Pyroxene europium valence oxybarometer: Effects of pyroxene composition, melt composition, and crystallization kinetics

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ABSTRACT

The behavior of multivalent elements such as Fe, Cr, V, and Eu in magmatic systems reflects the $f_{O_2}$ of the environment. In particular, Eu behavior in pyroxene from basaltic systems has been demonstrated to be an effective measure of $f_{O_2}$. We selected two nearly isochemoal lunar pigeonite basalts (15058, 15499), a lunar high-Ti basalt (75035), and Pasamonte (representing asteroid 4 Vesta, an unequilibrated eucrite), to explore other potential variables that may affect this indicator of $f_{O_2}$. All of these basalts crystallized at an $f_{O_2}$ of approximately IW-1, yet they experienced different cooling and crystallization histories and their pyroxenes exhibit a wide range of compositional trajectories within the pyroxene quadrilateral. There are several variables that influence the Eu/Eu* recorded in pyroxene that may compromise the determination of $f_{O_2}$. Previous experimental studies show that pyroxene composition influences the ability of pyroxene to accommodate REE and fractionate Eu$^{2+}$ from Eu$^{3+}$. We demonstrate that in addition to the influence of Ca in the M2 site, the Al content in the pyroxene and its influence on coupled substitutions will also influence the fractionation of Eu$^{2+}$ from Eu$^{3+}$. For example, the coupled substitution $\text{Si}^{4+} + \text{Ti}^{4+} \rightarrow \text{Al}^{3+} + \text{REE}^{3+}$ may accommodate REE$^{3+}$ in preference to Eu$^{2+}$, which is too large. Different pyroxene growth surfaces will incorporate Eu$^{2+}$ and Eu$^{3+}$ differently due to differences in growth rate, Al content, and site configuration. In consort with the pyroxene composition, fractionation of Eu$^{2+}$ from Eu$^{3+}$ will be aided by the Al content of the basaltic melt, which increases the activities of network-forming components such as CaAl$_2$O$_4$ and FeAl$_2$O$_4$ in the melt during pyroxene crystallization. The Al content will result in changing the partitioning behavior of Eu$^{2+}$ while having very little effect on Eu$^{3+}$. Melt composition, the appearance of plagioclase on the liquidus, and the kinetics of plagioclase crystallization are influenced by cooling rate. Data from the four basalts selected also suggest that Eu$^{2+}$/Eu$^{3+}$ in the melt remains buffered even with extreme differences in cooling rate and plagioclase crystallization kinetics. Unexpectedly, many of these same variables affect the substitution of multivalent V. If the $f_{O_2}$ determined from Eu behavior in pyroxene is not placed within a petrologic and crystal-chemical context, errors of 1 to 2 log units may result. The influence of these variables may be reduced by using multiple phases of plagioclase and pyroxene and ratioing $D_{\text{Eu}}$ to adjacent REE ($D_{\text{Eu}}$).

Keywords: Eu valence, V valence, pyroxene, oxybarometer, Moon, 4 Vesta

INTRODUCTION

The behavior of multivalent elements such as Fe, Cr, V, and Eu in magmatic systems reflects the $f_{O_2}$ of the environment (Fig. 1; cf. Papike et al. 2005). The oxidation state of these elements will influence the mineral assemblage (i.e., magnetite vs. Fe-metal) (Papike et al. 1998), crystallization sequence (i.e., early vs. late spinel) (McKay et al. 2004), and element partitioning (i.e., partitioning of Cr and V in olivine and spinel) (Shearer et al. 2005). The effect of $f_{O_2}$ on the relative proportions of divalent and trivalent Eu has proven to be a useful tool for estimating $f_{O_2}$ in a variety of magmatic systems (Fig. 1). This dependence of the ratio Eu$^{2+}$/Eu$^{3+}$ on $f_{O_2}$ can be illustrated by the reaction: Eu$^{2+} + \text{1/2O}_2 \rightarrow \text{Eu}^{3+} + \text{O}_2$. The concept of using Eu valence as a quantitative oxybarometer was initially demonstrated by Philpotts (1970) and Schnetzler and Philpotts (1970). The variation of $D_{\text{Eu}}^{\text{plagioclase-melt}}$ with oxygen fugacity has been determined experimentally by several workers and used to infer the redox conditions under which magmas have crystallized (e.g., Weill and Drake 1973; Weill et al. 1974; Drake 1975; Weill and McKay 1975). McKay (1989) experimentally calibrated the $D_{\text{Eu}}^{\text{plagioclase-melt}}$ and $D_{\text{Eu}}^{\text{pyroxene-melt}}$ for angrite melt compositions. That study not only demonstrated the power of using both minerals for estimating the redox conditions of angrite crystallization, but also hinted at the effect of melt composition on the behavior of Eu. Detailed crystal-chemical rationales for REE and Eu behavior in pyroxenes from lunar basalts were explored by Shearer and Papike (1989). The behavior of Eu in Martian basalts has been demonstrated to be an effective measure of $f_{O_2}$ (Wadhwa 2001). $D_{\text{Eu}}^{\text{pyroxene-melt}}$ has been calibrated experimentally for Martian basalts by McKay et al. (1986), McCanta and Rutherford (2002), and Musselwhite et al. (2003, 2004). These studies have demonstrated both the power of Eu valence as an oxybarometer and its dependence on several magmatic and mineralogical variables.

Here, we evaluate the effect of pyroxene and melt composition, crystallization sequence, and crystallization kinetics