ORIGIN OF THE APOLLO 15 GREEN GLASS. EVIDENCE FROM NI, CO, MN, V, AND CR;
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Introduction. The behavior of elements with siderophile and chalcophile characteristics have historically been used to place constraints on conditions and characteristics of the lunar mantle, the bulk composition of the Moon, the existence, nature, and evolution of a lunar core, and the evolutionary relationship between the Earth and the Moon [e.g. 1,2,3]. The source of some of this data has been primitive volcanic glasses that were returned from the Apollo and Luna missions. However, the understanding of these glasses, within a petrogenetic framework, is open to some interpretive problems. For example, the compositional variability in the Apollo 15 very low Ti picritic glasses has long been debated. Stolper [4] interpreted the major element variability in these glasses to be inconsistent with a volcanic origin. Numerous other studies [1,5,6,7] confirmed a magmatic origin but were unsuccessful in explaining the compositional variability. Galbreath et al [8] documented an unusual positive correlation between Co, generally considered to be compatible in basaltic systems, and incompatible elements such as REE, Ba, and Zr. They interpreted this relation as either a result of source mixing or magma mixing. Unfortunately, some of the subtleties of these relations were lost because of the precision of the ion microprobe techniques (7 to 15%). Further studies by Shearer and Papike [9] of very low Ti picritic glasses from other lunar sampling sites indicated that the mantle sources for these picritic magmas were extremely varied and consistent with the mixing models of [8]. Steele et al [10] documented similar compatible-incompatible element relations in the Apollo 15 very low Ti glasses based on INAA analyses of individual glass beads. Based on experimental studies [11], they concluded that this trace element behavior was a result of the incompatible element behavior of siderophile elements such as Ni and Co in basaltic systems at very low oxygen fugacities due to a higher proportion of Ni^0 and Co^0 in the melt. Subsequent studies [12,13,14] have indicated that, although this is a complex experimental and interpretive problem, the observations of [11] are probably incorrect. The purpose of this study is to use more precise ion microprobe analyses of these picritic glass beads from the Apollo 15 site to better understand the behavior of Co, Ni, Mn, Cr, and V at low lunar oxygen fugacities and to interpret the relationship among these glasses.

Experimental Technique. Our approach to better understanding the behavior of these elements is to analyze a suite of elements (Mn, Co, Ni, Cr, V) at high precision (better than 2%) using a Cameca IMS 4f ion microprobe. All of the Apollo 15 very low Ti picritic glasses analyzed in this study had been previously analyzed for major elements by electron microprobe, and for other trace elements (REE, Ba, Zr, Li, B, Be) using the ion microprobes at Woods Hole Oceanographic Institute and the University of New Mexico. Standards used in constructing calibration curves were well documented basaltic glasses. Conventional energy filtering techniques were used for the analysis of these elements.

Observations. Our observations for the first set of Apollo 15 glasses analyzed are presented in Figures A-F. As has been noted in previous studies [8, 10], the Apollo 15 very low Ti glasses exhibit a positive correlation between strongly compatible elements such as Ni (Figure A) and highly incompatible elements. This is inconsistent with the expected magmatic behavior of these elements and contrasts with the behavior of these elements observed in other lunar glass and crystalline mare basalts. This is illustrated by the high Ti glasses in Figure A. The reader is also referred to the more detailed observations [8, 10] that better illustrate the compositional variability in a larger sample population of the Apollo 15 glasses. In the Apollo 15 glasses thus far analyzed, there is a positive correlation between Co and Ni with a near constant Ni/Co ratio ($\approx$ 2). Manganese also exhibits a positive correlation with both Ni and Co although the Ni/Mn (.05 to .08) and the Co/Mn (.03 to .04) increase from the Green C glasses (lower incompatible element concentrations) to the Green A, D, and E glasses (higher incompatible element concentrations) (Figures C and D). This seemingly anomalous behavior **implies** that Ni and Co behave in more of a lithophile character than Mn,**if** these magmas are related by simple fractional crystallization or partial melting processes. Chromium is inversely correlated to Ni, Co, and Mn in the limited data set thus far collected. The Co/Cr ratio decreases from 0.015 to 0.025 from the Green C glasses to the Green A, D, and E glasses (Figure E). Chromium and V exhibit limited systematics with the V/Cr ratio varying between .030 and .034.

Discussion. Based on lunar metal compositions in the most primitive crystalline mare basalts [15], calculated Ds for these elements for olivine, orthopyroxene, metals, and sulfides, and assuming elements such as Ni and Co do not reside in the basaltic melt in the neutral valence state, the observed variations cannot be the result of fractional crystallization or partial melting processes in the strictest sense. First, it would be expected that the

Ni/Co ratio should be fractionated along the observed trends if that trend is a result of olivine or metal as a product of crystallization or melting. In low Ti crystalline mare basalts, the Ni/Co ratio decreases with crystal fractionation. Second, the Ni/Mn and Co/Mn ratios imply Mn is slightly more compatible in this basaltic system. In addition, the Mn-Cr-V relations are not consistent with that predicted from the experimental data of [16]. This data is also consistent with more recent experimental data [12,13,14] that may be interpreted to imply that Ni or Co do not become incompatible in this basaltic systems at low oxygen fugacities. Most importantly, the compositional variability in the high Ti glasses (that were also presumably derived from a very low f_{O2} mantle reservoir) indicate that Ni and Co behave compatibly relative to the incompatible lithophile elements (Figure A). Also, Ni/Co, Ni/Mn, and Co/Mn ratios are difficult to explain by the models of [8,9]. We suggest that the compositional variations observed in the Apollo 15 very low Ti glasses can be best explained by mixing models proposed by [8,9].

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