

**DIRECT MEASUREMENTS OF COPPER SPECIATION IN BASALTIC GLASSES USING X-RAY ABSORPTION SPECTROSCOPY: UNDERSTANDING THE ROLE OF SULFUR IN COPPER COMPLEXATION IN MELTS.** A. Lanzirotti<sup>1</sup>, L. Lee<sup>2</sup>, E. Head<sup>3</sup>, S. Sutton<sup>1</sup>, M. Newville<sup>1</sup>, M. McCanta<sup>4</sup>, A. Lerner<sup>5</sup>, P. Wallace<sup>5</sup>.<sup>1</sup>Center for Advanced Radiation Sources, Univ. of Chicago, Chicago, IL 60637 (lanzirotti@uchicago.edu); <sup>2</sup>Hawaiian Volcano Observatory, USGS, HI 96718; <sup>3</sup>Dept. of Earth Sci., Northeastern Illinois Univ., Chicago, IL 60625; <sup>4</sup>Dept. of Earth and Planet. Sci., Univ. of Tennessee, Knoxville, TN 37996; <sup>5</sup>Dept. of Earth Sci., Univ. of Oregon, Eugene, OR 97403.

**Introduction:** The solubility of metals such as copper (Cu) in silicate melts can be dependent on the oxygen fugacity ( $fO_2$ ) of the melt and the availability of potential ligands such as S and Cl. Understanding how these parameters control Cu solubility is important in modeling magma evolution and the driving mechanisms for core formation in terrestrial planets [1,2]. The sensitivity of Cu partitioning to these parameters will depend on what the stable Cu species are in the melt under given magmatic conditions. It is generally assumed that monovalent  $Cu^{+}$  oxygen species dominate in most terrestrial magmas, although some experimental studies have observed a weaker correlation between Cu solubility and melt S concentration. This may indicate that some degree of Cu-S complexing also occurs at high melt  $fS_2$ , possibly stabilizing some Cu in the melt as an oxy-sulfide species [3,4]. Preferential bonding of Cu in the melt to  $S^{2-}$  anions relative to  $O^{2-}$  would be expected to result in weaker dependency of Cu partitioning with magmatic  $fO_2$ .

This study provides a direct measurement of Cu speciation in natural basaltic glasses equilibrated at  $fO_2$ 's lower than the nickel-nickel oxide (NNO) buffer. At these  $fO_2$ 's sulfur in the melt should be present as a  $S^{2-}$  species. Measurement of the Cu speciation in magmatic glasses by X-ray Absorption Fine Structure (XAFS) spectroscopy should serve as a proxy for complexation of Cu in the magmatic liquid. XAFS is the only available methodology for directly measuring Cu speciation at the natural concentrations observed in most basalts (~100 ppm) and within small melt inclusions (typically < 100  $\mu m$  in diameter). Results are presented from several volcanic systems, but focus on samples collected from the 2008-2018 summit eruptions at Halema'uma'u at Kilauea, Hawai'i [5]. This suite of samples provides a unique opportunity to systematically evaluate how changes in Cu speciation correlate with magmatic S content in natural magmas.

**Methods:** Natural samples analyzed primarily include magmatic and volcanic glasses collected at the Kilauea summit vent at Halema'uma'u and from the 2018 Lower East Rift Zone (LERZ), Hawai'i between 2008 and 2018 [5, 6]. Samples were provided by the USGS Hawaiian Volcano Observatory (HVO). Additional natural glasses analyzed include MORB samples from the Juan de Fuca Ridge and East Pacific Rise and

from Mt. Etna and Nyamuragira volcanos. Natural samples consist of polished grain mounts which preserve both matrix glass and olivine-hosted melt inclusions (MI). Measured S concentrations in these natural samples vary from <100 ppm to >1000 ppm. A suite of 1-atm synthetic glasses of basaltic composition, with variable  $fO_2$ , were also analyzed. Cu K-edge micro-XAFS spectra were collected at Beamline 13-ID-E at the Advanced Photon Source. S and Cu abundances were also determined based on contemporaneous synchrotron micro-XRF analysis of the glasses.

**Results:** Cu XAFS spectroscopy of natural basaltic glasses equilibrated at  $fO_2$  lower than NNO shows that two primary Cu species are stabilized (Fig. 1), although in some samples both species may coexist.

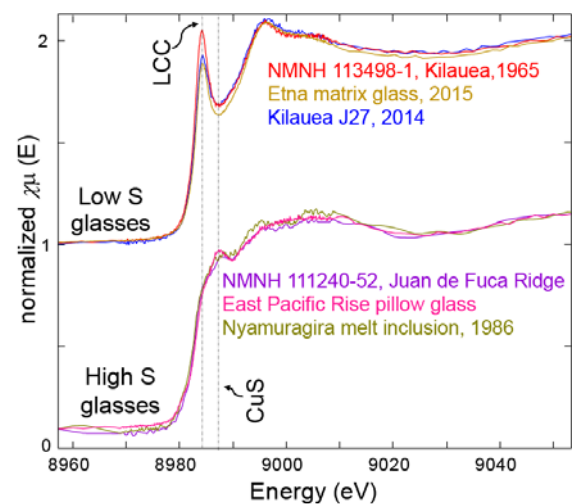


Figure 1: Cu XAFS spectra collected for natural magmatic glasses including high S (bottom) glass from MORB (Juan de Fuca, East Pacific Rise) and Nyamuragira alkaline basalt and low S (top) matrix glasses from the 1965 and 2014 Kilauea eruptions and lapilli from 2015 eruption at Mt. Etna. Dashed line labeled "LCC" shows energy of spectral maximum for Cu(I) complexes in a linear geometry and line labeled "CuS" shows energy of first maxima measured in covellite.

Which species dominates appears to correlate with the S content of the glass. In glasses with high measured S (>1000 ppm), such as MORB, the Cu XAFS spectra are indistinguishable from spectra measured in crystalline Cu(I)S standards (i.e. covellite). In glasses with

low measured S (<500 ppm), as found in degassed matrix glasses, the Cu XAFS spectra are most similar to spectra measured for aqueous linear Cu(I) complexes (LCC) [7]. We hypothesize that the Cu speciation in these low-S glasses most likely reflects the presence of Cu<sup>1+</sup>-O ligands in a linear geometry. This is consistent with results for 1-atm experimental glasses where  $fO_2$  was controlled, but S and Cl were not, allowing these volatiles to degas. The experimental glasses all yield similar LCC-type spectra, regardless of their  $fO_2$ .

To better understand the observed transition from sulfur- to oxygen- bound Cu species in natural melts, Cu speciation was also measured in MI and matrix glasses in samples collected from the 2008-2018 Kīlauea summit eruptions in Hawai'i [5,6]. These samples preserve a broad range in S concentration from <450

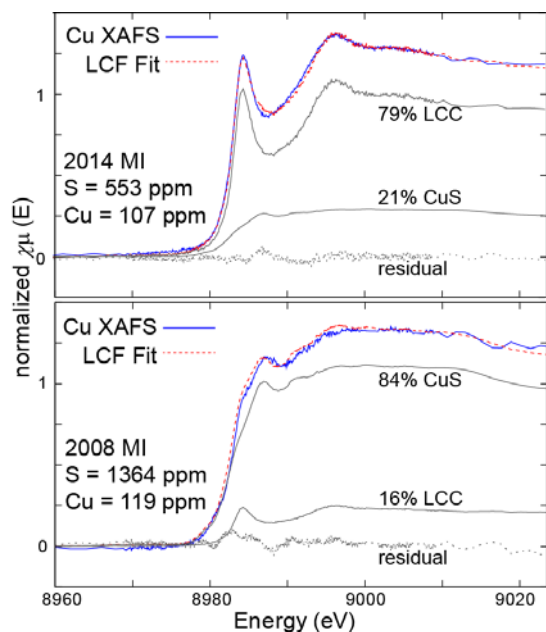


Figure 2: Linear combination fits (LCF) of Kīlauea glasses to predict their relative percentage of LCC species. Shown are fits for MI erupted in 2008 (bottom) and 2014 (top). Measured Cu XAFS spectra are shown as solid lines and the predicted fits, using CuS and LCC standards as the predictor components, are shown as dashed lines. Also plotted are the weighted component spectra for the fit and the residual.

ppm to >1000 ppm, which varies systematically as a result of S degassing. The highest S abundances measured in these glasses are lower than calculated sulfide saturation (SCSS) values

As was observed in the other natural glasses analyzed, Kīlauea summit MI with measured S abundances >1000 ppm yield Cu XAFS spectra similar to spectra measured for CuS-like species while MI and matrix glasses with S abundances <500 ppm yield Cu XAFS spectra characteristic of LCC, most likely representa-

tive of a linear, Cu<sup>1+</sup>-O species (Fig. 2). However, MI with intermediate S abundances between 500-1000 ppm yield spectra that are consistent with the presence of mixed LCC- and CuS-type species. These intermediate-type spectra can be quantitatively reproduced using a two-component linear mixing model, mixing between end member CuS-like and LCC species (Figs. 2 and 3). Cu abundance is not observed to change significantly over this transition (Fig. 2).

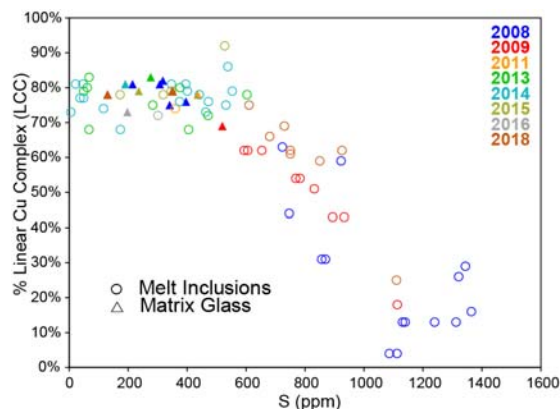


Figure 3: Plot of measured S abundance vs calculated %LCC for analyzed Kīlauea glasses. Matrix glasses are shown as solid triangles whereas MI are shown as open circles. Color-coding of the symbols indicates the date of eruption by year.

**Conclusions:** The results of this study show that in Kīlauea basaltic melts with S >1000 ppm, Cu is strongly complexed to S. Only below 1000 ppm does Cu begin to significantly complex with O, and Cu remains complexed to both ligands at the lowest S concentrations measured. Our LCF modeling suggests that even in melts with S concentrations <500 ppm, up to 20% of the Cu may remain bound to S ligands. Analysis of other natural glasses suggest this is not unique to Kīlauea glasses. In basaltic melts with moderate to high S content (i.e. near SCSS and  $fO_2 < NNO$ ), it appears that Cu-S complexing is strongly favored. This is consistent with studies that show Cu sulfide melt-silicate melt partition coefficients in MORB show little to no dependency on  $fO_2$  [8].

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