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1   **Textural and mineral chemical evidence for the cumulate origin and evolution of high-**

2   **titanium basalt fragment 71597**

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9   **Abstract**

10   Basalt fragment 71597 is the sole high-titanium mare basalt showing evidence for olivine

11   accumulation during formation. The petrogenesis of this unique sample was investigated using

12   quantitative textural analysis and major- and trace-element mineral geochemistry. Crystal size

13   distribution analysis identified two size populations of olivine, which we separate into cumulate

14   and matrix olivine. The spatial distribution of olivine also supports clustering of olivine crystals,

15   likely during accumulation. Observed mineral chemistry was consistent with an origin through

16   olivine accumulation, although where this occurred cannot be discerned (e.g., in ponded melts at

17   the base of or in the lunar crust, or within a thick high-Ti basalt flow). Attempts to place 71597

18   within a geochemical group were inconclusive both using subtraction of cumulate olivine from

19   bulk composition, and by modal recombination of major phases. However, equilibrium liquid

20   compositions of augite and plagioclase are determined to be consistent with an origin by

21   fractionation from the Type B2 chemical suite of Apollo 17 high-Ti basalts. This method of

22   classification has potential for placing other Type U ("Unclassified") basalts into chemical

23   suites.

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Introduction

29   Olivine cumulates have been recovered from multiple lunar locales, although they form

30   only a small part of the mare basalt sample collection. The majority of cumulates are low-

31   titanium (TiO_2 < 6 wt.%) composition comprising Apollo 12 ilmenite basalts 12005 and 12036

32   (Dungan and Brown 1977; Rhodes et al. 1977), several members of the Apollo 12 olivine basalt

33   suite (Neal et al. 1994), Apollo 15 basalts 15385 and 15387 (Ryder 1985), Apollo 14 clast

34   14305,122 (Taylor et al. 1983), and six fragments in lunar meteorite NWA 773 (Jolliff et al.

35   2003). The only high-Ti cumulate is basalt 71597 (8.4 wt% TiO_2), a 12.35 g fragment collected

36   with Apollo 17 mission rake samples (Murali et al. 1977; Warner et al. 1977). The composition

37   and formation of this fragment relative to Apollo 17 high-Ti basalts provides information on an

38   end-member of lunar volcanic textures.

39   Whole-rock analyses (major and trace element abundances) conducted by neutron

40   activation techniques (Murali et al. 1977) and mineral compositions (major element) have been

41   interpreted to indicate basalt 71597 experienced 24-27% olivine and possible minor ilmenite

42   accumulation (Warner et al. 1977). The evidence for accumulation described by Warner et al.

43   (1977) can be summarized in four main points:

44   • 71597 contains the highest whole-rock MgO content (15.8 wt%) and the highest modal

45   olivine abundance (19.3%) of any high-Ti basalt.

46 • Whole-rock REE abundances are lower than – but sub-parallel to – typical Apollo 17 high-

47 Ti basalts, indicating dilution by REE-poor olivine (± ilmenite).

48 • There is a bimodal distribution of olivine Fo-content between large, anhedral olivine cores

49 and small "matrix" olivine grains (Figure 1).

50 • It is unusual to find olivine crystals several millimeters in size in a coarse-grained matrix,

51 as large olivine crystals within other Apollo 17 samples are typically found as phenocrysts

52 in fine-grained basalts (*e.g.*, 74275).

53 Warner et al. (1979) further suggested 71597 originated in a Type B flow (after Rhodes et

54 al. 1976; separated into Type B1 and B2 by Neal et al. 1990). However, the small sample size of

55 71597 (12.35 g; Neal and Taylor 1993) and coarse grain size has precluded the determination of

56 an incontrovertibly representative whole-rock analysis, which means that 71597 remains

57 unclassified. Apollo 17 high-Ti basalts are classified into several groups (Types A, B1, B2, C, D,

58 and U for "unclassified") on the basis of whole-rock geochemistry (Rhodes et al. 1976; Warner

59 et al. 1979; Neal et al. 1990; Ryder 1990). Type A basalts contain 50-60% higher incompatible

60 trace element abundances than the other groups (Rhodes et al. 1976). Types B1 and B2 basalts

61 were split primarily on the basis of La/Sm ratios (Neal et al. 1990). Type C basalts contain high

62 MgO and Cr_2O_3, and have less ilmenite on the liquidus at early stages of crystallization. The

63 Type D group is defined by a single basalt fragment (,2144) from drive tube 79001, and has the

64 highest MgO/TiO_2 ratio and lowest incompatible trace element abundance of any other classified

65 Apollo 17 basalt (Ryder 1990). Classification schemes for Apollo 17 basalts are weighted toward

66 incompatible elements, and are thus strongly affected by the amount of mesostasis and late stage

67 components sampled. This effect is more pronounced in samples where <1 g material is used in

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68 bulk analyses (e.g., Haskin and Korotev 1977). Thus, the bulk composition of 71597 determined

69 using a 0.61 g subsample (Murali et al. 1977) still may not be representative.

70   The explanation for the origin of 71597 given by Warner et al. (1977) favors the

71 formation of large, skeletal olivine and ilmenite crystals towards the margins of a large flow that

72 accumulate via gravitational settling towards the flow's interior. Other processes, such as mixing

73 of magmas containing different crystal cargoes, have not been explored. Aspects of mare

74 volcanic processes and the nature of olivine accumulation (*e.g.*, gravitational settling during a

75 single, large flow versus magma mixing) can be addressed by mineral geochemistry and

76 quantitative petrographic analysis. We present electron probe microanalysis and laser ablation

77 inductively couple plasma mass spectrometry (LA-ICP-MS) analyses of mineral phases in two

78 new thin sections of basalt 71597. Microscale details of basalt evolution are recorded in core-to-

79 rim and inter-crystal compositional variations, and can best be constrained by *in-situ* techniques.

80 In addition, equilibrium liquid trace element compositions are used to constrain a petrogenetic

81 model of magma evolution. We also undertake quantitative petrography on 71597 through

82 Crystal Size Distribution (CSDs; Marsh 1988, 1998; Cashman and Marsh 1988; Higgins 2000,

83 2002, 2006; Higgins and Roberge 2003) and Spatial Distribution Patterns (SDPs; Jerram et al.

84 2003) analysis. Particularly relevant to this study is the work of Day and Taylor (2007) who

85 demonstrated that a combined CSD-SDP approach could show not only variability in cooling

86 rates, but also the importance of clumping and formation of clustered crystal frameworks during

87 the cooling of lunar lava flows. Additional studies have demonstrated the practicality of using

88 the CSD technique to differentiate endogenous mare basalts from impact melts (Cushing et al.

89 1999; Neal et al. 2015), and the CSD-SDP methods to equate Apollo 17 samples with

90 experimentally determined cooling rates (Donohue and Neal 2015).

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Samples and Methodology

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92   As noted above, the coarse grain size and small mass of 71597 has precluded an

93 unambiguously representative whole-rock analysis. This represents an issue of obtaining

94 representative CSD-SDP analyses of the sample due to its coarse grain size. In order to alleviate

95 the effect of non-representivity when undertaking a textural analysis of 71597, two thin sections

96 were requisitioned from sub-sample 71597,0, designated 71597,12 and 71597,13 (Figure 1). The

97 data obtained from each thin section were combined where possible, allowing for a more robust

98 statistical analysis.

99 **Crystal Size Distribution (CSD) and Spatial Distribution Profile (SDP) Methods**

100   The application of CSD and SDP methods to lunar basalts has been discussed in detail in

101 Day and Taylor (2007) and Donohue and Neal (2015). We present a brief summary here.

102 Quantitative textural analyses were conducted on digital photomicrograph mosaics (Figure 1).

103 Crystal outlines were manually traced in the *Adobe Photoshop©* program using reflected light

104 photomosaics for ilmenite, and plane polarized light photomosaics for olivine, pyroxene, and

105 plagioclase. Crystals larger than ~0.03 mm could be traced at the image resolution; smaller

106 crystals were not included in the analyses due to issues with resolution and intersection effects,

107 where grains smaller than the thin section thickness are underrepresented. Monomineralic layers

108 were processed in the image-processing program *ImageJ* (ver. 1.44m) (Schneider et al. 2012) to

109 determine crystal center coordinates (X,Y), major and minor crystal axis lengths and areas. Best-

110 fit 3D crystal dimensions were estimated from a database of major and minor axis lengths,

111 *CSDSlice* (Morgan and Jerram 2006). Stereological corrections were made using the

112 *CSDCorrections* (ver. 1.3.9) program (Higgins 2000) to calculate a semi-logarithmic CSD of

113 population density versus size. Crystal populations were split into size bins with five bins per

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114   decade (each size bin contains a range of crystal lengths 0.2 times larger than the previous).

115   Using more than five bins per decade introduces errors because there are fewer crystals in each

116   bin, and because more cycles of correction are needed during stereological conversion (Higgins

117   2000).

118   A reliable estimate of 3D crystal shape requires at least 75 total crystals (for tabular

119   morphologies); a minimum of 250 crystals is recommended for more acicular shapes (Morgan

120   and Jerram 2006). A size bin must contain three or more crystals in order to calculate upper and

121   lower uncertainties on the population density. The *CSDCorrections* program calculates a

122   goodness of fit (Q) of the data to a straight line, which allows for quantitative distinction

123   between linear ($Q > 0.1$), sub-linear (Q between 0.001 and 0.1) and non-linear ($Q < 0.001$) CSDs

124   (Higgins 2006). Sub-populations can also be isolated if a CSD appears kinked rather than curved.

125   A CSD is considered kinked if the profile can be divided into two (or more) linear segments with

126   unique slopes.

127   The CSD profile slope is a function of crystallization and is the inverse reciprocal of a

128   characteristic crystal length (C_L) for a given population (Marsh 1988). The C_L is the product of

129   growth rate (G) multiplied by residence time (τ). Growth rate is typically approximated based on

130   experimental work and for a given phase may vary by several orders of magnitude between and

131   even within specific studies (e.g., Burkhard 2005; Cabane et al. 2005; Vinet and Higgins 2010).

132   For example, it us evident that temperature plays a critical role in growth rate (e.g., Burkhard

133   2005), which changes throughout crystallization. Thus, without additional knowledge of the

134   system from which a phase crystallized, there are significant assumptions associated with

135   residence time calculations and, therefore, potentially significant errors are introduced.

136   Therefore, we do not use calculated absolute residence times as part of this study.

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137   The mineral SDPs can be used to investigate the relative ordering and frameworks of

138   mineral phases. Relative ordering is quantified by "R" values, where R is determined by

139   comparing observed phase distributions to a similarly-sized population of randomly packed

140   spheres (Jerram et al. 1996, 2003). R can be compared to the percent matrix (porosity) to

141   distinguish touching from non-touching frameworks, as well as the relative ordering or clustering

142   of phases. The SDP is a function of spatial relationships, and because we do not know exactly

143   the separation of the two thin sections, the SDP is calculated for individual thin sections.

144   Combining CSD and SDP analyses allows the effects of crystal nucleation and growth, magma

145   mixing (Martin et al. 2006), and the relative position of a given sample in lava flows and

146   intrusions (Jerram et al. 2003, 2010; Day and Taylor 2007; Donohue and Neal 2015).

147   **Major and trace element analysis**

148   Major element compositions of select ilmenite, pyroxene, plagioclase, and olivine

149   crystals were obtained using a JEOL JXA-8200 electron microprobe at the Earth and Planetary

150   Sciences Microanalysis Facility, Washington University in St. Louis (St. Louis, MO). The

151   microprobe was equipped with five wavelength-dispersive spectrometers and a JEOL (e2v /

152   Gresham) silicon-drift energy-dispersive spectrometer. Beam operating conditions were 15 kV

153   accelerating potential, 25 nA probe current, and a 5 micrometer spot size. A defocused beam

154   (~10 micrometers diameter) was used to avoid loss of volatiles (e.g., Na, K) during plagioclase

155   analyses.

156   Compositional analyses of several large (>10 μm) melt inclusions in olivine and ilmenite

157   crystals, as well as additional olivine (spot and line raster), armalcolite, and mesostasis analyses

158   were obtained using a Cameca SX50 electron microprobe at the University of Chicago (Chicago,

159   IL; see Supplementary Table S1). Line raster analyses were obtained across two large, partially

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160 resorbed olivines in 71597,12. Typical operating conditions were 15 kV accelerating potential

161 and a 30 nA probe current and a 1 or 5 micrometer spot size (for oxides and silicates,

162 respectively).

163   Trace element abundances of crystals were obtained using an Element2 inductively

164 coupled plasma mass spectrometer (ICP-MS) coupled to a UP213 Nd:YAG laser ablation system

165 at the Notre Dame Midwest Isotope and Trace Element Research Analytical Center (MITERAC,

166 Notre Dame, IN). Laser operating conditions were 5 Hz repetition rate and 5 ns pulse duration to

167 achieve <15 J/cm^2 fluence for 15-80 μm beam sizes. An optimum carrier gas (He) flow rate of

168 0.6 L min^{-1} was used to move ablated particles downstream to a 'Y'-connection where it was

169 mixed with Ar-gas and introduced to the mass spectrometer. The NIST SRM 610 (for olivine,

170 ilmenite, and armalcolite) and NIST SRM 612 (for plagioclase and pyroxene) glasses (Pearce et

171 al. 1997) were used for external calibration purposes. Detection limits (3σ) for pyroxene

172 calculated in GLITTER$^®$ (van Achterberg et al. 2001) were 0.001-0.03 ppm for Y, Nb, Cs, La,

173 Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Lu, Hf, Ta, Th, U; 0.03-1 ppm for Sc, Mn, Co, Ga, Rb,

174 Zr, Ba, Gd, Yb, Pb; 1-5 ppm for Cr, Ni, Sr; 5-10 ppm for Ti; and >200 ppm for Ca. Detection

175 limits for plagioclase were 0.03-1 ppm for Y, Sm, Eu, Dy, and Er, and similar to that for

176 pyroxene for other elements. Analyses of ilmenite and olivine were performed in medium

177 resolution (resolution = mass/peak width of ~4000) to reduce spectral interferences, but at the

178 cost of reduced sensitivity. Thus, detection limits for elements in olivine and Fe-Ti oxides were

179 0.08-5 ppm for Sc, V, Co, Y, Zr, Sr, Hf, Ta; 5-20 ppm for Cr and Mn; 20-100 ppm for Ti and Ni

180 in olivine; and 100-200 ppm for Ti in Fe-Ti oxides. The Ti-content obtained by microprobe was

181 utilized as the internal standard for ilmenite and armalcolite; similarly, MnO was the internal

182 standard for olivine, and CaO for plagioclase and pyroxene. Data were reduced using the

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183   GLITTER® software, which allows for time-resolved background (~50 seconds) and signal (~60

184   seconds) selection. Cracks, inclusions and adjacent phases were avoided using a combination of

185   transmitted and reflected light prior to ablation and confirmed by time-resolved signal review.

186   **Results**

187   **Textural Analysis**

188   In general, the two new thin sections are petrographically similar to the detailed

189   description given by Warner et al. (1977), although absolute mineral abundances differ. Manual

190   point-counting of 71597,12 (3,454 points over an area 67 mm^2) shows the sample contains 37%

191   pyroxene, 33% olivine, 15% plagioclase, and 15% opaques (ilmenite and trace armalcolite,

192   spinel, and troilite). Warner et al. (1977) conducted point-counting over a larger area (~240

193   mm^2), and report less olivine (19.3%), more plagioclase (28.3%), and other minor differences

194   compared point-counting results for 71597,12. Visual estimates of bulk fragments 71597,0 and

195   71597,5 range from 19-30% olivine (Warner et al. 1977; Neal and Taylor 1993).

196   Olivine CSD profiles for 71597,12 and ,13 were previously presented in Neal et al.

197   (2015). They are nearly identical and are multiply kinked, but the two largest size bins of the

198   71597,12 olivine CSD do not contain statistically significant numbers of crystals (n=2 each)

199   (Table 1, Figure 2a). In addition, only 43 olivine crystals could be reliably traced in 71597,13,

200   almost half the recommended minimum for CSD calculations (Morgan and Jerram 2006). A

201   more robust CSD was created by combining the olivine populations (n = 161) of 71597,12 and

202   ,13. The resulting CSD (Figure 2a) is consistent with the individual sample CSDs with kinks at

203   crystal lengths of ~0.4 mm and ~2.2 mm. However, the two largest size bins have the largest

204   error and do not represent a statistically unique population, especially given the low number of

205   crystals (n = 4) so we do not interpret this portion of the CSD as being a third distinct population

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206   of olivine crystals. Consideration of all crystals >0.4 mm in length yields a sub-linear CSD

207   profile (Q = 0.013) with a C_L of 0.57 mm. To avoid over-interpretation of the CSD data, we only

208   consider the olivine CSD as representing two populations (C_L of 0.07 mm and 0.57 mm) in

209   further calculations.

210   Ilmenite CSD profiles of both thin sections are indistinguishable, and strongly concave

211   upward (Q << 0.001) (Table 1, Figure 2b). Linear regression through the steep and shallow

212   segments of the ilmenite CSD profile yields slopes corresponding to characteristic lengths of 0.4

213   and 0.8 mm, respectively. The largest ilmenites (up to 1.1 mm as measured in thin section) are

214   similar in habit to but not as large as the elongate skeletal ilmenite (up to 5 mm) reported by

215   Warner et al. (1977). The CSD reconstructs 3D morphologies from 2D cross-sections. So, given

216   the X:Y:Z shape ratios calculated for ilmenite, the "true" length of a randomly-oriented prismatic

217   grain would likely be larger than the observed length. In addition, the CSD breaks population

218   density (number of crystals for the measured area) into a range of sizes. The points represent the

219   largest size of crystals in each bin, such that the 6.4 mm bin represents the population of crystals

220   of sizes ranging from ~4 to 6.4 mm. Therefore, the large crystal sizes observed by Warner et al.

221   (1977) are represented in the analysis here.

222   Pyroxene and plagioclase CSDs for 71597,12 are sub-linear with Q of 0.001 and 0.01,

223   respectively (Table 1, Figure 2c-d). The characteristic lengths range from 0.3-0.4 mm. There is

224   also a downturn of the CSD profile at the smallest crystal sizes for pyroxene and plagioclase, a

225   feature not observed in ilmenite or olivine CSDs. Pyroxene and plagioclase crystals extend to

226   size bins below the estimated limit of resolution of the CSD technique, and so this downturn

227   likely is due to an under-representation of these smaller crystal sizes.

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228   Spatial distribution profiles were determined for pyroxene (porosity, $P = 64\%$, $R = 1.03$),

229   plagioclase ($P = 89\%$, $R = 0.91$), ilmenite ($P = 94\%$, $R = 0.76$), and olivine ($P = 90\%$, $R = 0.59$)

230   in thin section 71597,12 (Table 1). Multiple thin sections cannot be combined for SDPs, as can

231   be done for CSDs, because the SDP calculation is based on nearest neighbor distances. These

232   SDP results are presented in Figure 3 along with SDP results of several Apollo 17 high-Ti basalts

233   (Donohue and Neal 2015). Olivine and pyroxene form a touching crystal framework in 71597

234   (Figure 3). The higher abundance of olivine appears to have offset the ilmenite and plagioclase

235   populations to higher densities compared to other high-Ti basalts. A similar relationship was

236   observed in low-Ti basalts (Day and Taylor 2007).

Petrography and Mineral Chemistry

238   Representative analyses of silicate, Fe-Ti oxide, and melt inclusion compositions are

239   presented in Table 2 and Table 3 (all analyses are available in Supplementary Table S1). Large

240   olivine crystals (Fo_{72-75}) typically exhibit normal zonation to higher-Fe margins (Fo_{66-72}) (Figure

241   4). However, this zonation is less gradual at sharp olivine-olivine contacts or where mantled by

242   titanaugite. Mantled olivines have a thin (<0.05 mm) reaction rim. The cores of large olivine

243   crystals are compositionally distinct from cores of small olivine crystals (Fo_{62-68}). The data

244   follow a crystal fractionation trend, wherein there is a corresponding decrease in Fo-content with

245   decreasing Cr (698-1880 ppm) and V (17-55 ppm), and increasing Y (1.5-7.1 ppm) (Figure 5).

246   Compared to olivine from other mare basalt suites as well as olivine vitrophyres, 71597 olivines

247   have unique compositions in terms of Ti/V and Cr/Y ratios on plots of Ti/V and Cr/V against Fo

248   contents (Figure 6).

249   Individual ilmenite compositions (n = 15) are homogeneous in regards to major element

250   abundance, with the range in Mg# (12-19) representing inter-crystal variation (Figure 7). Warner

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251 et al. (1977) noted a broader range in ilmenite Mg# of 4-29 (MgO = 1-8 wt%) from an

252 unreported number of crystals. Paired core and rim trace element analyses are also similar, with

253 the exception of Co in one crystal in 71597,12 and Cr and Co in one crystal of 71597,13. In both

254 cases, ilmenite rims show elevated Co abundance. There is inter-crystal variation, with a positive

255 correlation between Zr (~110 to 750 ppm) and Hf (~5 to 20 ppm) (Figure 7). Ilmenite typically

256 contains blebs and lamellae of rutile and Al-rich chromite (too small for analysis by LA-ICP-

257 MS), with inclusions of silicate melt, troilite, and/or Fe-metal.

258 The sole armalcolite crystal observed is partially rimmed by an ilmenite grain of average

259 composition. The armalcolite crystal itself is at the low MgO (5.6 wt%) and high Al_2O_3 (2.0

260 wt%) range of armalcolite compositions in Apollo 17 mare basalts (Dymek et al. 1975; Papike et

261 al. 1974; Warner et al. 1975; Warner et al. 1976a). Stanin and Taylor (1980) experimentally

262 constrained the relationship between the Fe/Ti^{3+} component and oxygen fugacity in armalcolite.

263 Our calculation of the Ti^{3+} component yielded an average oxygen fugacity, relative to the iron-

264 wüstite (IW) buffer, of IW-0.66 ± 0.2. This is within the range determined for high-Ti basalts

265 collected during the Apollo 17 mission, where armalcolite fO_2 was found to range from IW-0.4

266 to IW-0.8 (Stanin and Taylor 1980).

267 Pyroxene compositional variability is similar to that observed in Apollo 17 plagioclase-

268 poikilitic mare basalts (Figure 8, Table 3). Titanaugite is present as discrete crystals and as

269 mantles (up to 0.3 mm) on olivine. Pigeonite is limited to extreme margins of augite and small

270 crystals near the margins of partially resorbed olivine. There is only minor Fe-enrichment (up to

271 Fs_{35}) in the crystals investigated here, although Warner et al. (1977) found ~5 pyroxenes with up

272 to Fs_{50}. The Al/Ti ratio decreases from 2.4:1 in augite to ~2:1 in augite rims and pigeonite

273 crystals, and the absolute abundance of Al_2O_3 and TiO_2 also decreases from core to rim in

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274   individual crystals. Augite REE profiles are subparallel and convex upward with strong negative

275   Eu anomalies (Eu/Eu*, where Eu* = $\sqrt{[Sm_{CN} * Gd_{CN}]}$, "CN" = CI Chondrite Normalized")

276   (Figure 8). Pigeonite and augite crystals are LREE depleted and have steep profiles from La-Sm,

277   and relatively flat HREE profile. The La-Sm slope decreases with increasing total LREE

278   abundance.

279   Plagioclase exhibits minor core-to-rim compositional zonation from An_{90} to An_{84} (Figure

280   4). Poikilitic plagioclase grains contain 250-660 ppm Sr and 13-95 ppm Ba. One small grain

281   (~0.2 mm; An_{84}) in a partially resorbed olivine grain contains 1100 ppm Sr and 250 ppm Ba.

282   REE profiles are typical for lunar basalts, with large positive Eu-anomalies of 42 to 83. The

283   LREE profiles are flat, and inter-crystal REE-abundance varies by an order of magnitude (Figure

284   8).

285   Silicate melt inclusions are common in large, partially resorbed olivine crystals (>20 melt

286   inclusions in some olivines) and are ubiquitous in ilmenite laths. These melt inclusions generally

287   range in size from <0.01 mm to 0.05 mm. The majority of melt inclusions in olivine are

288   microcrystalline intergrowths of pyroxene and plagioclase, with occasional anhedral troilite or

289   ilmenite. Melt inclusions in ilmenite are generally glassy and occasionally contain troilite.

290   Compositions were determined by microprobe only (Supplementary Table S1) as the inclusion

291   size precluded trace element determinations by LA-ICP-MS. There was some degree of host

292   control on melt inclusion composition, where one melt inclusion in ilmenite contained lower

293   TiO_2 compared to those in olivine and spinel, and one inclusion in spinel contained higher Cr_2O_3

294   than others. The largest melt inclusion (0.08 mm) was heterogeneous, with two separate analyses

295   of 6.5 (center) and 4.5 (rim) wt% MgO. We did not have access to a heated stage to

296   rehomogenize these inclusions but this remains as an avenue for future study.

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Discussion

Evidence of crystal accumulation

299   Using the methodology of Longhi et al. (1978) to calculate the equilibrium olivine

300   composition for a given bulk composition, the Fe/Mg partition coefficient between melt and

301   olivine was adjusted for TiO_2 content (Delano 1980). The equilibrium olivine composition

302   calculated for 71597 using the bulk composition from Murali et al. (1977) is Fo_{83}, which is not

303   observed in this sample (Warner et al. 1977; this work). This suggests the bulk composition is

304   not representative of a liquid composition as the MgO abundance is inflated due to olivine

305   accumulation.

306   Jerram et al. (2003) have used SDP textural analysis to define crystal frameworks that

307   have high melt porosity and are loosely packed (produced from a mixed population of irregular-

308   shaped clusters or clumps of crystals), and more tightly packed frameworks with lower melt

309   porosity (produced from individual crystals). Figure 3 evaluates 71597 petrography in terms of R

310   and porosity, comparing the mineral data to those from other Apollo 17 high-Ti basalts

311   (Donohue and Neal 2015). Pyroxene is the most abundant groundmass phase in the Apollo 17

312   high-Ti basalts (e.g., Dymek et al. 1975; Neal et al. 1990) so it is not surprising that pyroxene

313   from all Apollo 17 basalts, including 71597, create a touching framework of crystals (Figure 3).

314   In comparison, the plagioclase analysis closest to the touching framework line ($P = \sim75\%$, $R =$

315   1.1) is from the equilibrated basalt 75015,52, which has the highest abundance of plagioclase (25

316   vol%) of the Apollo 17 basalts reported by Donohue and Neal (2015). Relative to other Apollo

317   17 basalts, plagioclase in 75015 has a lower calculated porosity (Figure 3), consistent with

318   compaction or overgrowth (e.g., Jerram et al. 1996, 2003). Olivine in 71597,12 has the lowest R

319   (0.59) of any phase, and is the sole non-pyroxene phase to create a touching crystal framework

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320   (Figure 3). Compared to other high-Ti basalt olivine, the 71597 olivine SDP is offset to a lower

321   *R* and decreased porosity. This is an indication of increased poor sorting (i.e. accumulation), an

322   interpretation further supported by the kinked olivine CSD reflecting two olivine crystal size

323   populations (Fig. 2a). The combination of SDP and CSD analyses support the observation that

324   olivine accumulation occurred as clusters in 71597 but was not a significant factor in any other

325   high-Ti basalt (*cf.*, Neal et al. 1990; Donohue and Neal 2015).

326   Crystal size distribution characteristics (CSD profile slope, y-intercept, and linearity)

327   vary between phases (Figure 2). However, direct comparisons first require accounting for

328   variable growth rates of the different phases in order to estimate residence time of the different

329   crystal cargoes present in 71597. It was noted above that growth rates are variable and are

330   dependent on many factors that change as a magma crystallizes, which leads to residence times

331   with large errors. We can, however, estimate relative residence times simply by examining the

332   gradients of the CSD profiles. For olivine and ilmenite, the CSDs are divided into two segments.

333   Warner et al. (1977) suggested there was some ilmenite accumulation in 71597, and here the

334   CSD has been subdivided at ~1 mm size bin. The populations of larger olivine and ilmenite

335   crystals have the lowest CSD gradients (-2.8 $\pm$ 0.3 and -1.5 $\pm$ 0.1, respectively), indicating

336   relatively longer residence times relative to other phases in 71597. This is consistent with the

337   either prolonged olivine and ilmenite crystallization or accumulation of these phases.

338   The variation in modal olivine between our analysis and that of Warner et al. (1977) and

339   Neal and Taylor (1993) indicates heterogeneous distribution of olivine at the thin section scale,

340   consistent with crystal accumulation, possibly as clusters of olivine. The bimodal Fo-content

341   distribution between large and matrix olivine (Figure 5) is also consistent with accumulation in

342   an evolving melt. Furthermore, compositional data suggest accumulation from a fractionating

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343 magma rather than from different magma batches, as there is no evidence of an antecryst origin

344 for some olivines or for mixing between magmas with olivine on the liquidus. Olivine

345 compositions also suggest that ilmenite was co-crystallizing with those containing the highest Fo

346 contents, but ceased crystallizing around Fo_{69} (Figure 6a).

347   The crystallization sequence and conditions for 71597 derived from textural analysis are

348 consistent with sample geochemistry. The general sequence of crystallization is olivine +

349 armalcolite → olivine + ilmenite → ilmenite + augite → ilmenite + augite + plagioclase →

350 pigeonite + plagioclase. The CSDs and general textures indicate olivine crystallized first at an

351 initial cooling rate of 1-3 degrees per hour (cf. Usselman et al. 1975; Usselman and Lofgren

352 1976; Donohue and Neal 2015). Olivine and ilmenite were on the liquidus prior to eruption, and

353 some matrix olivines likely crystallized at the surface. Ilmenite contains relatively high MgO

354 contents (3.2-5.2 wt% MgO here, up to 8 wt% noted by Warner et al. 1977) compared to other

355 Apollo 17 high-Ti basalts (0.17-4.87 wt% MgO), which may have resulted from reaction with

356 the evolving melt during crystallization. This reaction is supported by abundant exsolution

357 lamellae similar to those found in other re-equilibrated ilmenite from Apollo 17 basalts (e.g., El

358 Goresy and Ramdohr 1975). This relatively high-Mg content in ilmenite is likely buffered by

359 olivine resorption, with titanaugite and high-Ca plagioclase crystallization lowering CaO in the

360 residual melt (as evidenced by decreasing CaO content in plagioclase with decreasing compatible

361 element abundance) and leading to late pigeonite crystallization. There may also be a

362 contribution from isothermal diffusion, which can inhibit Fe-enrichment commonly observed

363 during pyroxene crystallization (e.g., Dungan and Brown 1977).

364 **Type source of 71597**

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365   Mineral compositions and CSDs can be used to evaluate not only crystallization history

366   but also source characteristics (e.g., Hui et al. 2011). Apollo 17 basalt 71597 is currently

367   unclassified (being part of the "Type U" classification of Rhodes et al. 1976) because of the

368   coarse grain size and small sample mass (12.35 g; Neal and Taylor 1993) making a

369   representative whole-rock analysis difficult to produce. This is why the whole rock data reported

370   by Murali et al. (1977) cannot be used to classify 71597. According to Haskin and Korotev

371   (1977), Haskin et al. (1977), and Ryder and Schuraytz (2001), coarse grained samples require up

372   to 5 grams of sample to be powdered in order to obtain a representative WR analysis. This would

373   require consuming almost half of the original 12.35 g that comprised 71597. Murali et al. (1977)

374   only used 0.612 g of this coarse-grained sample in their whole rock analysis, strongly suggesting

375   this is not representative of the true whole rock composition. The data obtained as part of this

376   study are used to propose a method for classifying 71597 within the chemical schemes already

377   proposed, thus enhancing the science return on these precious samples.

378   Apollo 17 high-Ti basalts are separated into groups (Types A, B1, B2, C, D) based on

379   whole-rock major and trace element abundances and ratios (Figure 9; Rhodes et al. 1976; Neal et

380   al. 1990; Ryder 1990). For example, the Type B basalt suite first identified by Rhodes et al.

381   (1976), and later split into Types B1 and B2, were divided based on whole rock rare earth

382   element (REE) and high field strength element (HFSE) abundances and La/Sm ratios (Neal et al.

383   1990). Prior to the split, Warner et al. (1979) proposed 71597 originated in a thick high-Ti basalt

384   flow of Apollo 17 Type B basalt composition. The fraction of olivine in the bulk analysis has

385   consequences for La, Sm, and Yb, which are controlled by the amount of mesostasis in the

386   analysis (Haskin and Korotev 1977). However, ratios of these olivine-incompatible elements

387   should be unaffected by olivine addition. Olivine (± ilmenite) accumulation should only dilute -

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388   and not fractionate – elements incompatible in olivine (and ilmenite - e.g., REEs). We attempted

389   to distinguish the Apollo 17 high-Ti basalt source group for 71597 by accounting for trace

390   element variation caused by olivine accumulation. The reported La/Yb ratio (0.63; Murali et al.

391   1977; Warner et al. 1977) is similar to Type B1 basalts, while the La/Sm ratio (0.77) is consistent

392   with Type B2 basalts (Figure 9b,c). The Yb/Sm ratio (1.23) is higher than all other A17 high-Ti

393   basalts (0.83-1.13). Uncertainty in the INAA-determined REE abundances reported by Murali et

394   al. (1977) are given only in general terms of ±1-5%. With this consideration, the Yb/Sm ratio of

395   71597 may then be within uncertainty of the upper limit of Type B1 basalts. However, calculated

396   pre-cumulate values for 71597 yield compositions outside any Apollo 17 group (Figure 9b),

397   Type B2 basalts (Figure 9c), and Type B1 basalts (Figure 9d). The conflicting groupings and

398   unique ratios of 71597 indicate at least some incompatible element ratios are not representative

399   of the whole-rock.

400   Major element oxide compositions of Apollo 17 high-Ti basalts group into trends (Figure

401   9) that can be explained by simple fractional crystallization evolution (*cf*. Neal et al. 1990).

402   Warner et al. (1977) showed that subtraction of 24-27% olivine from the measured 71597 bulk

403   composition brought the sample into the range of other high-Ti basalts (*cf*., Table 4 of Warner et

404   al. 1977). We expanded this model to include trace elements via Rayleigh fractionation.

405   Incompatible trace element fractionation results (Table 4 and Figure 9) for removal of 24% or

406   27% olivine (± 1% ilmenite) are essentially identical due to low olivine-melt and ilmenite-melt

407   partition coefficients. The resultant trace element compositions once again yield conflicting

408   classifications (Figure 9). The La/Yb ratio is consistent with Type B1 basalts, while La/Sm is

409   within the range of Type B2 basalts. The pre-cumulate abundances of La, Sm, and Cr are closest

410   to Type B1 basalts. Modeled Yb and Eu abundances do not distinguish between Type B1 and B2

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411   groups, and Co abundance is distinct only from Type B2 basalts. Therefore, either cumulate

412   71597 resulted from accumulation in a new magma type, one or more of the INAA-determined

413   REEs are not representative of the parent melt, or the simple model of olivine accumulation is

414   insufficient. An argument for any of these three possibilities would remain equivocal if only bulk

415   whole rock analyses were considered.

416   Equilibrium melt calculations theoretically yield compositions wherein mineral phases

417   crystallized. Melt compositions (Figure 10) were calculated for each phase by dividing trace

418   element abundances by mineral-specific partition coefficients for V, Cr, and the REEs (Table 5).

419   Olivine partition coefficients were calculated using the relationship of D to bulk MgO of Bédard

420   (2005). Other partition coefficients were determined at low fO$_2$ (between IW-0 and IW-2) and

421   with trace elements present at natural abundances (see references in Table 5). Equilibrium melts

422   could be explained by a model in which fractional crystallization evolution is modified by

423   olivine resorption (Figure 10b). Equilibrium liquid compositions calculated from the cores of

424   augite are similar to light REEs (LREE) or elevated above the heavy REEs (HREE) compared to

425   whole-rock values from Murali et al. (1977) (Figure 10c). The LREEs are more incompatible

426   than HREEs in olivine, and so this discrepancy may result from an unaccounted for dilution of

427   LREEs by olivine addition. Pigeonite equilibrium melts are similar to the compositional

428   dispersion observed in plagioclase (Figure 10c), but the majority are depleted in Eu, as seen on

429   Figure 10d. Pigeonite likely originated in olivine reaction rims after plagioclase crystallized,

430   which limited available Eu. Plagioclase equilibrium compositions follow the expected positive

431   correlation between La and Eu (Figure 10d).

432   Apollo 17 high-Ti basalts are classified primarily based on whole-rock trace element

433   compositional variation. The trace elements obtained for olivine in 71597 are similar to olivines

19

434   found in other chemical groups. In addition, the paucity of olivine in Type B1 basalts is not

435   conducive to such comparisons. Here, we utilize augite to trace source evolution, because augite

436   crystallizes early in high-Ti basalts, and has sufficient incompatible trace element abundance for

437   quantification by LA-ICP-MS analyses. On Figure 10d, the whole-rock fractionation trends of La

438   and Eu in Apollo 17 high-Ti basalts are compared to the plagioclase and pyroxene equilibrium

439   liquids. Pigeonite, as might be expected from a phase appearing late in the crystallization

440   sequence after modification by partial resorption, does not appear to represent true liquid

441   composition. Finally, the evolution from augite equilibrium melt to relatively late-stage

442   plagioclase most closely follows a fractional crystallization trend from a Type B2 basalt source

443   composition.

444

445   **Implications**

446   Through careful characterization of sample petrography and mineral geochemistry, we

447   are able to place constraints on the geochemical evolution of a unique Apollo sample and tie it to

448   the Type B2 mare basalt suite. The Type B2 suite comprises nine fine-grained vitrophyric-

449   olivine porphyritic basalts, and one plagioclase poikilitic basalt. Prior investigation suggesting a

450   spread in Rb-Sr and Sm-Nd isotopes for whole-rock samples indicated the Type B2 basalts were

451   affected by open system processes (Paces et al. 1991). We are not able to determine where

452   olivine accumulation occurred, but it could have been in ponded melts at the base of or in the

453   lunar crust, or within a thick high-Ti basalt flow. If it was the former, where multiple

454   components were mixing while olivine was crystallizing, further study of olivine melt inclusions

455   may be used to verify this process. If it was the latter case, then we would expect more coarse-

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456   grained material represented in the Type B2 sample suite, which might be present but

457   unrecognized in the Apollo sample collection.

458   Approximately one-third of high-Ti mare basalts returned by the Apollo 17 mission are

459   designated as Type U or "unclassified" basalts. These have remained unclassified for 40+ years

460   due to issues with obtaining representative bulk analyses, primarily due to small sample masses

461   and coarse grain sizes. The approach used here has the potential to place petrogenetic constraints

462   on these samples, and has demonstrated potential for classification and discrimination of Type U

463   basalts within the current whole-rock classification scheme for Apollo 17 high-Ti basalts, and

464   potentially identifying new basalt types. The Earth and the Moon share many similarities in

465   eruption styles of basalts. The characterization of end-member samples like 71597 will be

466   important for comparative analyses with the growing collection of mare basalt textures that have

467   been defined through quantitative analysis. Finally, application of these microscale techniques

468   will maximize the science potential of future robotic sample return missions to the Moon and

469   other planetary bodies.

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Revision 2

References

479 van Achterbergh, E., Ryan, C.G., Jackson, S.E., and Griffin, W.L. (2001) Data reduction

480 software for LA-ICP-MS: Appendix. In P.J. Sylvester, Ed., Laser ablation-ICP-mass

481 spectrometry in the Earth Sciences: Principles and applications, Vol. 29, pp. 239–243.

482 Mineralogical Association of Canada, Short Course Series.

483 Alexander, L., Snape, J.F., Crawford, I.A., Joy, K.H., and Downes, H. (2014) Searching for

484 nonlocal lithologies in the Apollo 12 regolith: A geochemical and petrological study of

485 basaltic coarse fines from the Apollo lunarsoil sample 12023,155. Meteoritics & Planetary

486 Science, 49, 1288–1304.

487 Bédard, J.H. (2005) Partitioning coefficients between olivine and silicate melts. Lithos, 83, 394–

488 419.

489 Bindeman, I.N., Davis, A.M., and Drake, M.J. (1998) Ion microprobe study of plagioclase-basalt

490 partition experiments at natural concentration levels of trace elements. Geochimica et

491 Cosmochimica Acta, 62, 1175–1193.

492 Burkhard, D.J.M. (2005) Nucleation and growth rates of pyroxene, plagioclase, and Fe-Ti oxides

493 in basalt under atmospheric conditions. European Journal of Mineralogy, 17, 675–686.

494 Cabane, H., Laporte, D., and Provost, A. (2005) An experimental study of Ostwald ripening of

495 olivine and plagioclase in silicate melts: Implications for the growth and size of crystals in

496 magmas. Contributions to Mineralogy and Petrology, 150, 37-53.

497 Cashman, K.V., and Marsh, B.D. (1988) Crystal size distribution (CSD) in rocks and the kinetics

498 and dynamics of crystallization II: Makaopuhi lava lake. Contributions to Mineralogy and

499 Petrology, 99, 292–305.

500 Cushing, J.A., Taylor, G.J., Norman, M.D., and Keil, K. (1999) The granulitic impactite suite:

22

502   Impact melts and metamorphic breccias of the early lunar crust. Meteoritics & Planetary

503   Science, 34, 185–195.

504   Day, J.M.D., and Taylor, L.A. (2007) On the structure of mare basalt lava flows from textural

505   analysis of the LaPaz Icefield and Northwest Africa 032 lunar meteorites. Meteoritics &

506   Planetary Science, 42, 3–17.

507   Delano, J.W. (1980) Chemistry and liquidus phase relations of Apollo 15 red glass: Implications

508   for the deep lunar interior. Proceedings of the 11th Lunar and Planetary Science Conference,

509   251-288.

510   Donohue, P.H., and Neal, C.R. (2015) Quantitative textural analysis of ilmenite in Apollo 17

511   high-titanium mare basalts. Geochimica et Cosmochimica Acta, 149, 115–130.

512   Dungan, M.A., and Brown, R.W. (1977) The petrology of the Apollo 12 ilmenite basalt suite.

513   Proceedings of the 8th Lunar Science Conference, 1339–1381.

514   Dygert, N., Liang, Y., and Hess, P.C. (2013) The importance of melt TiO_2 in affecting major and

515   trace element partitioning between Fe-Ti oxides and lunar picritic glass melts. Geochimica et

516   Cosmochimica Acta, 106, 134–151.

517   Dymek, R.F., Albee, A.L., and Chodos, A.A. (1975) Comparative mineralogy and petrology of

518   Apollo 17 mare basalts: Samples 70215, 71055, 74255, and 75055. Proceedings of the 6th

519   Lunar Science Conference, 49–77.

520   El Goresy, A., and Ramdohr, P. (1975) Subsolidus reduction of lunar opaque oxides: Textures,

521   assemblages, geochemistry, and evidence for a late-stage endogenic gaseous mixture.

522   Proceedings of the 6th Lunar Science Conference, 729–745.

523   Fagan, A.L., Neal, C.R., Simonetti, A., Donohue, P.H., and O'Sullivan, K.M. (2013)

524   Distinguishing between Apollo 14 impact melt and pristine mare basalt samples by

23

525   geochemical and textural analyses of olivine. Geochimica et Cosmochimica Acta, 106, 429–

526   445.

527   Hallis, L.J., Anand, M., and Strekopytov, S. (2014) Trace-element modelling of mare basalt

528   parental melts: Implications for a heterogeneous lunar mantle. Geochimica et Cosmochimica

529   Acta, 134, 289–316.

530   Haskin, L.A., and Korotev, R.L. (1977) Test of a model for trace element partition during closed-

531   system solidification of a silicate liquid. Geochimica et Cosmochimica Acta, 41, 921–939.

532   Haskin, L.A., Jacobs, J.W., Brannon, J.C., and Haskin, M.A. (1977) Compositional dispersions

533   in lunar and terrestrial basalts. Proceedings of the 8th Lunar and Planetary Science

534   Conference, 1731-1750.

535   Higgins, M.D. (2000) Measurement of crystal size distributions. American Mineralogist, 85,

536   1105–1116.

537   Higgins, M.D. (2002) Closure in crystal size distributions (CSD), verification of CSD

538   calculations, and the significance of CSD fans. American Mineralogist, 87, 171–175.

539   Higgins, M.D. (2006) Verification of ideal semi-logarithmic, lognormal or fractal crystal size

540   distributions from 2D datasets. Journal of Volcanology and Geothermal Research, 154, 8–16.

541   Higgins, M.D., and Roberge, J. (2003) Crystal size distribution of plagioclase and amphibole

542   from Soufrière Hills Volcano, Montserrat: Evidence for dynamic crystallization–textural

543   coarsening cycles. Journal of Petrology, 44, 1401–1411.

544   Hodges, F.N., and Kushiro, I. (1974) Apollo 17 petrology and experimental determination of

545   differentiation sequences in model moon compositions. Proceedings of the 5th Lunar

546   Conference, 505–520.

547   Hui, H., Oshrin, J.G., and Neal, C.R. (2011) Investigation into the petrogenesis of Apollo 14

Revision 2

548   high-Al basaltic melts through crystal stratigraphy of plagioclase. Geochimica et

549   Cosmochimica Acta, 75, 6439–6460.

550   Irving A. J., Merrill R. B. and Singleton D. E. (1978) Experimental partitioning of rare earth

551   elements and scandium among armalcolite, ilmenite, olivine and mare basalt liquid.

552   Proceedings of the 9th Lunar and Planetary Science Conference, 601–612.

553   Jerram, D.A., Cheadle, M.J., Hunter, R.H., and Elliott, M.T. (1996) The spatial distribution of

554   grains and crystals in rocks. Contributions to Mineralogy and Petrology, 125, 60–74.

555   Jerram, D.A., Cheadle, M.J., and Philpotts, A.R. (2003) Quantifying the building blocks of

556   igneous rocks: Are clustered crystal frameworks the foundation? Journal of Petrology, 44,

557   2033–2051.

558   Jerram, D.A., Davis, G.R., Mock, A., Charrier, A., and Marsh, B.D. (2010) Quantifying 3D

559   crystal populations, packing and layering in shallow intrusions: A case study from the

560   Basement Sill, Dry Valleys, Antarctica. Geosphere, 6, 537–548.

561   Jolliff, B.L., Korotev, R.L., Zeigler, R.A., and Floss, C. (2003) Northwest Africa 773: Lunar

562   mare breccia with a shallow-formed olivine-cumulate component, inferred very-low-Ti

563   (VLT) heritage, and a KREEP connection. Geochimica et Cosmochimica Acta, 67, 4857–

564   4879.

565   Klemme, S., Günther, D., Hametner, K., Prowatke, S. and Zack, T. (2006) The partitioning of

566   trace elements between ilmenite, ulvospinel, armalcolite and silicate melts with implications

567   for the early differentiation of the moon. Chemical Geology, 234, 251–263.

568   Laul, J.C., Schmitt, R.A., Robyn, M., and Goles, G.G. (1975) Chemical Composition of 18

569   Apollo 17 Rake Basalts and One Basalt Breccia. Proceedings of the 6th Lunar and Planetary

570   Science Conference, 492–493.

25

Always consult and cite the final, published document. See http:/www.minsocam.org or GeoscienceWorld

Revision 2

571   Longhi, J., Walker, D., and Hays, J.F. (1978) The distribution of Fe and Mg between olivine and

572   lunar basaltic liquids. Geochimica et Cosmochimica Acta, 42, 1545-1558.

573   Mallmann, G., and O'Neill, H.S.C. (2009) The crystal/melt partitioning of V during mantle

574   melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc,

575   Ti, Cr, Fe, Ga, Y, Zr and Nb). Journal of Petrology, 50, 1765–1794.

576   Marsh, B.D. (1988) Crystal size distribution (CSD) in rocks and the kinetics and dynamics of

577   crystallization I. Theory. Contributions to Mineralogy and Petrology, 99, 277–291.

578   Marsh, B.D. (1998) On the interpretation of crystal size distributions in magmatic systems.

579   Journal of Petrology, 39, 553–599.

580   Martin, V.M., Pyle, D.M., and Holness, M.B. (2006) The role of crystal frameworks in the

581   preservation of enclaves during magma mixing. Earth and Planetary Science Letters, 248,

582   787–799.

583   Masuda, A., Tanaka, T., Nakamura, N., and Kurasawa, H. (1974) Possible REE anomalies of

584   Apollo 17 REE patterns. Proceedings of the 5th Lunar Conference, 2, 1247–1253.

585   McCallum, I.S., and Charette, M.P. (1978) Zr and Nb partition coefficients: Implications for the

586   genesis of mare basalts, KREEP, and sea floor basalts. Geochimica et Cosmochimica Acta,

587   42, 859–869.

588   McDonough, W.F. and Sun, S.-S. (1995) The composition of the Earth. Chemical Geology, 120,

589   223–253.

590   Morgan, D.J., and Jerram, D.A. (2006) On estimating crystal shape for crystal size distribution

591   analysis. Journal of Volcanology and Geothermal Research, 154, 1–7.

592   Murali, A.V., Ma, M.-S., and Schmitt, R.A. (1977) Chemistry of 30 Apollo 17 rake basalts;

593   71597 a product of partial olivine accumulation. Abstracts of the 8th Lunar and Planetary

26

Revision 2

594   Science Conference, 703–704.

595   Neal, C.R. (2001) Interior of the Moon: The presence of garnet in the primitive deep lunar

596   mantle. Journal of Geophysical Research, 106, 27865–27886.

597   Neal, C.R., and Taylor, L.A. (1990) Modeling of lunar basalt petrogenesis: Sr isotope evidence

598   from Apollo 14 high-alumina basalts. Proceedings of the 20th Lunar and Planetary Science

599   Conference, 101–108.

600   Neal, C.R., and Taylor, L.A. (1993) Catalog of Apollo 17 Rocks Volume 2 - Central Valley, Part

601   1, 472 pp. NASA.

602   Neal, C.R., Taylor, L.A., Hughes, S.S., and Schmitt, R.A. (1990) The significance of fractional

603   crystallization in the petrogenesis of Apollo 17 Type A and B high-Ti basalts. Geochimica et

604   Cosmochimica Acta, 54, 1817–1833.

605   Neal, C.R., Hacker, M.D., Snyder, G.A., Taylor, L.A., Liu, Y.-G., and Schmitt, R.A. (1994)

606   Basalt generation at the Apollo 12 site, Part 2: Source heterogeneity, multiple melts, and

607   crustal contamination. Meteoritics, 29, 349–361.

608   Neal, C.R., Donohue, P.H., Fagan, A.L., O'Sullivan, K.M., Oshrin, J., and Roberts, S. (2015)

609   Distinguishing between basalts produced by endogenic volcanism and impact processes: A

610   non-destructive method using quantitative petrography of lunar basaltic samples. Geochimica

611   et Cosmochimica Acta, 148, 62–80.

612   Paces J.B., Nakai S., Neal C.R., Taylor L.A., Halliday A.N. and Lee D.-C. (1991) A strontium

613   and neodymium isotopic study of Apollo 17 high-Ti mare basalts: Resolution of ages,

614   evolution of magmas, and origins of source heterogeneities. Geochimica et Cosmochimica

615   Acta, 55, 2025–2043.

616   Papike, J.J., Bence, A.E., and Lindsley, D.H. (1974) Mare basalts from the Taurus-Littrow

617   region of the moon. Proceedings of the 5th Lunar Conference, 471–504.

618   Papike, J.J., Hodges, F.N., Bence, A.E., Cameron, M., and Rhodes, J.M. (1976) Mare basalts:

619   Crystal chemistry, mineralogy, and petrology. Reviews of Geophysics and Space Physics, 14,

620   475–540.

621   Pearce, N.J., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., and

622   Chenery, S.P. (1997) A compilation of new and published major and trace element data for

623   NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards Newsletter, 21,

624   115–144.

625   Rhodes, J.M., Hubbard, N.J., Wiesmann, H., Rodgers, K.V., Brannon, J.C., and Bansal, B.M.

626   (1976) Chemistry, classification, and petrogenesis of Apollo 17 mare basalts. Proceedings of

627   the 7th Lunar Science Conference, 1467–1489.

628   Rhodes, J.M., Brannon, J.C., Rodgers, K.V., Blanchard, D.P., and Dungan, M.A. (1977)

629   Chemistry of Apollo 12 mare basalts: Magma types and fractionation processes. Proceedings

630   of the 8th Lunar Science Conference, 1305–1338.

631   Ryder, G. (1985) Catalog of Apollo 15 Rocks Part 2. 15306-15468. Curatorial Branch

632   Publication, 72, 443 pp. NASA.

633   Ryder, G. (1990) A distinct variant of high-titanium mare basalt from the Van Serg core, Apollo

634   17 landing site. Meteoritics, 25, 249–258.

635   Ryder, G., and Schuraytz, B.C. (2001) Chemical variation of the large Apollo 15 olivine-

636   normative mare basalt rock samples. Journal of Geophysical Research, 106, 1435-1451.

637   Schnare, D.W., Day, J.M.D., Norman, M.D., Liu, Y., and Taylor, L.A. (2008) A laser-ablation

638   ICP-MS study of Apollo 15 low-titanium olivine-normative and quartz-normative mare

639   basalts. Geochimica et Cosmochimica Acta, 72, 2556–2572.

Revision 2

640 Schneider, C.A., Rasband, W.S., and Eliceiri, K.W. (2012) NIH Image to ImageJ: 25 years of

641   image analysis. Nature Methods, 9, 671–675.

642 Shih, C.-Y., Wiesmann, H., Bansal, B.M., Brannon, J.C., and Haskin, L.A. (1975) On the origin

643   of high-Ti mare basalts. Proceedings of the 6th Lunar Science Conference, 1255–1285.

644 Stanin, F.T., and Taylor, L.A. (1980) Armalcolite: An oxygen fugacity indicator. Proceedings of

645   the 11th Lunar and Planetary Science Conference, 117–124.

646 Sun, C., and Liang, Y. (2012) Distribution of REE between clinopyroxene and basaltic melt

647   along a mantle adiabat: effects of major element composition, water, and temperature.

648   Contributions to Mineralogy and Petrology, 163, 807–823.

649 Taylor, L.A., Shervais, J.W., Hunter, R.H., Shih, C.-Y., Bansal, B.M., Wooden, J.L., Nyquist,

650   L.E., and Laul, L.C. (1983) Pre-4.2 AE mare-basalt volcanism in the lunar highlands. Earth

651   and Planetary Science Letters, 66, 33–47.

652 Usselman, T.M., Lofgren, G.E., Donaldson, C.H., and Williams, R.J. (1975) Experimentally

653   reproduced textures and mineral chemistries of high-titanium mare basalts. Proceedings of

654   the 6th Lunar Science Conference, 997–1020.

655 Usselman, T.M., and Lofgren, G.E. (1976) The phase relations, textures, and mineral chemistries

656   of high-titanium mare basalts as a function of oxygen fugacity and cooling rate. Proceedings

657   of the 7th Lunar Science Conference, 1345–1363.

658 Vinet, N., and Higgins, M.D. (2010) Magma solidification processes beneath Kilauea Volcano,

659   Hawaii: A quantitative textural and geochemical study of the 1969-1974 Mauna Ulu lavas.

660   Journal of Petrology, 51, 1297–1332.

661 Vobecký, M., Frána, J., Bauer, J., Řanda, Z., Benada, J., and Kuncíř, J. (1971) Radioanalytical

662   determination of elemental compositions of lunar samples. Proceedings of the 2nd Lunar

29

Revision 2

663   Science Conference, 2, 1291–1300.

664 Walker, D., Longhi, J., and Hays, J.F. (1976) Heterogeneity in titaniferous lunar basalts. Earth

665   and Planetary Science Letters, 30, 27–36.

666 Warner, R.D., Keil, K., Prinz, M., Laul, J.C., Murali, A.V., and Schmitt, R.A. (1975)

667   Mineralogy, petrology, and chemistry of mare basalts from Apollo 17 rake samples.

668   Proceedings of the 6th Lunar Science Conference, 193–220.

669 Warner, R.D., Berkley, J.L., Mansker, W.L., Warren, R.G., and Keil, K. (1976a) Electron

670   microprobe analyses of spinel, Fe-Ti oxides and metal from Apollo 17 rake sample mare

671   basalts. Spec. Pub. #16, UNM Institute of Meteoritics, Albuquerque, 114 pp.

672 Warner, R.D., Warren, R.G., Mansker, W.L., Berkley, J.L., and Keil, K. (1976b) Electron

673   microprobe analyses of olivine, pyroxene and plagioclase from Apollo 17 rake sample mare

674   basalts, Spec. Pub. #15, UNM Institute of Meteoritics, Albuquerque, 121 pp.

675 Warner, R.D., Keil, K., and Taylor, G.J. (1977) Coarse-grained basalt 71597: A product of

676   partial olivine accumulation. Proceedings of the 8th Lunar Science Conference, 1429–1442.

677 Warner, R.D., Taylor, G.J., Conrad, G.H., Northrop, H.R., Barker, S., Keil, K., Ma, M.-S., and

678   Schmitt, R.A. (1979) Apollo 17 high-Ti mare basalts: New bulk compositional data, magma

679   types, and petrogenesis. Proceedings of the 10th Lunar and Planetary Science Conference,

680   225–247.

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682 **Figure Captions**

683 Figure 1. Plane-polarized light views and composites of traced phases of the two new thin

684 sections of 71597. (a) 71597,12 and (b) composite of traced ilmenite, olivine, plagioclase, and

685 pyroxene. Note pyroxene was only traced for half of the section. For (c) section 71597,13, only

686 (d) ilmenite and olivine were traced. The more subdued color of olivine and pyroxene on the

687 bottom half of 71597,13 is due to the lower thickness of the thin section. Crystals intersecting the

688 edge of the sections were not traced. Gray areas in (b) and (d) represent the sample area.

689 Figure 2. Crystal size distribution profiles for 71597,12 and ,13. (a) Olivine CSD profiles appear

690 to be multiply kinked, and (b) ilmenite CSDs are concave upward. The CSD profiles are sub-

691 linear for (c) pyroxene and (d) plagioclase.

692 Figure 3. R-value (relative ordering) versus Porosity (% matrix) for phases in Apollo 17 high-Ti

693 basalts (open symbols; Donohue and Neal 2015) and basalt 71597,12 (filled symbols). RSDL =

694 Random Sphere Distribution Line for modeled population of uniform spheres; points to the left

695 of the Touching Framework line (TF) form a touching framework of crystals. Besides olivine in

696 71597, plagioclase in coarse-grained Type A basalt 75015 is the only other non-pyroxene phase

697 to approach a clustered crystal distribution. The processes resulting in trends for related samples

698 are included schematically. Figure after Jerram et al. 2003.

699 Figure 4. Ranges of (a) olivine Fo and (b) plagioclase An compositions observed in 71597

700 compared to literature values for individual samples of other lunar basalt types. Data from Fagan

701 et al. (2013), Hallis et al. (2014), Schnare et al. (2008), and Neal and Taylor (1990).

702 Figure 5. Element variation diagrams for large olivine interiors (filled) and rims (open symbols)

703 as well as matrix olivine depicting (a) decreasing V (ppm) with melt evolution, and (b)

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704 corresponding increase in Y (ppm) abundance. Vertical lines indicate 1σ errors. Multiple

705 analyses of individual crystals are connected with a gray line.

706 Figure 6. Olivine forsterite variability versus (a) Ti/V and (b) Cr/Y versus olivine forsterite

707 contents. Fields drawn from literature: Apollo 12 (A12) ilmenite basalts, pigeonite basalts,

708 olivine basalts, Apollo 14 (A14) Groups A, B, and C basalts, Apollo 14 olivine vitrophyres

709 (OV), and Apollo 17 sample 74275 from Fagan et al. (2013); Apollo 15 (A15) olivine normative

710 and quartz normative basalts from Schnare et al. (2008).

711 Figure 7. Ilmenite major and trace element variation diagrams. 1σ errors for trace elements

712 indicated for each point where larger than the symbol.

713 Figure 8. (a) Composition of pyroxene projected onto pyroxene quadrilateral with data from

714 Warner et al. (1977) for comparison. (b) REE profiles of augite, pigeonite, and plagioclase of

715 71597 are typical of Apollo 17 basalts. Whole-rock values from 71597,1 (Murali et al. 1977).

716 Values for CI chondrite from McDonough and Sun (1995).

717 Figure 9. Compositional fields drawn from bulk rock analyses of Apollo 17 high-Ti basalts of (a)

718 TiO2 (wt.%) versus MgO (wt.%), (b) Sm (ppm) versus Cr/La, (c) La/Sm versus La (ppm), and

719 (d) Hf (ppm) versus La/Yb. Gray shaded circles are compositions resulting from 24% (dark gray)

720 and 27% (light gray) olivine subtraction from analysis of 71597,1 (black circle, Murali et al.

721 1977). Gray triangle represents subtraction of 27% olivine and 1% ilmenite.

722 Figure 10. Element variation diagrams for calculated equilibrium melts from crystal interiors

723 (filled symbols) and rims (open symbols). (a) Mg# versus V (ppm). (b) Cr/Y versus Cr (ppm)

724 with inferred magma compositional path shown (dashed line). (c) Chondrite-normalized

725 pyroxene and plagioclase equilibrium melt REE profiles compared to reported whole-rock and

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726 olivine subtracted compositions. (d) La versus Eu correlation of whole-rock compositions from

727 each group, and equilibrium liquid compositions of augite, pigeonite, and plagioclase. Fractional

728 crystallization (FC) paths for Types B1 and B2 basalts are from Neal et al. (1990) to 70%

729 crystallization. Two analyses of high-REE plagioclase are not shown, as they represent extreme

730 fractionation during late stage cooling. Calculations for removal of 24% olivine and 27% olivine

731 + 1% ilmenite (not shown) are within uncertainty of the -27% olivine on (c) and (d). Open

732 symbols in (a), (b), and (d) represent rim analyses. Literature bulk La and Eu values from

733 (Masuda et al. 1974; Laul et al. 1975; Shih et al. 1975; Warner et al. 1975; Rhodes et al. 1976;

734 Murali et al. 1977; Warner et al. 1979; Neal et al. 1990; Neal 2001).

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736 **Supplementary Material**

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738 Supplementary Table S1 (Deposit item)

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741   **Tables**

742   Table 1. Crystal size distribution data for major phases.

Phase split(s)	Area (mm2)	Crystals	vol %	Slope1		y-int1		Slope2		y-int2		shape parameters	R2	NND *average*	SDP *R* value
Olivine															
,12	102.2	118	16.4%	-9.04	± 1.70	4.55	± 0.49	-2.48	± 0.10	1.27	± 0.12	1:1.4:2	0.80	0.345	0.59
,13	61.7	43	19.2%	-8.47	± 1.15	4.15	± 0.35	-2.07	± 0.13	0.81	± 0.25	1:1.5:2.3	0.81	*n.a.*	*n.a.*
,12 + ,13	163.9	161	17.5%	-13.41	± 0.45	5.12	± 0.12	-1.76	± 0.39	0.09	± 0.79	1:1.4:1.9	0.84	*n.a.*	*n.a.*
Ilmenite															
,12	102.2	482	5.7%	-2.60	± 0.58	3.86	± 0.30	-1.53	± 0.17	2.29	± 0.49	1:1.25:7	0.78	0.116	0.76
,13	95.7	393	6.9%	-3.06	± 0.10	4.08	± 0.04	-1.63	± 0.21	1.73	± 0.59	1:1.7:6	0.73	0.113	0.65
,12 + ,13	197.9	875	6.3%	-2.28	± 0.30	3.57	± 0.15	-1.22	± 0.13	1.67	± 0.53	1:1.25:7	0.77	*n.a.*	*n.a.*
Plagioclase															
,12	102.2	286	10.9%	-2.25	± 0.13	2.93	± 0.20	-		-		1:1.7:4.5	0.79	0.260	0.91
Pyroxene															
,12	102.2	362	35.5%	-3.51	± 0.29	4.77	± 0.35	-		-		1:1.6:2.9	0.81	0.181	1.03

743   n.a.: not applicable. Vol % = volume percent.
744   Slope# and y-int# = slope and intercept of portions of CSD profiles representing different size populations.
745   NND: nearest neighbor distance (mm) to crystal of same phase.
746

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748 Table 2. Average olivine and Fe-Ti oxide mineral chemistry for 71597 and for mare basalt groups.

Phase	Large olivine				Matrix olivine		Ilmenite		Armalcolite		A17 Type A, B1, B2, C, U		A11 low-K, high-K		A12 Ilm, Ol, and Pigeonite suites		A14 high-Al and Ol. Vitrophyre		A15 KREEP & Ol normative	
	core	2σ	rim	2σ	core	2σ	average	2σ	average	2σ	Olivine	Ilmenite	Olivine	Ilmenite	Olivine	Ilmenite	Olivine	Ilmenite	Olivine	Ilmenite
n =	8		8		4		14		2											
wt.%																				
SiO$_2$	37.7	0.7	37.3	0.8	36.9	1.6					24.7 - 41.0	0.01 - 0.38	29.2 - 38.6	0.12 - 0.23	33.4 - 39.9	0.03 - 8.90	35.7 - 42.3	0.16	27.2 - 48.2	b.d. - 3.42
TiO$_2$							54.4	2.0	73.2	1.4	0.03 - 0.48	50.6 - 56.1		52.1 - 53.0	b.d. - 0.20	43.7 - 54.3	0.01 - 0.15	53.24	0.01 - 1.03	39.7 - 52.9
Al$_2$O$_3$							0.04	0.02	2.03	0.04	b.d. - 0.47	b.d. - 0.62	b.d. - 0.3		b.d. - 0.74	b.d. - 1.13	b.d. - 0.21	0.09		0.03 - 1.28
Cr$_2$O$_3$	0.21	0.06	0.18	0.08	0.15	0.02	0.73	0.26	1.39	0.15	0.04 - 0.37	0.15 - 1.11	0.02 - 0.28	0.52 - 2.12	0.05 - 0.74	b.d. - 0.75	b.d. - 1.39	0.35	b.d. - 0.51	b.d. - 1.08
FeO	25.4	2.9	27.8	2.6	30.7	2.40	39.9	2.5	17.6	1.1	15.6 - 46	34.8 - 46.4	25.4 - 68.7	44.4 - 45.1	20.7 - 65.3	41.7 - 47.3	11.6 - 41.8	45.3	22.6 - 67.8	42.5 - 56.7
MnO	0.28	0.05	0.29	0.05	0.33	0.12	0.37	0.07	0.07	0.04	0.18 - 0.48	0.3 - 0.59	0.22 - 1.10	0.45	b.d. - 0.52	0.27 - 0.43	0.10 - 0.42	0.47	0.26 - 0.75	0.19 - 0.39
MgO	36.1	3.0	34.1	2.4	31.9	2.37	4.47	0.95	5.54	0.13	19.5 - 44	0.1 - 8.7	0.5 - 36.5	0.75 - 1.35	3.54 - 40.1	b.d. - 3.17	23.6 - 48.7	0.72	0.45 - 34.4	0.04 - 2.12
CaO	0.26	0.02	0.26	0.03	0.26	0.03					0.2 - 0.78	0.06 - 0.44	0.26 - 0.33	0.01 - 0.10	0 - 0.34	b.d. - 2.51	0.03 - 0.85	0.05	0.24 - 11.7	0.004 - 0.36
TOTAL	100.05	0.73	100.07	0.94	100.26	1.14	99.91	0.96	99.85	2.22										
Ol. Fo%	72	4	69	3	65	3					37 - 82		1 - 73.3		9 - 78		50 - 88		1.22 - 70.5	
Ilm Mg#							17	3	36	2		0.22 - 29		2.9 - 5.1		0 - 11.9		2.8		0.10 - 8.12
ppm																				
Sc	15	8	14	9	18	7	101	20	233	24	7.73 - 15.0	83 - 104		123	4.42 - 85.6		1.31 - 37.18		7.9 - 44.5	17.2 - 32.9
Ti	462	142	417	112	584	357					219 - 962				102 - 865		30.7 - 3028		122 - 2930	
V	43	21	33	23	24	13	412	254	1399	118	26.4 - 51.5			107	20.5 - 157		9.95 - 121		27.1 - 316	47.5 - 153
Cr	1299	642	1061	514	946	489	3741	2349	7655	1074	991 - 1991	132 - 163			530 - 4840		140 - 3698		675 - 6047	532 - 1601
Mn	2129	441	2196	436	2581	912	2391	725	753	90	1358 - 2202				1626 - 5208		589 - 3245		1970 - 4028	1841 - 3309
Co	65	16	63	28	71	26	8	9	20	2	39.5 - 56.8	20.9		24	80.6 - 238		14.7 - 85.6		86.2 - 148	22.7 - 29.2
Ni	35	20	23	6							21.7 - 68.8				6.55 - 500		4.17 - 362		38.8 - 203	4.4 - 6.3
Zn							3	1							1.58 - 6.94					
Y	3	3	4	3	5	3					0.18 - 2.14				0.14 - 3.66		0.03 - 72.1		0.2 - 4.7	1.7 - 8.2
Zr			2		2		426	843	233	4					b.d. - 0.65				0.1 - 3.7	289 - 1127
Nb							51	178	32	1					b.d. - 0.37				0 - 0.1	43.2 - 75.8
Hf							19	50	12	2		17.4		11	b.d. - 0.02				0 - 0.2	6.9 - 18.1
Ta							3	7	3	4		4.9			b.d.				0	4.0 - 5.9
Sr							2	3	b.d.						b.d. - 0.43				0 - 3.0	2.1 - 2.3

749 b.d.: below detection limit; 2σ = two standard deviation of average value listed.
750 Literature data from Vobecký et al. (1971); Papike et al. (1974, 1976); Dymek et al. (1975); Warner et al. (1975, 1976a, 1976b, 1977);
751 Walker et al. (1976); Haskin and Korotev (1977); McCallum and Charette (1978); Neal et al. (1990); Schnare et al. (2008); Fagan et
752 al. (2013); Alexander et al. (2014); and Hallis et al. (2014).
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756   Table 3. Average compositions of pyroxene and plagioclase compared to major mare basalt groups.

Phase Analysis	Augite		Pigeonite		Plagioclase		A11 low-K and high-K		A12 Ilm, Ol, Plag basalts		A14 KREEP and high-Al		A15 KREEP and ONB		A17 Type A, B1, B2, C, U	
	average	2σ	average	2σ	average	2σ	*Pyroxene*	*Plagioclase*	*Pyroxene*	*Plagioclase*	*Pyroxene*	*Feldspar*	*Pyroxene*	*Feldspar*	*Pyroxene*	*Feldspar*
n =	13		5		19											
wt.%																
SiO_2	48.7	3.6	51.6	3.6	47.3	1.5	44.1 - 52.5	45.7 - 53.3	45.0 - 53.5	44.3 - 48.2	45.3 - 51.3	42.8 - 49.5	41.2 - 54.0	43.1 - 48.5	38.1 - 78.5	45.5 - 52.4
TiO_2	3.52	1.79	1.33	1.79	0.13	0.07	0.72 - 3.74	0.5	0.35 - 2.64	0.03 - 0.16	0.84 - 1.62	0.02 - 0.11	0.19 - 3.99		0.26 - 14.1	0.03 - 0.32
Al_2O_3	4.78	2.75	1.67	2.75	32.7	1.4	0.57 - 5.25	17.2 - 34.5	0.66 - 7.90	30.9 - 35.7	1.20 - 3.01	31.3 - 36.0	0.26 - 11.9	30.1 - 34.6	0.42 - 23.4	0.11 - 34.5
Cr_2O_3	0.91	0.40	0.39	0.40	-		0 - 0.61	0.04	0 - 1.54		0 - 0.73		0 - 1.44		0.04 - 1.12	
FeO	9.39	3.77	18.9	3.8	0.45	0.18	9.6 - 45.8	0.30 - 2.8	12.9 - 46.5	0.49 - 1.85	15.4 - 34.7	0.07 - 0.99	12.9 - 45.9	0.37 - 1.06	2.31 - 48	0.28 - 32.9
MnO	0.22	0.10	0.36	0.10	-		0 - 0.67	0.05	0 - 0.56	<0.05	0 - 0.53		0.18 - 0.80		0 - 0.62	
MgO	14.4	2.7	18.8	2.7	0.30	0.10	1.40 - 22.0	0.07 - 2.5	0.29 - 24.3	0.01 - 0.51	0.57 - 21.2	0.03 - 0.38	0.15 - 26.3	0.15 - 1.16	0.27 - 24.4	0.01 - 0.31
CaO	17.8	5.0	6.61	5.02	17.2	1.0	3.52 - 18.8	11.7 - 18.6	2.61 - 16.9	16.3 - 19.2	4.37 - 18.2	15.6 - 19.4	2.02 - 18.2	16.3 - 19.0	0.75 - 20.7	0.11 - 17.4
Na_2O	0.07	0.04	0.02	0.04	1.35	0.32	0 - 0.12	0.55 - 2.70	0 - 0.05	0.40 - 1.72	0 - 0.09	0.41 - 2.21	0 - 0.12	0.70 - 1.67	0 - 0.55	0.78 - 2.45
TOTAL	99.86	1.17	99.78	1.17	99.41	1.51										
Mg#	73	4	64	4	55	13	5 - 73	18 - 54	1 - 72	1 - 54			18 - 75			
En	44	6	55	6	-		0.6 - 63.4		0.41 - 67.0		5.8 - 63.7		1.9 - 80.1		0.9 - 67.1	
Fs	16	6	31	6	-				22.1 - 80.5						13.3 - 91.1	
Wo	40	12	14	12	-		0.55 - 43.5		6.55 - 42.2		7.5 - 33.7		2.6 - 36.2		5 - 49.3	
An	-		-		88	3		72.2 - 94.0		82.3 - 95.6		65.1 - 96.2		81.4 - 93.4		35.6 - 93.4
ppm																
Sc	196	270	220	270	b.d.		133	10.1	32 - 207	2.8 - 7.1			21.6 - 168	1.7 - 3.5	54 - 129	1
Ti	22566	10445	8432	10445	857	290			2840 - 16400	266 - 825			1409 - 12596	166 - 418		
Cr	4521	1617	1945	1617	6	3			132 - 22000	1.5 - 26.7			20.2 - 18636	2.4 - 13.9		
Mn	1437	483	591	483	57	7			760 - 8480	50.5 - 107			416 - 8191	42.7 - 83.2		
Co	10	5	12	5	0.4	0.3	22	8.5	10 - 159	b.d. - 1.7			7.7 - 140	0.3 - 1.6	14 - 24	0.84
Ga	1.2	0.4	0.7	0.4	11	26						2.3 - 85	0.3 - 2.3	4.2 - 13.3		
Sr	9.7	3.5	4.0	3.5	381	414			0.32 - 24	221 - 629		23.5 - 420	0.2 - 21.9	136 - 503		
Y	32	9	24	9	0.5	0.8			3.3 - 153	0.23 - 2.13	0.14 - 17.7		1.6 - 373	0.1 - 0.4		
Zr	25	14	11	14	b.d.		400		1.2 - 158	b.d. - 5.6			0.7 - 156	0.02 - 0.53		
Nb	0.09	0.07	0.07	0.07	0.02	0.02			0.4 - 3.5	b.d. - 0.78			0 - 1.5	0.01 - 0.02		
Ba	0.05	0.03	0.06	0.03	38	112	230	210	0.6 - 40	13.4 - 103		4.47 - 464	0 - 57.1	9.4 - 56.9		
La	0.31	0.16	0.14	0.16	0.36	0.93	12.2	16.4	0.05 - 4.21	0.28 - 1.29	0.18 - 7.7		0 - 1.9	0.1 - 0.5	0.44 - 1.4	0.84
Ce	1.63	0.53	0.78	0.53	0.98	2.64	30	47	0.11 - 10.6	0.59 - 2.46	0.44 - 14.2		0 - 9.5	0.4 - 1.3	2.6 - 7.8	2.6
Pr	0.46	0.12	0.23	0.12	0.14	0.37			0.08 - 2.51	b.d. - 0.36			0 - 2.6	0.04 - 0.15		
Nd	3.64	0.90	1.83	0.90	0.70	1.64		45	0.29 - 18.1	b.d. - 1.43	0.22 - 18		0.1 - 22.2	0.2 - 0.7		
Sm	2.34	0.63	1.23	0.63	0.21	0.54	11.2	7.1	0.33 - 10.5	b.d.	0.04 - 5.8		0 - 15.4	0.1 - 0.2	0.99 - 5.1	0.59
Eu	0.21	0.06	0.08	0.06	3.09	5.35	1.2	1.8	0.09 - 0.56	1.29 - 4.52		0.40 - 3.3	0 - 1.0	0.8 - 3.4	0.10 - 0.45	5.34
Gd	4.38	1.35	2.78	1.35	0.19	0.27		1.4	0.42 - 18.1	b.d.	0.09 - 51		0.1 - 33.0	0.04 - 0.15		
Tb	0.81	0.22	0.51	0.22	0.04	0.06	3.3		0.10 - 3.69	b.d.			0 - 7.8	0.01 - 0.02	0.42 - 2.0	0.09
Dy	6.17	1.74	4.24	1.74	0.13	0.21	20		0.64 - 27.2	b.d.	0.03 - 2.6		0.2 - 58.5	0.02 - 0.10		
Ho	1.30	0.34	0.96	0.34	0.02	0.04	3.3		0.10 - 6.16	b.d. - 0.08			0.1 - 14.2	0.01 - 0.02		

Er	3.65	0.93	2.96	0.93	0.06	0.08			0.30 - 17.8	b.d. - 0.21	0.03 - 9.3
Tm	0.53	0.16	0.46	0.16	0.02	0.01	4.6	1.3	0.08 - 2.83	b.d.	
Yb	3.55	0.78	3.27	0.78	0.08	0.09	11.2	5	0.44 - 21.2	b.d. - 0.25	0.03 - 2.5
Lu	0.47	0.14	0.49	0.14	0.012	0.004	1.65	0.56	0.09 - 3.27	b.d.	
Hf	1.75	0.96	0.79	0.96	*b.d.*		5.5	5	0.18 - 8.26	b.d. - 0.21	

(continued)

0.2 - 41.6	0.05		
0.2 - 40.5	0.07	2.4 - 7.2	0.27
0 - 5.8	0.011 - 0.012	0.37 - 0.92	0.034
0 - 6.4		0.58 - 1.2	0.15

757 Dashes indicate element not analyzed; b.d. = below detection limit.
758 Literature data from Hodges and Kushiro (1974); Papike et al. (1974, 1976); Dymek et al. (1975); Warner et al. (1975, 1976a, 1977); Haskin and Korotev (1977); Neal et al.
759 (1990); Schnare et al. (2008); Hui et al. (2011); Alexander et al. (2014); and Hallis et al. (2014).
760

761

762 Table 4. Results of fractionation calculations on 71597 composition.

	71597,1[a]	Olivine	$D_{Ol/L}$	$D_{ilm/L}$	olivine (± ilmenite) subtraction		
wt %					*24% ol*	*27% ol*	*27% ol + 1% ilm*
SiO$_2$	39.2	37.9			39.61	39.68	40.44
TiO$_2$	8.4	0.047			11.03	11.48	10.60
Al$_2$O$_3$	7.9				10.39	10.82	10.97
Cr$_2$O$_3$	0.47	0.22			0.55	0.56	0.56
FeO	19.8	24.3			18.49	18.26	17.84
MnO	0.237	0.26			0.23	0.23	0.23
MgO	15.8	37.1			8.96	7.79	8.03
CaO	7.9	0.26			10.31	10.72	10.87
Na$_2$O	0.29				0.38	0.40	0.40
K$_2$O	0.027				0.04	0.04	0.04
TOTAL	100	100.09			99.99	99.99	99.99
ppm							
Cr	3216	1854	0.92	10	3292	3303	2849
Co	43	64	3.5	2.2	21	19	19
La	3	[0.01]	0.011	0.029	3.9	4.1	4.2
Sm	3.9	[0.01]	0.0002	0.053	5.1	5.3	5.4
Eu	1	[0.01]	0.007	0.02	1.3	1.4	1.4
Yb	4.8	[0.01]	0.030	0.051	6.3	6.5	6.6
Hf	4.2	[0.01]	0.010	0.38	5.5	5.7	5.8
Cr/La	1072				836	806	686
La/Sm	0.77				0.77	0.77	0.77
Yb/Sm	1.23				1.22	1.22	1.22

763 [a]INAA Values reported in Murali et al. (1977). SiO$_2$ calculated to bring total to 100%.

764 $D_{Ol/L}$ values from equations of Bédard (2007), assuming initial bulk MgO was 9 wt%.
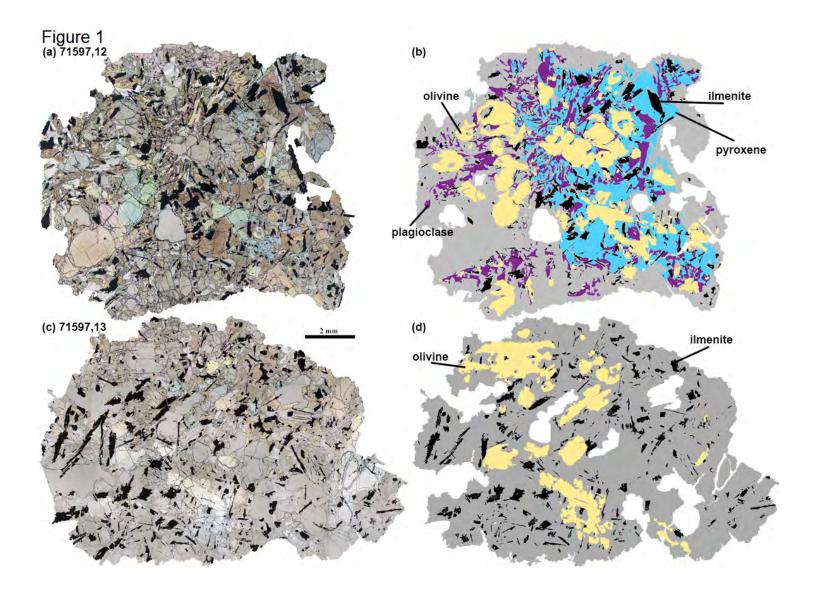
765 $D_{ilm/L}$ values from Haskin and Korotev (1977) except Hf (Klemme et al. 2006).
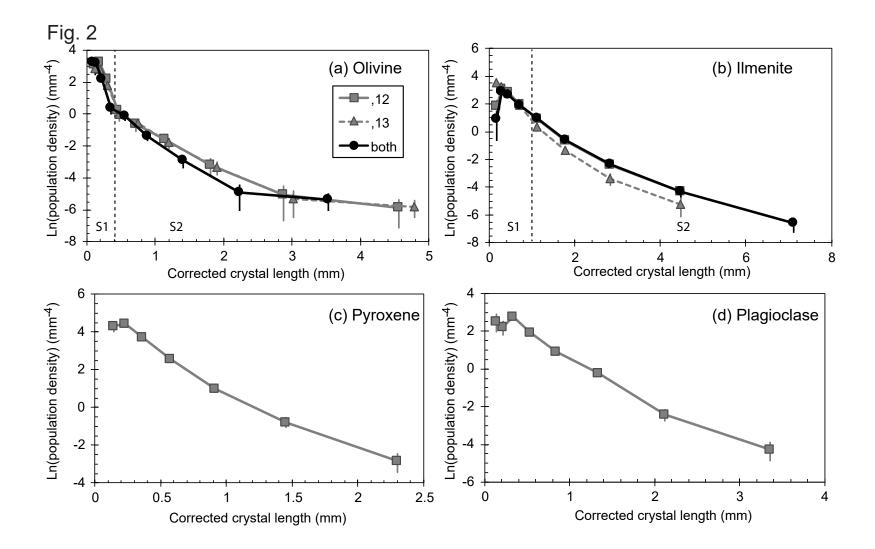
766   Table 5. Mineral-melt partition coefficients used in modeling of 71597.

	olivine	armalcolite	ilmenite	plagioclase		augite		pigeonite	
V	0.49[a]	6.7[c]	3.4[c]	0.010[h]		1.1[k]		0.33[a]	
Cr	0.91[a]	6.4[c]	10[g]	0.018	0.021[i]	3.3[g]		10[g]	
La	0.011[a]	0.006[d]	0.029[g]	0.013	0.022[j]	0.05	0.14[l]	0.004	0.023[l]
Ce	0.008[a]	0.007[d]	0.035[g]	0.015	0.022[j]	0.08	0.18[l]	0.006	0.035[l]
Pr	0.006[b]	0.007[d]	0.041[g]	0.037[g]		0.12	0.22[l]	0.01	0.052[l]
Nd	0.005[a]	0.008[d]	0.047[g]	0.012	0.018[j]	0.2	0.30[l]	0.021	0.098[l]
Sm	0.0002[a]	0.008[d]	0.053[g]	0.009	0.013[j]	0.24	0.33[l]	0.028	0.124[l]
Eu	0.007[a]	0.006[d]	0.020[g]	0.817	0.916[j]	0.26	0.36[l]	0.036	0.150[l]
Gd	0.004[a]	0.013[e]	0.081[g]	0.012[g]		0.28	0.37[l]	0.045	0.177[l]
Tb	0.01[a]	0.024[d]	0.095[g]	0.012[g]		0.29	0.38[l]	0.056	0.206[l]
Dy	0.01[a]	0.035[d]	0.013[c]	0.012[g]		0.29	0.40[l]	0.068	0.234[l]
Ho	0.016[a]	0.045[d]	0.018[c]	0.012[g]		0.29	0.43[l]	0.079	0.259[l]
Er	0.023[a]	0.056[d]	0.024[c]	0.001	0.004[j]	0.29	0.46[l]	0.09	0.280[l]
Tm	0.026[b]	0.060[f]	0.331[g]	0.012[g]		0.28	0.47[l]	0.1	0.297[l]
Yb	0.030[a]	0.070[d]	0.051[c]	0.012[g]		0.27	0.49[l]	0.109	0.310[l]
Lu	0.053[a]	0.070[e]	0.067[c]	0.011[g]		0.26	0.49[l]	0.117	0.321[l]

767   [a]Bédard (2005); [b]interpolated; [c]Dygert et al. (2013); [d]Neal et al. (1990); [e]Klemme et al.
768   (2006); [f]Irving et al. (1978); [g]Haskin and Korotev (1977); [h]Bindeman et al. (1998); [i]RTlnD;
769   [j]Hui et al. (2011); [k]Mallman and O'Neill (2009); [l]Sun and Liang (2012)

770

Figure 1

(a) 71597,12

(b)

olivine

ilmenite

pyroxene

plagioclase

(c) 71597,13

2 mm

(d)

olivine

ilmenite

Fig. 2

Fig. 3

Fig. 4

a (left panel)

Apollo 17
- 71597
- Type A
- Type C
- Type B2
- Type U
- Type U

Apollo 15
- ONB
- KREEP
- ONB

Apollo 14
- High-Al

Apollo 12
- Pigeonite
- Ilmenite
- Olivine
- Ilmenite

Apollo 11
- High-K
- Low-K
- High-K
- Low-K

Olivine Fo %

10   30   50   70   90

b (right panel)

Apollo 17
- 71597
- Type A
- Type C
- Type B2
- Type U
- Type U

Apollo 15
- ONB
- KREEP
- ONB

Apollo 14
- High-Al

Apollo 12
- Pig.
- Ilmenite
- Olivine
- Ilmenite

Apollo 11
- High-K
- Low-K
- High-K
- Low-K

Plagioclase An %

60   70   80   90   100

Fig. 5

Fig. 6

a

Ti/V

70
60
50
40
30
20
10
0

A12
+
A14

A15

71597

74275

A14
OV

40   50   60   70   80   90

Forsterite (%)

b

Cr / Y

100000

10000

1000

100

10

A15

A14

A12

74275

A14
OV

71597

40   50   60   70   80   90

Forsterite (%)

Fig. 7

Fig. 8
(a)

Di   Hd

● cores
○ rims
● Warner
   et al. (1977)

71157
70146
71095
70148

En   Fs

(b)

whole-rock

augite

pigeonite

plagioclase

CI chondrite normalized

1000

100

10

1

0.1

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Fig. 9

Fig. 10