Cu diffusion in a basaltic melt

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ABSTRACT

Recent studies suggest a potential role of diffusive transport of metals (e.g. Cu, Au, PGE) in the formation of magmatic sulfide deposits and porphyry-type ore deposits. However, diffusivities of these metals are poorly determined in natural silicate melts. In this study, diffusivities of copper in an anhydrous basaltic melt (<10 ppm H\textsubscript{2}O) were measured at temperatures from 1298 to 1581 °C, and pressures of 0.5 GPa, 1 GPa and 1.5 GPa. Copper diffusivities in anhydrous basaltic melt at 1 GPa can be described as:

\[ D_{Cu}^{basalt} = \exp[-(14.12 \pm 0.50) - \frac{11813 \pm 838}{T}] \]

where \( D_{Cu}^{basalt} \) is the diffusivity in m\textsuperscript{2}/s, \( T \) is the temperature in K, and errors are given at 1\( \sigma \) level.

A fitting of all experimental data considering the pressure effect is:

\[ D_{Cu}^{basalt} = \exp[-(13.59 \pm 0.81) - \frac{(12153 \pm 1229)+(620 \pm 241)P}{T}] \]

where \( P \) is the pressure in GPa, which corresponds to a pre-exponential factor \( D_0 = (1.25 \times 2.2) \times 10^{-6} \) m\textsuperscript{2}/s, an activation energy \( E_a = 101\pm10 \) kJ/mol at \( P = 0 \), and an activation volume \( V_a = (5.2\pm2.0) \times 10^{-6} \) m\textsuperscript{3}/mol.

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The diffusivity of copper in basaltic melt is high compared to most other cations, similar to that of Na. The high copper diffusivity is consistent with the occurrence of copper mostly as \text{Cu}^+ in silicate melts at or below NNO. Compared to the volatile species, copper diffusivity is generally smaller than water diffusivity, but about 1 order of magnitude higher than sulfur and chlorine diffusivities. Hence, Cu partitioning between a growing sulfide liquid drop and the surrounding silicate melt is roughly in equilibrium, whereas that between a growing fluid bubble and the surrounding melt can be out of equilibrium if the fluid is nearly pure H$_2$O fluid. Our results are the first copper diffusion data in natural silicate melts, and can be applied to discuss natural processes such as copper transport and kinetic partitioning behavior in ore formation, as well as copper isotope fractionation caused by evaporation during tektite formation.

**Keywords:** Copper diffusivity, kinetics, kinetic fractionation, copper isotope fractionation

### INTRODUCTION

As an important base metal widely used in construction and industry, enrichment of copper from a crustal average of 27 ppm (Rudnick and Gao 2014) to a typical minable concentration of a few thousand ppm has attracted much attention from economic geologists. Magmatic sulfide deposits and porphyry copper deposits are two main types of deposits that produce copper. In particular, porphyry-type deposits account for ~57% of world’s total discovered copper (Singer 1995).

As described by Naldrett (1989), magmatic sulfide ore deposits are typically related to a mafic or ultramafic magma. Cooling of the magma leads to the saturation of sulfur, and results in the nucleation and growth of sulfide liquid drops. Since sulfide drops have higher density than
the silicate melt, they will sink through the magma chamber, at the same time growing and scavenging ore elements (e.g. Cu, Ni, Au, Pt) from the surrounding magma. Given enough time, these sulfide drops will settle to the bottom of the magma chamber and form sulfide ore deposits (Zhang 2015). The mechanism for porphyry-type ore deposits to enrich copper is similar, but instead of a sulfide liquid phase settling down in the magma chamber for magmatic sulfide deposits, a fluid phase is saturated inside the magma, and rises through the magma chamber, scavenging and transporting ore metals (e.g. Cu, Au, Mo) to the top of the magma chamber. In both types of ore deposits, enrichment of the metals into the sulfide phase or fluid phase is controlled by at least two factors: (i) partitioning of the metal elements into the sulfide or fluid phase, which may depend on the presence of other elements, such as chlorine in the fluid phase, and (ii) diffusion of the metal elements through the silicate melt to the sulfide or fluid phase. For magmatic sulfide deposits, Mungall (2002a) modeled the kinetic control of metal partitioning assuming a sulfide drop is static inside the magma, and found that the enrichment factors of metals can differ by as large as a factor of 5 depending on the diffusivity of each metal. Zhang (2015) developed a quantitative model for magmatic sulfide deposits considering both sulfide sinking and growth in silicate magma. Metal behavior was also modeled in Zhang (2015) parametrically, concluding that as long as the metal diffusivity is larger than or similar to sulfur diffusivity that controls sulfide drop growth, partition of the metal into the sulfide liquid phase is close to equilibrium. Both Mungall (2002a) and Zhang (2015) used the empirical model by Mungall (2002b) to estimate metal diffusivities. The model of Mungall (2002b) indicates that copper diffusion is much faster than sulfur diffusion. Therefore, both authors concluded that partition of copper into the sulfide phase is close to equilibrium. On the other hand, Huber et al. (2012) developed a model for metal enrichment and transport by a fluid phase in a porphyry
system, and suggested that the efficiency of copper enrichment is dependent on the relative
diffusivity of copper to that of chlorine. Huber et al. (2012) used copper diffusion data from von
der Gonna and Russel (2000), with copper diffusivity being 1 order of magnitude smaller than
chlorine diffusivity. Therefore, copper partition into the fluid phase would not reach equilibrium
if the fluid bubbles ascend rapidly according to Huber et al. (2012).

In addition to metal enrichment processes discussed above, some other processes in ore
formation might also be kinetically controlled. For example, in magmatic sulfide deposits, after
sulfide liquid accumulation at the bottom of the magma chamber to form a sulfide liquid pool,
the interaction between the sulfide liquid pool and the magma might be diffusion-controlled
(Mungall 2002a). At the same time, metal extraction from other minerals into the sulfide melts is
controlled by diffusion of the metal in the mineral phase (e.g., extraction of Ni from olivine;
Zhang 2015). For porphyry-type ore deposits, re-dissolving of the sulfides and transport of their
metal elements from the more mafic magma to the silicic magma by a magmatic volatile phase is
also partially controlled by diffusivities of the metal elements in the melts (Nadeau et al. 2010,
2013).

Besides roles in copper ore formation, copper diffusivity is also an important parameter
in discussing copper isotope fractionation. Moynier et al. (2010) measured copper isotopes in
tektites, and found copper isotopes are more fractionated than zinc isotopes in the same set of
tektite samples. This is contrary to the notion that fractionation is due to volatile loss because
zinc has lower half-condensation temperature and is hence more easily lost than copper. The
authors explained their results by a higher diffusivity of copper than zinc in silicate melts,
implying that the isotope fractionation process was diffusion-limited.
Copper diffusion data in silicate melts are limited. Although there is a single study of copper diffusivity in a Na$_2$Si$_2$O$_5$ melt by von der Gonna and Russel (2000), there are currently no copper diffusion data in natural silicate melts. Cu diffusivity in the Na$_2$Si$_2$O$_5$ melt is unlikely applicable to Cu diffusion during copper ore formation from a natural silicate melt. Even though there is an empirical model by Mungall (2002b) to estimate diffusivity, as Behrens and Hahn (2009) and Zhang et al. (2010) pointed out, Mungall (2002b)’s diffusivity model may be orders of magnitude off in predicting diffusivities. Hence, experimental data are necessary for more quantitative prediction of the diffusion effects.

In this study, diffusion couple experiments are carried out to obtain copper diffusivities in a basaltic melt, and the results are used to discuss copper enrichment in ore formation, and to speculate on kinetic controls of copper isotope fractionation.

**EXPERIMENTAL AND ANALYTICAL METHODS**

**Starting glasses**

Two glasses with the same major element composition but different copper concentrations were synthesized for the diffusion couple experiments. A major element composition of Etna basalt was chosen since it has been well studied in terms of melt properties: both melt viscosity and sulfur diffusivity have been measured for this melt composition (Giordano and Dingwell 2003; Freda et al. 2005).

In order to synthesize the starting glasses, a total weight of ~6.5 g of oxides (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO) and carbonates (CaCO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$) were weighed based on the target composition of Etna basalt (Freda et al. 2005) and well mixed under alcohol in an agate mortar.
Then the mixture of the oxides and carbonates was divided into two halves, one of which was doped with Cu$_2$O to contain $\sim$1200 ppm Cu. Afterwards, approximately 0.6 g of the copper-free mixture and copper-containing mixture were put into separate graphite crucibles and fused at 1300 ºC for 3 hours together inside a Deltech furnace under a constant N$_2$ flow. After fusing, the two crucibles were taken out of the furnace and cooled in air to form two glass beads with a diameter of $\sim$8 mm.

The glasses synthesized were examined under optical microscope to ensure that they are bubble free, crystal free and homogeneous in color. A center section was cut from each glass bead and analyzed by electron microprobe to check its homogeneity before it was used for diffusion couple experiments. Average compositions of the synthesized glasses are shown in Table 1. In general, microprobe data show that the composition of the synthesized glass matches the target composition fairly well (difference $<$1 wt% for each major component). FeO concentration was found to decrease slightly ($\sim$8% relative) towards the surface of the glass beads. Cu concentration was also found to be slightly inhomogeneous, with lower concentration near the surface of the glass beads ($\sim$1000 ppm) than at the center of the glass beads ($\sim$1300 ppm) (Fig. 1). To avoid possible effects of inhomogeneity in glass composition to our experiments, only center parts of the synthetic glasses were used for diffusion couple experiments.

H$_2$O and CO$_2$ concentrations in the synthetic Etna basaltic glasses are below $\sim$10 ppm and $\sim$100 ppm, respectively, based on FTIR measurements using a Perkin-Elmer Spectrum GX FTIR spectrometer at the University of Michigan.
Experimental procedure

All diffusion couple experiments were conducted in a piston-cylinder apparatus at the University of Michigan. An illustration of the experimental design for our diffusion couple experiments can be found in Fig. 2, and the experimental procedures are as follows. First, two glass cylinders with a diameter of 2.0 mm and height of 1.5 mm were prepared, one from copper-free and the other from copper-containing synthetic glass beads. The choice of 1.5 mm height of each glass cylinder used in our experiments is a compromise between two factors. One factor is that shorter cylinders lead to shorter experimental charge and hence smaller temperature variation across the whole charge. The other is that the cylinder must be tall enough so that Cu diffusion would not reach the boundary of the glass during the experiment. The glass cylinders were doubly polished using progressively finer silicon carbide sandpapers and a finish on 0.1-µm alumina powder. Afterwards, the two glass cylinders were ultrasonically cleaned in acetone and then in alcohol. After drying in vacuum for about 1 hour, the two glass cylinders were placed together and fit snugly into a 4.0-mm outer-diameter graphite capsule. The copper-free glass was placed on top since it is expected to have a slightly lower density. The graphite capsule was fit into an MgO pressure medium, then placed inside a graphite furnace, and then into a BaCO₃ outer pressure medium. Geometry of the sample assemblage was designed so that the interface is at the center of the graphite furnace to minimize temperature gradient across the capsule (Fig. 2). A type-S thermocouple (Pt90Rh10-Pt) was used to measure the temperature during an experiment. The length of each part of the sample assemblage was measured after an experiment to examine whether the interface was at the center of the graphite furnace during the experiment. The distance of the thermocouple tip to the diffusion interface was typically 2.5 to 3 mm. Temperature correction was made using the calibration of Hui et al. (2008). Temperature at the
interface of the diffusion couple was used as the experimental temperature. The temperature at
the two ends of the diffusion couple is estimated to be 10 to 20 °C below the interface
temperature using the calibration of Hui et al. (2008).

Experiments were conducted at pressures of 0.5 to 1.5 GPa at a 0.5 GPa increment. A 5%
pressure correction is applied based on calibration by Ni and Zhang (2008) on the same piston
cylinder apparatus. During an experimental run, the pressure was first increased slowly and
smoothly to 15% higher than the target pressure (10% in the case of 1.5 GPa experiment) using a
pressure controller. Then the whole sample assemblage was relaxed at this pressure and 200 °C
for at least 2.5 hours to close gaps inside the assemblage. Both pressure and temperature were
maintained automatically in this step. After relaxation, the temperature was brought up to the
designated temperature in ~60 s by a programmed heating procedure. No temperature overshoot
occurred during heating-up, and temperature fluctuation was within ±1 °C during the
experiments. Due to high Cu diffusivity, only a short duration was needed in the diffusion couple
experiments (2 to 7 minutes at 1298 °C to 1581 °C) to generate a long enough profile. After a
designated duration, the assemblage was quenched with a cooling rate of about 100 °C/s (based
on direct measurement) by turning off the power. During quench, the pressure was maintained by
a manually controlled ENERPAC electric pump (except for Cudiffcp 4.4 and Cudiffcp 7.2, for
which the pressure was maintained by the pressure controller). The whole sample assemblage
was then preserved inside an epoxy resin disc and polished to expose the center section for
electron microprobe analysis.

Since the experimental duration was only 2 to 7 minutes, the effect of heating up (taking
~1 min) needs to be considered. Quenching is rapid and hence the effect is small, but the small
effect is also accounted for in the following correction applied to obtain the effective duration for
all experiments. Based on the solution to the diffusion problem for time-dependent $D$ (e.g., Zhang, 2008, Eq. 3-54b), the following equation was used to calculate the effective duration at the experimental temperature $T_0$:

$$t_c = \int_0^t \frac{\exp(-E / RT)}{\exp(-E / RT_0)} dt$$

where $t_c$ is the effective duration, $E$ is the activation energy for Cu diffusion, $R$ is the gas constant, $T$ is recorded experiment temperature (including temperature recorded during heating up and that during cooling down) corrected to the interface position, and $T_0$ is the plateau interface temperature. At the beginning an estimated $E$ was used for the effective duration correction. After enough experiments were done, $E$ was obtained by fitting the Arrhenius equation and $t_c$ was corrected again until $t_c$ and $E$ do not change anymore. Copper diffusion has a small activation energy, leading to a relatively large duration correction of ~35 s.

Analytical methods

Major element composition and copper concentration profiles were measured in WDS mode using the Cameca SX-100 electron microprobe at the University of Michigan. Major oxide concentrations (SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, MgO, CaO, Na$_2$O and K$_2$O) of the synthetic glasses were measured with an acceleration voltage of 15 kV, a beam current of 10 nA in focused mode, and a counting time of 30 to 40 seconds on the peak and 15 to 20 seconds on each side of the backgrounds. The following standards were used for the microprobe analysis: albite (ALBA) for Na, forsterite (FOBO) for Mg and Si, sillimanite (SILL) for Al, potassium feldspar (GKFS) for K, wollastonite (WOLL) for Ca, geikielite (GEIK) for Ti, and ferrosilite (FESI) for Fe. Cu concentrations were measured in separate sessions using a point beam with an acceleration
voltage of 15 kV and a beam current of 40 nA. The standard for Cu concentration measurement is chalcopyrite (CPY). Three spectrometers were employed to count Cu at the same time. The counting time is 240 s on the Cu Kα peak and 120 s on either side of the background to achieve a detection limit of ~80 ppm for Cu. The analytical error given by the microprobe based on counting statistics is ~80 ppm (1σ). NIST SRM 610 was used as a secondary standard for Cu in our analysis. The average concentration of Cu in SRM 610 was reported by Pearce et al. (1997) to be 422±42 ppm. Our microprobe analysis yielded a Cu concentration of 464 ppm to 516 ppm on SRM 610. The shift of absolute concentrations results in a shift of the entire copper diffusion profile. However, if the amount of shift were similar for both the low and high copper concentration ends, the diffusivity obtained from the profile would not be affected. In order to evaluate whether the shift in absolute copper concentration has significant effect on copper diffusivity, the sample Cudiffcp 3.1 was analyzed twice on two different days. The entire copper concentration profile measured on two days shifted ~200 ppm from each other. However, after the background correction, the two profiles measured on different days closely match each other (Fig. 3). The diffusivities fitted from the two analyses of different days are <2% different from each other, which is much smaller than the fitting error (1σ fitting error is about 10%) and hence negligible.

RESULTS

Copper diffusion profiles and fitting

Ten successful diffusion couple experiments have been conducted. In addition to the 10 experiments reported here in Table 1, two more experiments were carried out but are classified as unsuccessful. One experiment at 0.5 GPa and 1300 ºC shows abnormal concentration profile,
which might be due to initial Cu concentration inhomogeneity. The other experiment at 1.5 GPa and 1300 ºC crystallized because the pressure was too high for the given temperature. Both experiments are excluded from the data.

Fig. 4 shows optical microscope images of two successful experiments. For each diffusion couple, at least three Cu concentration traverses ~250 µm apart from each other were measured to examine the reproducibility and possible convection. In five out of the ten experiments (Cudiffcp 1.2, Cudiffcp 3.1, Cudiffcp 4.2, Cudiffcp 4.3 and Cudiffcp 4.4), the interface survived the quench process and the sample glasses were crack-free after the experiment. In these cases, the physical interface position was indicated by the two dents on both sides of the glasses, as shown in Fig. 4a.

For the other five experiments (Cudiffcp 1.1, Cudiffcp 2.1, Cudiffcp 5.1, Cudiffcp 6.1 and Cudiffcp 7.2), a crack occurred almost exactly along the interface (Fig. 4b). In order to prevent loss of glass during polish, epoxy was added multiple times to protect the cracks. After microprobe analyses, copper concentration profiles on both sides of the crack were compared: if necessary, a distance correction is made so that the profile across the crack is smooth. As a result, a 7.5 µm and 12.5 µm correction to the concentration profiles was applied for experiments Cudiffcp 2.1 and Cudiffcp 6.1, while no correction was applied to experiments Cudiffcp 1.1, Cudiffcp 5.1 and Cudiffcp 7.2.

Cu concentration profiles in all experiments besides Cudiffcp 3.1 are shown in Fig. 5. The concentration profiles were fit by the solution to a one-dimensional diffusion couple with constant diffusivity (Crank 1975):

\[
C = \frac{C_0 + C_1}{2} + \frac{C_0 - C_1}{2} \operatorname{erf} \frac{x - x_0}{\sqrt{4Dt}}
\]  

(3)
where $C_0$ is the initial Cu concentration at the Cu-free half of the diffusion couple (defined as $x-x_0 > 0$); $C_1$ is the initial Cu concentration at the Cu-bearing half (defined as $x-x_0 < 0$); $D$ is copper diffusivity and $x_0$ is the position of the interface. Since copper diffusivity is high, there is concern that copper diffusion might have reached the ends of the diffusion couple. This would cause error in fitting using Eq. 3, which assumes an infinite diffusion medium. Visual examination of the data and fitting of the profiles indicate that for the longer-duration or higher-temperature experiments (Cudiffcp 1.1, Cudiffcp 5.1 and Cudiffcp 7.2) diffusion seems to have reached the two ends. Numerical fitting using the solution for finite diffusion medium was carried out for these three experiments (curves shown in Fig. 5), and the resulting diffusivities were only 3-5% higher than that assuming infinite diffusion medium.

Temperature and pressure dependence of copper diffusivity

Experimental run conditions and results for all successful experiments are summarized in Table 2. An Arrhenius plot of all copper diffusivities obtained in this study is shown in Fig. 6. Diffusion data of the five experiments at 1 GPa and 1314-1575 ºC in anhydrous basaltic melt can be expressed by the following Arrhenius relation:

$$D_{\text{Cu}}^{\text{basalt}} = \exp\left[-(14.12 \pm 0.50) - \frac{11813 \pm 838}{T}\right], \quad r^2=0.985$$  

(4)

where $D_{\text{Cu}}^{\text{basalt}}$ is in m$^2$/s, $T$ is temperature in K, and errors are at 1σ level. The above equation reproduces the five experimental ln$D$ values to within 0.09 ln$D$ units. The activation energy corresponding to Eq. 4 is 98.2 ± 7.0 kJ/mol. This small activation energy (~100 kJ/mol) means that the temperature dependence of copper diffusivity is relatively small compared to other elements, and is consistent with Cu diffusing as Cu$^+$. 
To evaluate the pressure effect on copper diffusivity, two experiments were done at 1.5 GPa and three experiments were done at 0.5 GPa (see Fig. 6). Two of the three 0.5 GPa experiments gave diffusivities that are ~20% higher than the 1 GPa diffusivities, while diffusivity from the other 0.5 GPa experiment fell 12% below the 1 GPa trend. Two 1.5 GPa experiments gave diffusivities 12% and 29% below the 1 GPa diffusivities respectively.

Although the 0.5 GPa experiments have relatively larger errors (these are still small errors for diffusion studies), a fit of all measured copper diffusivities at 1298 ºC to 1581 ºC and 0.5 to 1.5 GPa gives:

$$D_{Cu_{basalt}} = \exp\left[-(13.59 \pm 0.81) - \frac{(12153 \pm 1229) + (620 \pm 241)P}{T}\right], \quad r^2=0.938$$

where $D_{Cu_{basalt}}$ is diffusivity in m²/s, $T$ is temperature in K, $P$ is pressure in GPa, and errors are at 1σ level. Eq. 5 corresponds to a pre-exponential factor $D_0=(1.25 \times 2.2) \times 10^{-6}$ m²/s, an activation energy $E_a=101 \pm 10$ kJ/mol and an activation volume $V_a=(5.2 \pm 2.0) \times 10^{-6}$ m³/mol for copper diffusion in anhydrous basaltic melt. The above equation is able to reproduce all our experimental ln$D$ values to within 0.23 ln$D$ units.

Possible complications and other sources of error

Since basaltic melts have low viscosities at our experimental condition (about $10^0$ to $10^{1.3}$ Pa·s at temperatures from 1581 ºC to 1298 ºC using the viscosity model for Etna basalt by Giordano and Dingwell 2003), there is concern about whether convection has occurred during the experiments. Effort was made to examine whether convection is an issue in our experiments. First, at least three traverses 200 µm to 300 µm apart from each other were measured on every sample. If convection occurred, the three traverses would likely diverge, and diffusivities
obtained from these traverses may be significantly different from each other. The results show that, diffusivities fitted to individual traverses in one sample are typically within ~20% from the overall diffusivity, indicating no obvious convection. Second, two experiments (Cudiffcp 1.1 and Cudiffcp 1.2) were conducted at the same temperature and pressure but with different duration (465 s vs 163 s, almost a factor of 3 difference). As can be found in Table 2, relative diffusivity difference between the two experiments is only about 8%, within our experimental error. Both the consistency between diffusivities from Cudiffcp 1.1 and Cudiffcp 1.2 and the agreement between different traverses in the same experiment suggest that the occurrence of convection is unlikely in our experiments.

Temperature uncertainty may cause error in the data. As discussed in Methods, temperature at the two ends of the diffusion couple can be 10 to 20 °C lower than the interface temperature. Hence, the error caused by temperature uncertainty is estimated using this maximum temperature uncertainty of 20 °C. Based on the activation energy of 98.2 kJ/mol for Cu diffusivity at 1 GPa, the uncertainty of 20 °C can result in errors in $D_{Cu}$ of 10% at 1300 °C and 7% at 1600 °C. The uncertainty in Cu diffusivity due to pressure uncertainty is negligible because copper diffusivity changes less than 20% when pressure changes by 0.5 GPa.

Another possible source of error is the effective run duration contributed by heating and cooling. As a compromise to the high Cu diffusivity, most of our experiments were designed to be only ~2 min long. Under this circumstance, the heating and quenching processes contribute about 20% to 30% to the effective run duration, meaning Cu diffusivity is changed by 20% to 30% with the duration correction. However, the method we used to correct the duration (Eq. 2) is accurate if the activation energy of Cu diffusion is constant.
As mentioned earlier, cracks occurred along the interface of five samples during quench (Cudiffcp 1.1, Cudiffcp 2.1, Cudiffcp 5.1, Cudiffcp 6.1 and Cudiffcp 7.2) and the cracks are almost perfectly horizontal, and hence the distance across the crack cannot be determined by comparing different traverses. For these five experiments, corrections were done by comparing the trend of copper concentration profiles on both sides of the crack. As a result, a 7.5 µm and 12.5 µm correction to the concentration profiles was applied for experiments Cudiffcp 2.1 and Cudiffcp 6.1, while no correction was applied to experiment Cudiffcp 1.1, Cudiffcp 5.1 and Cudiffcp 7.2. This resulted in a 3% increase in diffusivity obtained from Cudiffcp 2.1 and a 2% increase in diffusivity obtained from Cudiffcp 6.1.

The synthetic starting glasses are not perfectly homogeneous in copper concentration. In the 8-mm-diameter copper-bearing synthetic glass, copper concentration can be ~1300 ppm at the center and ~1000 ppm near the boundary (Fig. 1). However, considering that the glass cylinder used for experiments is only about 1.5-mm tall, the copper concentration difference across the glass cylinder is ~100 ppm, which is only slightly above our analytical error of ~80 ppm. Therefore the Cu concentration gradient in the starting glasses is unlikely to cause significant error.

**DISCUSSION**

**Comparison with existing copper diffusivity data**

For multivalent ions, valence state of the ion plays an important role in its diffusivity in silicate melts and minerals. Ions in the lower valence state typically have higher diffusivities because of the weaker bonding between these ions and surrounding melt structure (Zhang 2010). Examples of multivalent ions in silicate melts include Fe$^{2+}$ and Fe$^{3+}$, Sn$^{2+}$ and Sn$^{4+}$, etc. Copper
is also a multivalent element in the natural system, and is commonly found as 0, +1 or +2 in natural occurrence. In the study of copper solubility in a mafic melt, Ripley and Brophy (1995) plotted log copper solubility versus $\log f_{O_2}$, and found that copper dissolves into the melt predominantly in +1 valence state at or below NNO. The high Cu diffusivity and low activation energy for Cu diffusion observed in our study are consistent with Cu being univalent. Therefore in this study, we regard our measured copper diffusivity as $Cu^+$ diffusivity.

As mentioned in the Introduction, we know of only one study reporting $Cu^+$ diffusivities in Na$_2$Si$_2$O$_5$ melt (von der Gonna and Russel 2000) using a voltammetry method. They reported $Cu^+$ diffusivity to be $5.01 \times 10^{-11}$ m$^2$/s at 1100 ºC with activation energy of 92.1 kJ/mol. Their diffusivities of copper in Na$_2$Si$_2$O$_5$ glass melt are plotted in Fig. 7 (green open squares) to compare with those measured in this study (red solid circles, diamonds and triangles). $Cu^+$ diffusivities in Na$_2$Si$_2$O$_5$ glass melt are smaller than those in basaltic melt by a factor of about 3 with similar activation energy.

Mungall (2002b) developed a model to calculate ion diffusivities in silicate melt. Calculated $Cu^+$ diffusivities in basaltic melt using his model are plotted in Fig. 7 as a grey solid line, and are about 3 to 5 times the diffusivities determined by our experiments. The model by Mungall (2002b) shows larger errors in reproducing the diffusivities in the Na$_2$Si$_2$O$_5$ melt. At 1100ºC, calculated $Cu^+$ diffusivities using his model are two orders of magnitude larger than the experimental data by von der Gonna and Russel (2000).

**Comparison of copper diffusivity with that of other elements in anhydrous basaltic melts**

Diffusivity data for selected elements in basaltic melts are also plotted in Fig. 7. From the figure, Cu diffusivity is almost identical to Na diffusivity at ~1400 ºC, lower than Li diffusivity
by a factor of about 3 and significantly higher than diffusivities of all other cations shown in Fig. 7. At 1300 °C, Cu diffusivity is ~10 times Ca and Co diffusivity, 18 times Mg diffusivity, and ~30 times S and Fe diffusivity. Since Cu diffusion has smaller activation energy than all other elements shown in Fig. 7, when temperature increases, Cu diffusivity increases slower than other elements. At 1500 °C Cu diffusivity is only ~5 to 10 times higher than Mg, Fe, Co, S and Ca. However when temperature decreases, Cu diffusivity decreases slower than all other elements shown in Fig. 7, and becomes larger than Na diffusivity. At 1100 °C, Cu diffusivity will be ~200 times Fe diffusivity, 67 times Mg diffusivity, 35 times Co diffusivity, ~25 times Ca diffusivity and 2.5 times Na diffusivity.

To examine the role of valence and size of cations, the radius of Cu⁺ was compared to other monovalent cations. For self-consistency, the ionic radii of Li⁺, Cu⁺ and Na⁺ in octahedral sites (0.076, 0.077, and 0.102 nm, respectively, Shannon 1976) are compared. If diffusivities of univalent cations in a given melt are mainly determined by the ionic radii (Mungall 2002b), Cu⁺ diffusivity would be similar to Li⁺ diffusivity. The fact that Cu⁺ diffusivity is a factor of 3 smaller than Li⁺ diffusivity but similar to Na⁺ diffusivity indicates that other ionic characters (e.g., electronegativity, the presence of d electrons, different co-ordination number, etc.) also play a role in determining the diffusion rate.

Applications

The role of copper diffusion in magmatic sulfide deposit formation has been discussed above in the Introduction. The major conclusions by Mungall (2002a) and Zhang (2015) were consistent in that, if the diffusivity of a metal is much larger than sulfur diffusivity in basaltic melt, the partitioning of the metal into the sulfide phase can be regarded as in equilibrium. Both
Mungall (2002a) and Zhang (2015) used the diffusivity model by Mungall (2002b) to estimate metal diffusivities in their study, and found Cu\(^+\) to be one of the most mobile elements in basaltic melt. Our results suggest that Mungall’s model overestimated copper diffusivity in basaltic melt by a factor of 2 to 4. However, our measured copper diffusivity is still ~30 times higher than sulfur diffusivity in basaltic melt. Therefore copper partition into the sulfide melt can be regarded as equilibrium partitioning in most cases.

High copper diffusivity in basaltic melt might also play a role in metal transport by a magmatic vapor phase (MVP). Nadeau et al. (2013) carried out a melt-inclusion study on samples from Merapi volcano, Indonesia, and found that copper was more enriched in shallower felsic melts (~45 ppm) than in deeper mafic melts (~25 ppm), which is opposite to the trend normally observed in arc magmas. The unusual behavior of Cu could not be explained by crystal fractionation or combined assimilation and fractionation. Nadeau et al. (2010) suggested a mechanism in which copper was transported from the mafic magma to the felsic magma by an MVP enriched in copper. Since water diffusivity in basalt is high (Fig. 7), the growth of an MVP inside the magma is rapid. In this process, because the diffusivity of copper is lower than that of H\(_2\)O but higher than that of other metal elements (except for Li and Na), copper would not reach equilibrium concentration in the MVP but would be more efficiently enriched in the aqueous volatile phase than the other metal elements. One complication is that, the partition coefficient of copper between the volatile phase and the silicate melt phase strongly depends on chlorine and sulfur contents in the volatile phase (e.g., Candela and Holland 1984; Williams et al. 1995; Simon et al. 2006 and Zajacz et al. 2008). Hence, enrichment of copper in the MVP would be controlled by diffusion of sulfur or chlorine from the silicate melt to the MVP. As can be seen in Fig. 7, \(D_{\text{Cu}} > D_{\text{Cl}} > D_{\text{S}}\) assuming water content in silicate melt does not change the sequence. Therefore,
in pure H$_2$O fluid phase, Cu concentration in the fluid phase would be even lower than that indicated by the low partition coefficient, but if the fluid bubble is enriched in chlorine or sulfide, copper partitioning between the fluid and melt phases would be roughly in equilibrium, while Cl and S concentrations in the fluid bubble would be lower than that indicated by equilibrium partitioning. Nadeau et al. (2013) did not specify the composition of the MVP in his study, but a study by Zajacz and Halter (2009) found evidence for sulfur-rich vapor in melt and vapor inclusions hosted by plagioclase. In that case, copper partitioning during the metal transportation by an MVP is likely equilibrium partitioning again.

High copper diffusivity may also be responsible for rapid Cu loss from tektites, resulting in large kinetic copper isotope fractionation. Moynier et al. (2010) measured copper isotope ratios in tektites, and found almost all the tektites are greatly enriched in heavy Cu isotope ($< \delta^{65}\text{Cu} < +6.98\%$), where $\delta^{65}\text{Cu} = ((^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}/(^{65}\text{Cu}/^{63}\text{Cu})_{\text{standard}}-1) \times 1000\%$. Because tektites might have been heated to a temperature as high as >2800 °C (Walter 1967) for a short period of time, and the half-condensation temperature for copper is 1037 K (Lodders 2003), Moynier et al. (2010) proposed that copper isotopes were fractionated by evaporation loss, with lighter isotopes escaping more rapidly into the volatile phase. However, by comparing with their previous study of zinc isotope fractionation in tektites (Moynier et al. 2009), the authors found zinc isotopes to be less fractionated than copper isotopes in the same set of samples ($\delta^{66/64}\text{Zn}$ up to 2.49‰ comparing to $\delta^{65/63}\text{Cu}$ up to 6.98‰). If Cu and Zn loss is due to open system volatization (such as Raleigh fractionation in which a tektite droplet is uniform compositionally and isotopically), because zinc has a much lower half-condensation temperature ($T_c \sim 726$ K, Lodders 2003) than Cu, zinc isotopes would be more fractionated than copper isotopes, opposite to the observations. Moynier et al. (2010) explained the more fractionated copper isotopes than
zinc isotopes by the higher diffusivity of Cu$^+$ than Zn$^{2+}$ in silicate melts, and argued that the isotopic fractionation in tektites was controlled by the competition between the evaporation flux and the diffusion flux. They employed the diffusivity model by Mungall (2002b) and found Cu$^+$ diffusivity to be about 2 orders of magnitude higher than Zn$^{2+}$ diffusivity, and used this result to explain why copper isotopes are more fractionated than zinc isotopes. Using literature Zn$^{2+}$ diffusion data in rhyolitic melt (Baker and Watson, 1988) and our Cu$^+$ diffusion data, and assuming melt composition does not affect Cu$^+$ diffusivity significantly (our preliminary data reported in Ni et al., 2015 show that Cu$^+$ diffusivity in anhydrous rhyolitic melt is only ~50% smaller than Cu$^+$ diffusivity in basalt), Cu$^+$ diffusivity is about 3 orders of magnitude higher than Zn$^{2+}$ diffusivity (Fig. 7). Hence, Cu and Zn diffusion data are consistent with the explanation by Moynier et al. (2010).

**IMPLICATIONS**

Our copper diffusion data in basaltic melt show that, copper diffusivity in anhydrous basaltic melt is as high as that of sodium at ~1400 ºC, and has a small activation energy (~100 kJ/mol). The measured copper diffusivities are ~3 times smaller than the values predicted by a previous diffusivity model in the same melt, and ~3 times larger than reported copper diffusivities in the Na$_2$Si$_2$O$_5$ melt. In basaltic melt, copper diffusivity is ~30 times higher than sulfur diffusivity, indicating that during the formation of magmatic sulfide deposit, when immiscible sulfide liquid drops separate from the host magma and settle to the bottom of the magma chamber, the partitioning of copper into the sulfide liquid phase can be regarded as equilibrium partitioning. In the process of porphyry-type deposit formation, where metal transport from the more mafic magma to the more felsic magma by a magmatic volatile phase is
possible, high diffusivity of copper also ensures the efficiency of copper diffusion into and away from the volatile phase. Because of the high diffusivity of copper in basaltic melt, kinetic limitation of copper partitioning during ore formation is less likely a concern. This also means copper may be diffusively fractionated from other ore elements with smaller diffusivity.

The results of our study can also be used to discuss the kinetic role in evaporation loss and isotope fractionation of volatile elements in impact glasses. The more fractionated copper isotopes than zinc isotopes as observed in tektites can be explained by the higher diffusivity of Cu⁺ than Zn²⁺ in silicate melts, despite the lower condensation temperature for zinc than copper. Similar processes may also happen to lunar volcanic and impact glasses on the surface of Moon.

ACKNOWLEDGEMENTS

We thank two anonymous reviewers for their constructive comments, and James Jolles for informal comments. P. Ni thanks Zhengjiu Xu for training and help with piston-cylinder experiments, Gordon Moore, Yang Chen and Yi Yu for help with microprobe analysis and Chenghuan Guo for discussion about synthesizing glasses. This work was partially supported by NSF grants EAR-1019440 and EAR-1524473. The electron microprobe used in this study was acquired using NSF grant EAR-9911352.

REFERENCES CITED


**FIGURE 1.** Copper concentration profiles measured across the center sections of four synthesized glass beads. Distances shown in the figure are relative to the approximate center of the glass beads.

**FIGURE 2.** Illustration of the experimental design for our diffusion couple experiments (modified from Wang et al. 2009). Interface between the two glass halves are aligned to be at the center of the graphite heater to minimize temperature gradient. The scale in the figure is not exact.

**FIGURE 3.** Cu diffusion profile of experiment Cudiffcp 3.1. Probe results obtained on two different days are in open symbols and closed symbols respectively. Traverses 3 to 5 were moved down by 194 ppm to account for the background shift relative to traverses 1 and 2. The diffusivity given in the figure is based on fit of all 5 traverses after the correction for the background shift.

**FIGURE 4.** Optical microscope images of experimental charges. (a) Cudiffcp 3.1; (b) Cudiffcp 7.2. The Cu-free glass is on the top while the Cu-bearing glass is at the bottom. In (a), two pieces of glasses were welded together after the experiment; position of the interface is indicated by the two dents on both sides of the glasses. In (b), there is a large crack right at the interface after the experiment. Red dashed lines show the position of microprobe traverses.

**FIGURE 5.** Cu concentration profiles for all diffusion couple experiments in this study. Different symbols in each plot represent different traverses analyzed on the sample perpendicular to the interface.
**FIGURE 6.** Arrhenius plot of all copper diffusion data obtained in this study. The linear fitting is for 1 GPa experiments only. Errors shown on diffusivities are at 1σ level.

**FIGURE 7.** Comparison of Cu diffusivities obtained in this study to literature diffusivity data for other elements in anhydrous basaltic melts unless otherwise indicated. a. Cu diffusivities at 0.5 GPa from this study; b. Cu diffusivities at 1.5 GPa from this study; c. Cu diffusivities at 1 GPa from this study; d. Cu diffusivities in dry basaltic melt by Mungall’s model (Mungall 2002b); e. Cu diffusivities in Na$_2$Si$_2$O$_5$ melt at 1000-1400°C and1 bar (von der Gonna and Russel 2000); f. S diffusivities at 1225-1450 °C and 0.5-1 GPa (Freda et al. 2005); g. H$_2$O$_t$ diffusivities at 1 wt% water, 400-1500 °C, and ≤ 1 GPa (Zhang and Ni 2010); h. Cl tracer diffusivities at 1250-1450 °C and 0.5-1 GPa (Alletti et al. 2007); i. Li tracer diffusivities at 1300-1400 °C and 1 bar (Lowry et al. 1981); j. Na tracer diffusivities at 1300-1400 °C and 1 bar (Lowry et al. 1982); k. Co tracer diffusivities at 1300-1400 °C and 1 bar (Lowry et al. 1982); l. Zn diffusivities in anhydrous rhyolite melt at 898-1400 °C and 0.01–1 GPa (Baker and Watson 1988).
### Table 1. Chemical compositions of the synthesized basaltic glasses.

<table>
<thead>
<tr>
<th>wt%</th>
<th>Et1 ave</th>
<th>Et1Cu ave</th>
<th>Et2 ave</th>
<th>Et2Cu ave</th>
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<tr>
<td></td>
<td>sd (1σ)</td>
<td>sd (1σ)</td>
<td>sd (1σ)</td>
<td>sd (1σ)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>47.26</td>
<td>0.39</td>
<td>46.18</td>
<td>0.72</td>
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<tr>
<td>TiO₂</td>
<td>1.62</td>
<td>0.06</td>
<td>1.63</td>
<td>0.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.52</td>
<td>0.27</td>
<td>18.17</td>
<td>0.64</td>
</tr>
<tr>
<td>FeO₁</td>
<td>10.47</td>
<td>0.21</td>
<td>10.67</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>5.83</td>
<td>0.07</td>
<td>5.84</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO</td>
<td>10.69</td>
<td>0.06</td>
<td>10.69</td>
<td>0.06</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.45</td>
<td>0.12</td>
<td>4.45</td>
<td>0.08</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.03</td>
<td>0.04</td>
<td>1.90</td>
<td>0.04</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>122</td>
<td>35</td>
<td>1174</td>
<td>121</td>
</tr>
<tr>
<td>Total</td>
<td>99.88</td>
<td>99.65</td>
<td>99.76</td>
<td>99.98</td>
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</tbody>
</table>

Reported data are electron microprobe measurements of far-field compositions on the samples after experiments, except for Cu, whose concentrations are measured on original glasses before experiments. At least 20 points were analyzed and averaged for each glass composition. Details about the microprobe analysis can be found in Analytical Methods.
## Table 2. Summary of experimental conditions and results.

<table>
<thead>
<tr>
<th>Exp#</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>$t_1$ (s)</th>
<th>$t_2$ (s)</th>
<th>$D \times 10^{12}$ m$^2$/s</th>
<th>Error (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cudiffcp 1.1</td>
<td>1</td>
<td>1314</td>
<td>429.3</td>
<td>464.6</td>
<td>403.7*</td>
<td>37.1</td>
</tr>
<tr>
<td>Cudiffcp 1.2</td>
<td>1</td>
<td>1314</td>
<td>124.2</td>
<td>162.4</td>
<td>439.4</td>
<td>26.8</td>
</tr>
<tr>
<td>Cudiffcp 2.1</td>
<td>1</td>
<td>1397</td>
<td>126.4</td>
<td>162.7</td>
<td>678.3</td>
<td>43.7</td>
</tr>
<tr>
<td>Cudiffcp 3.1</td>
<td>1</td>
<td>1509</td>
<td>105.1</td>
<td>140.5</td>
<td>930.9</td>
<td>6.3</td>
</tr>
<tr>
<td>Cudiffcp 4.2</td>
<td>0.5</td>
<td>1313</td>
<td>122.1</td>
<td>157.2</td>
<td>505.8</td>
<td>55.9</td>
</tr>
<tr>
<td>Cudiffcp 4.3</td>
<td>0.5</td>
<td>1306</td>
<td>119.9</td>
<td>157.7</td>
<td>514.3</td>
<td>71.7</td>
</tr>
<tr>
<td>Cudiffcp 4.4</td>
<td>0.5</td>
<td>1298</td>
<td>131.2</td>
<td>161.8</td>
<td>355.3</td>
<td>31.9</td>
</tr>
<tr>
<td>Cudiffcp 5.1</td>
<td>1</td>
<td>1575</td>
<td>95.6</td>
<td>137.7</td>
<td>1237.3*</td>
<td>157.5</td>
</tr>
<tr>
<td>Cudiffcp 6.1</td>
<td>1.5</td>
<td>1410</td>
<td>125.7</td>
<td>151.1</td>
<td>465.5</td>
<td>28.9</td>
</tr>
<tr>
<td>Cudiffcp 7.2</td>
<td>1.5</td>
<td>1581</td>
<td>107.9</td>
<td>140.4</td>
<td>1104.6*</td>
<td>68.8</td>
</tr>
</tbody>
</table>

$P$ is corrected pressure; $T$ is corrected temperature; $t_1$ is the recorded duration at the target temperature ±1 °C; $t_2$ is the corrected duration using the method described in Experimental Procedure.

*Diffusivities of these three experiments were fitted using the solution for a finite diffusion medium as explained in the text.
Fig. 1

![Graph showing Cu content vs. distance from center (mm)](image_url)
Figure 2

Graphite furnace

BaCO3 pressure medium

MgO

Graphite disc

Capsule

Type S thermocouple

Graphite

Cu-free glass

Cu-doped glass

Graphite
cap

2.0mm

1.5 mm

4.0mm

1.5 mm
Fig. 3

Cudiffcp 3.1

1509 °C
1 GPa
140.5 s
$D=930.9 \mu m^2/s$

Cu (wt%)
Fig. 4b

Cudiffcp
7.2

Graphite capsule

Line1 top
Line2 top
Line3 top

Interface

1000 μm

Line1 bottom
Line2 bottom
Line3 bottom

MgO
Fig. 5a

Cudiffcp 1.1

1314 °C
1 GPa
465 s

\( D = 403.7 \, \mu m^2/s \)

(a) (finite method)
Fig. 5b

![Graph showing Cu (wt%) vs. Distance from interface (μm) for different lines with fitting.](image)

- **Cu (wt%)**
- **Distance from interface (μm)**

**Legend:**
- Blue circles: Line 1
- Green squares: Line 2
- Red triangles: Line 3
- Black line: Fitting curve

**Data Points:**
- **1314 °C**
- **1 GPa**
- **162.4 s**
- **$D=439.3 \, \mu m^2/s$**
Fig. 5c

Cudiffcp 2.1

1397 °C
1 GPa
162.7 s
$D=678.4 \, \mu m^2/s$

Cu (wt%) vs Distance from interface (µm)

- 1397 °C
- 1 GPa
- 162.7 s
- $D=678.4 \, \mu m^2/s$
Fig. 5d

Cudiffcp 4.2

d)

1313 °C
0.5 GPa
157.2 s
$D=505.8 \, \mu m^2/s$

Cu (wt%) vs. Distance from interface (μm)
Fig. 5e

The figure shows a plot of Cu (wt%) against distance from the interface (µm) at 1306 °C, 0.5 GPa, and 157.7 s. The diffusion constant, $D$, is calculated to be 514.3 µm²/s.
Fig. 5f

Cudiffcp 4.4

1298 °C
0.5 GPa
161.8 s

$D = 355.3 \, \mu m^2/s$

Cu (wt\%) vs. Distance from interface (µm)

- Line 1
- Line 2
- Line 3
- Fitting

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Fig. 5g

Cudiffcp 5.1

![Graph showing Cu concentration vs. distance from interface. The graph includes data points and lines of best fit. Key parameters: 1575 °C, 1 GPa, 138 s, $D=1237.3 \mu m^2/s$ (finite method).]
**Fig. 5h**

![Graph showing Cu (wt%) concentration over distance from interface (µm).](image)

- Temperature: 1410 °C
- Pressure: 1.5 GPa
- Time: 151.1 s
- Diffusion coefficient: $D = 465.5 \mu m^2/s$
Fig. 5i

Cudiffcp 7.2

1581 °C
1.5 GPa
140 s
$$D=1104.6 \, \mu m^2/s$$
(Finite method)

\[ \text{Cu (wt\%)} \]

\[ \text{Distance from interface (\mu m)} \]

Line 1
Line 2
Line 3
Finite fitting
Fig. 6

Cu diffusivities in basalt

\[ \ln D = m_1 M_0 + m_2 \]

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>-11.813</td>
<td>0.8375</td>
</tr>
<tr>
<td>m2</td>
<td>-14.122</td>
<td>0.4969</td>
</tr>
</tbody>
</table>

Chisq: 0.013654
R: 0.99255

1 GPa
0.5 GPa
1.5 GPa