XANES measurements of Cr valence in olivine and their applications to planetary basalts

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Abstract

In this work we present a series of experiments that examine the relationship between oxygen fugacity and Cr valence ratio in olivine grown from a basaltic liquid. These experiments are specifically targeted for an olivine-rich martian basalt composition that was modeled after the bulk chemistry of the meteorite Yamato 980459 (i.e., Y-98). The chromium valence ratio in the olivine crystals was measured with X-ray absorption near edge spectroscopy (XANES) at the Advanced Photon Source, Argonne National Laboratory. Results from the XANES measurements indicate that the ratio of divalent to trivalent Cr in the olivine is not only systematically correlated with $f_{O_2}$, but is also reflective of the molar $Cr^{3+}/Cr^{2+}$ in the silicate liquid from which it grew. In this way, measurements of Cr valence in olivine phenocrysts can yield important information about the oxygen fugacity and molar $Cr^{3+}/Cr^{2+}$ of its parental liquid in the absence of a quenched melt phase. Although the results from the experiments presented in this work specifically apply to the Y-98 parental melt, the concepts and XANES analytical techniques discussed within the text present a novel, generalized methodology that may be applicable to any olivine-bearing basalt. Furthermore, the XANES-based measurements are made on a micrometer-scale, thus potential changes of the $Cr^{3+}/Cr^{2+}$ in the melt during crystallization could be examined with a great deal of spatial detail.

Keywords: XANES, Cr valence, redox equilibria, martian basalts

Introduction

Oxidation state, basaltic magmas, and their mantle sources

Quantifying and understanding the redox evolution of basaltic liquids and their mantle source regions has been a major theme in magmatic petrology for over 30 years (Fudali 1965; Arculus et al. 1981; Ballhaus 1993; Carmichael 1991; Brandon and Draper 1996; Canil 2002; Kelley and Cottrell 2009). Oxygen fugacity is a critical variable that exerts profound influence on basaltic phase equilibria, magmatic differentiation paths, C-O-H-S volatile speciation, metallic core segregation, and even peridotite rheology (Mathez 1984; Wood et al. 1990; Carmichael 1991; Righter 2003; Shearer et al. 2006; Mackwell 2008). In general, calculating the oxidation state of planetary basalts is a vexing problem. Oxygen fugacity calculations for planetary basalts are frequently impeded by: (1) the paucity of glassy material that could be used to infer $f_{O_2}$ from direct measurements of Fe$^{2+}$/Fe$^{3+}$; (2) difficulties associated with redox-sensitive mineral assemblages that are susceptible to subsolidus re-equilibration (e.g. the Fe-Ti oxides); and (3) understanding how calculated $f_{O_2}$ values fit into the temporal evolution and petrologic context of the sample. More often than not, the relationship between the $f_{O_2}$ values calculated for a crystallized basaltic sample and the $f_{O_2}$ of its mantle source region is difficult to discern due to post-melting compositional modification during ascent and differentiation.

Despite these difficulties, many studies have produced robust $f_{O_2}$ estimates for the olivine-phyric Shergottite-Nakhliite-Chassignite (SNC) suite meteorites. These estimates have been made using various different oxybarometers. The $f_{O_2}$ values calculated for the olivine-phyric martian basalts show a curious degree of dispersion in that the calculated $f_{O_2}$ values range from IW-0.5 to IW+4.4 (Wadhwa 2001; Herd 2003; and Shearer et al. 2006). Calculated $f_{O_2}$ values have even been observed to vary by two to three orders of magnitude in a single sample depending on which mineral pairs and compositions were used in the calculations.

In light of these difficulties and uncertainties, there is naturally much impetus to develop more sensitive methods with which to calculate $f_{O_2}$ values for not only the olivine-phyric martian meteorites, but also a generalized methodology that is applicable to any crystallized basaltic material. Measurements of the formal valence state of trace Cr that is present in olivine present a potential solution to this problem. Such measurements may yield important insight into the oxidation state of the parental liquid while circumventing problems associated with the lack of glassy material or reset mineral equilibria.

The utility of chromium as a petrogenetic tracer and a redox indicator

The consequences of variable $Cr^{3+}/Cr^{2+}$ in basaltic melts have long been recognized as playing a critical role in dictating the