

Earliest high-Ti volcanism on the Moon: ^{40}Ar - ^{39}Ar , Sm-Nd, and Rb-Sr isotopic studies of Group D basalts from the Apollo 11 landing site

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Abstract—High-Ti basalts from the Apollo collections span a range in age from 3.87 Ga to 3.55 Ga. The oldest of these are the common Apollo 11 Group B2 basalts which yield evidence of some of the earliest melting of the lunar mantle beneath Mare Tranquillitatis. Rare Group D high-Ti basalts from Mare Tranquillitatis have been studied in an attempt to confirm a postulated link with Group B2 basalts (Jerde *et al.*, 1994). The initial Sr isotopic ratio of a known Group D basalt (0.69916 ± 3 at 3.85 Ga) lies at the lower end of the tight range for Group B2 basalts ($^{87}\text{Sr}/^{86}\text{Sr} = 0.69920$ to 0.69921). One known Group D basalt and a second postulated Group D basalt yield indistinguishable initial ϵ_{Nd} (1.2 ± 0.6 and 1.2 ± 0.3) and again lie at the lower end of the range for the Group B2 basalts from Apollo 11 ($+2.0 \pm 0.4$ to $+3.9 \pm 0.6$, at 3.85 Ga). A third sample has isotopic ($^{87}\text{Sr}/^{86}\text{Sr} = 0.69932 \pm 2$; $\epsilon_{\text{Nd}} = 2.5 \pm 0.4$; at 3.59 Ga; as per Snyder *et al.*, 1994b) and elemental characteristics similar to the Group A high-Ti basalts returned from the Apollo 11 landing site.

Ages of ^{40}Ar - ^{39}Ar have been determined for one known Group D basalt and a second postulated Group D basalt using step-heating with a continuous-wave laser. Suspected Group D basalt, 10002,1006, yielded disturbed age spectra on two separate runs, which was probably due to ^{39}Ar recoil effects. Using the "reduced plateau age" method of Turner *et al.* (1978), the ages derived from this sample were 3898 ± 19 and 3894 ± 19 Ma. Three separate runs of known Group D basalt 10002,116 yielded $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of 3798 ± 9 Ma, 3781 ± 8 Ma, and 3805 ± 7 Ma (all errors 2σ). Furthermore, this sample has apparently suffered significant ^{40}Ar loss either due to solar heating or due to meteorite impact. The loss of a significant proportion of ^{40}Ar at such a time means that the plateau ages underestimate the "true" crystallization age of the sample. Modelling of this Ar loss yields older, "true" ages of 3837 ± 18 , 3826 ± 16 , and 3836 ± 14 Ma. These ages overlap the ages of Group B2 high-Ti basalts (weighted average age = 3850 ± 20 Ma; range in ages = 3.80 to 3.90 Ga).

The combined evidence indicates that the Group D and B2 high-Ti basalts could be coeval and may be genetically related, possibly through increasing degrees of melting of a similar source region in the upper mantle of the Moon that formed >4.2 Ga ago. The Group D basalts were melted from the source first and contained 3–5 \times more trapped KREEP-like liquid than the later (by possibly only a few million years) Group B2 basalts. Furthermore, the relatively LREE- and Rb-enriched nature of these early magmas may lend credence to the idea that the decay of heat-producing elements enriched in the KREEP-like trapped liquid of upper mantle cumulates, such as K, U, and Th, could have initiated widespread lunar volcanism.

INTRODUCTION

Lunar basalts are higher in total Fe and Fe/Mg and generally lower in Al_2O_3 (<15 wt%), Na_2O (0.5 wt%), and K_2O than terrestrial basalts (Neal and Taylor, 1992). These characteristics, combined with the total lack of H_2O , leads to much lower viscosity, allowing the basalts to flow readily on the surface of the Moon and cover large basins with relatively thin flow-units. High-Ti basalts (>9 wt% TiO_2) from the Moon have no terrestrial equivalent. In fact, terrestrial basalts seldom reach 4 wt% TiO_2 (BVSP, 1981).

High-Ti basalts are the most abundant basalt group in the Apollo collections (Neal and Taylor, 1992). They are particularly conspicuous at the Apollo 11 and Apollo 17 landing sites. Furthermore, because they are considered to be melts of the uppermost mantle of the Moon (Snyder *et al.*, 1992, and references therein), they are paramount to an understanding of the evolution of the Moon's upper mantle as well as the differentiation of the magma ocean which crystallized to form the mantle (Snyder *et al.*, 1994b).

Five separate groups of high-Ti basalts have been recognized in returned samples from Mare Tranquillitatis (Apollo 11 landing site):

Groups A, B1, B2, B3, and D (Beaty and Albee, 1978). Group A is characterized by high K (>0.2 wt% K_2O) and REE ($\text{La} = 20$ – 34 ppm) and is the youngest, with an average age of 3.59 ± 0.04 Ga (Snyder *et al.*, 1994b). This group may consist of the crystallization products of a parent similar to the Apollo 17 orange glasses (Jerde *et al.*, 1994). Groups B1 and B3 exhibit low K (<0.12 wt% K_2O) and REE ($\text{La} = 4$ – 10 ppm) and have similar average ages of 3.67 ± 0.02 and 3.71 ± 0.02 Ga, respectively (Snyder *et al.*, 1994b). Group B2 basalts are characterized by relatively high REE ($\text{La} = 10$ – 24 ppm), yet low K (<0.08 wt% K_2O), and are by far the oldest group of high-Ti basalts found in the Apollo collections, with an average age of 3.85 ± 0.02 Ga (Snyder *et al.*, 1994b). Jerde *et al.* (1994) hypothesized that Group B2 basalts represented the parents of the more REE-enriched ($\text{La} = 32$ – 34 ppm) Group D basalts. In this model, Group D basalts would be derived from Group B2 basalts by simple addition of whitlockite (*i.e.*, trapped liquid). However, age information on the Group D basalts was nonexistent.

The purpose of this study is to determine ages, on a known Group D basalt (10002,116) and a suspected Group D basalt

TABLE 1. Nd and Sr isotopic composition of Apollo 11 high-Ti basalts.

Rock	wt.(mg)	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr*	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr ₍₀₎ †	T _{LUNI} ‡	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd*	¹⁴³ Nd/ ¹⁴⁴ Nd	ε _{Nd} (T)	T _{LUM} §
10002,98 (A)	31	4.67	168	0.0799	0.703751 ± 13	0.69963 ± 2	4.09	18.8	54.3	0.2089	0.513053 ± 12	2.5 ± 0.4	4.28
10002,116 (D)	29							21.9	67.6	0.1960	0.512684 ± 13	1.2 ± 0.3	4.29
10002,1006 (D)	21	1.35	139	0.0279	0.700709 ± 20	0.69916 ± 3	4.17	19.6	60.2	0.1972	0.512715 ± 12	1.2 ± 0.6	4.29

* Errors on the ⁸⁷Rb/⁸⁶Sr and ¹⁴⁷Sm/¹⁴⁴Nd ratios are <0.5% and <0.1%, respectively.

† ⁸⁷Sr/⁸⁶Sr initial ratios and ε_{Nd}(T) were calculated assuming and age of 3.59 Ga for 10002,98 and 3.85 Ga for 10002,116 and 10002,1006.

‡ T_{LUNI} (in Ga) calculated as per Nyquist *et al.* (1973).

§ T_{LUM} (in Ga) = 1/λ × ln[(¹⁴³Nd/¹⁴⁴Nd - 0.516149)/(¹⁴⁷Sm/¹⁴⁴Nd - 0.318) + 1]. T_{LUM} yields a model age at which the sample was in equilibrium with a Lunar Upper Mantle with a ¹⁴⁷Sm/¹⁴⁴Nd = 0.318 (Snyder *et al.*, 1994b) and which has a present-day ¹⁴³Nd/¹⁴⁴Nd = 0.516149.

(10002,1006; Snyder *et al.*, 1994a), as well as Nd and Sr isotopic compositions of these important, albeit rare, high-Ti basalts. A third sample taken from the Apollo 11 soil 10002, sample 10002,98, was also analyzed and classified as a Group A basalt.

SAMPLE PREPARATION AND ANALYTICAL METHODS

Based upon previous studies which suggested that they may be Group D basalts, three samples were selected for isotopic analyses. Further investigation of the samples lead to the conclusion that one of the samples, 10002,98, is actually a Group A basalt. All three samples were sieved from soil sample 10002 at the NASA-Johnson Space Center, Houston, Texas. Individual rock chips were either handpicked by our group or previously handpicked by other workers in the clean laboratories of the Curatorial Facility at NASA-JSC. Sample 10002,98 consisted of four fragments of 790 mg mass, nominally described as "basaltic." Macroscopic observation allowed the classification of all four fragments as vuggy olivine basalts. One of the fragments, free of microimpact features and weighing ~150 mg, was separated out and processed for isotopic analyses. Sample 10002,116 was the potted butt from a thin-section made of the parent sample (104). This potted butt was estimated at 160 mg and was set in epoxy. The epoxy was removed sequentially by treatment with methylene chloride and acetone (B. M. Bansal, pers. comm.). Sample 10002,1006 was an 85 mg mare basalt chip picked from the 2–4 mm fraction of soil subsample 10002,89. Approximately 44 mg was used for INA analysis (Snyder *et al.*, 1994a) and the remainder (~40 mg) was used for Ar-Ar, Rb-Sr, and Sm-Nd isotopic analyses.

Age calibration for the ⁴⁰Ar/³⁹Ar analyses was accomplished assuming a K-Ar age of 1071 Ma for standard hornblende 3gr (Roddick, 1983). The standard mineral grains were irradiated within the same Al foil packets as the lunar basalt sample grains, thereby virtually eliminating any problems due to neutron flux gradients. The samples were irradiated for 14 days in location L-67 of the Phoenix-Ford Memorial nuclear reactor at the University of Michigan. Laser step-heating was performed using a defocused laser beam from a Coherent INNOVA model 70 Ar ion laser. Each heating step lasted 1 min, followed by 2 min of gas clean up with 2 SAES 10 l/s ST-101 alloy getters.

Argon analyses were performed using a MAP-215 mass spectrometer equipped with a Balzers electron multiplier. All measurements were corrected for blanks, mass discrimination and neutron-induced interferences. Fusion system blanks were performed frequently (typically every fourth sample fraction) and the blanks at masses 36 to 40 were, in order, ~8 × 10⁻¹⁴, 1.3 × 10⁻¹³, 3 × 10⁻¹⁴, 5 × 10⁻¹⁴ and 3 × 10⁻¹² ml STP. Mass discrimination was measured once per day using an aliquot of ~2.5 × 10⁻⁹ ml STP of atmospheric Ar. All Ar isotope ratios were corrected for interference due to nuclear reactions with K and Ca, and the ³⁶Ar peak was corrected for contributions from the decay of ³⁶Cl.

All ages were calculated assuming an initial ⁴⁰Ar/³⁶Ar ratio of 1.17, which was derived from isochron analysis of the high temperature fractions of the comparatively ³⁶Ar-rich sample 10002,1006. The assumed initial ⁴⁰Ar/³⁶Ar ratio is nearly unity and is similar to values measured for the solar-wind component (*e.g.*, Ozima and Podosek, 1983; Shaeffer *et al.*, 1976).

Samples were prepared for Rb-Sr and Sm-Nd isotopic analyses by crushing in acetone in a boron carbide mortar under a flow of better than class 100 air and then dissolved in HF, HNO₃, and HCl. Isotope dilution measurements were made on a 10–15% split of this solution with ⁸⁷Rb-⁸⁴Sr and ¹⁴⁹Sm-¹⁵⁰Nd mixed spikes. Total-process blanks for chemical procedures were always <10 pg Rb, 120 pg Sr, 10 pg Sm, and 50 pg Nd. Isotopic data for Sr and Nd were obtained by multidynamic analysis on a VG Sector multiple collector mass spectrometer. All Sr and Nd isotopic analyses are normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219,

respectively. Analyses of SRM 987 Sr and La Jolla Nd standards were performed throughout this study and gave weighted averages (at the 95% confidence limit, external precision) of ⁸⁷Sr/⁸⁶Sr = 0.710250 ± 0.000011, and ¹⁴³Nd/¹⁴⁴Nd = 0.511854 ± 0.000011, respectively. Internal, within-run, statistics are almost always of comparable to higher precision than the external errors (see Table 1 for within-run statistics of samples which are comparable to those of the standards). All isotope dilution measurements utilized static mode multiple collection.

By convention, the Nd isotopic data are also presented in Table 1 in ε_{Nd} units, with deviation relative to a chondritic uniform reservoir, CHUR (DePaolo, 1976):

$$\epsilon_{Nd} = \left[\frac{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{sample}} - \frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{CHUR}} \right)}{\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{CHUR}}} \right] \times 10^4 \quad \text{Eq. (1)}$$

Model ages (or single-stage evolution ages) have been calculated for both Nd and Sr isotopes and are given under the headings T_{CHUR} and T_{LUNI}, respectively, in Table 1, where,

$$T_{LUNI} = \frac{1}{\lambda} \times \ln \left[\left(\frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} - 0.69903 \right)}{\frac{^{87}\text{Rb}}{^{86}\text{Sr}}} \right) + 1 \right] \quad \text{Eq. (2)}$$

and,

$$T_{CHUR} = \frac{1}{\lambda} \times \ln \left[\left(\frac{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} - 0.512638 \right)}{\left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}} - 0.1966 \right)} \right) + 1 \right] \quad \text{Eq. (3)}$$

The T_{LUNI} model age is determined relative to a suggested lunar initial ⁸⁷Sr/⁸⁶Sr = LUNI = 0.69903 at 4.55 Ga (Nyquist *et al.*, 1973). The T_{CHUR} model age is determined relative to a present-day chondritic uniform reservoir (CHUR) with ¹⁴³Nd/¹⁴⁴Nd = 0.512638 and ¹⁴⁷Sm/¹⁴⁴Nd = 0.1966. Errors in the model ages are estimated from consideration of errors in the parent-daughter ratios and measured isotopic ratios.

PETROGRAPHY AND CHEMISTRY OF GROUP D HIGH-TI BASALTS

The most conspicuous feature of high-Ti lunar basalts is the large amount of modal ilmenite (6–17%). Early examination of samples returned from the Apollo 11 mission allowed the separation of the high-Ti basalts into two groups, fine-grained vesicular rocks (Group A) and coarse-grained vuggy rocks (Group B) (LSPET, 1969). Chemical compositions of the basalts confirmed these subdivisions and showed that the Group A basalts were also elevated in K₂O (>>0.2 wt%) and La (>20 ppm) relative to Group B basalts (Gast and Hubbard, 1970; Compston *et al.* 1970a,b). Subsequent petrographic and chemical analyses of the Apollo 11 high-Ti basalts led to further subdivisions of the Group B samples into B1, B2, and B3 varieties (Beaty and Albee, 1978). A fifth group of basalts, distinct from Group B, was suggested for a set of

fragments found in Apollo 11 soils (Beaty *et al.*, 1979). These were classified as the Group D basalts.

Of the 156 high-Ti basalts which have been studied from the Moon (approximately one-half from the Apollo 11 landing site), only four have been determined to be of Group D. All of the Group D basalts are fragments from soils: 10002,116(,121), 10085,808(,918), 10085,836(,923), and 10002,1006 (Beaty *et al.*, 1979; Snyder *et al.*, 1994a). The petrography and chemistry of the first three of these fragments are discussed in detail by Beaty *et al.* (1979). They concluded that, although the high-La in these samples makes them akin to high-K (Group A) suite samples, the Group D basalts can be distinguished by early Cr-spinel, high modal olivine content (0.2–3.7%), relatively low modal ilmenite (5.7–12.4%), and lath-shaped plagioclase. Furthermore, the Group D basalts can be distinguished from low-K (Groups B1, B2, and B3) high-Ti basalts by their intersertal texture, by having plagioclase as a late crystallizing phase and by the relative abundance of whitlockite (0.54% as compared to 0.27% for the Group B2 basalts; Beaty and Albee, 1978; Jerde *et al.*, 1994). Snyder *et al.* (1994a) subsequently discovered a possible fourth Group D basalt (10002,1006) in their study of 2–4 mm fragments from soil 10002. The bulk-rock chemical composition of this sample is given in Table 2 along with those of the other Group D high-Ti basalts. The placement of Group D basalts in the K_2O vs. La discrimination diagram, relative to other Apollo 11 high-Ti basalts, is indicated in Fig. 1. Group D basalts are enriched in the REE, but not K. Therefore, their petrogenesis cannot include simple KREEP addition, but most likely is due to simple addition of a relatively small proportion (0.2%) of the REE-rich mineral whitlockite (Jerde *et al.*, 1994).

Based on the high Rb content alone, sample 10002,98 would appear to be distinct from the Group D basalts and similar to Group A high-Ti basalts. Considering that Group A basalts have K/Rb ratios that average ~450, and La/Sm ratios of ~1.3, the K_2O content of this sample would be ~0.25 wt% and the La abundance should be ~25 ppm. Therefore, on a conventional La- K_2O plot (Fig. 1) used for high-Ti basalt classification, 10002,98 would lie squarely within the Group A field.

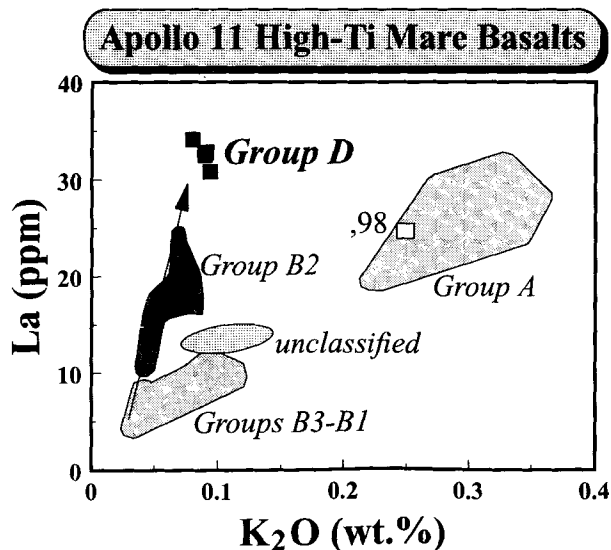


FIG. 1. Plot of K_2O (wt%) vs. La (ppm) for all Apollo 11 high-Ti basalts. Fields for the different basalt groups are also shown as well as the data for Group D basalts.

TABLE 2. Whole-rock chemical compositions of Group D basalts.

Parent Sub-sample Probe Mount	10002* ,1006	10002 ,116 ,121	10085 ,808 ,918	10085 ,836 ,923
SiO ₂	—	41.2	44.0	40.7
TiO ₂	—	8.6	10.0	6.7
Al ₂ O ₃	—	11.8	10.8	11.6
FeO	18.8	19.0	20.6	19.7
MnO	0.275	0.249	0.275	0.252
MgO		8	7	7
CaO	10.7	11.5	11.2	11.9
Na ₂ O	0.38	0.37	0.37	0.40
K ₂ O	0.094	0.090	0.091	0.080
P ₂ O ₅		0.28	0.15	0.21
Cr ₂ O ₃	0.24	0.30	0.39	0.30
Sc	81.6	76	77	81
V		100	89	102
Co	14.3	15	20	15
Zr	388	320	630	500
Ga	5.1			
Rb	4.8			
Sr	162			
Ba	333	160	220	230
La	30.8	32.5	32.8	34.1
Ce	91.4	88	98	93
Nd	60.4	68	81	77
Sm	21.7	21.5	24.6	23.7
Eu	1.99	1.91	2.02	1.85
Tb	4.73	4.6	4.9	4.7
Dy	31.2	31	32	32
Yb	16.3	16.0	17.0	17.3
Lu	2.30	2.23	2.48	2.47
Hf	12.0	12.3	13.0	12.4
Ta	1.45	1.8	1.6	1.8
Th	2.81	3.1	2.3	2.1

* From Snyder *et al.* (1994a).

ARGON-40/ARGON-39 AGE SPECTRA

Age spectra have been determined on three separate runs of Group D basalt 10002,116 (Fig. 2) and two runs of a suspected Group D basalt, 10002,1006 (Fig. 3) (Snyder *et al.*, 1994a). The age spectra for sample 10002,116 exhibit plateau segments over the last 70% to 80% of the ³⁹Ar gas release. The three runs yield plateau ages of 3798 ± 9 Ma, 3781 ± 8 Ma, and 3805 ± 7 Ma, with a weighted average of 3795 ± 14 Ma (all errors 2σ). The ages determined for 10002,116 are similar (within analytical uncertainty) to an age of 3.83 ± 0.03 Ga determined for Group B2 basalt 10029 and are within the total possible range of Group B2 basalt ages (3.80 to 3.90 Ga), although they are below the weighted average age of 3.85 ± 0.02 Ga (Snyder *et al.*, 1994b).

The age spectra for two runs of suspected Group D basalt 10002,1006 both show a significant sag to lower apparent ages for the high-temperature fractions and no "true" plateau (Fig. 3). Given the extremely large range of Ca/K values for minerals in this sample, plus the likely small grain size of the K-bearing phases, we suspect that this nonideal behavior is due to internal redistribution of ³⁹Ar caused by recoil. Therefore, we have used a technique, detailed by Turner *et al.* (1978), to calculate "reduced plateau" ages, which minimizes the effects of ⁴⁰Ar loss from low-retentivity sites, while at the same time averaging out the effects of ³⁹Ar recoil between phases with contrasting Ca and K concentrations. The

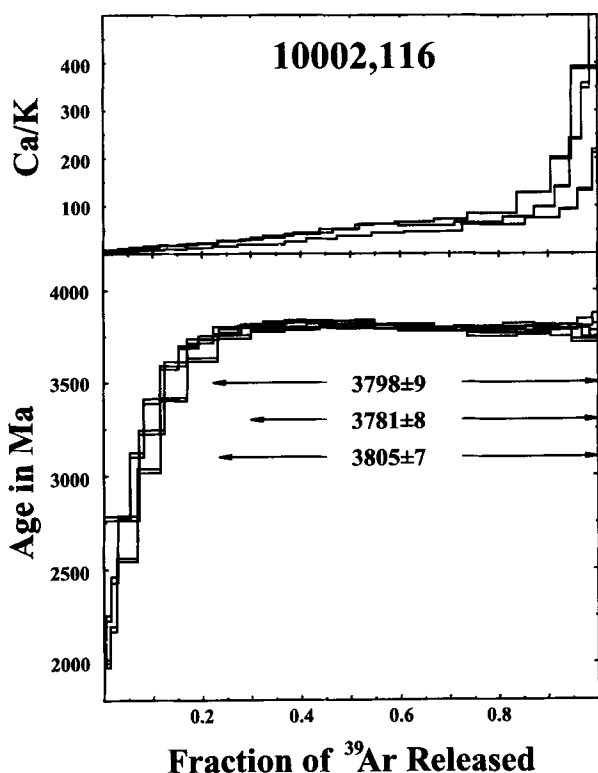


FIG. 2. Plot of Ar age spectra for three runs of basalt sample 10002,116. The fraction of ³⁹Ar released during step-heating is plotted relative to the age (below) and the Ca/K ratio (above).

reduced plateau ages are 3900 ± 18 Ma and 3894 ± 19 Ma (average = 3897 ± 13 Ma), and these ages are only slightly greater than the total gas ages of 3880 ± 19 and 3879 ± 19 Ma, respectively.

The apparent age of sample 10002,1006 is significantly higher than the measured age for Group D basalt 10002,116 and is in excess of those reported from most Group B2 basalts, although within the total measured age range (including errors) of 3.80 to 3.90 Ga. However, the average ⁴⁰Ar/³⁹Ar age of 3896 ± 13 Ma is similar to a Sm-Nd internal isochron determined for basalt 10062 (3880 ± 60 Ma; Papanastassiou *et al.*, 1977), albeit much younger than the ⁴⁰Ar/³⁹Ar age for 10062 of 3970 ± 110 Ma (Guggisberg *et al.*, 1979). Basalt 10062 was considered to be unclassified (Beaty and Albee, 1978), but it is most similar in terms of petrography and chemistry to the Group B2 basalts. It is possible that 10062 is an early manifestation of the Group B2 basalts at Mare Tranquillitatis and that 10002,1006 is also an evolved derivative of these early melts. Conversely, the age of 10002,1006 could correspond to that of an extensive group of impact melts generated at about this time (Ryder, 1990; Bogard, 1995, and references therein).

MODELLING ARGON-40 LOSS AND REFINING THE FORMATION AGE OF 10002,116

The age spectra of Group D basalt 10002,116 suggest that this rock has either suffered significant, episodic ⁴⁰Ar loss at ~2.0 Ga or continuous loss prior to this time. Turner (1971) accounted for the Ar loss in several Apollo 11 mare basalts by solar heating on the lunar surface over a period of tens of millions of years. Regardless of the mechanism, the loss of a significant amount of ⁴⁰Ar at such

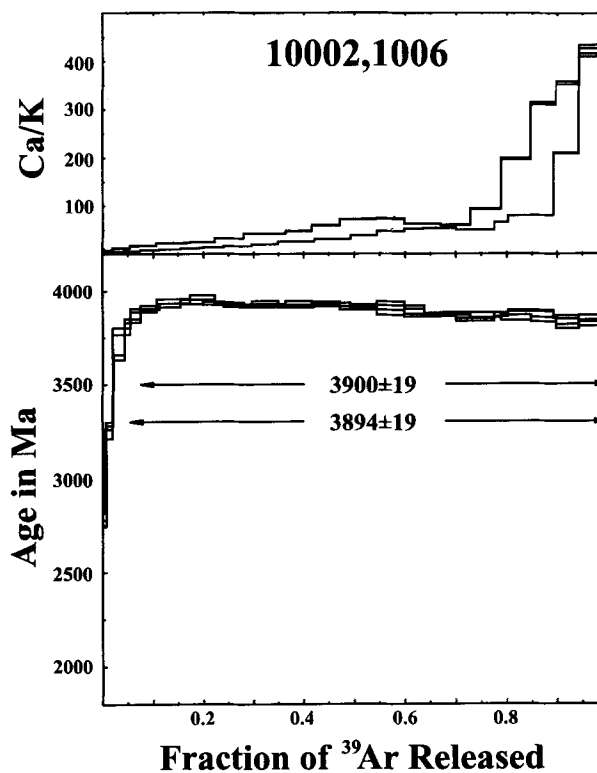


FIG. 3. Plot of Ar age spectra for two runs of basalt sample 10002,1006. The fraction of ³⁹Ar released during step-heating is plotted relative to the age (below) and the Ca/K ratio (above).

an earlier time would mean that the reduced plateau ages underestimate the age of the sample. Therefore, we wish to further refine the age interpretation for this sample by modelling each of the three runs assuming a single blocking event followed by a single episode of Ar loss. This is achieved by using the method of Turner (1968) and is based on the theoretical age spectral shape one would expect due to diffusive loss of Ar at some time after a sample's formation. The basic theory behind this approach is presented in Turner (1968) and assumes, first, that the effective grain size for diffusion is defined approximately by a sphere of radius *a*. The sample will presumably lose Ar via a volume diffusion mechanism, where its diffusion coefficient is a function of temperature (*T*) and is denoted as *D*. Further, it is assumed that *D* is related to *T* by the Arrhenius relationship:

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \tag{Eq. (4)}$$

where *D*₀ is a frequency factor and *E* is an activation energy. For an isotope which is initially uniformly distributed within the sphere, the fraction of this isotope which is released as a function of time is given by the following diffusion equation (from Carslaw and Jaeger, 1959):

$$f(x) = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2\pi^2x) \tag{Eq. (5)}$$

where

$$x = \int_0^t \left[\frac{D(\tau)}{a^2}\right] d\tau \tag{Eq. (6)}$$

The original formation or "blocking" age is τ_0 and at some time in the past, τ_1 , the sample suffered a "sudden" (*i.e.*, short compared to the decay constant of ^{40}K) loss of ^{40}Ar . We denote the time integral of D/a^2 for this event as x_m , and therefore the fraction of gas released at that time would have been $f(x_m)$.

When the sample is step-heated in the laboratory, diffusive loss both of ^{40}Ar and ^{39}Ar occurs. Whereas the ^{39}Ar is uniformly distributed, the ^{40}Ar is not because of the earlier loss in nature. We can find out the time integrals of D/a^2 for the lab step-heating procedure by measuring the fractions of ^{39}Ar released for the various steps (g_i) and then use the inverse function for $f(x)$ to get the corresponding lab x_i . That is:

$$x_i = f^{-1}(g_i) \quad \text{Eq. (7)}$$

There are reasonable approximations of this inverse function in Carslaw and Jaeger (1959) and an "expected" or "model" age spectrum based only on the three parameters τ_0 , τ_1 , and x_m (or equivalently $f(x_m)$) can be calculated. The apparent ages t_i are given by:

$$e^{\lambda t_i} = e^{\lambda \tau_1} + (e^{\lambda \tau_0} - e^{\lambda \tau_1}) \left\{ \frac{[f(x_i + x_m) - f(x_{i-1} + x_m)]}{[f(x_i) - f(x_{i-1})]} \right\} \quad \text{Eq. (8)}$$

Finally, these three parameters are adjusted using a Levenberg-Marquardt technique to give an error weighted least squares fit to the data (Press *et al.*, 1992). The results of this modelling are given in Fig. 4 and Table 3. The fitted crystallization ages for the three separate runs of 10002,116 are 3837 ± 18 , 3826 ± 16 , and 3836 ± 14 Ma (errors are estimated). These ages overlap the weighted average age for Group B2 high-Ti basalts (3850 ± 20 Ma) and provide further circumstantial evidence of a possible genetic relationship between the Group B2 and Group D basalts (Beaty and Albee, 1978; Jerde *et al.*, 1994).

NEODYMIUM AND STRONTIUM ISOTOPIC COMPOSITIONS

For the first time, Group D basalt rocklets have been analyzed for their Sm-Nd and Rb-Sr isotopic compositions (Table 1). These

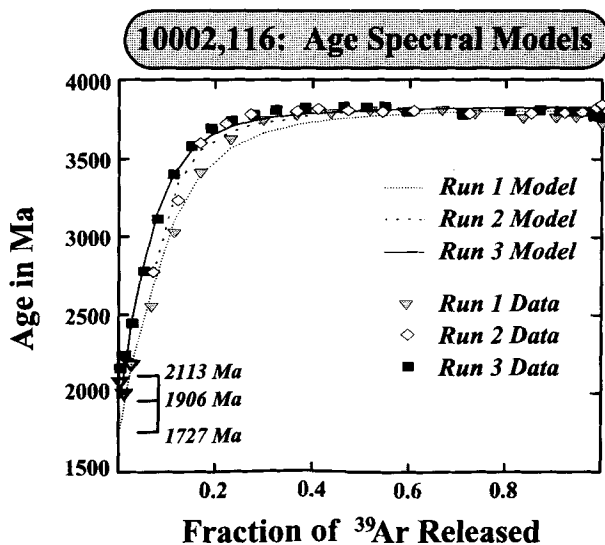


FIG. 4. Plot of modelled age spectra assuming an Ar loss event as discussed in the text. The fraction of ^{39}Ar released during step-heating is plotted relative to the modelled age.

TABLE 3. Results of age modelling of ^{40}Ar loss for 10002,116.

	% ^{40}Ar Lost	Loss Age (Ma)	Initial Age (Ma)
Run 1	11.4	2113	3837
Run 2	13.1	1727	3826
Run 3	9.7	1906	3836

Group D basalts have the lowest $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (0.1960 and 0.1972) measured for lunar high-Ti basalts, which exhibit a range from 0.2061 to 0.2623 (Papanastassiou *et al.*, 1977; Paces *et al.*, 1991; Snyder *et al.*, 1994b) and are similar to CHUR. Therefore, model ages for these rocks that are referenced to a chondritic bulk Moon (T_{CHUR}) are unrealistic or undefined.

The Nd and Sr isotopic compositions of the Group D basalts are at the lower end of the range for the Group B2 basalts from Apollo 11 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.69920$ to 0.69921 and $\epsilon_{\text{Nd}} = +2.0$ to $+3.9$ at 3.85 Ga; Papanastassiou *et al.*, 1977; Unruh *et al.*, 1984; and Snyder *et al.*, 1994b). Although the Group B2 and Group D basalts are similar in age, the Nd and Sr initial ratios suggest that there are differences in the sources for these two groups (Figs. 5 and 6).

The sample classified as a Group A basalt, 10002,98, has a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio (0.2089) that is slightly higher than previously analyzed Group A basalts (0.2061 to 0.2072; Papanastassiou *et al.*, 1977; Snyder *et al.*, 1994b) and an $^{87}\text{Rb}/^{86}\text{Sr}$ ratio (0.0799) that is substantially lower than other Group A basalts (0.101 to 0.106). Thus, this sample has the highest initial $^{87}\text{Sr}/^{86}\text{Sr}$ (0.69963 ± 2 at 3.59 Ga; the weighted average age of Group A basalts; Snyder *et al.*, 1994b) measured for any Group A high-Ti basalt (Fig. 5). This rock also has a much higher $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio (even at 3.85 Ga) than either the B2 or D basalts, due in large part to the elevated Rb abundance of this sample (Table 1). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, along with the ϵ_{Nd} of 2.5 ± 0.4 (at 3.59 Ga), is consistent with this sample representing a Group A high-Ti basalt.

DISCUSSION

The low $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for the Group D samples, similar to CHUR, are unique among lunar high-Ti mare basalts. These low $^{147}\text{Sm}/^{144}\text{Nd}$ ratios lead to the calculation of model T_{CHUR} ages that

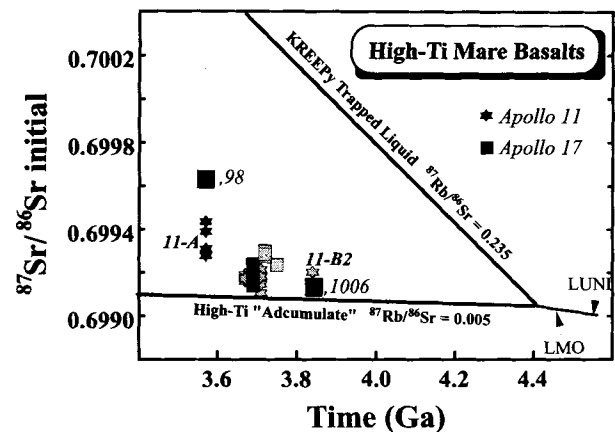


FIG. 5. Plot of time (in Ga) vs. $^{87}\text{Sr}/^{86}\text{Sr}$ for all lunar high-Ti basalts and data for the Group D basalt (10002,1006) and "new" Group A basalt (10002,98). These $^{87}\text{Sr}/^{86}\text{Sr}$ initial values were calculated assuming ages determined from $^{40}\text{Ar}/^{39}\text{Ar}$ analyses in this paper and an age of 3.59 Ga for 10002,98 (as per the weighted average age of Group A high-Ti basalts from Snyder *et al.*, 1994).

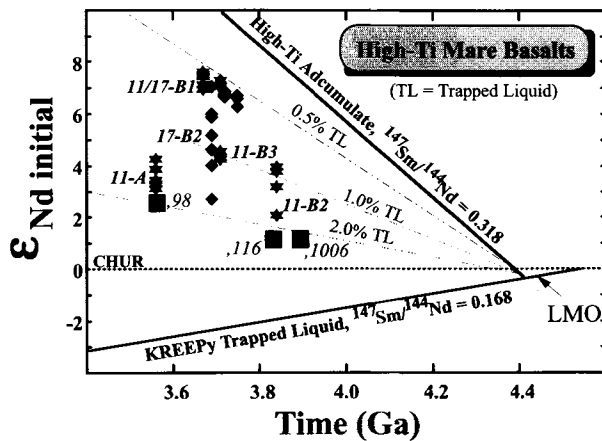


FIG. 6. Plot of time (in Ga) vs. ϵ_{Nd} for all lunar high-Ti basalts and including the data for the two Group D high-Ti basalts (10002, 116 and 10002, 1006) and one Group A high-Ti basalt (10002, 98). Solid lines show the evolution of the "most depleted" lunar upper mantle and the KREEP (trapped liquid) reservoirs, and the dashed lines indicate percentages of this trapped KREEP-like liquid in the "most depleted" source.

are unrealistic and thus, yield evidence that they were not derived in a single stage from an undepleted, chondritic reservoir. However, if one assumes that these rocks were crystallized from magmas that were derived from a depleted upper mantle, then reasonable estimates for model ages are forthcoming. Snyder *et al.* (1995) have defined such a parameter (T_{LUM}) that yields the maximum age of separation of lunar basaltic magmas from a depleted upper mantle adcumulate. This depleted upper mantle model assumes no trapped KREEP-like liquid and is the most LREE-depleted, ilmenite-bearing, source (*i.e.*, it has the highest possible $^{147}\text{Sm}/^{144}\text{Nd}$, 0.318) calculated from the lunar magma ocean (LMO) modelling of Snyder *et al.* (1992). Addition of KREEP-like liquid to this source would serve to decrease the model ages.

Depleted lunar mantle model (T_{LUM}) ages for the two Group D high-Ti basalts (4.28 to 4.29 Ga) are similar to those of Group A (4.22 to 4.28 Ga), Group B3 (4.25 to 4.27 Ga), and Group B2 (4.33 Ga) high-Ti basalts. Only the Group B1 high-Ti basalts have demonstrably different T_{LUM} ages of 4.02 to 4.05 Ga. These ages suggest that the heterogeneities found in the sources of most high-Ti basalts were locked in at ~4.3 to 4.2 Ga (*i.e.*, the sources for most high-Ti basalts were last equilibrated at this time). This is in general agreement with Papanastassiou *et al.* (1977), Paces *et al.* (1991) and Snyder *et al.* (1994b) who have shown that the sources for most of the high-Ti basalts were formed early (possibly as the final dregs of the LMO were crystallizing) and that heterogeneities were locked in during its inception and not created by later processes.

The Nd and Sr isotopic heterogeneities in the sources of most low-K high-Ti mare basalts (such as Groups B2 and D) could be the consequence of events unique to the Moon. In the late stages of LMO crystallization, when ilmenite was a liquidus phase, upper mantle cumulates trapped variable yet small amounts of residual LMO liquid (Snyder *et al.*, 1994b; Snyder *et al.*, 1992). A lack of recycling in the lunar environment would allow these slightly different portions of essentially the same source to diverge along separate isotopic evolutionary paths. Adcumulates with more trapped liquid would have higher contents of the heat-producing elements U, Th, and K and would likely melt first. Therefore, the earliest phase of volcanism at Mare Tranquillitatis (3.80 to 3.90 Ga

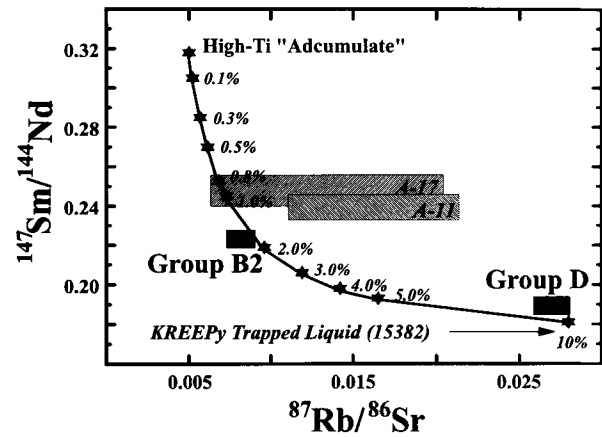


FIG. 7. Plot of $^{87}\text{Rb}/^{86}\text{Sr}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$ for the two Group D basalts and for a previously measured Group B2 basalt (Snyder *et al.*, 1994). A mixing curve between a postulated high-Ti perfect adcumulate in the upper mantle of the Moon and late, trapped, KREEP-like liquid (represented by lunar rock 15382) is shown to indicate variability in the source region(s) of Apollo 11 and 17 basalts. Percentages of trapped liquid are indicated on the curve by stars. Also shown are fields for other Apollo 11 and Apollo 17 high-Ti basalts (with the exception of Group A basalts from Apollo 11).

ago, Group B2 and/or possibly D) involved the melting of a source which was relatively enriched in this KREEP-like trapped liquid (Figs. 6 and 7) and the resultant magmas were slightly more aluminous, less titaniferous, and possessed a lower Mg# than the later B3 basalts (Snyder *et al.*, 1994b). The volume of this KREEP-like trapped liquid would be small, but, because of its high LILE content, could greatly affect the isotopic ratios of basaltic magmas that would have intruded through the upper crust en route to the surface of the Moon.

Based on this scenario, one might predict that the Group D basalts should have erupted just prior to Group B2 volcanism (possibly within a few million years; the difference being unresolvable by current age dating), because the Group D basalts have not only slightly lower ϵ_{Nd} values, but much lower $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (0.1960–0.1972) and higher $^{87}\text{Rb}/^{86}\text{Sr}$ (0.0279) ratios than the Group B2 basalts (0.2206 and 0.00785, respectively; Snyder *et al.*, 1994b). The explanation for these differences could be found in slight age differences and/or the proportion of trapped KREEP-like liquid in the magma. Rare Group D basalts would have contained a trapped KREEP-like liquid component that was 4–5 \times more abundant than that found in Group B2 basalts (Fig. 7). These rare Group D basalts may represent the earliest volcanic activity on the eastern nearside as revealed in samples returned by the Apollo missions. That the earliest volcanism is relatively LREE-enriched, and exhibits the lowest ϵ_{Nd} values of high-Ti basalts, may be an indication that the mechanism for initiating lunar volcanism was indeed the radioactive decay of U, Th, and K, which are key components of the KREEP-like trapped liquid found in such abundance in these samples.

However, one important aspect of the chemistry of the Group D basalts has yet to be satisfactorily explained. Whereas one might expect such samples, with a large proportion of trapped KREEP-like component, to exhibit elevated K, all Group D samples are distinguished by their relative depletion in K. This K depletion, yet REE-enrichment, is largely due to the influence of whitlockite, which is relatively abundant in these samples (Beaty and Albee, 1978; Beaty *et al.*, 1979; and Jerde *et al.*, 1994). Neal and Taylor

(1991) postulated that whitlockite may be evidence of metasomatism in the highlands of the Moon caused by the immiscibility of KREEP. In fact, Jerde *et al.* (1994) postulated that Group D basalts were directly related to Group B2 basalts through the simple addition of 0.27 to 0.54 modal% whitlockite. The convergence of T_{LUM} model ages of most high-Ti basalts (including Group B2 and D) at 4.2 to 4.3 Ga and the existence of a rough whole-rock "age" for all high-Ti mare basalts of 4.46 ± 0.17 Ga (Snyder *et al.*, 1994b) argues against late metasomatism of lunar basalts and/or their source regions, or the simple addition of whitlockite during extrusion at 3.8 to 3.9 Ga. However, if metasomatism did occur it must have been coeval with source formation at 4.2 to 4.3 Ga ago.

CONCLUSIONS

The hypothesized genetic link between common Group B2 and rare Group D basalts at the Apollo 11 landing site has been strengthened through ^{40}Ar - ^{39}Ar age dating of two Group D basalts. The ages of the Group D basalts (3.83 and 3.90 Ga) overlap the ages of the Group B2 basalts (age range of 3.80 to 3.90 Ga; Snyder *et al.*, 1994b). One group D basalt, 10002,116, yields an approximate Ar-loss age of ~ 2 Ga. This Ar-loss age could be due to local impact events (including micrometeorite impacts), may indicate a significant impact at this time, or may be due simply to solar heating of the lunar surface.

The Nd and Sr isotopic analyses of Group D basalts also indicate that the earliest phase of lunar volcanism melted a source which was relatively fertile (*i.e.*, enriched in heat producing elements U and Th, as well as the LREE) as compared to other volcanic episodes. This is shown by the relatively low ϵ_{Nd} values for Groups B2 (+2.0 to +3.9) and D basalts (+1.2) as compared to later low-K, Groups B1 and B3, high-Ti basalts (+4.3 to +7.6; Snyder *et al.*, 1994b).

The sources of most low-K high-Ti mare basalts were formed 300 to 400 Ma prior to the onset of melting. The mechanism for initiation of melting was likely heat generated by radioactive decay of elements such as U, Th, and possibly K.

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REFERENCES

- BEATY D.W. AND ALBEE A. (1978) Comparative petrology and possible genetic relations among the Apollo 11 basalts. *Proc. Lunar Planet. Sci. Conf.* **9th**, 359–463.
- BEATY D. W. AND ALBEE A. L. (1980) The geology and petrology of the Apollo 11 landing site. *Proc. Lunar Planet. Sci. Conf.* **11th**, 23–35.
- BEATY D. W., HILL S. M. R., ALBEE A. L., MA M.-S. AND SCHMITT R. A. (1979) The petrology and chemistry of basaltic fragments from the Apollo 11 soil, part I. *Proc. Lunar Planet. Sci. Conf.* **10th**, 41–75.
- BOGARD D. D. (1995) Impact ages of meteorites: A synthesis. *Meteoritics* **30**, 244–268.
- BVSP (1981) *Basaltic Volcanism on the Terrestrial Planets*. Pergamon Press, Elmsford, New York. 1286 pp.
- CARSLAW H. S. AND JAEGER J. C. (1959) *Conduction of Heat in Solids*. Oxford University Press, New York, New York. 510 pp.
- COMPSTON W., ARRIENS P. A., VERNON M. J. AND CHAPPELL B. W. (1970a) Rubidium-strontium chronology and chemistry of lunar material. *Science* **167**, 474–476.
- COMPSTON W., CHAPPELL B. W., ARRIENS P. A. AND VERNON M. J. (1970b) The chemistry and age of Apollo 11 lunar material. *Proc. Apollo 11 Lunar Sci. Conf.*, 1007–1028.
- DEPAOLO D. J. (1976) Nd isotopic variations and petrogenetic models. *Geophys. Res. Lett.* **3**, 249–252.
- GAST P. W. AND HUBBARD N. J. (1970) Abundance of alkali metals, alkaline, and rare earths, and strontium-87/strontium-86 ratios in lunar samples. *Science* **167**, 485–487.
- GUGGISBERG S., EBERHARDT P., GEISS J., GROGLER N., STETTLER A., BROWN G. M. AND PECKETT A. (1979) Classification of the Apollo-11 mare basalts according to Ar^{39} - Ar^{40} ages and petrological properties. *Proc. Lunar Planet. Sci. Conf.* **10th**, 601–615.
- JERDE E. A., SNYDER G. A., TAYLOR L. A., LIU Y. G. AND SCHMITT R. A. (1994) The origin and evolution of lunar high-Ti basalts: Periodic melting of a single source at Mare Tranquillitatis. *Geochim. Cosmochim. Acta* **58**, 515–527.
- LAYER P. W., HALL C. M. AND YORK D. (1987) The derivation of $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of single grains of hornblende and biotite by laser step-heating. *Geophys. Res. Lett.* **14**, D757–D760.
- LSPET (Lunar Sample Preliminary Examination Team) (1969) Preliminary examination of lunar samples from Apollo 11. *Science* **165**, 1211–1227.
- LUDWIG K. L. (1990) *ISOPLOT: A Plotting and Regression Program for Radiogenic-isotope Data for IBM-PC Compatible Computers, Version 2.01*. USGS Open-File Report 88–557. 79 pp.
- NEAL C. R. AND TAYLOR L. A. (1991) Evidence for metasomatism of the lunar highlands and the origin of whitlockite. *Geochim. Cosmochim. Acta* **55**, 2965–2980.
- NEAL C. R. AND TAYLOR L. A. (1992) Petrogenesis of mare basalts: A record of lunar volcanism. *Geochim. Cosmochim. Acta* **56**, 2177–2211.
- NYQUIST L. E., HUBBARD N. J., GAST P. W., BANSAL B. M., WIESMANN H. AND JAHN B.-M. (1973) Rb-Sr systematics for chemically defined Apollo 15 and 16 materials. *Proc. Lunar Sci. Conf.* **4th**, 1823–1846.
- OZIMA M. AND PODOSEK F. A. (1983) *Noble Gas Geochemistry*. Cambridge Univ. Press, New York, New York. 365 pp.
- PACES J. B., NAKAI S., NEAL C. R., TAYLOR L. A., HALLIDAY A. N. AND LEE D.-C. (1991) A strontium and neodymium isotopic study of Apollo 17 high-Ti mare basalts: Resolution of ages, evolution of magmas, and origins of source heterogeneities. *Geochim. Cosmochim. Acta* **55**, 2025–2043.
- PAPANASTASSIOU D., DEPAOLO D. J. AND WASSERBURG G. J. (1977) Rb-Sr and Sm-Nd chronology and genealogy of mare basalts from the Sea of Tranquillity. *Proc. Lunar Planet. Sci. Conf.* **8th**, 1639–1672.
- PRESS W. H., TEUKOLSKY S. A., VETTERLING W. T. AND FLANNERY B. P., Eds. (1992) *Numerical Recipes in C*. Cambridge University Press, New York, New York. 230 pp.
- RODDICK J. C. (1983) High precision intercalibration of ^{40}Ar - ^{39}Ar standards. *Geochim. Cosmochim. Acta* **47**, 887–898.
- RYDER G. (1990) Lunar samples, lunar accretion, and early bombardment of the Moon. *EOS* **71**, 322–323.
- SCHAEFFER O. A., HUSSAIN L. AND SCHAEFFER G. A. (1976) Ages of highlands rocks: The chronology of lunar basin formation revisited. *Proc. Lunar Sci. Conf.* **7th**, 2067–2092.
- SNYDER G. A., TAYLOR L. A. AND NEAL C. R. (1992) A chemical model for generating the sources of mare basalts: Combined equilibrium and fractional crystallization of the lunar magmasphere. *Geochim. Cosmochim. Acta* **56**, 3809–3823.
- SNYDER G. A., JERDE E. A., TAYLOR L. A., LEE D.-C. AND HALLIDAY A. N. (1994a) A sortie for pristine rocks at Mare Tranquillitatis: A ferroan anorthosite, a new Group D basalt, and the isotopic composition of Group D high-Ti basalts (abstract). *Lunar Planet. Sci.* **25**, 1299–1300.
- SNYDER G. A., LEE D.-C., TAYLOR L. A., HALLIDAY A. N. AND JERDE E. A. (1994b) Evolution of the upper mantle of the Earth's moon: Neodymium and strontium isotopic constraints from high-Ti mare basalts. *Geochim. Cosmochim. Acta* **58**, 4795–4808.
- SNYDER G. A., NEAL C. R., TAYLOR L. A. AND HALLIDAY A. N. (1995) Mantle sources of lunar volcanism in the Ocean of Storms: Evidence from trace-element and Nd isotopic chemistry of fine-grained basalts at Apollo 12 (abstract). *Lunar Planet. Sci.* **26**, 1331–1332.
- TURNER G. (1968) The distribution of potassium and argon in chondrites. In *Origin and Distribution of the Elements* (ed. L. H. Ahrens), pp. 387–398. Pergamon, London, U.K.
- TURNER G. (1971) ^{40}Ar - ^{39}Ar ages from the lunar maria. *Earth Planet. Sci. Lett.* **11**, 169–191.
- TURNER G., ENRIGHT M. C. AND CADOGAN P. H. (1978) The early history of chondrite parent bodies inferred from ^{40}Ar - ^{39}Ar ages. *Proc. Lunar Planet. Sci. Conf.* **9th**, 989–1025.
- UNRUH D. M., STILLE P., PATCHETT P. J. AND TATSUMOTO M. (1984) Lu-Hf and Sm-Nd evolution in lunar mare basalts. *Proc. Lunar Planet. Sci. Conf.* **14th**, B459–B477.
- YORK D. (1969) Least-squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.* **5**, 320–324.