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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 isochemical 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 ${}^{T}Si^{4+} + {}^{M2}R^{2+} \rightarrow {}^{T}Al^{3+} + {}^{M2}REE^{3+}$ 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 $CaAl_2O_4$ and $FeAl_2O_4$ in the melt during pyroxene crystallization. The Al content will result in changing the partitioning behavior of Eu^{3+} while having very little effect on Eu^{2+}. 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, co-crystallizing phases (i.e., plagioclase and pyroxene) and ratioing D_{Eu} to adjacent REE ($D_{Sm, Gd}$).

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