CONTEMPORANEOUS FORMATION OF DIVERSE LUNAR MAGMA OCEAN RESIDUAL LIQUIDS: THE ROLE OF HERCYNITIC SPINEL H. Nekvasil[1], D. H. Lindsley[1] and N. J. DiFrancesco[1], [1]Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, Hanna.Nekvasil@stonybrook.edu.

Introduction: With the increased recognition that diverse lithologies of the early lunar crust and sources of mare basalts have similar ages (e.g., [1], [2]) there is a need to identify lunar magma ocean (LMO) processes that could induce diversification of the residual liquids and residual crystalline assemblages. We are focusing on the difference in plagioclase behavior, namely the absence of Na-enrichment in ferroan anorthosites, yet normal behavior of plagioclase in other ancient lithologies of the lunar crust highlands to gain insight into possible diversification processes. Here we explore the role that local fractionation of hercynitic spinel could play in such diversification and its effect on plagioclase and LMO residual liquid compositions.

Hercynitic spinel and the plagioclase pseudoazeotrope: We [3] have shown that the compositional evolution of highly anorthitic plagioclase at pressures above 0.35 GPA in basaltic melt deviates from the well-known plagioclase melting loop and is governed by a pseudoazeotrope at ~An94. This topology, inherited from the simple plagioclase system at high pressure (Fig. 1), inhibits the classic Ab-enrichment of anorthitic plagioclase with dropping temperature and instead produces slight An-enrichment. In the LMO, this inhibition of Ab enrichment could occur over a wide temperature interval over which the Mg' of the ferromagnesian minerals coprecipitating with plagioclase would show major variation (as observed in lunar anorthosites, e.g., [4]-[6]).

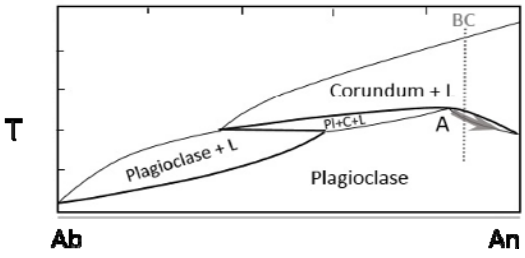

Figure 1. Schematic of the binary plagioclase system demonstrating the topology of a pseudoazeotrope (A) arising from the destabilization of the anorthite melt component to produce a corundum-like melt species and eventual saturation with corundum (C). For bulk compositions more anorthitic A, the first plagioclase will be more albitic than the bulk composition and become more anorthitic with dropping temperature (gray arrow). Modified from [7].

The extension of the pseudoazeotrope to lower pressures in simplified basaltic systems with high An contents determined by [3] and seen in experimental LMO simulated melts by [8] can be envisioned as arising from both the breakdown of anorthite melt component at elevated pressure and the high temperature interaction of olivine and anorthite melt components to produce aluminous spinel, silica, and $CaSiO_3$ "melt species" (R1)

$$2CaAl_2Si_2O_8(m) + (Mg,Fe)_2SiO_4(m) \rightarrow 2(Mg,Fe)Al_2O_4(m) + 2CaSiO_3(m) + 3SiO_2(m). \quad \text{R1}$$

For conditions (i.e., bulk composition and temperature) at which significant reaction occurs, the activity of the spinel melt species may become high enough to allow saturation with the equivalent crystalline phase (hercynitic spinel). With decreasing temperature, backreaction of R1 would dissolve the crystalline spinel back into the liquid to maintain equilibrium. However, spinel with its high density has a propensity for settling out. As shown in Figure 2, this occurs even within the time frame of a laboratory experiment.

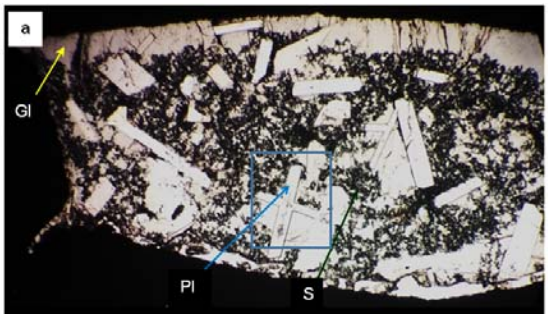

Figure 2. Dynamic cooling experiment on the composition (An95)67(Fo50)33 at 0.7 GPa in a graphite capsule showing spinel (S), plagioclase (Pl) and glass (Gl). The capsule is oriented such that the top is towards the top of the page .Note the settling of the spinel (small black grains). (From [3])

The effect of spinel fractionation on magma diversification. Spinel loss (fractionation) would do two important things. First, it restricts the amount of backreaction of R1 and production of An melt component, thus decreasing the An/An+Ab ratio of the residual system and impeding the An-enrichment of the plagioclase. Second, it would increase the amount of normative pyroxene and silica melt components.

The simplified system olivine-plagioclase provides information of the effect of fractionating minerals on residual liquid compositions and can guide our understanding of what might happen in complex multicomponent melts. Figure 3 shows the computed individual effect of removal of plagioclase, olivine, and hercynitic spinel on the normative olivine and plagioclase in the residual melt. Importantly spinel fractionation decreases both the normative olivine and plagioclase content of the residual liquid (as indicated by R1), suggesting the formation of a range of residual liquidsdepending upon the relative efficacy of plagioclase flotation and olivine and spinel settling.

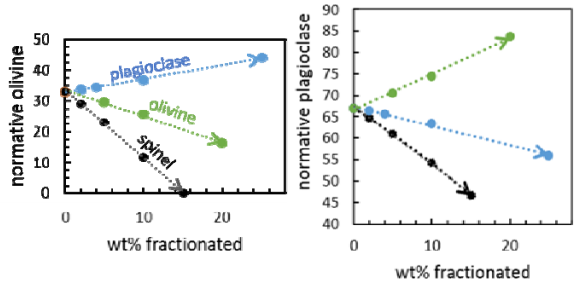

Figure 3. Computed variation in normative olivine and plagioclase of the residual liquid for the bulk composition of Fig. 2 during fractionation of plagioclase, olivine, or spinel vs. amount of the phase removed from the system.

The residual liquid after spinel fractionation is not only depleted in olivine and plagioclase components, but enriched in silica and pyroxene species through R1. The rise in silica content of the residual melts can be seen in Figure 4a. The normative pyroxene constituents, hypersthene and diopside, that arose purely from the dissociation in the melt (R1), increases with increasing degree of spinel fractionation (as shown in Figure 4a).

Spinel loss shifts the bulk composition towards Ab (just as corundum loss would shift the composition BC towards Ab in Figure 1) and this is reflected in a decrease in normative AN number of the melt with increasing amount of spinel loss (Fig. 4b). This shift can actually extend past the pseudoazeotrope to the Ab side of the pseudoazeotrope; such residual liquids would crystallize plagioclase with normal Ab enrichment with dropping temperature (e.g., Fig. 1).

These results suggest that hercynitic spinel fractionation could have resulted, at least locally, in LMO residual liquids that were compositionally quite distinct (specifically, more albitic, more silica-rich, and enriched in pyroxene components) from the highly Ab-depleted silica-poor residual liquids in equilibrium with the plagioclase that floated to form the rocks of the ferroan anorthosite suite.

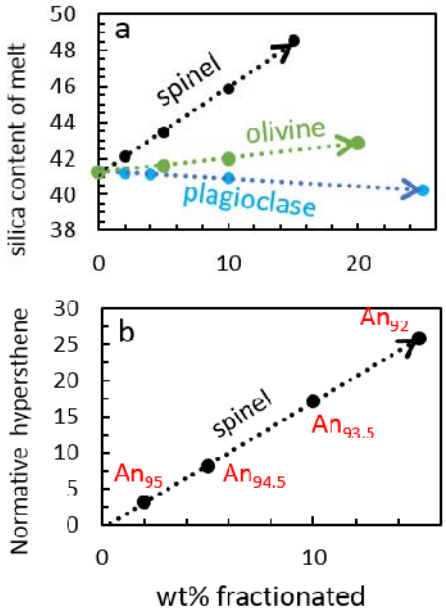

Figure 4. Computed variation in silica content (a) and normative hypersthene (b) of the residual liquid for the bulk composition in Figure 2 after fractionation of spinel, olivine, or plagioclase. (b) also shows the decrease in normative An number of the residual melt with increasing amount of crystalline spinel loss from the system. Normative diopside is found in the residual liquids at nearly the same abundance as hypersthene. Together they may induce the crystallization of pigeonite and low-Ca pyroxene at high temperature.

Summary: Hercynitic spinel is an expected phase to crystallize from olivine and anorthite-rich melts and its potential role in diversifying residual liquids in the LMO should not be ignored. Spinel fractionation provides a mechanism for producing basaltic "sodic" melts in which plagioclase shows normal behavior contemporaneous with production of the low silica, highly Na-depleted melts associated with the formation of the plagioclase that gave rise to the ferroan anorthosite suite.

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