

Fe-Mn-Mg IN PLAGIOCLASE FROM LUNAR BASALT AND HIGHLAND SAMPLES

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INTRODUCTION: Measurements of Fe and Mn in plagioclase from lunar samples and achondrites using the synchrotron x-ray fluorescence microprobe (SXRF) have revealed variation of both the absolute Fe and Mn contents and the Fe/Mn ratio in plagioclase {1}. These elements are critical in fractionation of magmas involved in petrogenesis of both highland rocks and mare basalts and show significant difference depending on the environment.

Early work on Fe and Mn has focussed on their abundances in bulk rock and in mafic silicates in which they are either major or minor elements. Feldspar contains only trace levels of these elements and measurements have proven difficult because the presence of microscopic inclusions can obscure the true feldspathic concentrations. Measurements of the Fe and Mn content by SXRF are coupled with major element and precise Fe and Mg measurements by electron microprobe (EMP), of the same spot, to allow the role of contamination to be assessed critically. By careful selection of inclusion free areas to be analysed and by using a 5 μ m synchrotron beam, analysis of clean plagioclase volumes by both techniques have been achieved. Since feldspar contains less Fe than almost every other coexisting phase (except some SiO₂ polymorphs) the presence of contamination in the SXRF analyses is readily revealed by increased Fe_{sxrf} relative to Fe_{emp}. Less than 1% contamination by a mafic silicate can double the apparent Fe_{sxrf} content of SXRF measurement in Fe poor anorthosite derived feldspars. In 78235, for example, inclusions of metal and pyroxene in the plagioclase, produce an array of Fe/Mn measurements defining mixing lines between the feldspar and the inclusion species. However, in most clean feldspar, the variation of absolute Fe content of the feldspar is correlated with the Fe/(Fe+Mg) ratio of the sample. The Fe/(Fe+Mg) ratios of the highland feldspar are typically significantly higher than the coexisting mafic silicates (e.g. in 15415 FFM_{fel} is \approx 45-60 whereas the coexisting mafics have ratios of about 30-40). (This difference also provides a test for the presence of contamination of the feldspar analyses by micron-scale inclusions.)

Feldspar from both highlands samples and several types of mare basalts has been measured in samples EET87521; 14310, 15076, 15415, 15475, 15555, 60035, 67435, 67915, 70035, 78235. Within this suite, the Fe content of feldspar ranges from 500ppm to 8000ppm and the Fe/Mn ratio of the feldspar ranges from 18 to 80. Fe/Mn ratios of bulk samples reflect the ratios of the mafic silicates and are typically considered to be fairly constant and high (70-100). Measurement of Fe/Mn in pyroxene typically has a range from 45-80 while olivine ranges from 60-120. Within any sample, however, variation of Fe/Mn is correlated with the Fe/(Fe+Mg) ratio of the pyroxene and the feldspar.

The increase of Fe/Mn with ffm indicates that the partition coefficients for Fe and Mn between feldspar and liquid are different. Both pyroxene-liquid and feldspar-liquid equilibria have trends of increasing Fe relative to Mn suggests that $D_{Mn} > D_{Fe}$, suggesting that Mn is more compatible than Fe during differentiation processes. In mare basalt samples such as EET87521, strong fractionation of Fe and Mg is preserved and the range of Fe/Mn is compatible with a single fractionation sequence in which Fe/Mn increases monotonically with Fe/(Fe+Mg). When data for highland feldspar are compared with the basaltic sequences, despite a continuous range of Fe/(Fe+Mg), there are distinct differences between the suites (Figure 1). The highlands samples such as 15415 and the Apollo 16 suite have lower Fe/Mn ratios at any given Fe/(Fe+Mg). Figure 1 suggests that those assemblages in which plagioclase was the earliest crystallizing phase, tend to have the lowest Fe/Mn in the plagioclase.

The lower Fe/Mn ratios in highlands feldspar relative to mare feldspar may reflect a fundamental difference between highlands magmatism and the later mare magmatism. Low ratios suggest that Mn was enriched relative to Fe during the early highlands magmatism. While the higher Fe/Mn ratios of the mare samples might reflect Mn depletion by volatilization, this mechanism seems incompatible with the relative abundances of other similarly volatile elements such as Na. More probably, the early differentiation of the lunar highlands involved a phase capable of extracting Mn from the primordial source regions. The most efficient fractionation

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would involve the mafic silicates as these minerals are the hosts for much of the lunar Mn. However, the higher Fe/Mn ratios of mafic silicates indicate that cocrystallization of mafics and plagioclase tends to enrich Mn in the feldspar relative to Fe. Thus, fractionation of pyroxene, and especially olivine is likely to decrease the Fe/Mn of the residue. The higher Fe/Mn in the later sources for the mare basalts are, therefore, unlikely to reflect such mafic fractionation trends. A more likely effect is the fractionation of anorthite itself. Removal of plagioclase from the primordial highlands source to form the highlands crust would force the Fe/Mn of the residue to increase, especially if that source had a low Fe content. While the absolute abundance of both Fe and Mn in plagioclase is low, and the effect of plagioclase removal on these elements seems unlikely to have a major effect on the crustal Fe/Mn ratios, the mass balance constraints of the relative abundances of feldspar and the mafic silicates crystallizing in the early crust must be clarified to assess the importance of this mechanism. However, since mare basalt REE patterns characteristically reflect plagioclase depletion of their source regions, this mechanism may have some validity. Since highland and mare basalt feldspar with similar Fe/(Fe+Mg) ratios have different Fe/Mn ratios, the variation of Fe/Mn with Fe/(Fe+Mg) is not sufficient explain the apparent increase in Fe/Mn from the highland to the mare provenances. At present, however, the relationships between ferroan suite of the highlands and the most magnesian mare samples is unclear. In addition, pressure and oxygen fugacity differences between the source regions of the mare basalts and the earlier highlands may alter the partitioning of Fe and Mn between feldspar and liquid. Future experiments using X-ray absorption near edge structure (XANES) measurements may reveal the oxidation state of Fe and Mn in these samples, which in comparison with fO_2 controlled will constrain the fO_2 conditions of formation {2}.

CONCLUSIONS: (1) Fe/Mn variations in plagioclase correlate with Fe/(Fe+Mg) variations and reflect the fractionation of a silicate magma. (2) Highlands plagioclase has lower Fe/Mn than mare basalt plagioclase at constant Fe/(Fe+Mg). (3) The higher ratios of the mare basalt plagioclase are consistent with the earlier removal of plagioclase to form the lunar highlands crust which, in turn, may have increased the Fe/Mn ratios of the sources of the later mare magmas.

References: {1} Delaney et al., 1989: LPSC XX, 238; {2} Sutton et al. this volume.

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