

Structural role of Cu in synthetic silicate glasses by XANES spectroscopy

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9 shifts from 15/12/2006 to 18/12/2006

Beam quality good. Some delays were encountered setting up the monochromator and multichannel fluorescence detection.

No other beamtime on other beamlines for this research project

Introduction

Understanding how the local environment of Cu changes as a function of composition, pressure, temperature and oxygen fugacity is essential in order to explain the partitioning behaviour of this element and its role in a wide number of magmatic processes [1-2]. The speciation of Cu in low T aqueous geochemical environments (the solubility of the ore component in the aqueous fluid is a critical parameter in the formation of various ore deposits) and the metal mobility, toxicity and bioavailability are also strongly dependent on the structural configuration of Cu [3-4]. Despite the importance of these studies, very little is known about how the structural environment of Cu influences the chemical and geochemical behaviour of glasses [5-7]. Here we first examine the pre-edge region of the Cu K-edge XANES spectrum of several Cu-bearing crystalline oxide and silicate standards. We then investigate the Cu K-edge XANES spectra of several series of Cu-bearing silicate glasses with various base chemical composition and total Cu concentration, formed at differing oxygen fugacities (fO_2) in order to find systematic correlations between these chemical parameters and the local structural environment of copper.

Experiment

Synthetic glass samples ranged in both base chemical composition (sodium disilicate NS2, haplogranitic HPG8, anorthite-diopside AnDi) and total Cu content (between 1 to 10 % Cu oxide component). Samples were crushed and ground to powder form and placed on a flat plate for Cu K-edge XANES spectroscopy. No special sample environment such as controlled atmosphere or high (or low) temperature or high pressure conditions were required. Relatively low Cu concentrations in the vitreous samples required that the spectra be collected in fluorescence mode using the high-purity 13-element Ge detector. Spectra of Cu-bearing crystalline standards with known structure and oxidation state (e.g. diopside, cuprite, kinkite) were also acquired in order to calibrate the energy and to model the edge shape (edge energy, white line energy, intensity and width, pre-edge peak energy and intensity) according to Cu coordination number, polyhedral shape and oxidation state.

Results

The combination of a high-resolution Si (311) monochromator and multichannel fluorescence detection allowed us to observe even weak features in the pre-edge region of the Cu K-edge (Fig. 1). Whereas moderate to strong pre-edge peaks were observed in the cases of cuprite and hemimorphite, the spectra of diopside and kinkite showed negligible intensities, even though further up the main edge their spectra include shoulders, which have been interpreted to results from

1s→ 4p transitions in tetrahedrally coordinated species [8-9]. The spectrum of cuprite displays the strongest pre-edge peak among the standards due to its low oxidation state, low coordination number and linear geometry. Divalent copper in diopside and kinkite, however, is incorporated as higher coordinated species with variable degrees of distortion and their pre-edge intensities are extremely weak. For each glass series, as many as four different samples ranging in oxygen fugacity at which the glass was formed was examined by Cu K-edge XANES spectroscopy. The spectra are characterized by a pre-edge feature that is nearly coincidental with the position of the main edge, superimposed along its steep slope, making background correction for quantitative analysis of the pre-edge difficult. An example set of data is illustrated in Fig. 2 for a synthetic haplogranitic glass with 5% Cu showing 2-Gaussian fits of background-subtracted normalized intensities. The centroid position of the pre-edge peak remains relatively constant as a function of oxygen fugacity suggesting little variation in the overall oxidation state of copper. In contrast, the intensity (area under the peak) of the pre-edge peak is quite sensitive to fO_2 which suggests that the small changes in the overall oxidation state result in large variations in the fraction of divalent copper in tetrahedral coordination. Similar observations were also made in the case of Cu-bearing glasses of moderately polymerized An-Di composition and the more depolymerized NS2 composition. Such variations, particularly if tetrahedrally coordinated Cu acts as a network-forming cation like Si^{4+} and Al^{3+} , are likely to strongly influence the rheological properties of Cu-bearing silicate liquids.

Fig. 1 Pre-edge regions of the Cu K-edge XANES spectrum for selected crystalline standard compounds, demonstrating the strong variation of intensity and centroid position of the pre-edge peak, depending on local structural environment of Cu.

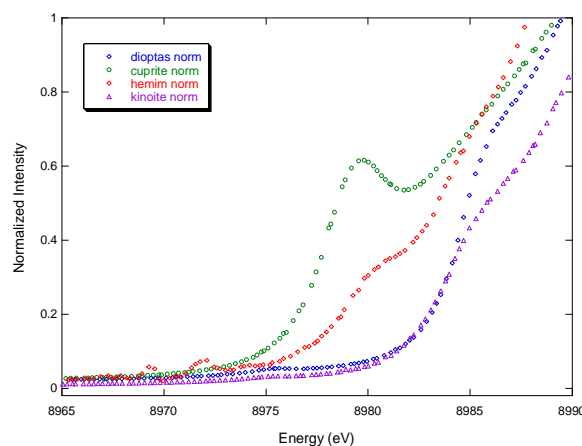
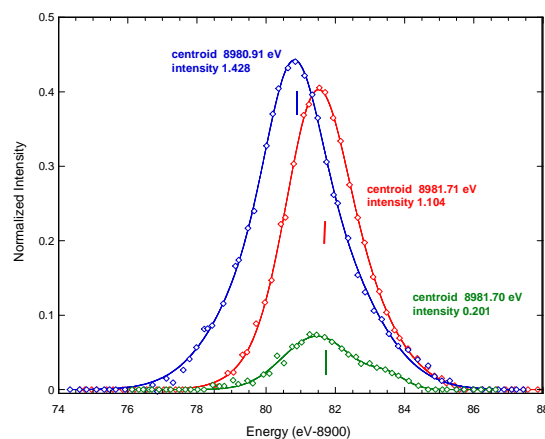


Fig. 2 Fitted (2 Gaussians) pre-edge regions of the Cu K-edge XANES spectra of HPG8 glasses containing 5% copper. Larger variations in pre-edge intensity are observed compared to changes in its centroid position.



Future Perspectives

Additional XANES data over a wider range of chemical compositions would allow us to predict how Cu behaves in a variety of geochemical environments. A developing model for the characterization of the local structure surrounding Cu and other transition elements in amorphous materials complemented by independent Cu redox measurements would also allow us to predict the

rheological and other physical properties of magmatic liquids in a wide range of volcanological settings, as these properties are expected to be sensitive to the variability of the structural environment of Cu. As Cu oxidation state and coordination are also likely to be influenced by the presence and amount of dissolved H₂O in silicate liquids, it is also important to characterize hydrous Cu-bearing glasses using XANES spectroscopy.

References

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Publications

None currently

Conferences

None currently