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Copper and Li diffusion in plagioclase, pyroxenes, olivine and apatite, and consequences for the composition of melt inclusions

Andreas Audétat[a,*], Li Zhang[b], Huaiwei Ni[b]

[a] Bayerisches Geoinstitut, Universität Bayreuth, 95447 Bayreuth, Germany
[b] School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

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Abstract

Silicate melt inclusions are an important tool to reconstruct original concentrations of volatiles and metals in silicate melts, as these constituents are partly lost during magma solidification. However, melt inclusions analyzed in co-precipitated minerals in volcanic rocks commonly show strongly divergent Cu contents, raising doubts about the validity of their composition. To understand the origin of this divergence a multiple approach was followed. First, the phenomenon was documented by recording petrographic details of five volcanic samples and analyzing 189 melt inclusions by laser-ablation ICP-MS. Second, diffusion experiments on gem-quality plagioclase, clinopyroxene, orthopyroxene, apatite and olivine were performed in a gas mixing furnace to constrain diffusion coefficients of Cu and to a lesser extent of Li. Third, re-equilibration experiments were performed on melt inclusions within plagioclase crystals to induce changes in their Cu and Li contents.

The LA-ICP-MS analyses reveal that plagioclase-hosted and orthopyroxene-hosted melt inclusions in volcanic rocks commonly contain an order of magnitude more Cu than melt inclusions in co-precipitated clinopyroxene and olivine. Plagioclase-hosted melt inclusions in intrusive rocks, on the other hand, do not show this divergence. The diffusion experiments conducted on minerals find that Cu and Li diffusion in plagioclase is extremely fast ($\log D = -13.0$ to $-11.5\ \mathrm{m^2\,s^{-1}}$ at 1000 °C) and in both cases occurs via two separate diffusion mechanisms. Copper diffusion coefficients in apatite, clinopyroxene, orthopyroxene and olivine are 2–3 orders of magnitude lower but are still high compared to most other elements. Both the re-equilibration experiments on melt inclusions and quantitative modeling based on the measured diffusion coefficients demonstrate that at 1000 °C plagioclase-hosted melt inclusions can re-equilibrate their Cu and Li content with that of the surrounding magma within a few hours to a few weeks, whereas apatite-, clinopyroxene-, orthopyroxene- and olivine-hosted melt inclusions require tens of years to hundreds of years to do so. Abnormally high Cu contents of plagioclase- and orthopyroxene-hosted melt inclusions appear to result from postentrapmental Cu gain. In the case of orthopyroxene-hosted melt inclusions Cu seems to have been gained as a consequence of postentrapmental sidewall crystallization, which triggered the formation of sulfide globules that acted as a Cu sink. This process likely occurred at depth in magma chambers. Plagioclase-hosted melt inclusions, on the other hand, seem to have gained Cu in exchange for hydrogen that diffused out of the melt inclusions during or after volcanic eruption. Our results suggest that Cu (and also Li) concentrations measured in melt inclusions have to be generally treated with caution, and that particular prudence has to be used in the case of plagioclase and orthopyroxene hosts.

Keywords: Copper diffusion; Lithium; Melt inclusions; Experimental; Postentrapmental modification; LA-ICP-MS

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* Corresponding author.
E-mail address: andreas.audetat@uni-bayreuth.de (A. Audétat).

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1. INTRODUCTION

Melt inclusions are defined here as small droplets of silicate melt that were trapped in minerals during their growth in magmas (Audétat and Lowenstern, 2014). They represent an important tool to reconstruct original volatile contents and metal concentrations in silicate melts because such information cannot reliably be obtained from whole-rock samples. However, it was noticed that melt inclusions do not always behave as closed systems. For example, it has been experimentally demonstrated that quartz-hosted melt inclusions can diffusively gain or lose significant amounts of Na, Li, Ag, Cu in a matter of a few days (Kamenetsky and Danyushevsky, 2005; Zajacz et al., 2009; Audétat and Lowenstern, 2014; Rottier et al., 2017), that olivine-hosted melt inclusions commonly lost Fe (Danyushevsky et al., 2000), and that H_2 and molecular H_2O can be quickly lost or gained during heating experiments (Massare et al., 2002; Portnyagin et al., 2008; Gaetani et al., 2012). Several studies noticed that melt inclusions hosted in plagioclase contained much higher Cu than ones hosted in other, co-precipitated minerals (Halter et al., 2005; Zajacz and Halter, 2007; Agangi and Reddy, 2016), which was interpreted to reflect co-trapment of Cu-rich volatile or sulfide phase in the plagioclase-hosted melt inclusions (Zajacz and Halter, 2009; Agangi and Reddy, 2016). However, in view of the high Cu mobility in quartz (which affects also the Cu content of fluid inclusions; e.g., Lerchbaumer and Audétat, 2012) it may also be feasible that the discrepancy was caused by postentrapmental Cu diffusion through the host mineral. This suspicion is fueled by the fact that plagioclase can be artificially colored red by heat-treatment of in Cu-rich environment (Emmett and Douthit, 2009). However, according to our knowledge no Cu diffusion coefficients have been published for any common magmatic minerals so far (Zhang and Cherniak, 2010).

The aim of the present work is fivefold: (1) to document systematic discrepancies in the Cu content of natural melt inclusions hosted in various minerals, (2) to constrain Cu diffusion coefficients for common igneous minerals, (3) to experimentally demonstrate that Cu can rapidly diffuse into or out of plagioclase-hosted melt inclusions, (4) to quantitatively model Cu re-equilibration times of melt inclusions in various host minerals, and (5) to discuss the potential mechanisms that lead to abnormally high Cu contents of certain melt inclusions. Because some experiments simultaneously allowed determination of Li diffusion coefficients we also report data on Li. However, this dataset is less complete than that for Cu.

2. METHODS

2.1. Characterization of natural, melt inclusion-bearing samples

In order to document systematic variations in the Cu content of natural melt inclusions, five volcanic samples containing melt inclusions in co-precipitated minerals were studied. Samples *PG18* and *PG21* were collected from Miocene trachyandesite flows from the Pine Grove area in Utah, USA, containing phenocrysts of plagioclase, clinopyroxene, orthopyroxene, spinel and olivine. Sample *Death4* is a young (ca. 2 Ma old) basaltic andesite from Death Valley, California, USA, containing phenocrystic plagioclase, clinopyroxene, olivine, orthopyroxene and spinel. Sample *CC4* was taken form an Eocene basaltic andesite flow exposed along Costilla Creek in the Questa Caldera, New Mexico, USA, containing phenocrysts of plagioclase, clinopyroxene, orthopyroxene and altered olivine and spinel. Sample *CC3* was collected from a slightly older, andesitic to dacitic volcanic unit in the same area and contains phenocrysts of plagioclase, amphibole, clinopyroxene, biotite, spinel and orthopyroxene. Further details on sample location, age, and mineralogy are provided in supplementary Table S1. A thick section scan of sample *PG18* and photomicrographs of contained melt inclusions are shown in Fig. 1, whereas similar images taken from samples *Death4*, *CC4* and *CCS* are provided in supplementary Figs. S1–S3. Sample *PG21* is mineralogically identical to *PG18* but consists of frothy rather than massive lava. Although all samples are of volcanic origin, many of the contained melt inclusions are not glassy. For example, orthopyroxene-hosted melt inclusions in sample *PG18* contain large daughter crystals (Fig. 1c), whereas plagioclase- and clinopyroxene-hosted melt inclusions contain numerous small microlites (Fig. 1b, d).

From each mineral phase of a given sample, between 2 and 48 melt inclusions were measured by LA-ICP-MS using a 193 nm ArF Excimer laser (GeolasPro, Coherent, USA) attached to a quadrupole mass spectrometer (Elan DRC-e, Perkin Elmer, Canada). The laser was operated at 10 Hz and an energy density of 3–10 J cm^{-2} at the sample surface. The sample chamber was flushed with He gas at a rate of 0.4 l min^{-1}, to which 5 ml min^{-1} H_2 was added on the way to the ICP-MS. Measured isotopes include ^{7}Li, ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{30}Si, ^{31}P, ^{39}K, ^{43}Ca, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{62}Ni, ^{65}Cu, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{133}Cs, ^{137}Ba, ^{140}Ce and ^{208}Pb, measured using dwell times of 10–50 ms. The ICP-MS was tuned to a ThO rate of 0.07 ± 0.02% and a rate of doubly-charged ^{42}Ca ions of 0.2–0.3% based on measurements on NIST SRM 610 glass. Entire, unexposed melt inclusions were drilled out of their host without prior re-homogenization, choosing a circular laser pit that was slightly larger than the melt inclusion. The contribution of excess ablated host to the mixed signal was numerically subtracted using constraints from whole-rock data (Halter et al., 2004). Plagioclase-hosted melt inclusions were corrected based on the trend of FeO_{tot} vs. SiO_2, i.e., plagioclase host was subtracted from the mixed signal until the remaining composition fit on the FeO_{tot} vs. SiO_2 trend defined by whole-rock data. Clinopyroxene-hosted melt inclusions were corrected based on the trend of CaO vs. SiO_2 or Al_2O_3 vs. SiO_2, orthopyroxene-hosted ones based on Al_2O_3 vs. SiO_2 or MgO vs. SiO_2, and olivine-hosted ones based on Al_2O_3 vs. SiO_2. In sample *Death4* all melt inclusions were calculated using the Al_2O_3 content of the glassy matrix as internal standard. To monitor potential variations in sulfur contents we also measured ^{32}S, but the results are only semiquantitative because they depend strongly on