Copper isotope fractionation during chemical diffusion in basaltic melt

My proposed research to do at the Geophysical Laboratory is to study Cu isotope fractionation during chemical diffusion by combining gas-mixing furnace experiments, piston cylinder experiments and Cu isotope measurements.

Background

In the periodic table, many elements have multiple stable isotopes that are naturally occurring. Different isotopes of one element have tiny differences in their chemical and physical properties. Therefore they can be fractionated by various chemical and physical processes in nature. In general, isotope fractionation can be categorized into two types: 1) equilibrium fractionation, in which heavier isotopes are usually enriched in stronger bonds; 2) kinetic isotope fractionation, in which light isotopes are usually enriched in the product. Stable isotope geochemistry has a wide range of applications, such as understanding the hydrologic cycle, tracking the origin of rocks and pollutants, understanding mixing of geochemical end members and geothermometers, etc.

Recent advances in analytical techniques, especially the application of Multicollector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS), has enabled us to analyze a wider range of stable isotope systems with improved precision, especially on transition metals and heavy metals (Hoefs, 2015 [1]). Earliest Cu isotope measurements were mainly using thermal ionization mass spectrometry (Shields et al., 1965 [2]). Recent development in analytical method using MC-ICP-MS (Marechal et al., 1999 [3]) significantly improved the precision of Cu isotope measurement in geological and biological samples.

With the increasing amount of studies on Cu isotope system, Cu isotope fractionation at low temperatures was found to be mainly controlled by redox reactions between Cu(I) and Cu(II) species (e,g, Zhu et al., 2002 [4]). While at magmatic conditions, Cu isotope fractionation is likely affected by its chalcophile/siderophile and volatile properties. The chalcophile behavior of Cu is one important factor for multiple formation processes of Cu-bearing ore deposits. Many recent studies explored the possibility of using Cu isotopes as a proxy to understand Cu ore deposit formation (e.g. Maher and Larson, 2007 [5]; Li et al., 2010 [6]). On the other hand, Cu is also moderately siderophile (e.g. Righter et al., 2010 [7]), leads to a possibility of Cu isotope fractionation during core formation processes of planetary bodies. More importantly, Cu is volatile at high temperatures, with a half condensation temperature of 1037 K (Lodders, 2003 [8]), makes Cu isotopes sensitive to evaporation processes at high temperatures. For example, a fractionation of up to 4.5‰ in $\delta^{65/63}$Cu in lunar soil was reported by Moynier et al. (2006) [9]. In terrestrial impact samples, $\delta^{65/63}$Cu can be fractionated to as high as 6.99‰ in tektites (Moynier et al., 2010 [10]). In addition to traditional MC-ICP-MS analysis, in-situ analysis of Cu isotopes in metals and sulfides by coupling a laser ablation system and an MC-ICP-MS has been developed and applied in multiple studies (e.g. Graham et al., 2004 [11]; Li et al., 2010 [6]; Lazarov and Horn, 2015 [12]).

Isotope fractionation during chemical diffusion is one type of kinetic isotope fractionation, and can also be called "dynamic isotope fractionation". During dynamic isotope fractionation, diffusivities of two isotopes of an element are related to their masses by $D_1/D_2 = (m_2/m_1)^\beta$, where D_1, D_2, m_1, m_2 are the diffusivities and molecular masses of the two isotopes respectively, and β is an empirical factor. Dynamic isotope fractionation has been experimentally studied for Ge and Ca in molten oxides (Richter et al., 1999 [13]), and for Li and Ca in silicate melts (Richter et al., 2003 [14]). Dynamic isotope fraction of Cu is interesting to study, one reason is that Cu diffusivity is high in silicate melts (similar to Na, Ni and Zhang, 2016 [15]), making it possible to generate relatively large scale of isotope fractionation in given time. It is important especially at high temperatures, as equilibrium fractionation becomes weaker at high temperature. Copper dynamic isotope fraction might play a role in many of the processes discussed above. One example is during Cu isotope fractionation in tektites. As mentioned in the previous paragraph, tektites are usually enriched in the heavy isotope of Cu. Interestingly, Cu isotopes were found to be more fractionated than Zn in tektites,

although Cu is less volatile than Zn ($T_{1/2}$=726 K and 1037 K for Zn and Cu, Lodders, 2003 [8]). To explain this phenomenon, the authors suggested the possible role of diffusion rate in controlling degassing of Cu and Zn, because Cu^{+} diffuses much faster than Zn^{2+}. However, this explanation also indicates that Cu isotope fraction in tektites can be partly due to the dynamic isotope fractionation during Cu diffusion, which is poorly understood. A simplified model of Cu isotope fractionation in tektites during evaporation is shown in Fig. 1.

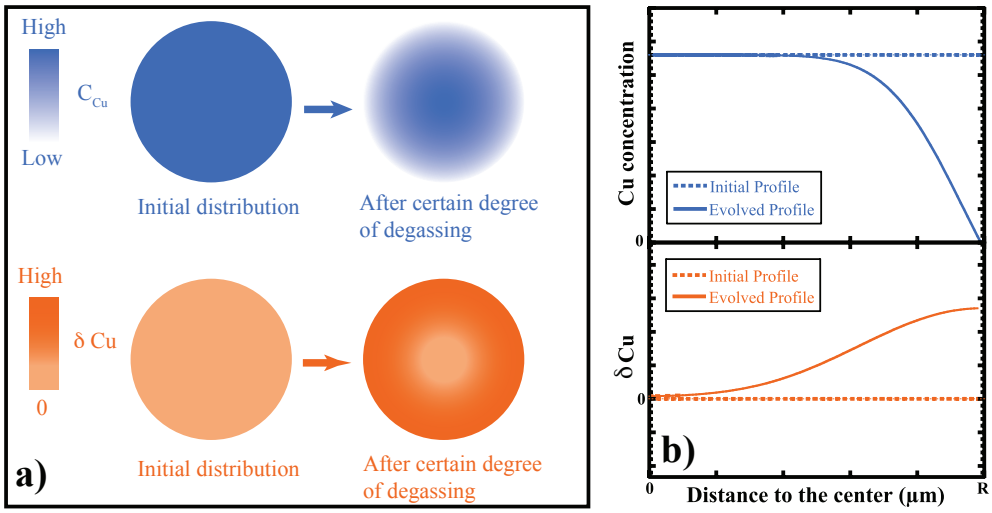

Figure 1: Semi-quantitative illustration of a simplified model for Cu degassing and isotope fractionation in a spherical tektite. This model assumes static diffusion (no convection) and zero Cu concentration at the surface. a) Change of Cu concentration profile and Cu isotope profile of a spherical tektite. Copper is lost from the rim and heavy Cu isotopes are also enriched near the rim. b) Plot of the Cu concentration and isotope profiles along the radius of the spherical tektite from the center to the rim.

Therefore, this proposal aims at combining the previous success of Cu diffusion couple experiments (Ni and Zhang, 2016 [15]) and improved methods of Cu isotope measurement (e.g. Marechal et al., 1999 [3]; Moynier et al., 2006 [9]; Moynier et al., 2010 [10]; Chen et al., 2016 [16], etc.) to study dynamic isotope fractionation of Cu in basaltic melt. Effort will also be made to analyze Cu isotope fractionation profile in the diffusion couple by LA-MC-ICP-MS.

Proposed study

The proposed experiments consist mainly of three steps: 1) synthesizing basaltic glasses using a gas-mixing vertical furnace; 2) diffusion couple experiment using a piston cylinder; 3) Cu isotope measurement using MC-ICP-MS or LA-MC-ICP-MS.

An illustration of dynamic Cu isotope fractionation in a diffusion couple experiment is shown in Fig. 2. Initially the two sides of the couple have different Cu concentrations but the same $\delta^{65/63}$Cu value representing the natural Cu isotope ratio(Fig. 2a). As the experiment goes on, Cu diffuses from the high concentration end to the low concentration end. Since the lighter ^{63}Cu diffuses faster than ^{65}Cu, an enrichment of ^{63}Cu is achieved near the diffusion front on the lower Cu concentration side of the diffusion couple (Fig. 2b). Given enough time, the system reaches equilibrium with an ambient concentration profile (Fig. 2c). Isotopic variations in the system are also erased once the equilibrium state is reached.

1) Synthesizing basaltic glasses

Basaltic glasses with two different starting Cu concentrations need to be synthesized from oxides for the diffusion couple experiments. The method will be similar to our previous approach in Ni and Zhang (2016) [15]. Oxides and carbonates will be weighed according to the target basaltic composition, with a correction of LOI. Then they will be mixed using a mortar and pistol, before doped with different amount

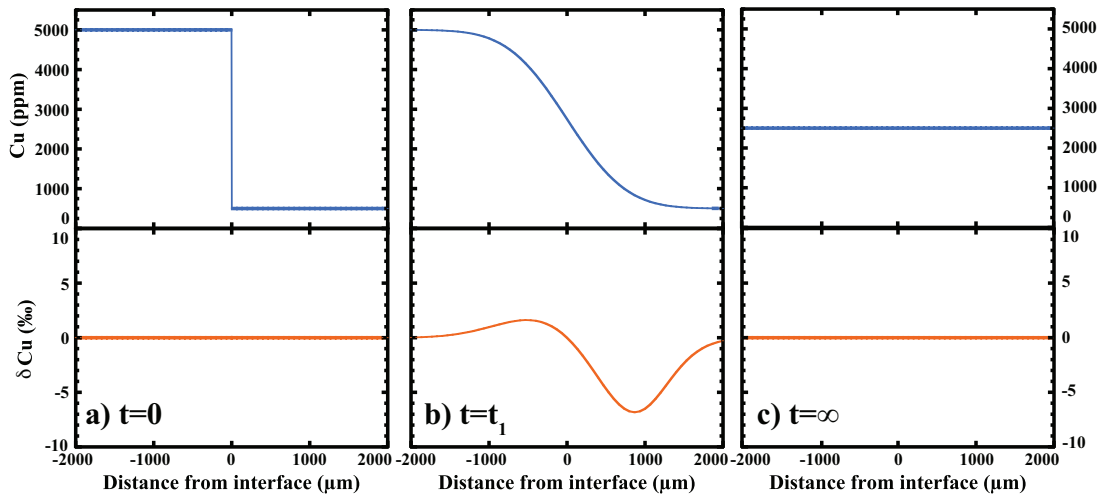

Figure 2: Evolution of Cu concentration and isotope profiles in a diffusion couple experiment. The two halves of the diffusion couple are basaltic glasses with similar matrix compositions but 500 ppm and 5000 ppm starting Cu concentrations, respectively. Calculations were done assuming $\beta = 0.5$. (a) At $t = 0$, Cu concentration profile across the diffusion couple is a step function, but the isotopic profile is uniform, representing the natural Cu isotope compositions; (b) At $t = t_1$, Cu concentration profile is an error function, while the isotope profile reaches one maximum and one minimum near the diffusion fronts on the two sides of the diffusion couple; (3) At $t = \infty$, Cu concentration profile reaches equilibrium, and the isotope fractionations were erased.

of Cu_2O oxide, and mixed again. A certain amount of oxide and carbonate mixture will be weighed and placed into a graphite capsule, then fused at 1400°C under a constant N_2 flow in a vertical furnace for 2 to 3 hours, forming bubble-free and crystal-free glass beads. A section from the synthesized glass beads will be cut and polished to check for chemical homogeneity under electron microprobe.

The targeting Cu concentrations for the two starting glasses will be 5000 ppm and 500 ppm respectively. The choice of Cu concentrations is controlled mainly by three factors: **a)** solubility of Cu at glass synthesizing conditions (∼1 wt% at NNO, Ripley and Brophy, 1995 [17]); **b)** enough amount of Cu in a section on the low concentration end for precise isotope analysis; **c)** maximizing concentration ratio between the two sides of diffusion couple to maximize Cu isotope fractionation.

2) Diffusion couple experiments

Once the starting glasses are synthesized, they will be cut and prepared into cylinders for piston cylinder experiments. An illustration of the experiment capsule design is shown in Fig. 3. The experiments will be similar to those in Ni and Zhang (2016) [15], but a 3/4 inch pressure vessel will be used to allow the usage of a larger diameter of sample in the experiments. In addition, longer glass cylinders will be used in the experiments to increase the total length of the sample for sectioning and Cu isotope analyses. A detailed illustration of the entire experiment charge can be found in Ni and Zhang (2016) [15].

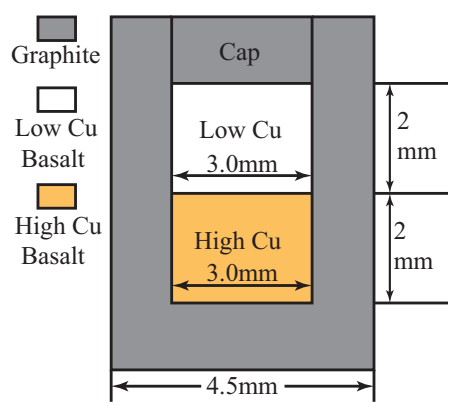

Figure 3: Capsule geometry of the designed copper diffusion experiments.

Length of each half of the diffusion couple is limited to 2 mm because of the consideration of temperature gradient across the experiment charge. At an experiment temperature of 1300 °C, temperature variation across a 4-mm diffusion couple can be 20 °C, according to temperature calibration done on the piston cylinder at University of Michigan (Hui et al. 2008) [18].

Copper concentration profiles will be measured by electron microprobe or LA-ICP-MS, prior to the possible need of destroying the sample for isotope analysis. Diffusivity coefficients extracted from the profiles

will be compared to Ni and Zhang (2016) [15] to check whether they are within reasonable range. At least three traverses along the diffusion couple will be measured to make sure convection is absent during the experiments.

3) Cu isotopic measurments

Analysis of the Cu isotope profiles will be first tried with a laser system coupled with an MC-ICP-MS. Starting glasses for the two halves of the diffusion couple will be analyzed beforehand with traditional MC-ICP-MS method to correct for the matrix effect during LA-MC-ICP-MS analysis. Since both sides of the diffusion couple have very similar major element composition, the matrix effect is expected to be constant across the diffusion couple, making it possible for the LA-MC-ICP-MS analysis to succeed.

If the LA-MC-ICP-MS method turns out to be unsuccessful, the samples will be cut into 9 sections for Cu isotope measurements using wet chemistry and MC-ICP-MS. Depending on the availability of cutting or drilling method available in the lab, the best approach will be used to minimize sample loss and maximize the number of sections to be measured. Assuming the samples will be cut using a fine-diamond saw, a kerf loss of $\sim$200μm is expected at each cutting position. Assuming a quench crack occurs at the interface, the sample can be further divided into 9 sections as shown in Fig. 4a.

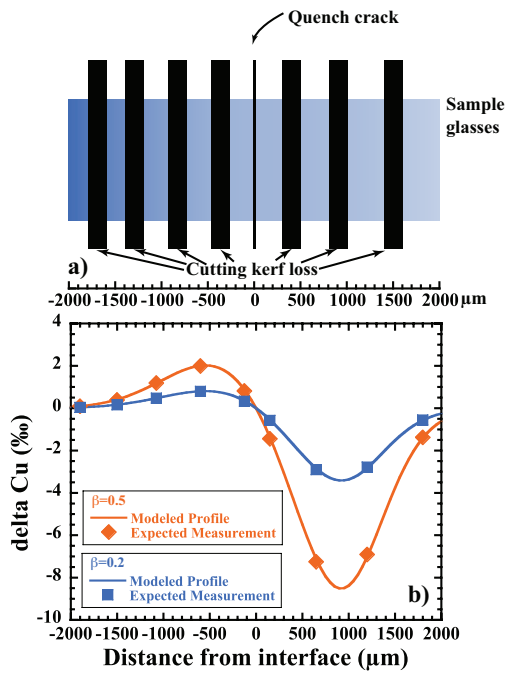

Figure 4: Illustration of a) planned sample sectioning by cutting and b) expected isotope measurements of 9 cutted sections corresponding to $\beta = 0.5$ and $\beta = 0.2$.

Each section of the glass will be cleaned ultrasonically in water, and then fully dissolved in HNO_3/HF. The solution sample will be run through an anion exchange resin to separate Cu from major elements and Zn, before measured using an MC-ICP-MS. Detailed steps of sample processing and Cu isotope measurement will be similar to those in Chen et al. (2016) [16]. The expected outcome profile will be similar to Fig. 4b, with a best fit isotope profile going through measured isotope points. The most critical data points are those two that are near the diffusion front, because they vary the most depending on different β values. Once successful, experiments at multiple temperatures will be done to see if a temperature effect on β factor is resolvable.

Anticipated results

The expected outcome of β factor for dynamic Cu isotope fractionation from the proposed study might be important to help understand: 1) the mechanism of Cu diffusion in silicate melts; 2) the contribution of dynamic Cu isotope fractionation to the fractionation of Cu isotopes in impact glasses (e.g. tektites, lunar impact glasses); 3) the potential role of kinetic control in Cu-bearing ore formation processes; and 4) possible Cu isotope fractionation during rapid core assimilation processes.

The high diffusivity and low activation energy for Cu diffusion in silicate melts indicates that Cu is possibly diffusing as a relatively simple molecular (e.g. Cu^+ or CuO^-). The experimentally determined β factor for dynamic Cu isotope fractionation can be used to infer the diffusion species of Cu in silicate melts. For example, a β factor of 0.5 means Cu is diffusing as Cu^+; a β factor close to 0.41 might suggest that Cu is diffusing as CuO^-; while a β factor smaller than 0.41 means Cu is likely diffusing as a more complicated cluster in silicate melts.

As mentioned above in the background, Cu isotopes in tektites and various lunar materials are fractionated during evaporation processes. Fractionation of Cu isotopes during evaporation processes can be affected by at least two processes: 1) dynamic Cu isotope fractionation during diffusion transport of Cu to the evap-

oration surface; 2) evaporation of Cu from surface melt to the vapor phase. An experimentally determined β factor is crucial in quantitatively understanding Cu isotope fractionation during the first process. From a broader scale, the proposed study would enhance our understanding on evaporation processes during impact events.

Recent studies suggest a potential role of kinetic control in Cu-bearing ore formation processes. Either in the case of magmatic sulfide deposit formation, where sulfide drops form and scavenge chalcophile elements (e.g. Cu, Au, Pt) down through a magma chamber, or in the case of porphyry-type deposit formation, where a magmatic fluid phase enrich and transport metal elements (e.g. Cu, Au, Mo) from the silicate magma to the shallower crust, an experimentally determined β factor for dynamic Cu isotope fractionation can be used to assess the possibility of kinetic control in these processes. For example, if the β factor is found to be significant, a role of Cu diffusion control would likely result in observable Cu isotope fractionation between the Cu ore deposit and its source magma. Similarly, given the possibility of Cu diffusion control on Cu re-equilibrium between the core and the mantle during rapid core assimilation processes in a terrestrial body, a Cu isotope fractionation would likely occur if the β factor for dynamic isotope fractionation is significant enough.

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