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The formation and evolution of the Moon's crust inferred from the Sm-Nd isotopic systematics of highlands rocks

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Abstract

Ages determined for magnesian and ferroan anorthosite crustal rock suites overlap, suggesting they formed contemporaneously. A notable exception is the Sm-Nd age determined on Mg-suite gabbronorite 67667 which is at least 100 Ma younger than the youngest ferroan anorthosite. New chronologic measurements determined on 67667 yield concordant Sm-Nd and Rb-Sr mineral isochron ages of 4349 ± 31 Ma and 4368 ± 67 Ma. Furthermore, a whole rock Sm-Nd isochron of Mg-suite rocks from the Apollo 14, 15, 16, and 17 landing sites yields an age of 4348 ± 25 Ma, indicating that Mg-suite magmatism was widespread and roughly contemporaneous on the lunar nearside. Analysis of Sm-Nd internal isochron ages confirms that Mg-suite magmatism was restricted to a period between about 4.33 and 4.35 Ga at the Apollo 14, 15, 16, and 17 landing sites and was synchronous with magmatism at the Apollo 16 site associated with the ferroan anorthosite suite between 4.35 and 4.37 Ga. Magnesian- and ferroan anorthosite suite rocks with ages younger than ~4.33 Ga appear to have experienced slow cooling in the deep lunar interior, so that the ages record when the samples cooled below the closure temperature of the Sm-Nd isotopic system and not the time they crystallized.

The ages determined for Mg-suite and ferroan anorthosite suite rocks are concordant with the age determined for the formation of urKREEP of 4350 ± 34 Ma using the Sm-Nd isotopic systematics of 67667 and measurements completed on norite 78238, troctolite 76535, KREEP basalt 15386, and gabbronorite NWA 773. Crystallization ages of Mg-suite and FAS are also concordant with the age we previously determined for the formation of the mare basalt source region of 4336 ± 10 Ma using the ^{146}Sm-^{142}Nd isotopic compositions of mare basalts. The similarity of ages for Mg-suite magmatism, ferroan anorthosite suite magmatism, urKREEP formation, and formation of the mare basalt source regions implies the processes that produced these rocks were petrogenetically linked. Late and rapid solidification of a lunar magma ocean can account for the concordance of ferroan anorthosite suite rocks, urKREEP, and the mare basalt source regions. However, the major and trace element compositions of Mg-suite magmas preclude them from being a primary differentiation product of the lunar magma ocean. Instead, the Mg-suite could be produced as a result of mixing of magma ocean solidification products associated with density driven overturn occurring immediately after, or perhaps during, solidification of the lunar magma ocean. This scenario not only accounts for the chronology of the various rock suites, but is consistent with the petrogenesis of the Mg-suite that involves the interaction between pre-existing Mg-rich, plagioclase-rich, and urKREEP-rich cumulates of the magma ocean.

1. Introduction

The lunar crust is comprised of three major suites of plutonic rocks. The first is the ferroan anorthosite suite (FAS), which is characterized by high modal abundances of calcic plagioclase with minor Fe-rich orthopyroxene and olivine, and which is thought to represent floatation cumulates produced after ~70% solidification of a primordial magma ocean (Wood et al., 1970; Smith et al., 1970; Snyder et al., 1992). The second suite of lunar plutonic crustal rocks is called the magnesium (Mg) -suite because it comprises rocks that contain mafic minerals with high Mg#s (Mg/Mg + Fe). The third suite is known as the Alkali-suite because these rocks contain high abundances of alkali elements relative to other lunar rocks. In addition, both the Mg- and Alkali-

suite rocks have elevated abundances of incompatible elements (e.g. K, REE, and P) indicating that products of the last-stage of crystallization of the magma ocean (urKREEP) contributed to their petrogenisis (e.g., Shervais and McGee, 1999; Shearer et al., 2015). Although the petrogenetic relationship between the Mg-suite and urKREEP is debated (e.g., Shearer et al., 2015; Elardo et al., 2020) the involvement of urKREEP in the petrogenesis of the Mg- and Alkali-suites has led to the supposition that the crystallization ages of these rocks should postdate crystallization ages of FAS LMO floatation cumulates (Papike et al., 1998; Shearer et al., 2015).

Chronologic investigations completed over the last 50 years do not support this simple petrogenetic model however. Ferroan anorthosite suite rocks have ages that range from 4.29 to 4.55 Ga, whereas ages of Mg-suite rocks range from 4.18 to 4.51 Ga (see summaries in Nyquist and Shih, 1992; Nyquist et al., 2001, Snyder et al., 1995; 2000, Papike et al., 1998, Shearer and Papike, 2005, Shearer et al., 2006, and Borg et al., 2015). Although few unambiguous ages have been determined for Alkali-suite rocks, detrital zircons from lunar soils and breccias associated with this suite yield ages that are well within the range defined by the Mg-suite samples (Grange et al. , 2009, 2011; Meyer et al. , 1996; Nemchin et al. 2006, 2008, 2009a, 2009b; Pidgeon et al., 2007). The existing chronology, therefore, implies that all three suites of lunar crustal rocks were produced contemporaneously over several hundred million years. Obviously, this interpretation is predicated on the assumption that every age determined for a lunar highland sample is correct. Several studies have observed, however, that chronologic investigations of single samples by various investigators often do not yield the same age (Papike et al., 1998; Nyquist et al., 2001; Borg et al., 2015). This indicates that that some ages are erroneous, potentially contributing to the apparent age overlap between Mg-suite, FAS, and Alkali-suite rocks.

The most recent chronologic investigations of Mg-suite and FAS magmatism suggest these magmatic events were confined to a more restricted period in lunar history (Borg et al., 2015). For example, ages of FAS samples that have been determined in the last 10 or so years range from 4.30 Ga (Marks et al., 2019) to 4.36 Ga (Borg et al., 2011), whereas recent age determinations of Mg-suite rocks range from 4.28 Ga (Carlson et al., 2014) to 4.33 Ga (Edmunson et al. 2009). Furthermore, Sio et al. (2020) demonstrated that FAS and Mg-suite rocks, that have been dated using the same analytical methods and corrected for thermal neutron capture by the same algorithms, lie within error of a single 4.37 ± 0.05 Ga Sm-Nd isochron consistent with derivation of both suites of rocks from the same undifferentiated magma source at about the same time. Thus, the nearly identical Sm-Nd isotopic systematics of FAS and many Mg-suite rocks suggest that they could be produced by the same event on the Moon as suggested by Shervais and McGee (1999).

A notable inconsistency with the hypothesis that FAS and Mg-suite magmatism are cogenetic is the presence of relatively young ages determined on two Mg-suite rocks (67667, 72255) and one Alkali-suite (Clast 'b' 14304). The most noteworthy of these is the Sm-Nd age of 4.18 ± 0.06 Ga that was determined on the gabbronorite 67667 by Carlson and Lugmair (1981), because there is no obvious indication that this age is erroneous (Borg et al., 2015). Recent Sm isotopic measurements on 67667 completed by Carlson et al. (2014) demonstrated, however, that 67667 experienced a flux of thermal neutrons that probably affected the age determination. Furthermore, the Sm-Nd age of 67667 was not confirmed by a second chronometric system, such as Rb-Sr, that would alleviate the need to redetermine it. The goal of this work is to reanalyze 67667 using modern techniques in order to substantiate the previous age determination. If the young age of 4.18 ± 0.06 Ga is confirmed, then Mg-suite rocks are unlikely to share a common petrogenisis with FAS because they would be produced over an extended period of time beyond

which the magma ocean is likely to have existed. On the other hand, the petrogenesis of the Mg-suite may be linked to magma ocean processes responsible for the origin of the anorthositic crust, as suggested by Shervais and McGee (1999), if 67667 has Sm-Nd isotopic systematics that are similar to other FAS and Mg-suite samples.

2. Petrographic, geochemical, and chronologic characterization of 67667

Sample 67667 is a 7.9 gram rake sample collected near the rim of North Ray Crater at the Apollo 16 landing site and represents one of the few Mg-suite samples from this landing site. It is classified as a gabbronorite by James and Flohr (1983) and Shearer et al (2015) and contains 50-58 modal percent olivine, 21-23% plagioclase, 15-21% orthopyroxene, 5% clinopyroxene, and 1% Fe-Ti-Cr oxide minerals ilmenite and chromite (Warren and Wasson, 1979; Hanson et al., 1980). The high modal abundance of olivine, low abundance of plagioclase, combined with their respective Mg- and Ca-rich compositions make 67667 an mineralogically unique lunar sample. The sample is heavily cataclastized and at least some of the plagioclase has been maskelynitized (Warren and Wasson, 1979; Hansen et al., 1980). Immersed in the cataclastic matrix are distinct polymineralic and monomineralic regions (Figure 1). The polymineralic regions are dominated by olivine and pyroxene and may represent original cumulate textures (Figure 1). The monomineralic regions contain multiple grains of either low-Ca pyroxene or plagioclase and were interpreted by Hansen et al. (1980) to represent individual cumulus minerals disrupted during the formation of the cataclastic texture. Hansen et al. (1980) noted that there is no evidence for metamorphic recrystallization after cataclasis although the sample is brecciated with only a few relict grains remaining. Despite evidence of shock, previous petrologic investigations have not reported the presence of impact melt in 67667. Warren and Wasson (1979) note that 67667 has low siderophile

element abundances, minerals with limited compositional ranges, and metal grains with low Ni/Co and is therefore pristine. As such, they argue 67667 is monomict-brecciated plutonic product of endogenous lunar magmatism.

Sample 67667 is one of only a handful of Mg-suite samples that contain zoned cumulus minerals (Papike et al., 1998). Olivine in 67667 has a limited compositional range from Fo_{75} to Fo_{70} and, as with olivine in most Mg-suite samples, has very low Cr_2O_3 (Shearer et al., 2015). The composition of orthopyroxene ranges from $En_{80}Fs_{16}Wo_4$ to $En_{69}Fs_{29}Wo_2$. Some orthopyroxene demonstrates fine, ~1 micron, exsolution lamellae of clinopyroxene (Figure 1). Individual high-Ca pyroxene has a composition of $En_{46}Fs_{11}Wo_{43}$ with more Ca-poor compositions attributed to very-fine exsolution lamellae of low-Ca pyroxene with a thickness of <1 micron. Unlike the low-Ca pyroxene, the high-Ca pyroxene exhibits very little variation in the enstatite component. The composition of most of the plagioclase is An_{93} with rare and localized zoning to An_{72}. As a consequence, 67667 falls in the Mg-suite field defined on a plot of anorthite content of plagioclase versus Mg# of mafic silicates (Figure 2A).

Based on the grain size of silicates comprising the individual regions in 67667, Hansen et al. (1980) conclude that the initial igneous texture was originally fine-grained, with an average grain size of ~1mm, suggesting that it formed in a shallow intrusion in the lunar crust. This conclusion is consistent with the exsolution textures observed in some low-Ca pyroxenes. Using the approach calibrated by McCallum et al. (2006), and further demonstrated by Shearer et al. (2012) and Marks et al. (2019), 67667 crystallized initially in a shallow intrusion within a few kilometers of the lunar surface (1-3 km). Hanson et al. (1980) used a variety of mineral geothermometers (Ca-Fe-Mg pyroxene, oxide-silicate) to estimate mineral blocking-temperatures during cooling from near-magmatic (1070°C) to subsolidus (820°C).

149 Like most Mg-suite rocks, 67667 is strongly enriched in incompatible elements with rare
150 earth element abundances of ~20x chondrites. However, unlike most lunar Mg-suite samples, the
151 REE pattern of 67667 does not have an Eu anomaly. It also has relatively high Ti/Sm and Sc/Sm
152 ratios indicative of the significant role that urKREEP plays in the petrogenesis of 67667. This is
153 confirmed by abundances of Sr, Y, Ba, and K in plagioclase minerals that are about twice as high
154 as typical Mg-suite samples (Steele et al., 1980; Shearer and Papike, 2005; Shearer et al., 2015).
155 The gabbronorite 67667 thus appears to represent a somewhat unusual member of the Mg-suite.

156 The sample was dated using the Sm-Nd system by Carlson and Lugmair (1981) who
157 obtained an age of 4176 ± 61 Ma (see recalculation of age in Borg et al., 2015). The initial ε^{143}Nd
158 is positive, 0.82 ± 0.96, but within uncertainty of 0 to slightly negative as predicted for an ancient
159 LREE-enriched lunar rock. Similarly, the mean squared of weighted deviates (MSWD) associated
160 with the isochron regression is low (1.2) leading Borg et al. (2015) to conclude that the age was
161 reliably determined. However, the age was not confirmed using a second chronometer, such as
162 Rb-Sr or U-Pb, and is substantially younger than ages determined on most Mg-suite rocks.
163 Furthermore, the Sm-Nd isotopic composition of 67667 whole rock lies near an isochron defined
164 by other Mg-suite rocks that has a slope of corresponding to an age of~4.30 Ga (Carlson and
165 Lugmair, 1981; Carlson et al., 2014; Sio et al., 2020) suggesting the mineral isochron age of 4.18
166 Ga could be erroneous.

167

168 **3. Methods**

169 **3.1 Mineral separations, digestions, and elemental compositions**

A 280 mg piece of gabbronorite 67667 was broken into chips in a sapphire mortar and pestle. A ~5 mg chip was removed and set aside for Ar-Ar analysis, and the remainder was gently crushed and then sieved at 100-200 mesh (149-74 μm), 200-325 mesh (74-44 μm) and < 325 mesh. Two whole rock fractions were taken from the 200-325 and <325 size fractions (Figure 3). Minerals were purified from the remaining material using a Frantz Isobarrier separator in combination with hand-picking. As noted by Carlson and Lugmair (1981), obtaining pure mineral fractions proved difficult, given the fractured nature of the sample and the limited color difference between Mg-rich silicate phases. As a consequence, mineral separates were produced by consolidating grains with similar textures, shapes, and to a lesser extent, colors. The modal proportions of the hand-picked fractions are estimated from their major element abundances (see below).

Prior to digestion, the mineral fractions were leached in 2N HCl for 10 minutes to remove potential contaminants as well as phosphate minerals that could potentially limit the spread in $^{147}Sm/^{144}Nd$ ratios. The whole rock fractions were not leached. After leaching, the mineral separates and unleached whole rocks were digested on a hot plate in a combination of HF, HCl, HNO_3 acids. Small aliquots (~5%) were quantitatively separated from the digested solutions for major and trace element analyses using a ThermoScientific Element XR ICP-MS. Elemental concentrations were quantified by external calibration using USGS rock standards. An indium internal standard was added to all samples and standards in order to correct for matrix suppression and instrumental drift throughout the runs. To assess accuracy of the measurements and effectiveness of the dissolution procedure separate aliquots of BCR-2 and BHVO-2 were dissolved alongside the samples and analyzed as unknowns. Based on long term analyses of these QC standards the typical accuracy of major and trace element analyses is within 10% of published

values. The major and trace element data are presented in Table 1. The remaining 95% fractions were spiked with ^{87}Rb-^{86}Sr and ^{149}Sm-^{150}Nd isotopic tracers in proportions dictated by the Sr and Nd concentrations measured for the fractions by ICPMS. In addition, whole-rock 2 was split and Rb, Sr, Sm, and Nd abundances were determined by isotope dilution on one aliquot (0.02 mg), and Rb, Sr, Sm, and Nd isotope compositions were determined on the other (6.60 mg). Unfortunately, relatively large blank/sample ratios associated with the 0.02 mg aliquot that contained only 9.4 pg Rb, 2.3 ng Sr, 48 pg Sm, and 148 pg Nd, contributed significant uncertainty to the ^{87}Rb/^{86}Sr and ^{147}Sm/^{144}Nd ratios.

3.2 Chemical separations and thermal ionization mass spectrometry

After several dry-downs on the hot plate, to ensure that equilibrium was established between the isotopic tracers and the samples, the samples were centrifuged to confirm that no solids remained undissolved. Initial chemical separations of Rb, Sr, and REE were completed in 2N and 6N HCl using 26 cm long, 0.7 cm diameter primary quartz columns filled with Eichrom AG50W-X8 200-400 mesh resin. Samarium and neodymium were purified from the REE fractions using 33 cm long, 0.1 cm diameter, pressurized quartz columns filled with ammonia form of AG50W-X8 200-400 mesh resin. Samples were loaded in 1% $HClO_4$ and eluted in 0.2M alpha-hydroxyisobutyric acid adjusted to a pH of 4.45. The Sm and Nd elutions were directly loaded onto 2 mL columns loaded with Eichrom AG50W-X8 200-400 mesh resin that were stacked below the REE columns. Alpha-hydroxyisobutyric acid was removed from the Sm and Nd cuts using water, 2N HCl, 2N HNO_3, and 6N HCl. Processing blanks associated with the digestion and chemical separation procedure used here were measured to be 7.5 ± 0.9 pg for Rb, 23 ± 7 pg for Sr, 1.6 ± 0.5 pg for Nd and 0.8 ± 0.6 pg for Sm.

All isotopic analyses were completed at Lawrence Livermore National Laboratory (LLNL) using a ThermoScientific Triton thermal ionization mass spectrometer. Rubidium was loaded on single zone refined Re filaments in 2N HCl with a 99.999% pure Ta_2O_5 emitter. Mass fractionation was corrected using runs of unspiked 67667 whole-rock 2 analyzed during the course of the investigation. Strontium was also loaded on single zone refined Re filaments in 2N HCl with the Ta_2O_5 emitter and run at 2-5 x 10^{-11} amps ^{88}Sr for 200 ratios of 8 second integrations. Fractionation was corrected assuming $^{86}Sr/^{88}Sr = 0.1194$. Although ^{87}Rb was monitored during the analyses, none was observed. The NBS-987 Sr isotope standard was run 6 times for 200 ratios at signal intensities of 3 to 5 x 10^{-11} amps of ^{88}Sr and averaged $^{87}Sr/^{86}Sr = 0.710248 \pm 9$. Samarium was loaded in 2N HNO_3 onto a zone refined Re filament and analyzed as Sm^+ using a second Re filament. All Sm isotopes along with interferences from Nd (^{146}Nd) were measured statically for 200 ratios of 8 seconds integration each. Instrument fractionation was corrected assuming $^{147}Sm/^{152}Sm = 0.56083$. Samarium concentrations were calculated using Sm isotopic composition determined on 67667 whole-rock 2 ($\varepsilon^{149}Sm = -3.7 \pm 0.1$ and $\varepsilon^{150}Sm = +7.1 \pm 0.2$) which agreed with the values determined on 67667 by Carlson et al. (2014). This resulted in a small, but significant, adjustment of the $^{147}Sm/^{144}Nd$ ratios of -0.05 to -0.27%. The measure $^{143}Nd/^{144}Nd$ ratios were corrected for neutron capture by 4 ppm following the relationships illustrated in Borg et al. (2019).

Neodymium was run as both a metal (Nd^+) and an oxide (NdO^+). The smallest Nd fractions (olivine leach and whole-rock 2 ID), as well as roughly 10% of the large Nd fractions (Plagioclase, Plagioclase-Rejects 1, Plagioclase-Rejects 2, Pyroxene-Rejects 2, Olivine-Pyroxene, Olivine, and whole-rock 1) were loaded on single zone refined filaments in Ta_2O_5 emitter and run as NdO^+. The samples were run in static mode with 8 second integrations and amplifiers equipped with 10^{11}

ohm resistors. Samples ranged in size from 148 pg to 15 ng. Measured $^{144}Nd^{16}O$ beam intensities ranged from 0.05 to 2 x 10^{-11} amps with ionization efficiencies ranging from 3 to 9 percent. Oxide, mass fractionation, spike, and interfering element corrections were made off-line assuming $^{146}Nd/^{144}Nd = 0.7219$. Interfering elements monitored during the course of these runs included ^{139}LaO, ^{140}CeO, ^{141}PrO, and ^{149}SmO. Eleven $^{143}Nd/^{144}Nd$ and $^{142}Nd/^{144}Nd$ measurements of 5 ng loads of the LaJolla Nd standard averaged 0.511844 ± 13 and 1.141838 ± 21 (2 stdev). Larger Nd samples were loaded in 2N HCl onto zone refined Re filaments and analyzed as Nd^+ using a second Re filament. These were analyzed in static mode for 100 to 500 ratios of 8 second integrations. Fractionation was corrected assuming $^{146}Nd/^{144}Nd = 0.7219$. Cerium and Sm interferences were monitored using ^{140}Ce and ^{149}Sm. Although ^{149}Sm signals were trivial, ^{140}Ce often required corrections on $^{142}Nd/^{144}Nd$ ratios of 30 ppm. Eight $^{143}Nd/^{144}Nd$ and $^{142}Nd/^{144}Nd$ measurements of 500 ng JNdi standards averaged 0.512106 ± 5 and 1.141839 ± 9. All of the $^{143}Nd/^{144}Nd$ values measured on the 67667 fractions by NdO^+ and Nd^+ agreed within 25 ppm. In general, the oxide measurements of $^{143}Nd/^{144}Nd$ had higher internal precision, longer duration runs, and runs of higher intensity and are consequently those reported in Table 2. The $^{142}Nd/^{144}Nd$ values in Table 3 are a combination of Nd^+ and NdO^+ runs, whichever yielded a lower analytical uncertainty.

3.3 Noble gas mass spectrometry

Whole-rock fragments of 67667 were loaded into an aluminum disc alongside Fish Canyon sanidine neutron fluence monitors and irradiated for 50 hours at the Oregon State University TRIGA reactor in the Cadmium-Lined In-Core Tube (CLICIT). Noble gas extractions were performed in the Livermore Noble Gas Lab at LLNL. An ~4 mg whole-rock fragment was loaded into a Pt-Ir alloy tube that was crimped at both ends. The capsule was then placed into an ultra-high vacuum laser chamber and heated with a 75 W diode laser co-axially aligned with optical

pyrometer at temperatures between 450 °C to >1400 °C following procedures described in Cassata et al. (2018). The released Ar was purified using SAES getters and analyzed in peak hopping mode using a Nu Instruments Noblesse mass spectrometer. Complete analytical details are provided in the supplementary materials (Table S1). The proportion of cosmogenic Ar in each step was calculated based on a two-component deconvolution of the measured $^{38}Ar/^{36}Ar$ ratio, assuming a cosmogenic $^{38}Ar/^{36}Ar$ ratio of 1.54 (Wieler, 2002) and a trapped $^{38}Ar/^{36}Ar$ ratio of 0.19 (e.g., Levine et al., 2007). The apparent cosmic ray exposure ages of each degassing step were calculated from the ratio of cosmogenic ^{38}Ar ($^{38}Ar_{cos}$) to reactor-produced ^{37}Ar from Ca ($^{37}Ar_{Ca}$) and ^{39}Ar from K ($^{39}Ar_K$) following the approach of Shuster and Cassata (2015) using the $^{38}Ar_{cos}$ production rate from Ca of Turner et al. (1971) and relative production rate from K of Eugster and Michel (1995). The production ratio of $^{37}Ar_{Ca}/^{39}Ar_K$ per unit weight of Ca and K was taken as 0.508 ± 0.013 (specific to the OSU TRIGA reactor CLICIT tube; Renne et al., 2010). $^{40}Ar/^{39}Ar$ ages were calculated using the ^{40}K decay constants and standard calibration of Renne et al. (2011), interfering nuclear reaction constants of Renne et al. (2013), and potassium isotopic abundances of Steiger and Jäger (1977). Data were corrected for cosmogenic ^{40}Ar assuming a cosmogenic $^{40}Ar/^{38}Ar$ ratio of 0.2 (Lammerzahl and Zahringer, 1966). No corrections were applied for trapped ^{40}Ar. Uncertainties on ages are quoted at 2σ throughout the paper.

4. Results

4.1. Major and trace element analyses

Major and trace element analyses were completed on the whole rock and mineral fractions from 67667 (Table 1). The compositions determined here for whole-rock 1 and whole-rock 2 are

283 a good match to those published for 67667 bulk sample by Warren and Wasson (1979). The bulk
284 rock composition of 67667 is compared to other Mg-suite rocks, ferroan anorthosites, mare basalts,
285 and KREEP basalts in Figure 2B-F. The Ti/Sm and Sc/Sm of 67667 are generally higher than
286 other olivine-rich Mg-suite rocks and KREEP basalts (Figure 2B-C). Consistent with olivine
287 compositions, the bulk Cr_2O_3 is similar to other olivine-rich Mg-suite rocks (Figure 2D).
288 Incompatible elements, such as Th (Figure 2D) and Ba, are higher in 67667 than in the dunites and
289 troctolites of the Mg-suite, but similar to the norites and gabbronorites. As expected for olivine-
290 othopyroxene-plagioclase cumulates, these two incompatible elements are significantly lower in
291 concentration than the KREEP basalts and the quartz monzodiorites. Both Ni and Co are elevated
292 in concentration compared to the olivine-rich Mg-suite lithologies reflecting the presence of non-
293 meteoritic metal in 67667. These chemical characteristics demonstrate that 67667 is a unique
294 lithologic member of the Mg-suite.

295 Using the major element compositions in Table 1 and mineral compositions determined
296 using an electron microprobe by Hansen et al. (1980), the proportions of phases comprising the
297 various fractions analyzed for Rb-Sr and Sm-Nd isotopes have been estimated. The proportions
298 of phases are presented in Table 2. The calculated mineral mode of the whole rocks indicates our
299 bulk sample is composed of 53% olivine, 20% orthopyroxene, 19% plagioclase, 7%
300 clinopyroxene, and 1% ilmenite. This is in excellent agreement with the proportions of phases
301 determined by petrographic examination of thin sections (see above). The modes calculated for
302 the mineral fractions demonstrates that, despite our best efforts to isolate plagioclase, pyroxene,
303 and olivine mineral grains, the mineral fractions are not particularly pure. For example, olivine is
304 ubiquitous in all mineral fractions, and is never below 30%. Fortunately, the presence of olivine
305 has little effect on the isotopic systematics of the fractions because it contains very little Rb, Sr,

306 Sm, or Nd. Thus, although the Plagioclase 1 fraction contains only 61% plagioclase, it has 30%
307 olivine and just 9% pyroxene, and is therefore is a reasonable proxy for the isotopic composition
308 of pure plagioclase. The olivine fraction is not pure either. It contains only 72% olivine, and 28%
309 impurities of plagioclase, and pyroxene which dominate its isotopic systematics. Likewise, mafic
310 minerals rejected from the Plagioclase 1 separate by hand-picking contain the majority of
311 pyroxene. The Plagioclase-Rejects 1 contains 39% pyroxene (25% clinopyroxene and 14%
312 orthopyroxene), whereas the Plagioclase-Rejects 2 contains 48% pyroxene (47% clinopyroxene
313 and 1% orthopyroxene). The impure nature of the mineral fractions is a likely manifestation of
314 the limited sample mass available for this investigation, the brecciated nature of the sample itself,
315 and the color similarity between olivine and pyroxene.

316 The concentrations of Sr, Sm, and Nd of the mineral and whole rock fractions determined
317 by ICPMS are in very good agreement with those measured by isotope dilution. The two whole
318 rocks measured here have ~20 times chondritic abundances of REE, flat REE patterns, and lack
319 Eu anomalies (Figure 4) supporting previous trace element measurements completed by Warren
320 and Wasson (1979). The REE patterns of the mineral fractions reflect their modal mineralogy.
321 For example, the olivine mineral fraction has the same REE pattern, but only about half the total
322 REE, as the whole rocks. This is consistent with the fact that although the abundance of olivine is
323 higher in the olivine fraction, the proportions of pyroxene and plagioclase are comparable in the
324 olivine and whole rock fractions (Table 2). Likewise, positive Eu anomalies are only observed in
325 the plagioclase-rich fractions which include Plagioclase 1 and Plagioclase-Reject 1. The
326 Plagioclase-Reject 2 fraction demonstrates a small negative Eu anomaly indicative of the removal
327 of plagioclase from this fraction by hand-picking. The most LREE-depleted pattern is that of the
328 Plagioclase-Reject 2 which, along with Plagioclase-Reject 1 fraction, demonstrates a very slightly

convex downward shape. Both patterns are similar to the patterns observed in lunar clinopyroxene (Papike et al., 1998) and reflect the presence of relatively large proportions of clinopyroxene and low proportions of plagioclase in these mineral fractions (Table 2).

4.2 Ar-Ar systematics

Sample 67667 yields two distinct release spectra associated with plagioclase- and pyroxene-derived gas (Figure 5). The plagioclase age spectrum (lower Ca/K), which comprises the first ~60% of the total ^{39}Ar released, yields initial step ages that increase from ~3600 Ma to a weighted average of 3890 ± 16 [28] Ma (MSWD = 0.49; complete external uncertainties in brackets, which include J-value, standard age, and decay constant uncertainties) defined by 50% of the total ^{39}Ar released (~80% of the plagioclase portion of the release spectrum). The pyroxene age spectrum (higher Ca/K), which comprises the last ~40% of the total ^{39}Ar released, yields discordant initial step ages that increase from ~3600 Ma to weighted average of 4073 ± 16 [34] Ma (MWSD = 0.89) defined 22% of the total ^{39}Ar released at the highest temperatures (~60% of the pyroxene portion of the release spectrum). Both of these ages are younger than the Rb-Sr and Sm-Nd ages (discussed below), suggesting they record a post crystallization history wherein an impact event or events caused significant heating of 67667. The plagioclase age is interpreted as a maximum constraint on the metamorphic age of the sample. The ^{38}Ar cosmic ray exposure age inferred from the plagioclase portion of the age spectrum is 34.2 ± 0.5 [3.9] Ma (MSWD = 0.63; complete external uncertainties in brackets, which include J-value, $^{37}Ar_{Ca}/^{39}Ar_{K}$ production ratio, and $^{38}Ar_{cos}$ production rate uncertainties, the latter of which is assumed to be 10%). This relatively young exposure age is consistent with the measured Sm isotopic composition of 66776, which indicates that the sample has been exposed to a modest flux of thermal neutrons on the lunar surface.

352 **4.3 Sm-Nd Isotopes**

353 Samarium-neodymium isotopic data are presented in Table 3. These data exhibit a
354 substantial range of $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ values. Both the measured $^{147}Sm/^{144}Nd$ and
355 $^{143}Nd/^{144}Nd$ of the mineral fractions and whole rocks correlate with the proportions of mineral
356 phases estimated in each fraction from their major element compositions. This is illustrated on
357 Figure 6A where the mode of plagioclase/(mode of plagioclase + clinopyroxene) for each fraction
358 is plotted against the measured $^{143}Nd/^{144}Nd$ ratios. The linearity of this line (R^2 = 0.997)
359 demonstrates that plagioclase and clinopyroxene control the distribution of REE in 67667 as is
360 expected given the low abundances of REE in olivine, orthopyroxene, and ilmenite. Note that
361 phosphate, potentially present in 67667, has been mostly removed from the leached mineral
362 fractions that define the line and therefore is not a major contributor to the Sm-Nd isotopic
363 systematics of these fractions.

364 All eight of the leached mineral fractions and whole rocks define a line on a Sm-Nd
365 isochron plot that corresponds to an age of 4351 ± 31 Ma with an initial epsilon ^{143}Nd of 0.04 ±
366 0.11 and an MSWD of 1.8. The isochron age changes to 4349 ± 31 with an initial epsilon ^{143}Nd
367 of -0.19 ± 0.10 and an MSWD of 1.6 if the whole rock data point analyzed by Carlson et al. (2014)
368 is included in the calculation (Figure 7). This data was corrected for neutron capture using the
369 same algorithms used here (Sio et al., 2020), and was obtained using the same Sm-Nd isotopic
370 tracers. As a consequence, this is our preferred age. The only fraction that lies off the isochron is
371 the leachate of the olivine fraction. The leachate contains about a third of the total REE in the
372 olivine fraction after picking. This suggests that a leachable phase, such as phosphate, hosts a
373 significant proportion of REE in 67667. Uneven distribution of phosphates in various aliquots of
374 67667 could account for the ~20% difference in Sm and Nd abundances measured here and by

Carlson and Lugmair (1981). The leachate was taken from the unwashed olivine fraction after hand-picking and probably contains an additional blank contribution from the picking reagents and glassware. Thus, an under-estimation of the Sm and Nd blanks could account for the slight divergence of the olivine leachate from the isochron defined by the other fractions. Alternatively, REE could be partially mobilized during impact metamorphism such that most liable component in the rock was disturbed. This explanation is consistent with the Ar-Ar systematics of 67667 that indicate that it experienced a complex impact history (Figure 5).

The Sm-Nd age reported here is approximately 170 Ma older than the age of 4176 ± 61 Ma reported by Carlson and Lugmair (1981). The reason for this difference is unclear. Although correction of the measured $^{147}Sm/^{144}Nd$ ratios for neutron capture were not discussed in Carlson and Lugmair (1981), they were completed (Carlson, personal communication), eliminating this potential explanation. The mineral fractions analyzed here were leached in weak HCl, whereas those analyzed by Carlson and Lugmair (1981) were not. Phosphates are easily mobilized during shock associated with impacts, contain a significant amount of REE, and are easily leachable in weak HCl. Note however that the olivine leach lies to the right of our 4349 Ma isochron, whereas the plagioclase and whole rocks analyzed by Carlson and Lugmair (1981) lie to the left. Thus, removal of the leached component from our mineral fractions shifts them towards those of Carlson and Lugmair (1981), minimizing the age difference between the two investigations. In addition, the unleached whole rocks analyzed in this investigation lie on the 4349 Ma Sm-Nd isochron, implying leaching does not strongly effect their Sm-Nd isotopic systematics. Thus, there is no obvious explanation why the two Sm-Nd age determinations should differ so dramatically. Nevertheless, such discrepancies are common in lunar chronologic investigations (Borg et al., 2015).

The initial epsilon ^{143}Nd determined from the isochron regression is -0.19 ± 0.10. The uncertainty is calculated using the technique of Fletcher and Rosman, (1982) that calculates the deviation of the isochron from a chondritic $^{143}Nd/^{144}Nd$ isotopic composition of 0.51263 at a $^{147}Sm/^{144}Nd$ value of 0.196 (Bouvier et al., 2008). This reduces the uncertainty on the initial Nd isotopic composition calculated traditionally from the extrapolation of the regression to $^{147}Sm/^{144}Nd = 0$ from about 1.0 to 0.10. Note that the $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ values used in these calculations differ from those we have previously reported since 1997. This results in the reduction of the initial epsilon ^{143}Nd by 0.22 units. If uncertainties on the CHUR parameters reported by Bouvier et al. (2008) are incorporated into the calculation the initial epsilon ^{143}Nd is -0.19 ± 0.30.

The initial Nd isotopic composition is consistent with derivation of 67667 from a source region that has a chondritic REE pattern. The $^{147}Sm/^{144}Nd$ ratio calculated for this source, assuming it formed at 4567 Ma, is 0.1980 ± 0.0037 and is within error of the chondritic $^{147}Sm/^{144}Nd$ ratio. This is consistent with the slightly LREE-enriched REE pattern of the whole-rocks (Figure 4), because LREE behave slightly more incompatibly during partial melting and fractional crystallization than HREE. Thus, the REE systematics of the source region from which 67667 was derived is indistinguishable from an undifferentiated chondritic reservoir. This could reflect the fact that 67667 was derived from a previously undifferentiated Moon, or alternatively that 67667 s produced from sources that formed close to the time the Moon first differentiated. In this case, the Nd isotopic composition of the Mg-suite magma sources would still be chondritic, because there would be insufficient time for significant decay of ^{147}Sm to occur.

A regression through a plot of $^{147}Sm/^{144}Nd$ versus $^{142}Nd/^{144}Nd$ (Figure 6B) yields an age of 4337 $^{+66}/_{-120}$ Ma and has an initial $\varepsilon^{142}Nd$ of -0.12 ± 0.04. The age is calculated using the

parameters previously outlined by Borg et al. (2019). The ^{147}Sm-^{142}Nd data for 67667 falls on the isochron defined by the mare basalt source regions and FAS mineral separates that has a slope corresponding to an age of 4336 ± 10 Ma and an initial ε^{142}Nd of -0.15 ± 0.05. The relatively large uncertainty in the calculated 67667 age reflects the limited variation in ^{142}Nd/^{144}Nd relative to the large uncertainty associated with the ^{142}Nd/^{144}Nd measurements. Nevertheless, the fact that variation in ^{142}Nd/^{144}Nd is observed among the 67667 mineral fractions, and that the ^{147}Sm-^{142}Nd isochron age is concordant with the ^{147}Sm-^{143}Nd isochron age, suggests that ^{146}Sm was alive when 67667 crystallized. This would not be true if 67667 had an age of 4.18 Ga as previously reported.

4.4 Rb-Sr Isotopes

Rubidium and strontium isotopic data determined from the 67667 mineral fractions and whole rocks is presented in Table 3. There is limited spread in the measured ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr ratios of all but one fraction. The ^{87}Rb/^{86}Sr ratios of the leached mineral fractions and whole rocks only vary from 0.0076 to 0.0125, and ^{87}Sr/^{86}Sr differs by only 437 ppm among these fractions. The spread in the Rb-Sr isotopic data is increased by about 30% if the whole rock data point analyzed by Carlson et al. (2014) is included (Wr-C14). In contrast, the olivine leachate is highly radiogenic with ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr ratios of 0.321 and 0.7295, respectively. The Sr abundance in the mineral and whole rock fractions closely follows the abundance of plagioclase in the fraction (Figure 6B). Note however, that the ^{87}Sr/^{86}Sr ratios of the mineral fractions do not correlate with the plagioclase modes. This suggests that the lack of variation of ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr in the mineral fractions does not solely reflect the ubiquitous presence of plagioclase. Instead it is a manifestation of the fact that mineral phases that comprise the 67667 mineral fractions have similar Rb/Sr ratios. Interestingly, the plagioclase fraction does not define the lowest point on the Rb-Sr isochron (Figure 8). Instead, the lowest point is defined by the Plagioclase-Reject 1 fraction that

444 contains only ~30% plagioclase. The relatively elevated $^{87}Rb/^{86}Sr$ of the Plagioclase fraction
445 probably reflects the observation that plagioclase in 67667 is characterized by unusually high
446 abundances of Rb, K, and Ba (Steele et al., 1980). The phase responsible for the low $^{87}Rb/^{86}Sr$ of
447 the Plagioclase-Reject 1 fraction is not identified.

448 Despite the limited range of $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ of the leached mineral fractions and
449 whole rock of Carlson et al. (2014), the data define a linear array with a slope corresponding to an
450 age of 4368 ± 67 Ma (Figure 8). This age is within uncertainty of the Sm-Nd age defined in Figure
451 7. The Rb-Sr regression has a MSWD of 1.9 indicating that it has a high probability of being
452 within uncertainty of the errors determined for the $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios. The relatively
453 large uncertainty determined on the age reflects the fact that the fractions have only ~625 ppm
454 variation in $^{87}Sr/^{86}Sr$. Note that the olivine leachate, and two whole rock fractions lie above the
455 isochron. A line regressed through the olivine leachate and plagioclase fractions has a slope
456 corresponding to an age that is greater than 6 Ga, and intersects the two whole rock data points.
457 The $^{87}Sr/^{86}Sr$ of the leachate is too high to result from a large blank contribution, suggesting that
458 the Rb-Sr system has been slightly disturbed by a post-crystallization impact event or events such
459 as those recorded in by the Ar-Ar systematics of 67667. The disturbance appears to have most
460 strongly affected the labile component, represented by the olivine leachate. One possibility is that
461 heating associated with an impact event mobilized and removed some Rb from grain boundaries
462 that disproportionately contributed to the Rb-Sr isotopic systematics of the leachate. This
463 disturbed component is present in the two unleached whole-rock fractions, but appears to have
464 been mostly removed from the leached mineral fractions and the whole rock analyzed by Carlson
465 et al. (2014). The disparate behavior of Rb-Sr in the various whole rock fractions may reflect the
466 fact that the two whole-rocks analyzed here were derived from the finest sieved fractions (not used

for the mineral fractions) that could contain a disproportionate amount of mobilized Rb. In contrast, the whole rock of Carlson et al. (2014) was derived from a bulk chip.

The initial $^{87}Sr/^{86}Sr$ ratio determined for 67667 from the Rb-Sr isochron is 0.699116 ± 0.000010. This value is similar to values previously measured for other Mg-suite rocks including troctolite 76535 (0.699100 ± 0.000009; Borg et al., 2017) and norite 78238 (0.699074 ± 0.000022; Edmunson et al., 2009), suggesting that most, maybe all, Mg-suite rocks are derived from sources with very low long-term Rb/Sr ratios. The $^{87}Rb/^{86}Sr$ of Mg-suite sources are calculated using a single stage model assuming derivation from a reservoir with Basaltic Best Initial (BABI) initial value for $^{87}Sr/^{86}Sr$ of 0.69898 at 4567 Ma. Note that more sophisticated two stage models, such as those constructed for Sm-Nd, are not warranted given the limited variation determined for their initial $^{87}Sr/^{86}Sr$ ratios and the similarity of these ratios to the initial value of the Solar System. Using a single-stage model, the source of 67667 is calculated to have an $^{87}Rb/^{86}Sr$ ratio of 0.040 ± 0.009. The value estimated for the source of 67667 is just within error of the average value estimated for the bulk Moon of 0.020 ± 0.012 (Anders, 1977; Taylor 1982; Wänke et al., 1977), but significantly lower than the average value estimated for bulk Earth of 0.081 ± 0.018 (Anderson, 1983; Ringwood, 1991; Taylor and McLennan, 1985; Wänke et al., 1984), urKREEP of 0.302 ± 0.047 (Warren, 1986), or primitive chondritic meteorites of 0.853 ± 0.017 (Anders and Grevesse, 1989). The $^{87}Rb/^{86}Sr$ ratio estimated for the 67667 source is also within error of $^{87}Rb/^{86}Sr$ ratios determined from the Rb-Sr isotopic systematics of other Mg-suite rocks including 78238 (0.028 ± 0.011) and 76535 (0.026 ± 0.018), consistent with derivation of all of these rocks from similar, perhaps even common, source regions. The observation that the source region(s) of the Mg-suite have $^{87}Rb/^{86}Sr$ ratios that are within error of estimates for the bulk Moon suggests they had either experienced minimal differentiation prior to the extraction of Mg-suite magmas, or that the sources

formed near the time of primordial differentiation of the Moon and still had $^{87}Sr/^{87}Sr$ ratios approximating those of the bulk Moon at the time the rocks crystallized. The latter scenario seems most plausible given the highly fractionated incompatible element systematics of Mg-suite rocks.

From this analysis it is apparent that the Sm-Nd and Rb-Sr isotopic systematics of 67667 are very similar to other Mg-suite rocks, so that despite having a somewhat unique composition and representing one of the few Mg-suite samples from the Apollo 16 landing site, its petrogenesis is indicative of the origin of the broader group of Mg-suite rocks. The following discussion uses the isotopic systematics of 67667 in conjunction with other Mg-suite rocks, FAS samples, and KREEP-rich basalts to constrain the age and origin of various lunar lithologies.

5. Discussion

5.1. Chronology of the Moon

5.1.1 The age of the highlands crust

The Sm-Nd and Rb-Sr age determined here for 67667 are similar to ages that have been reported previously for other Mg-suite rocks including norite 78238 (4334 ± 34 Ma and 4359 ± 24 Ma; Edmunson et al., 2009), norite clast from breccia 15445 (4332 ± 79 Ma; Sm-Nd age only, Gaffney et al., 2015), noritic breccia 77215 (4283 ± 23 and 4374 ± 45 Ma; Carlson et al., 2014), and troctolite 76535 (4307 ± 11 Ma and 4279 ± 52 Ma; Borg et al., 2017). The Sm-Nd and Rb-Sr ages for three of the five samples are concordant, suggesting these record geologic events on the Moon. In contrast, the Sm-Nd age of 77215 is 91 Ma younger than the Rb-Sr age, suggesting the isotopic systematics of this rock are partially disturbed. Like the Sm-Nd age of 77215, both the Sm-Nd and Rb-Sr ages of 76535 are slightly younger than the ages determined on 67667, 15445,

and 78238. This likely reflects the fact that this rock was derived from the greatest depth and experienced the slowest cooling of any rock in the Apollo collection (Nord et al., 1976; McCallum et al., 2006; Elardo et al., 2012). As a consequence, the Sm-Nd and Rb-Sr ages of this sample record the time the rock cooled below the closure temperature of ~850 °C for the Sm-Nd and Rb-Sr systems and not the time the rock was emplaced in the lower crust or upper mantle (McCallum et al., 2006; Borg et al., 2017). Sample 77215 might also have experienced slow cooling before the brecciation event that partially disturbed its isotopic systematics (Carlson et al., 2014). The range of Sm-Nd and Rb-Sr ages of Mg-suite samples that we have determined, and that we believe most reliably record crystallization of the samples (67667, 15445, and 78238), varies from about 4.33 to 4.35 Ga. The limited age range is remarkable given the fact that these samples were collected at three different Apollo landing sites and that these landing sites are over 1100 km apart. Thus, the most reliable crystallization age determinations completed on Mg-suite rocks suggests that Mg-suite magmatism was widespread, but confined a time interval of ~20 Ma around 4.34 ± 0.01 Ga.

One Mg-suite rock 73255 has yielded a Sm-Nd age of 4246 ± 48 Ma (Carlson and Lugmair, 1981b) that is outside the 4.34 ± 0.01 Ga range defined by the other Mg-suite samples. In addition, Rb-Sr ages of 4528 ± 92 Ma and 4161 ± 89 Ma have been determined for dunite 74217 (Papanastassiou and Wasserburg, 1975) and norite 72255 (Compston et al., 1975), respectively. If correct, these data would expand the range of Mg-suite magmatism from 4.16 to 4.53 Ga. However, two of these ages are based on the Rb-Sr system that is more easily disturbed by impact metamorphism than Sm-Nd suggesting they may be erroneous. Furthermore, all of these ages meet only a limited set of criteria used to evaluate their reliability (Borg et al., 2015). Therefore there is a reasonable chance that the ages of 73255, 74217, and 72255 are erroneous.

The range of ages we have determined on Mg-suite rocks is very similar to Sm-Nd ages determined recently on several FAS samples from the Apollo 16 landing site including 60025 (4367 ± 11 Ma; Borg et al., 2011), 60016 (4302 ± 28 Ma; Marks et al., 2019), and 62237 (4350 ± 73 Ma; Sio et al., 2020). The similarity is maintained even more profound if rocks that exhibit evidence for slow cooling, such as 76535 and 60016, or are potentially disturbed by post-crystallization impact processes, i.e. 77215, are removed from the comparison. Samarium-neodymium ages of moderately to quickly cooled FAS and Mg-suite samples (60025, 62237, 78238, 15445, and 67667) span almost identical ranges of 4.35 to 4.37 Ga and 4.33 to 4.35 Ga respectively. The ages of the Mg-suite may be very slightly younger than the ages determined on FAS samples, although it is impossible to delineate whether this age difference is real given the analytical uncertainties associated with the chronometry and the limited number of samples that have been analyzed. However, taking the existing data at face value implies that the maximum difference between the Mg-suite and FAS is only a few Ma.

Again, it should be noted that there are two FAS samples that yield Sm-Nd ages outside the range of 4.35 to 4.37 Ga. These include FAS sample 67016 (4576 ± 160 Ma; Alibert et al., 1994) and FAS clast in meteorite Y86032 (4438 ± 34 Ma; Nyquist et al., 2006). Sample 67016 has an age that is as old as the solar system, has a large uncertainty, and exhibits a strongly positive initial ^{143}Nd value that combine to suggest the age could be erroneous. Although sample Y86032 has coherent Sm-Nd isotopic systematics it contains mineral phases characterized by REE abundances that are 5 to 8 times higher than typical FAS samples (Papike et al., 1997) indicating it contains an evolved KREEP-like component. This is problematic because the Sm-Nd age of Y86032 is older than all but one model age for urKREEP (see below).

557 The Alkali-suite is the third major magmatic suite, along with the Mg-suite and FAS, that
558 comprise the lunar crust. It is primarily represented by breccia clasts in rocks from the Apollo 14
559 landing site. The clasts are the most felsic samples from the Moon containing Fe-rich pyroxene in
560 conjunction with granophyres of silica and K-feldspar, as well as accessory phases such as
561 phosphate and zircon (Taylor et al., 1980; Marvin et al., 1991). Only one attempt has been made
562 to date a sample from the Alkali-suite using the Sm-Nd and Rb-Sr isotopic system. Unfortunately,
563 this investigation yielded badly discordant Sm-Nd and Rb-Sr ages of 4.11 ± 0.05 and 4.33 ± 0.08
564 Ga, respectively (Snyder et al., 1995). Furthermore, potential disturbance of the Sm-Nd system
565 by neutron capture was not monitored by measuring the isotopic composition of Sm or Gd. As a
566 consequence, despite the larger uncertainty on the isochron, the Rb-Sr age may be the best
567 indicator of the crystallization age of the sample. If this interpretation is correct, then Alkali-suite
568 magmatism may have been contemporary with Mg-suite magmatism. Age data of zircons found
569 in soils, and in a few alkali-suite rocks, determined by SIMS seem to confirm this interpretation
570 (Grange et al., 2009, 2011; Meyer et al., 1996; Nemchin et al. 2006, 2008, 2009a, 2009b; Pidgeon
571 et al., 2007). Compilations of zircon ages by Borg et al. (2015) demonstrate a peak at 4340 ± 20
572 Ma. This suggests that Mg-suite and Alkali-suite magmatism was contemporaneous within the
573 resolution of the chronometry between 4.33 and 4.35 Ga.

574 *5.1.2. The age of urKREEP formation*

575 Crystallization of the LMO produced the FAS suite, the Mg-rich cumulates involved in the
576 petrogenesis of the Mg-suite and mare basalts, and, after extensive crystallization, urKREEP.
577 Model ages of LMO mafic cumulates and urKREEP have been generated to constrain their
578 formation ages. The first attempts to define the age of the formation of urKREEP resulted in ages
579 of 4.36 ± 0.06 and 4.42 ± 0.07 Ga (Carlson and Lugmair, 1979; Nyquist and Shih, 1992). These

were generated using the Sm-Nd and Rb-Sr isotopic systematics of KREEP-rich samples. Model urKREEP Sm-Nd (and Lu-Hf) ages have also been obtained by plotting the age (T) and initial isotopic composition (I) of rocks on T-I diagrams (Edmunson et al., 2009; Sprung et al., 2013; Gaffney and Borg, 2014). These model ages are defined by the intersection of the line regressed through the data with an isotope evolution curve for the undifferentiated Moon assumed to be represented by chondritic meteorites. This approach works well for samples rich in urKREEP because this geochemical component dominates the Sm-Nd and Lu-Hf isotopic systematics of the host rocks. In other words, the initial isotopic compositions determined from the isochrons documents the isotopic evolution of urKREEP through time. An age of 4350 ± 34 (MSWD = 0.44) is calculated (Figure 9) from the Sm-Nd isotopic systematics of the Mg-suite rocks discussed here (67667, 15445, 78238, 76535) and basaltic rocks previously analyzed that are enriched in the urKREEP component including KREEP basalt 15386 (Borg et al., 2019) and KREEP-rich gabbronorite NWA 773 (Borg et al., 2009). Although the likely disturbance of the Sm-Nd data results in the exclusion of 77215 from the best age calculation, the calculated intercept of the regression on Figure 9 changes minimally to 4368 ± 26 (MSWD = 0.82) if it is included. This Sm-Nd model age of urKREEP formation is in remarkable agreement with the Lu-Hf model age of urKREEP formation of 4353 ± 37 Ma calculated by Gaffney and Borg (2014) and portends near simultaneous production of urKREEP and the highlands crust.

Barboni et al. (2017) used Pb-Pb ages of zircons combined with their Hf isotopic compositions to calculate a 4.51 Ga model age for the formation of urKREEP. Unlike the whole rock data of Sprung et al. (2013) and Gaffney and Borg (2014) the zircon data do not define a linear array on a plot of age versus initial Hf isotopic composition. As a consequence, a precise age cannot be calculated by regressing a line through the zircon data on a plot similar to that

603 presented in Figure 9. Instead, Barboni et al. (2017) define the age as the intercept between a
604 urKREEP Hf evolution curve and a chondritic Hf evolution curve assuming the former intersects
605 the zircon point with the oldest age and lowest Hf isotopic composition. Not only is this age
606 defined by a single zircon analysis, the urKREEP evolution curve assumes urKREEP has a
607 $^{176}Lu/^{177}Hf$ ratio of 0. In fact, urKREEP is estimated to have a $^{176}Lu/^{177}Hf$ ratio closer to 0.018 ±
608 0.002 (Warren 1989). If this value is used to calculate an intercept, urKREEP is modeled to have
609 formed prior to the solar system.

610 Maurice et al. (2020) have taken a different approach to determine when urKREEP formed
611 and obtained ages that are significantly younger than those discussed above. These authors suggest
612 that the Moon solidified over 100 to 200 Ma. As a result, the magma ocean is LREE enriched, as
613 a result of crystallization of mafic silicates, for a substantial period of time. Using the Sm-Nd
614 isotopic data for KREEP-rich samples and LMO Sm-Nd isotopic systematics consistent with an
615 early and slowly evolving LMO they calculate an age of urKREEP formation of 4.22 to 4.27 Ga.
616 These ages are difficult to reconcile with older ages determined on KREEP-rich Mg-suite rocks
617 such as 67667 because the isochron ages determined on several Mg-suite rocks are older than the
618 modeled age for the formation of the urKREEP component they contain.

619 *5.1.3. The age of lunar magma ocean mantle cumulates*

620 Model ages for the formation of the mare basalt source regions have been calculated many
621 times based on their measured ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd isotopic compositions and
622 crystallization ages. The weighted average of mare basalt source formation ages determined by
623 Nyquist et al. (1995), Rankenburg et al. (2006), Boyet and Carlson (2007), Brandon et al. (2009),
624 McLeod et al. (2014), and Borg et al (2019) is 4333 ± 8 Ma (95% confidence, MSWD = 1.5). The

uncertainty on the ^{146}Sm half-life is relatively large (Meissner et al., 1987), and if included in the age calculation expands the uncertainty to 4333 ± 30 Ma.

The age of LMO solidification can also be estimated from the ^{147}Sm-^{143}Nd isotopic compositions of highlands crustal rocks. A ^{147}Sm-^{143}Nd isochron plot of Mg-suite samples is presented in Figure 10, where a slope regressed through the data corresponds to an age of 4348 ± 25 Ma. The data for Mg-suite whole rocks are from Carlson et al., (2014), Sio et al. (2020), Gaffney et al., 2015), and this investigation. This age is in excellent agreement with a similar calculations performed on Mg-suite samples by Carlson and Lugmair (1981a) that yielded and age of 4.33 ± 0.08 Ga. Petrogenetic models for the origin of Mg-suite demonstrate that these rocks are mixtures of urKREEP, mafic cumulates, and probably anorthositic plagioclase derived from solidification of the LMO (Shearer et al., 2015; Elardo et al., 2020). As a consequence, the slope of the isochron defines the age at which the various LMO solidification products were produced. This interpretation is further supported by the fact that FAS samples listed in Table 4, analyzed by Boyet et al. (2015), Marks et al. (2019), and Sio et al. (2020), and corrected for neutron capture effects by Sio et al. (2020), lie on, or very near, the Mg-suite whole rock isochron (Figure 10). There is more scatter in the FAS data than in the Mg-suite data most likely reflecting the additional difficulty of determining the ^{147}Sm/^{144}Nd ratios of neutron irradiated samples with high proportions of plagioclase. This arises from the fact that the Sm isotopic composition of these samples is not only modified by neutron capture on ^{149}Sm, but by the production of ^{152}Sm through the capture of neutrons on Eu (Borg et al., 1999).

This analysis demonstrates that there is a preponderance of ~4.35 Ga ages observed in lunar samples and genetically related magmatic suites. Furthermore, many of these samples have similar Sm-Nd isotopic systematics that suggest they are derived from similar, or even identical, magmatic

sources that have experienced only a limited amount of elemental fractionation from an assumed chondritic isotopic composition. Petrogenetic models for the origin of the Moon that account for these observation are discussed below.

5.2 Contemporaneous solidification and overturn of the LMO

Simultaneous, or near simultaneous, production of FAS and Mg-suite magmas is not predicted by the magma ocean model of lunar differentiation. In other words, petrogenetic models imply that FAS should pre-date Mg-suite rocks. This stems from the fact that the Mg-suite is composed of components that are themselves thought to be crystallization products of the LMO (e.g., Shearer et al., 2015). The most obvious example of this is urKREEP which dominates the incompatible element geochemical signature of Mg-suite magmas (Shervais and McGee, 1999; Warren, 1988; Hess et al. 1978; Hess 1989). Other examples include the Mg-rich component that is likely derived from early formed LMO olivine and orthopyroxene bearing cumulates, and an Al-rich component that has some petrogenetic relationship to anorthosite flotation cumulates in the lunar crust (Warren and Wasson, 1977; Longhi, 1981; James and Flohr, 1983; Warren, 1986; Ryder, 1991; Papike et al., 1994, 1996). Any petrogenetic model for the origin of the Moon must account for the contemporaneous or near-contemporaneous formation of the Mg-suite with the ferroan anorthosite suite, Mg-rich cumulates, and urKREEP. Simple, rapid and late crystallization of the LMO can account for the contemporaneous formation of the Mg-rich cumulates, FAS, and urKREEP between 4.34 and 4.37 Ga. The LMO model is strongly supported by its unique ability to account for the widespread occurrence of Ca-Fe-rich anorthosites on the lunar surface, the composition of the mare basalt source regions, and the formation of urKREEP. Thus, a mechanism to produce Mg-suite in this context is sought.

The simplest petrogenetic scenario that temporally links Mg-suite magmatism with LMO solidification is if the Mg-suite is produced during LMO solidification as suggested by Wood (1975), Longhi and Boudreau (1979), and McCallum (1983). However, Raedeke and McCallum (1980) demonstrated that FAS and Mg-suite rocks have mineral and major element compositions that cannot be produced from the same parental magmas. The incompatible trace element ratios of these two rock suites are also inconsistent with production from a common parent (Shearer et al., 2015). Another possibility was suggested by Hess (1994) and Hess and Parmentier (1995) who argued that LMO solidification and Mg-suite magmatism could be linked temporally if Mg-suite magmas formed by decompression melting associated with mantle overturn. This would allow Mg-rich magmas to interact with anorthositic plagioclase and urKREEP that was present in the mantle and crust. This hypothesis is supported by Elkins-Tanton et al. (2011) who noted that the wide range of FAS ages, as well as the overlap with an equally large range of ages of Mg-suite rocks, could reflect overturn of the LMO in a slowly cooling LMO. In this case slow cooling of the LMO was speculated to reflect tidal heating of the Moon by the Earth. The restricted, overlapping ages of Mg-suite, FAS, and urKREEP, as well as the mare basalt source regions, eliminates the need for prolonged cooling of the LMO. Instead, if overturn is indeed required to produce Mg-suite magmas, then it must occur within a few Ma of the time of primordial solidification of the LMO. This is consistent with the calculated $^{147}Sm/^{144}Nd$ and $^{87}Rb/^{86}Sr$ ratios of the Mg-suite sources that require them to be undifferentiated, or to have been produced near the time the LMO differentiated.

Elkins-Tanton et al. (2002) argued that solid ilmenite-clinopyroxene bearing cumulates would not sink on a post-LMO Moon as a result of Rayleigh-Taylor instabilities. However, they noted that a clinopyroxene + ilmenite liquid is negatively buoyant and could sink under such

conditions. This provides a mechanism to temporally link overturn with primordial solidification of the LMO. Likewise, experimental studies by Prissel et al. (2016) suggest that some plagioclase undersaturated Mg-suite melts were produced by decompression melting of early LMO cumulates. Additional modeling of compositional overturn of magma oceans completed by Boukaré et al. (2018), Morison et al. (2019), Li et al. (2019), and Zhao et al. (2019) demonstrate that overturn on the Moon could even occur contemporaneously with the last stages LMO solidification. In this scenario overturn is driven by progressive Fe-enrichment of the cumulate pile as it solidifies. These overturn scenarios seem to fit the chronologic data well. They account for the temporal relationships between the formation of LMO cumulates and Mg-suite magmatism. They also are consistent with the range of Mg-suite samples that have been dated reliably so far. If Mg-suite magmas, significantly younger than 4.33 Ga are found, then a more complicated relationship between LMO solidification and Mg-suite magmatism will be required. Until such samples are identified, the existing chronology points to a tight relationship between LMO solidification and overturn resulting in ubiquitous ~4.35 Ga ages for the formation of numerous suites of lunar rocks.

5.3 Ramifications for the preponderance of 4.35 ages

As noted above, crystallization ages of Mg-suite and FAS, as well as formation ages of the mare basalt source regions, and urKREEP are tightly scatter around 4.35 Ga. The best estimates for the timing of these events, as averaged from the ages outlined above, are: Mg-suite = 4345 ± 10 Ma, FAS = 4359 ± 9 Ma, urKREEP formation = 4350 ± 34 Ma, and formation of the mare basalt source region = 4333 ± 30 Ma. These ages are within uncertainty of one another and span only 26 Ma. Furthermore, the materials dated are likely produced throughout the various stages of LMO solidification. The mafic mare basalt sources for example, likely formed early in LMO crystallization sequence, whereas FAS samples formed after ~70% crystallization of the LMO

716 (Elkins-Tanton, 2011), and urKREEP formed near the very end of solidification. The compressed
717 nature of these ages suggests that once solidification began, the LMO cooled relatively rapidly. A
718 maximum duration of LMO solidification permissible within the uncertainties estimated for these
719 ages is ~40 Ma. This is consistent with shorter, 10s of Ma, estimates of LMO solidification
720 timescales (e.g. Elkins-Tanton et al., 2011), but contrasts with some longer, 100-200 Ma, estimates
721 (e.g. Solomon and Longhi, 1977; Maurice et al., 2020).

722 The U-Pb systematics of the Earth have been used to estimate the age of the Giant Impact
723 at 4421 ± 5 (Connelly and Bizzaro, 2016), whereas Maurice et al. (2020) estimated the accretion
724 age of the Moon to be 4425 ± 25 Ma. The age of the Giant Impact and the age estimated for the
725 accretion of the Moon precede the earliest potential age for the onset of LMO solidification,
726 represented by the 4333 ± 30 Ma ^{146}Sm-^{142}Nd model age for the formation of the mare basalt
727 sources, by a minimum of 37 to 53 Ma. At face value this age interval seems consistent with
728 prolonged cooling of the LMO. However, most thermal models for LMO solidification suggest
729 that initial cooling was relatively rapid until formation of a buoyant plagioclase-rich crust formed
730 after ~70% solidification (Solomon and Longhi, 1977; Elkins-Tanton et al., 2011; Maurice et al.,
731 2020). Note that some more ancient ages for the Giant Impact and accretion of the Moon, such as
732 those suggested by Barboni et al., (2017) and Thiemans et al. (2019), around 4.51-4.52 Ga make
733 the gap between lunar formation and lunar differentiation event larger. In any case, the time gap
734 between formation and differentiation of the Moon implies either: (1) the Moon accreted relatively
735 slowly after the Giant Impact, (2) an additional heat source kept the Moon mostly molten after it
736 accreted, or (3) some or all of these age estimates, or associated uncertainties, are incorrect.

737 **5.4 Evolution of KREEP magmatism**

738 Magmatic activity of samples characterized by a KREEP-rich geochemical signature (Mg-
739 suite, Alkali-suite, KREEP basalts) extends from ~4.35 Ga to 2.99 Ga (Borg et al. 2009). Younger
740 episodes of basaltic volcanism, ≤ 1.0 Ga, are observed within the Procellarum KREEP Terrane
741 (PKT) and produce lavas with high concentrations of heat producing elements, such as Th
742 (Hiesinger et al., 2011). It therefore appears likely that magmatism associated with KREEP may
743 extend over a period of at least 3.35 billion years. Over this period of time the thermal and
744 dynamical states of the lunar mantle changed dramatically (e.g., Shearer et al., 2005 and references
745 within), so that the mechanisms for the production of KREEP-rich magmas must also have
746 evolved.

747 The limited duration of Mg-suite magmatism indicates that the first episode of KREEP
748 magmatism was related to a single short-term event hypothesized to be associated with primordial
749 solidification and subsequent overturn of the LMO. This involved a dynamic mantle event that
750 resulted not only the downwelling of dense, Fe-Ti-rich LMO cumulates, but also the upwelling of
751 hot (>1600°C) early-formed LMO cumulates (high Mg# olivine and orthopyroxene) to the base of
752 the lunar crust (Elkins-Tanton et al., 2002; 2011). The Mg-suite parental magmas were produced
753 either through decompressional melting of the upwelling mantle (Shearer and Papike, 2005; Prissel
754 et al., 2016;) or melting of a hybrid mantle source resulting from the mixing of hot upwelled mantle
755 with shallow LMO crystallization products, such as FAS and urKREEP, at the base of the lunar
756 crust (Shearer and Papike, 2005; Longhi et al., 2010; Shearer et al., 2015). Although urKREEP is
757 an important component of Mg-suite magmas within the PKT, recent remote sensing data indicate
758 that Mg-suite lithologies without a urKREEP signature are globally distributed across the
759 feldspathic highlands outside the PKT (e.g., Pieters et al., 2014; Prissel et al., 2016). Furthermore,
760 some feldspathic meteorites, presumably from outside the PKT, have Mg-suite lithologies that are

761 essentially devoid of a urKREEP geochemical component (e.g., Gross et al., 2014; 2020). Thus,
762 the presence of urKREEP is not a prerequisite for the production of Mg-suite magmas. Instead,
763 production of the Mg-suite appears to be tied to a short lived, high temperature, dynamic mantle
764 event, such as LMO overturn.

765 Magmatism associated with urKREEP continued for another ~3.20 billion years after
766 production of the last Mg-suite rocks. It is typified by KREEP basalts derived from the lunar
767 interior such as those collected from the Apollo 15 and 17 sites, meteorites such as NWA 773, and
768 younger eruptive units identified by orbital observations (e.g., unit P60 near Aristarchus crater).
769 This magmatism became increasingly restricted to the interior of the PKT with time (Nemchin et
770 al., 2008) suggesting a relationship between magmatic activity and the presence of urKREEP. Late
771 basaltic magmatism involved a urKREEP component that could have initiated melting through
772 heat-generated by the decay of the radioactive elements it contained. Thus, the heat source for
773 KREEP-rich magmatism changed over time. Initially, the petrogenesis of KREEP-bearing Mg-
774 suite magmas was driven by heat derived from early differentiation of the Moon in the deep lunar
775 interior. It involved high temperatures and high degrees of partial melting and incorporated the
776 urKREEP component only if it was available. The heat source of Mg-suite magmatism was not
777 urKREEP. In contrast, later KREEP-rich magmatism is associated with lower temperatures and
778 lower degrees of partial melting and was probably driven by the heat generated locally by the
779 decay of radioactive elements in KREEP.

780 **6. Conclusion**

781 Gabbronorite 67667 yields concordant Sm-Nd and Rb-Sr ages of 4349 ± 31 Ma and 4368
782 ± 67 Ma, respectively. These ages are similar to other ages determined on Mg-suite samples. A
783 compilation of all Mg-suite samples dated using the Sm-Nd system and corrected for neutron

784 capture using the same techniques indicates the Mg-suite was emplaced in the lunar crust at the
785 Apollo 14, 15, 16, and 17 landing sites contemporaneously between 4.33 and 4.35 Ga. Although
786 the dataset is small, it implies that Mg-suite magmatism was confined to a short period in lunar
787 history. The age of Mg-suite magmatism is concordant with the age of FAS magmatism (4.36 ±
788 0.01 Ga), urKREEP formation (4.35 ± 0.03 Ga), and formation of the mare basalt source regions
789 (4.34 ± 0.01 Ga). Despite contemporaneous, or near contemporaneous production of these magma
790 suites, their geochemical characteristics preclude them from being cogenetic. Whereas FAS, the
791 mare basalt source regions, and urKREEP could be produced during late and rapid primordial
792 solidification of the LMO, the Mg-suite must be produced by another mechanism. One possibility
793 is that the Mg-suite is produced during density driven overturn of the LMO that occurred during,
794 or immediately after, it solidified. This would not only account the range of measured ages, but
795 for the calculated $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ ratios of the Mg-suite sources that closely
796 approximate estimates for the bulk, undifferentiated, Moon.

797

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Figure Captions.

Figure 1. Backscatter electron images of 67667. A. Textures and mineralogy of 67667. Texture is partial defined by distinct regions immersed in a cataclastic matrix. O = olivine, P = plagioclase, Pyx = pyroxene (both high-Ca and low-Ca pyroxene), Cr = chromite, ilm = ilmenite. Box area is image in B. Scale bar = 500μm. B. Monomineralic and polymineralic regions of pyroxene and olivine. Box area is image in C. C. Polymineralic region of cumulate pyroxene consisting of both high-Ca and low Ca pyroxene. Pyroxene region is within olivine.

Figure 2. Comparison of 67667 with other lunar lithologies. Sample 67667 in red squires. Fields for other lithologies are indexed. Individual data points for olivine-poor and olivine-rich Mg-suite lithologies are plotted. A. Anorthite content of plagioclase versus Mg# of mafic silicates. B. Mg/Mg+Fe versus Ti/Sm. C. Mg/Mg+Fe versus Sc/Sm. D. Mg/Mg+Fe versus Cr_2O_3 (wt.%). E. Mg/Mg+Fe versus Th. F. Co versus Ni.

Figure 3. Mineral separation procedure for 67667. Shaded fractions were analyzed for Rb-Sr and Sm-Nd isotopic analysis.

Figure 4. Rare earth element patterns for 67667 whole rock and mineral fractions. Data normalized to chondritic values of Anders and Grevesse (1989)

Figure 5. ^{40}Ar-^{39}Ar age of whole rock 67667 versus cumulative ^{39}Ar released during stepwise heating. Ages, uncorrected and corrected for cosmogenic ^{40}Ar, are shown in dashed blank lines and red, respectively. The Ca/K ratio of the released fraction is shown in gray. The arrows denote the steps included in the age calculation.

Figure 6. Plots of calculated mineral modes versus Sr concentrations as well as Sr and Nd isotopic compositions. A. Plot of mode fraction of Plagioclase/(Plagioclase + Clinopyroxene) in mineral separates and whole rocks versus their measured Sr (open circles) and Nd (solid circles) isotopic compositions. B. Plot of mode of Plagioclase in mineral separates and whole rocks versus their measured Sr abundances (solid circles) and isotopic compositions (open circles). Note that the "Plagioclase" point is the concentration of pure plagioclase measured using an electron microprobe by Hansen et al. (1980), and does not have a corresponding $^{87}Sr/^{87}Sr$ ratio.

Figure 7. Sm-Nd isochron plots. A. ^{147}Sm-^{143}Nd isochron plot of mineral fractions and whole rocks for 67667. The calculated regression (solid line) through all the data, excluding the Olivine leachate fraction (open symbol) yields an age of 4349 ± 31 Ma and an initial epsilon Nd value 0.03 ± 0.10. Wr-C14 whole rock data point is from Carlson et al. (2014). Inset depicts deviation of data from isochron (dashed line) in epsilon units. B. ^{147}Sm-^{142}Nd isochron plot of mineral fractions and whole rocks for 67667. Symbols same as in A. All data fall with uncertainty of the 4337 $^{+66}/_{-120}$ Ma isochron.

Figure 8. Rb-Sr isochron plot of mineral fractions and whole rocks for 67667. Wr-C14 is from Carlson et al. (2014). Inset depicts deviation of data from isochron (dashed line) in epsilon units. All data fall except the whole rocks (open circles) and the olivine leachate (not plotted) fall with uncertainty of the 4368 ± 67 Ga isochron. Ages calculated using 87Rb decay constant $\lambda = 1.402 \times 10^{-11} yr^{-1}$.

Figure 9. Age versus initial Nd isotope plot of urKREEP rich samples. Data from Borg et al. (2017; 2009), Edmunson et al (2009), Gaffney and Borg (2014), this study. A model age for urKREEP formation of 4350 ± 34 Ma is calculated by the intercept of a line regressed through the data with a line modeling the evolution of an undifferentiated (chondritic) Moon. The slope of the line corresponds to a $^{147}Sm/^{144}Nd$ ratio of 0.171 which is in good agreement with the values of 0.166 estimated for urKREEP by Warren (1988).

Figure 10. Whole rock isochron plot of Mg-suite samples from Apollo 14, 15, 16, and 17 landing sites (solid circles) yield age of 4348 ± 25 Ma. FAS whole rock samples (open circles) plotted for comparison. All samples corrected for neutron capture using algorithms in Borg et al. (2019) and normalized to $^{143}Nd/^{144}Nd$ values for JNdi value of 0.512105. Data listed in Table 4 and are from Carlson et al., (2014), Sio et al. (2020), Gaffney et al., 2015; 2019), Boyet et al. (2015) and this investigation.

1125 Table 1. Major and trace element compositions of mineral fractions

	Plag	Plag-Rej 1	Plag-Rej 2	Px-Rej 2	Ol-Px	Oliv	Wr-1	Wr-2
[SiO_2]	43.23	45.46	44.18	42.03	41.91	40.56	42.96	41.52
TiO_2	0.23	0.82	1.56	3.57	0.75	0.28	0.90	1.10
Al_2O_3	21.96	10.17	6.24	4.93	4.96	3.74	6.85	6.90
Cr_2O_3	0.05	0.23	0.39	0.15	0.16	0.09	0.14	0.14
FeO	8.57	12.58	12.65	18.69	18.72	20.72	17.24	17.68
MnO	0.09	0.16	0.18	0.21	0.21	0.21	0.19	0.19
MgO	12.57	20.39	21.98	25.66	28.79	31.67	26.23	26.58
CaO	12.67	9.91	12.67	4.66	4.39	2.68	5.33	5.69
Na_2O	0.52	0.19	0.10	0.05	0.05	0.00	0.11	0.11
K_2O	0.12	0.06	0.05	0.05	0.04	0.05	0.06	0.09
P_2O_5	0.39	0.33	0.38	0.27	0.21	0.23	0.19	0.41
Ni	5.85	7.80	7.58	18.2	15.8	15.4	53.0	51.9
Co	8.95	11.8	12.2	18.2	19.2	20.9	24.1	25.5
Sc	7.09	27.0	48.6	23.2	20.0	12.1	17.3	17.8
Zr	17.3	39.0	97.4	71.9	33.8	16.2	31.0	33.2
Nb	1.38	2.72	4.57	18.9	3.50	1.47	4.28	5.63
Sr	397	181	99	84	79	61	114	119
Ba	213	93	57	54	51	44	73	83
Y	11.0	28.6	56.4	30.5	23.7	14.3	22.4	22.4
La	3.39	3.15	3.45	3.39	2.95	2.34	3.54	3.70
Ce	7.91	8.49	10.8	9.27	7.79	5.92	9.26	9.54
Pr	1.14	1.38	2.01	1.52	1.22	0.90	1.42	1.44
Nd	4.88	6.95	11.0	7.32	5.85	4.10	6.70	6.87
Sm	1.38	2.55	4.71	2.61	2.06	1.58	2.19	2.27
Eu	2.89	1.43	0.91	0.78	0.69	0.53	0.92	0.94
Gd	1.58	3.35	6.54	3.42	2.64	1.61	2.69	2.78
Tb	0.30	0.70	1.33	0.71	0.53	0.37	0.53	0.53
Dy	1.81	4.70	9.54	4.86	3.75	2.21	3.61	3.67
Ho	0.38	1.04	2.03	1.06	0.85	0.51	0.80	0.78
Er	1.08	2.94	5.74	3.20	2.48	1.59	2.29	2.32
Tm	0.17	0.45	0.82	0.50	0.41	0.27	0.35	0.34
Yb	1.18	2.67	4.98	3.21	2.49	1.75	2.18	2.27
Lu	0.20	0.40	0.67	0.50	0.39	0.29	0.33	0.33
Hf	0.67	1.39	2.82	2.64	1.10	0.60	0.94	1.12
U	0.16	0.22	0.62	0.28	0.20	0.11	0.19	0.17
Th	0.39	0.67	1.44	0.85	0.63	0.38	0.58	0.58

1126 Major elements reported in weight percent oxides. SiO_2 estimated from total.
1127 Trace elements reported in ppm.

Table 2. Modes of Mineral Fractions

Fraction	Plag	Olivine	Opx	Cpx	Ilm	Plag/(Plag + Cpx)
Wr-1 & -2	0.19	0.53	0.20	0.07	0.01	0.73
Plag	0.61	0.30	0.03	0.06	0.00	0.91
Plag-Rej 1	0.27	0.33	0.14	0.25	0.01	0.52
Plag-Rej 2	0.15	0.36	0.01	0.47	0.01	0.24
Px-Rej 2	0.12	0.45	0.28	0.09	0.06	0.57
Ol-Px	0.12	0.59	0.20	0.08	0.01	0.60
Ol	0.10	0.72	0.15	0.03	0.00	0.76

Table 3. Rb-Sr and Sm-Nd isotopic data

Sample	67667 Plag-1	67667 Plag-Rej 1	67667 Plag-Rej 2	67667 Px-Rej 2	67667 Oliv-Px	67667 Oliv	67667 Mafics	67667 Oliv Leach	67667 Wr-1	67667 Wr-2	14321 Troc. Clst Wr	15445 Norite Clst Wr
Wt. (mg)	8.21	5.95	5.11	20.13	25.74	33.65	4.51	---	26.30	0.02	150.43	77.3
Rb (ppm)	1.216	0.471	0.328	0.284	0.268	0.271	0.178	---	0.472	0.476	0.787	1.658
Sr (ppm)	386.2	179.8	94.6	85.9	80.7	62.3	49.7	---	116.3	117.4	179.15	128.72
$^{87}Rb/^{86}Sr$	0.009118	0.007603	0.010087	0.009570	0.009594	0.012584	0.010365	0.3203	0.011752	0.0117	0.01272	0.03726
+/-	0.000046	0.000038	0.000050	0.000048	0.000048	0.000063	0.000052	0.0016	0.000059	0.0013	0.00013	0.00037
$^{87}Sr/^{86}Sr$	0.6996919	0.6995988	0.6997505	0.6997229	0.6997209	0.6999046	0.6997676	0.729533	0.6999869	0.6999715	0.6998854	0.7014615
+/-	0.0000048	0.0000046	0.0000048	0.0000057	0.0000044	0.0000048	0.0000059	0.000018	0.0000038	0.0000052	0.0000044	0.0000070
Sm (ppm)	1.380	2.604	4.585	2.778	2.089	1.346			2.282	2.4	2.665	1.623
Nd (ppm)	4.995	7.156	10.96	7.847	6.097	4.349			7.124	7.4	11.992	5.798
$^{147}Sm/^{144}Nd$	0.16701	0.21995	0.25304	0.21402	0.20709	0.18708		0.15119	0.19329	0.1918	0.13435	0.16923
+/-	0.00017	0.00022	0.00025	0.00021	0.00021	0.00019		0.00015	0.00019	0.0021	0.00013	0.00017
$^{143}Nd/^{144}Nd$	0.511797	0.513313	0.514277	0.513130	0.512931	0.512358		0.511213	0.512535	0.512502	0.510835	0.511817
+/-	0.000007	0.000004	0.000008	0.000005	0.000003	0.000004		0.000006	0.000003	0.000003	0.000002	0.000002
$^{142}Nd/^{144}Nd$	1.141816	1.141826	1.141844	1.141836	1.141835	1.141814		1.141809	1.141830	1.141815	1.141779	1.141800
+/-	0.000019	0.000011	0.000020	0.000014	0.000009	0.000010		0.000018	0.000020	0.000012	0.000004	0.000004

67667 Nd isotopic data corrected for neutron capture by $^{143}Nd/^{144}Nd$ = 4 ppm and $^{142}Nd/^{144}Nd$ = 8 ppm

Table 4 Mg-suite and FAS whole rock data used in Sm-Nd whole rock isochron

Sample	$^{147}Sm/^{144}Nd$	±	$^{143}Nd/^{144}Nd$	±
Mg-suite				
14321	0.13435	0.00013	0.510835	0.000010
76535	0.15592	0.00014	0.511443	0.000010
15445	0.16923	0.00017	0.511826	0.000010
77215	0.17540	0.00018	0.512007	0.000010
76238	0.17480	0.00017	0.511996	0.000010
76355	0.18100	0.00018	0.512169	0.000010
67667	0.19329	0.00019	0.512535	0.000010
73255	0.23800	0.00020	0.513818	0.000010
FAS				
65315	0.15280	0.00015	0.511323	0.000014
62255	0.15400	0.00015	0.511381	0.000010
15415	0.15900	0.00016	0.511535	0.000014
60025	0.15892	0.00016	0.511542	0.000010
60016	0.16083	0.00017	0.511598	0.000010
62237	0.18093	0.00027	0.512143	0.000011
65315	0.15280	0.00015	0.511323	0.000014

Data corrected for neutron capture and normalized to JNdi = 0.512105. Date from Carlson et al., (2014), Sio et al. (2020), Gaffney et al., 2015; 2019), Boyet et al. (2015), and this investigation.