Lunar Crustal History from Isotopic Studies of Lunar Anorthosites

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Abstract

Anorthosites occur ubiquitously within the lunar crust at depths of ~3-30 km in apparent confirmation of the Lunar Magma Ocean (LMO) hypothesis. We present recent chronological studies of anorthosites that are relevant both to the LMO hypothesis and to the lunar cataclysm hypothesis. Old (~4.4 Ga) ages have been determined for some Apollo 16 anorthosites, and primitive initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been measured for several, but well-defined Rb-Sr ages concordant with the Sm-Nd ages have not been determined until now. Lunar ferroan anorthosite (FAN) 67075, a Feldspathic Fragmental Breccia (FFB) collected near the rim of North Ray Crater, has concordant Sm-Nd and Rb-Sr ages of 4.47±0.07 Ga. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ determined from the Sm-Nd isochron corresponds to $\varepsilon_{\text{Nd}}$,$_{\text{CHUR}}=0.3\pm0.5$ compared to a Chondritic Uniform Reservoir, or $\varepsilon_{\text{Nd}}$,$_{\text{HEDPB}}=-0.6\pm0.5$ compared to the initial $^{143}\text{Nd}/^{144}\text{Nd}$ of the HED Parent Body. Lunar anorthosites often have $\varepsilon_{\text{Nd}}$,$_{\text{CHUR}}>0$ when compared to CHUR, apparently inconsistent with derivation from a single lunar magma ocean. If lunar initial $^{143}\text{Nd}/^{144}\text{Nd}$ is taken equal to that in the HED parent body, $\varepsilon_{\text{Nd}}$,$_{\text{HEDPB}}<0$ for most anorthosites, but enough variability remains among the anorthosite data alone to suggest that lunar anorthosites do not derive from a single source, i.e., they are not all products of the LMO. An anorthositic clast from desert meteorite Dhofar 908 has an $^{39}\text{Ar}-^{40}\text{Ar}$ age of 4.42±0.04 Ga, within the error limits the same as the age of FAN 67075, and also the same as the 4.36-4.41±0.035 Ga $^{39}\text{Ar}-^{40}\text{Ar}$ age of anorthositic clast Y-86032,116 in Antarctic meteorite Yamato-86032. We conclude: (i) Lunar anorthosites come from diverse sources. Orbital geochemical studies confirm variability in lunar crustal composition. We suggest that the variability extends to anorthosites alone as shown by the Sm-Nd data and the existence of magnesian anorthosites (MAN), sodic anorthosites (SAN), and “An93 anorthosites” in addition to FAN. (ii) Anorthositic clasts in lunar meteorites retain “high” Ar-Ar ages compared to Apollo anorthosites, a hint that “cataclysmic” impacts were less energetic in the mostly farside source regions of these meteorites than on the lunar nearside.

Introduction: Anorthosites occur ubiquitously within the lunar crust at depths of ~3-30 km in apparent confirmation of the Lunar Magma Ocean (LMO) hypothesis (Ohtake et al. 2009). The type of anorthosites most frequently observed in the lunar sample collection is ferroan anorthosites, or FANs. FANs typically contain >90% modal plagioclase. They are characterized by values of Mg’ ~<70 in their mafic minerals, where Mg’ is defined as

$$
\text{Mg’} = 100 x \{|\text{MgO}|/(|\text{MgO}| + |\text{FeO}|)\}
$$

and [MgO] and [FeO] are the molar abundances of MgO and FeO, respectively, in mafic minerals, i.e., olivine and pyroxene. FANs also are characterized by An values >An96, where

$$
\text{An} = 100 x \{|\text{CaO}|/(|\text{CaO}|+|\text{Na}_2\text{O}|+|\text{K}_2\text{O}|)\}
$$

and [CaO], [Na$_2$O], and [K$_2$O] are the molar abundances of CaO, Na$_2$O, and K$_2$O, respectively, in plagioclase (Papike et al., 1998). Because of their relatively high FeO content, which, it has been argued, would make them buoyant in a global LMO (Warren, 1990) FANs are widely accepted as having formed the initial lunar crust via flotation accumulation at the surface of the primordial LMO. However, it is becoming increasingly apparent that FANs are not the only type of anorthosites occurring in the present lunar highlands crust. In this paper we consider three additional lunar anorthosite types: “magnesian anorthosite” (MAN, Takeda et al., 2006; Arai et al., 2007), “sodic anorthosite” (SAN, Norman and Taylor, 1992) and “An93
We recently have dated lunar FAN 67075, a Feldspathic Fragmental Breccia (FFB) collected near the rim of North Ray Crater, by the Sm-Nd and Rb-Sr techniques (Nyquist et al., 2010). This is the first time that concordant ages have been obtained by these techniques on a lunar FAN. In combination with the chronological information provided by the Sm-Nd and Rb-Sr methods, the initial isotopic ratios $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ present in the anorthosites when they solidified provide constraints on the Sm/Nd and Rb/Sr ratios, respectively, in precursor materials. In the case of lunar FANs, the “precursor materials”, are assumed to be present in the LMO. But, not all of the different types of lunar anorthosite can come from a single LMO, implying more complex magmatic evolution in the lunar highlands crust.

We also have dated an anorthositic white clast (WC) and surrounding matrix in lunar meteorite Dhofar 908 by the $^{39}\text{Ar}/^{40}\text{Ar}$ technique and measured whole rock (WR) Sm-Nd data for a companion sample of the white clast. We discuss the significance of the ages of these and other anorthosites for the early magmatic and bombardment history of the moon.

**Mg’ vs. An for the studied anorthosites:** Fig. 1 shows Mg’ in mafic minerals vs. An in plagioclase for the anorthosites discussed in this paper. We emphasize FAN 67075 in the discussion because the new Sm-Nd and Rb-Sr data for it provide some pieces hitherto missing from the FAN puzzle. Fig. 1 shows that Mg’ ~55 and An~97 for 67075 are typical of lunar FANs as shown in the lower elongated field. FAN clasts occur ubiquitously in lunar highland meteorites like Yamato 86032, hereafter Y-86032. Although Y-86032 has been studied by many authors, the studies of a slab cut from the meteorite (cf. Nyquist et al., 2006; Yamaguchi et al., 2010) serve best to put the results of these studies into the physical and compositional context of the lunar crust at the location from which this rock was launched into space by the impact of a large meteorite ~7-10 Ma ago (Nyquist et al., 2006). The texture of Yamato-86032 is that of “breccias within a breccia” as is also the case for most of the lunar highlands meteorites. However, preserved within the breccia generations are a few “pristine” anorthosite clasts consisting of rare mafic minerals (olivine, orthopyroxene, and augite) adhering to plagioclase fragments. In Fig. 1, the compositional data for these clasts are shown by red squares, green circles, and a blue triangle according to whether the mafic mineral analysed was olivine (olv), orthopyroxene (opx), or augite (aug), respectively. The Yamato-86032 clasts are designated by “NCn” in Fig. 1, where “N” identifies the polished thin section (PTS) in which they were observed, and “n” was assigned according to the sequence of analysis. The rectangle labeled “An93” in Fig. 1 shows the reconstructed composition of An 93 anorthosite. (cf. Yamaguchi et al., 2010, for more detailed descriptions).

The composition of An 93 anorthosite shown in Fig. 1 was inferred from analyses of several hundred individual olivine and plagioclase grains in the “Light Gray” (LG) breccia lithology that comprised a major portion of the slab cut from Y-86032. Although LG contained rare mineral grains of other origins, the combined mineralogical, chemical, and isotopic data for LG shows “An93 anorthosite” to be the dominant lithology, as discussed in Nyquist et al. (2006) and Yamaguchi et al. (2010). Other anorthosites represented in Fig. 1 are the magnesian anorthosite clast (MAN) from Dhofar 489 (Takeda et al., 2006) and three sodic anorthosite (SAN) clasts from Apollo 16 breccia 67016: subsamples 334, 339, and 346 (Norman and Taylor, 1992).

**Rare Earth Elements (REE) in the anorthosites:** Trace element abundances in the studied anorthosites are shown in Figs. 2 and 3. Interestingly, although the major mineral composition of 67075 places it squarely among the FAN suite, its Rare Earth Element (REE)
abundances more closely match those of the dominantly An93 anorthosite sample Y-86032,28 than those of the “typical” FANs 60025, 62236, 61016, and 15415, the abundances of which plot within the shaded blue band in Fig. 2. This raises the issue of whether the REEs in 67075 are atypically high for a FAN, or whether those in the more well-known FANs are atypically low. Haskin et al. (1981), for example, concluded that it was difficult to account for the compositions and mineralogy of lunar anorthosites in terms of simple fractional crystallization from the LMO. In particular, they suggested that mafic phases in anorthosites accumulated from a magma ocean might be expected to be modally more abundant than observed in the most plagioclase-rich anorthosites, and that these mafic phases had been removed via reheating events. They appealed to impact tectonics as a heat source, suggesting that such processes might be regarded as integral parts of the overall mechanisms producing lunar anorthosites. They noted that the low $^{87}\text{Sr}/^{86}\text{Sr}$ in FANs required very early separation of Rb from Sr in the rocks. Their mechanism is local in nature, and therefore one might expect to find some FANs from which such early removal of Rb had not occurred. We briefly examine this hypothesis with the aid of Fig. 3, which compares Rb, Sr, Sm, and Nd abundances determined at the Johnson Space Center (JSC) for the anorthosites as part of the isotopic analyses.

**Rb, Sr, Sm, Nd abundances in anorthosites:** The abundances of the alkali element Rb, the alkaline earth element Sr, and the REE Sm and Nd in 67075 and plagioclase separated from it support the observations of Haskin et al. (1981). The abundances of the two REE in our bulk sample, as measured by the mass spectrometric isotope dilution technique, are in good agreement with those from the literature as seen by comparing Figs. 2 and 3. In the case of 67075, the analyses are of the same subsample as analysed at JSC by Hubbard et al. (1974) and again in by Shih et al. (2005). This observation supports the atypically high (for a FAN) REE abundances in the bulk rock of 67075. Moreover, the abundances of all these elements are a factor of ~2-4 higher even in plagioclase separated from 67075 compared to bulk analyses of the FANs with the lowest abundances of these elements. Also, Rb in bulk 67075 is high compared to those FANs with the lowest Rb content, in apparent agreement with the supposition by Haskin et al. (1981) that moderately volatile Rb has been lost from most FANs via reheating events. In fact, Fig. 3 shows that six Apollo 16 FANs are separated into two groups on the basis of their Rb contents: A high-Rb group with Rb > 0.39 ppm (e.g., 62236, 67215, and 67075), and a low-Rb group with Rb < 0.15 ppm (e.g., 15415, 61016, and 60025). Refractory, divalent, Sr has comparatively constant abundances in all of these FANs. The same is true of refractory, mostly divalent Eu (Fig. 2).

As will be shown below, the Sr and Nd isotopic data for 67075 are fully consistent with the hypothesis that it is a good candidate to be a flotation cumulate from the LMO. Adopting this hypothesis for the moment, it is interesting to note that the Heavy Rare Earth Element (HREE) abundances in Yamato-86032,28 LG (~An93 anorthosite) are nearly identical to those for FAN 67075, and that the Light Rare Earth Elements (LREE) differ by less than a factor of three between these two rocks. From a trace element viewpoint, it...
seems possible that both are derivative from the same or very similar parent magmas. As we will show, the isotopic systematics are permissive of such a scenario, but the lower An content of the An93 anorthosites compared FAN 67075 suggests the An93 anorthosites crystallized at a later stage of magma evolution.

**Crystallization Age of 67075 from Rb-Sr Data:**

Although $^{39}$Ar-$^{40}$Ar ages of ~3.95-4.04 Ga (1 Ga = 10$^9$ yrs) have been reported for 67075 (Turner et al., 1973; Huneke et al., 1977), our Rb-Sr and Sm-Nd ages for this anorthosite are both 4.47±0.07 Ga, i.e., completely concordant. The Sm-Nd isochron has already been presented (Nyquist et al., 2010). Similarly old Sm-Nd ages have been determined for Apollo 16 anorthosites 60025 (Carlson and Lugmair, 1988) and 67215 (Norman et al., 2003), but this is the first time that a well-defined Rb-Sr age that is concordant with the Sm-Nd ages have been determined for a lunar anorthosite. Figure 4 shows the Rb-Sr isochron.

Among 12 analyses of bulk and mineral separates from 67075, several show some evidence of minor isotopic disturbance. This is particularly true of the whole rock (WR) sample. A leachate from the whole rock WR(l) suggests that the disturbance is most likely related to mobilization of moderately volatile Rb, in this case via Rb loss. In an experimental study, Nyquist et al. (1991) showed that heating lunar basalt 15555 in vacuo for a week caused significant loss of Rb. The losses were ~40% and ~85%, at 800°C and 1000°C, respectively. For 67075, the probable time of Rb loss was during the reheating event which reset the $^{39}$Ar-$^{40}$Ar age to 3.98±0.05 Ga. The time-temperature parameters of the 67075 event are unknown, but in the experimental study, Ar was nearly quantitatively lost from those phases contributing to the first ~50% of the $^{39}$Ar release at 800°C, and substantially lost from even the most retentive phases at 1000°C. It thus appears that, compared to the two experiments, the amount of reheating experienced by 67075 corresponded most closely to the 800°C event. Additional quantification of the reheating event could be sought via mineralogical/petrological studies.

Some of the Rb present in 67075 may have existed in late-crystallizing minor phases sensitive to reheating. However, the major phases appear to have been largely unaffected, and define an isochron for which all of the data lie within 1 part in 10,000 in $^{87}$Sr/$^{86}$Sr, i.e., within 1 $\varepsilon$-unit of the best-fit isochron (cf. Fig. 4 inset). The points lying on the isochron include not only the residues after leaching of the major minerals plagioclase (Plag), pyroxene (Px), and a combined pyroxene-ilmenite separate (px+ilm), but also the leachates from the plagioclase separates, Plag2(l) and Plag3(l) (Fig. 4).

The latter are apparently enriched in Rb due to leaching of plagioclase surfaces enriched in Rb (and K) by crystal zoning during igneous crystallization. Plag3(l), the highest point on the isochron was a leachate with 1N HCl, whereas Plag2(l) was a leachate with stronger 2N HCl, and was somewhat less enriched in Rb over Sr. These two points with the residue of a mixed (pyroxene + ilmenite) separate plus the low Rb/Sr plagioclase data define the isochron. We consider that the age of 4.47±0.07 Ga derived from the isochron fit to these data is robust within its error limits. Initial $^{87}$Sr/$^{86}$Sr ($I_{87}$) = 0.699045±14 from the isochron fit, where the 2σ error limits apply to the last digits.

**Rb-mobilization among FANs ~4.0 Ga ago:** Further evidence that the Rb-disturbances recorded in 67075 originated at the time of Ar-out-gassing ~3.98 Ga ago is provided by the Rb-Sr isotopic systematics of bulk samples of anorthosites, mostly Apollo 16 FANs. Fig. 5 shows that the isotopic data for the bulk anorthosites tend to scatter between the 4.47±0.07 Ga primary isochron for 67075 and a secondary isochron corresponding to an ~4.0 Ga age for major Rb-mobilization. The reference isochron for 4.00 Ga shown in the figure is from Nyquist et al. (2006) and was constructed for the Light Gray lithology (,28LG, 2N HCl, whereas Plag2(l) was a leachate with stronger 2N HCl, and was somewhat less enriched in Rb over Sr. These two points with the residue of a mixed (pyroxene + ilmenite) separate plus the low Rb/Sr plagioclase data define the isochron. We consider that the age of 4.47±0.07 Ga derived from the isochron fit to these data is robust within its error limits. Initial $^{87}$Sr/$^{86}$Sr ($I_{87}$) = 0.699045±14 from the isochron fit, where the 2σ error limits apply to the last digits.

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anorthosites dates an event that affected KREEP-rich rocks as well. Possibly the event dated is the formation of the Nectaris basin, the age of which was placed at 3.89±0.02 Ga ago by Stöffler and Ryder (2001). Alternatively, KREEP accompanied by volatilized Rb, as well as some of the anorthositic breccias may have been delivered to the Apollo 16 via the impact that formed the Imbrium basin in the KREEP-rich Procellarum KREEP Terrain (PKT) (Norman et al., 2010). Nevertheless, the fact that the secondary Rb-Sr isochron for the Apollo 16 samples (Fig. 5) shows an age contemporaneous with that recorded in impact melt in the Yamato-86032 meteorite, thought to derive from the lunar farside (Nyquist et al., 2006), is a strong indication that the LHB was global in extent.

That data for some anorthosites, like 15415, for example, lie to the right of the secondary isochron in Fig. 5 is further evidence of the volatility of Rb in the lunar environment. Because of the low Rb abundance in the rock itself, it is easily “contaminated” with mobilized Rb as already noted. The relatively young Rb-Sr model age of ~2.7 Ga for 15415 suggests such Rb mobilization occurred post-LHB and comparatively recently, perhaps associated with Rb volatilization accompanying formation of a moderately-sized crater local to the Apollo 15 site.

Thus, there is ample evidence that Rb volatility has played a role in the history of lunar anorthosites. Such evidence lends further plausibility to the suggestion of Haskin et al. (1981) that Rb volatility also may have played an earlier role, since the impact rate during the accre tionary phase of the moon must have greatly exceeded even that occurring during the Late Heavy Bombardment. Perhaps the accretionary impacts played a role in establishing the dichotomy between the high-Rb and low-Rb FANs that is evident in Fig. 3, for example. That plagioclase separated from high-Rb 67075 mimics the Rb, Sr, Sm, and Nd systematics of the low-Rb FANs suggests that they may be the residue of one or more processes that stripped them of volatile Rb hosted mainly in plagioclase itself as well as of the mafic phases hosting REE. This possibility, first suggested by Haskin et al. (1981) merits serious consideration and investigation.

Another observation from the Rb-Sr data that is of significance in the context of this paper is that the Rb-Sr systematics of Y-86032,28 LG, dominantly An93 anorthosite, are identical to those of low-Rb FANs like 60015 and 60025. This observation implies that igneous differentiation of magmas from those giving rise to An93 anorthosites was an early and perhaps primary lunar magmatic process.

**Sm-Nd Age of 67075 and εNd of Lunar Anorthosites:** A Sm-Nd isochron corresponding to an age T = 4.47±0.07 Ga for 67075 was reported by Nyquist et al., (2010a). Fig. 6 reproduces their data including a comparison to the Sm-Nd data for a CHondritic Uniform Reservoir (CHUR) and to the HED (Howardite-Eucrite-Diogenite) Parent Body (HEDPB).

The Sm-Nd age of 67075 of 4.47±0.07 Ga is in perfect agreement with its Rb-Sr age. The latter was calculated using the decay constant, \( \lambda_{87^{\text{Rb}}} = 0.01402 \text{ Ga}^{-1} \) as recommended by Begemann et al. (2001) following the work of Minster et al. (1982). It should be noted that ages using this value of the decay constant
The units at the age of the solar system of 4.568 Ga (Jacobsen and Wasserburg, 1984) means the initial reservoir. The reference reservoir is often used to CHUR values of Jacobsen and Wasserburg (1984). However, we have determined several internal mineral isochrons for both basaltic and cumulate eucrites (Nyquist et al., 2004; 2006). Values of $\varepsilon_{\text{Nd}}$ relative to a reference Sm-Nd reservoir are defined in the usual way:

$$\varepsilon_{\text{Nd},\text{REF}} = [\varepsilon_{\text{Nd},\text{sam}} - \varepsilon_{\text{Nd},\text{CHUR},\text{REF}}] \times 10^6.$$

Here the subscripts “I”, “sam”, and “REF” mean “initial”, “sample”, and “reference reservoir”, respectively. Thus, $\varepsilon_{\text{Nd},\text{sam}}$ means the initial $\varepsilon_{\text{Nd}}$ ratio in a rock sample when it crystallized, and $\varepsilon_{\text{Nd},\text{REF}}$ means the initial $\varepsilon_{\text{Nd}}$ ratio in the reference reservoir. The reference reservoir is often chosen to be “CHUR” for a “CHondritic Uniform Reservoir” (Jacobsen and Wasserburg, 1984). However, we have determined several internal mineral isochrons for both basaltic and cumulate eucrites (Nyquist et al., 2004) from the Howardite-Eucrite-Diogenite parent body (HED PB) which give values of $\varepsilon_{\text{Nd}}$ higher than the Jacobsen and Wasserburg (1984) value of $\varepsilon_{\text{Nd}}$ for 60025 done at JSC (Shih et al., 2005) and plotted at $T = 4.42\pm0.02$ Ga (Carlson and Lugmair, 1988). The new values of $(T, \varepsilon_{\text{Nd}})$ for 67075, as well as for the mineral isochron for combined data from Yamato 86032,28 LG and 44DG are in agreement at $\varepsilon_{\text{Nd}}$ values slightly more positive than would be found in a CHUR reservoir at the corresponding ages, but slightly negative relative to HEDPB. Thus, we think that at least for data from our laboratory the value of initial $\varepsilon_{\text{Nd}}$ is $0.505937$ for the HED PB is a better reference for lunar initial $\varepsilon_{\text{Nd}}$ data. (The Nd isotopic data are normalized to $146\text{Nd}/144\text{Nd} = 0.724140$ and adjusted to $143\text{Nd}/144\text{Nd} = 0.511138$ for Ames Nd metal standard (Wasserburg et al., 1981; Nyquist et al., 1990). For the HED PB reference, the Sm-Nd isotopic systematics of the aforementioned anorthosites, plus 67215, and the An97 anorthosite found in Y-86302,116 GC are all consistent with derivation from an LMO initially chondritic in REE abundances.

**Discussion:**

**Petrogenesis of the lunar crust**

Because the $\varepsilon_{\text{Nd}}$ values increase with time proportionally to $147\text{Sm}/144\text{Nd}$, the $\varepsilon_{\text{Nd}}$ values for reservoirs in which $147\text{Sm}/144\text{Nd}$ is $> 0.1967$ become progressively more positive for samples of younger ages derived from such reservoirs, whereas for reservoirs in which $147\text{Sm}/144\text{Nd}$ is $< 0.1967$ the $\varepsilon_{\text{Nd}}$ values become progressively more negative. Here we define the parameter

$$\mu = 147\text{Sm}/144\text{Nd}.$$
Fig. 7 illustrates the measured Sm-Nd data for bulk ("whole rock") anorthosite samples. Whereas, some FANS, shown by yellow squares in the diagram, have $^{147}\text{Sm}/^{144}\text{Nd}$ values $< 0.1967$ (CHUR), as expected for plagioclase cumulates from the LMO, values of $^{147}\text{Sm}/^{144}\text{Nd} \approx 0.1967$ are approximately equally probable. Data shown as red or pink squares are for anorthosites that formed via flotation on the LMO contemporaneously (Borg et al., 1999). Thus, FAN 62236 could not have formed via flotation on the LMO contemporaneously with the older FANs.

The (T, $\varepsilon_{\text{Nd}}$) diagram for many of the samples as shown in Fig. 7. The data used in Fig. 8 are largely independent of those used for Fig. 7, but the two figures convey similar conclusions. For example, Fig. 8 illustrates that the reason why data for the bulk sample of FAN 62236 fall off the $\approx 4.42$ Ga isochron in Fig. 7 is because this FAN is really $\approx 4.29$ Ga old as obtained from a Sm-Nd internal mineral isochron (Borg et al., 1999). Thus, FAN 62236 could not have formed via flotation on the LMO contemporaneously with the older FANs.

The (T, $\varepsilon_{\text{Nd}}$) values of 62236, probably magnesian anorthosite Dho 908WC, and possibly FAN 67215 suggest an alternate style of petrogenesis. The Nd that was incorporated into these rocks when they crystallized must have undergone prior evolution in source regions with $\mu \geq 0.1967$, even though the present-day rocks have $\mu$-values significantly below 0.1967. That some igneous differentiation must have occurred within the crust is illustrated by bulk rock $\mu$-values $> 0.1967$ as shown in Fig. 7. The Precursor source for 62236 must have been significantly enriched in mafic minerals because $\mu \approx 0.33$ would be required to account for Nd-isotopic evolution away from that in 67075 within the time interval from 4.47 to 4.29 Ga ago. This is a high $\mu$-value, but not impossibly so. Fig. 6 shows that pyroxene separated from 67075 had similarly high $^{147}\text{Sm}/^{144}\text{Nd}$ ($\mu$) values.

The Sm-Nd data for Dho 908WC also indicate prior evolution in a source region with Sm/Nd greater than the chondritic value, and indicate a similar, mafic, precursor as for 62236. The situation for Dho 908WC is somewhat ambiguous because it was not possible to obtain an internal isochron for this monomineralic clast. The data are shown at the age obtained from an isochron formed with the data from a "white" (W) clast Y-86032,133W, assuming that the clasts represent similar anorthosites that are likely to be contemporaneous. Both lunar meteorites are likely from the farside, but their places of origin are nearly certainly different (Karuji et al., 2010). Nevertheless, both are characterized by An$_{97}$ anorthosite (Yamaguchi et al., 2010 and Yamaguchi, p. comm.). Although Mg" for Dho 908 WC is indeterminate, a reasonable assumption is that both could have formed from the same large-scale parental magma. In this case, because the Sm-Nd data for both lie above the $\approx 4.42$ Ga reference isochron in Fig. 7, the parental magma is not the same as for 67075, i.e., the
LMO, but could have been a “magma sea” of more localized extent. Because of the possibility that these two clasts are not cogenetic, the Sm-Nd age derived from them is best considered to be only an estimate of their time of formation.

The $^{39}\text{Ar} - ^{40}\text{Ar}$ age of Dho 908WC is individually defined at 4.42±0.04 Ga (Nyquist et al., 2010). The Dho 908WC datum plotted at this age (open symbol in Fig. 8) suggests a precursor source region with $\mu$ equal or greater than for the source of 62236, and perhaps formed slightly earlier. It is impossible to plot an equivalent datum for Y-86032,133W because the $^{39}\text{Ar} - ^{40}\text{Ar}$ data indicate that this clast was strongly outgassed at ~3.8 Ga, the breccia assembly age of Y-86032, and reach maximum values of only ~4.23 Ga, a lower limit on the crystallization age of this clast (Nyquist et al., 2006).

We emphasize that the Sm-Nd data for Dho 908WC and Y86032,133W are important in spite of the fact that it was impossible to determine a precisely defined internal isochron for Y86032,133W or an internal isochron for Dho 908WC. As noted above, the bulk rock data for these clasts plot above the 4.42 Ga reference isochron in Fig. 8, showing that they were not formed contemporaneously with those FANs defining the reference isochron. The data for Dho 908WC and Y86032,133W show that the 62236 data are not unique in indicating precursor source regions with elevated $\mu$-values.

In Fig. 8 the data for the majority of bulk FANs are represented by the elongated blue parallelogram, and are fully consistent with internal mineral isochron data for 60025, 67075, and the combined data for Y-86032,28LG and .44DG. These rocks appear to be the oldest lunar anorthosites, and thus to be the best candidates to have been derived from the LMO. We suggest that source regions like those required for 62236, Dho 908, and Y-86032,133 might have been dominantly mafic plutons formed within an earlier lunar crust, and subsequently remelted during later impact or tectonic events. The RREE and other trace elements extracted during remelting may have been carried via migrating magmas to mix with magmas produced by remelting more trace element-poor plutons of generally feldspathic composition. Another possibility is that these anorthosites crystallized from magma seas formed comparatively late during lunar accretion, and which incorporated some Nd from lunar upper mantle cumulates formed late in the crystallization sequence of the main LMO (cf. Snyder and Taylor, Fig. 5, cumulates formed after ~90-99 per cent solidification (PCS) of the LMO). In this case, an explanation is required as to why Nd from the LREE-enriched residual magma (“urKREEP”) was excluded, however.

Another circumstance suggested by the (T, $\varepsilon_{\text{Nd}}$) data is illustrated in Fig. 8 for Y-86032,116GC, plotted at its $^{39}\text{Ar} - ^{40}\text{Ar}$ age (Nyquist et al., 2006), and possibly for 67075 and the other FANs as well if the lunar initial Sm-Nd systematics were equal to those in the HEDPB. In that case, a hypothetical evolution line for LREE-enriched precursors with $\mu = 0.121$ and starting at the (T,$\varepsilon_{\text{Nd}}$) parameters for the HEDPB simultaneously passes through the (T, $\varepsilon_{\text{Nd}}$) data points for 67075, and Y-86032,116GC (GC = gray clast). This evolutionary path could approximate that in residual magma in the LMO as it becomes progressively enriched in LREE. Alternatively, comparison to the 67075 isochron diagram (Fig. 6) shows that among major mineral processes, such low $\mu$-values are expected only for plagioclase. Comparison to Fig. 7 shows that similar $\mu$-values occur in bulk anorthosites like 60025 and 15415. Rocks for which the (T, $\varepsilon_{\text{Nd}}$) data plot along this evolution line either crystallized directly from the LMO, or incorporated Nd derived mostly from the LMO and/or plagioclase at late stages of lunar crust formation.

Indepedently of detailed models for lunar crustal genesis, the dispersion of $^{147}\text{Sm} / ^{144}\text{Nd}$ values among bulk lunar FANS from ~0.15 to >~0.20 as is illustrated in Fig. 7 shows the effect of magmatic differentiation either accompanying primary igneous processes, or driven by remelting following tectonic or impact processes as envisioned by Haskin et al. (1981). Thus, we envision the lunar crust to have been a physically dynamic environment in which complex styles of magmatism frequently occurred.

**Comparison to U-Pb chronology and the “lunar cataclysm”**

The U-Pb and Pb-Pb dating methods are in principle capable of yielding more precise ages than either the Rb-Sr or the Sm-Nd method. The results of two U-Pb studies seem particularly significant in the context of the present discussion, and are considered briefly in the following.

Oberli et al. (1979) reported U-Pb systematics for 67075 showing that it contains a high proportion of “unsupported” radiogenic Pb, and that its U-Pb data are consistent with the linear array of lunar crustal anorthosites between a $^{207}\text{Pb} / ^{206}\text{Pb}$ age of ~3.86 Ga and a concordia intercept age of 4.47±0.03 Ga, which they interpreted as the age of the lunar crust. This “upper intercept” U-Pb age is in perfect agreement with our Rb-Sr and Sm-Nd ages for 67075.

The work of Oberli et al. (1979) continued the earlier U-Pb studies of Tera et al. (1974) and Tera and Wasserburg (1974). A well-known conclusion of those
studies is that all of the then-available U-Pb data for lunar crustal rocks formed a linear array on a U-Pb concordia diagram intersecting concordia at ~3.95 Ga and ~4.42 Ga, respectively. Tera et al. (1974) and Tera and Wasserburg (1974) interpreted this linear data array to mean that the lunar crust formed at ~4.42 Ga, and that a “terminal cataclastic bombardment” affected the moon at ~3.95 Ga. (This “terminal cataclasm” also has been called the Late Heavy Bombardment, LHB) by other workers. The data array used by Tera and Wasserburg (1974) to reach these conclusions included KREEP-rich rocks, however. Indeed the reference isochron to which they referred was anchored to the data for KREEP-basalt (or impact melt rock) 14310. KREEP-rich rocks are so enriched in U, and therefore radiogenic Pb, that data from them are weighted heavily in any analysis that includes them. Recent studies of Oberli et al. (1979) added a number of KREEP-poor highland rocks to the U-Pb data of Tera and Wasserburg (1974), and thereby found slightly modified values for the concordia intercepts. In particular, the upper intersection age became 4.47±0.03 Ga as noted above. They also obtained a “cataclysm age” of 3.83 (+0.10, -0.05) Ga from an internal 207Pb/206Pb-204Pb/206Pb isochron for leachates and leachate-residues for lunar highlands regolith breccia 66075. They made no attempt to distinguish this age, obtained for an individual lunar anorthosite from the age of the general lunar cataclasm. Oberli et al. (1979) also reported an internal 207Pb/206Pb-204Pb/206Pb isochron age of 4.17±0.02 Ga for highlands breccia 78155, accompanied by an 39Ar-40Ar age with the same value. They interpreted these ages as predating the more generally defined lunar cataclasm. A two-stage model yielded an upper concordia intersection age of 4.51±0.04 Ga for 78155, which Oberli et al. (1979) interpret as an alternative estimate of the “crustal formation age”. Although consistent with 4.47±0.03 Ga within the mutual error limits, both ages indicate relatively early crustal formation as compared to the Sm-Nd ages of anorthosites summarized in Fig. 7.

Recently, Connelly and Borg (2010) revisited the Pb isotopic systematics of FAN 60025. Using modern methods and instrumentation, they report a “preliminary” 207Pb/206Pb-204Pb/206Pb internal age of 4382±8 Ma for this FAN (1 Ma = 10^6 years). This precise, but comparatively young, age for 60025 would move it to the extreme low-age end of the 67075 error parallelogram in the (T,εNd) diagram (Fig. 8). This result undercuts the previously widely held assumption that this FAN is typical of the type of flotation cumulates to be expected on the LMO. Anorthosite 60025 is one of the “pure” ferroan anorthosites (PFA) considered by Warren (1990) in presenting his plagioclase flotation model for the LMO, for example.

Either of the “crustal formation” ages suggested by Tera and Wasserburg (1974), or Oberli et al. (1979) are consistent within error limits with the concordant Rb-Sr and Sm-Nd ages determined here for 67075. However, further resolution of ages among lunar anorthosites is important if one considers that the lunar crust is composed of a variety of crustal rocks, which could have different characteristic ages. This possibility has hitherto been accepted for the so-called Mg-suite rocks, which are widely interpreted as being present within an anorthositic lunar crust of “FAN” composition. However, the above discussion illustrates that there is growing evidence that lunar FANs are not all contemporaneous. This circumstance has hitherto been most vividly evident in the unusually young (for a FAN) age of ~4.29 Ga for FAN 62236 (Borg et al., 1999). Interestingly, anorthosite 62236 has low overall REE abundances like 60025, and was one of the “mafic” ferroan anorthosites (MFA) considered by Warren (1990) in formulating his plagioclase flotation model of LMO evolution. Both PFA and MFA, to use Warren’s terms, have Mg’ values of ~0.62 (MFA) to 0.63 (PFA). Thus, the ages and Sm-Nd isotopic systematic of these two FANs have a direct bearing on models of lunar crust formation via flotation accumulation of plagioclase.

The age variation visible in the Sm-Nd data has been less visible in the data from other chronometers for several reasons. Among these reasons are: (a) U-Pb ages of highland rocks mostly show the effect of redistribution of volatile Pb during the lunar cataclasm as noted by Tera et al. (1974) and in the subsequent work of Oberli et al. (1979) and others. (b) 39Ar-40Ar ages of highland rocks are easily reset by post-impact thermal annealing, so that most 39Ar-40Ar ages of lunar highland rocks also show the ~3.9 Ga lunar cataclasm age; (c) Rb-Sr ages of highland rocks, although often not totally reset during the cataclastic bombardment, were relatively pervasively disturbed, so that reliable crystallization ages often cannot be determined by this method. A further complicating factor is that the mineral isochron methods, i.e., Sm-Nd and Rb-Sr, require analysis of two or more mineral phases, and lunar anorthosites are nearly monomineralic plagioclase.
The \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) data for lunar meteorites, however, seem to present a more hopeful situation for determining the crystallization ages of lunar meteoritic anorthosites. This situation appears to be related to the fact that lunar highlands meteorites come from random positions on the lunar surface, including in particular the lunar farside, and unlike the case for the returned lunar samples, do not come exclusively from the lunar nearside. However, the \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages of anorthosites in lunar meteorites compared to anorthosites from the lunar nearside

\(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages of anorthosites in lunar meteorites compared to anorthosites from the lunar nearside

Fig. 9 summarizes \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages of anorthositic clasts studied at JSC for the Yamato-86032, Dho 489, and Dho 908 lunar highlands meteorites and compares them to \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages for anorthosites returned from the nearside of the moon by the Apollo and Luna missions. Both sample suites contain a few samples with \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages within the range of \(\sim 3.4\text{–} 4.5\) Ga crystallization ages of these lunar crustal rocks. However, the \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) age distribution of the nearside returned samples is skewed towards younger values than is the case for the meteoritic clasts. This effect would be more visibly pronounced if (a) the \(\sim 3.8\) Ga impact melt clast Y-86032, 30 dating breccia assembly were turned samples is skewed towards younger values than

The \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages for Apollo and meteoritic anorthosites are difficult to degas even in the laboratory. We thus tentatively ascribe the typically younger \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages found for anorthosites from the lunar nearside to a greater external energy input accompanying the impact formation of the large nearside meteorites. So far, among the lunar highlands meteorites that have been studied, each of them has had at least one anorthositic clast with a “pre-cataclysm” age. The recently determined \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) age of Dho 908 WC (Nyquist et al., 2010) is included among the \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages summarized in Fig. 8. Although Dho 908 WC contained a significant amount of terrestrial atmospheric Ar that degassed at low temperatures in a stepped temperature extraction, the last six extractions releasing 86-97% of the \(^{39}\text{Ar}\) gave nearly constant ages of \(4.42\pm 0.04\) Ga. This value is probably the best available age for the formation of this clast. That the age indicated by the combined Sm-Nd data for Dho 908 WC and Y-86032, 133W agrees with this \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) age within error limits (cf., Fig. 8), suggests that those two clasts represent similar anorthositic lithologies formed approximately contemporaneously, but at different places in the lunar highlands crust as discussed above.

The breccia matrix of the Dho 908 meteorite contained some trapped solar wind Ar, as well as \(^{40}\text{Ar}\) reimplanted from the lunar atmosphere. Nevertheless, a precise age of 4266\pm 20 Ma was obtained from an isochron plot in the \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) study (Nyquist et al., 2010b).

The \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages found for Dho 908 are comparable to \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages previously determined for clasts from the lunar highlands meteorites Dho 489 and Y-86032 (Takeda et al., 2006; Nyquist et al., 2006), and higher than \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages of \(\sim 3.95\text{–}4.04\) Ga for 67075 (Turner et al., 1973; Huneke et al., 1977), for example. \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages for two other FANs included in Fig. 9 are 3.93\pm 0.08 Ga for 67215 (Norman et al., 2003), and 4.15\pm 0.12 Ga for 60025 (Bogard, unpublished). These ages are in the range of the \(^{207}\text{Pb}/^{206}\text{Pb}\) ages attributed to the lunar cataclysmic bombardment by Tera et al. (1974), and clearly were reset or partially reset at that time. In contrast, anorthositic clasts in two of the lunar meteorites, Yamato 86032 and Dhofar 908, retain older \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages of \(\sim 4.35\text{–}4.42\) Ga, consistent with the Sm-Nd ages of the clasts (Fig. 9). The tendency for \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages from lunar meteorites to be greater than for those for returned samples from the lunar nearside is illustrated by the difference in the means of the two age distributions shown in the upper and lower panels, respectively, of Fig. 9: The mean \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) age for the returned meteorites is 4.22\pm 0.20 Ga, whereas the mean \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) age for the returned samples is 4.03\pm 0.28 Ga.

Anorthosites are difficult to degas even in the laboratory. We thus tentatively ascribe the typically younger \(^{39}\text{Ar}\)-\(^{40}\text{Ar}\) ages found for anorthosites from the lunar nearside to a greater external energy input accompanying the impact formation of the large nearside
lunar basins thereby leading to a generally greater degree of degassing of the nearside anorthosites.

**Conclusions:**

The earliest lunar anorthositic crust formed more than 4.4 Ga ago. This conclusion differs little from previous results, and thus previously widely-held views among lunar scientists. Nevertheless, an issue remains as to whether the time of crustal formation is closer to ~4.5 Ga ago than ~4.4 Ga ago. There is an impressive concordance between the Rb-Sr and Sm-Nd ages of 67075 and the earlier suggested “lunar crustal” age of 4.47±0.03 to 4.51±0.04 Ga based on U-Pb systematics. Also, a short period for lunar differentiation of ~50 Ma has been suggested based the short-lived Hf-W chronometer. The recent, apparently high-precision 207Pb-206Pb age of 4382±9 Ma for “typical” FAN 60025 underscores the possibility of multiple episodes of magmatism in the lunar crust, even for ferroan anorthosites.

Lunar anorthosites appear to come from diverse sources. The range of variability among lunar anorthosites in major element and trace element composition, ages, and initial Nd-isotopic compositions show that they do not derive from a single magma source. Thus, they cannot all be products of a global LMO. We note that orbital geochemical studies confirm variability in lunar crustal composition (Cahill et al., 2009; Ohtake et al., 2009).

The REE abundances of LMO-related magmas (or flotation cumulates) probably resembled those of 67075 and An93 anorthosites more than those of severely REE-depleted anorthosites like 60025. The large range in REE abundances and 147Sm/144Nd ratios among FANs, accompanied by the observation that both of these parameters in severely REE-depleted FANs like 60025 are nearly identical to the same parameters in plagioclase separated from 67075 is suggestive that the mafic phases were “squeezed out” of the latter, as suggested by Haskin et al. (1981). The existence of high-Rb and low-Rb FANs appears to be another manifestation of the same process, and is suggestive that the process is volatility related, since mafic phases are not good hosts for Rb. Rather, the lost Rb probably came from plagioclase, the major host of K and therefore Rb in anorthosites.

The Rb-Sr and Sm-Nd isotopic systematics of An93 anorthosite are identical to those of the oldest FANs. Unfortunately, pristine examples of “An93 anorthosite” have not yet been identified. Nevertheless, “whole rock” samples of Y-86032,28LG, predominantly An93 anorthosite, plot precisely on the ~4.4 Ga Rb-Sr and Sm-Nd bulk rock isochrons for FANs, and a combined mineral isochron for Y-86032,28LG and Y-86032,44 DG (~FAN) gives an age of 4.43±0.03 Ga. The Rb/Sr ratio of An93 anorthosite is intermediate to those of the high-Rb and low-Rb FANs. We believe these observations strongly suggest magmatic differentiation events within the lunar that were contemporaneous with its earliest formation.

The Rb/Sr and Sm/Nd isotopic systematics of magnesian anorthosites (“MAN”) remain poorly defined. So far, the only examples of this potentially important lithology are found in so-called “hot desert” meteorites. The intrinsic Rb/Sr systematics of hot desert meteorites are completely overprinted by terrestrial contamination. The present Sm-Nd and age data of the Dho 908 white clast (WC) suggest that its petrogenesis resembles that of isotopically unusual FAN 62236 more than that of FAN 67075. From a Sm-Nd isotopic viewpoint, 67075 is a better candidate to be a product of the LMO than 62236. Although Dho 906 belongs to the Dho 489 family of meteorites in which magnesian anorthosites were discovered by Takeda et al. (2006), the classification of Dho 908 as magnesian anorthosite is uncertain. Another possibility is that it is a metamorphosed FAN (A. Yamaguchi, p. comm., and Nyquist et al., 2010b). Better Sm-Nd data for magnesian anorthosites are highly desirable.

Anorthositic clasts in lunar meteorites that are apparently derived from the lunar farside tend to retain their crystallization ages in their 39Ar-40Ar age spectra. On the basis of the few currently available analyses, it appears that the 39Ar-40Ar ages of anorthositic clasts in lunar highland meteorites are less likely to have been reset by secondary heating events than anorthosites returned by the Apollo and Luna programs. This observation is a hint that “cataclysmic” impacts were less energetic in the source regions of these meteorites than on the lunar nearside.

Whether or not the apparent lunar asymmetry displayed by the 39Ar-40Ar data also is evident in the isotopic systematics of the other radiometric dating systems is not discernible from the available data. However, if “large” samples suitable for dating by isochron techniques were returned from the lunar farside, for example, it is probable that Rb-Sr ages could be reliably determined for some of them. It also is possible that some of the scatter observed in the bulk anorthosite data of Fig. 8 at low 147Sm/144Nd values is impact-related. A reduced level of impact-related scatter in the Sm-Nd data would make the accompanying conclusions concerning lunar crustal evolution more robust. Also, verification of the lunar cataclysm as a truly global event, as opposed to the result of a few large, basin-forming impacts on the lunar nearside, would be of fundamental importance. Thus, it seems probable that our picture of lunar crustal chronology would...
change in important ways if additional lunar samples were returned from the lunar farside by either automated or crewed missions.

References


