QUANTIFYING AND CORRECTING THE EFFECTS OF ANISOTROPY IN XANES MEASUREMENTS OF CHROMIUM VALENCE IN OLIVINE: IMPLICATIONS FOR A NEW OLIVINE OXYBAROMETER

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ABSTRACT

Chromium valence ratios in igneous olivine may hold a wealth of redox information about the melts from which they crystallized. It has been experimentally shown that the Cr²⁺/ΣCr of olivine varies systematically with $f_{O_2}$, therefore measurements of Cr valence in olivine could be employed as a quantitative oxybarometer. In situ synchrotron µ-XANES analyses of Cr valence ratios of individual olivine phenocryts in thin section have the potential to unlock this stored magmatic redox information on a fine spatial scale. However, there are still obstacles to obtaining accurate XANES measurements of cation valence in crystalline materials, as the results from these measurements can be compromised by anisotropic absorption effects related to the crystallographic orientation of the sample. Improving the accuracy of XANES measurements of Cr valence ratios in olivine by calibrating an anisotropy correction is a vital step in developing Cr valence measurements in olivine as a rigorous oxybarometer. To accomplish this goal, we have used an integrated approach that combined experiments, electron backscatter diffraction analysis, and XANES measurements in olivine to systematically examine how orientation affects the resultant Cr K-edge XANES spectra and the Cr valence ratios that are calculated from them. The data set generated in this work was used to construct a model that mitigates the effects of anisotropy of the calculated Cr²⁺/ΣCr values. The application of this correction procedure as a part of spectral processing improves the overall accuracy of the resultant Cr²⁺/ΣCr values by nearly a factor of five. The increased accuracy of the XANES measured Cr valence ratios afforded by the anisotropy correction reduces the error on calculated $f_{O_2}$ values from approximately ±1.2 to ±0.25 log units.

Keywords: XANES, Cr valence, anisotropy, olivine, oxybarometer

INTRODUCTION

Synchrotron X-ray absorption near edge structure (XANES) measurements of the valence ratios of multivalent cations in quenched glasses and minerals are a potentially powerful tool for understanding the redox histories of magmatic rocks. Recently the experimental study of Bell et al. (2014) demonstrated that the XANES-based measurements of Cr²⁺/ΣCr in olivine could potentially be employed as a sensitive indicator of magmatic oxygen fugacity. This experimental study demonstrated how synchrotron µ-XANES measurements of the Cr valence ratio in olivine could potentially be used as a method for assessing magmatic oxygen fugacity. The results of this study showed that the measured Cr²⁺/ΣCr in the olivine varied systematically with the imposed experimental $f_{O_2}$. These experiments led the authors to suggest that Cr valence measurements in olivine combined with an experimental calibration may be exploited as a new quantitative oxybarometer for igneous rocks.

The basic principle underpinning the Cr valence in olivine (hereafter referred to as the CrViO) oxybarometer relies on the fact that the Cr valence ratio measured in an igneous olivine is directly linked to that of the liquid from which it grew and thus can be exploited to obtain information on magmatic oxygen fugacity. Numerous experimental partitioning studies present data suggesting that the values of $D^{Cr_{2+}}_{ol-liq}$ for both Cr²⁺ and Cr³⁺ are nearly equivalent for basaltic magmas (Gaetani and Grove 1997; Mallmann and O’Neill 2009). The observation that olivine shows nearly the same partition affinity for either Cr²⁺ or Cr³⁺ is the reason that it is especially well suited to serve as a high-fidelity mineralogical recorder of the Cr valence ratio of the liquid from which it crystallized. This point is of considerable importance, as measurements of Cr valence in olivine phenocrysts in igneous rocks can provide a unique pathway for accessing redox information about the parent magma, even in the absence of a quenched liquid or glassy melt inclusions.

The pioneering experiments and XANES analyses of Berry and O’Neill (2004) and Berry et al. (2006) conclusively demonstrated that the Cr²⁺/ΣCr ratios of basaltic melts are indeed a systematic function of $f_{O_2}$, and therefore by analogy Cr valence ratios can be theoretically be utilized to calculate $f_{O_2}$ values in the same way that measurements of Fe²⁺/ΣFe in a silicate melts are used for this task. It should, however, be emphasized that simply retrieving a magmatic liquid’s Cr²⁺/ΣCr ratio via the olivine proxy is not, in of itself, a direct measure of magmatic oxygen fugacity,