Revision 2

1 # Cu diffusion in a basaltic melt

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5 **ABSTRACT**

6 Recent studies suggest a potential role of diffusive transport of metals (e.g. Cu, Au, PGE)

7 in the formation of magmatic sulfide deposits and porphyry-type ore deposits. However,

8 diffusivities of these metals are poorly determined in natural silicate melts. In this study,

9 diffusivities of copper in an anhydrous basaltic melt (<10 ppm H_2O) were measured at

10 temperatures from 1298 to 1581 ºC, and pressures of 0.5 GPa, 1 GPa and 1.5 GPa. Copper

11 diffusivities in anhydrous basaltic melt at 1 GPa can be described as:

$$D_{Cu}^{basalt} = \exp\left[-(14.12\pm0.50)-\frac{11813\pm838}{T}\right]$$

13 where D_{Cu}^{basalt} is the diffusivity in m^2/s, T is the temperature in K, and errors are given at 1σ level.

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

$$D_{Cu}^{basalt} = \exp\left[-(13.59\pm0.81)-\frac{(12153\pm1229)+(620\pm241)P}{T}\right]$$

16 where P is the pressure in GPa, which corresponds to a pre-exponential factor $D_0 = (1.25$

17 $\overset{\times}{\div}2.2)\times10^{-6}$ m^2/s, an activation energy $E_a = 101\pm10$ kJ/mol at $P = 0$, and an activation volume

18 $V_a = (5.2\pm2.0)\times10^{-6}$ m^3/mol.

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19   The diffusivity of copper in basaltic melt is high compared to most other cations, similar

20   to that of Na. The high copper diffusivity is consistent with the occurrence of copper mostly as

21   Cu^+ in silicate melts at or below NNO. Compared to the volatile species, copper diffusivity is

22   generally smaller than water diffusivity, but about 1 order of magnitude higher than sulfur and

23   chlorine diffusivities. Hence, Cu partitioning between a growing sulfide liquid drop and the

24   surrounding silicate melt is roughly in equilibrium, whereas that between a growing fluid bubble

25   and the surrounding melt can be out of equilibrium if the fluid is nearly pure H_2O fluid. Our

26   results are the first copper diffusion data in natural silicate melts, and can be applied to discuss

27   natural processes such as copper transport and kinetic partitioning behavior in ore formation, as

28   well as copper isotope fractionation caused by evaporation during tektite formation.

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

30

31   **INTRODUCTION**

32   As an important base metal widely used in construction and industry, enrichment of

33   copper from a crustal average of 27 ppm (Rudnick and Gao 2014) to a typical minable

34   concentration of a few thousand ppm has attracted much attention from economic geologists.

35   Magmatic sulfide deposits and porphyry copper deposits are two main types of deposits that

36   produce copper. In particular, porphyry-type deposits account for ~57% of world's total

37   discovered copper (Singer 1995).

38   As described by Naldrett (1989), magmatic sulfide ore deposits are typically related to a

39   mafic or ultramafic magma. Cooling of the magma leads to the saturation of sulfur, and results in

40   the nucleation and growth of sulfide liquid drops. Since sulfide drops have higher density than

41 the silicate melt, they will sink through the magma chamber, at the same time growing and

42 scavenging ore elements (e.g. Cu, Ni, Au, Pt) from the surrounding magma. Given enough time,

43 these sulfide drops will settle to the bottom of the magma chamber and form sulfide ore deposits

44 (Zhang 2015). The mechanism for porphyry-type ore deposits to enrich copper is similar, but

45 instead of a sulfide liquid phase settling down in the magma chamber for magmatic sulfide

46 deposits, a fluid phase is saturated inside the magma, and rises through the magma chamber,

47 scavenging and transporting ore metals (e.g. Cu, Au, Mo) to the top of the magma chamber. In

48 both types of ore deposits, enrichment of the metals into the sulfide phase or fluid phase is

49 controlled by at least two factors: (i) partitioning of the metal elements into the sulfide or fluid

50 phase, which may depend on the presence of other elements, such as chlorine in the fluid phase,

51 and (ii) diffusion of the metal elements through the silicate melt to the sulfide or fluid phase. For

52 magmatic sulfide deposits, Mungall (2002a) modeled the kinetic control of metal partitioning

53 assuming a sulfide drop is static inside the magma, and found that the enrichment factors of

54 metals can differ by as large as a factor of 5 depending on the diffusivity of each metal. Zhang

55 (2015) developed a quantitative model for magmatic sulfide deposits considering both sulfide

56 sinking and growth in silicate magma. Metal behavior was also modeled in Zhang (2015)

57 parametrically, concluding that as long as the metal diffusivity is larger than or similar to sulfur

58 diffusivity that controls sulfide drop growth, partition of the metal into the sulfide liquid phase is

59 close to equilibrium. Both Mungall (2002a) and Zhang (2015) used the empirical model by

60 Mungall (2002b) to estimate metal diffusivities. The model of Mungall (2002b) indicates that

61 copper diffusion is much faster than sulfur diffusion. Therefore, both authors concluded that

62 partition of copper into the sulfide phase is close to equilibrium. On the other hand, Huber et al.

63 (2012) developed a model for metal enrichment and transport by a fluid phase in a porphyry

3

64 system, and suggested that the efficiency of copper enrichment is dependent on the relative

65 diffusivity of copper to that of chlorine. Huber et al. (2012) used copper diffusion data from von

66 der Gonna and Russel (2000), with copper diffusivity being 1 order of magnitude smaller than

67 chlorine diffusivity. Therefore, copper partition into the fluid phase would not reach equilibrium

68 if the fluid bubbles ascend rapidly according to Huber et al. (2012).

69   In addition to metal enrichment processes discussed above, some other processes in ore

70 formation might also be kinetically controlled. For example, in magmatic sulfide deposits, after

71 sulfide liquid accumulation at the bottom of the magma chamber to form a sulfide liquid pool,

72 the interaction between the sulfide liquid pool and the magma might be diffusion-controlled

73 (Mungall 2002a). At the same time, metal extraction from other minerals into the sulfide melts is

74 controlled by diffusion of the metal in the mineral phase (e.g., extraction of Ni from olivine;

75 Zhang 2015). For porphyry-type ore deposits, re-dissolving of the sulfides and transport of their

76 metal elements from the more mafic magma to the silicic magma by a magmatic volatile phase is

77 also partially controlled by diffusivities of the metal elements in the melts (Nadeau et al. 2010,

78 2013).

79   Besides roles in copper ore formation, copper diffusivity is also an important parameter

80 in discussing copper isotope fractionation. Moynier et al. (2010) measured copper isotopes in

81 tektites, and found copper isotopes are more fractionated than zinc isotopes in the same set of

82 tektite samples. This is contrary to the notion that fractionation is due to volatile loss because

83 zinc has lower half-condensation temperature and is hence more easily lost than copper. The

84 authors explained their results by a higher diffusivity of copper than zinc in silicate melts,

85 implying that the isotope fractionation process was diffusion-limited.

4

86   Copper diffusion data in silicate melts are limited. Although there is a single study of

87   copper diffusivity in a $Na_2Si_2O_5$ melt by von der Gonna and Russel (2000), there are currently no

88   copper diffusion data in natural silicate melts. Cu diffusivity in the $Na_2Si_2O_5$ melt is unlikely

89   applicable to Cu diffusion during copper ore formation from a natural silicate melt. Even though

90   there is an empirical model by Mungall (2002b) to estimate diffusivity, as Behrens and Hahn

91   (2009) and Zhang et al. (2010) pointed out, Mungall (2002b)'s diffusivity model may be orders

92   of magnitude off in predicting diffusivities. Hence, experimental data are necessary for more

93   quantitative prediction of the diffusion effects.

94   In this study, diffusion couple experiments are carried out to obtain copper diffusivities in

95   a basaltic melt, and the results are used to discuss copper enrichment in ore formation, and to

96   speculate on kinetic controls of copper isotope fractionation.

97

98   **EXPERIMENTAL AND ANALYTICAL METHODS**

99   **Starting glasses**

100   Two glasses with the same major element composition but different copper

101   concentrations were synthesized for the diffusion couple experiments. A major element

102   composition of Etna basalt was chosen since it has been well studied in terms of melt properties:

103   both melt viscosity and sulfur diffusivity have been measured for this melt composition

104   (Giordano and Dingwell 2003; Freda et al. 2005).

105   In order to synthesize the starting glasses, a total weight of ~6.5 g of oxides (SiO_2, TiO_2,

106   Al_2O_3, Fe_2O_3, MgO) and carbonates ($CaCO_3$, Na_2CO_3, K_2CO_3) were weighed based on the target

107   composition of Etna basalt (Freda et al. 2005) and well mixed under alcohol in an agate mortar.

5

108 Then the mixture of the oxides and carbonates was divided into two halves, one of which was

109 doped with Cu_2O to contain ~1200 ppm Cu. Afterwards, approximately 0.6 g of the copper-free

110 mixture and copper-containing mixture were put into separate graphite crucibles and fused at

111 1300 ºC for 3 hours together inside a Deltech furnace under a constant N_2 flow. After fusing, the

112 two crucibles were taken out of the furnace and cooled in air to form two glass beads with a

113 diameter of ~8 mm.

114   The glasses synthesized were examined under optical microscope to ensure that they are

115 bubble free, crystal free and homogeneous in color. A center section was cut from each glass

116 bead and analyzed by electron microprobe to check its homogeneity before it was used for

117 diffusion couple experiments. Average compositions of the synthesized glasses are shown in

118 Table 1. In general, microprobe data show that the composition of the synthesized glass matches

119 the target composition fairly well (difference <1 wt% for each major component). FeO

120 concentration was found to decrease slightly (~8% relative) towards the surface of the glass

121 beads. Cu concentration was also found to be slightly inhomogeneous, with lower concentration

122 near the surface of the glass beads (~1000 ppm) than at the center of the glass beads (~1300 ppm)

123 (Fig. 1). To avoid possible effects of inhomogeneity in glass composition to our experiments,

124 only center parts of the synthetic glasses were used for diffusion couple experiments.

125   H_2O and CO_2 concentrations in the synthetic Etna basaltic glasses are below ~10 ppm

126 and ~100 ppm, respectively, based on FTIR measurements using a Perkin-Elmer Spectrum GX

127 FTIR spectrometer at the University of Michigan.

128

6

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 $BaCO_3$

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

7

152   interface of the diffusion couple was used as the experimental temperature. The temperature at

153   the two ends of the diffusion couple is estimated to be 10 to 20 ºC below the interface

154   temperature using the calibration of Hui et al. (2008).

155   Experiments were conducted at pressures of 0.5 to 1.5 GPa at a 0.5 GPa increment. A 5%

156   pressure correction is applied based on calibration by Ni and Zhang (2008) on the same piston

157   cylinder apparatus. During an experimental run, the pressure was first increased slowly and

158   smoothly to 15% higher than the target pressure (10% in the case of 1.5 GPa experiment) using a

159   pressure controller. Then the whole sample assemblage was relaxed at this pressure and 200 ºC

160   for at least 2.5 hours to close gaps inside the assemblage. Both pressure and temperature were

161   maintained automatically in this step. After relaxation, the temperature was brought up to the

162   designated temperature in ~60 s by a programed heating procedure. No temperature overshoot

163   occurred during heating-up, and temperature fluctuation was within ±1 ºC during the

164   experiments. Due to high Cu diffusivity, only a short duration was needed in the diffusion couple

165   experiments (2 to 7 minutes at 1298 ºC to 1581 ºC) to generate a long enough profile. After a

166   designated duration, the assemblage was quenched with a cooling rate of about 100 ºC/s (based

167   on direct measurement) by turning off the power. During quench, the pressure was maintained by

168   a manually controlled ENERPAC electric pump (except for Cudiffcp 4.4 and Cudiffcp 7.2, for

169   which the pressure was maintained by the pressure controller). The whole sample assemblage

170   was then preserved inside an epoxy resin disc and polished to expose the center section for

171   electron microprobe analysis.

172   Since the experimental duration was only 2 to 7 minutes, the effect of heating up (taking

173   ~1 min) needs to be considered. Quenching is rapid and hence the effect is small, but the small

174   effect is also accounted for in the following correction applied to obtain the effective duration for

8

175 all experiments. Based on the solution to the diffusion problem for time-dependent D (e.g.,

176 Zhang, 2008, Eq. 3-54b), the following equation was used to calculate the effective duration at

177 the experimental temperature T_0:

$$
178 \qquad t_c = \frac{\int_0^t \exp(-E/RT)\,dt}{\exp(-E/RT_0)} \qquad (2)
$$

179 where t_c is the effective duration, E is the activation energy for Cu diffusion, R is the gas

180 constant, T is recorded experiment temperature (including temperature recorded during heating

181 up and that during cooling down) corrected to the interface position, and T_0 is the plateau

182 interface temperature. At the beginning an estimated E was used for the effective duration

183 correction. After enough experiments were done, E was obtained by fitting the Arrhenius

184 equation and t_c was corrected again until t_c and E do not change anymore. Copper diffusion has a

185 small activation energy, leading to a relatively large duration correction of ~35 s.

186

187 **Analytical methods**

188   Major element composition and copper concentration profiles were measured in WDS

189 mode using the Cameca SX-100 electron microprobe at the University of Michigan. Major oxide

190 concentrations (SiO_2, TiO_2, Al_2O_3, FeO_t, MgO, CaO, Na_2O and K_2O) of the synthetic glasses

191 were measured with an acceleration voltage of 15 kV, a beam current of 10 nA in focused mode,

192 and a counting time of 30 to 40 seconds on the peak and 15 to 20 seconds on each side of the

193 backgrounds. The following standards were used for the microprobe analysis: albite (ALBA) for

194 Na, forsterite (FOBO) for Mg and Si, sillimanite (SILL) for Al, potassium feldspar (GKFS) for K,

195 wollastonite (WOLL) for Ca, geikielite (GEIK) for Ti, and ferrosilite (FESI) for Fe. Cu

196 concentrations were measured in separate sessions using a point beam with an acceleration

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197   voltage of 15 kV and a beam current of 40 nA. The standard for Cu concentration measurement

198   is chalcopyrite (CPY). Three spectrometers were employed to count Cu at the same time. The

199   counting time is 240 s on the Cu Kα peak and 120 s on either side of the background to achieve a

200   detection limit of ~80 ppm for Cu. The analytical error given by the microprobe based on

201   counting statistics is ~80 ppm (1σ). NIST SRM 610 was used as a secondary standard for Cu in

202   our analysis. The average concentration of Cu in SRM 610 was reported by Pearce et al. (1997)

203   to be 422±42 ppm. Our microprobe analysis yielded a Cu concentration of 464 ppm to 516 ppm

204   on SRM 610. The shift of absolute concentrations results in a shift of the entire copper diffusion

205   profile. However, if the amount of shift were similar for both the low and high copper

206   concentration ends, the diffusivity obtained from the profile would not be affected. In order to

207   evaluate whether the shift in absolute copper concentration has significant effect on copper

208   diffusivity, the sample Cudiffcp 3.1 was analyzed twice on two different days. The entire copper

209   concentration profile measured on two days shifted ~200 ppm from each other. However, after

210   the background correction, the two profiles measured on different days closely match each other

211   (Fig. 3). The diffusivities fitted from the two analyses of different days are <2% different from

212   each other, which is much smaller than the fitting error (1σ fitting error is about 10%) and hence

213   negligible.

214

215   **RESULTS**

216   **Copper diffusion profiles and fitting**

217   Ten successful diffusion couple experiments have been conducted. In addition to the 10

218   experiments reported here in Table 1, two more experiments were carried out but are classified

219   as unsuccessful. One experiment at 0.5 GPa and 1300 ºC shows abnormal concentration profile,

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220 which might be due to initial Cu concentration inhomogeneity. The other experiment at 1.5 GPa

221 and 1300 ºC crystallized because the pressure was too high for the given temperature. Both

222 experiments are excluded from the data.

223   Fig. 4 shows optical microscope images of two successful experiments. For each

224 diffusion couple, at least three Cu concentration traverses ~250 μm apart from each other were

225 measured to examine the reproducibility and possible convection. In five out of the ten

226 experiments (Cudiffcp 1.2, Cudiffcp 3.1, Cudiffcp 4.2, Cudiffcp 4.3 and Cudiffcp 4.4), the

227 interface survived the quench process and the sample glasses were crack-free after the

228 experiment. In these cases, the physical interface position was indicated by the two dents on both

229 sides of the glasses, as shown in Fig. 4a.

230   For the other five experiments (Cudiffcp 1.1, Cudiffcp 2.1, Cudiffcp 5.1, Cudiffcp 6.1

231 and Cudiffcp 7.2), a crack occurred almost exactly along the interface (Fig. 4b). In order to

232 prevent loss of glass during polish, epoxy was added multiple times to protect the cracks. After

233 microprobe analyses, copper concentration profiles on both sides of the crack were compared: if

234 necessary, a distance correction is made so that the profile across the crack is smooth. As a result,

235 a 7.5 μm and 12.5 μm correction to the concentration profiles was applied for experiments

236 Cudiffcp 2.1 and Cudiffcp 6.1, while no correction was applied to experiments Cudiffcp 1.1,

237 Cudiffcp 5.1 and Cudiffcp 7.2.

238   Cu concentration profiles in all experiments besides Cudiffcp 3.1 are shown in Fig. 5.

239 The concentration profiles were fit by the solution to a one-dimensional diffusion couple with

240 constant diffusivity (Crank 1975):

241
$$C = \frac{C_0 + C_1}{2} + \frac{C_0 - C_1}{2} \operatorname{erf} \frac{x - x_0}{\sqrt{4Dt}}$$ (3)

11

242   where C_0 is the initial Cu concentration at the Cu-free half of the diffusion couple (defined as $x-$

243    $x_0 > 0$); C_1 is the initial Cu concentration at the Cu-bearing half (defined as $x-x_0 < 0$); D is copper

244   diffusivity and x_0 is the position of the interface. Since copper diffusivity is high, there is concern

245   that copper diffusion might have reached the ends of the diffusion couple. This would cause error

246   in fitting using Eq. 3, which assumes an infinite diffusion medium. Visual examination of the

247   data and fitting of the profiles indicate that for the longer-duration or higher-temperature

248   experiments (Cudiffcp 1.1, Cudiffcp 5.1 and Cudiffcp 7.2) diffusion seems to have reached the

249   two ends. Numerical fitting using the solution for finite diffusion medium was carried out for

250   these three experiments (curves shown in Fig. 5), and the resulting diffusivities were only 3-5%

251   higher than that assuming infinite diffusion medium.

252

253   **Temperature and pressure dependence of copper diffusivity**

254   Experimental run conditions and results for all successful experiments are summarized in

255   Table 2. An Arrhenius plot of all copper diffusivities obtained in this study is shown in Fig. 6.

256   Diffusion data of the five experiments at 1 GPa and 1314-1575 °C in anhydrous basaltic melt can

257   be expressed by the following Arrhenius relation:

$$D_{Cu}^{basalt} = \exp\left[-(14.12 \pm 0.50) - \frac{11813 \pm 838}{T}\right], \quad r^2 = 0.985 \tag{4}$$

259   where D_{Cu}^{basalt} is in m^2/s, T is temperature in K, and errors are at 1σ level. The above equation

260   reproduces the five experimental ln$D$ values to within 0.09 ln$D$ units. The activation energy

261   corresponding to Eq. 4 is 98.2 ± 7.0 kJ/mol. This small activation energy (~100 kJ/mol) means

262   that the temperature dependence of copper diffusivity is relatively small compared to other

263   elements, and is consistent with Cu diffusing as Cu$^+$.

12

264   To evaluate the pressure effect on copper diffusivity, two experiments were done at 1.5

265   GPa and three experiments were done at 0.5 GPa (see Fig. 6). Two of the three 0.5 GPa

266   experiments gave diffusivities that are ~20% higher than the 1 GPa diffusivities, while

267   diffusivity from the other 0.5 GPa experiment fell 12% below the 1 GPa trend. Two 1.5 GPa

268   experiments gave diffusivities 12% and 29% below the 1 GPa diffusivities respectively.

269   Although the 0.5 GPa experiments have relatively larger errors (these are still small errors for

270   diffusion studies), a fit of all measured copper diffusivities at 1298 ºC to 1581 ºC and 0.5 to 1.5

271   GPa gives:

$$D_{Cu}^{basalt} = \exp\left[-(13.59 \pm 0.81) - \frac{(12153 \pm 1229) + (620 \pm 241)P}{T}\right], r^2 = 0.938 \qquad (5)$$

273   where D_{Cu}^{basalt} is diffusivity in m^2/s, T is temperature in K, P is pressure in GPa, and errors are at

274   1σ level. Eq. 5 corresponds to a pre-exponential factor $D_0 = (1.25 \overset{\times}{\div} 2.2) \times 10^{-6}$ m^2/s, an activation

275   energy $E_a = 101 \pm 10$ kJ/mol and an activation volume $V_a = (5.2 \pm 2.0) \times 10^{-6}$ m^3/mol for copper

276   diffusion in anhydrous basaltic melt. The above equation is able to reproduce all our

277   experimental ln$D$ values to within 0.23 ln$D$ units.

278

279   **Possible complications and other sources of error**

280   Since basaltic melts have low viscosities at our experimental condition (about 10^0 to $10^{1.3}$

281   Pa·s at temperatures from 1581 ºC to 1298 ºC using the viscosity model for Etna basalt by

282   Giordano and Dingwell 2003), there is concern about whether convection has occurred during

283   the experiments. Effort was made to examine whether convection is an issue in our experiments.

284   First, at least three traverses 200 μm to 300 μm apart from each other were measured on every

285   sample. If convection occurred, the three traverses would likely diverge, and diffusivities

13

286   obtained from these traverses may be significantly different from each other. The results show

287   that, diffusivities fitted to individual traverses in one sample are typically within ~20% from the

288   overall diffusivity, indicating no obvious convection. Second, two experiments (Cudiffcp 1.1 and

289   Cudiffcp 1.2) were conducted at the same temperature and pressure but with different duration

290   (465 s vs 163 s, almost a factor of 3 difference). As can be found in Table 2, relative diffusivity

291   difference between the two experiments is only about 8%, within our experimental error. Both

292   the consistency between diffusivities from Cudiffcp 1.1 and Cudiffcp 1.2 and the agreement

293   between different traverses in the same experiment suggest that the occurrence of convection is

294   unlikely in our experiments.

295   Temperature uncertainty may cause error in the data. As discussed in Methods,

296   temperature at the two ends of the diffusion couple can be 10 to 20 ºC lower than the interface

297   temperature. Hence, the error caused by temperature uncertainty is estimated using this

298   maximum temperature uncertainty of 20 ºC. Based on the activation energy of 98.2 kJ/mol for

299   Cu diffusivity at 1 GPa, the uncertainty of 20 ºC can result in errors in D_{Cu} of 10% at 1300 ºC

300   and 7% at 1600 ºC. The uncertainty in Cu diffusivity due to pressure uncertainty is negligible

301   because copper diffusivity changes less than 20% when pressure changes by 0.5 GPa.

302   Another possible source of error is the effective run duration contributed by heating and

303   cooling. As a compromise to the high Cu diffusivity, most of our experiments were designed to

304   be only ~2 min long. Under this circumstance, the heating and quenching processes contribute

305   about 20% to 30% to the effective run duration, meaning Cu diffusivity is changed by 20% to

306   30% with the duration correction. However, the method we used to correct the duration (Eq. 2) is

307   accurate if the activation energy of Cu diffusion is constant.

14

308   As mentioned earlier, cracks occurred along the interface of five samples during quench

309   (Cudiffcp 1.1, Cudiffcp 2.1, Cudiffcp 5.1, Cudiffcp 6.1 and Cudiffcp 7.2) and the cracks are

310   almost perfectly horizontal, and hence the distance across the crack cannot be determined by

311   comparing different traverses. For these five experiments, corrections were done by comparing

312   the trend of copper concentration profiles on both sides of the crack. As a result, a 7.5 µm and

313   12.5 µm correction to the concentration profiles was applied for experiments Cudiffcp 2.1 and

314   Cudiffcp 6.1, while no correction was applied to experiment Cudiffcp 1.1, Cudiffcp 5.1 and

315   Cudiffcp 7.2. This resulted in a 3% increase in diffusivity obtained from Cudiffcp 2.1 and a 2%

316   increase in diffusivity obtained from Cudiffcp 6.1.

317   The synthetic starting glasses are not perfectly homogeneous in copper concentration. In

318   the 8-mm-diameter copper-bearing synthetic glass, copper concentration can be ~1300 ppm at

319   the center and ~1000 ppm near the boundary (Fig. 1). However, considering that the glass

320   cylinder used for experiments is only about 1.5-mm tall, the copper concentration difference

321   across the glass cylinder is ~100 ppm, which is only slightly above our analytical error of ~80

322   ppm. Therefore the Cu concentration gradient in the starting glasses is unlikely to cause

323   significant error.

324

325   <div align="center">**DISCUSSION**</div>

326   **Comparison with existing copper diffusivity data**

327   For multivalent ions, valence state of the ion plays an important role in its diffusivity in

328   silicate melts and minerals. Ions in the lower valence state typically have higher diffusivities

329   because of the weaker bonding between these ions and surrounding melt structure (Zhang 2010).

330   Examples of multivalent ions in silicate melts include Fe^{2+} and Fe^{3+}, Sn^{2+} and Sn^{4+}, etc. Copper

15

331 is also a multivalent element in the natural system, and is commonly found as 0, +1 or +2 in

332 natural occurrence. In the study of copper solubility in a mafic melt, Ripley and Brophy (1995)

333 plotted log copper solubility versus $\log f_{O_2}$, and found that copper dissolves into the melt

334 predominantly in +1 valence state at or below NNO. The high Cu diffusivity and low activation

335 energy for Cu diffusion observed in our study are consistent with Cu being univalent. Therefore

336 in this study, we regard our measured copper diffusivity as Cu^+ diffusivity.

337   As mentioned in the Introduction, we know of only one study reporting Cu^+ diffusivities

338 in $Na_2Si_2O_5$ melt (von der Gonna and Russel 2000) using a voltammetry method. They reported

339 Cu^+ diffusivity to be 5.01×10^{-11} m^2/s at 1100 ºC with activation energy of 92.1 kJ/mol. Their

340 diffusivities of copper in $Na_2Si_2O_5$ glass melt are plotted in Fig. 7 (green open squares) to

341 compare with those measured in this study (red solid circles, diamonds and triangles). Cu^+

342 diffusivities in $Na_2Si_2O_5$ glass melt are smaller than those in basaltic melt by a factor of about 3

343 with similar activation energy.

344   Mungall (2002b) developed a model to calculate ion diffusivities in silicate melt.

345 Calculated Cu^+ diffusivities in basaltic melt using his model are plotted in Fig. 7 as a grey solid

346 line, and are about 3 to 5 times the diffusivities determined by our experiments. The model by

347 Mungall (2002b) shows larger errors in reproducing the diffusivities in the $Na_2Si_2O_5$ melt. At

348 1100ºC, calculated Cu^+ diffusivities using his model are two orders of magnitude larger than the

349 experimental data by von der Gonna and Russel (2000).

350

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

352   Diffusivity data for selected elements in basaltic melts are also plotted in Fig. 7. From the

353 figure, Cu diffusivity is almost identical to Na diffusivity at ~1400 ºC, lower than Li diffusivity

16

354   by a factor of about 3 and significantly higher than diffusivities of all other cations shown in Fig.

355   7. At 1300 ºC, Cu diffusivity is ~10 times Ca and Co diffusivity, 18 times Mg diffusivity, and

356   ~30 times S and Fe diffusivity. Since Cu diffusion has smaller activation energy than all other

357   elements shown in Fig. 7, when temperature increases, Cu diffusivity increases slower than other

358   elements. At 1500 ºC Cu diffusivity is only ~5 to 10 times higher than Mg, Fe, Co, S and Ca.

359   However when temperature decreases, Cu diffusivity decreases slower than all other elements

360   shown in Fig. 7, and becomes larger than Na diffusivity. At 1100 ºC, Cu diffusivity will be ~200

361   times Fe diffusivity, 67 times Mg diffusivity, 35 times Co diffusivity, ~25 times Ca diffusivity

362   and 2.5 times Na diffusivity.

363   To examine the role of valence and size of cations, the radius of Cu^+ was compared to

364   other monovalent cations. For self-consistency, the ionic radii of Li^+, Cu^+ and Na^+ in octahedral

365   sites (0.076, 0.077, and 0.102 nm, respectively, Shannon 1976) are compared. If diffusivities of

366   univalent cations in a given melt are mainly determined by the ionic radii (Mungall 2002b), Cu^+

367   diffusivity would be similar to Li^+ diffusivity. The fact that Cu^+ diffusivity is a factor of 3

368   smaller than Li^+ diffusivity but similar to Na^+ diffusivity indicates that other ionic characters

369   (e.g., electronegativity, the presence of d electrons, different co-ordination number, etc.) also

370   play a role in determining the diffusion rate.

371

372   **Applications**

373   The role of copper diffusion in magmatic sulfide deposit formation has been discussed

374   above in the Introduction. The major conclusions by Mungall (2002a) and Zhang (2015) were

375   consistent in that, if the diffusivity of a metal is much larger than sulfur diffusivity in basaltic

376   melt, the partitioning of the metal into the sulfide phase can be regarded as in equilibrium. Both

17

377 Mungall (2002a) and Zhang (2015) used the diffusivity model by Mungall (2002b) to estimate

378 metal diffusivities in their study, and found Cu^+ to be one of the most mobile elements in basaltic

379 melt. Our results suggest that Mungall's model overestimated copper diffusivity in basaltic melt

380 by a factor of 2 to 4. However, our measured copper diffusivity is still ~30 times higher than

381 sulfur diffusivity in basaltic melt. Therefore copper partition into the sulfide melt can be

382 regarded as equilibrium partitioning in most cases.

383   High copper diffusivity in basaltic melt might also play a role in metal transport by a

384 magmatic vapor phase (MVP). Nadeau et al. (2013) carried out a melt-inclusion study on

385 samples from Merapi volcano, Indonesia, and found that copper was more enriched in shallower

386 felsic melts (~45 ppm) than in deeper mafic melts (~25 ppm), which is opposite to the trend

387 normally observed in arc magmas. The unusual behavior of Cu could not be explained by crystal

388 fractionation or combined assimilation and fractionation. Nadeau et al. (2010) suggested a

389 mechanism in which copper was transported from the mafic magma to the felsic magma by an

390 MVP enriched in copper. Since water diffusivity in basalt is high (Fig. 7), the growth of an MVP

391 inside the magma is rapid. In this process, because the diffusivity of copper is lower than that of

392 H_2O but higher than that of other metal elements (except for Li and Na), copper would not reach

393 equilibrium concentration in the MVP but would be more efficiently enriched in the aqueous

394 volatile phase than the other metal elements. One complication is that, the partition coefficient of

395 copper between the volatile phase and the silicate melt phase strongly depends on chlorine and

396 sulfur contents in the volatile phase (e.g., Candela and Holland 1984;Williams et al. 1995; Simon

397 et al. 2006 and Zajacz et al. 2008). Hence, enrichment of copper in the MVP would be controlled

398 by diffusion of sulfur or chlorine from the silicate melt to the MVP. As can be seen in Fig. 7,

399 $D_{Cu} > D_{Cl} > D_S$ assuming water content in silicate melt does not change the sequence. Therefore,

18

400   in pure H_2O fluid phase, Cu concentration in the fluid phase would be even lower than that

401   indicated by the low partition coefficient, but if the fluid bubble is enriched in chlorine or sulfide,

402   copper partitioning between the fluid and melt phases would be roughly in equilibrium, while Cl

403   and S concentrations in the fluid bubble would be lower than that indicated by equilibrium

404   partitioning. Nadeau et al. (2013) did not specify the composition of the MVP in his study, but a

405   study by Zajacz and Halter (2009) found evidence for sulfur-rich vapor in melt and vapor

406   inclusions hosted by plagioclase. In that case, copper partitioning during the metal transportation

407   by an MVP is likely equilibrium partitioning again.

408   High copper diffusivity may also be responsible for rapid Cu loss from tektites, resulting

409   in large kinetic copper isotope fractionation. Moynier et al. (2010) measured copper isotope

410   ratios in tektites, and found almost all the tektites are greatly enriched in heavy Cu isotope (+1.99‰

411     $< \delta^{65}Cu < +6.98‰$), where $\delta^{65}Cu = ((^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{standard}-1)\times1000‰$. Because

412   tektites might have been heated to a temperature as high as >2800 ºC (Walter 1967) for a short

413   period of time, and the half-condensation temperature for copper is 1037 K (Lodders 2003),

414   Moynier et al. (2010) proposed that copper isotopes were fractionated by evaporation loss, with

415   lighter isotopes escaping more rapidly into the volatile phase. However, by comparing with their

416   previous study of zinc isotope fractionation in tektites (Moynier et al. 2009), the authors found

417   zinc isotopes to be less fractionated than copper isotopes in the same set of samples ($\delta^{66/64}Zn$ up

418   to 2.49‰ comparing to $\delta^{65/63}Cu$ up to 6.98‰). If Cu and Zn loss is due to open system

419   volatization (such as Raleigh fractionation in which a tektite droplet is uniform compositionally

420   and isotopically), because zinc has a much lower half-condensation temperature ($T_c \sim 726$ K,

421   Lodders 2003) than Cu, zinc isotopes would be more fractionated than copper isotopes, opposite

422   to the observations. Moynier et al. (2010) explained the more fractionated copper isotopes than

19

423   zinc isotopes by the higher diffusivity of Cu^+ than Zn^{2+} in silicate melts, and argued that the

424   isotopic fractionation in tektites was controlled by the competition between the evaporation flux

425   and the diffusion flux. They employed the diffusivity model by Mungall (2002b) and found Cu^+

426   diffusivity to be about 2 orders of magnitude higher than Zn^{2+} diffusivity, and used this result to

427   explain why copper isotopes are more fractionated than zinc isotopes. Using literature Zn^{2+}

428   diffusion data in rhyolitic melt (Baker and Watson, 1988) and our Cu^+ diffusion data, and

429   assuming melt composition does not affect Cu^+ diffusivity significantly (our preliminary data

430   reported in Ni et al., 2015 show that Cu^+ diffusivity in anhydrous rhyolitic melt is only ~50%

431   smaller than Cu^+ diffusivity in basalt), Cu^+ diffusivity is about 3 orders of magnitude higher than

432   Zn^{2+} diffusivity (Fig. 7). Hence, Cu and Zn diffusion data are consistent with the explanation by

433   Moynier et al. (2010).

434

435   **IMPLICATIONS**

436   Our copper diffusion data in basaltic melt show that, copper diffusivity in anhydrous

437   basaltic melt is as high as that of sodium at ~1400 ºC, and has a small activation energy (~100

438   kJ/mol). The measured copper diffusivities are ~3 times smaller than the values predicted by a

439   previous diffusivity model in the same melt, and ~3 times larger than reported copper

440   diffusivities in the $Na_2Si_2O_5$ melt. In basaltic melt, copper diffusivity is ~30 times higher than

441   sulfur diffusivity, indicating that during the formation of magmatic sulfide deposit, when

442   immiscible sulfide liquid drops separate from the host magma and settle to the bottom of the

443   magma chamber, the partitioning of copper into the sulfide liquid phase can be regarded as

444   equilibrium partitioning. In the process of porphyry-type deposit formation, where metal

445   transport from the more mafic magma to the more felsic magma by a magmatic volatile phase is

446   possible, high diffusivity of copper also ensures the efficiency of copper diffusion into and away

447   from the volatile phase. Because of the high diffusivity of copper in basaltic melt, kinetic

448   limitation of copper partitioning during ore formation is less likely a concern. This also means

449   copper may be diffusively fractionated from other ore elements with smaller diffusivity.

450   The results of our study can also be used to discuss the kinetic role in evaporation loss

451   and isotope fractionation of volatile elements in impact glasses. The more fractionated copper

452   isotopes than zinc isotopes as observed in tektites can be explained by the higher diffusivity of

453   Cu^+ than Zn^{2+} in silicate melts, despite the lower condensation temperature for zinc than copper.

454   Similar processes may also happen to lunar volcanic and impact glasses on the surface of Moon.

455

456   **ACKNOWLEDGEMENTS**

463

464   **REFERENCES CITED**

465   Alletti, M., Baker, D.R., and Freda, C. (2007) Halogen diffusion in a basaltic melt. Geochimica

466   et Cosmochimica Acta, 71, 3570-3580.

467   Baker, D.R., and Watson, E.B. (1988). Diffusion of major and trace elements in compositionally

468   complex Cl-and F-bearing silicate melts. Journal of Non-Crystalline Solids, 102, 62-70.

21

469   Behrens, H., and Hahn, M. (2009) Trace element diffusion and viscous flow in potassium-rich

470   trachytic and phonolitic melts. Chemical Geology, 259, 63-77.

471   Candela, P.A., and Holland, H.D. (1984) The partitioning of copper and molybdenum between

472   silicate melts and aqueous fluids. Geochimica et Cosmochimica Acta, 48, 373-380.

473   Crank, J. (1975) The Mathematics of Diffusion. Oxford, UK: Clarendon Press.

474   Freda, C., Baker, D.R., and Scarlato, P. (2005) Sulfur diffusion in basaltic melts. Geochimica et

475   cosmochimica acta, 69, 5061-5069.

476   Giordano, D., and Dingwell, D. (2003) Viscosity of hydrous Etna basalt: implications for

477   Plinian-style basaltic eruptions. Bulletin of Volcanology, 65, 8-14.

478   Huber, C., Bachmann, O., Vigneresse, J.L., Dufek, J., and Parmigiani, A. (2012) A physical

479   model for metal extraction and transport in shallow magmatic systems. Geochemistry,

480   Geophysics, Geosystems, 13.

481   Hui, H., Zhang, Y., Xu, Z., and Behrens, H. (2008) Pressure dependence of the speciation of

482   dissolved water in rhyolitic melts. Geochimica et Cosmochimica Acta, 72, 3229-3240.

483   Lodders, K. (2003) Solar system abundances and condensation temperatures of the

484   elements. The Astrophysical Journal, 591, 1220.

485   Lowry, R.K., Reed, S.J.B., Nolan, J., Henderson, P., and Long, J.V.P. (1981) Lithium tracer-

486   diffusion in an alkali-basaltic melt—an ion-microprobe determination. Earth and Planetary

487   Science Letters, 53, 36-40.

488   Lowry, R.K., Henderson, P., and Nolan, J. (1982) Tracer diffusion of some alkali, alkaline-earth

489   and transition element ions in a basaltic and an andesitic melt, and the implications

490   concerning melt structure. Contributions to Mineralogy and Petrology, 80, 254-261.

491 Moynier, F., Beck, P., Jourdan, F., Yin, Q.Z., Reimold, U., and Koeberl, C. (2009) Isotopic
492   fractionation of zinc in tektites. Earth and Planetary Science Letters, 277, 482-489.

493 Moynier, F., Koeberl, C., Beck, P., Jourdan, F., and Telouk, P. (2010) Isotopic fractionation of
494   Cu in tektites. Geochimica et Cosmochimica Acta, 74, 799-807.

495 Mungall, J.E. (2002a) Kinetic controls on the partitioning of trace elements between silicate and
496   sulfide liquids. Journal of Petrology, 43, 749-768.

497 Mungall, J.E. (2002b) Empirical models relating viscosity and tracer diffusion in magmatic
498   silicate melts. Geochimica et Cosmochimica Acta, 66, 125-143.

499 Nadeau, O., Williams-Jones, A.E., and Stix, J. (2010) Sulphide magma as a source of metals in
500   arc-related magmatic hydrothermal ore fluids. Nature Geoscience, 3, 501-505.

501 Nadeau, O., Stix, J., and Williams-Jones, A.E. (2013) The behavior of Cu, Zn and Pb during
502   magmatic–hydrothermal activity at Merapi volcano, Indonesia. Chemical Geology, 342, 167-
503   179.

504 Naldrett, A.J. (1989) Magmatic sulfide deposits. Oxford University Press.

505 Ni, H., and Zhang, Y. (2008) H_2O diffusion models in rhyolitic melt with new high pressure
506   data. Chemical Geology, 250, 68-78.

507 Ni P., Zhang Y., Simon A. & Gagnon J. (2015) Goldschmidt Abstracts, 2015 2269.

508 Pearce, N.J., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., and
509   Chenery, S.P. (1997) A compilation of new and published major and trace element data for
510   NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards newsletter, 21,
511   115-144.

512 Ripley, E.M., and Brophy, J.G. (1995) Solubility of copper in a sulfur-free mafic
513   melt. Geochimica et cosmochimica acta, 59, 5027-5030.

514   Rudnick, R.L., and Gao, S. (2014) Composition of the continental crust, Treatise on

515   Geochemistry (2nd edition), pp. 1-51.

516   Shannon, R.T. (1976) Revised effective ionic radii and systematic studies of interatomic

517   distances in halides and chalcogenides. Acta Crystallographica Section A: Crystal Physics,

518   Diffraction, Theoretical and General Crystallography, 32, 751-767.

519   Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., and Heinrich, C.A. (2006) Copper

520   partitioning in a melt–vapor–brine–magnetite–pyrrhotite assemblage. Geochimica et

521   Cosmochimica Acta, 70, 5583-5600.

522   Singer, D.A. (1995) World class base and precious metal deposits; a quantitative

523   analysis. Economic Geology, 90, 88-104.

524   von der Gonna, G., and Russel, C. (2000) Diffusivity of various polyvalent elements in a

525        $Na_2O \cdot 2SiO_2$ glass melt. Journal of non-crystalline solids, 261, 204-210.

526   Walter, L.S. (1967) Tektite compositional trends and experimental vapor fractionation of

527   silicates. Geochimica et Cosmochimica Acta, 31, 2043-2063.

528   Wang, H., Xu, Z., Behrens, H., and Zhang, Y. (2009) Water diffusion in Mount Changbai

529   peralkaline rhyolitic melt. Contributions to Mineralogy and Petrology, 158, 471-484.

530   Williams, T.J., Candela, P.A., and Piccoli, P.M. (1995) The partitioning of copper between

531   silicate melts and two-phase aqueous fluids: an experimental investigation at 1 kbar, 800 C

532   and 0.5 kbar, 850 C. Contributions to Mineralogy and Petrology, 121, 388-399.

533   Zajacz, Z., Halter, W.E., Pettke, T., and Guillong, M. (2008) Determination of fluid/melt

534   partition coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions:

535   controls on element partitioning. Geochimica et Cosmochimica Acta, 72, 2169-2197.

536   Zajacz, Z., and Halter, W. (2009) Copper transport by high temperature, sulfur-rich magmatic

537   vapor: Evidence from silicate melt and vapor inclusions in a basaltic andesite from the

538   Villarrica volcano (Chile). Earth and Planetary Science Letters, 282, 115-121.

539   Zhang, Y. (2008) Geochemical Kinetics. Princeton University Press.

540   Zhang, Y. (2010) Diffusion in minerals and melts: theoretical background. Reviews in

541   Mineralogy and Geochemistry, 72, 5-59.

542   Zhang, Y. (2015). Toward a quantitative model for the formation of gravitational magmatic

543   sulfide deposits. Chemical Geology, 391, 56-73.

544   Zhang, Y., and Ni, H. (2010) Diffusion of H, C, and O components in silicate melts. Reviews in

545   Mineralogy and Geochemistry, 72, 171-225.

546   Zhang, Y., Ni, H., and Chen, Y. (2010) Diffusion data in silicate melts. Reviews in Mineralogy

547   and Geochemistry, 72, 311-408.

548

549 **FIGURE 1.** Copper concentration profiles measured across the center sections of four synthesized

550 glass beads. Distances shown in the figure are relative to the approximate center of the glass

551 beads.

552

553 **FIGURE 2.** Illustration of the experimental design for our diffusion couple experiments (modified

554 from Wang et al. 2009). Interface between the two glass halves are aligned to be at the center of

555 the graphite heater to minimize temperature gradient. The scale in the figure is not exact.

556

557 **FIGURE 3.** Cu diffusion profile of experiment Cudiffcp 3.1. Probe results obtained on two

558 different days are in open symbols and closed symbols respectively. Traverses 3 to 5 were

559 moved down by 194 ppm to account for the background shift relative to traverses 1 and 2. The

560 diffusivity given in the figure is based on fit of all 5 traverses after the correction for the

561 background shift.

562

563 **FIGURE 4.** Optical microscope images of experimental charges. (a) Cudiffcp 3.1; (b) Cudiffcp

564 7.2. The Cu-free glass is on the top while the Cu-bearing glass is at the bottom. In (a), two pieces

565 of glasses were welded together after the experiment; position of the interface is indicated by the

566 two dents on both sides of the glasses. In (b), there is a large crack right at the interface after the

567 experiment. Red dashed lines show the position of microprobe traverses.

568

569 **FIGURE 5.** Cu concentration profiles for all diffusion couple experiments in this study. Different

570 symbols in each plot represent different traverses analyzed on the sample perpendicular to the

571 interface.

572   **FIGURE 6.** Arrhenius plot of all copper diffusion data obtained in this study. The linear fitting is

573   for 1 GPa experiments only. Errors shown on diffusivities are at 1σ level.

574

575   **FIGURE 7.** Comparison of Cu diffusivities obtained in this study to literature diffusivity data for

576   other elements in anhydrous basaltic melts unless otherwise indicated. a. Cu diffusivities at 0.5

577   GPa from this study; b. Cu diffusivities at 1.5 GPa from this study; c. Cu diffusivities at 1 GPa

578   from this study; d. Cu diffusivities in dry basaltic melt by Mungall's model (Mungall 2002b); e.

579   Cu diffusivities in $Na_2Si_2O_5$ melt at 1000-1400°C and1 bar (von der Gonna and Russel 2000); f.

580   S diffusivities at 1225-1450 ºC and 0.5-1 GPa (Freda et al. 2005); g. H_2O_t diffusivities at 1 wt%

581   water, 400-1500 ºC, and ≤ 1 GPa (Zhang and Ni 2010); h. Cl tracer diffusivities at 1250-1450 ºC

582   and 0.5-1 GPa (Alletti et al. 2007); i. Li tracer diffusivities at 1300-1400 ºC and 1 bar (Lowry et

583   al. 1981); j. Na tracer diffusivities at 1300-1400 ºC and 1 bar (Lowry et al. 1982); k. Co tracer

584   diffusivities at 1300-1400 ºC and 1 bar (Lowry et al. 1982); l. Zn diffusivities in anhydrous

585   rhyolite melt at 898-1400 ºC and 0.01–1 GPa (Baker and Watson 1988).

586

587   **TABLE 1.** Chemical compositions of the synthesized basaltic glasses.

wt%	Et1		Et1Cu		Et2		Et2Cu	
	ave	sd (1σ)	ave	sd (1σ)	ave	sd (1σ)	ave	sd (1σ)
SiO_2	47.26	0.39	46.18	0.72	46.92	0.51	47.27	0.46
TiO_2	1.62	0.06	1.63	0.04	1.67	0.05	1.66	0.05
Al_2O_3	17.52	0.27	18.17	0.64	17.72	0.85	17.21	0.40
FeO_t	10.47	0.21	10.67	0.14	10.58	0.20	10.73	0.25
MgO	5.83	0.07	5.84	0.10	5.89	0.13	5.88	0.08
CaO	10.69	0.06	10.69	0.06	10.51	0.08	10.58	0.05
Na_2O	4.45	0.12	4.45	0.08	4.40	0.11	4.43	0.08
K_2O	2.03	0.04	1.90	0.04	2.06	0.04	2.10	0.04
Cu (ppm)	122	35	1174	121	82	22	1193	93
Total	99.88		99.65		99.76		99.98	

588   Reported data are electron microprobe measurements of far-field compositions on the samples

589   after experiments, except for Cu, whose concentrations are measured on original glasses before

590   experiments. At least 20 points were analyzed and averaged for each glass composition. Details

591   about the microprobe analysis can be found in Analytical Methods.

592

28

593   **TABLE 2.** Summary of experimental conditions and results.

Exp#	P (GPa)	T (°C)	Duration (s)		D (10^{-12} m²/s)	Error (1σ)
			t_1 (s)	t_2(s)		
Cudiffcp 1.1	1	1314	429.3	464.6	403.7*	37.1
Cudiffcp 1.2	1	1314	124.2	162.4	439.4	26.8
Cudiffcp 2.1	1	1397	126.4	162.7	678.3	43.7
Cudiffcp 3.1	1	1509	105.1	140.5	930.9	6.3
Cudiffcp 4.2	0.5	1313	122.1	157.2	505.8	55.9
Cudiffcp 4.3	0.5	1306	119.9	157.7	514.3	71.7
Cudiffcp 4.4	0.5	1298	131.2	161.8	355.3	31.9
Cudiffcp 5.1	1	1575	95.6	137.7	1237.3*	157.5
Cudiffcp 6.1	1.5	1410	125.7	151.1	465.5	28.9
Cudiffcp 7.2	1.5	1581	107.9	140.4	1104.6*	68.8

594   P is corrected pressure; T is corrected temperature; t_1 is the recorded duration at the target

595   temperature ±1 °C; t_2 is the corrected duration using the method described in Experimental

596   Procedure.

597   *Diffusivities of these three experiments were fitted using the solution for a finite diffusion

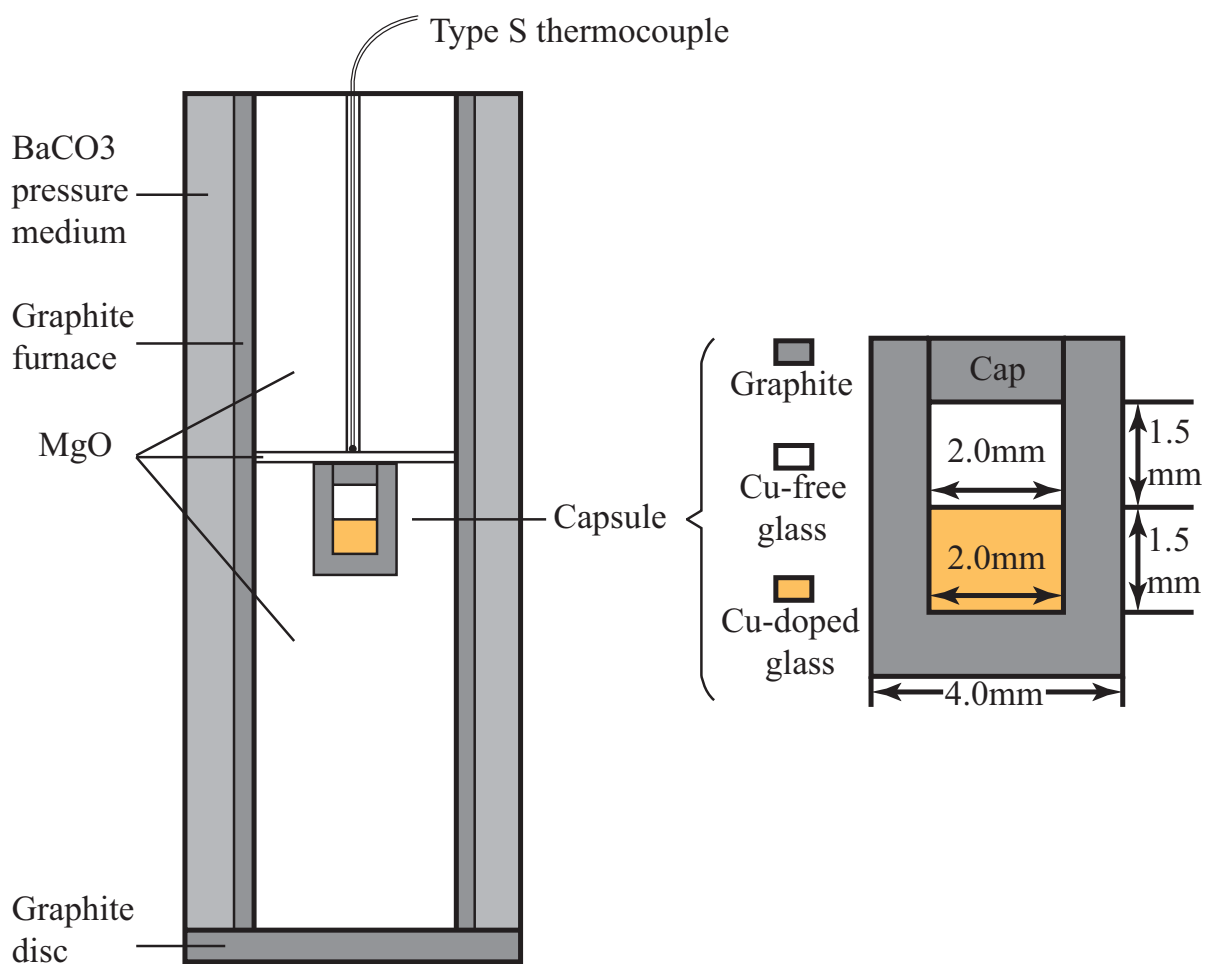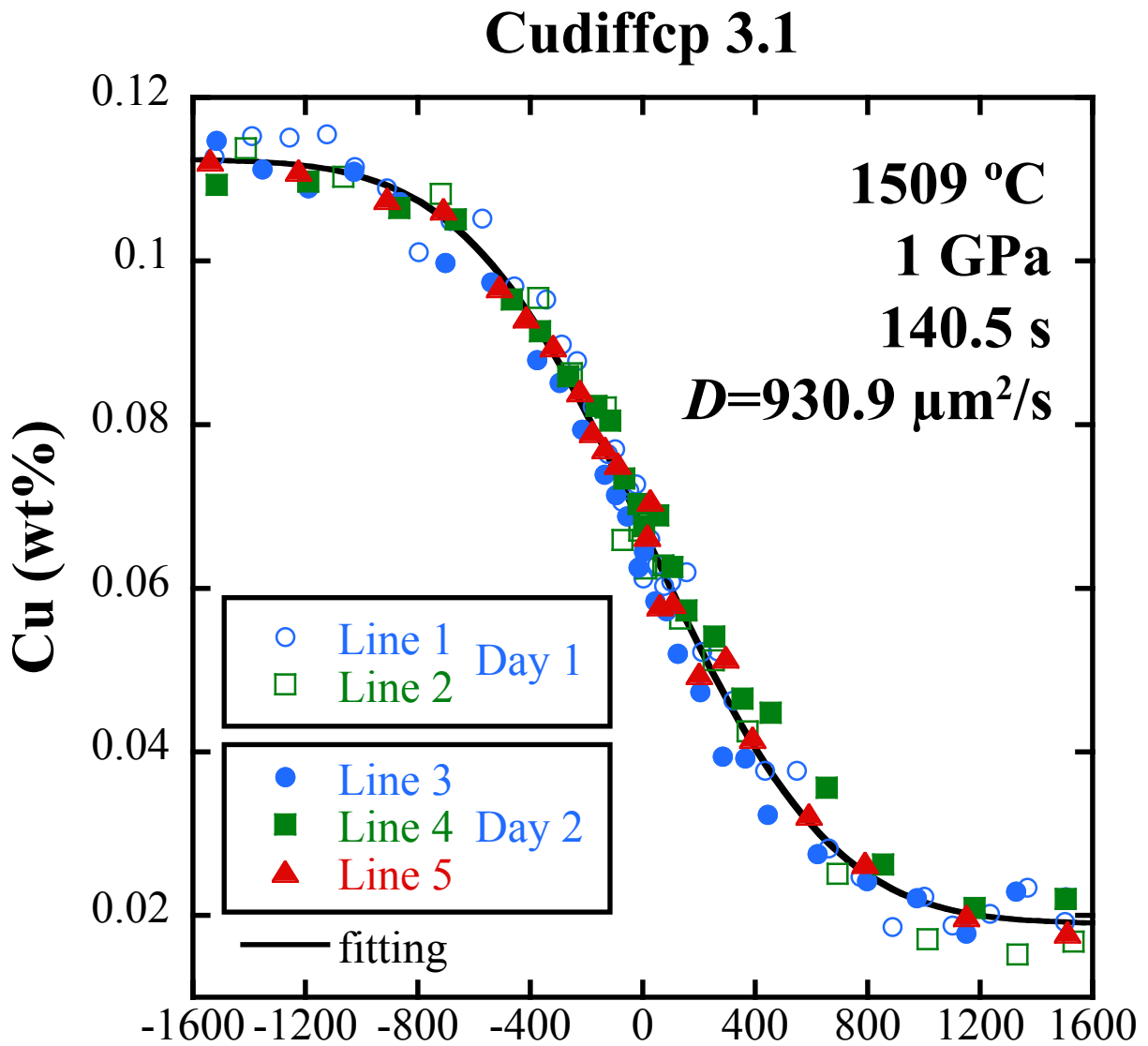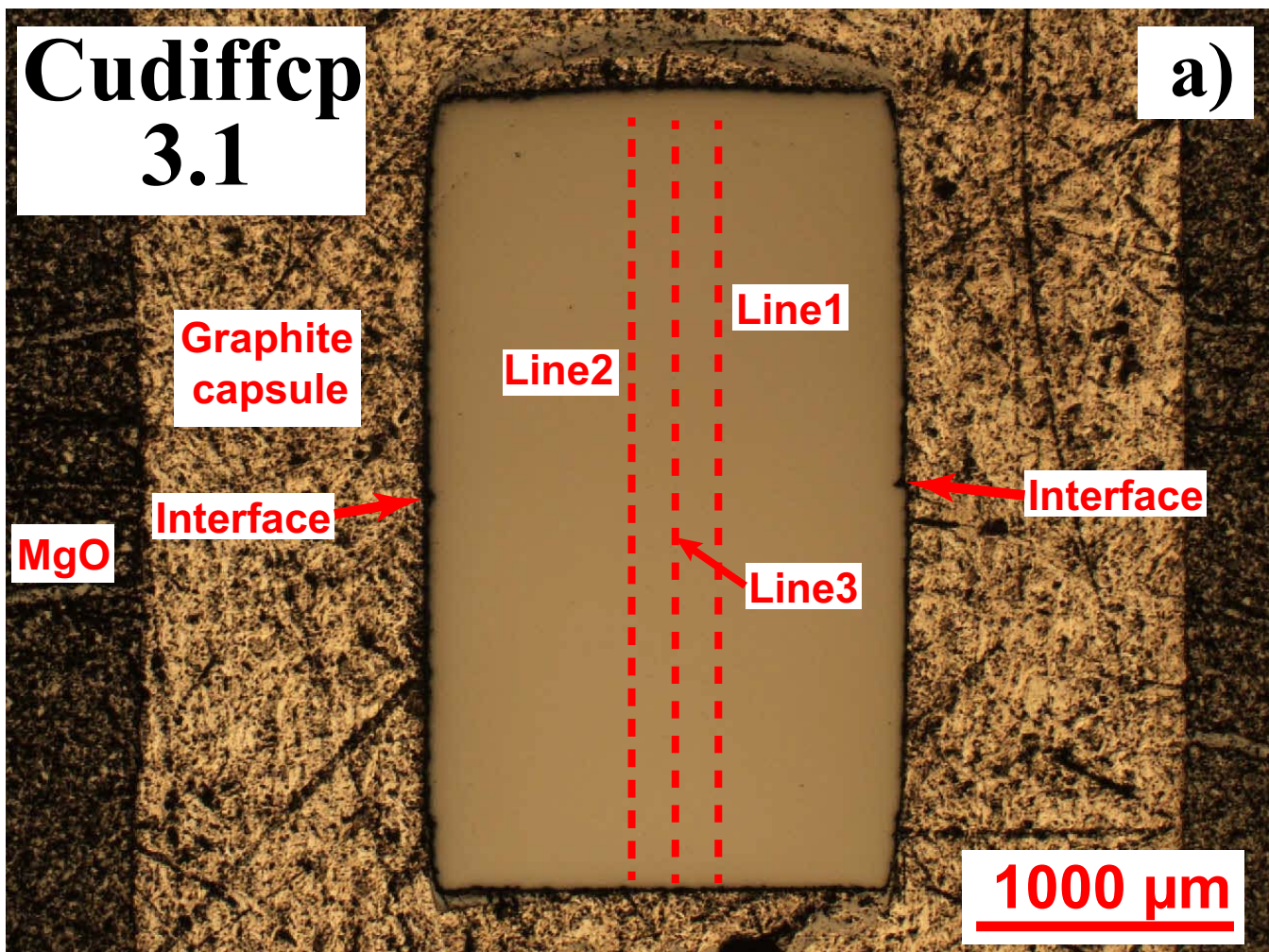598   medium as explained in the text.

Fig. 1

Figure 2

Fig. 3

Cudiffcp 3.1

Fig. 4a

Fig. 4b

Fig. 5a

Cudiffcp 1.1

a)

1314 ºC
1 GPa
465 s
D=403.7 μm²/s
(finite method)

Legend:
- Line1
- Line2
- Line3
- Line 4
- Finite fitting

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

Fig. 5b

Cudiffcp 1.2

b)

1314 ºC
1 GPa
162.4 s
D=439.3 µm²/s

Legend:
- Line 1
- Line 2
- Line 3
- fitting

Cu (wt%)
Distance from interface (µm)

Fig. 5c

Cudiffcp 2.1

c)

1397 ºC
1 GPa
162.7 s
D=678.4 µm²/s

- Line 1
- Line 2
- Line 3
- fitting

Cu (wt%)

Distance from interface (µm)

Fig. 5d

Cudiffcp 4.2

d)

1313 °C
0.5 GPa
157.2 s
D=505.8 μm²/s

Legend: Line 1, Line 2, Line 3, fitting

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

Fig. 5e

Cudiffcp 4.3

e)

1306 ºC
0.5 GPa
157.7 s
D=514.3 μm²/s

Legend: Line 1, Line 2, Line 3, fitting

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

Fig. 5f

Cudiffcp 4.4

f)

1298 ºC
0.5 GPa
161.8 s
D=355.3 μm²/s

Line 1
Line 2
Line 3
fitting

Cu (wt%)

Distance from interface(μm)

Fig. 5g

Cudiffcp 5.1

g)

1575 °C
1 GPa
138 s
D=1237.3 µm²/s
(finite method)

Cu (wt%)

Distance from interface(µm)

- Line 1
- Line 2
- Line 3
- Finite fitting

Fig. 5h

Cudiffcp 6.1

Fig. 5i

Cudiffcp 7.2

1581 ºC
1.5 GPa
140 s
D=1104.6 µm²/s
(Finite method)

i)

Line 1
Line 2
Line 3
Finite fitting

Cu (wt%)

Distance from interface(µm)

Fig. 6

Cu diffusivities in basalt

Fig. 7