 0.5°C over the height of the autoclave.

The autoclave was loaded with one open quartz ampoule containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Figure 1). A known mass of H_2O -HCl solution (HCl, optima-grade) with a predetermined composition was placed at the bottom of the autoclave using a syringe in order to prevent contact of solid CuCl_2 and liquid. Care was taken to ensure that the mass introduced did not saturate the system with liquid under the experimental conditions, and CuCl_2 only dissolved in dry vapor. After each run, the autoclaves were removed from the oven and quenched in cold water, and the condensates were collected for analysis. Several milliliters of 1:5 HNO_3 were added to dissolve any copper precipitated on the walls of the autoclaves. The concentrations of dissolved copper in the condensates and washing solutions were determined by atom absorption spectroscopy (PE5100).

2 Experimental results

To determine the duration required for the reaction to reach equilibrium, a series of kinetic experiments were performed for 1 to 16 days. At the given temperature, equilibrium was attained 8 days later (Table 1 and Figure 2). Figure 2 shows that once equilibrium was reached, the solubility of CuCl_2 was reproducible to approximately $\pm 5\%$. On the basis of the results of kinetic experiments, all subsequent runs were conducted for 9 days.

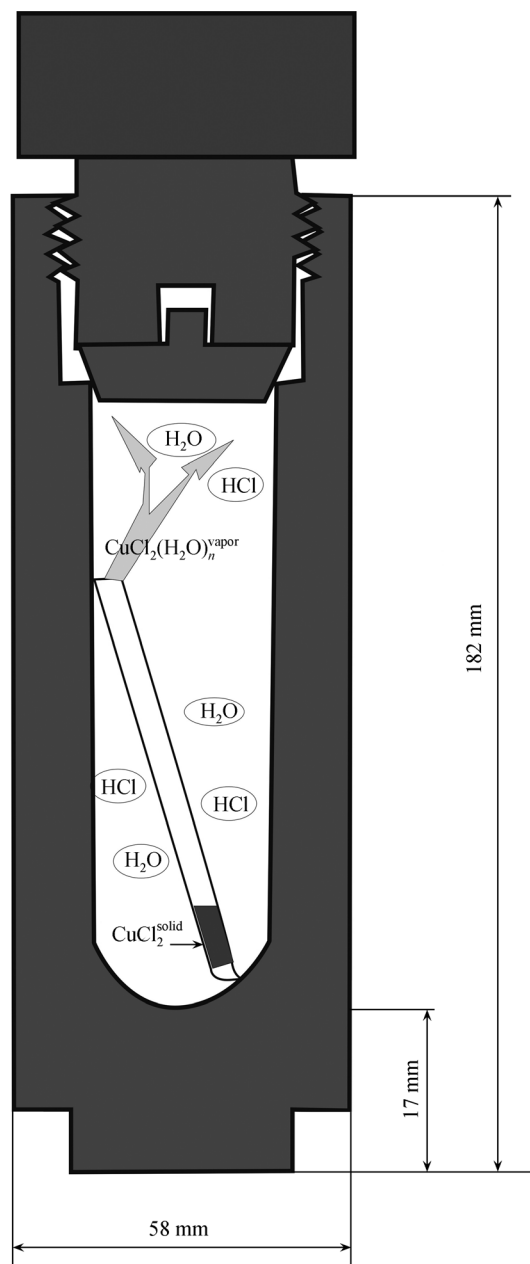


Figure 1 Sketch of a titanium autoclave used in this study. The autoclave contains a CuCl_2 reagent-bearing quartz capsule.

Table 1 Solubility of CuCl_2 in vapor phase as a function of time

Time (d)	$T(^{\circ}\text{C})$	$f_{\text{H}_2\text{O}} (\times 10^6 \text{Pa})$	$\text{Cu}^{\text{vapor}} (\mu\text{g/g})$
1	330	3.921	14.22
2	330	3.921	18.78
4	330	3.921	37.02
6	330	3.921	53.11
8.5	330	3.921	69.21
10	330	3.921	70.90
13.5	330	3.921	65.50
16	330	3.921	68.00

$f_{\text{H}_2\text{O}}$ is the fugacity of H_2O ; Cu^{vapor} is the concentration of dissolved Cu in the vapor phase.

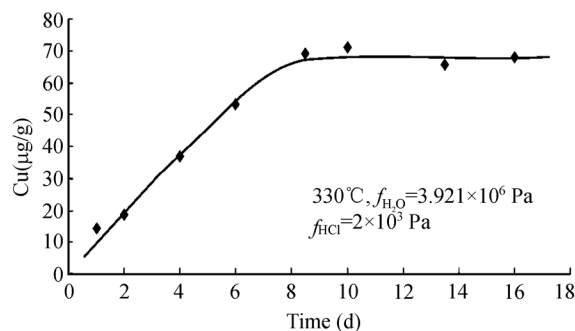


Figure 2 The solubility of copper in vapor as a function of time.

The dependence of the concentrations of CuCl_2 in water vapor on the partial pressure of HCl is illustrated in Table 2 and Figure 3. In this figure, the slope is equal to zero, so it is evident that CuCl_2 solubility is independent of f_{HCl} within the limit of experimental errors, at constant temperature and partial fugacity of H_2O . This indicates that in the dominant gaseous copper species the stoichiometrical ratio $\text{Cu}:\text{Cl}$ is equal to 1: 2.

Table 2 Concentration of copper in water vapor versus the partial pressure of HCl^{gas}

$T(^{\circ}\text{C})$	$f_{\text{H}_2\text{O}}(\times 10^6 \text{Pa})$	pH	$\log f_{\text{HCl}}(\text{Pa})$	$\text{Cu}^{\text{vapor}}(\times 10^{-6})$
350	4.169	0.07	4.86	67.47
350	4.169	1.09	3.85	73.08
350	4.169	1.09	3.85	73.00
350	4.169	1.31	3.64	70.50
350	4.169	1.69	3.25	66.60
350	4.169	1.93	3.02	74.75
350	4.169	3.02	1.93	68.00

$f_{\text{H}_2\text{O}}$ is the fugacity of H_2O ; $\log f_{\text{HCl}}$ is the log of the fugacity of HCl in vapor phase; Cu^{vapor} is the concentration of dissolved Cu in the vapor phase.

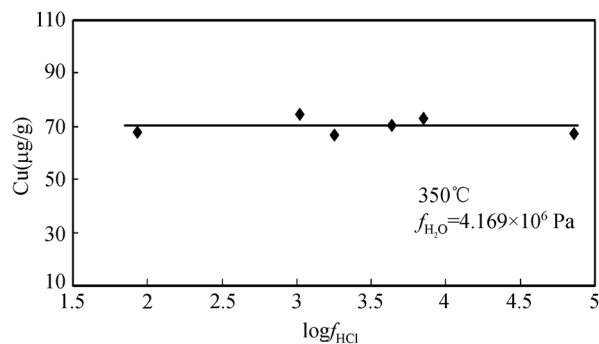


Figure 3 The solubility of copper in vapor versus $\log f_{\text{HCl}}$ at constant $f_{\text{H}_2\text{O}}$.

For comparison of the data collected at different temperatures, experiments specially designed to investigate the dependence of solubility on $f_{\text{H}_2\text{O}}$ were conducted over the same restricted range of f_{HCl} . At temperatures of 330°C, 350°C, and 370°C, the concentrations of copper in the vapor phase determined from our experiments are listed in Table 3, and shown as a function of $\rho_{\text{H}_2\text{O}}$ and $f_{\text{H}_2\text{O}}$ in Figures 4 and 5, respectively. From both figures, it can be seen that the isothermal concentrations of copper in vapor tend to increase sharply with increasing H_2O fugacity, that is to say, copper fugacity correlates positively with the fugacity of water vapor. At the same time, from Figure 4, it can also be seen that the solubility of copper in vapor increases slightly with increasing temperature at constant $\rho_{\text{H}_2\text{O}}$, but the effect of water vapor density on the solubility of copper is higher than that of the temperature.

Table 3 Solubility and mole fraction of CuCl_2 in the vapor phase at 330°C, 350°C and 370°C

$T(^{\circ}\text{C})$	$P_{(\text{H}_2\text{O})}(\times 10^6 \text{Pa})$	$\log P_{(\text{H}_2\text{O})}$	$\phi_{\text{H}_2\text{O}}$	$\log f_{\text{H}_2\text{O}}$	$\text{Cu}^{\text{vapor}}(\mu\text{g/g})$	$\log X_{\text{Cu}}$
330	4.767	6.68	0.907	6.64	80.00	-4.64
330	5.582	6.75	0.892	6.70	104.17	-4.53
330	6.353	6.80	0.878	6.75	142.50	-4.39
330	7.200	6.86	0.863	6.79	231.25	-4.18
330	7.815	6.89	0.852	6.82	276.60	-4.11
350	4.468	6.65	0.922	6.61	70.50	-4.70
350	5.260	6.72	0.909	6.68	111.25	-4.50
350	6.745	6.83	0.884	6.78	210.94	-4.22
350	8.101	6.91	0.863	6.84	264.50	-4.13
370	4.650	6.67	0.927	6.63	90.72	-4.59
370	5.485	6.74	0.915	6.70	120.42	-4.47
370	6.107	6.79	0.906	6.74	172.50	-4.31
370	7.062	6.85	0.892	6.80	187.03	-4.28
370	7.062	6.85	0.892	6.80	189.53	-4.27
370	8.518	6.93	0.871	6.87	328.13	-4.03
370	9.392	6.97	0.858	6.91	385.00	-3.96
370	10.048	7.00	0.849	6.93	411.90	-3.93
370	11.087	7.04	0.835	6.97	503.75	-3.85

P is the partial pressure of H_2O ; $\phi_{\text{H}_2\text{O}}$ is the fugacity coefficient of H_2O ; Cu^{vapor} is the concentration of dissolved Cu in the vapor phase; $\log X_{\text{Cu}}$ is the log of the Cu mole fraction in vapor phase.

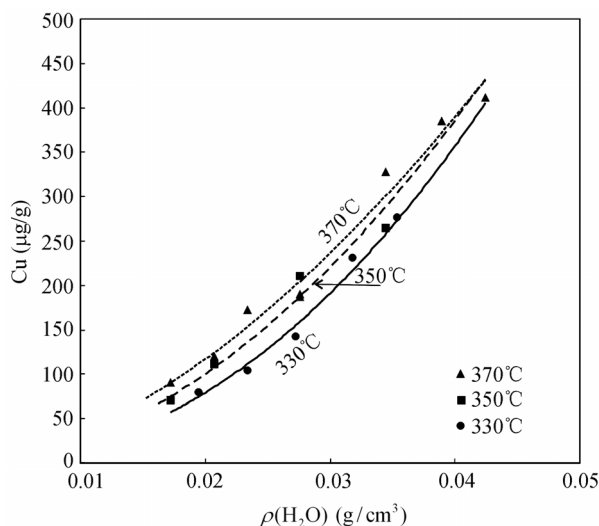


Figure 4 The concentrations of CuCl_2 in water vapor versus water vapor density obtained in experimental runs at 330°C, 350°C and 370°C.

3 Discussion

3.1 Data analysis

In our calculations, we assumed that f_{HCl} and f_{Cu} were negligible (when HCl was present in the experiments) compared to $P_{\text{H}_2\text{O}}$. Values of $P_{\text{H}_2\text{O}}$ were calculated from the equation of Kestin et al.^[22], and the mole of copper in vapor was calculated from the concentrations of copper in quenched condensates. The mole fraction of copper is therefore given by the equation:

$$X_{\text{CuCl}_2} = \frac{M_{\text{CuCl}_2}}{M_{\text{H}_2\text{O}} + M_{\text{CuCl}_2}} \cong \frac{M_{\text{CuCl}_2}}{M_{\text{H}_2\text{O}}},$$

where X_{CuCl_2} is the mole fraction of copper in vapor, and M is the mole concentrations of the corresponding compound.

As the concentrations of copper in vapor increase with increasing $P_{\text{H}_2\text{O}}$, it can be assumed that the dominant species has the stoichiometrical $\text{CuCl}_2(\text{H}_2\text{O})_n^{\text{gas}}$. The formation of this species can be described by the reaction:



where n is the hydration number of the copper species in vapor. Our experiment data were interpreted on the assumption that the vapor was an ideal mixture of non-ideal gases, and therefore it obeyed Raoult's Law. So the fugacity of copper in vapor is expressed as

$$f_{\text{CuCl}_2 \cdot (\text{H}_2\text{O})_n} \cong f_{\text{H}_2\text{O}} \times X_{\text{CuCl}_2(\text{H}_2\text{O})_n}.$$

The equilibrium constant for reaction 1 is given by

$$\log K_1 = \log X_{\text{CuCl}_2(\text{H}_2\text{O})_n} - (n-1) \log f_{\text{H}_2\text{O}} - \log f_{\text{CuCl}_2^{\text{solid}}}. \quad (2)$$

While holding temperature constant, differentiating eq. (2) with respect to $\log f_{\text{H}_2\text{O}}$, we obtained

$$\left(\frac{\partial \log X_{\text{CuCl}_2(\text{H}_2\text{O})_n}}{\partial \log f_{\text{H}_2\text{O}}} \right)_T \cong n-1,$$

where $n-1$ is the slope of $\log X_{\text{CuCl}_2(\text{H}_2\text{O})_n}$ versus $\log f_{\text{H}_2\text{O}}$, as shown in Figure 5. At the temperatures of 330°C, 350°C and 370°C, the slope values are ~ 3.0 , ~ 2.6 , and ~ 2.3 , respectively, so the substituted hydration numbers are ~ 4.0 , ~ 3.6 , and ~ 3.3 and the dominant copper species in vapor are $\text{CuCl}_2(\text{H}_2\text{O})_{4.0}^{\text{gas}}$, $\text{CuCl}_2(\text{H}_2\text{O})_{3.6}^{\text{gas}}$, and $\text{CuCl}_2(\text{H}_2\text{O})_{3.3}^{\text{gas}}$.

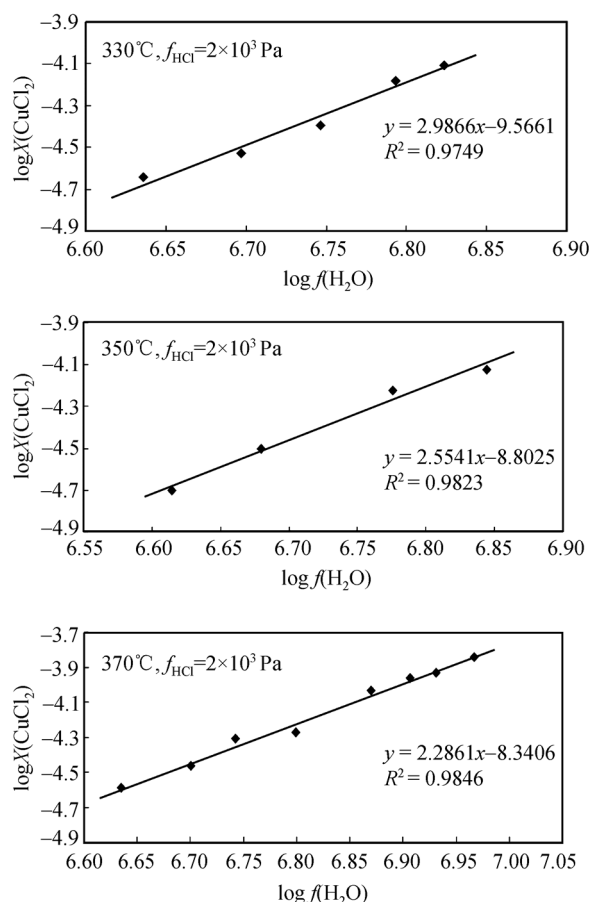


Figure 5 Diagram of $\log X_{\text{CuCl}_2}$ versus $\log f_{\text{H}_2\text{O}}$ at constant f_{HCl} and temperatures of 330°C, 350°C and 370°C.

3.2 Comparison with other studies

Results of these experiments show that CuCl_2 is transported as hydrated species $\text{CuCl}_2(\text{H}_2\text{O})_n^{\text{gas}}$ in water vapor.

With increasing temperature from 330°C to 370°C, the hydration number tends to decrease from 4.0 to 3.3. This situation is similar to what was reported in previous research^[14,16,17]. Migdisov et al.^[14] concluded that AgCl has a hydration number of three between 300°C and 360°C. Archibald et al.^[16,17] reported a variable hydration number for AuCl, from 5 at 300°C to 3 at 360°C; for CuCl, from 7.6 at 280°C to 6 at 320°C. As proposed by Archibald et al.^[16,17] for gold and copper, the decrease of hydration number should be attributed to the decrease of stability of the solvation shell with increasing temperature.

Through experimental studies, it is discovered that the behavior of CuCl₂ is similar to that of CuCl^[17] in water vapor, their solubility all correlate positively with the water vapor pressure, but the concentrations of CuCl₂ are two orders of magnitude higher than those of CuCl under the same experimental conditions, and are at least ten orders of magnitude higher than those of CuCl^[17] in the water-free system. Relatively, CuCl₂ is more easily dissolved in water vapor than CuCl.

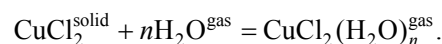
In the process of magmatic-hydrothermal evolution, low density vapor will appear, which contains many volatile components (H₂O, HCl, H₂S, SO₂, CO₂ and so on). In addition, the data obtained from our experiments show that the chloride-bearing water vapor can enhance the capacity of copper transport in vapor, and other researchers also suggest that copper may exist as a HS-bearing complex in the vapor^[23–25]. Which ligand is dominant in copper transport? This needs more experimental researches. Anyway, our experimental data on the solubility of CuCl₂ in chloride-bearing water vapor

show that interaction between vapor solvent and copper would enhance the solubility of copper in water vapor. Therefore, in special geological environments (e. g. magmatic degassing process or evolution of magmatic-hydrothermal fluid), vapor-phase fluid may play an important role in the formation of copper deposits.

4 Conclusions

Results of these experiments show that the CuCl₂ of appreciable concentrations can be transported in chloride-bearing water vapor. At the constant temperature, the solubility of copper in the vapor phase tends to increase with increasing $f_{\text{H}_2\text{O}}$, but under the same experimental conditions, the solubility of CuCl₂ is about two orders of magnitude higher than that of CuCl in water vapor. Relatively, CuCl₂ is more easily dissolved in water vapor than CuCl.

The increase of solubility of CuCl₂ is attributed to the interactions between copper and water vapor, and copper is dissolved as hydrated species in water vapor. The complexes are proposed to have been formed through the reaction:



The hydration number n decreases slightly with increasing temperature. At the temperatures of 330°C, 350°C and 370°C, the dominant copper species in vapor are CuCl₂(H₂O)_{4.0}, CuCl₂(H₂O)_{3.6} and CuCl₂(H₂O)_{3.3}, respectively.

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- Gemmell J B. Geochemistry of metallic trace elements in fumarole condensates from Nicaraguan and Costa Rican volcanoes. *J Volcanol Geoth Res*, 1987, 33: 161–181 [DOI]
- Giggenbach W F, Matsuo S. Evaluation of results from Second and Third IAVCEI field workshops on volcanic gases, Mt Usu, Japan, and white island, New Zealand. *Appl Geochem*, 1991, 6: 125–141 [DOI]
- Le Guern F, Bernard A. A new method for sampling and analyzing sublimates: Application to Merapi Volcano, Java. *J Volcanol Geoth Res*, 1982, 12: 133–146 [DOI]
- Menyailov I A, Nikitina L P. Chemistry and metal contents of magmatic gases: the new tolbachik volcanoes gas (Kamchatka). *Bull Volcano*, 1980, 43: 197–207
- Taran Y A, Hedenquist J W, Korzhinsky M A, et al. Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. *Geochim. Cosmochim. Acta*, 1995, 59: 1749–1761 [DOI]
- Taran Y A, Bernard A, Gavilanes J C, et al. Native gold in mineral precipitates from high temperature volcanic gases of Colima volcano, Mexico. *Appl Geochem*, 2000, 15: 337–346 [DOI]
- Wahrenberger C, Seward T M, Dietrich V. Volatile trace-element transport in high-temperature gases from Kudryavy volcano (Iturup, Kurile Islands, Russia). *Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry*, 2002, 7: 307–327
- Heinrich C H, Ryan C G, Mernagh T P, et al. Segregation of Ore Metals between Magmatic brine and vapor: A fluid inclusion study using PIXE microanalysis. *Econ Geol*, 1992, 87: 1566–1583
- Heinrich C A, Günther D, Audétat A, et al. Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology*, 1999, 27: 755–758 [DOI]
- Ulrich T, Günther D, Heinrich C A. Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. *Nature*, 1999, 399: 676–679 [DOI]
- Lowenstern J B, Mahood G A, Rivers M L, et al. Evidence for extreme

- partitioning of copper into a magmatic vapor phase. *Science*, 1991, 252: 1405—1409[DOI]
- 12 Audétat A, Günther D, Heinrich C A. Causes for large-scale zonation around mineralized plutons: fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Econ Geol*, 2000, 95: 1563—1581[DOI]
- 13 Chen T H, Yue S C. Role of gaseous phase in the formation of hydrothermal ore deposits. *J Hefei University of Technology (in Chinese)*, 2001, 24(4): 470—476
- 14 Migdisov Art A, Williams-Jones A E, Suleimenov O M. Solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures. *Geochim Cosmochim Acta*, 1999, 63: 3817—3827[DOI]
- 15 Migdisov Art A, Williams-Jones A E. An experimental study of cassiterite solubility in HCl-bearing water vapour at temperature up to 350°C. Implications for tin ore formation. *Cheml Geol*, 2005, 217: 29—40[DOI]
- 16 Archibald S M, Migdisov Art A, Williams-Jones A E. The stability of Au-chloride complexes in water vapor at elevated temperatures and pressures. *Geochim Cosmochim Acta*, 2001, 65: 4413—4423[DOI]
- 17 Archibald S M, Migdisov Art A, Williams-Jones A E. An experimental study of the stability of copper chloride complexes in water vapor at elevated temperatures and pressures. *Geochim Cosmochim Acta*, 2002, 66: 1611—1619[DOI]
- 18 Zakaznova-Iakovleva V P, Migdisov Art A, Suleimenov O M, et al. An experimental study of stibnite solubility in gaseous hydrogen sulphide from 200 to 320°C. *Geochim Cosmochim Acta*, 2001, 65: 289—298 [DOI]
- 19 Williams-Jones A E, Migdisov Art A, Archibald A M, et al. Vapor-transport of ore metals. *Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry*, 2002, 7: 279—305
- 20 Pokrovski G B, Zakirov I V, Roux J, et al. Experimental study of arsenic speciation in vapor phase to 500°C: Implications for As transport and fractionation in low-density crustal fluids and volcanic gases. *Geochim Cosmochim Acta*, 2002, 66(19): 3453—3480[DOI]
- 21 Zhang R-H, and Hu S-M. A case study of the influx of upper mantle fluids into the crust. *J Volcanol Geoth Res*, 2002, 118: 319—338[DOI]
- 22 Kestin J, Sengers J V, Kamgar-parsi B, et al. Thermophysical properties of fluid H₂O. *J Phys Chem Ref Data*, 1984, 13: 175—183
- 23 Sun W D, Arculus R J, Kamenetsky V S, et al. Release of gold-bearing fluids in convergent margin magmas prompted by magnetite crystallization. *Nature*, 2004, 431: 975—978[DOI]
- 24 Heinrich C A, Driesner T, Stefánsson A, et al. Magmatic vapor contraction and the transport of gold from the porphyry environment to epithermal ore deposits. *Geology*, 2004, 32: 761—764[DOI]
- 25 Pokrovski G S, Roux J, Harrichoury J-C. Fluid density control on vapor-liquid partitioning of metals in hydrothermal systems. *Geology*, 2005, 33: 657—660[DOI]