

APOLLO 17 HIGH-TI BASALT EVOLUTION: WHOLE ROCK VS. MINERAL CRYSTALLIZATION TRENDS. P. H. Donohue* and C. R. Neal, Department of Civil Engineering & Geological Sciences, University of Notre Dame, Notre Dame, IN (*pdonohu1@nd.edu).

Introduction: *In-situ* trace element geochemical studies are the leading edge in petrologic research, which until recently was dominated by characterization of whole-rock (WR) and major phase mineralogical studies. They allow a higher level of fidelity in evaluating basalt evolution and have been shown in many cases to reveal more than was apparent in WR studies [e.g., 1]. In this study we investigate the Apollo 17 high-Ti mare basalts from the Taurus-Littrow Valley of the Moon. These basalts represent multiple source regions (e.g., [2]), and on the basis of WR compositional and mineralogical variations have been separated into 5 types (A, B1, B2, C, and D) [3-6].

A fundamental question in petrologic studies is whether crystallizing phases are in equilibrium with whole rock composition. Answering such a question reveals details about the evolution of a sample that would not be evident from whole rock data alone. Although an estimate of olivine disequilibrium can be obtained by using whole-rock Mg/Fe to calculate the Fo content of olivine in equilibrium with it [7,8] no such relationship is available for ilmenite.

Samples & Methods: The petrography of 18 Apollo 17 high-Ti basalts was examined via thin section. Crystal size distributions (CSDs) were generated for major phases (e.g., ilmenite, olivine, pyroxene, plagioclase) to obtain quantitative information on crystal populations. A typical CSD is a plot of population density vs size, and allows us to calculate properties of crystallization kinetics (e.g., cooling rate, growth rate, residence time [9]). Sharp changes (“kinks”) in a CSD slope may also indicate multiple crystal populations. Ilmenite CSDs for Apollo 17 high-Ti basalts fall into one of two categories, either linear or concave up.

CSD characterizations [10] were used to guide geochemical analysis in order to obtain major, minor and trace element abundances for a representative set of crystals for each sample. Major and minor element analyses were obtained on a JEOL JXA-8200 Electron Microprobe (EMP) at Washington University in St. Louis, except for two samples (71597 and 74235) which were characterized on a Cameca SX50 EMP at the University of Chicago. Trace element analyses were performed at the University of Notre Dame on an Element2 high-resolution inductively coupled plasma mass spectrometer (ICP-MS) coupled to a UP213 Nd:YAG New Wave laser ablation system. Trace element analyses have been obtained primarily for ilmenite as it is present and abundant in all samples. Data were also obtained for olivines in one Type C basalt

and armalcolite in two Type B2 samples. Analysis of additional samples and phases (*i.e.*, pyroxene and plagioclase) could not be completed in time for abstract submission due to an ICP-MS repair.

To assess whether mineral phases are in equilibrium with the whole rock, partition coefficients (K_d s) were used to calculate the equilibrium liquid from which each crystal would have crystallized using the equation $C_L = C_X/K_d$ where C_L is the element concentration in the equilibrium liquid, C_X is measured abundance of element X in the mineral phase. Previously published whole rock trace element abundances and literature partition coefficient values were used. We note that relatively few studies generate ilmenite and olivine crystals of similar composition to those found in Apollo 17 high-Ti basalts (Fig. 1).

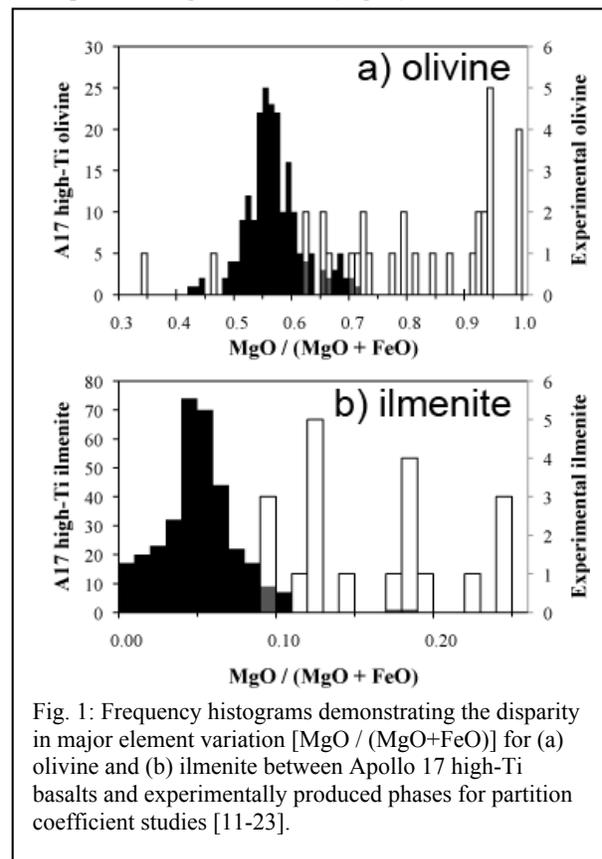


Fig. 1: Frequency histograms demonstrating the disparity in major element variation [MgO / (MgO+FeO)] for (a) olivine and (b) ilmenite between Apollo 17 high-Ti basalts and experimentally produced phases for partition coefficient studies [11-23].

Results: This study focuses on three samples: 75015 is a compositional Type A, coarse-grained plagioclase-poikilitic basalt with a curved ilmenite CSD; 70315, a compositional Type B1, coarse-grained plagioclase-poikilitic basalt with a straight ilmenite CSD; and 74275, a compositional Type C, fine-grained oli-

vine-porphyritic basalt with a curved ilmenite CSD and non-linear olivine CSD.

A comparison of whole rock to calculated equilibrium liquids is presented in Fig. 2 for Sc and Co, two elements nominally compatible in basaltic crystal phases. The ilmenite Kds of Sc (2.2) and Co (2.5) [12] are similar and thus should behave similarly (*i.e.*, decrease at a constant ratio), which we observe in 75015. Some ilmenite in 74275 and 70315 have equilibrium liquids higher than whole rock abundance. There is a gap in equilibrium liquid Sc and Co composition between ilmenite and olivine (Sc $Kd = 0.3$ [21]; Co $Kd = 2.2$ [20]) in 74275 (Fig. 2), which may be a product of the number of crystals analyzed or there was a gap between the crystallization of these phases.

Discussion: Whole rock compositions represent an average of component phases, and thus normally plot between major phases (Fig. 2a). This appears to be the case for ilmenite and olivine in 74275, which are early-forming but not co-crystallizing phases as they produce different equilibrium liquid compositions. Co-crystallizing mineral phases should have equilibrium

liquid compositions that are identical. Disequilibrium is indicated if the WR compositions plots outside the box formed by constituent mineral compositions.

Disequilibrium in whole rock compositions may represent multiple crystal populations or result from magma mixing. In addition, care must be taken in selecting appropriate Kds as they can vary with mineral chemistry, and we have noted above that there is a scarcity of relevant experimental data. Current thinking is that the curved CSDs of 75015 and 74275 are a product of textural coarsening, suggesting an equilibrium assemblage is present. This will be tested by the acquisition of trace element data from the remaining mineral phases [10,27].

Additional phases are necessary to rule out disequilibrium effects on 75015 and 70315, as whole rock compositions do not appear to be controlled solely by ilmenite. Pyroxene Kds for Sc (1.6) and Co (1.2) [21] are similar to ilmenite and would deplete magma composition at a similar ratio to that seen in ilmenite in 75015. Ilmenite is an early crystallizing phase (starting prior to pyroxene and plagioclase) in 70315, whereas ilmenite is a later stage and less abundant phase in 75015. This is supported by the differences in ilmenite Sc content for these two basalts (Fig. 2b).

References: [1] Hui *et al.* (2011) *GCA* 75, 6439-6460. [2] Paces J.B. *et al.* (1991) *GCA* 55, 2025-2043. [3] Neal C. R. *et al.* (1990) *GCA* 54, 1817-1833. [4] Longhi J. *et al.* (1974) *PLSC*, 5th, 447-469. [5] Warner R. D. *et al.* (1979) *PLPSC*, 10th, 225-247. [6] Ryder G. (1990) *MaPS* 25, 249-258. [7] Longhi J. *et al.* (1978) *GCA* 42, 1545-1558. [8] Delano J.W. (1980) *PLPSC* 11, 251-288. [9] Higgins M. D. (1996) *JVGR* 70, 37-48. [10] Donohue P. H. & Neal C. R. (2011) *LPS* 42, Abstract #2568. [11] van Kan Parker M. *et al.* (2011) *GCA* 75, 4179-4193. [12] Klemme S. *et al.* (2006) *Chem. Geol.* 234, 251-263. [13] McKay *et al.* (1986) *JGR*, 91(B4), D229-D237. [14] Nakamura Y. *et al.* (1986) *JGR*, 91(B4), D239-D250. [15] Irving A. J. *et al.* (1978) *PLPSC*, 9th, 601-612. [16] McCalum I. S. & Charette M. P. (1978) *GCA* 42, 859-869. [17] McKay G. A. & Weill D. F. (1976) *PLSC*, 7th, 2427-2447. [18] Akella J. & Boyd F. R. (1973) *PLSC*, 4th, 1049-1059. [19] Mallman G. & O'Neill H. St.C (2009) *J. Pet.* 50, 1765-1794. [20] Mysen B. O. (2006) *GCA* 70, 3121-3138. [21] Neal C. R. & Kramer G. Y. (2006) *Am. Min.* 91, 1521-1535. [22] McKay G. A. (1986) *GCA* 50, 69-79. [23] Ringwood A. E. (1970) *JGR* 75, 6453-6479. [24] Neal C. R. (2001) *JGR* 106, 27865-27885. [25] Rhodes J. M. (1976) *PLSC*, 7th, 1467-1489. [26] Warner R. D. (1975) *Conf. Origins Mare Bas. & Implic. Lunar Evol.*, 179-183. [27] Higgins M. D. (1998) *J. Pet.* 39, 1307-1323.

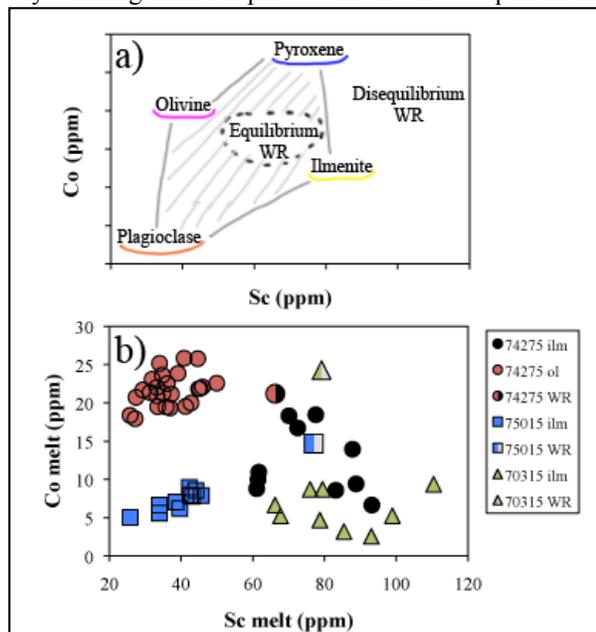


Fig. 2: Scandium and Cobalt trace element (TE) variation diagrams. a) Theoretical distribution of Sc and Co for major phases in mare basalts (label names at relative TE abundances). For this example the whole rock composition would be in equilibrium if it plotted within the shaded region. Whole rock values outside of this region are not in equilibrium with the crystal assemblage. Whole rock data from [24-26]; b) Ilmenite equilibrium liquids and olivine (74275 only). Equilibrium assemblages should have WR compositions plotting on equilibrium liquid trends. More data are being collected and will be presented at LPS 43.