

Copper partitioning between granitic silicate melt and coexisting aqueous fluid at 850 °C and 100 MPa

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Abstract Experiments on the partitioning of Cu between different granitic silicate melts and the respective coexisting aqueous fluids have been performed under conditions of 850 °C, 100 MPa and oxygen fugacity (f_{O_2}) buffered at approaching Ni–NiO (NNO). Partition coefficients of Cu ($D_{\text{Cu}} = c_{\text{fluid}}/c_{\text{melt}}$) were varied with different alumina/alkali mole ratios [$\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$, abbreviated as Al/Alk], Na/K mole ratios, and SiO_2 mole contents. The D_{Cu} increased from 1.28 ± 0.01 to 22.18 ± 0.22 with the increase of Al/Alk mole ratios (ranging from 0.64 to 1.20) and Na/K mole ratios (ranging from 0.58 to 2.56). The experimental results also showed that D_{Cu} was positively correlated with the HCl concentration of the starting fluid. The D_{Cu} was independent of the SiO_2 mole content in the range of SiO_2 content considered. No D_{Cu} value was less than 1 in our experiments at 850 °C and 100 MPa, indicating that Cu preferred to enter the fluid phase rather than the coexisting melt phase under most conditions in the melt-fluid system, and thus a significant amount of Cu could be transported in the fluid phase in the magmatic-hydrothermal environment. The results indicated that Cu favored partitioning into the aqueous fluid rather than the

melt phase if there was a high Na/K ratio, Na-rich, peraluminous granitic melt coexisting with the high Cl^- fluid.

Keywords Cu · Experimental study · Partition coefficient · Granitic silicate melt · Aqueous fluid

1 Introduction

The porphyry copper deposit is the most important source of Cu in the world, as it accounts for about 50 %–60 % of the world's Cu production (Sinclair 2007). Porphyry copper deposits are spatially and temporally related to felsic and to intermediate porphyritic intrusions. This has led many investigators to examine the relationship between magmatic activity and hydrothermal ore genesis (Frank et al. 2011). Studies are in general agreement that magma provides the heat and metallogenic materials for the porphyry deposits (Sillitoe 1979, 1989, 2010; Sinclair 2007). It has been hypothesized that the majority of the Cu found in the deposits was derived from the melt (Sinclair 2007). Most researchers believed that the porphyry deposits were formed when the metals in the ore-forming fluid were precipitated due to the boiling and/or un-mixing of fluid (Sillitoe 2010). The close spatial relationship between the felsic porphyry rocks and the ore bodies strengthens the melt-ore link, but the details of the Cu transport in the porphyry environment are still not clear over a range of pressure, temperature, compositions of fluids and silicate melts.

The transformation of silicate melt and fluid from the original melt resulted in the element partitioning behavior between the melt and fluid phases (Audétat et al. 2000; Kamenetsky et al. 2004). This is an important step for the formation of the porphyry ore deposits (Hedenquist and

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Lowenstern 1994; Shinohara 1994; Candela and Piccoli 1995; Barnes 1997; Ulrich et al. 1999). During phase transformation, the fluid and silicate melt compositions immediately influence the element partitioning behavior between the silicate melt and fluid (Bodnar et al. 1985; Heinrich et al. 1999; Kamenetsky et al. 2004; Rusk et al. 2004), causing the variation of element species and concentrations in fluid, followed by the formation of various kinds of hydrothermal deposits (Halter and Webster 2004). Thus, it is important to know the partitioning behavior of Cu between granitic silicate melts and coexisting fluids.

The partitioning behavior of metals between silicate melts and fluids can be affected by a number of parameters, including temperature, pressure, oxygen fugacity, and compositions of fluid and melt. Previous studies on Cu partitioning between aqueous fluids and silicate melts have focused on various aqueous fluid systems at ~700–1000 °C and 50–400 MPa (Khitarov et al. 1982; Candela and Holland 1984; Keppler and Wyllie 1991; Williams et al. 1995; Bai and Koster van Groos 1999; Simon et al. 2006; Frank et al. 2011; Zajacz et al. 2012). Their data show that the $D_{\text{Cu}}(\text{fluid/melt})$ values can vary from 0.1 to 433, with most of them being greater than 1. The available experimental data of Cu partitioning between fluids and melts show that the Cu partitioning into the fluid phase is significantly enhanced with the presence of chloride (NaCl/KCl or HCl) in the system, with positive correlations between the $D_{\text{Cu}}(\text{fluid/melt})$ values and the Cl^- concentrations in the fluids (Khitarov et al. 1982; Candela and Holland 1984; Keppler and Wyllie 1991; Williams et al. 1995; Bai and Koster van Groos 1999; Simon et al. 2006; Frank et al. 2011). Data of Simon et al. (2006) demonstrate that the presence of sulfur enhances the partitioning of Cu from melts into magmatic volatile and brine phases, as the $D_{\text{Cu}}^{\text{v/m}}$ value of the S-bearing system is five times of that of the S-free system. Recently, Tattitch et al. (2015) reported that the $D_{\text{Cu}}(\text{brine/vapor})$ values increase from $25(\pm 6)$ at $X_{\text{CO}_2} = 0.10$, to $100(\pm 30)$ at $X_{\text{CO}_2} = 0.38$ in the CO_2 -bearing vapor–brine–melt system.

In natural systems, analyses of Cu-rich, low-density fluid bubbles, trapped in melt inclusions in quartz of silicic volcanic rocks from the 1912 Valley of Ten Thousand Smokes, Alaska (Lowenstern 1993) and in the CO_2 -dominated vapor bubbles from quartz phenocrysts of rhyolites from Pantelleria, Sicily (Lowenstern et al. 1991), show the $D_{(\text{vapor/melt})}$ values for Cu to be from 100 to 1000. Rare natural data on Cu partitioning between fluids and silicic melts in granitic-pegmatite (Zajacz et al. 2008) and magmatic-hydrothermal (Audétat and Pettke 2003; Vikent'ev et al. 2012) systems agree with the range of experimentally measured values in the laboratory.

However, there is a lack of experimental data about the influence of silicate melt compositions [Al/(Na + K), Na/

K, SiO_2] on the partitioning behavior of Cu between the melt and fluid phases. Only some data reported by Bai and Koster van Groos (1999) show that the decrease of ASI of the silicate melt results in a decrease of the D_{Cu} values for the Cl-bearing system. In the experiments in this paper, the fluid-melt partition coefficients of Cu were determined as a function of the melt compositions (e.g., Al/Alk mole ratios, Na/K mole ratios, and SiO_2 mole contents, where the Al/Alk mole ratio is the molar ratio of Al_2O_3 divided by the sum of $\text{Na}_2\text{O} + \text{K}_2\text{O}$) and the concentrations of chlorine in the co-existing fluids at 850 °C, 100 MPa, in order to constrain the Cu partitioning behavior between the melt and fluid phases in a fluid-melt system evolved from the representative porphyry magma.

2 Experimental methods

2.1 Starting materials

The starting chemical compositions of the individual haplogranite gels were determined by X-ray fluorescence (XRF) and are provided in Table 1. The method used to compound the haplogranitic gels is presented in detail by Hamilton and Henderson (1968). The gels were prepared from reagent grade TEOS, Na_2CO_3 , KHCO_3 , and Al_2O_3 . The Al/Alk mole ratios and Na/K mole ratios of these haplogranitic gels are varied around a basic point with composition of $(\text{Qtz}_{0.38}\text{Ab}_{0.33}\text{Or}_{0.29})$, which is the ternary minimum composition of the water-saturated melt, with the liquids at a temperature of about 710 °C and a vapor pressure of 100 MPa (Tuttle and Bowen 1958; Zhang 1992). In order to conform to Henry's Law, a small amount of Cu_2O powder was added for the synthesis of the haplogranite gels.

The haplogranitic gel was fused to glass in the Pt crucibles in a silicon–molybdenum electric oven at 1300 °C for 2 h. The glasses were then mounted onto a polymer casting resin, polished, and examined for the compositional homogeneity by using a scanning electron microscope (Fig. 1). The data show that major elements (Si, Al, Na, K) were distributed homogeneously in the glass, indicating that the glasses were compositionally homogeneous.

2.2 Experimental apparatus

Experiments were conducted using an externally-heated cold-seal rapid quench pressure vessel (RQV) (Fig. 2), which mainly includes three parts (reaction system, pressure system, and temperature control system). The vessel of the reaction system has 30 mm in its outer diameter, 8 mm in its inner diameter, 450 mm in length, with the distilled water as the pressure medium of the reaction

Table 1 Major element (wt%) and Cu ($\mu\text{g/g}$) concentrations of haplogranitic gels

Gel	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	Na/K ^a	Al/Alk ^a	Cu
L1-1	76.87	10.63	5.748	6.573	1.33	0.64	$9.90(\pm 0.59) \times 10^2$
L1-2	75.81	11.59	5.291	6.092	1.32	0.76	$9.87(\pm 0.59) \times 10^2$
L1-3	75.85	13.46	4.842	5.494	1.34	0.97	$10.50(\pm 0.63) \times 10^2$
L1-4	74.90	13.97	4.350	5.144	1.29	1.10	$9.63(\pm 0.58) \times 10^2$
L1-5	74.87	14.74	4.228	4.942	1.30	1.20	$10.23(\pm 0.61) \times 10^2$
L2-1	77.24	12.98	4.695	5.374	1.33	0.96	$8.86(\pm 0.53) \times 10^2$
L2-2	76.39	12.90	2.979	7.868	0.58	0.96	$8.45(\pm 0.51) \times 10^2$
L2-3	77.35	12.94	4.059	6.292	1.33	0.96	$8.44(\pm 0.51) \times 10^2$
L2-4	77.57	13.11	5.188	4.684	1.68	0.96	$8.45(\pm 0.51) \times 10^2$
L2-5	77.41	12.90	5.473	4.000	2.08	0.97	$8.72(\pm 0.52) \times 10^2$
L2-6	77.06	12.94	5.771	3.420	2.56	0.98	$8.45(\pm 0.51) \times 10^2$
L3-1	76.79	12.66	4.345	5.216	1.27	0.99	$9.56(\pm 0.57) \times 10^2$
L3-2	66.71	18.75	6.133	7.411	1.26	1.03	$9.66(\pm 0.57) \times 10^2$
L3-3	72.03	15.67	5.362	6.515	1.25	0.99	$9.88(\pm 0.59) \times 10^2$
L3-4	74.48	14.03	4.747	5.799	1.24	1.00	$9.54(\pm 0.57) \times 10^2$
L3-5	78.97	10.79	3.607	4.850	1.13	0.96	$9.76(\pm 0.59) \times 10^2$

^a Al/Alk and Na/K are calculated as mole content

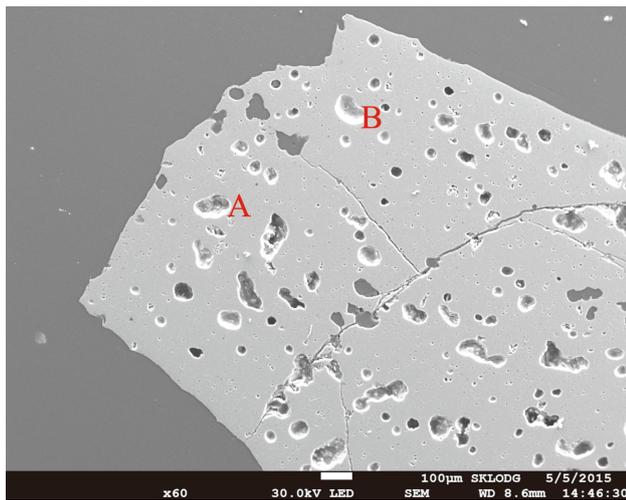


Fig. 1 A SEM image of haplogranitic glass. Pores (such as A and B) are produced by rapid quench. They are distributed randomly in the haplogranitic glass

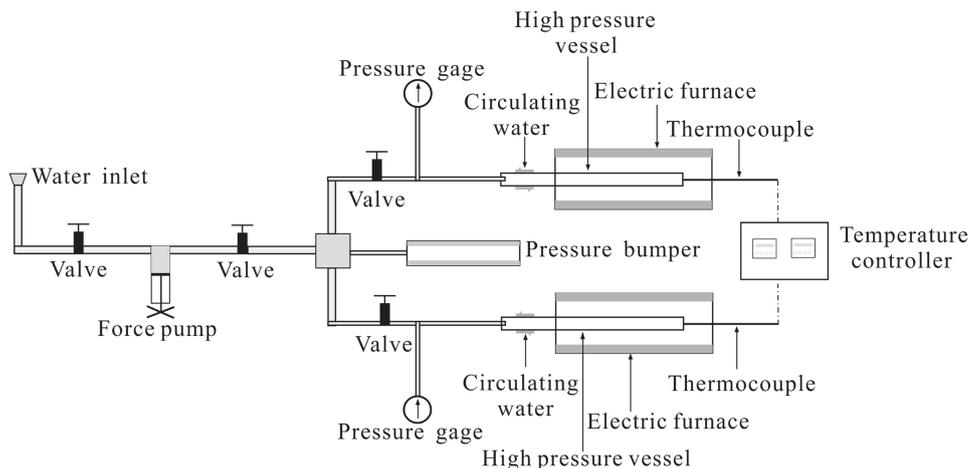
system. The exterior cooling kettle (~ 200 mm long) of the vessel is cooled by a water-circulating jacket during the entire experimental run, in order to protect the vessel during the rapid quench. The vessel was removed from the furnace and tilted vertically to allow the capsule to slide to the cool-end of the vessel and quenched to room temperature in 1 min at the end of the experiment. A manual spiral pump was used to enhance the pressure of the pressure system. Valves and buffers were used to keep a constant pressure condition. Pressures were measured with a Bourdon-type gauge, which was manufactured by the Jinan Great Wall Instrumentation Factory and has an

uncertainty of ± 5 MPa. The temperature control system, produced by the Shanghai Automation Instrumentation Co., Ltd., has applied an XTMD-1000P controller with a temperature error of ± 1 °C. A calibrated sheathed Pt-Pt90Rh10 thermocouple was inserted into a shallow hole at the end of the vessel to connect the reaction system and the temperature control system. There is a constant temperature zone in the reaction system to keep the same conditions during various experiments. The Ni-rich alloy of the vessel (GH49, containing ca. 60 wt% Ni) and a Ni-based filler rod generated an oxygen fugacity that was intrinsically buffered near the NNO at temperatures of ~ 800 – 850 °C and a water pressure of 100 MPa (Chou 1987; Taylor et al. 1992).

2.3 Experimental procedures

Experiments were conducted in gold capsules with a length of ~ 60 mm, outer diameter of 5 mm, and inner diameter of 4.5 mm. Approximately 200 mg of haplogranite powder and 200 μl solution were loaded into each capsule. The capsule was crimped and bathed in ice water while being sealed with an oxyacetylene torch to minimize volatile losses, with less than ± 0.5 mg being lost from the capsules after sealing. They were then baked in an oven overnight at 110 °C to check for leakage. If the weight loss was less than ± 0.5 mg, the capsules were placed into the externally-heated cold-seal rapid quench pressure vessel, sealed, pressurized to about one-third of the desired final pressure, and then heated to the desired temperature and pressure. Experiments were done for several days at constant

Fig. 2 Sketch of the RQV experimental apparatus



temperature and pressure and finally quenched isobarically within 1 min.

The capsules were then removed from the vessels, cleaned, and weighed to check for any leakage that may have happened during the experiments. Capsules that had a weight loss of over ± 0.5 mg were discarded. Then, the eligible capsules were pierced with a stainless steel needle and the solution was removed with a microsyringe into a 10 ml test tube. The solution was then weighed and diluted with 5 wt% HNO_3 to a volume of 10 ml, with an uncertainty of ± 1 %. After the solution was removed, the glass was obtained by splitting the capsule. Then, the inside of the capsule and the outside of the glass bead were cleaned with 5 wt% HNO_3 . The cleaning solution was moved to a 50 ml test tube with an error of ± 0.1 ml, similar to the concentration of Cu in the aqueous fluid. Therefore, achieving equilibrium between the haplogranite melt and fluid in the capsule was an important precondition. A series of experiments have been done to check how long the equilibrium could be reached for the partition of elements (Candela and Holland 1984; Williams et al. 1995; Frank et al. 2003, 2011; Chen 1989; Tang 2003). Based on the data from the studies above, each of our experiments had to be run for 5 days, in order to make sure the equilibrium between the haplogranite melt and the fluid in the capsule was reached.

3 Analytical techniques

The major elements of the glasses were analyzed by using a PANalytical Axios-advance XRF spectrometer on fused lithium-tetraborate glass pellets. Analytical precision, as determined by the Chinese National standard GSR-1, was generally around 1 %–5 %. The Cu concentrations of the haplogranitic gels and recovered quenched aqueous fluids were analyzed by using a Finnigan MAT ELEMENT

inductively coupled plasma source mass spectrometer (ICP-MS) following the procedures described by Qi et al. (2000). Part of the product glasses were milled to 200 mesh in an agate mortar, then 50 mg of the glass powder was dissolved by 1 ml of purified HF and HNO_3 in a Teflon crucible, and the solutions also were analyzed by using ICP-MS. Rhodium was used as an internal standard to monitor signal drift during counting. The international standards GBPG-1 and OU-6 were used for analytical quality control. The relative analytical precision was generally less than 5 %.

Simon et al. (2007) verified that compositions of aqueous fluids trapped as quartz-hosted inclusion and glass-hosted inclusion, and those recovered from the capsule after quench are generally consistent at the 2δ uncertainty level, though those compositions were analyzed by using three entirely different instrumental techniques (i.e., LA-ICP-MS, INAA and AAS). Therefore, in our experiments, the Cu contents of the recovered quenched aqueous fluids analyzed with the ICP-MS represent the concentration of Cu in the fluids at high temperature and pressure, while the Cu contents of the produced glasses indicate those of the melts.

During the quenching process, a small amount of the solutions included in some pores or inclusions of the glasses could influence the actual Cu concentrations of the melts. In order to estimate the influence, a small portion of product glass was mounted onto a polymer casting resin, polished, and observed under optical microscope. Microscopic observations verified that the glass was homogeneous and crystal-free, with many pores or inclusions (Fig. 3). Among these pores or inclusions, only 1 %–5 % of them in volume are actual fluid inclusions, which were checked using Laser Raman Spectrometry. Raman spectra indicate that these inclusions contain some water (Fig. 4), in which Cu and other components, such as NaCl, KCl and HCl, could be presented. Therefore, it is estimated that

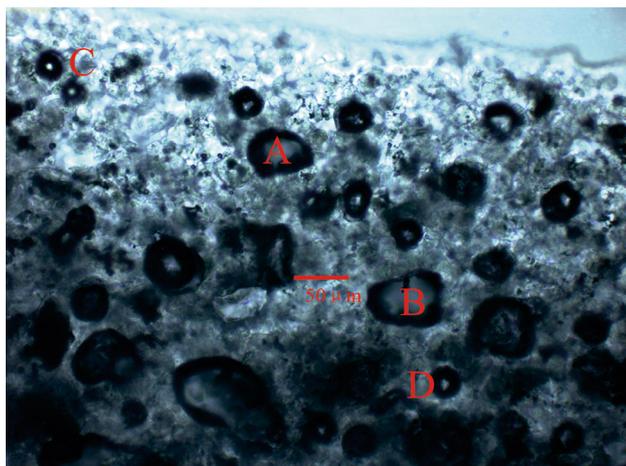


Fig. 3 Photomicrograph of pores or inclusions in product glass. The dark areas like A or B are mostly pores produced by quenching of the melts (95 %). Only 1 %–5 % of them (C and D) contain water verified by Raman spectroscopy

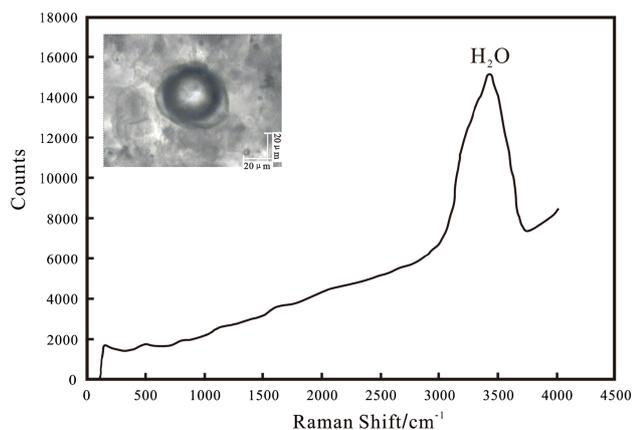


Fig. 4 Raman spectrum of water contained in a pore in product glass

there is an uncertainty of about $\pm 5\%$ for the Cu concentrations of the melts.

4 Results and discussion

4.1 Influence of Al/Alk mole ratio of the melt

In Group A of Table 2, the L1 series gels with various Al/Alk mole ratios and similar Na/K mole ratios were used as starting melts and the 0.1 mol/l HCl solution was used as the starting fluid. Cu partition coefficients vary from 1.28 ± 0.01 to 10.09 ± 0.10 when Al/Alk mole ratios range from 0.64 to 1.20. Evidently, the D_{Cu} is positively correlated with the Al/Alk mole ratios (Fig. 5). This infers that Cu partitioning is distinctly affected by the melt composition changing from peralkaline to peraluminous. It

can be seen that the higher Al/Alk mole ratios for the melts, the more Cu partitions into the coexisting aqueous fluids. However, the higher the alkali contents of the melts, the more Cu partitions into the melts.

The network of silicate melts constitutes of the basic structure of magma. In silicate melts, Si^{4+} and Al^{3+} are called network-former cations, while Na^{+} and K^{+} are called network-modifier cations. The ratio between the network-modifier cation and network-former cation defines the degree of melt polymerization. The increase of Al/Alk mole ratios means an increase of the degree of polymerization but a relative decrease of non-bridging oxygen (NBO) available. Some elements, such as Cu, Pb, Zn, Mo, and so on, form six-coordinate (or >6) complexes in the silicate melts (Bai and Koster van Groos 1999), with a positive correlation to the NBO (Farges et al. 1991, 1992). Therefore, with the increase of the Al/Alk mole ratios, the solubility of the element Cu in the silicate melts is reduced, resulting in an increase of the partition coefficient of Cu between fluids and melts.

4.2 Influence of Na/K mole ratio of the melt

The influences of the Na/K mole ratio on the Cu partition coefficients are listed in Group B of Table 2. In Group B, the L2 series gels with various Na/K mole ratios and similar Al/Alk mole ratios were used as the starting melts and the 0.1 mol/l HCl solution was used as the starting fluid. The Cu partition coefficients vary from 1.35 ± 0.01 to 22.18 ± 0.22 , when the Na/K ratios range from 0.58 to 2.56. Evidently, the D_{Cu} is positively correlated with the Na/K mole ratio (Fig. 6). This implies that Cu is more favorable to be partitioned into the aqueous fluid for a Na-rich melt-fluid system than a K-rich melt-fluid system.

The standard enthalpy of formation of Na_2O and K_2O are -416 and -363.17 kJ/mol, respectively. In addition, the Pauling radius of Na^{+} (95 pm) is smaller than that of K^{+} (133 pm), while the electronegativity of Na^{+} is larger than that of K^{+} (Huheey et al. 2006). Based on these parameters, the structure of a melt becomes more and more stable with the increase Na/K mole ratio, resulting in the decrease of capability for accommodating Cu in the melt phase. Hence, Cu tends to be enriched in the fluids rather than the melt. In addition, the Cu partition coefficients are increased with an increase of the Na/K ratios of the melt. This agrees with the fact that the Na ion is in favor of the Cu enrichment in fluids by Holland (1972).

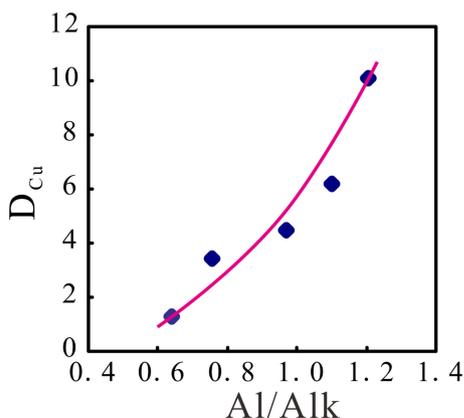
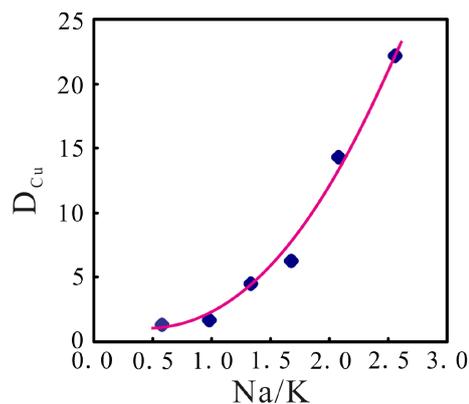
4.3 Influence of the SiO_2 mole content

The influences of the SiO_2 mole content on the Cu partition coefficients are listed in Group C of Table 2. In Group C,

Table 2 Data for the partitioning of Cu between various silicate melts and coexisting aqueous fluids

Gel	Fluid	Na/K ^a	Al/Alk ^a	SiO ₂ (mole content)	C _{fluid} (μg/g)	C _{melt} (μg/g)	D _{Cu}
Group A							
L1-1	0.1 M HCl	1.33	0.64	82.74 ± 3.84	6.58 ± 0.33	5.14 ± 0.31	1.28 ± 0.01
L1-2	0.1 M HCl	1.32	0.76	82.71 ± 3.79	10.80 ± 0.54	3.16 ± 0.19	3.42 ± 0.03
L1-3	0.1 M HCl	1.34	0.97	82.46 ± 3.79	78.28 ± 3.91	17.47 ± 1.05	4.48 ± 0.04
L1-4	0.1 M HCl	1.29	1.10	82.64 ± 3.75	27.40 ± 1.37	4.41 ± 0.26	6.21 ± 0.06
L1-5	0.1 M HCl	1.30	1.20	82.44 ± 3.74	12.11 ± 0.61	1.20 ± 0.07	10.09 ± 0.10
Group B							
L2-1	0.1 M HCl	0.58	0.96	83.17 ± 3.86	40.60 ± 2.03	30.10 ± 1.81	1.35 ± 0.01
L2-2	0.1 M HCl	0.98	0.96	83.12 ± 3.82	35.50 ± 1.78	21.70 ± 1.30	1.64 ± 0.02
L2-3	0.1 M HCl	1.33	0.96	83.24 ± 3.88	78.28 ± 3.91	17.47 ± 1.05	4.48 ± 0.04
L2-4	0.1 M HCl	1.68	0.96	83.13 ± 3.87	7.14 ± 0.36	1.14 ± 0.07	6.26 ± 0.06
L2-5	0.1 M HCl	2.08	0.97	83.35 ± 3.87	50.14 ± 2.51	3.50 ± 0.21	14.33 ± 0.14
L2-6	0.1 M HCl	2.56	0.98	83.34 ± 3.85	73.20 ± 3.66	3.30 ± 0.20	22.18 ± 0.22
Group C							
L3-1	0.1 M HCl	1.27	1.01	83.66 ± 3.85	78.28 ± 3.91	17.47 ± 1.05	4.48 ± 0.04
L3-2	0.1 M HCl	1.26	0.97	75.44 ± 3.84	25.29 ± 1.26	4.55 ± 0.27	5.56 ± 0.06
L3-3	0.1 M HCl	1.25	1.01	79.48 ± 3.34	13.75 ± 0.69	1.91 ± 0.11	7.20 ± 0.07
L3-4	0.1 M HCl	1.24	1.00	81.80 ± 3.60	48.28 ± 2.41	3.63 ± 0.22	13.30 ± 0.13
L3-5	0.1 M HCl	1.13	1.04	85.61 ± 3.95	10.06 ± 0.50	1.62 ± 0.10	6.21 ± 0.06
Group D							
L1-3	0.01M HCl	1.34	0.97	82.46 ± 3.79	11.05 ± 0.55	3.86 ± 0.23	2.98 ± 0.03
L1-3	0.05 M HCl	1.34	0.97	82.46 ± 3.79	6.25 ± 0.31	1.76 ± 0.11	3.55 ± 0.04
L1-3	0.1 M HCl	1.34	0.97	82.46 ± 3.79	78.28 ± 3.91	17.47 ± 1.05	4.48 ± 0.04
L1-3	0.5 M HCl	1.34	0.97	82.46 ± 3.79	163.00 ± 8.15	18.05 ± 1.08	9.03 ± 0.09
L1-3	1.00 M HCl	1.34	0.97	82.46 ± 3.79	103.77 ± 5.19	18.00 ± 1.08	5.75 ± 0.06
L1-3	2.00 M HCl	1.34	0.97	82.46 ± 3.79	90.73 ± 4.54	5.15 ± 0.31	17.61 ± 0.17

^a Al/Alk and Na/K are calculated as mole content

**Fig. 5** Relationship between D_{Cu} and Al/Alk of melt**Fig. 6** Relationship between D_{Cu} and Na/K mole ratio

the L3 series gels with similar Al/Alk mole ratios and Na/K mole ratios were used as the starting melts and the 0.1 mol/l HCl solution was used as the starting fluid. The Cu

partition coefficients vary from 4.48 ± 0.04 to 13.30 ± 0.13 , with the SiO₂ mole content ranging from 75.44 ± 3.84 to 85.61 ± 3.95 . It can be seen in Fig. 7 that

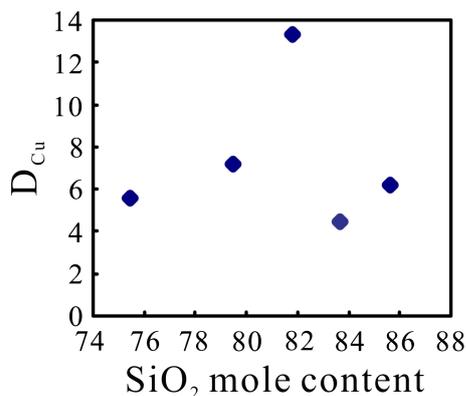


Fig. 7 Relationship between D_{Cu} and SiO_2 mole content

there is no linear correlation between the Cu partition coefficient and the SiO_2 mole content.

The SiO_2 mole content is the most important parameter controlling the various kinds of structures of silicate melts. The capability for accommodating elements varies widely with different kinds of melt structures (from island silicates to framework silicates). In this study, all silicate melts are supersaturated with SiO_2 . Consequently, the SiO_2 mole content of the melt is not obviously influenced by the Cu partition coefficients between the liquid and melt.

4.4 Influence of HCl concentration in starting fluids

In Group D, L1-3 gels with Al/Alk mole ratio of 0.97 and Na/K mole ratio of 1.34 were used as the starting melt and different HCl solutions were used as the starting fluids (Table 2). The Cu partition coefficients vary from 2.98 ± 0.03 to 17.61 ± 0.17 , with the HCl concentrations of solutions ranging from 0.01 to 2.00 mol/l. The results of this study are consistent with those of previous ones (Khitarov et al. 1982; Candela and Holland 1984; Keppler and Wyllie 1991; Williams et al. 1995; Bai and Koster van Groos 1999; Simon et al. 2005; Frank et al. 2011). It can be

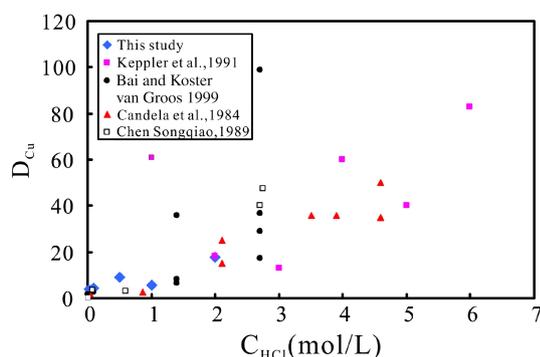


Fig. 8 Relationship between D_{Cu} and HCl concentrations in starting fluids

seen in Fig. 8 that there is a positive linear correlation between the Cu partition coefficient and the Cl concentration of the fluid.

Volatile elements, particularly F and Cl, play an important role in magmatic hydrothermal ore-forming systems (Webster 1990). For example, halogens affect various processes, such as the timing of vapor saturation, the compositional variations by complexing with metals, and types of mineralization in hydrothermal metallogenic system (Hu et al. 2008). Chlorine prefers to be distributed in aqueous fluids with a maximum Cl distribution coefficient of 117 (Webster 1992a, b; Bureau et al. 2000). Cu prefers to complex with Cl in aqueous fluids (Khitarov et al. 1982; Candela and Holland 1984; Keppler and Wyllie 1991; Williams et al. 1995; Bai and Koster van Groos 1999; Simon et al. 2005; Frank et al. 2011), so the Cu partitioning coefficients are increased with an increase of Cl concentrations in the fluids.

5 Implications

The metallogenic system of the porphyry ore deposits is complicated, as the compositions of melts, vapor, and brine fluids are extremely varied throughout the ore-forming process. Our data have demonstrated that the melt composition is also an important factor governing the partitioning behavior of Cu between fluids and melts, besides the chlorine and sulfur in fluids. Whole rock analyses of ore-bearing porphyry rocks obviously show their Al/Alk and Na/K mole ratios are both larger than 1 in Fig. 9 (Zhou 2011; Wang 2013; Hou et al. 2003). These geological and experimental results imply that Cu prefers to partition into the aqueous fluids to form Cu-rich ore-forming fluids in the system of peraluminous granitic melt or Na-rich melt coexisting with HCl-rich aqueous. Fluids (vapor and/or brine) can be exsolved from magmatic melts when they are saturated in the melts under conditions of certain temperatures and pressure (Robb 2013). The total quantity of Cu scavenged from the melts by the exsolved fluids can easily supply enough Cu to form a world-class Cu-porphyry deposit (Sinclair 2007).

In natural systems, the exsolution of the magmatic volatile phase (MVP), which always occur during the later stage of the fractional crystallization of the magma, resulted in the partition of Cu between the MVP and melt (Candela 1997). Therefore, the contents Al_2O_3 , Na_2O , and K_2O (or $Na_2O + K_2O$) of the primary melt cannot be used to evaluate its metallogenic potentiality, as those contents in the melt are variable during the fractional crystallization process. Our study presents that the parameters (Al/Alk, Na/K mole ratios) of evolved magmas are more suitable for indicating the metallogenic potentiality of the melt. The

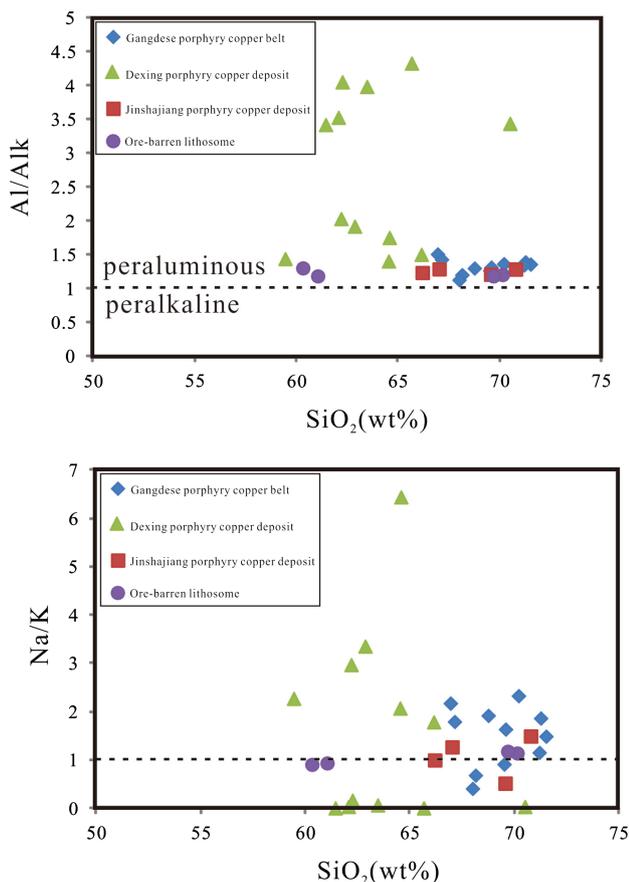


Fig. 9 Plots of Al/Alk and Na/K mole ratios versus SiO₂ contents of Copper deposits (Data cited: Zhou 2011; Wang 2013; Hou et al. 2003) Al/Alk and Na/K are calculated in mole content. Al/Alk is the mole ratio of Al₂O₃ divided by the sum of Na₂O + K₂O

D_{Cu} (fluid/melt) values (1.28–22.18) presented by our work are consistent with the values obtained by previous researchers from the natural samples (Lowenstern et al. 1991; Lowenstern 1993; Audétat and Pettker 2003; Vikent'ev et al. 2012; Zajacz et al. 2008). Therefore, it is believed that our Cu partition coefficients between fluids and silicate melts could be used as a parameter to estimate the possible amount of Cu derived from source magma of porphyries in a geological model, such as that shown by Pokrovski et al. (2013).

Herein, our Cu partitioning data obtained from the above experiments have been applied to discuss how copper could be efficiently removed from a silicate melt into an evolving fluid in the fluid-melt system. We selected the following parameters for the simulation: mean Cu partitioning value (10), volume of granite melts (100 km³), density of melts (2.5 g/cm³), content of water (5 wt%), Cu concentration in granite melts (50 ppm). In addition, the system is supposed to be closed so that the Cu amounts are limited to the given volume of the melts. After the

equilibration of Cu in the fluid and melt two-phases, the calculated Cu mass in fluid is 4.17×10^6 tons. The model indicates that 33.3 % of the Cu would be removed from the melt into the fluid. This calculation reveals that a large amount of Cu could be extracted from the silicate melt into the coexisting fluid, even if the Cu partitioning values are relatively small (such as 1–10). This implies that the variation of compositions of silicate melts could result in the large variation of Cu mass transferred from the melt into the fluid.

Simultaneously, considering the influence of fluid compositions (such as S, CO₂ and HCl) on the Cu partition coefficients (Simon et al. 2006; Zajacz et al. 2008; Frank et al. 2011; Tattitch et al. 2015; this study), a Cu partitioning value of 50 without exaggeration has been assumed to calculate the efficiencies of Cu removal from the melt into the fluid. On the basis of the calculation, 8.93×10^6 tons out of the total 1.25×10^7 tons of Cu in the melt could be extracted from the melt into the fluid, showing the efficiency of removal to be about 71.5 %. This shows the extent of Cu partition between the fluid and silicate melt phases, which should play a dominant controlling role for the formation of porphyry Cu deposits. Such calculations, while representing a simplification of nature's processes, suggest that a partition coefficient may have a significant influence on the behavior of copper in magmatic systems.

6 Conclusions

The results of our experiments have shown that the Cu partition coefficients show a positive correlation with the concentration of HCl in the starting fluid. Furthermore, the composition of a melt evidently constrains the Cu partitioning between the granitic silicate melt and coexisting aqueous fluid. Cu partition coefficients are increased with the increases of Na/K and Al/Alk mole ratios in the melt, indicating that Cu is more favorable to be partitioned into the fluid phase in the peraluminous granitic melt (especially Na-rich)-fluid system compared to the peralkaline and K-rich granitic melt-fluid system.

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