A NEW MECHANISM FOR GENERATING THE CALCIUM ENRICHMENT OF LUNAR FERROAN ANORTHOSITE. H. Nekvasil[1], N. J. DiFrancesco[1], A. E. Coraor[2], and D. H. Lindsley[1], [1]Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 Hanna.Nekvasil@stonybrook.edu, [2] Cornell University, Ithaca, NY.

Introduction: We propose a new explanation for the lack of Na-enrichment in plagioclase of ferroan anorthosites - an explanation with major implications for the composition of the LMO and the petrologic relationship of ancient lunar lithologies.

The observation of ferroan anorthosite with highly anorthitic plagioclase on the lunar surface has been a foundational part of the current paradigm of lunar crust formation and has shaped our view of the compositional nature of the lunar magma ocean (LMO). Our understanding of the compositional evolution of the mineral plagioclase during cooling and crystallization [1] has led to the logical conclusion that the low Mg# of ferromagnesian minerals associated with highly anorthitic plagioclase requires a very feldspar component- (and Na-) depleted LMO composition and requires extensive crystallization of ferromagnesian phases prior to saturation with plagioclase. However, as discussed by [2] there is evidence that at high pressures, plagioclase compositional evolution at high An contents differs markedly from the classic behavior at low pressure (in which Na-enrichment occurs with dropping temperature); instead, plagioclase may become more anorthitic with dropping temperature (and dropping Mg# of co-precipitating ferromagnesian minerals) ([3], Fig. 1). This likely arises from the differential breakdown of the anorthite component in the melt, lowering its activity and producing corundum melt species, but decreases in the amount of the corundum species with dropping temperature.

Such change in plagioclase behavior with pressure would provide a powerful new constraint on early lunar processes. For example, it would allow for a more feldspar-enriched LMO with earlier saturation of plagioclase at high Mg#, formation of anorthitic plagioclase at the later stages of crystallization once the Mg# decreased and flotation of this An-rich plagioclase because of the more Fe-enriched melt (as per [4]), all while allowing the same LMO closer to the surface to produce anorthitic plagioclase early at high Mg# that would become more albitic upon cooling (as seen in other old lunar lithologies).

The change in plagioclase behavior in Figure 1 is at too high a pressure to be relevant to the LMO. However, it is possible that such a decrease in anorthite activity in the melt could be achieved by spinel formation through reaction of anorthite and olivine melt components. As determined experimentally by [2], this is not the case at low pressure, where normal zoning of plagioclase was obtained experimentally even in the presence of spinel. Thus, the typical low pressure melting loop shown in Figure 1 would dictate anorthitic plagioclase compositional evolution even in magmas rich in ferromagnesian components.

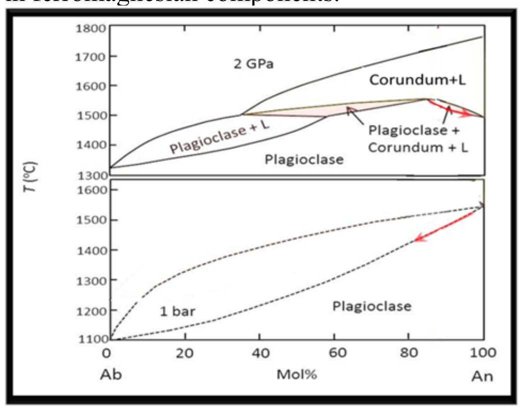


Figure 1. Plagioclase evolution at high pressure vs. 1 bar (red arrows). High pressure diagram based on [3]. A bulk composition in the region of the red arrows would produce plagioclase with reverse zoning at high pressure, but normal zoning at low pressure.

The primary question addressed in this study is whether an azeotropic configuration occurs in the presence of spinel at depths of relevance to the LMO, specifically 80-150 km.

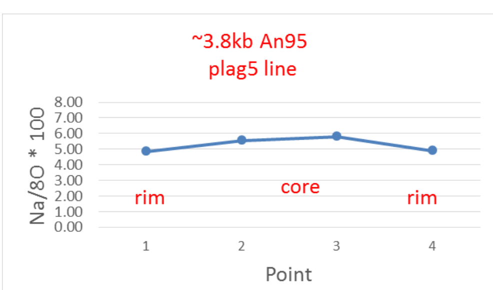
Experimental strategy: A series of experiments were designed to evaluate normal (Ab-enrichment) vs. reverse zoning (An-enrichment) of anorthitic plagioclase during dynamic cooling experiments. If an azeotrope exists at moderate pressures it would lie at a composition no more albitic than An93, since plagioclase of this composition in lunar lithologies always shows normal zoning. For this reason, a projected composition of An_{95} was chosen. In order to attain Mg numbers of relevance to lunar compositions, a projected olivine composition of $Fo_{50}Fa_{50}$ was selected, with a ratio of 67% plagioclase 33% olivine for the bulk composition. An additional mix was made of $(An_{90})_{67}$ $(Fo_{50}Fa_{50})_{33}$ to bracket the location of the possible azeotrope.

Experimental details: The two mixes were made of dried reagents. Fe sponge was used with hematite to ensure that primarily FeO was initially present. The mixes were loaded into a graphite capsules, dried at 800 °C under vacuum in the presence of a Fe-sponge oxygen getter at 600 °C , and the capsules loaded into Ba carbonate piston-cylinder assemblies. Each sample was pressurized to 3.8 kbar (An95) and 7.0 kbar (An95 and An90) and then melted at 1350 °C. After melting, the sample was cooled isobarically over several days until a final crystallization temperature of 1150°C was reached. Slightly lower melting temperatures were used for the 3.8 kbar experiments to compensate for a lower liquidus (i.e., 1300° vs 1350° C).

Results: Each experiment produced euhedral plagioclase crystals, glass, and spinel. The spinel varied from euhedral crystals at higher temperature to small anhedral grains at lower temperature.

Line electron microprobe (American Museum of Natural History) analyses through plagioclase crystals (Figs. 2-4) were carried out using a 20 nA beam current and a focused electron beam with a 5µm spot size. There was no indication of any loss of Na during chemical analysis. [Na/8O*100 is a proxy for normative Ab content (mol%).]

Figure 2. Characteristic line scans of plagioclase from the bulk composition $(An95)_{67}(Fo50Fa50)_{33}$, showing reverse zoning during dynamic cooling at 7 kbar.



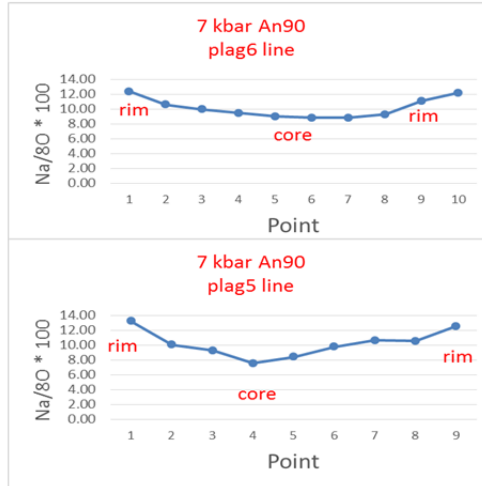


Figure 4. Characteristic line scans of plagioclase from the albitic composition $(An90)_{67}(Fo50Fa50)_{33}$, showing the expected normal zoning at 7 kbar

Conclusions. The reverse zoning of plagioclase for the An95 composition at 7 kbar, but not for the An90 composition, and the absence of zoning at 3.8 kbar, strongly supports the presence of an azeotrope between An90 and An95 at 7 kbar and higher pressure, and its absence at 3.8 kbar and lower pressure. Thus, calcic plagioclase formed at 75-140 km in the LMO would show no Na enrichment; instead, it would start crystallizing from the LMO with higher Ab content than that of FAN plagioclase and evolve to higher An content with dropping temperature. Normal zoning below 3.8 kbar suggests that at shallow levels of the LMO, highly anorthitic plag could have formed at a much earlier stage of crystallization than at depth, that is, while the Mg# was still high.

This result forms a new basis for reconsidering the LMO composition, the stage at which plagioclase first formed in the LMO, the nature of KREEP, magmas formed by mantle overturn, and the relationship between the ferroan anorthosites and old rocks such as the Mg-suite lithology types.

References: [1]Bowen N.L (1913) *Am J. Sci.* 35, 577-599. [2] Nekvasil H. et al. (2014) *45th LPSC, Abstr.* #81.[3] Lindsley, D.H. (1968*) NY State Museum and Science Service Mem*. 18, 39-46.[4] Warren P.H. (1990) *Am Min*. 75, 46-58.
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Figure 3. Characteristic line scan of plagioclase from the bulk composition (An95)67(Fo50Fa50)33, showing no (or minimal) zoning during dynamic cooling at 3.8 kbar.