Cu and Fe diffusion in rhyolitic melts during chalcocite “dissolution”:
Implications for porphyry ore deposits and tektites

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ABSTRACT

Copper diffusion plays an important role in natural processes, such as metal transport during the formation of magmatic-hydrothermal porphyry-type ore deposit and Cu isotope fractionation during tektite formation. Copper diffusion data in natural silicate melts, however, are limited. In this study, chalcocite (Cu2S) “dissolution” experiments were carried out by using chalcocite-rhyolite diffusion “couples” to study Cu (and S) diffusion in rhyolitic melts. Instead of chalcocite dissolution as initially expected, our experiments show that Cu is transferred from the chalcocite crystal to the rhyolitic melt, and Fe is transferred from the rhyolitic melt to chalcocite, whereas the S concentration profile in the rhyolitic melt is essentially flat. From the Cu and Fe exchange profiles in the rhyolitic melts, Cu diffusivities and Fe diffusivities are obtained and reported.

Copper diffusivity in rhyolitic melts containing 0.10 to 5.95 wt% H2O at temperatures of 750 to 1391°C and pressures of 0.5 to 1.0 GPa can be described as:

\[ D_{\text{Cu}}^{\text{Rhy}} = \exp \left[ -(14.75 \pm 0.35) - (0.23 \pm 0.10)w - \frac{(11647 \pm 491) - (698 \pm 117)w}{T} \right] \]

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which allows the estimation of an activation energy for diffusion in dry rhyolitic melts to be 96.8±4.1 kJ/mol. In the above equation, diffusivity ($D$) is in m$^2$/s, $T$ is the temperature in K, $w$ is the H$_2$O concentration in the rhyolitic melts in wt% and all errors reported are at 1σ level.

Combining Cu diffusion data from this study and previous data in basaltic melt gives a general equation for Cu diffusivity in natural silicate melts:

$$D_{Cu} = \exp \left[-(17.3\pm0.9)+(3.8\pm1.5)(\text{Si}+\text{Al}-\text{H}) - \frac{(4403\pm1094)+(9700\pm1921)(\text{Si}+\text{Al}-\text{H})}{T}\right],$$

where Si+Al-H is the cation mole fraction of Si plus Al minus H in the silicate melt on a wet basis.

Iron diffusivities obtained in this study in anhydrous to 6 wt% H$_2$O rhyolite are combined with previous data to get a general equation for Fe diffusion in rhyolitic melts:

$$D_{Fe}^{Rhy} = \exp \left[-(16.1\pm1.7) - \frac{(19859\pm2541)-(1218\pm135)w}{T}\right].$$

Our data demonstrate that Cu diffusion is faster than H$_2$O or Cl in rhyolitic melts containing 6 wt% water, which indicates that the scavenging and transport of Cu by a magmatic volatile phase during formation of porphyry-type ore deposits is not limited by diffusion of Cu. Based on our experimental data, Cu diffusivity is almost 4 orders of magnitude higher than Zn in anhydrous rhyolitic melts, which supports the explanation of more diffusive loss of Cu leading to more fractionated Cu isotopes than Zn isotopes in tektites.

**Key words**: copper diffusion, iron diffusion, porphyry-type deposits, kinetic fractionation
INTRODUCTION

Porphyry-type ore deposits are important sources for metals, such as Cu, Au, Mo and Ag, comprising~57%, 10%, 99% and 13%, respectively, of the world’s total discovered quantities of these metals (Singer 1995). In order to form a porphyry-Cu deposit, the Cu concentration must be enriched from a crustal average concentration of ~30 ppm (Rudnick and Gao 2014) to a typical mineable grade of ~0.2 to 2 wt% in the porphyry environment (Simon and Ripley 2011). This 2 to 3 orders of magnitude enrichment is accomplished by, among other things, the efficient scavenging of Cu by a magmatic volatile phase (MVP) exsolved from silicate melts in Earth’s upper continental crust (e.g. Candela 1997; Wilkinson 2013). The exsolution of an MVP from silicate melts can occur by decompression, which reduces the solubility of volatiles in the melt (i.e., first boiling; Audetat and Simon 2012), or crystal fractionation that occurs during cooling of magma in shallow level magma chambers (i.e., second boiling, Candela 1997; Audetat and Simon 2012). Since the exsolved MVP bubbles are less dense than the surrounding silicate magma, at a volume fraction >10% the bubbles can form an interconnected network and rise through the magma chamber (Candela 1991; Parmigiani et al. 2016), simultaneously scavenging ore metals, such as Cu, Au, Mo and Ag from the surrounding melt, and possibly also via resorption of metal sulfides (Audetat and Simon 2012). Huber et al. (2012) quantitatively modeled the partitioning and transport of metals by an MVP that ascends through a magma chamber, and determined that the efficiency of metal extraction (i.e., the total quantity of a metal removed from the magma chamber and transported into the overlying porphyry environment) is dependent on a balance between diffusion of the metal in the silicate melt, and the advection of the MVP through the magma chamber. They showed that elements with high diffusivities will more likely reach equilibrium with the MVP and be efficiently transported, whereas elements...
with low diffusivities might not equilibrate with a rapidly ascending MVP and, therefore, become less efficiently scavenged and transported. Such an effect can lead to diffusive fractionation of metals, and hence variability of metal ratios in magmatic-hydrothermal ore deposits.

Moynier et al. (2009, 2010) studied Cu and Zn isotope systematics in tektites, and found that Cu isotopes are more fractionated than Zn isotopes in the same batch of tektites. The fractionation of Cu and Zn isotopes in tektites can be explained by the evaporative loss of Cu and Zn from the tektites during their formation, when a short period of high temperature was experienced (as high as >2800 °C, Walter 1967). However, if condensation temperature alone controlled isotope fractionation, the greater degree of fractionation of Cu isotopes relative to Zn isotopes is inconsistent with the lower half condensation temperature of Zn \( T_{1/2} \sim 726 \) K, Lodders 2003) than Cu \( T_{1/2} \sim 1037 \) K, Lodders 2003). The authors invoked a “diffusion-limited” mechanism, and suggested that the more fractionated Cu isotope signature is due to the higher diffusivity of Cu\(^+\) than Zn\(^{2+}\) in silicate melt. The higher diffusivity of Cu would lead to more rapid loss of Cu from the tektite during heating, and would result in more fractionated Cu isotopes than Zn isotopes in tektites.

Despite the potential role of Cu diffusion in magmatic-hydrothermal porphyry-type ore formation and tektite and other isotope fractionation processes, Cu diffusion data are limited. To our knowledge, only two experimental studies on Cu diffusion have been conducted. Von der Gonna and Russel (2000) studied Cu diffusion in a Na\(_2\)O·2SiO\(_2\) melt using a voltammetry method. Ni and Zhang (2016) investigated Cu diffusion in anhydrous basaltic melt by the diffusion couple method. Because porphyry-type deposits typically originate from water-saturated intermediate to felsic magmas (Simon and Ripley 2011), and tektites are often
“rhyolitic” in terms of their silica content (e.g., Cassidy et al. 1969), Cu diffusion data from these two studies cannot be directly applied to elucidate the evolution of porphyry-type ore deposits or isotope fractionation in tektites. In this study, we report Cu diffusion data in rhyolitic melts containing 0.1 to 5.9 wt% H2O from chalcocite “dissolution” experiments, and discuss the implications of the data in the context of natural processes of porphyry-type Cu deposit formation and Cu isotope fractionation in tektites.

EXPERIMENTAL AND ANALYTICAL METHODS

Starting materials

In this study, chalcocite “dissolution” experiments were carried out to determine Cu diffusivities over the temperature range of 750 °C to 1391 °C in silicate melts with rhyolitic compositions and with H2O concentrations ranging from “anhydrous” (0.10 ~ 0.24 wt%) to 5.9 wt%. “Dissolution” is referred to in quotation marks because, even though the experiments were initially designed as chalcocite dissolution to study the diffusion of both Cu and S, the actual chemical reaction observed in our experiments is close to “metal exchange” as discussed below.

A cluster of chalcocite (Cu2S) crystals purchased from a gem dealer was used as the starting material. As examined using scanning electron microscope (SEM) and election microprobe (EMP), the chalcocite crystals are mostly pure Cu2S (20.36 wt% S, 81.10 wt% Cu and 0.00 wt% Fe), but occasionally have inclusions of bornite (Cu5FeS4) and Cu metal (compositions plotted in Fig. 1). When preparing samples for the experiments, care was taken to avoid any impurities in the chalcocite crystal. Six rhyolitic glasses with H2O concentrations from 0.1 wt% to 5.9 wt% were used for this series of experiments. The major element compositions
and H₂O concentrations of the starting glasses are summarized in Table 1. Among these rhyolitic glasses, NCO is a natural glass from the Newberry Crater, Oregon; bb7b-25 is a natural obsidian glass from the Mono Crater, California; CIT is a natural obsidian glass from Coso Range, California, which was previously used for infrared (IR) spectral calibration by Newman et al. (1986); and GMR+2, GMR+4 and GMR+6 are glasses synthesized by hydration of obsidians from Glass Mountain, California, which were previously used in studies for viscosity and water speciation of rhyolites (Hui and Zhang 2007; Hui et al. 2008). The SiO₂ concentration in the rhyolites, on a dry weight basis, ranges from 73.4 to 76.7 wt% (the concentrations reported in Table 1 include H₂O). Glass cylinders rather than powders were used for the experiments. These starting glass cylinders already contain dissolved H₂O, and no liquid H₂O was added into the capsule during the experiment.

**Piston cylinder experiments**

In preparation for piston cylinder experiments, a chalcocite crystal and rhyolitic glass were first cut and prepared into long cylinders with a diameter of ~2 mm. A wafer was then cut from each of the cylinders, with a thickness of ~1 mm for the chalcocite wafer and 1 to 2 mm for the rhyolitic glass wafer depending on the estimated profile length for each experiment. The wafers were doubly polished with progressively finer sandpapers, finishing with 0.3-μm alumina powders. After examination under optical microscope, chalcocite and rhyolitic glass wafers with the least amount of impurities were chosen for experiments. After cleaning and drying, the wafers were placed into a graphite capsule, with the rhyolite glass on top and the denser chalcocite at the bottom. The graphite capsule was fit tightly into a drilled hole of an MgO rod, then into a graphite furnace, and finally into a barium carbonate pressure medium. Effort was
made to place the interface right at the center of the graphite furnace to minimize temperature
gradients across the sample.

All piston cylinder experiments were carried out at the University of Michigan. The
pressure was measured by a Heise digital pressure gauge. A 5% correction is applied to the
nominal pressure based on the calibration by Ni and Zhang (2008) on the same piston cylinder
apparatus. The experimental charge was pressurized to 15% above the target pressure, and then
allowed to relax overnight at 200 ºC to close gaps inside the assembly. After relaxation, the
sample was heated up to the target temperature in ~50 s using a programmed temperature
controller. Pressure was maintained manually using an Enerpac electric pump. The pressure
fluctuation was within 1% during the experiment, ~10% during heating up and ~20% during
quench. Temperature was measured by a Type-S thermocouple (Pt90Rh10-Pt) and controlled by
a Eurotherm controller. Temperature correction based on the distance from the thermocouple tip
to the interface was applied using the calibration of Hui et al. (2008). The thermocouple tip is
typically 2 to 2.5 mm away from the interface. The temperature variation across the sample is
usually ≤13 ºC. No temperature overshoot was observed during the experiment, and the
temperature fluctuation recorded by the temperature controller was ±1 ºC during the experiment.
After a designated duration, the assembly was quenched to room temperature at a rate of ~100
ºC/s by turning off the power. The whole sample assembly was recovered from the piston
cylinder apparatus and preserved in epoxy. Because of the strong secondary fluorescence effect
for Cu analysis by EMP as realized in the preliminary analyses (see analytical methods), the
chalcopyrite crystal was removed from the sample charge before probe analysis. Removal of the
chalcopyrite crystal was done by first doubly polishing the sample to a thin wafer (<1 mm thick),
and then cutting through the graphite capsule and physically pushing the chalcopyrite out of the
sample disc with tweezers. The hole in the sample disc after chalcocite removal was filled with epoxy to better preserve the sample glass. The rhyolitic melt does not wet the chalcocite crystal, and there is typically a gap between chalcocite and glass produced by expansion of the assembly during depressurization during and after quench, thus reducing the difficulty in the removal process. The chalcocite crystal is usually a whole undamaged piece after removal, which is then preserved in a separate epoxy disc.

Analytical methods

**EMP analyses of major elements.** Major element compositions and Cu concentrations were analyzed in separate sessions using the CAMECA SX-100 electron microprobe at the University of Michigan. Major oxides were analyzed using a 5 nA focused beam with an accelerating voltage of 15 kV. Standards used for the analyses are: albite (ALBA) for Na, natural rhyolitic glass (VGRH) for Si, potassium feldspar (GKFS) for K, wollastonite (WOLL) for Ca, synthetic ferrosilite (FESI) for Fe, synthetic geikielite (GEIK) for Ti, forsterite (FOBO) for Mg and sillimanite (SILL) for Al. Counting time for each element was 20 to 40 seconds on the peak, and 10 to 20 seconds on each side of the background. A special routine was employed for counting Na (extrapolating to photon counts at zero time) to correct for Na loss during analysis.

**Secondary fluorescence effect in EMP analysis for Cu.** Although the strong secondary fluorescence effect on Cu analysis using EMP was avoided by removing chalcocite crystal from the capsule after experiment, a brief description of the effect is included below as a reference for future studies. Our test analyses before we decided to remove chalcocite from the experimental charge show that secondary fluorescence effect is a significant concern in EMP analysis for trace
amount of Cu (i.e. hundreds of ppm) when a Cu-rich phase is within hundreds of micrometers of
the analytical spot. In our test analyses, a chalcocite wafer and a rhyolitic glass wafer (CIT) were
polished and placed into a graphite capsule, then preserved in epoxy and polished to the center
section for EMP analysis. Traverses were measured in the glass perpendicular to the contact
between the chalcocite crystal and the glass, and the results are plotted in Fig. 2a (Line 1 through
Line 3). The results show that the secondary fluorescence effect for Cu is especially large in
EMP analysis compared to other elements such as Zr (Harrison and Watson 1983; Zhang and Xu
2016), Cr (Zhao et al. 2015), and Sn (Yang et al. 2016), for example. Copper concentration in
this natural glass is low and roughly uniform (2.7±1.1 ppm, based on analyses of Chal-Rhy-4-2).
The secondary fluorescence profile, however, yields over 6000 ppm Cu near the contact with the
chalcocite, 1000 ppm Cu at 100-µm distance away from the chalcocite, and extends more than
200 µm into the glass (Fig. 2a).

Secondary fluorescence effect for Cu analysis was also estimated by Monte Carlo
simulations using the software package PENEPMA (Llovet and Salvat 2008). The geometry
used in the simulation was set up following the sample orientation, where a chalcocite crystal
(Cu₂S) and a rhyolitic glass (CIT) were placed on a plane right next to each other. The electron
beam was applied perpendicular to the glass surface with an initial energy of 15 keV. Movement
of the electrons and all secondary particles and X-rays was tracked until their energies were
below 7 keV. A pseudo-spectrometer covering the entire sample surface was used to record X-
ray spectra from 7 kV to 15 kV. About 5 million electrons were simulated at each spot to achieve
a statistical precision of ~1% on the Cu Kα peaks. Then the X-ray spectra obtained from Monte
Carlo simulations were convolved assuming a spectral resolution of 40 eV, after which the peak
heights of Cu Kα were measured. The same simulation was run on a target of Cu metal as the
standard, and peak count ratios on sample over standard are plotted in Fig. 2b, and compared to
EMP measurements by three wavelength-dispersive X-ray spectrometers. Two key conclusions
can be drawn from the comparison. Firstly, the Monte Carlo simulation matches the
measurements well. Secondly, the secondary fluorescence effect on each WDS detector is
different based on its relative orientation to the sample (Fig. 2b). According to the
measurements, the WDS detector records higher counts of secondary fluorescence signal of Cu
Kα if the chalcocite side of the couple is facing the detector (Spectrometer 4). This phenomenon
is similar to the findings of a previous study on secondary fluorescence effect of Nb Kα in an
Nb-Pd₃HfAl couple (Fournelle et al. 2005). One possible explanation is that chalcocite has a
smaller mass attenuation coefficient for Cu Kα than rhyolitic glass, so that more Cu Kα X-rays
survived the pathway through the chalcocite crystal and reached the detector.

The Cu diffusion profiles in our samples are typically hundreds of micrometers long, with
an interface concentration of less than 1000 ppm. The strong secondary fluorescence effect
completely overwhelms the actual Cu diffusion profile (Fig. 2a, Line 4). Hence, we decided to
remove chalcocite from our sample charge after experiment for precise EMP analysis of Cu.

**EMP analyses of Cu.** With chalcocite removed, Cu concentrations were measured on glass in
dedicated EMP sessions for Cu alone with three spectrometers counting Cu Kα peak for 240 s at
the same time, and then 120 s counting on background on each side of the peak. A focused beam
was used for the anhydrous rhyolite glasses (NCO and CIT), while a 10 µm scanning beam was
used for the hydrous glasses (bb7b-25, GMR+2, GMR+4 and GMR+6) to minimize the beam
damage during the analysis. The beam current was 40 nA when the interface Cu concentrations
were high (e.g. higher than 500 ppm), achieving a detection limit of ~80 ppm. Otherwise a beam
current of 100 nA was used to achieve a detection limit of ~50 ppm for Cu. Previously analyzed major element compositions of the glasses (Table 1) were input into the software for ZAF correction. NIST SRM 610 was used as a secondary standard to verify the EMP analysis of Cu. The reported Cu concentration in NIST 610 is 421.7 ppm (Pearce et al. 1997), and our analyses yielded 420 to 540 ppm Cu during different sessions for this standard, indicating that EMP analyses of Cu may have systematic errors up to 120 ppm. EMP data of Cu concentrations are relatively low in precision compared to Laser-ablation ICP-MS (see below), but have higher spatial resolution (<10 µm), which helps to capture the short quench profile near the interface. In addition, the multiple electron microprobe traverses verifies the horizontal homogeneity and help to rule out the concern of convection in our experiments.

Laser-ablation ICP-MS analyses of Cu. Copper concentration profiles were also analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the University of Windsor. All LA-ICP-MS data reported in this study were analyzed by using a PhotonMachines Analyte Exicite 193 nm, short-pulse-width (sub 4 ns), Ar-F excimer laser ablation system coupled with an Agilent 7900, fast-scanning quadrupole ICP-MS. The operating conditions are summarized in Table 2. Copper concentration profiles were obtained by analyzing multiple spots along a traverse perpendicular to the interface. For each spot analysis, a 25-µm-diameter laser beam was used to ablate the sample surface at a frequency of 25 Hz for a duration of 30 s. The first few seconds of each transient laser signal were excluded during data processing to eliminate possible signal contribution from surface contamination (Pettke et al. 2012). NIST 610 synthetic glass standard was analyzed at least every hour for use as an external calibration standard and to assess
instrumental drift. The isotope $^{44}$Ca was used as the internal calibration standard to compensate for differences in ablation behavior between calibration standards and unknowns, and to obtain Cu concentrations. A detection limit of ~ 0.04 ppm for Cu was achieved for our analysis using the operating conditions presented in Table 2.

**FTIR analyses.** Concentrations of H$_2$O in the starting glasses and in glasses after diffusion experiments were measured using a Perkin-Elmer GX Fourier Transform Infrared Spectrometer (FTIR) at the University of Michigan. Sample glasses were typically doubly polished to ~500 µm thickness for analysis. An NIR source and a CaF$_2$ beamsplitter were used. Molecular water and OH concentrations were determined by measuring the absorption peaks at 5230 and 4515 cm$^{-1}$ respectively. The baselines were fit with a flexi curve as shown in Zhang et al. (1997). Total H$_2$O concentrations were obtained by summing the concentrations of both species calculated by using calibrated molar absorptivities from Newman et al. (1986).

To assess possible H$_2$O loss during the experiments, the H$_2$O concentration was measured in hydrous glass after the highest-temperature experiments at each H$_2$O concentration (Chal-Rhy-1-2, Chal-Rhy-3-1, Chal-Rhy-7-1 and Chal-Rhy-14-1). For all four experiments, the amount of H$_2$O loss was negligible (<0.1 wt%) near the interface and at the center part of the glass where Cu diffusion profiles were measured. Therefore, measured H$_2$O concentrations in the starting glasses (Table 1) were adopted as the H$_2$O concentrations in the melt for all the experiments.

**RESULTS**
One example of the sample charge after an experiment is shown in Fig. 3a. The rhyolitic glasses show different optical features after the experiments. In general, synthetic hydrous glasses after low temperature experiments (Chal-Rhy-8-1, Chal-Rhy-11-1, Chal-Rhy-13-1) are opaque and slightly crystallized. Synthetic hydrous glasses after high temperature experiments (Chal-Rhy-3-1, Chal-Rhy-3-2, Chal-Rhy-7-1, Chal-Rhy-12-1, Chal-Rhy-14-1) show reddish color near the interface (e.g. Fig 4a, 4b). The reddish color in these glasses is caused by Cu-bearing nanoparticles in the glasses, as verified by high-magnification SEM images. These particles are too small in size (~75 nm in diameter) for their exact chemical composition to be quantified by SEM or EMP. Consistent diffusivities (within 20% difference) extracted from the time-series experiments (Chal-Rhy-3-1 and Chal-Rhy-3-2) that both contain Cu-bearing nanoparticles (Fig. 4a, 4b) suggest that these particles likely formed during quench. Because the analytical spot size is large, which averaged the nanoparticles in each spot, the nanoparticles do not affect the determination of diffusivities in our experiments. For all other experiments, the resulting glasses are transparent and colorless. An image of the sample charge after removing the chalcocite crystal is shown in Fig. 3b. Experimental conditions and results of all successful experiments are summarized in Table 3.

Absence of S diffusion profile

The original purpose of our experimental design was to obtain both Cu and S diffusivities in rhyolitic melts, as the dissolution of chalcocite (Cu$_2$S) would release Cu and S into the melt at an atomic ratio of 2:1. In addition, S diffusivity is lower than Cu diffusivity by a factor of 30 or more at the experimental temperatures, at least in basaltic melt (Ni and Zhang 2016). Hence, S concentration in the rhyolitic melt near the interface would be high and the difference between
interface S and far-field S concentrations would be easily measurable if chalcocite simply
dissolved into the rhyolitic melt. Despite success in obtaining Cu diffusion profiles, however, we
were unable to detect any S diffusion profile in the rhyolitic glass after the experiments. That is,
S concentration variation in the rhyolitic glass is consistently below the detection limit of ±20
ppm. After careful examination of the experimental charge and by repeating the experiments, we
recognized that the lack of S diffusion profile was not due to experimental errors, sample
preparation, or the analysis. Instead, S stayed in the chalcocite phase at our experimental
conditions. However, because:(i) S concentration in chalcocite is high, (ii) the chalcocite wafers
used in the experiments are relatively large in size, and (iii) S diffusion distance in chalcocite can
be significant, S concentration change in “chalcocite” after the experiments is small and is
difficult to detect. In order to better understand the chemical reaction happening during the
experiment, one experiment (Chal-Rhy-2-2) was specially conducted at 1096°C, in which we put
a 15-µm-thick wafer of chalcocite sandwiched between two 1.5-mm-thick rhyolitic glass wafers
(Fig. 5). The purpose of this experimental design was to use a small volume of chalcocite relative
to rhyolitic glass, with which we might be able to detect a change in chalcocite composition. The
composition of the chalcocite before the experiment was verified by EMP to be essentially pure
chalcocite (Cu$_{1.96}$Fe$_{0.00}$S). After the experiment, the composition of run-product “chalcocite” has
a composition of Cu$_{7.16}$Fe$_{0.27}$S$_4$, which roughly falls between the compositions of chalcocite
(Cu$_2$S) and bornite (Cu$_5$FeS$_4$), as shown in Fig. 1. This result indicates that during the experiment,
chalcocite lost Cu to and gained Fe from the surrounding rhyolitic melt, while S essentially
remained in the sulfide phase. In addition to the change of chalcocite composition in Chal-Rhy-
2-2, Cu and Fe diffusion profiles in the glass also agree with the loss of Cu to the melt and gain
of Fe from the melt. Results of experiment Chal-Rhy-2-2 explain why a S diffusion profile was
not observed in the rhyolitic melt, and also show that our experiments are better characterized as
Cu-Fe exchange experiments between chalcocite and rhyolitic melt, rather than chalcocite
“dissolution” experiments.

Cu diffusion profiles and fitting

Typically three EMP traverses and one LA-ICP-MS traverse were analyzed perpendicular
to the interface to obtain the Cu concentration profiles in the separated glass wafer of each
sample. All EMP and LA-ICP-MS Cu diffusion profiles besides those in Fig. 4 are plotted in Fig.
6. The Cu concentrations measured using EMP are often somewhat higher than determined using
LA-ICP-MS (e.g., Chal-Ryh-1-2 in Fig. 6a), which is likely due to the imperfect choice of the
WDS background for EMP analyses. Near (within 45 µm) the interface, the Cu concentration
decreases toward the interface in the high-spatial-resolution EMP profile in Fig. 6a. This is
because during quench, Cu preferentially partitions into the chalcocite phase as temperature
decreases, leading to a Cu concentration decrease in the rhyolitic glasses near the interface.
Similar effects have been observed previously, typically within ~20 µm distance from the
mineral-melt interface (Zhang et al. 1989; Chen and Zhang 2008; Yu et al. 2016; Zhang and Xu
2016). LA-ICP-MS has lower spatial resolution, and only the first point close to the interface
might be affected by this decrease. The presence of this quench-affected profile indicates that a
negligible amount of melt is lost during separation of the chalcocite crystal (Zhang et al. 1989;
Chen and Zhang 2008; Yu et al. 2016). When fitting the profiles to obtain Cu diffusivities, the
portion of the profiles affected by quench was excluded. Assuming interface motion is negligible
because chalcocite is not dissolving (total Cu mass gained by the melt is less than that contained
in 1 µm chalcocite, meaning negligible interface motion anyway), the Cu concentration profiles
were fitted by the analytical solution to the one-dimensional diffusion in semi-infinite medium with constant interface concentration (Crank 1975) to obtain Cu diffusivities:

\[
C = C_\infty + (C_0 - C_\infty) \text{erfc} \frac{x}{2\sqrt{Dt}},
\]

(1)

where \(C_0\) is the Cu concentration at the interface; \(C_\infty\) is the initial Cu concentration of the rhyolitic glass; \(x\) is the distance in the melt to the interface; \(D\) is Cu diffusivity and \(t\) is the experimental duration. Three parameters, \(C_0, C_\infty\) and \(D\) for each experiment, were obtained from curve fitting of the Cu concentration profile.

For experiment Chal-Rhy-3-1, which had the longest duration, it appears that diffusion reached the far-field boundary (Fig. 4a). Therefore, the Cu diffusion profile of Chal-Rhy-3-1 was fit with a different method, assuming a finite diffusion medium and an initial Cu concentration of 3.4 ppm (based on experiment Chal-Rhy-3-2, which used the same starting glass as Chal-Rhy-3-1).

Fitting results of all the experiments for both EMP and LA-ICP-MS results are summarized in Table 3. Although both EMP and LA-ICP-MS data were acquired for Cu diffusion profiles, Cu diffusivities fit from the LA-ICP-MS data were adopted for further discussion, while the high spatial resolution EMP data helped capture the short quench profile near the interface, and the multiple EMP traverses in each experiment helped to alleviate the concern of convection.

Fe diffusion profiles and fitting

Iron was observed to partition into the chalcocite during our experiments. Fe concentration profiles were measured by EMP to determine Fe diffusivities in the rhyolitic glasses (Fig. 7). Typically four traverses were analyzed by EMP perpendicular to the interface,
and the results are consistent with each other. Compared to the Cu diffusion profile in the same sample, the Fe diffusion profile is much shorter (e.g. Fig. 6a and Fig. 7a), which is consistent with the expectation that divalent Fe$^{2+}$ diffuses at a much lower rate than monovalent Cu$^{+}$ (Ni and Zhang 2016). Among the 15 experiments, resolvable Fe diffusion profiles were obtained in 8 experiments, as reported in Table 3. The remaining experiments either have an Fe diffusion profile that is too short (Chal-Rhy-4-2, Chal-Rhy-4-3 and Chal-Rhy-5-1) to be precisely analyzed, or exhibit anomalous behavior of Fe (experiment Chal-Rhy-8-1 has a flat Fe concentration profile in the rhyolitic glass; for Chal-Rhy-10-1, Fe concentration increases towards the interface). The anomalous behavior of Fe in experiments might be caused by the presence of bornite (Cu$_5$FeS$_4$) inclusions in the starting chalcocite. A small amount of bornite can greatly affect Fe activity in the chalcocite, but Cu activity would be affected to a much smaller degree. The Fe concentration profiles are fitted using Eq. (1), where the interface concentration ($C_0$) is lower than the far field concentration ($C_\infty$) for Fe diffusion. All the fitted Fe diffusivities are reported in Table 3.

**DISCUSSION**

**Possible convection**

Because rhyolitic melts typically have high viscosities ($\sim 10^3$ to $10^7$ Pa·s at our experimental conditions according to the viscosity model by Hui and Zhang 2007), convection is unlikely a problem in our experiments. Nonetheless, two experiments (Chal-Rhy-3-1 and Chal-Rhy-3-2) were conducted with different durations of $\sim 2$ min and $\sim 30$ min to check for possible convection. The two experiments gave similar Cu diffusivities that are within 20% difference, implying no convection in our experiments (Fig. 4a, b). In addiction, multiple traverses were measured in
each experiment to verify that convection did not affect the diffusion profiles. Typically three
EMP traverses ~200 μm away from each other were analyzed in each sample. Convection would
lead to inconsistent profiles along different traverses, which is not the case for our experiments
(Fig. 6). For LA-ICP-MS analysis, typically only one traverse was analyzed for each sample, but
three LA-ICP-MS traverses ~300 μm away from each other were analyzed for the experiment at
the highest temperature (Chal-Rhy-10-1). As can be seen in Fig. 6h, the concentration profiles
observed along three traverses match almost perfectly with each other, indicating that convection
was unlikely.

Sources of error

Uncertainty in temperature measurements is often an important source of error in diffusion
studies. Because the activation energy of Cu diffusion is small, the error caused by temperature
measurement uncertainties is within 10% for Cu diffusivities. Uncertainty in pressure
measurement is also a negligible source of error, because based on our results, no obvious
dependence of Cu diffusivity on pressure can be resolved from the 0.5 GPa and 1 GPa
experiments.

Another source of error in our experiments is from diffusion during heating and
quenching, especially because our shortest experimental duration is only ~2 min. Correction of
the effective experimental duration was done using the solution to diffusion problems with a
time-dependent diffusivity (Zhang 2008):

\[
t_c = \frac{\int_0^t \exp(-E/RT) dt}{\exp(-E/RT_0)},
\]
where \( t_e \) is the effective experimental duration in seconds, \( T_0 \) is the target temperature in K, \( T \) is the recorded temperature corrected to the interface, and \( E \) is the activation energy of Cu diffusion. The above equation is theoretically rigorous for diffusion couple experiments, and the effect of heating (~50 s) and cooling (~10 s) is accounted for as equivalent duration at the target temperature. In this study, however, not only the diffusivity \( (D) \), but also the interface Cu concentration \( (C_0) \) in Eq. (1) is temperature dependent. Hence, an error might occur while using this correction method for our study. Because \( \ln C_0 \) for experiments in 4 wt% and 6 wt% H2O rhyolitic melts is approximately linearly dependent on \( 1/T \), the diffusion equation is numerically solved given the recorded temperature history with \( C_0 \) and \( D \) as a function of temperature. One example of the simulated profile is shown in Fig. 6j, where both the EMP profile and the LA-ICP-MS profile were modeled. As can be seen in the figure, the simulated profile fits the measured concentration profile well. In particular, the quench-affected part of the EMP profile is also well reproduced. After excluding the first ~40 \( \mu \)m of the modeled profiles, fitting the simulated “data” using Eq. (1) and effective duration from Eq. (2) recovers the input diffusivity within 5%. Therefore, effective experimental durations calculated using Eq. (2) are valid, and are shown in Table 3.

Dependence of Cu diffusivity on temperature, pressure and melt composition

All Cu diffusivities determined in this study are summarized on an Arrhenius plot in Fig. 8a, together with Cu diffusivities from previous studies as a comparison. Copper diffusivities obtained using Newberry Crater Obsidian (NCO) at 0.5 GPa and 1 GPa fall onto a single linear trend, indicating that the pressure dependence of Cu diffusion is insignificant. In order to examine the effect of major element composition on Cu diffusion, we compare Cu diffusion in
anhydrous silicate melts with different compositions. As can be seen in Fig. 8a, Cu diffusivities measured in two anhydrous rhyolitic glasses NCO (73.5 wt% SiO$_2$) and CIT (76.5 wt% SiO$_2$) by this study are in agreement within error. Copper diffusivity in anhydrous rhyolitic melts is about 0.5 natural logarithm units lower than in anhydrous basaltic melt (Ni and Zhang 2016) and about 0.5 natural logarithm units higher than in an anhydrous Na$_2$Si$_2$O$_5$ melt, in which Cu diffusivity was determined using a voltammetry method (von der Gonna and Russel 2000). Hence, Cu diffusivity in silicate melts is only weakly dependent on major element composition. The lower Cu$^+$ diffusivity in anhydrous Na$_2$Si$_2$O$_5$ melt with NBO/T = 1 than in both anhydrous rhyolitic melt with NBO/T ≈ 0 and anhydrous Etna basalt with NBO/T ≈ 3/4 is somewhat unusual and may imply that Cu diffusivity determined using voltammetry is less reliable. Copper diffusivities calculated using the model by Mungall (2002) with a melt composition equivalent to NCO are also plotted in Fig. 8a for comparison. The calculated Cu diffusivities are a factor of 3 to 6 higher than our experimental data.

The concentration of H$_2$O in rhyolite has a stronger effect than major element compositions on Cu diffusivity. At 1000°C, every 2 wt% H$_2$O in the rhyolitic melt approximately doubles Cu diffusivity. Among monovalent elements, the effect of H$_2$O on Cu diffusion is greater than on Na (Zhang et al. 2010), but smaller than on Cs (Watson 1981). Fitting Cu diffusivities in anhydrous rhyolitic melts and rhyolitic melts containing 4 wt% and 6 wt% H$_2$O (Fig. 8a) give results as follows:
where diffusivities are in m²/s, T is temperature in K, and errors are given in 1σ.

Fitting results show that, increasing H₂O content in rhyolitic melts not only increases Cu diffusivity, but also decreases the activation energy. Activation energy of Cu diffusion in anhydrous rhyolitic melts is 99.4±5.8 kJ/mol, decreasing to 71.2±2.4 kJ/mol in 4 wt% H₂O rhyolitic melts and to 61.8±3.6 kJ/mol in 6 wt% H₂O rhyolitic melts. The decrease of activation energy is approximately linear with increasing H₂O concentration in the rhyolitic glass (Fig. 8b). Even in anhydrous rhyolitic melt, activation energy of Cu diffusion is small (~100 kJ/mol), consistent with our expectation that Cu is diffusing as Cu⁺ in the silicate melt.

If we consider H₂O concentration in the rhyolitic melt as an independent parameter, and fit all Cu diffusivities by minimizing \[ \sum [(\ln D_{i,\text{meas}}-\ln D_{i,\text{calc}})/\sigma_i]^2 \], where \( \ln D_{i,\text{meas}} \), \( \ln D_{i,\text{calc}} \), and \( \sigma_i \) are the logarithm of measured diffusivity, that of calculated diffusivity and 1σ error for \( \ln D_{i,\text{meas}} \), respectively, we obtain the following expression of Cu diffusivity in rhyolitic melts containing 0.1 to 6 wt% water:

\[
D_{\text{Cu}}^{\text{rhy}} = \exp\left[-(14.75 \pm 0.35) - (0.23 \pm 0.10) w - \frac{(11647 \pm 491) - (698 \pm 117) w}{T}\right], r^2=0.9849 \quad (4)
\]

where \( w \) is H₂O concentration in the rhyolitic melt in wt% and \( T \) is temperature in K. Eq. (4) reproduces all of our Cu diffusivity data to within 0.19 natural logarithm units.
Because we now have Cu diffusion data in rhyolitic melts and basaltic melts (Ni and Zhang 2016), effort was made to model all Cu diffusion data in natural silicate melts. In order to incorporate melt composition as a factor in Cu diffusivity, mole percent of Si+Al on wet basis was first tried to fit the data. Previously, Yu et al. (2015) used the single compositional parameter of Si+Al to successfully model SiO2 diffusivity in rhyolitic and anhydrous basaltic melts. Zhang and Xu (2016) were also able to use Si+Al to model Zr diffusivity in rhyolitic melts. Fitting our Cu diffusion data with Si+Al, however, does not reproduce the diffusivities in basaltic melts well. After some trials, we found that a single parameter of Si+Al-H can be used to account for melt composition in fitting Cu diffusivities in anhydrous basaltic melts and rhyolitic melts at 750°C to 1575 °C and 0.5 to 1.5 GPa:

\[
D_{Cu} = \exp \left\{ a + b(Si+Al-H) - \frac{c + d(Si+Al-H)}{T} \right\}, \quad r^2=0.9869
\]  

with \(a=-17.3\pm0.9, \ b=3.8\pm1.5, \ c=4403\pm1094\) and \(d=9700\pm1921\). In Eq. (5) \(D_{Cu}\) is in m²/s and \(T\) is temperature in K, and errors are given in 1σ. Eq. (5) reproduces Cu diffusivities in rhyolitic and basaltic melts (Ni and Zhang 2016) to within 0.35 natural logarithm units, with a 1σ standard deviation of 0.11 natural logarithm units. The success of using Si+Al-H instead of Si+Al in fitting Cu diffusivities indicates that the effect of H₂O in the melt on Cu diffusion is more than the simple dilution of network-forming cations as previously found for Zr diffusion (Zhang and Xu 2016) and Si diffusion (Yu et al. 2015). The difference in the compositional dependence of Cu diffusivity versus Si and Zr diffusivity may be attributed to the difference between the low-field strength ion Cu and high field strength ions Zr and Si.

As discussed earlier, the pressure effect on Cu diffusion is small. Incorporating pressure in the fitting yields a fitting error that is larger than the absolute value of the fitted parameter. In addition, applying Eq. (5) on Cu diffusivities in Na₂Si₂O₅ melt (von der Gonna and Russel 2000)
yields errors of up to 1.7 lnD units, meaning either our Cu diffusivity model does not apply to a melt composition of Na$_2$Si$_2$O$_5$, or Cu diffusivities obtained by the voltammetry method is less reliable, as discussed earlier.

**Dependence of Fe diffusivities on temperature and H$_2$O concentration in rhyolitic melt**

Iron diffusivities obtained in this study are summarized on an Arrhenius plot in Fig. 9. As can be seen in the figure, our Fe diffusivity data in anhydrous rhyolitic melt at 1 GPa approximate those reported in Baker and Watson (1988). Concentration of H$_2$O in the starting glass has a strong effect on Fe diffusivity. At 1050°C, every 1 wt% H$_2$O increases Fe diffusivity by a factor of ~3. Because not all the experiments yielded reliable Fe diffusivities, only in 4 wt% H$_2$O rhyolitic glasses produced enough data points to fit the Arrhenius equation:

$$D_{Fe}^{4wt\%H_2O} = \exp\left[-(14.45 \pm 0.66) - \frac{16845 \pm 809}{T}\right], r^2=0.9977$$  \hspace{1cm} (6)

where diffusivity is in m$^2$/s and $T$ is temperature in K. The activation energy corresponding to Eq. (6) is 140.0±6.7 kJ. The above equation reproduces our experimental data to within 0.06 lnD units.

Combining our Fe diffusion data in anhydrous and hydrous rhyolite melts with data in Baker and Watson (1988), a general equation for Fe diffusivity in rhyolitic melts as a function of temperature and H$_2$O concentration is obtained as follows:

$$D_{Fe}^{Rhy} = \exp\left[-(16.1 \pm 1.7) - \frac{(19859 \pm 2541)-(1218 \pm 135)w}{T}\right], r^2=0.8359$$  \hspace{1cm} (7)

where diffusivity is in m$^2$/s and $w$ is H$_2$O concentration in wt%. For the fitting of Eq. (7), because Fe diffusivities from Baker and Watson (1988) have larger errors (~0.25 natural logarithm units on average) than our data (~0.08 natural logarithm units), Cu diffusivities from
this study are weighted 9 times as important as the data from Baker and Watson (1988) to reflect
the 3 times difference in error. The equation above corresponds to an activation energy of
165±21 kJ/mol for Fe diffusion in dry rhyolitic melts. Eq. (7) reproduces most data of this study
and the study of Baker and Watson (1988) to less than 0.7 natural logarithm units, except for
three data points in anhydrous rhyolitic melts, which are off by 0.9, 0.9 and 1.5 natural logarithm
units respectively (Fig. 9).

For the diffusion of Fe, there is always concern as to whether Fe is diffusing as Fe$^{2+}$ or
Fe$^{3+}$ in the experiments. As discussed in Zhang et al. (2010), Fe diffusion can be expressed as a
linear combination of its Fe$^{2+}$ and Fe$^{3+}$ components:

\[
D_{\text{Fe}} = X_{\text{Fe}^{2+}} D_{\text{Fe}^{2+}} + X_{\text{Fe}^{3+}} D_{\text{Fe}^{3+}} \tag{8}
\]

where \(X_{\text{Fe}^{2+}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})\) and \(X_{\text{Fe}^{3+}} = \text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})\), respectively. Ferric iron has higher
valence and is expected to diffuse at a much lower rate than Fe$^{2+}$ in the melt. Therefore, the
diffusion of Fe is usually due to the contribution of Fe$^{2+}$, as long as its relative abundance is high.
Because our experimental durations are short, the oxidation state of Fe in the glass is likely
controlled by the initial ferric/ferrous iron ratio. Rapid diffusion of H$_2$ or CO, however, can occur
along the chalcocite-rhyolite interface and reduce Fe$^{3+}$ in the rhyolitic glasses, thus increasing
\(X_{\text{Fe}^{2+}}\) values. One way to evaluate whether Fe$^{2+}$ or Fe$^{3+}$ is dominant in our experiments is to
compare Fe diffusivities to Mg$^{2+}$ diffusivities for a similar melt composition. This is because
Fe$^{2+}$ and Mg$^{2+}$ are identical in valence and similar in size and hence are expected to have similar
diffusivities. On the other hand, Fe$^{3+}$ is trivalent and is expected to have significantly lower
diffusivity than Mg$^{2+}$. As can be seen in Fig. 10, Fe diffusivities in anhydrous rhyolitic melts
determined in this study are slightly higher than Mg$^{2+}$ diffusivities in an anhydrous haplogranitic
melt (Fig. 10), indicating that Fe diffusivities obtained in this study are mostly Fe$^{2+}$ diffusivities.
Comparison to diffusivities of other elements in rhyolitic melts

Diffusivities of Cu and Fe are plotted in Fig. 10 to compare with other elements in rhyolitic melts. According to Cu solubility and partitioning studies in basaltic, andesitic, and rhyolitic melts (e.g., Ripley and Brophy 1995; Holzheid and Lodders 2001; Zajacz et al. 2012; Zajacz et al. 2013; Liu et al. 2015), Cu dissolves into the silicate melt mostly as Cu\(^+\) when oxygen fugacity is below FMQ+4.4 (or NNO+3.6). Because oxygen fugacity in natural magmas is usually within NNO±2 (Carmichael and Ghiorso 1990), and assuming that the valence state of Cu does not change significantly with silicate melt composition, Cu should exist in most natural magmas as Cu\(^+\). Although the oxygen fugacity was not controlled during our experiments, the use of graphite capsules provides a relatively reducing environment (below NNO based on measured CO\(_2\) concentrations in the melt; Holloway 1992), and it is expected that Cu is diffusing as Cu\(^+\) in our experiments. This conclusion is in accordance with the high diffusivity and low activation energy of Cu based on our diffusion data. Comparison of Cu diffusivity to diffusivities of alkali elements in anhydrous rhyolitic melt shows that, \(D_{Li} \approx D_{Na} > D_{Cu} > D_{K}\), with \(D_{Cu}\) approximately 1 order of magnitude smaller than \(D_{Li}\) and \(D_{Na}\), and about \(1\) natural logarithm unit higher than \(D_{K}\) (Fig. 10). According to Shannon (1976), in octahedral sites, Cu\(^+\) has an ionic radius of 0.77 Å, similar to Li\(^+\) (0.76 Å), smaller than Na\(^+\) (1.02 Å), and significantly smaller than K\(^+\) (1.38 Å). These cations are compared at a fixed coordination number for self-consistency, although they are not necessarily 6-coordinated in the silicate melt. The fact that Cu diffusivity is larger than K diffusivity, but 1 order of magnitude smaller than that of Li and Na for anhydrous rhyolitic melt means that monovalent cation diffusivity cannot be predicted based on ionic
radius. On the other hand, the activation energies for Cu, Li, Na and K in anhydrous rhyolitic melts are similar. Their diffusivity trends are sub-parallel to each other, as can be seen in Fig. 10.

As shown in Fig. 10, Fe diffusivity in dry rhyolitic melt NCO is slightly higher than that of Mg in a synthetic granitoid (HPG8) melt (Mungall et al. 1999), similar to that of Zn in the same melt (Mungall et al. 1999), and much smaller than those of monovalent cations. The HPG8 melt, which contains 79.6 wt% SiO₂, is more silicic than NCO melt (73.5 wt% SiO₂), and hence the lower Mg diffusivity in HPG8 relative to Fe diffusivity in NCO is probably largely due to the bulk compositional differences. Diffusivity of Fe is about three orders of magnitude smaller than Cu diffusivity, and about four orders of magnitude smaller than Li or Na diffusivity. The activation energy of Fe diffusion is also significantly higher than Cu or alkali elements. This can be seen in Fig. 10 from the steeper slope for Fe and Zn diffusivities than for the alkalis. In addition, the effect of H₂O content on Fe diffusion is greater than on Cu diffusion. Iron diffusivity in rhyolitic melt with 6 wt% H₂O is almost 4 orders of magnitude higher than that in anhydrous rhyolitic melts (Fig. 9), whereas the difference between Cu diffusivities in 6 wt% H₂O rhyolitic melt and anhydrous rhyolitic melts is only about 1 order of magnitude (Fig. 10). The difference is consistent with literature data that demonstrate that dissolved H₂O typically has a much stronger effect on the diffusivity of divalent cations than on monovalent cations in silicate melts, or more generally, H₂O has a larger effect on elements with smaller diffusivities (Zhang et al. 2010).

The new Cu⁺ and Fe²⁺ diffusivities reported here allow us, to update the relative diffusivity sequence of Zhang et al. (2010) in dry rhyolitic melts as follows:

\[
\text{Li} \approx \text{Na} > \text{Cu}^+ > \text{K} > \text{Ar} \approx \text{CO}_2 \approx \text{Cl} \approx \text{Rb} \approx \text{Sb} \approx \text{F} > \text{Ba} \approx \text{Cs} \approx \text{Sr} > \text{Ca} > \text{Fe}^{2+} \approx \text{S} \approx \text{Mg} \\
> \text{Be} \approx \text{B} \approx \text{Ta} \approx \text{Nb} \approx \text{Y} \approx \text{REE} > \text{Zr} \approx \text{U} \approx \text{Hf} \approx \text{Ge} \approx \text{Th} \approx \text{Si} \approx \text{P}
\]  

(9)

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In rhyolitic melts with 6 wt% H₂O, the sequence of diffusivities is:

$$\text{Cu}^+ > \text{H}_2\text{O} > \text{CO}_2 > \text{Cl} > \text{Fe}^{2+} > \text{S}$$  \hspace{1cm} (10)

At 1123 K, Cu diffusivity is \(~50\) times Cl diffusivity in anhydrous rhyolitic melts and \(~30\) times Cl diffusivity in rhyolitic melts with 6 wt% water. Also plotted in Fig. 10 are S diffusion data in 6 wt% H₂O rhyolitic melts from Baker and Rutherford (1996). Although the S diffusivities vary by almost two orders of magnitude over the temperature range 850 to 900 °C, the data indicate that S diffusivity is much lower than Cl and Fe²⁺ diffusivity. Copper diffusivity is 4 to 5 orders of magnitude higher than S diffusivity in anhydrous rhyolitic melts and 6 wt% H₂O rhyolitic melt. One complication is that S diffusivities from Baker and Rutherford (1996) were obtained from anhydrite (CaSO₄) dissolution at an oxygen fugacity buffered by MNO, which is approximately FMQ+4.5 (O’Neill and Pownceby 1993). This indicates that S was diffusing in the form of S⁶⁺ or sulfate (SO₄²⁻) in their experiments, instead of sulfide (S²⁻) under the more reducing conditions typical of arc-related magmatic systems. Based on a study by Behrens and Stelling (2011), however, diffusivities of sulfide and sulfate are similar, at least in a soda lime (SiO₂-CaO-Na₂O) silicate melt. If diffusivities of sulfide and sulfate in natural silicate melt are also similar, our comparison of Cu and S diffusivities would not be affected by the diffusion species of S in silicate melts.

**Implications**

Prior to this study, the complete absence of experimental Cu diffusion data for rhyolitic melts required any assessment of Cu mobility in magmatic systems to use Cu diffusivities in an anhydrous Na₂Si₂O₅ melt (von der Gonna and Russel 2000) or theoretical values based on the model of Mungall (2002). Here, we use our new Cu diffusion data for rhyolite melts to assess the
transfer and partitioning behavior of Cu in an MVP-saturated magma. Our new Cu diffusion data suggest that, in a fluid-saturated magma (melt + crystals + MVP) wherein Cu behaves incompatibly in the fractionating crystal assemblage, the concentration of Cu in the MVP exsolved from a hydrous rhyolitic melt would always be close to equilibrium partitioning, because Cu diffusivity in the melt is higher than that of water and other elements (Fig. 10) (e.g., Zhang 2015). Experimental studies show that the Cu content of the MVP increases with increasing Cl content of the MVP (Audetat and Simon 2012; Zajacz et al. 2012) wherein Cu is complexed with Cl (i.e., CuCl; Candela and Holland 1984) or in the form of alkali-copper-chloride complex (e.g., Na/(K)CuCl₂; Zajacz et al. 2011). Thus, the diffusion of Cl from the melt to the MVP plays a key role not only in the Cl concentration in the MVP, but also in the partitioning of Cu between the melt and the MVP. That is, once an MVP bubble forms, the ability of the bubble to scavenge Cu depends on the Cl concentration in the MVP and hence the diffusion of Cl from the melt to the MVP. The rapid diffusion of Cu would ensure that Cu partitioning between the MVP and the melt is always approximately in equilibrium, whether the MVP is made of individual bubbles or forms percolation clusters buoyantly rising through the melt. Once Cl concentration in the MVP is modeled, the Cu concentration in the MVP can be estimated from batch equilibrium partitioning. This conclusion is different from the modeling results of Huber et al. (2012), mainly because a much lower Cu diffusivity (almost two orders of magnitude lower than our experimental data) from von der Gonna and Russel (2000) was used in their study.

Our Cu diffusion data can also be applied to elucidate the Cu and Zn isotope signatures of tektites, such as in the studies of Moynier et al. (2009, 2010). These studies reported significant depletion of both Cu (from typical upper crustal concentration of 28 ppm to ~2 ppm) and Zn.
(from typical upper crustal concentration of 67 ppm to ~20 ppm) in tektites, where the typical upper crustal concentrations are from Rudnick and Gao (2014). In accordance with the depleted abundances of Zn and Cu, both metals exhibit enrichment of their heavy isotopes (+1.22‰ < $\delta^{66/64}$Zn < +2.49‰; +1.98‰ < $\delta^{65/63}$Cu < +6.99‰). To explain the more fractionated Cu isotope signature relative to Zn, Moynier et al. (2010) used the diffusion model of Mungall (2002) to estimate Cu$^+$ diffusivity to be 2 orders of magnitude greater than Zn$^{2+}$ diffusivity at 1150 ºC. Based on experimental data from this study and from Baker and Watson (1988), however, the difference is almost 4 orders of magnitude at 1150 ºC (Fig. 10). In general, our Cu diffusion data support the explanation by Moynier et al. (2010) that the more fractionated Cu isotope signature in tektites is likely due to the higher Cu diffusivity than Zn. It would be desirable to measure Cu and Zn concentration profiles in individual tektites to assess Cu and Zn loss, and to model the isotopic fractionation.

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References:


**Figure captions**

**Figure 1.** Composition of chalcocite, bornite, and pure copper in the natural chalcocite cluster and the “chalcocite” after experiment in Chal-Rhy-2-2 in the Cu-Fe-S ternary system (atomic percent). Composition of the “chalcocite” after experiment (purple crosses) in Chal-Rhy-2-2 roughly falls in between chalcocite and bornite.

**Figure 2.** a) Apparent Cu concentration profiles due to secondary fluorescence, measured in natural CIT glass next to a piece of chalcocite. Line 1 was measured from the contact to the far field; Line 2 was measured when there is a tiny gap filled with epoxy between the chalcocite and the glass; Line 3 was measured from the far field towards the contact; Line 4 was measured in experimental charge Chal-Rhy-2-2, with a real Cu diffusion profile in the rhyolitic glass but overwhelmed by the secondary fluorescence effect. b) Comparison of Monte Carlo simulated Cu secondary fluorescence profile to electron microprobe measurements. The vertical axis is the raw Cu Kα peak counts ratio on sample over Cu metal standard, without ZAF correction. An \( \frac{I_x}{I_{std}} = 0.005 \) roughly corresponds to a Cu concentration of 0.6 wt%. In the simulation, the effect of the orientation of the spectrometer is also examined: spectrometer 4 is oriented toward the chalcocite side of the chalcocite-rhyolite couple, leading to higher Cu secondary fluorescence signals than spectrometers 3 and 5.

**Figure 3.** a) Microscope image of a sample charge after piston cylinder experiment. The chalcocite and the rhyolitic glass were naturally separated during quench probably because
rhyolitic melts do not wet on chalcocite. b) Microscope image of the same sample charge after
double polishing, the removal of the chalcocite wafer, and analyses. Dark spots on the glass are
laser ablation traverse spots and the red dashed lines show probe traverses for Cu concentration
analysis.

**FIGURE 4.** Two experiments (forming a time series; one experiment in (a) and the other in (b)) to
examine possible convection and the effect of Cu nanoparticles on Cu diffusivity extraction. The
two experiments differ in duration by a factor of 12. Both products contain red Cu-bearing
nanoparticles after the experiment. The Cu concentration profiles are plotted together with an
image section of the sample glass to show correlations between the Cu concentration profile in
the glass and existence of the Cu-bearing nanoparticles. The longer-duration experiment (Chal-
Rhy-3-1) has a longer Cu diffusion profile, leading to the existence of Cu-bearing particles in a
much wider region from the interface. Similar diffusivities (<20% different) obtained from these
two experiments indicate that these particles had negligible effect on the diffusivities. a) Three
EMP traverses and a traverse of LA-ICP-MS spots were analyzed for Chal-Rhy-3-1. The
diffusivity provided in the figure is based on fitting result using the finite method. b) Sample
Chal-Rhy-3-2 was measured by LA-ICP-MS only. The first point from the interface in open
orange circle is likely affected by the short quench profile and is excluded from fitting.

**FIGURE 5.** Special experiment (Chal-Rhy-2-2) designed to examine the behavior of chalcocite
during its “dissolution”. “Dissolution” is in quotation marks because the reaction is better
described as “metal exchange” instead of “dissolution”. One thin wafer of chalcocite was
sandwiched between two rhyolitic glasses in the experiment. The two rhyolitic glasses separated
during quench, and the gap was filled with epoxy for protection during polish. The chalcocite was found containing 2.4 atom% Fe, 35.0 atom% S and 62.6 atom% Cu after the experiment, indicating an exchange of Cu and Fe with the rhyolitic melts.

**Figure 6.** Copper diffusion profiles measured in this study (except for Chal-Rhy-3-1 and Chal-Rhy-3-2, which are in Fig. 4). Solid symbols are LA-ICP-MS data (often one traverse only; except for Chal-Rhy-10-1). Open orange circles indicate LA-ICP-MS data that are affected by the quench effect and excluded from fitting. All other symbols are for EMP traverses (3 or more). In j, the profiles are modeled considering the temperature effect on the interface Cu concentration. Details about the modeling can be found in “sources of error”.

**Figure 7.** Iron diffusion profiles obtained in this study that are used to extract Fe diffusivities in Table 3. At least four electron microprobe traverses were analyzed perpendicular to the interface for each sample. Fitting results for the experiments using Eq. (1) are also provided in the figures.

**Figure 8.** a) Arrhenius plot of all Cu diffusivities obtained in this study, together with those in anhydrous basalt (Ni and Zhang 2016, at 0.5, 1 and 1.5 GPa), dry sodium silicate melt (von der Gonna and Russel 2000, at 1bar) and calculated using the model of Mungall 2002 in NCO. Experimental pressure is 0.5 GPa unless otherwise specified. Error bars reported for diffusivities in natural silicate melts are all in 1σ (often smaller than the symbol). Diffusivities in anhydrous rhyolite, 4wt% H₂O rhyolite and 6wt% H₂O rhyolite are fitted with linear functions respectively. In general, Cu diffusivities show negligible dependence on pressure and weak dependence on
major element composition, but relatively strong dependence on H2O concentration. b) Plot of activation energy versus concentration of H2O in rhyolitic melts. Error bars are in 1σ. Increasing H2O concentration in rhyolitic melts decreases the activation energy roughly linearly.

**FIGURE 9.** Iron diffusivities obtained in this study and from Baker and Watson 1988. All error bars shown are in 1σ. For some of the data points, error bars are smaller than the symbol size. Lines are calculated from the best-weighted fit of all data (Eq. 7).

**FIGURE 10.** Comparison of Cu diffusivities and Fe diffusivities to diffusivities of other elements in rhyolitic melts. Fitting of Fe diffusivities in anhydrous rhyolitic melt is adopted from Fig. 9. Data sources: Cu and Fe (anhydrous and 6 wt% H2O rhyolitic melt, this study); Fe (anhydrous rhyolitic melt, diffusion couple method, P=1000 MPa, T= 1100 to 1400 ºC, Baker and Watson 1988); Li (anhydrous rhyolitic melt, tracer diffusivity, P=0.1 MPa, T=297 to 909 ºC, Jambon and Semet 1978); Na (anhydrous rhyolitic melt, P=0.1 MPa, extrapolated from T=138 to 502 ºC, Jambon 1982); K (anhydrous rhyolitic melt, P=0.1 MPa, T=372 to 845 ºC, Jambon 1982); Cs (anhydrous rhyolitic melt, Ni and Zhang 2008); Cl (anhydrous rhyolitic melt, P=0.1 to 100 MPa, T=850 to 1400 ºC, Bai and Koster van Groos 1994); Cl (6.9 wt% H2O rhyolitic melt, P=100 and 200 MPa, T=850 ºC, Bai and Koster van Groos 1994); Zn (diffusion couple method, P=10 and 1000 MPa, T=898 to 1400 ºC, Baker and Watson 1988); Mg (synthetic granitoid melt HPG8, P=0.1 MPa, T=1137 to 1600 ºC, Mungall et al. 1999); S (anhydrite dissolution, anhydrous and 6.1 to 6.3 wt% H2O rhyolitic melt, P=100 to 200 MPa, T=850 to 1100 ºC, MNO oxygen buffer, Baker and Rutherford 1996).
**TABLE 1.** Chemical composition of the rhyolitic glasses used for this study. Major element compositions were measured by electron microprobe on starting glasses. Details for the EMP analyses can be found in Analytical Methods. About 15 points were analyzed on each glass sample and the average composition is reported below. All compositions are in wt%.

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<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeOᵢ</th>
<th>MgO</th>
<th>CaO</th>
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<tr>
<td>NCO</td>
<td>73.45</td>
<td>0.23</td>
<td>14.04</td>
<td>2.00</td>
<td>0.14</td>
<td>0.75</td>
<td>5.35</td>
<td>4.30</td>
<td>0.10</td>
<td>100.36</td>
</tr>
<tr>
<td>CIT</td>
<td>76.51</td>
<td>0.05</td>
<td>12.48</td>
<td>1.02</td>
<td>0.02</td>
<td>0.41</td>
<td>4.32</td>
<td>4.92</td>
<td>0.24</td>
<td>99.97</td>
</tr>
<tr>
<td>bb7b-25</td>
<td>75.26</td>
<td>0.06</td>
<td>12.26</td>
<td>1.05</td>
<td>0.02</td>
<td>0.52</td>
<td>3.96</td>
<td>4.85</td>
<td>1.80</td>
<td>99.78</td>
</tr>
<tr>
<td>GMR+2</td>
<td>72.07</td>
<td>0.26</td>
<td>13.41</td>
<td>1.65</td>
<td>0.27</td>
<td>1.22</td>
<td>4.12</td>
<td>4.44</td>
<td>1.99</td>
<td>99.43</td>
</tr>
<tr>
<td>GMR+4</td>
<td>70.53</td>
<td>0.26</td>
<td>13.16</td>
<td>1.71</td>
<td>0.27</td>
<td>1.20</td>
<td>4.03</td>
<td>4.35</td>
<td>3.89</td>
<td>99.40</td>
</tr>
<tr>
<td>GMR+6</td>
<td>69.22</td>
<td>0.25</td>
<td>12.94</td>
<td>1.66</td>
<td>0.27</td>
<td>1.17</td>
<td>3.90</td>
<td>4.20</td>
<td>5.95</td>
<td>99.56</td>
</tr>
</tbody>
</table>

*Concentration of H₂O was measured by FTIR, each value is the average of ~10 analysis on the same sample.
### Table 2. Instrumental parameters and operating conditions of the LA-ICP-MS

<table>
<thead>
<tr>
<th>Laser-ablation system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser system</td>
<td>PhotonMachines 193 nm short pulse width Analyte Excite excimer laser ablation system</td>
</tr>
<tr>
<td>Energy</td>
<td>6.33 J/cm²</td>
</tr>
<tr>
<td>Spot size</td>
<td>25 µm</td>
</tr>
<tr>
<td>Pulse rate</td>
<td>25 Hz</td>
</tr>
<tr>
<td>Carrier gas flow</td>
<td>1.2 L/min (He)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ICP-MS system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument model</td>
<td>Agilent 7900</td>
</tr>
<tr>
<td>RF power</td>
<td>1250 W</td>
</tr>
<tr>
<td>Auxiliary gas flow rate</td>
<td>0 L/min (no make up or dilute gas used)</td>
</tr>
<tr>
<td>Nebulizer gas flow rate</td>
<td>0.8 L/min (Ar)</td>
</tr>
<tr>
<td>Interface cones</td>
<td>Agilent Ni Sampler cone #G3280-67040</td>
</tr>
<tr>
<td></td>
<td>Agilent Ni Skimmer cone #G3280-67041</td>
</tr>
<tr>
<td>Dwell time</td>
<td>10 ms on $^{43}$Ca, $^{44}$Ca, $^{57}$Fe, $^{63}$Cu and $^{65}$Cu</td>
</tr>
<tr>
<td>Background</td>
<td>30 s</td>
</tr>
</tbody>
</table>
Table 3. Summary of experimental conditions and results.

<table>
<thead>
<tr>
<th>Exp#</th>
<th>P (GPa)</th>
<th>T (ºC)</th>
<th>Starting glass</th>
<th>Duration (s)</th>
<th>(D_{Cu} (\times 10^{-12} \text{m}^2/\text{s})) EMP</th>
<th>(D_{Fe} (\times 10^{-12} \text{m}^2/\text{s})) ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chal-Rhy-1-2</td>
<td>0.5</td>
<td>1101 bb7b-25</td>
<td></td>
<td>428.9 464.8</td>
<td>113.0±8.1 126.1±5.8</td>
<td>113.0±8.1 126.1±5.8</td>
</tr>
<tr>
<td>Chal-Rhy-2-2*</td>
<td>0.5</td>
<td>1096 GMR+2</td>
<td>n.a.</td>
<td>n.a. n.a.</td>
<td>n.a. n.a.</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-3-1**</td>
<td>0.5</td>
<td>1001 GMR+2</td>
<td>1804.4 1830.8</td>
<td>n.a. 95.5±3.6</td>
<td>95.5±3.6</td>
<td>0.166±0.005</td>
</tr>
<tr>
<td>Chal-Rhy-3-2</td>
<td>0.5</td>
<td>1003 GMR+2</td>
<td>118.9 146.7</td>
<td>n.a. 80.7±1.5</td>
<td>80.7±1.5</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-4-2</td>
<td>0.5</td>
<td>1099 CIT</td>
<td>909.9 932.9</td>
<td>56±13 92.8±3.9</td>
<td>92.8±3.9</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-4-3</td>
<td>0.5</td>
<td>1088 NCO</td>
<td>906.8 936.1</td>
<td>69±14 80.2±5.5</td>
<td>80.2±5.5</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-5-1</td>
<td>0.5</td>
<td>1006 NCO</td>
<td>902.8 930.2</td>
<td>50±14 38.6±2.0</td>
<td>38.6±2.0</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-7-1</td>
<td>0.5</td>
<td>941 GMR+6</td>
<td>244.7 286.7</td>
<td>277±45 215.6±6.1</td>
<td>215.6±6.1</td>
<td>2.39±0.21</td>
</tr>
<tr>
<td>Chal-Rhy-8-1</td>
<td>0.5</td>
<td>750 GMR+6</td>
<td>231.9 279.4</td>
<td>36.2±6.6 68.1±0.9</td>
<td>68.1±0.9</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-9-1</td>
<td>1</td>
<td>1303 NCO</td>
<td>120.8 148.7</td>
<td>223±14 241.4±4.3</td>
<td>241.4±4.3</td>
<td>0.273±0.028</td>
</tr>
<tr>
<td>Chal-Rhy-10-1</td>
<td>1</td>
<td>1391 NCO</td>
<td>118.9 153.4</td>
<td>483±20 372.5±6.6</td>
<td>372.5±6.6</td>
<td>1.75±0.11</td>
</tr>
<tr>
<td>Chal-Rhy-11-1</td>
<td>0.5</td>
<td>854 GMR+6</td>
<td>246.4 284.3</td>
<td>157±15 126.6±1.4</td>
<td>126.6±1.4</td>
<td>n.a. n.a.</td>
</tr>
<tr>
<td>Chal-Rhy-12-1</td>
<td>0.5</td>
<td>954 GMR+4</td>
<td>239.3 270.2</td>
<td>97.4±6.6 110.1±3.4</td>
<td>110.1±3.4</td>
<td>0.548±0.025</td>
</tr>
<tr>
<td>Chal-Rhy-13-1</td>
<td>0.5</td>
<td>856 GMR+4</td>
<td>247.4 279.4</td>
<td>76±13 61.9±2.1</td>
<td>61.9±2.1</td>
<td>0.195±0.033</td>
</tr>
<tr>
<td>Chal-Rhy-14-1</td>
<td>0.5</td>
<td>1049 GMR+4</td>
<td>120.1 152.7</td>
<td>195.7±7.5 187.5±6.0</td>
<td>187.5±6.0</td>
<td>1.482±0.073</td>
</tr>
</tbody>
</table>

Note: P is corrected pressure; T is corrected interface temperature; \(t_1\) is recorded duration at target temperature ±1 ºC; \(t_2\) is effective duration calculated using Eq. (2). All reported errors are at 1σ level.

*Experiment Chal-Rhy-2-2 was specially designed to study the composition change of chalcocite crystal during experiment. Therefore no diffusivities were determined for the experiment.

**Copper diffusivity in Chal-Rhy-3-1 was fit assuming diffusion in finite medium using the same initial Cu concentration as Chal-Rhy-3-2.
Fig. 1
Fig. 2a

![Graph showing Cu distribution with different lines representing different conditions.

Legend:
- Red circles: Line 1
- Green squares: Line 2 (with gap)
- Blue crosses: Line 3 (analyze towards interface)
- Purple triangles: Line 4 (with a real profile)

Graph axes:
- Y-axis: Cu (wt%)
- X-axis: Distance from interface (µm)

The graph illustrates the Cu distribution profile across the interface with different probe traverses and analysis conditions.
Fig. 2b
**Fig. 3a**

- Chal-Rhy-3-1
- MgO
- Graphite
- Chalcocite
- Rhyolitic glass
- Thermo-couple
- Epoxy

a) 1 mm
Fig. 3b

Chal-Rhy-3-1

Thermocouple

Rhyolitic glass

Epoxy

1 mm
Fig. 4a

Epoxy Graphite Sample Glass Interface Far-field Region with Cu-bearing particles

Chal-Rhy-3-1

$T=1001 \, ^{\circ}C$

$P=0.5 \, \text{GPa}$

$t=1830.8 \, \text{s}$

$D_{Cu}=95.5 \, \mu m^2/s$

a)
Fig. 4b

- Epoxy
- Sample Glass
- Graphite

**Interface**

**Far-field**

**Region with Cu-bearing particles**

**Chal-Rhy-3-2**

- $T = 1003 \, ^\circ\text{C}$
- $P = 0.5 \, \text{GPa}$
- $t = 146.7 \, \text{s}$
- $D_{\text{Cu}} = 80.7 \, \mu\text{m}^2/\text{s}$
Fig. 5
Fig. 6a
Fig. 6b

![Graph showing Cu concentration vs. distance from interface (μm) with different lines representing various conditions.](image-url)
Fig. 6c

Chal-Rhy-4-3

- Line 1
- Line 2
- Line 3
- Probe fitting
- LAICPMS fitting

Cu (wt%) vs Distance from interface (μm)
Fig. 6d

![Graph showing Cu (wt%) vs. Distance from interface (μm)](image-url)

- **Chal-Rhy-5-1**
- **Lines:** Line 1, Line 2, Line 3
- **Curve:** Probe fitting
- **Data Points:** LA-ICP-MS
Fig. 6e
Fig. 6f

Chal-Rhy-8-1

- Line 1
- Line 2
- Line 3
- Line 4
- Fitting
- LAICPMS

Cu (wt%) vs. Distance from interface (µm)
Fig. 6g

![Graph showing Cu concentration (wt%) against distance from the interface (μm) for Chal-Rhy-9-1. The graph includes data points and lines for different lines (1.1, 1.2, 2.1, 2.2, 3.1, 3.2) and fitting lines for LAICPMS and probe fitting.](image-url)
Fig. 6h

Chal-Rhy-10-1

- Line 1
- Line 2
- Line 3
- Probe fitting
- LAICPMS Line1
- LAICPMS Line2
- LAICPMS Line3
- ICPMS fitting

Cu (wt%) vs. Distance from interface (μm)
Fig. 6i

![Graph showing copper concentration (wt%) vs. distance from interface (µm) for Chal-Rhy-11-1. The graph includes data points and lines representing different lines and a probe fitting, with line 1, line 2, line 3, and LAICPMS indicated.](image-url)
Fig. 6j

![Graph showing Cu (wt%) vs Distance from interface (µm) for Chal-Rhy-12-1. The graph includes markers for Line 1, Line 2, Line 3, Test profile, LAICPMS, Modeled LAICPMS, and Modeled probe. The y-axis represents Cu (wt%) ranging from 0 to 0.07, and the x-axis represents Distance from interface (µm) ranging from 0 to 1400.]
Fig. 6k

Chal-Rhy-13-1

Cu (wt%)

Distance from interface (μm)

Line 1
Line 2
Line 3
Probe fitting
LA-ICP-MS

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Fig. 6l

Chal-Rhy-14-1

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

- Line 1
- Line 2
- Line 3
- Line 4
- Fitting
- LAICPMS
Fig. 7a

Chal-Rhy-1-2

\[ C = C'_0 + (C_0 - C'_0) \text{erfc}(x/\sqrt{Dt}) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 )</td>
<td>0.12081</td>
<td>0.02632</td>
</tr>
<tr>
<td>( C'_0 )</td>
<td>1.0203</td>
<td>0.0043182</td>
</tr>
<tr>
<td>( D )</td>
<td>0.18478</td>
<td>0.01110</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.11378</td>
<td>NA</td>
</tr>
<tr>
<td>( R )</td>
<td>0.9812</td>
<td>NA</td>
</tr>
</tbody>
</table>
Fig. 7b

\[ C = C_0 + (C_0 - C_w) \text{erfc}(x/\sqrt{4Dt}) \]

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 )</td>
<td>0.16087</td>
<td>0.01787</td>
</tr>
<tr>
<td>( C_w )</td>
<td>1.7065</td>
<td>0.005581</td>
</tr>
<tr>
<td>( D )</td>
<td>0.16619</td>
<td>0.00521</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.13423</td>
<td>NA</td>
</tr>
<tr>
<td>R</td>
<td>0.9955</td>
<td>NA</td>
</tr>
</tbody>
</table>
C = C_0 + (C_w - C_0) \text{erfc}(x/\sqrt{4Dt})

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_0</td>
<td>0.94834</td>
<td>0.020428</td>
</tr>
<tr>
<td>C_w</td>
<td>1.5745</td>
<td>0.0064853</td>
</tr>
<tr>
<td>D</td>
<td>2.47970</td>
<td>0.22277</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.097008</td>
<td>NA</td>
</tr>
<tr>
<td>R</td>
<td>0.97423</td>
<td>NA</td>
</tr>
</tbody>
</table>

Fig. 7c


\[ C = C_\infty + (C_0 - C_\infty) \text{erfc}(x/\sqrt{D\bar{t}}) \]

**Fig. 7d**

**Chal-Rhy-9-1**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 )</td>
<td>0.21942</td>
<td>0.099538</td>
</tr>
<tr>
<td>( C_\infty )</td>
<td>1.9288</td>
<td>0.01008</td>
</tr>
<tr>
<td>( D )</td>
<td>0.27294</td>
<td>0.02756</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.30911</td>
<td>NA</td>
</tr>
<tr>
<td>R</td>
<td>0.96594</td>
<td>NA</td>
</tr>
</tbody>
</table>
Fig. 7e

Chal-Rhy-10-1

\[ C = C_0 + (C_0 - C_\infty) \text{erfc}(x/\sqrt{Dt}) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 )</td>
<td>0.21457</td>
<td>0.044429</td>
</tr>
<tr>
<td>( C_\infty )</td>
<td>1.9851</td>
<td>0.01011</td>
</tr>
<tr>
<td>( D )</td>
<td>1.7506</td>
<td>0.1073</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.48842</td>
<td>NA</td>
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<tr>
<td>R</td>
<td>0.98381</td>
<td>NA</td>
</tr>
</tbody>
</table>
Fig. 7f

Chal-Rhy-12-1

\[ C = C_o + (C_o - C_w) \text{erfc}(x/\sqrt{4Dt}) \]

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_o )</td>
<td>0.31817</td>
<td>0.022806</td>
</tr>
<tr>
<td>( C_w )</td>
<td>1.5989</td>
<td>0.0057701</td>
</tr>
<tr>
<td>( D )</td>
<td>0.55396</td>
<td>0.02557</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.079989</td>
<td>NA</td>
</tr>
<tr>
<td>( R )</td>
<td>0.99371</td>
<td>NA</td>
</tr>
</tbody>
</table>
Fig. 7g

Chal-Rhy-13-1

\[ C = C_0 + (C_0 - C_w) \text{erfc}(x/\sqrt{Dt}) \]

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_0)</td>
<td>0.75172</td>
<td>0.062905</td>
</tr>
<tr>
<td>(C_w)</td>
<td>1.5921</td>
<td>0.011346</td>
</tr>
<tr>
<td>(D)</td>
<td>0.19775</td>
<td>0.03364</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.26</td>
<td>NA</td>
</tr>
<tr>
<td>R</td>
<td>0.92954</td>
<td>NA</td>
</tr>
</tbody>
</table>
Fig. 8a

-24
-23.5
-23
-22.5
-22
-21.5
-21
-20.5

0.5 0.6 0.7 0.8 0.9 1
1000/T (T in K)

-20.5 1600 1400 1200 1000 800
T (°C)

Dry basalt
2wt% H₂O rhyolite
4wt% H₂O rhyolite
6wt% H₂O rhyolite
NCO (anhydrous)
NCO (1GPa)
CIT (anhydrous)
NCO (Mungall 2002)
dry Na₂Si₂O₅ melt

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Cite as Authors (Year) Title. American Mineralogist, in press.
(DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-2017-5885

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Fig. 8b

The graph shows the relationship between activation energy (kJ/mol) and water content (wt%). The equation is given as $y = a + b \cdot x$. The table provides the values for $a$, $b$, Chisq, and R, with their respective errors. The graph includes data points with error bars.
Fig. 9
Fig. 10

![Graph showing diffusion coefficients (D) plotted against the inverse temperature (1000/T) for various elements and water contents.](image-url)