CHEMICAL GRADIENTS IN GLASS ADJACENT TO OLIVINE IN EXPERIMENTAL CHARGES AND APOLLO 15 GREEN GLASS VITROPHYRES. D. A. Kring, LPI (currently Dept. Geol., I. U., Bloomington, IN 47405) and G. A. McKay, SN4, NASA-JSC, Houston, TX 77058.

Production of chemical diffusion gradients in silicate melts adjacent to growing crystals is a well known phenomenon [e.g., 1-3]. In at least two instances, such gradients have been attributed to olivine growth during rapid quench of experimental runs [4,5]. To determine if such gradients are present in our crystal/liquid partitioning experiments, and to assess their potential for producing erroneous partition coefficient measurements, we performed a series of detailed microprobe traverses in glass adjacent to olivine in charges from these experiments, and observed gradients in all cases. We also performed such traverses on two Apollo 15 Green Glass vitrophyre samples (GGV), and observed similar gradients. In this abstract we discuss the origins of these gradients and their implications for experimental partitioning studies and for the thermal history of GGV.

Charges consisting of wire-suspended 100mg beads of synthetic low-Ti mare and LKFM basalt were heated above their liquidus, cooled to below olivine saturation (1200-1250°C), held at constant T for up to 1000hr, and air-quenched at >6000/min. In all cases, microprobe traverses adjacent to olivine revealed zones of depletion of Mg and Fe, and enrichment of Ca, Si, Ti, and Al. Typical profiles for Mg, Ca, and Al are shown in Fig. 1. The width of the enrichment or depletion zones decreases in the order Mg>Ca>Fe>Ti>Si>Al, reflecting differing cation diffusivities.

Chemical boundary zones in charges held at constant T for 1000hr did not differ significantly in width from those held for only 20 hrs, thus indicating that the gradients were produced during the quench, rather than during primary growth of olivine. Crystallization of a layer of olivine only a few tenths of a micrometer thick, undetectable by conventional microprobe techniques, is required to produce the observed Mg depletion. Boundary zones are narrower for LKFM than for mare basalt (MB) compositions. This may reflect lower diffusivity in the higher viscosity LKFM composition, or the lower temperature from which LKFM runs were quenched (1200°C vs. 1250°C for MB)[5].

We observed similar chemical zoning in two GGV samples described by [6], 15301,120 and 15501,44. Typical profiles are shown in Fig. 2. Because of the pervasiveness of olivine crystals, no traverses were performed for glass regions more than 40 micrometers in width. Hence all traverses are double-ended (i.e., there is an olivine crystal within 1-2 micrometers of each endpoint, Fig. 2). In all cases dif-
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Fusion effects appear to extend completely across the region between olivine crystals. Note in particular that the effects of Al diffusion extend farther in GGV than in MB, suggesting either higher diffusivity, slower cooling, or quenching from higher T for GGV.

Apparent KD values ([Fe/MgOL]/[Fe/MgGL]) were computed using olivine analyses performed "2 micrometers from the interface and glass analyses from along the profiles for both MB and GGV. For MB, apparent KD values calculated using glass near the interface are always well below the equilibrium value for this composition (e.g., 0.27 vs. 0.33 for eq.), and rise to the equilibrium value beyond the boundary zone. Kd's for GGV exhibit similar behavior. Different behavior for the variation of apparent KD values along concentration gradients adjacent to olivine was observed by [7] in an experimental charge quenched from 1050°C after being cooled at ~10⁶/min from 11980°C. In this case, the apparent KD calculated from glass nearest the interface most closely approached the equilibrium value, and increased above this value as glass farther and farther from the interface was used.

We propose the following interpretations for the above observations: (1) In the experiment of [7], steady state chemical diffusion gradients were established early in crystallization, and the analyzed portion of the olivine grain crystallized in surface equilibrium with the Mg-depleted liquid boundary layer from which it grew. (2) In the MB experiment, olivine was in equilibrium with the bulk liquid before quenching. During the quench, a sub-micron overgrowth of olivine formed, depleting adjacent liquid in olivine components, including Mg. This overgrowth is too small to be detected by microprobe techniques. It may have maintained surface equilibrium with liquid adjacent to the interface, in which case the overgrowth would be strongly zoned towards Mg depletion. The concentration gradients established during the quench did not reach a steady state. (3) In contrast to our MB and LKFM experiments, the experiment of [7] shows no evidence for chemical gradients produced during the quench. This could be due to lower diffusivity in the more viscous liquid in their experiment, to the lower temperature from which their run was quenched, or to other unidentified causes. (4) Lower-than-equilibrium apparent KD values at the olivine-liquid interface in GGV suggest that steady-state gradients had not been established at the time of formation of the analyzed olivine, and hence that this olivine grew during cooling which was much more rapid than in the experiment of [7] (~10⁶/min). The larger extent of Al diffusion in GGV relative to MB suggests that the gradients formed during slower cooling than the >600⁰/min quench of the MB experiments, but does not rule out a subsequent rapid quench at >600⁰/min, which may have slightly modified the original diffusion gradients. Because a <1mm sphere of GG will cool by radiation to a cold environment at >600⁰/min [8], it appears likely that either GGV olivines formed before droplet formation, or else the droplets cooled in a warm environment, such as an eruption cloud. The observed diffusion gradients appear to be broadly consistent with olivine growth at cooling rates of ~10⁶⁰⁰⁰ C/min proposed for these samples on textural grounds [6].