

Letter

AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY

Competition between two redox states in silicate melts: An in-situ experiment at the Fe $K$-edge and Eu $L_{3}$-edge†

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ABSTRACT

The understanding of redox equilibria as well as the knowledge of the elemental distribution in magmatic melts are of fundamental importance to constrain the genesis of magmas. In particular, the partitioning of trace elements (e.g., Eu) has demonstrated to be a useful tool for estimating the redox conditions in Earth and planetary materials. However, for a more complete comprehension of Eu in silicate melts, information regarding the effects of temperature ($T$), redox conditions, compositions, and the possible interference of other multivalent elements is still lacking. Here we provide new data on the oxidation states of two commonly coexistent multivalent elements (Eu and Fe) in melts, acquired by “in situ” dispersive X-ray absorption spectroscopy experiments at high temperatures and at different oxygen fugacity conditions. This work, for the first time, shows the possibility to monitor in real-time the behavior and valence variations of two elements under varying environmental conditions (like $T$ and redox state).

Keywords: Europium, iron, oxidation states, silicate melts, in-situ dispersive XAS

INTRODUCTION

Rare earth element (REE) patterns of igneous rocks provide useful information on the conditions and processes during magma formation (e.g., Schnetzler and Philpotts 1970; Henderson 1984; Blundy and Wood 2003). Among the 15 REE, europium is the only one stable in a divalent form, and many authors in the past decades have used Eu valence as a quantitative oxybarometer in magmatic systems (e.g., Philpotts 1970; Drake 1975; McKay 1989; Wadhwa 2001; Karner et al. 2010). The distribution and behavior of multivalent elements (Fe, Cr, V, Eu) reflect the prevailing redox conditions of their environment (Shearer et al. 2006), and their oxidation states will influence the mineral crystallization and the element partitioning in various geochemical systems. Thus, a complete understanding of transition and RE elements is important for the geochemical and petrological interpretations of magmatic processes and partition properties between melt and crystals in many planetary materials. This requires the determination of the ratios of oxidation states by means of a quantitative knowledge of the effects of composition, $T$, and redox environment ($f_{o_{2}}$).

In previous studies (Cicconi et al. 2009, 2012) it was experimentally demonstrated that Eu behavior in silicate glasses is primarily controlled by the bulk composition and then by temperature and redox conditions of the melt. In particular, Fe has been shown to affect Eu oxidation states (Cicconi et al. 2012). Since Fe is the most abundant transition element, and its redox state also affects the physical properties of magma, we dedicated our attention to the interaction between Eu and Fe. Schreiber (1977) suggested that the higher reduction potential of the Fe$^{2+}$-Fe$^{3+}$ redox couple in silicate melts, in comparison with the reduction potential of Eu$^{3+}$-Eu$^{2+}$, implies that Fe$^{2+}$ could oxidize all the Eu$^{3+}$ present. This interaction in silicate glasses was also described for Fe and Ce (Schreiber et al. 1980).

To experimentally visualize the Eu kinetic reduction and therefore to understand how Fe influences Eu-bearing melts, we have carried out a direct determination of Eu and Fe valence states by dispersive X-ray absorption spectroscopy (XAS).

SAMPLES AND ANALYTICAL TECHNIQUES

The sample investigated has an Fe-rich (~14 wt%) basaltic composition (Fe-Bas). The starting material has been prepared from dried oxides and carbonates in stoichiometric proportions. The mixture was homogenized in an agate mortar and melted to obtain a glass ($T = 1400$ °C), which was then finely ground and doped with 5 wt% EuO$_{2}$. The resulting glass was checked by optical microscopy and scanning electron microscopy to ensure homogeneity and the absence of crystalline phases (Cicconi et al. 2012 for details on the syntheses; Table 1).

To carry out the high-temperature (HT) X-ray absorption near-edge structure (XANES) experiments, the samples were loaded as microgram-powders in the 1 mm hole of the Pt-Ir10% heating wire of the microfurnace designed following the idea developed by Mysen and Frantz (1992) and previously used for in situ XANES