INTRA-CRYSTALLINE BEHAVIOR OF TRACE ELEMENTS IN PYROXENE FROM MARE BASALTS WITH DIFFERENT $f_{O_2}$ - CRYSTALLIZATION HISTORIES. C.K. Shearer and J.J. Papike, Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131-1126

Pyroxenes are sensitive to variants in their cooling histories and intensive thermodynamic parameters, and, therefore, are useful in deciphering the evolution of mare basalts [1,2,3,4]. Bence and Papike [2] demonstrated that major and minor element zoning trends in pyroxene can be correlated with differences in bulk-rock compositions, emplacement histories, and intensive parameters such as T and $f_{O_2}$. Shearer et al. [5] demonstrated that trace element zoning characteristics in selected lunar pyroxenes are intimately related to the interplay among the efficiency of the crystallization process, the kinetics at the crystal-melt interface, the kinetics of plagioclase nucleation, and the characteristics of the crystal chemical substitutions within both the pyroxene and the associated crystallizing phases.

Several lines of evidence suggest a more reducing crystallization history for mare basalt sample 14053 relative to other mare basalts: late stage mineral assemblage of hedenbergite + fayalite + SiO$_2$ + plagioclase [2] and the breakdown of fayalite to iron metal + silica glass + tridymite [6]. Based on these textural and mineralogical observations, Bence and Papike [2] concluded that extremely low $f_{O_2}$ (approximately $10^{-16}$ [7]) affected the major and minor element zoning in the pyroxene. In particular, they noted that the Ti$^{3+}$/Ti$^{4+}$ in pyroxene increased during pyroxene crystallization. The timing of the very low $f_{O_2}$ conditions, its cause, and its effect on trace element behavior is unknown. The purpose of this study is to compare the trace element zoning trends of 14053 with those of a more reducing crystallization history for mare basalt which crystallized under higher $f_{O_2}$ to elucidate the conditions of 14053 crystallization and the role of changing $f_{O_2}$ on trace element behavior in mare basalts.

Basalt types represented by 14053 and 15555 were selected for comparison in this study. Both samples have delayed plagioclase crystallization, similar cooling and crystallization histories [2], and similar compositional trajectories on the pyroxene quadrilateral. They are dissimilar in that they apparently crystallized at different $f_{O_2}$ (14053 at $f_{O_2} \approx 10^{-16}$ at 1000°C and 15555 at $f_{O_2} \approx 10^{-13}$ at 1000°C) during at least part of their crystallization history. They also differ in Al$_2$O$_3$ content [2]. Individual grains were analyzed by both secondary ion mass spectrometry (SIMS) and electron microprobe (EMP). Beam diameter for the SIMS analysis was approximately 10-25 μm. We make the following observations concerning trace element zoning in the pyroxene from 15555 and 14053:

1. V and Cr are (+) correlated in pigeonite and augite. V and Cr decrease from early pigeonite to late augite.

2. With crystallization, Ti increases in both 15555 and 14053. Pyroxene in 15555 shows the greatest variation in Ti (400 ppm to 11,000 ppm) relative to 14053 (4000 ppm to 9500 ppm), but Ti/Al ratio changes more abruptly in 14053 [2]. This suggests that during late pyroxene crystallization components $R^2$Ti$^3$SiAlO$_6$ and $R^2$Ti$^4$Al$_2$O$_6$ are important in pyroxene from 14053.

3. Co (measured as Co/Si which is proportional to Co) remains constant throughout pyroxene crystallization in 14053, but increases in the late pyroxene in 15555.

4. Zr and Sr are (+) correlated throughout pyroxene crystallization. Both Zr and Sr increase with crystallization indicating their incompatible behavior in pyroxene. In late augite, Zr increases at a greater rate than Sr. This may be attributed to differential changes in $K_D$ of Sr relative to Zr with changing pyroxene composition (primarily Ca in M2). Minor deviations from this observed behavior may be due to differences in $K_D$ for growth directions normal to (110) relative to normal to (010).
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(5) The (-) Eu anomaly remains constant throughout pyroxene crystallization with \( \text{Eu}/\text{Gd} = 0.04 \) to 0.08. This Eu anomaly is not substantially affected by plagioclase crystallization because Eu\(^{3+} \) is effectively partitioned into pyroxene relative to Eu\(^{2+} \) and the plagioclase effect is diluted by the low Eu distribution coefficient for the more abundant pyroxene.

(6) Eu is (+) correlated with Sr and Zr. Late augite exhibits Eu (and REE) enrichment relative to this general relationship. This may be attributed to (a) behavioral differences between Sr-Zr and Eu-REE due to kinetic surface effects or (b) relative change in \( K_D \) as Ca concentration in M2 site changes.

(7) The Eu\(^{2+}/\text{Eu}^{3+} \) in the mare basaltic melt is a function of \( f_{O_2} \). As Eu\(^{2+} \) and Eu\(^{3+} \) preferentially substitute into plagioclase and pyroxene, respectively, the Eu anomaly in plagioclase and pyroxene reflect \( f_{O_2} \). (Eu/Gd) plag/(Eu/Gd) pyroxene in the two basalts are approximately the same (90-106). The Eu/Gd in plagioclase was measured in those grains which penetrate the pyroxene grains. Compared to the (Eu/Gd) plag/(Eu/Gd) fassaitic pyroxene \( f_{O_2} \) calibration [8], pyroxene and plagioclase crystallized near the iron-wustite buffer in both samples.

This trace element data indicates that reduction of 14053 did not occur during the crystallization of the complexly zoned pyroxene. Most likely, 14053 and 15555 crystallized at similar \( f_{O_2} \). The increase in Ti\(^{3+}/\text{Ti}^{4+} \) during pyroxene crystallization [2] may be crystal chemically imposed rather than a product of changing \( f_{O_2} \). Mare basalt 14053 crystallized much more plagioclase than 15555 (pyx/plag = 1.25 and 2.6, respectively) resulting in the increase of the Ti/Al ratio in 14053 pyroxene. Ti\(^{3+}/\text{Ti}^{4+} \) increased in the pyroxene in response to structural charge balance constraints. The reduction observed in this sample is apparently a late-magmatic or subsolidus process. It may be the result of (1) impact processes during or following primary crystallization or (2) unusual eruptive processes involving reduction type mechanisms suggest by [9].

References: