

**Co AND Ni AS INCOMPATIBLE ELEMENTS IN THE LUNAR MANTLE:  
IMPLICATIONS FOR  $fO_2$  AND THE PETROGENESIS OF APOLLO 15 GREEN GLASS.**  
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**Introduction:** Several investigators have suggested that the compositional trends shown by Apollo 15 green glass Group B reflect processes that involved mixing in a heterogeneous mantle source region [1, 2, 3]. Others have speculated that complex igneous mechanisms such as sulfide liquid immiscibility [4], high pressure relationships [5], or another, poorly-understood process [e.g., 6] may have caused the variations. Most of these theories were advanced because no quantitative model could explain simultaneously all inter-element relationships in terms of equilibrium melting of a single parent rock or fractional crystallization of a homogeneous magma. Through recent studies that have combined major- and trace-element analysis [7, 8], we have confirmed that the compositional systematics of Group B do not *immediately* suggest simple igneous mechanisms.

**Theoretical/Experimental:** Positive correlations between Co, Ni and Sm values [7, 8] are important clues to the nature of the source region and the petrogenesis of Group B. It is unusual for Ni and Sm to behave similarly in mafic igneous systems because  $Ni^{2+}$  is compatible with ferromagnesian minerals while  $Sm^{3+}$  is not.

Recent investigations of the behavior of Ni show that its solubility in silicate melts and crystals remains substantial (~0.2 wt. %) even at very low values of  $fO_2$ , where it is no longer present in the  $2^+$  valence state [9]. This causes the Ni distribution coefficient ( $D_{Ni}$ ) to vary with  $fO_2$ . We have extended these previous experimental investigations to include compositions similar to green-glass Group B. We have found that, at high  $fO_2$ , the value of  $D_{Ni}$  is that which we expect for the  $2^+$  oxidation state (i.e., compatibility with olivine; Fig. 1). As  $fO_2$  is lowered, the  $D_{Ni}$  value decreases substantially (presumably because of a change in valence state; [9]) until at very low values of  $fO_2$ , Ni becomes incompatible in olivine and pyroxene (Fig. 1).  $D_{Ni}$  at low  $fO_2$  was found to be ~0.6 in olivine, while that measured for orthopyroxene was 0.59. Similar values are expected for  $D_{Co}$  (experiments are underway to determine the partitioning behavior of Co in both minerals). Because NiO is more readily reduced than FeO, the  $fO_2$  necessary to reduce most Ni (and probably Co) to the metallic state is still several orders of magnitude higher than that required to reduce an appreciable proportion of FeO to metal. Thus, under conditions where Co and Ni exist predominantly as metallic atoms, Fe could remain lithophile, which would be consistent with behavior shown by Group B [10].

**Modelling and Discussion:** Preliminary modelling suggests that batch equilibrium melting [11] of a homogeneous source region under conditions of low  $fO_2$  could, in part, explain the compositional behavior of Group B (Fig. 2). Although much of the variation in the sample set is explained by this mechanism, some variation greater than analytical uncertainty remains, and likely has a different origin, perhaps local source heterogeneity. The amount of melting required by our model is generally consistent with that proposed by other investigators for the green-glass source region [12].

Thus, the trace-element behavior shown by Group B could be explained by a simple and conventional igneous mechanism, if Ni and Co behaved as mildly incompatible elements. The major-element behavior of Group B could be explained by this same model if pressure in the source region were sufficient (see Colson and Steele, this volume). This model has implications for the oxidation state of the lunar mantle, which is still under debate. Some investigators predict relatively oxidizing conditions at depth (e.g., wüstite-magnetite buffer; [13]). Others suspect that such conditions would not be consistent with some geochemical features observed in lunar samples [14]. Our estimate of source  $fO_2$  based on Ni behavior in green glass is lower than previous evaluations (i.e., well below iron-wüstite buffer). However, an independent estimate that we made using thermodynamic data [15, 16] suggests that the  $fO_2$  of the mantle source region may not be as low as that implied in this model, although it would still be below previously-surmised values according to this calculation (Fig. 1).

**Conclusions:** Experimentally-determined D values indicate that Ni behaves as an incompatible element in olivine and orthopyroxene under conditions of very low  $fO_2$ . Modelling that utilizes these D values suggests that simple batch equilibrium melting could have produced the trace-element trends exhibited by Apollo 15 green glass Group B, a result that is consistent for major elements as well. If this model is an appropriate description of this group, the source region is constrained to be both deep and highly reducing.

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ACKNOWLEDGEMENTS: We thank NASA for support through UA/NASA space engineering center for utilization of local planetary resources, and through grant NAG 9-56.

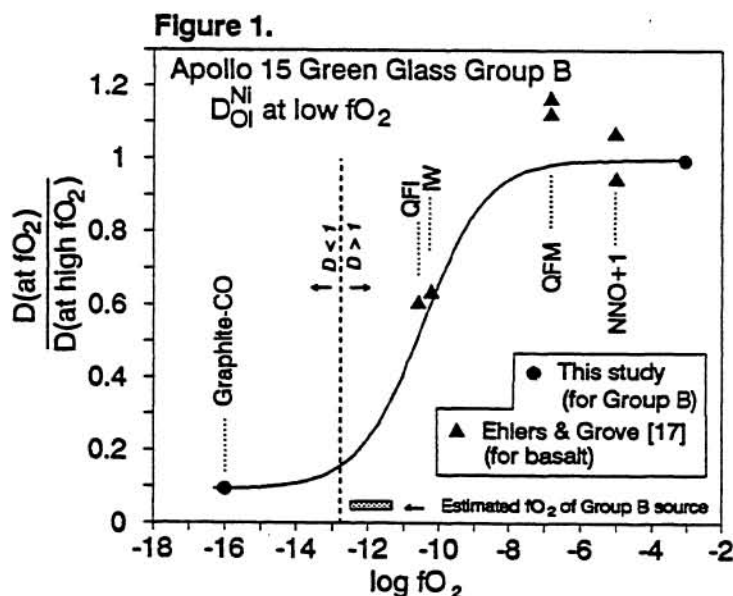


Figure 1. Plot illustrating the behavior of Ni over a range of  $fO_2$  values. At high  $fO_2$ , Ni behaves as a compatible element in material of green glass composition, with  $D_{Ni}^{Ni}$  -6. As  $fO_2$  decreases,  $D_{Ni}^{Ni}$  drops substantially. The shape of the curve is algebraically derived from equilibrium constants involving Ni in different valence states. The  $fO_2$  for the source region (shaded rectangle) was estimated using thermodynamic relationships and the reaction  $FeO \leftrightarrow Fe + \frac{1}{2}O_2$ . This calculation assumed equilibrium between silicate and metal, and yielded only an approximate  $fO_2$  value because activity values for Fe and FeO were estimated, and because of uncertainty in the free energy of reaction.

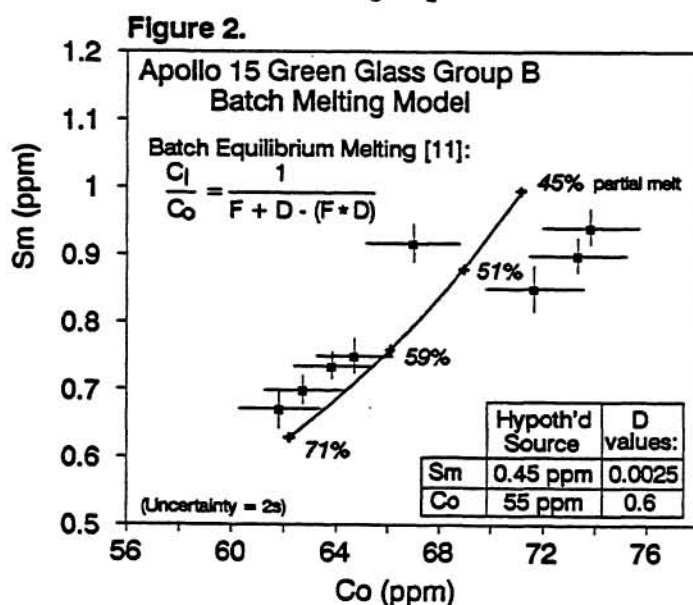


Figure 2. Comparison of the Group B trend with that predicted by batch equilibrium melting [11] for Sm and Co. The D value of 0.6, measured for Ni, is used in modelling Co because we have not acquired precise Ni data for these green glass particles, and because the behavior of Co is probably comparable to that of Ni under the same conditions of  $fO_2$ . The unusual positive trend is, to a first approximation, successfully reproduced using this model.