

**COMPOSITIONAL VARIATIONS IN MARE-BASALT PLAGIOCLASE PRODUCED BY DIFFERING CRYSTALLIZATION REGIMES.** Odette B. James and James J. McGee, U.S. Geological Survey, Reston, VA 22092

*Introduction.* We have begun a study of lunar mare basalts to define the nature of igneous variations of minor components in lunar plagioclases. Thus far we have analyzed the plagioclases in two Apollo 15 basalts. We plan to expand our studies to include correlation of pyroxene compositional variations with plagioclase compositional variations, estimation of plagioclase/melt distribution coefficients for FeO and MgO, and analysis of other basalts. Our goal in this study is to be able to use compositional variations to distinguish igneous from metamorphic lunar plagioclase and to deduce crystallization and reequilibration processes in samples where textures are ambiguous.

*Textures and mineralogy.* We have studied 15384 and 15388. Basalt 15384 is a medium-grained olivine-bearing mare basalt [1]. There are local patches of coarsely variolitic intergrowths of pyroxene and plagioclase, but most of the rock is a hypidiomorphic-granular intergrowth of these minerals and olivine. Basalt 15388 is an olivine-free feldspathic microgabbro [1]. This rock has two textural domains: 1) early crystallized, coarse-grained variolitic intergrowths of pyroxene and plagioclase; and 2) later crystallized, coarse-grained hypidiomorphic-granular intergrowths of lath-shaped plagioclase, equant pyroxene, and interstitial opaque oxides and cristobalite. (The hypidiomorphic-granular domains clearly crystallized later than the variolitic domains because they contain the late-stage minerals and locally contain vugs.) The variolitic textures are similar to textures produced by experimental crystallization of liquids supersaturated with plagioclase [2,3]. Locally, there are sparse large pyroxene phenocrysts.

*Plagioclase compositions.* Plagioclase from the different textural domains in 15388 shows different compositional variations; in our analyses, we distinguished "early" plagioclase (within variolitic intergrowths), "intermediate" plagioclase (at edges of variolitic intergrowths and in centers of large laths), and "late" plagioclase (in outer zones and edges of large laths). The early 15388 plagioclase and all the 15384 plagioclase show identical trends of variation of FeO and MgO with An (100 x molar Ca/Ca+Na+K). There is a strong negative correlation of both these oxides with An (Fig. 1a,b), but  $mg'$  (100 x molar Mg/Mg+Fe) is nearly constant and relatively high (Fig. 1c). The late 15388 plagioclase shows a different trend. As the edges of grains are approached, An content decreases, MgO is constant or decreases slightly, FeO increases markedly, and thus  $mg'$  decreases greatly (Fig. 1a-c). The relationship of the two trends in 15388 indicates that the first plagioclase to crystallize had relatively low An, high FeO, and the highest MgO. Subsequent early plagioclase was reversely zoned; An increased and both FeO and MgO decreased. Content of An was at a maximum, and content of FeO was at a minimum, in the intermediate plagioclase. The late plagioclase was zoned normally; An and MgO decreased and FeO increased.

*Substitution mechanisms.* Our data permit determination of the extent of operation of different substitution mechanisms in the plagioclase. Previous studies [4-5] have shown that Fe and Mg enter lunar plagioclase primarily as  $Ca(Fe,Mg)Si_3O_8$ ; in this component, Fe and Mg are in tetrahedral sites, substituting for Al and Si, and charge is balanced by a coupled substitution of Ca for Na. Lesser amounts of Fe and Mg enter lunar plagioclase as  $(Fe,Mg)Al_2Si_2O_8$ ; in this component, Fe and Mg substitute for Ca in octahedral sites. Lunar plagioclase also incorporates  $\square Si_4O_8$  (also referred to as "excess" Si); in this component, Si substitutes for Al in tetrahedral sites, and charge is balanced by vacancies in octahedral sites [6]. Plots of various cation sums (method modified from [4]) distinguish the effects of different mechanisms. In all plots, the parameters are chosen such that compositions in the solid solution series  $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$ , or "pure" plagioclase, plot at a single point. Compositional variations produced by the three substitution mechanisms occur along vectors marked by arrows. In a plot of Al-Ca vs. Al+Si (Fig. 1d), the effects of substitution of octahedral Fe+Mg ( $(Fe,Mg)Al_2Si_2O_8$ ) and "excess" Si ( $\square Si_4O_8$ ) are opposed, roughly cancelling each other, and the decrease of Al+Si from the ideal value of 4 cations per 8 oxygens indicates that tetrahedral Fe+Mg is 0.0099-0.0305 (cations per 8 oxygens) in 15388 and 0.0141-0.0352 in 15384. The 15384 plagioclase and the earliest 15388 plagioclase contain the most tetrahedral Fe+Mg. As crystallization proceeds, the extent of this substitution decreases. It is at a minimum in the intermediate 15388 plagioclase, but it increases again in the late 15388 plagioclase. In a plot of Si-Na-K vs. Al+Si (Fig. 1e), substitution of octahedral Fe+Mg ( $(Fe,Mg)Al_2Si_2O_8$ ) produces no effect, and the effects of tetrahedral Fe+Mg ( $Ca(Fe,Mg)Si_3O_8$ ) and "excess" Si ( $\square Si_4O_8$ ) are emphasized. The difference of Si-Na-K from the  $Ca(Fe,Mg)Si_3O_8$  vector indicates that the amount of "excess" Si is 0.0054-0.0219 (cations per 8 oxygens) in 15384 and 0.0063-0.0358 in 15388. The earliest 15388 plagioclase contains moderate amounts of "excess" Si. As crystallization proceeds, the "excess" Si decreases. It is at a minimum in the intermediate plagioclase but increases again in the late plagioclase. In a plot of Al-Ca+2(Fe+Mg) vs. Si+Al+Fe+Mg (Fig. 1f), substitution of tetrahedral Fe+Mg ( $Ca(Fe,Mg)Si_3O_8$ ) produces no effect, and the effects of substitution of octahedral Fe+Mg ( $(Fe,Mg)Al_2Si_2O_8$ ) and "excess" Si ( $\square Si_4O_8$ ) are emphasized. This plot shows that the content of octahedral Fe+Mg is roughly constant in the plagioclases of both rocks and averages 0.0154 (cations per 8 oxygens) in 15388 and 0.0129 in 15384. The amount of octahedral Fe+Mg in the plagioclase does not vary with time in the crystallization sequence.

*Conclusion and summary.* We interpret the "early" and "late" trends of plagioclase compositional variation as being produced by two different crystallization regimes. The "early" trend (shown by 15384 plagioclase and early crystallized 15388 plagioclase) appears to result from crystallization of a melt undercooled with respect to plagioclase nucleation (similar zoning trends in the plagioclase of mare basalt 12021 were interpreted in the same way [7]). The "late" trend (shown by late crystallized 15388 plagioclase) seems to represent equilibrium crystallization. The earliest plagioclase to crystallize incorporated more Na, Fe, Mg, and Si than would be incorporated in crystals in equilibrium with the melt; most of the Fe+Mg substituted for tetrahedral Si+Al, as  $Ca(Fe,Mg)Si_3O_8$ . As the plagioclase crystallized, its composition approached the equilibrium composition ("intermediate" 15388 plagioclase). The components  $Ca(Fe,Mg)Si_3O_8$  and  $\square Si_4O_8$  were at a minimum in this plagioclase. Subsequent crystallization produced a plagioclase that was normally zoned and incorporated progressively increasing contents of  $CaFeSi_3O_8$  and  $\square Si_4O_8$ . The content of octahedral Fe+Mg ( $(Fe,Mg)Al_2Si_2O_8$ ) was roughly constant throughout crystallization.

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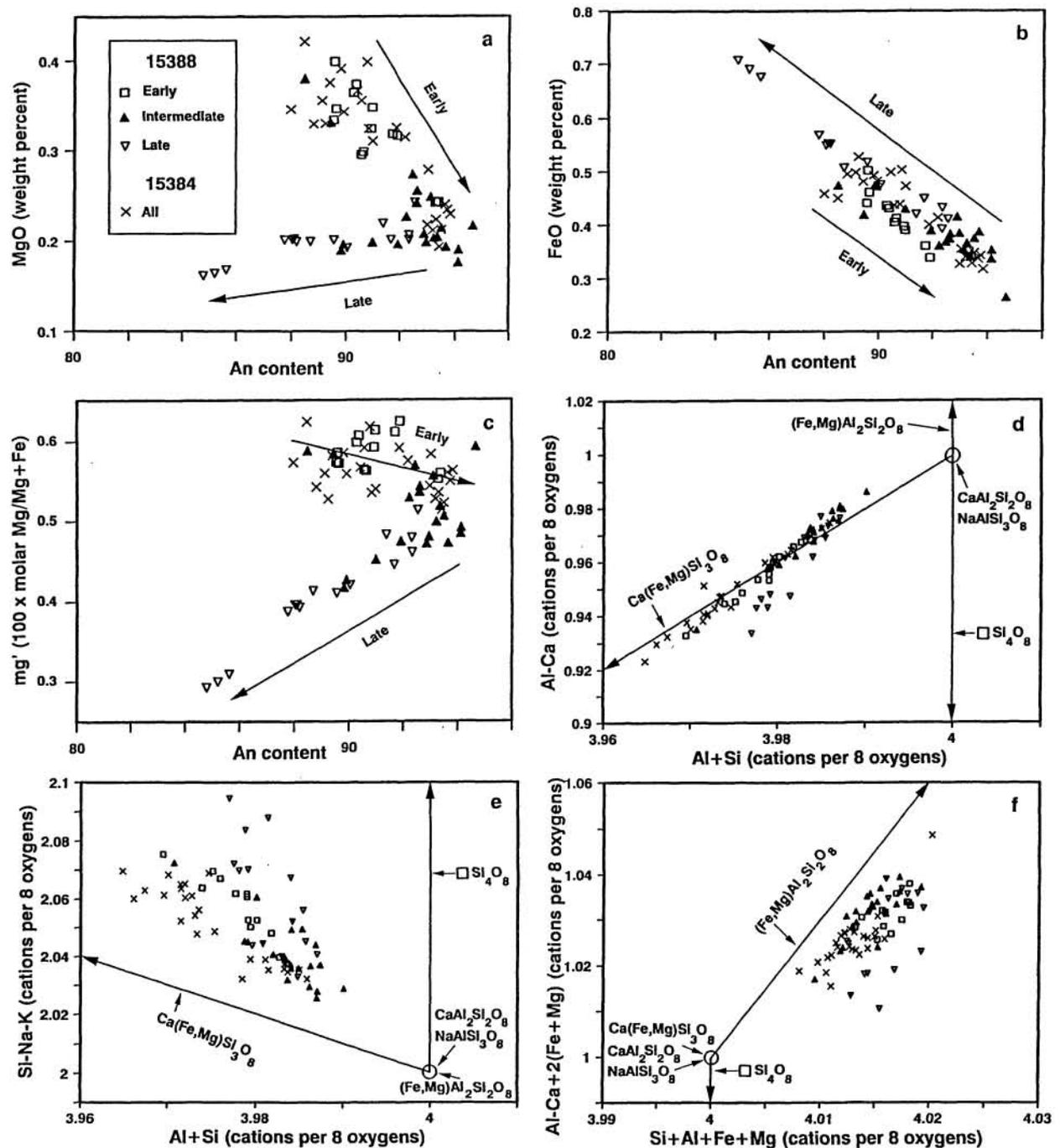


Figure 1. Compositions of plagioclases in 15388 and 15384. (a) MgO vs. An (100 x molar Ca/Ca+Na+K) content. Trends shown by early and late crystallized 15388 plagioclases are marked by arrows, whose points indicates the inferred direction of compositional change with time. (b) FeO vs. An content. Arrows and symbols as in a. (c)  $mg'$  vs. An content. Arrows and symbols as in a. (d) Al-Ca vs. Al+Si. Symbols as in a. Substitution vectors are marked by arrows; pure plagioclase (in the solid solution series  $NaAlSi_3O_8$ - $CaAl_2Si_2O_8$ ) plots at the center of the circle. (e) Si-Na-K vs. Al+Si (cations per 8 oxygens). Symbols as in a. Substitution vectors are marked by arrows; pure plagioclase and plagioclase in which Fe and Mg substitute for Ca ( $(Fe,Mg)Al_2Si_2O_8$ ) plot at the center of the circle. (f) Al-Ca+2(Fe+Mg) vs. Si+Al+Fe+Mg. Symbols as in a. Substitution vectors are marked by arrows; pure plagioclase and plagioclase in which Fe and Mg substitute for Si and Al ( $Ca(Fe,Mg)Si_3O_8$ ) plot at the center of the circle.