

## Research



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# Rb-Sr, Sm-Nd and Lu-Hf isotope systematics of the lunar Mg-suite: the age of the lunar crust and its relation to the time of Moon formation

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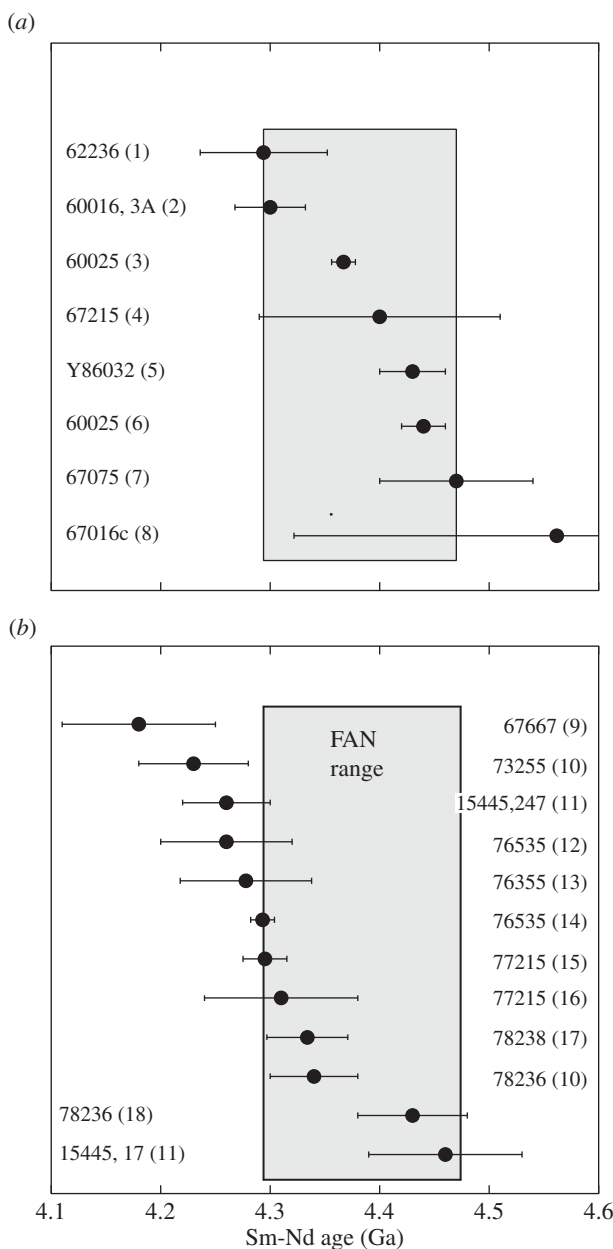
New Rb-Sr,  $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$  and Lu-Hf isotopic analyses of Mg-suite lunar crustal rocks 67667, 76335, 77215 and 78238, including an internal isochron for norite 77215, were undertaken to better define the time and duration of lunar crust formation and the history of the source materials of the Mg-suite. Isochron ages determined in this study for 77215 are: Rb-Sr =  $4450 \pm 270$  Ma,  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  =  $4283 \pm 23$  Ma and Lu-Hf =  $4421 \pm 68$  Ma. The data define an initial  $^{146}\text{Sm}/^{144}\text{Sm}$  ratio of  $0.00193 \pm 0.00092$  corresponding to ages between 4348 and 4413 Ma depending on the half-life and initial abundance used for  $^{146}\text{Sm}$ . The initial Nd and Hf isotopic compositions of all samples indicate a source region with slight enrichment in the incompatible elements in accord with previous suggestions that the Mg-suite crustal rocks contain a component of KREEP. The Sm/Nd— $^{142}\text{Nd}/^{144}\text{Nd}$  correlation shown by both ferroan anorthosite and Mg-suite rocks is coincident with the trend defined by mare and KREEP basalts, the slope of which corresponds to ages between 4.35 and 4.45 Ga. These data, along with similar ages for various early Earth differentiation events, are in accord with the model of lunar formation via giant impact into Earth at ca 4.4 Ga.

# 1. Introduction

The time and duration of lunar highlands crust formation plays an unusually important role in models for lunar origin because of the suggestion that much of the highlands crust grew by plagioclase flotation from a crystallizing magma ocean [1]. In the magma ocean model for the Moon, an initially extensively molten Moon first crystallized mafic silicates that sank into the mantle to form the source regions of much later mare basalt magmatism [2,3]. After some 70–80% crystallization of the magma ocean, plagioclase began to crystallize from what was by then a dense iron-rich differentiated magma leading the plagioclase to float to form the ferroan anorthosite (FAN) clan of lunar highlands rocks [4]. The extraction of plagioclase from the magma ocean imprinted the later mafic cumulates in the lunar interior with a deficiency in Eu relative to neighbouring rare earth elements (REEs) that is reflected in the negative Eu anomalies of some mare basalts [5]. Further crystallization resulted in a residual liquid strongly enriched in incompatible elements that was given the name KREEP for its enrichment in potassium, REE and phosphorus, among many other incompatible elements [6]. The final component of the lunar highlands crust is a group of plagioclase-rich rocks that are distinguished from FANs by their higher Mg/Fe ratios, the presence of abundant mafic phases, and substantially higher incompatible element contents. This group of highlands rocks is known as the Mg-suite [7]. The parental magmas to the Mg-suite cumulate rocks usually are assumed to be partial melts of cumulates in the lunar interior [8], although an alternative is that the parental magmas originate from large impacts [9].

Where chronology enters the picture is that the magma ocean model predicts stratigraphic relationships in the rocks crystallized from the magma ocean. In this model, the mafic cumulate sources of the mare basalts form first, followed shortly by FANs, then by KREEP. The mare basalt source age and ferroan anorthosite age should be similar given the rapid crystallization of a magma ocean devoid of a thick, insulating crust [10]. Crystallization to the point of forming KREEP could take longer, perhaps up to 150 Ma [11], because of the high radioactive heat-producing capacity of KREEP and the fact that this last portion of magma ocean crystallization would take place with the surface boundary insulated by the thick highlands crust. If they indeed are later igneous intrusions into the crust, the Mg-suite rocks should yield ages no older than those of the FANs although a range to younger ages might be expected. Accurate chronology for lunar highlands rocks thus has the potential to test both whether the magma ocean model is correct and, if so, constrain the time of initial differentiation of the Moon.

Figure 1 illustrates that the age range of Mg-suite rocks is large and extends to relatively young (e.g. 4.18 Ga) ages. The oldest Mg-suite rocks overlap with the age range reported for FANs. How much of the age range of both the FANs and the Mg-suite reflects the true range of crystallization ages of crustal rocks as opposed to later metamorphic disturbance has been the subject of much work [14,21,23,28,29]. Obtaining convincingly accurate and adequately precise ages for lunar crustal rocks has proved difficult. Neither the Mg-suite nor FANs contain high closure temperature U-rich minerals, such as zircon that has proved itself as a precise and accurate chronometer of igneous rock crystallization. FANs have extremely low incompatible element contents, and because all the long-lived radioactive chronometers, except Re-Os, involve incompatible elements, analyses of FANs are unusually susceptible to both laboratory blank and natural contamination. FANs also are composed primarily of plagioclase, to the point that the presence of even minor mafic phases is interpreted as a sign of a polymict nature [30]. Mg-suite samples have much higher incompatible element abundances and mafic phases that clearly crystallized from the same parental magma as the plagioclase. Many Mg-suite samples show evidence of shock metamorphism including formation of maskelynite and the presence of impact melt glass. Finally, exposure of the lunar surface to cosmic ray irradiation produces secondary neutrons that can substantially influence the isotopic composition of samples that have long exposure histories, with important consequences for  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  and Lu–Hf results [31–35].



**Figure 1.** Sm-Nd isochron ages for rocks from the (a) FAN and (b) Mg-suite groups of highlands rocks. Data from: 1—Borg *et al.* [12]; 2—Marks *et al.* [13]; 3—Borg *et al.* [14]; 4—Norman *et al.* [15]; 5—Nyquist *et al.* [16]; 6—Carlson & Lugmair [17]; 7—Nyquist *et al.* [18]; 8—Alibert *et al.* [19]; 9—Carlson & Lugmair [20]; 10—Carlson & Lugmair [21]; 11—Shih *et al.* [22]; 12—Lugmair *et al.* [23]; 13—Edmunson *et al.* [24]; 14—Borg *et al.* [25]; 15—this study; 16—Nakamura *et al.* [26]; 17—Edmunson *et al.* [27] and 18—Nyquist *et al.* [28].

Given these issues and the importance of lunar crustal chronology to the understanding of Moon formation and early differentiation, we have been revisiting the lunar highlands sample collection in order to apply modern analytical approaches that involve several different isotope systems and the improved precision of modern mass spectrometric techniques in an attempt better illuminate the correct interpretation of both the ages and initial isotopic compositions

of lunar highlands rocks. This paper reports results for Rb-Sr,  $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$  and Lu-Hf measurements of whole rock samples of feldspathic ilmenite 67667, cataclastic magnesian anorthosite 76335 and norite 78238 along with minerals separated from the Mg-suite norite 77215 and compares the results with recent data for other highlands rocks to derive constraints on the early history of the Moon.

## 2. Sample descriptions and previous chronological results

Troctolitic anorthosite 76335 consists of 88% plagioclase and 12% olivine with a number of trace phases including minor orthopyroxene, chromite and phosphate [36]. 76335 provided a Sm-Nd age of  $4278 \pm 60$  Ma with an initial  $\epsilon^{143}\text{Nd}$  of  $0.06 \pm 0.39$ , but the rock has been significantly shocked as indicated by disturbed Rb-Sr systematics [24]. Cumulate norite 78238 is one of several (78235–78238) that were sampled from a glass covered noritic boulder at Apollo 17, station 8. The rocks are about 50:50 plagioclase and orthopyroxene with accessory minerals including clinopyroxene, phosphates and veins of shock-melted glass [37]. This group of rocks have been the subject of many chronological investigations including Ar-Ar ( $4.11 \pm 0.02$  Ga, [38]); Rb-Sr ( $4.38 \pm 0.02$ , [28];  $4.37 \pm 0.05$ , [27]); Sm-Nd ( $4.43 \pm 0.05$  Ga, [28];  $4.34 \pm 0.04$  Ga, [21];  $4.33 \pm 0.04$  Ga, [27]) and U-Pb ( $4.43 \pm 0.06$  Ga, [39]), all of which show disturbance due to the shock this rock has experienced. Apollo 16 feldspathic ilmenite 67667 consists of 50% olivine, 21% orthopyroxene, 5% clinopyroxene, 23% plagioclase and 1% ilmenite [40]. As with most highlands samples, 67667 displays ample evidence of shock. 67667 has been dated by Sm-Nd at  $4.18 \pm 0.07$  Ga with an initial  $\epsilon^{143}\text{Nd}$  of  $0.8 \pm 1.6$  [20].

Apollo 17 sample 77215 consists of a number of brecciated pigeonite-anorthite cumulate clasts cut and surrounded by melt rock. Chao *et al.* [41] concluded that 77215 crystallized and cooled slowly at a depth of approximately 10 km and was then excavated by an impact and mixed with impact melts of similar noritic composition. They suggest further that 77215 may have been derived from the same parental magma as 78238 and related norites. Ar-Ar study of subsample 77215, 45a provided ages of 3.96 to 4.05 Ga, interpreted as the time of impact excavation [42]. Nakamura *et al.* [26] reported Rb-Sr and Sm-Nd results for 77215. Correcting their data to a value of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025$  for the NIST-987 standard and refitting the data using Isoplot [43] and a  $^{87}\text{Rb}$  decay constant of  $1.402 \times 10^{-11} \text{ yr}^{-1}$  [44], their Rb-Sr results for all splits define a scattered array (MSWD = 203) with slope corresponding to an age of  $4313 \pm 320$  Ma with initial  $^{87}\text{Sr}/^{86}\text{Sr} = 0.6997 \pm 0.0012$  (errors at the 95% confidence level). The two high-density separates analysed are the primary cause of scatter on the isochron. Excluding these two points from the line fitting, the remaining eight data points define a reasonably precise (MSWD = 2.6) isochron of age  $4371 \pm 52$  Ma with initial  $^{87}\text{Sr}/^{86}\text{Sr} = 0.69910 \pm 0.00013$ .

Accounting for interlaboratory bias in the Sm-Nd data of Nakamura *et al.* [26] is difficult for a number of reasons. They report data for a variety of standards, but none of the standards measured in the USGS laboratory at that time were measured by other groups, making it impossible to directly compare measured  $^{143}\text{Nd}/^{144}\text{Nd}$  data. Their Nd data are fractionation corrected to  $^{142}\text{Nd}/^{146}\text{Nd}$ , which is sensitive to interference from  $^{142}\text{Ce}$  and also propagates the variable  $^{142}\text{Nd}$  abundance caused by decay of  $^{146}\text{Sm}$  into the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio. Nakamura *et al.* [26] report significant  $^{142}\text{Ce}$  interferences in the range of  $10^{-4}$ – $10^{-5}$ . The effect of variable  $^{142}\text{Nd}$  is small because of the limited  $^{142}\text{Nd}$  variation in a lunar rock of this age. With their fractionation scheme, the  $^{146}\text{Nd}/^{144}\text{Nd}$  they measure in standards is 0.72198, which is higher than the 0.7219 value now used by most workers for fractionation correction of Nd isotope ratios. Re-correcting their data for mass fractionation to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  will raise their reported  $^{143}\text{Nd}/^{144}\text{Nd}$  values by a factor of 1.000055. Nakamura *et al.* [26] report data for a whole rock aliquot of the Juvinas eucrite, which can serve as another comparison with modern Sm-Nd data assuming that the Juvinas point lies on a 4.56 Ga isochron that passes through the average chondrite data of Bouvier *et al.* [45]. The Nakamura *et al.*'s [26] data for Juvinas, however, plot above the 4.56 Ga isochron because either  $^{143}\text{Nd}/^{144}\text{Nd}$  is too high by a factor of 1.000155, or  $^{147}\text{Sm}/^{144}\text{Nd}$  is

too low by a factor of 1.0136. Ignoring the correction suggested by the Juvinas comparison, their Sm-Nd data for mineral separates and whole rock aliquots from 77215 provide a Sm-Nd isochron age of  $4373 \pm 69$  Ma (MSWD = 1.0) with initial  $\epsilon^{143}\text{Nd} = -2.8 \pm 2.2$ . Using the Juvinas comparison and increasing their reported  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios by a factor of 1.0136 causes the data to define an isochron of  $4316 \pm 68$  Ma with initial  $\epsilon^{143}\text{Nd} = -4.3 \pm 2.2$ . Although problematic, the Nakamura *et al.*'s [26] data imply that the Sm-Nd crystallization age of 77215 is between 4.32 and 4.37 Ga.

Nunes *et al.* [46] report U-Pb results for whole rock and mineral separates from 77215. Recalculating their results using Isoplot provides a highly scattered Pb-Pb array of age  $4417 \pm 130$  Ma using all data points. At the radiogenic end of the array, data for pyroxene have substantially lower  $^{207}\text{Pb}/^{206}\text{Pb}$  at higher  $^{206}\text{Pb}/^{204}\text{Pb}$  than do whole rock measurements. A line fit to the whole rock and plagioclase data alone provides an age of  $4377 \pm 210$  Ma (MSWD = 22), while a line fit to the plagioclase and pyroxene data alone provides an age of  $4007 \pm 360$  Ma (MSWD = 1055). Both the scatter and young age of the pyroxene-plagioclase tie line suggest substantial disturbance of the U-Pb system in the mafic phases of 77215, something that is also observed in the Rb-Sr data of Nakamura *et al.* [26].

### 3. Procedures

Whole rock chips were crushed to powder in an agate mortar. A 143 mg aliquot of 77215 was crushed in an agate mortar and sieved to obtain 71.6 mg of a size fraction between 106 and 250  $\mu\text{m}$ . The less than 106  $\mu\text{m}$  fraction was used both for the total-spiked whole rock measurement with a separate aliquot (26.2 mg) dissolved and processed without spike. The sieved fraction was passed through a Frantz isodynamic separator in order to separate plagioclase from mafic phases. The final non-magnetic fraction consisted primarily of plagioclase with a small percentage of black grains that were removed by hand picking. The pyroxene fraction contained a fair amount of plagioclase and so was crushed further, sieved and passed again through the Frantz magnetic separator followed by a final handpicking to remove impurities.

Samples were weighed into 15 ml Savillex PFA Teflon beakers to which appropriate quantities of isotopically enriched  $^{87}\text{Rb}$ ,  $^{84}\text{Sr}$  and mixed  $^{150}\text{Nd}$ - $^{149}\text{Sm}$  and  $^{176}\text{Lu}$ - $^{178}\text{Hf}$  spikes were added. For this work, a highly enriched  $^{150}\text{Nd}$  (99.988 atom %) spike was used that allowed determination of the  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio for total-spiked samples with only minor correction needed for spike contribution to the isotopic composition. This newly prepared mixed Sm-Nd spike was calibrated against the same standard solutions prepared from AMES Sm and Nd metal used in the work of Boyet & Carlson [47]. The most recent calibration of the Lu-Hf spike, done in September 2013, showed Lu and Hf concentration reproducibility in four independent calibrations of 0.12% and 0.04%, respectively.

A blank, treated identically to the samples, but without sample added, was run in parallel with the samples. Sample digestion followed procedures described in Carlson *et al.* [48] and Boyet & Carlson [47]. The total procedural blank measured during this analysis period is Rb = 318 pg, Sr = 91 pg, Nd = 10 pg, Sm = 1.9 pg, Lu = 1.6 pg and Hf = 50 pg. These blanks are less than 0.12% of the analysed sample amounts for all Sr, Sm, Nd, Lu and Hf analyses. Rb blanks are less than 0.3–2.7% (77215 pyroxene) of the analysed amounts. Blank corrections have been made for all analyses.

A second whole rock Lu-Hf analysis of 77215 was performed at LLNL on a separate sample aliquot. After complete dissolution using Parr digestion vessels, the sample was split and one aliquot was spiked with a mixed  $^{180}\text{Hf}$ - $^{176}\text{Lu}$  tracer. Hafnium was purified following the procedures of Connelly *et al.* [49]. The REE cut from the cation exchange column was passed through an  $\alpha$ -hydroxyisobutyric acid column (0.1 M, pH = 4.10) to purify Lu. Purified Hf and Lu were analysed on the Nu Plasma HR MC-ICP-MS at LLNL.

Sr, Nd and Sm isotopic compositions were measured on the DTM Thermo-Fisher Triton thermal ionization mass spectrometer using procedures similar to those described in Carlson



*et al.* [50] and Qin *et al.* [51]. Each Sr ratio involved 8-s integrations with amplifier rotation used during runs of 262 (77215 pyroxene) to 400 (all other samples) ratios. Signal strengths of  $^{88}\text{Sr}$  ranged from  $2.5 \times 10^{-11}$  amps for 77215 pyroxene to  $10\text{--}17 \times 10^{-11}$  amps for all other samples.

Nd was analysed as  $\text{Nd}^+$  from double Re filaments using a two-step dynamic routine described in Carlson *et al.* [50]. The 77215 analyses involved  $^{144}\text{Nd}$  signal sizes of approximately  $1.6 \times 10^{-11}$  amps for a total of 240 ratios for pyroxene, 270 ratios for plagioclase and 360 ratios for the whole rock. All other whole rock analyses used  $^{144}\text{Nd}$  signal sizes of approximately  $2 \times 10^{-11}$  amps for 270 (67667), 960 (76335) or 1620 (78238) ratios. Average ratios for four runs of the JNdi standard run with the whole rocks (except 77215) are  $^{142}\text{Nd}/^{144}\text{Nd} = 1.141839 \pm 0.000011$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512109 \pm 0.000006$  (errors are  $2\sigma$ ). The averages for three filaments of the JNdi standard run 1 year later in the same barrel as the 77215 samples are  $^{142}\text{Nd}/^{144}\text{Nd} = 1.141840 \pm 0.000006$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512118 \pm 0.000005$ . The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios measured for the samples are adjusted to a value of 0.512115 for the JNdi standard, which is equivalent to  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511853$  for the La Jolla Nd standard as determined on consecutive runs of the JNdi and La Jolla standards.  $^{147}\text{Sm}/^{146}\text{Nd}$  was  $2 \times 10^{-6}$  or lower for most runs with the exception of 78238 ( $2 \times 10^{-5}$ ) and 77215 pyroxene ( $1.1 \times 10^{-5}$ ).  $^{140}\text{Ce}/^{146}\text{Nd}$  was less than  $5 \times 10^{-5}$  for most whole rocks and the 77215 pyroxene, but was  $1.3 \times 10^{-4}$  for plagioclase and  $3.5 \times 10^{-4}$  for 76335 whole rock. Corrections for  $^{142}\text{Ce}$  interference on  $^{142}\text{Nd}$  were applied for all samples.

Signal sizes of  $^{152}\text{Sm}$  of  $0.8\text{--}1.5 \times 10^{-11}$  amps were obtained for all samples with the data reflecting the average of 120 ratios taken with 8 s integrations using amplifier rotation. Mass fractionation was corrected to  $^{147}\text{Sm}/^{152}\text{Sm} = 0.56081$  and to  $^{147}\text{Sm}/^{154}\text{Sm} = 0.65916$ , the latter to check on the possibility of production of  $^{152}\text{Sm}$  via neutron capture on  $^{151}\text{Eu}$ . Using this latter fractionation correction, after spike correction, no sample displayed  $^{152}\text{Sm}/^{154}\text{Sm}$  ratios more than three parts in 10 000 higher than the standard. Given this minimal, if any, effect on the  $^{152}\text{Sm}$  relative abundance due to neutron exposure, Sm concentrations were calculated using the  $^{147}\text{Sm}/^{152}\text{Sm}$  fractionation correction. The Sm isotopic composition measured for an unspiked aliquot of 77215 whole rock (table 1) shows no resolvable deficit in  $^{149}\text{Sm}$ . Unspiked aliquots of Sm from 78238 and 76535 were measured in separate studies [25,34] and showed  $\epsilon^{149}\text{Sm}$  of  $-27.4$  and  $-13.5$ , respectively, relative to terrestrial Sm. After correction for the spike contribution to  $^{150}\text{Sm}$  (table 1), and using the  $^{150}\text{Sm}\text{--}^{149}\text{Sm}$  relationship for lunar samples with significant neutron capture histories from Boyet & Carlson [52], the estimated  $\epsilon^{149}\text{Sm}$  calculated from the spiked runs were  $-27.0$ ,  $-12.3$  and  $-3.0$  for 78238, 76355 and 67667, respectively. For calculating the Sm concentration and the corrections for neutron capture on  $^{142}\text{Nd}$ , the measured unspiked  $^{149}\text{Sm}$  values were used for 77215 and 78238, while for 76335 and 67667, the estimates of the  $^{149}\text{Sm}$  deficit obtained from the spike-corrected  $^{150}\text{Sm}$  values measured in this study were used. The neutron exposure of these samples required negligible corrections for 77215 and 67667, but the significant neutron exposures seen by 76335 and 78238 required corrections to  $^{142}\text{Nd}/^{144}\text{Nd}$  of 11 and 22 ppm, respectively, using the approach of Rankenburg *et al.* [32].

Rb, Lu and Hf were measured on the DTM Nu-Plasma-HR, multicollector ICP-MS. Instrumental mass fractionation for Rb and Lu was corrected using standards interspersed with the sample analyses. Signal sizes for  $^{85}\text{Rb}$  were  $0.6\text{--}2.8 \times 10^{-11}$  amps for all samples except 77215 pyroxene ( $7.9 \times 10^{-13}$  amps). Lu signal sizes were between  $^{175}\text{Lu} = 0.4$  and  $2 \times 10^{-11}$  amps for all whole rocks, but only  $6.5 \times 10^{-13}$  amps for 77215 pyroxene and  $1.5 \times 10^{-13}$  amps for 77215 plagioclase.

Solutions containing Hf were aspirated into the ICP-MS using an MCN-6000 desolvating nebulizer and  $50 \mu\text{l min}^{-1}$  Teflon nebulizer. Signal sizes of  $^{178}\text{Hf}$  were between 1.5 and  $6 \times 10^{-11}$  amps. Measured ratios of the monitored interferences to the  $^{177}\text{Hf}$  signal did not exceed 0.00006 for any sample. Ratios are calculated statically using 10 s integrations. Most samples were run for 80 ratios with the exception of 77215 whole rock and plagioclase (55 ratios) and 77215 pyroxene (49 ratios). Seven runs of the JMC-475 Hf standard run with all whole rocks but 77215 produced an average  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282145 \pm 0.000003$ . Five runs of the same standard run during the 77215 analytical session provided an average  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282138 \pm 0.000010$ .

**Table 1.** Sm and Hf isotopic composition. Sm fractionation corrected to  $^{147}\text{Sm}/^{152}\text{Sm} = 0.56081$ , Hf to  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  with  $^{176}\text{Hf}/^{177}\text{Hf}$  reported relative to 0.282160 for the JMC-475 Hf standard. Spike-corrected ratios reflect the values after stripping spike contribution, but the primary spiked isotope ratios ( $^{149}\text{Sm}/^{152}\text{Sm}$  and  $^{178}\text{Hf}/^{177}\text{Hf}$ ) are reported as measured.  $\varepsilon$  is the deviation in parts in 10 000 from the value of the ratio in the standard.

	$^{144}\text{Sm}/^{152}\text{Sm}$	$^{148}\text{Sm}/^{152}\text{Sm}$	$^{149}\text{Sm}/^{152}\text{Sm}$	$^{150}\text{Sm}/^{152}\text{Sm}$	$^{154}\text{Sm}/^{152}\text{Sm}$	$n$		
standard (DTM)	0.114946	0.420419	0.516840	0.275981	0.850812	2		
$2\sigma$	0.000015	0.000010	0.000011	0.000008	0.000012			
standard (LLNL)	0.114997	0.420438	0.516853	0.275993	0.850792	54		
$2\sigma$	0.000007	0.000013	0.000001	0.000005	0.000026			
							$\varepsilon^{149}\text{Sm}$	$\varepsilon^{150}\text{Sm}$
unspiked 77215 (DTM)	0.114968	0.420444	0.516841	0.276036	0.850795	0.02	2.00	
$2\sigma$	0.000003	0.000004	0.000005	0.000003	0.000008	0.09	0.11	
78238 (LLNL)	0.114986	0.420446	0.515437	0.277383	0.850658	−27.4	50.8	
$2\sigma$	0.000002	0.000003	0.000003	0.000002	0.000005	0.06	0.07	
spike corrected								
77215WR	0.114973	0.420440	0.911588	0.276084	0.850760	7638	3.73	
77215Px	0.114962	0.420421	0.780324	0.275978	0.850758	5098	−0.11	
77215PI	0.114985	0.420434	0.720466	0.276051	0.850735	3940	2.53	
67667	0.114971	0.420432	0.827814	0.276177	0.850772	6017	7.10	
76355	0.115005	0.420428	0.810244	0.276660	0.850594	5677	24.61	
78238	0.114979	0.420449	0.777587	0.277428	0.850697	5045	52.42	
	$^{174}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{178}\text{Hf}/^{177}\text{Hf}$	$^{180}\text{Hf}/^{177}\text{Hf}$	$\varepsilon^{180}\text{Hf}$			
standard	0.008653	0.282138	1.467481	1.886825				
$2\sigma$	0.000006	0.000010	0.000051	0.000079	0.42			
spike corrected								
77215WR	0.008658	0.282778	1.504768	1.886893	0.36			
77215Px	0.008647	0.282601	1.569252	1.886919	0.50			
77215PI	0.008633	0.281421	1.477830	1.886838	0.07			
76355	0.008663	0.281029	1.499380	1.886738	−0.46			
78238	0.008661	0.282554	1.536428	1.886611	−1.13			
67667	0.008655	0.282187	1.515238	1.886896	0.38			

The stable Hf isotope compositions, after spike correction, for each sample are reported in table 1. Given the limited neutron exposure of 77215 and 67667, concentration and spike correction calculations for these two samples were done assuming stable Hf isotopic compositions equal to those of the terrestrial standard. For 78238 and 76355, concentration calculations were done iteratively first using terrestrial standard Hf, then a Hf isotopic composition adjusted for the  $^{180}\text{Hf}/^{177}\text{Hf}$  calculated from the spike corrected value found in the first iterative step. In this second step, the deviation of the sample's  $\varepsilon^{178}\text{Hf}$  from the standard was assumed to equal 0.607 times that of the  $\varepsilon^{180}\text{Hf}$  based on fitting the lunar basalt data from Sprung *et al.* [35]. Using the same dataset, the neutron correction to  $\varepsilon^{176}\text{Hf} = 1.64^* \varepsilon^{180}\text{Hf}$  and is therefore −0.82 for 76355 and −2.0 for 78238.

**Table 2.** Isotopic results for Mg-suite samples. Sr isotopic composition fractionation corrected to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . The average value for  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained for NIST-987 Sr =  $0.7102561 \pm 0.0000013$  ( $n = 5$ ), but the data in the table are reported relative to a value of 0.71025. Nd is fractionation corrected to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ , with  $^{143}\text{Nd}/^{144}\text{Nd}$  reported relative to a value of 0.512115 for the JNdi Nd standard. Hf is fractionation corrected to  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  and reported relative to a value of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$  in the JMC-475 Hf standard. All fractionation correction is done assuming exponential mass dependency.  $^{142}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  are corrected for neutron capture as explained in the text. The LLNL Hf isotopic data were measured on an unspiked aliquot.

	77215 WR	77215-WR (LLNL)	77215 Plag	77215 Px	78238 WR	76355 WR	67667 WR
weight (g)	0.0685	0.1200	0.0159	0.0128	0.0911	0.1372	0.0742
[Rb] ppm	2.67		6.59	1.09	1.40	0.998	0.587
[Sr] ppm	92.6		216	7.80	83.8	157	117
$^{87}\text{Rb}/^{86}\text{Rb}$	0.0834		0.0884	0.4041	0.0483	0.0183	0.0145
$^{87}\text{Sr}/^{86}\text{Sr}$	0.704124		0.704723	0.724811	0.702287	0.700235	0.700043
$2\sigma$	0.000004		0.000003	0.000010	0.000004	0.000004	0.000004
[Sm] ppm	3.520		8.350	2.224	2.425	1.104	2.812
[Nd] ppm	12.13		47.78	6.082	8.386	3.689	8.805
$^{147}\text{Sm}/^{144}\text{Nd}$	0.1754		0.1566	0.2210	0.1748	0.1810	0.1930
$^{143}\text{Nd}/^{144}\text{Nd}$	0.512016		0.511491	0.513320	0.511988	0.512171	0.512538
$2\sigma$	0.000004		0.000004	0.000005	0.000001	0.000002	0.000004
$^{142}\text{Nd}/^{144}\text{Nd}$	1.141812		1.141806	1.141831	1.141816	1.141817	1.141829
$2\sigma$	0.000008		0.000007	0.000010	0.000003	0.000004	0.000008
[Lu] ppm	0.642	0.671	0.444	0.897	0.370	0.115	0.395
[Hf] ppm	2.700	3.483	3.501	3.988	1.687	1.258	2.112
$^{176}\text{Lu}/^{177}\text{Hf}$	0.03375	0.02734	0.01801	0.03193	0.0311	0.0130	0.0266
$^{176}\text{Hf}/^{177}\text{Hf}$	0.282778	0.282240	0.281421	0.282601	0.282554	0.281029	0.282187
$2\sigma$	0.000006	0.000010	0.000006	0.000009	0.000003	0.000005	0.000004

Results are reported in table 2. All line fitting in this paper is done using Isoplot [43]. Uncertainties assigned to Rb/Sr and Sm/Nd ratios are 0.1% and 0.5%, respectively. Given the small Lu signal sizes obtained for the 77215 mineral separates, the Lu/Hf ratios for the separates are assigned an error of 1% compared with the typical 0.5% for the whole rocks. Age uncertainties are reported at the 95% confidence level. Decay constants used for calculating ages are  $^{87}\text{Rb} = 1.402 \times 10^{-11} \text{ yr}^{-1}$  [44],  $^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ yr}^{-1}$  [53] and  $^{176}\text{Lu} = 1.867 \times 10^{-11} \text{ yr}^{-1}$  [54,55].  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  ages will be compared using decay constants of  $6.73 \times 10^{-9} \text{ yr}^{-1}$  [56] with Solar System initial  $^{146}\text{Sm}/^{144}\text{Sm} = 0.0084$  [57] and the more recently measured value of  $1.02 \times 10^{-8} \text{ yr}^{-1}$  [58], which requires the Solar System initial  $^{146}\text{Sm}/^{144}\text{Sm}$  to be adjusted to 0.0094. Chondrite reference parameters used in this paper are  $^{147}\text{Sm}/^{144}\text{Nd} = 0.196$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51263$ ,  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$  and  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$  from Bouvier *et al.* [45]. Uncertainties on initial Nd and Hf isotopic compositions are calculated using the approach of Fletcher & Rosman [59].

## 4. Results

The Sm-Nd data for 77215 define a  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  isochron of  $4283 \pm 23 \text{ Ma}$  (MSWD = 3.0) and initial  $^{143}\text{Nd}/^{144}\text{Nd} = 0.507039 \pm 0.000027$  for an initial  $\epsilon^{143}\text{Nd} = -0.35 \pm 0.09$  (figure 2). The data also define a good linear correlation in Sm/Nd versus  $^{142}\text{Nd}/^{144}\text{Nd}$  although the total range



in  $^{142}\text{Nd}/^{144}\text{Nd}$  is only 22 ppm. The slope of the line corresponds to an initial  $^{146}\text{Sm}/^{144}\text{Sm} = 0.00193 \pm 0.00092$  and an initial  $^{142}\text{Nd}/^{144}\text{Nd} = 1.141744 \pm 0.00006$  corresponding to  $\varepsilon^{142}\text{Nd} = -0.16 \pm 0.05$  relative to terrestrial Nd at that time. Using the 103 Ma half-life and Solar System initial  $^{146}\text{Sm}/^{144}\text{Sm} = 0.0084$ , the slope corresponds to an age of  $4348^{+57}_{-96}$  Ma. The age is calculated to be  $4413^{+38}_{-63}$  Ma when using the half-life from Kinoshita *et al.* [58]. The data reported here are clearly offset to higher  $^{143}\text{Nd}/^{144}\text{Nd}$ , or lower Sm/Nd, compared with the data reported by Nakamura *et al.* [26]. All of the Mg-suite whole rocks, except for 67667, lie within uncertainty of the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  line defined by 77215 (figure 2b), but are not used in the age calculation for 77215.

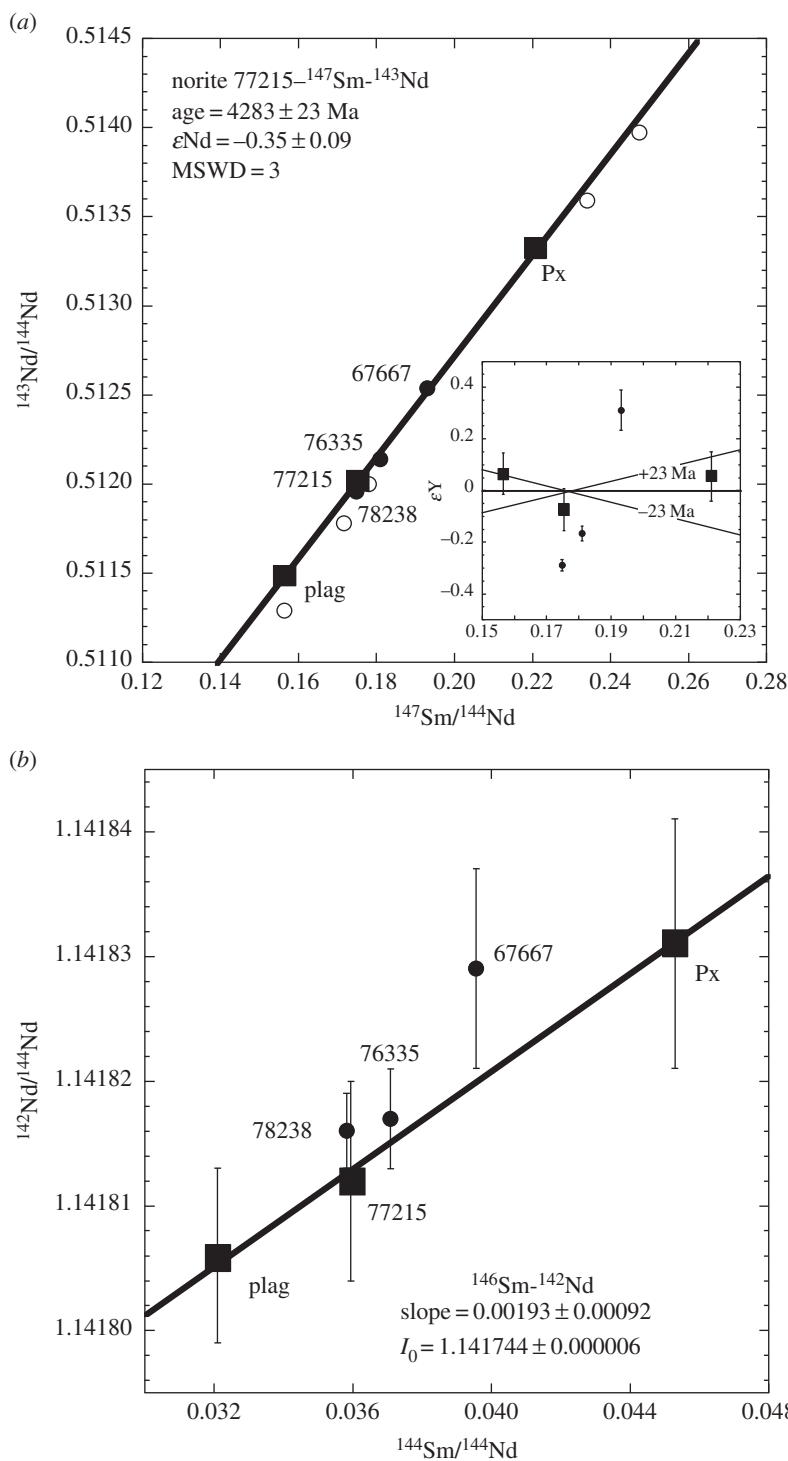
The four Lu-Hf data for 77215 define a linear array (MSWD = 2.6) with a slope that corresponds to an age of  $4421 \pm 68$  Ma with initial  $^{176}\text{Hf}/^{177}\text{Hf} = 0.27988 \pm 0.00004$  or initial  $\varepsilon\text{Hf} = -0.5 \pm 1.4$  (figure 3). The whole rock fraction measured here has a Lu/Hf ratio that does not lie between those of the pyroxene and plagioclase. The three other whole rock Mg-suite data also have been plotted on the 77215 isochron diagram in figure 3, but were not used in the calculation of the 77215 isochron. The whole rock data lie between 0.2 and 1.0  $\varepsilon$  above the 77215 isochron, suggesting that these Mg-suite samples share a similar petrogenetic history. Leaving out the much younger 67667, the remaining four whole rock data, for rocks with overlapping internal isochron ages, define a line that corresponds to an age of  $4347 \pm 29$  Ma (MSWD = 0.3) and initial  $^{176}\text{Hf}/^{177}\text{Hf} = 0.279930 \pm 0.000013$  ( $\varepsilon\text{Hf} = -0.5 \pm 0.5$ ).

The 77215 mineral data define a three point Rb-Sr best fit line with slope corresponding to an age of  $4450 \pm 270$  Ma (MSWD = 2) with initial  $^{87}\text{Sr}/^{86}\text{Sr} = 0.69888 \pm 0.00042$  (figure 4). At the low Rb/Sr end of the isochron, the whole rock and plagioclase separates do not plot on the isochron within uncertainty. They define two-point tie lines of 4400 Ma (plagioclase) and 4459 Ma (whole rock) with the pyroxene data. In the three data reported here, as with Lu-Hf, the whole rock has a Rb/Sr ratio that does not lie between the Rb/Sr ratios of the mineral separates implying that there is a phase in the whole rock with sufficiently low Rb/Sr and high Sr content compared with plagioclase to account for the offset of the whole rock point from the plagioclase separate. Our plagioclase separate also has substantially higher Rb/Sr ratio than did the plagioclase analysed by Nakamura *et al.* [26]. Including the data from Nakamura *et al.* [26], after adjusting to a value of NIST-987 = 0.710250 and assigning an uncertainty of  $\pm 1\%$  to their reported Rb/Sr ratios, the combined dataset defines an isochron of  $4374 \pm 45$  Ma (MSWD = 2.1) and initial  $^{87}\text{Sr}/^{86}\text{Sr} = 0.69908 \pm 0.00011$ , leaving off their two high-density mineral separates, which lie well above the line defined by the remaining samples. The other three Mg-suite whole rocks analysed here fall close to the 77215 mineral isochron but are not included in the age determination for 77215.

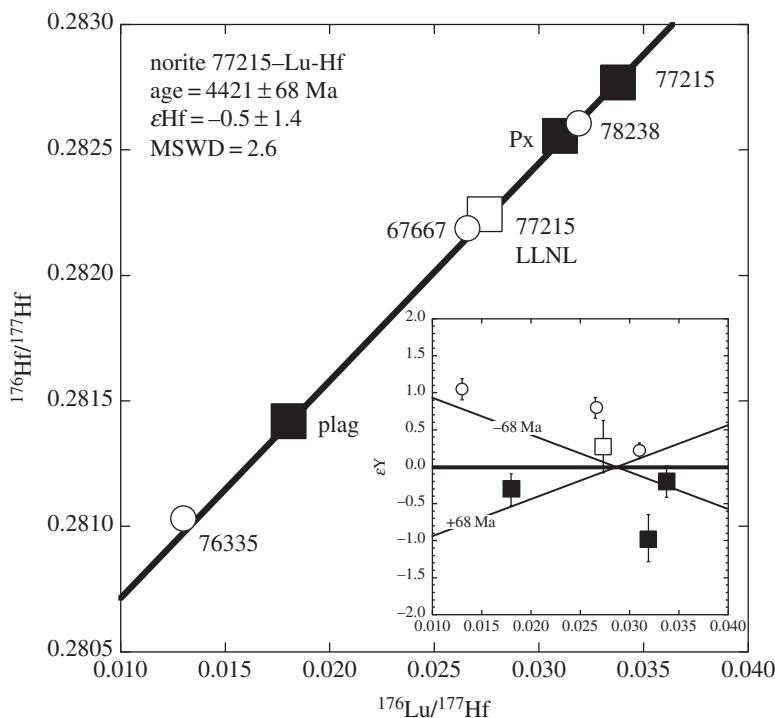
## 5. Discussion

### (a) 77215 mineral systematics

The small size (143 mg) of the starting sample used here and that (70 mg) used in the study of Nakamura *et al.* [26] make it unlikely that the 'whole rock' aliquots actually represent the whole rock composition of the 77215 norite. Nevertheless, the Rb and Sr concentrations for the whole rock splits from the two studies are within 14% and 7%, respectively. While the Sm and Nd concentrations differ by 22–24% between the two studies, the whole rock Sm/Nd ratios differ by only 1.7%. The greatest difference between our and the Nakamura *et al.*'s [26] data is for the Sm and Nd concentration of plagioclase. Our plagioclase separate has approximately twice as much Sm and Nd as did the plagioclase separate analysed by Nakamura *et al.* [26], but with nearly identical Sm/Nd ratios. Chao *et al.* [41] list an approximate mode for 77215 of 51.8% plagioclase, 44.6% orthopyroxene and a number of phases present at approximately 1% or less. With this mode, the Nd concentrations measured here for plagioclase and pyroxene would lead to a whole rock with approximately 19 ppm Nd, some 60% higher than the measured value. We interpret this



**Figure 2.** Sm-Nd isochron diagrams for 77215. Data measured here for 77215 are shown by filled squares along with the data for other Mg-suite whole rocks (filled circles). The open circles are the data from Nakamura *et al.* [26] that are as reported in that study after refractionation correction to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . The inset to part (a) shows the deviation of the individual points, in parts in 10 000 from the 77215 internal isochron.

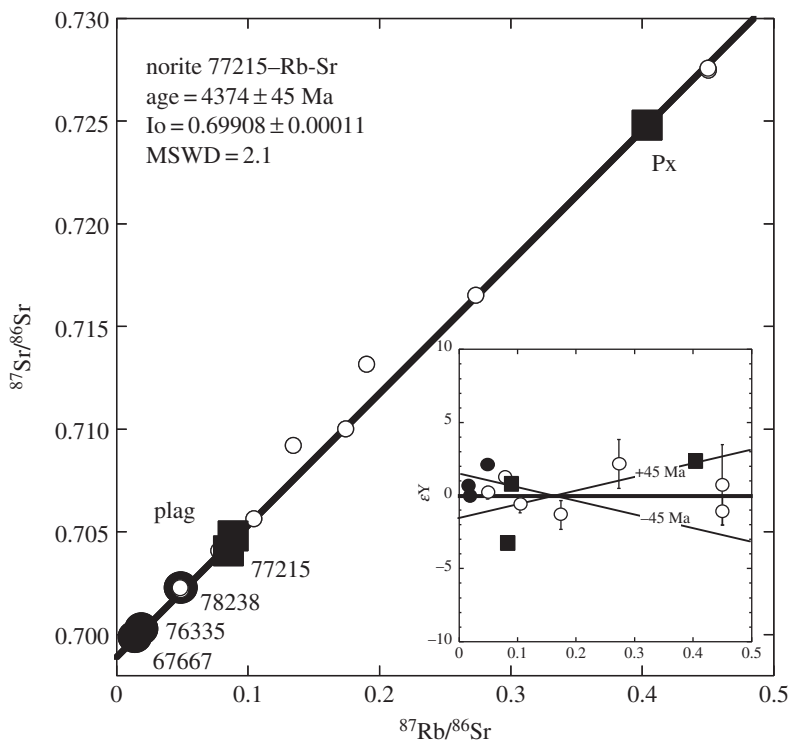


**Figure 3.** Lu–Hf isochron diagram for 77215 minerals and whole rock (squares) and other Mg-suite samples (circles). The open square denotes the 77215 whole rock sample measured at LLNL. The inset shows deviations of the data, in parts in 10 000 from the 77215 internal isochron. Only the data for 77215 are used to determine the lines shown in the figure.

combination of observations to suggest that our plagioclase separate contained a REE-rich phase in addition to plagioclase. One candidate is whitlockite. Chao *et al.* [41] note that whitlockite is found in the 77215 mesostasis that often is associated with aggregates of plagioclase. Using a Nd concentration of 13 000 ppm and Lu content of 200 ppm [60] as an estimate of the whitlockite REE concentrations in 77215, and the Nd concentrations measured in 77215 plagioclase by Nakamura *et al.* [26], the concentration of Nd in our plagioclase separate could be explained by the presence of 0.13% whitlockite. Assuming an Nd/Lu ratio of 340 in the 77215 plagioclase, as seen in plagioclase from Mg-suite troctolite 76535 [61], then using the same mixing model, 0.13% whitlockite in our plagioclase separate would result in the Lu concentration increasing from 0.046 ppm for pure plagioclase to 0.3 ppm for the whitlockite contaminated separate. The measured concentration is 0.43 ppm, thus the contamination of the plagioclase separate with per-mil amounts of whitlockite is a possible explanation for the Sm and Nd concentration difference between the plagioclase measured here and that reported by Nakamura *et al.* [26].

In combination with the more extensive Rb–Sr dataset reported by Nakamura *et al.* [26], this study derives ages for 77215 of: Rb–Sr =  $4374 \pm 45$  Ma,  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  =  $4283 \pm 23$  Ma,  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  = 4348 Ma (103 Ma half-life) to 4413 Ma (68 Ma half-life) and Lu–Hf =  $4421 \pm 68$  Ma. The  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  age determined here is marginally younger, but within uncertainty of the  $4373 \pm 69$  Ma age determined from refitting the data from Nakamura *et al.* [26], but our initial  $\epsilon_{\text{Nd}}$  is higher by approximately 2  $\epsilon$  units.

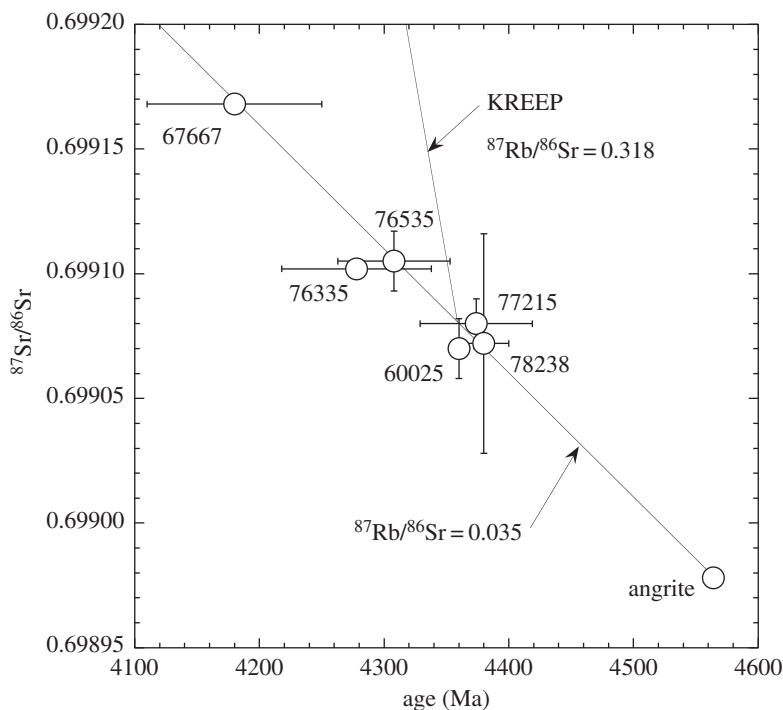
As with many studies of lunar highlands samples, this study finds discordant ages for different isotope systems when applied to exactly the same mineral and whole rock separates. Choosing which age best represents the crystallization age of the rock depends on applying subjective criteria. In reality, none of the ages need to reflect accurate crystallization ages as the lack of concordance from the different systems is a clear indication of disturbance of the radioisotope



**Figure 4.** Rb-Sr isochron diagram for 77215 minerals and whole rock (squares) and Mg-suite whole rocks (filled circles). Additional data (open circles) from Nakamura *et al.* [26]. Inset shows deviation in parts in 10 000 of the individual data from the best fit line to the data reported here and all but the two high-density separates from Nakamura *et al.* [26]. Only data for 77215 are used to determine the lines shown in the figure.

systems. For 77215, post-crystallization disturbance of its isotope systematics is clearly indicated by *ca* 3.9–4.0 Ga ages from both Ar-Ar [42] and U-Pb [46]. Although they give overlapping ages, both the Rb-Sr and Lu-Hf data for 77215 scatter about any best fit line outside of the analytical error of the individual points reflective of disturbance whose effect on the age provided by these systems is uncertain. The most precise age for 77215 is the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age of  $4283 \pm 23$  Ma, but this age is the youngest of all the ages determined here. While the Sm-Nd system is commonly suggested to be the most robust to resisting shock-related metamorphic disturbance, all the isochrons reported here depend on data for plagioclase, a mineral with a known low closure temperature and the propensity to turn to glass (maskelyite) during shock events. In addition, the plagioclase measured here, based on its REE concentrations, clearly cannot be pure plagioclase, but likely contains whitlockite, another mineral with a low closure temperature that is thus easily reset by shock. Our conclusion, unfortunately, has to be that the isotope systematics are disturbed and that the best estimate for the crystallization age of 77215 lies between its  $4283 \pm 23$  Ma  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  age and its  $4421 \pm 68$  Ma Lu-Hf age.

This age range for 77215 overlaps with two other recently redated Mg-suite rocks, 76535 ( $^{147}\text{Sm}$ - $^{143}\text{Nd} = 4306 \pm 11$  Ma [61]) and 78236 ( $^{147}\text{Sm}$ - $^{143}\text{Nd} = 4334 \pm 37$  Ma [27]), and with recently determined ages for FANs 60025 ( $4360 \pm 3$  Ma [14]) and 60016 ( $4300 \pm 32$  Ma [13]). Several Mg-suite samples have provided younger ages, but only three, 15445, 17 [22], 78236 [28] and 74217 [62] have provided ages as old as the older FANs (figure 1). The age determined for 72417 is based on Rb-Sr analyses mostly of different chips from this dunitic clast. The age of 15445 [22] is based on a Sm-Nd isochron that has highly scattered Rb-Sr systematics that do not support the Sm-Nd age. A second clast (15445, 247) from the same sample provides a much younger



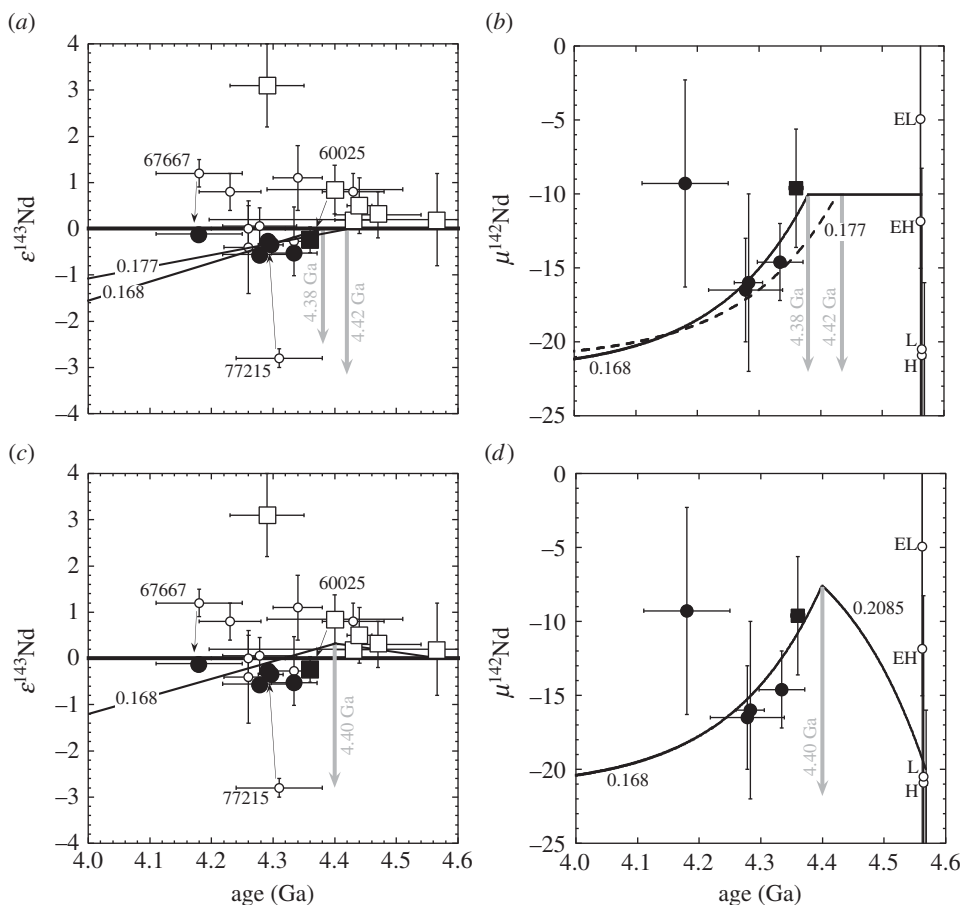
**Figure 5.** Sr isotope evolution diagram. Data for the angrite parent body initial from Hans *et al.* [63], 60025 from Carlson & Lugmair [17] and 76535 from Borg *et al.* [61]. The KREEP evolution line starts at the KREEP Sm-Nd model age of 4.36 Ga.

( $4.28 \pm 0.03$  Ga) Sm-Nd age. The old age for 78236 has not been reproduced in other studies of this same sample [21] or its related sample 78238 [27]. Our conclusion is that the available chronological data for Mg-suite and FANs from the lunar highlands are not sufficiently precise, nor free of evidence for shock disturbance, to convincingly resolve either the age range of the FANs or whether Mg-suite rocks extend to ages older than the youngest FANs. What is clear is that none of the highlands samples studied so far provide convincing evidence for their formation prior to *ca* 4.4–4.5 Ga.

## (b) History of the Mg-suite source

Regardless of the actual crystallization age of individual Mg-suite samples, their very elevated incompatible element abundances suggest the influence of a common, and highly differentiated, component in their magmatic source regions in the lunar interior. This is perhaps most clearly shown by the clustering of the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of the individual Mg-suite samples, and FAN 60025, along a single Sr isotope evolution line evolving with  $^{87}\text{Rb}/^{86}\text{Sr} = 0.035$  (figure 5). The estimated  $^{87}\text{Rb}/^{86}\text{Sr}$  of KREEP is 0.318 [6], so the Mg-suite source could not have had such a high Rb/Sr ratio for more than 20–30 Ma prior to the crystallization age of the samples without evolving higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  than measured for the samples (figure 5).

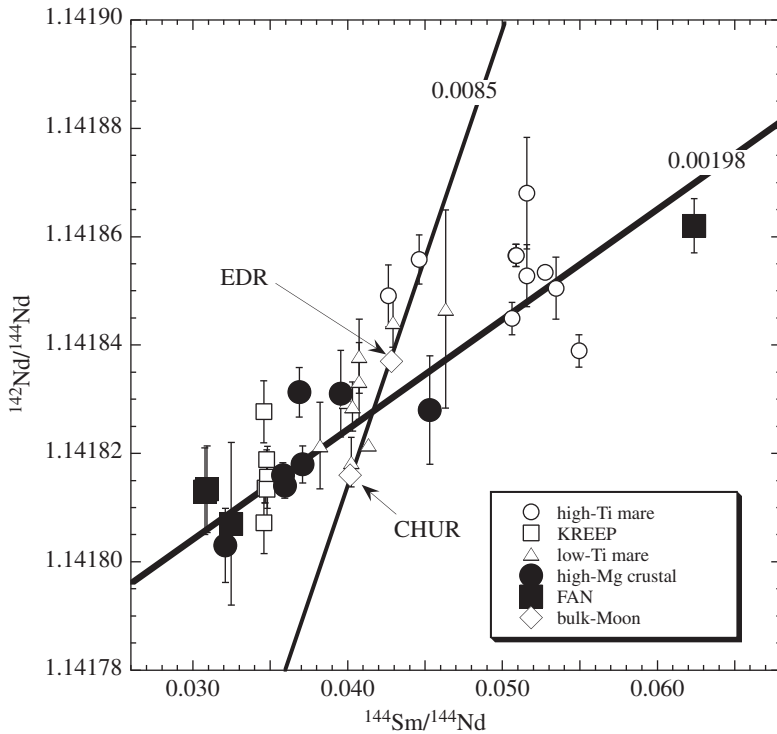
The derivation of the Mg-suite from a common source is supported by the excellent linearity of the whole rock Lu-Hf isochron defined by the data for the three Mg-suite samples with overlapping crystallization ages (excluding the younger 67667). The slope of this line corresponds to an age of  $4347 \pm 29$  Ma with initial  $\varepsilon_{\text{Hf}} = -0.5 \pm 0.5$ . This age has chronological significance only if the three rocks that define the line formed at the same time, from the same source, but we note the close correspondence of this age with the Sm-Nd and Lu-Hf model ages for KREEP [34,35,64].



**Figure 6.** Initial  $\epsilon^{143}\text{Nd}$  (parts in 10 000 deviation of initial  $^{143}\text{Nd}/^{144}\text{Nd}$  from the average chondrite reference [45]) and  $\mu^{142}\text{Nd}$  (ppm difference between the initial  $^{142}\text{Nd}/^{144}\text{Nd}$  and the value the terrestrial standard would have at the formation age of the sample when age corrected on the assumption of a chondritic Sm/Nd ratio). Open circles are literature data as cited in the caption for figure 1. The open square is the data for FAN 60025 [17] and the filled square for the same sample from Borg *et al.* [25]. Filled circles are the Mg-suite data reported here. Evolution lines in parts (a,b) assume a source with chondritic Sm/Nd ( $^{147}\text{Sm}/^{144}\text{Nd} = 0.196$ ; [45]) followed by evolution with the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios shown by the labels on the lines/curves. Evolution lines in parts (c,d) assume an evolution starting from the average  $^{142}\text{Nd}/^{144}\text{Nd}$  of ordinary chondrites (L, H) [31,47,50,65] with superchondritic Sm/Nd [47] until 4.4 Ga then with a  $^{147}\text{Sm}/^{144}\text{Nd} = 0.168$ , similar to estimated for KREEP [64]. Data for the average  $^{142}\text{Nd}/^{144}\text{Nd}$  in enstatite chondrites (EL, EH) from Gannoun *et al.* [66].

Figure 6a shows that the more recent data for the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  of both FAN 60025 and the Mg-suite samples measured here converge towards values that are just slightly below those expected for a source evolving with chondritic Sm/Nd ratio. The new data thus do not support the observation of earlier studies that most highlands rocks had slightly superchondritic  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios at the time of their formation. We suggest that this difference likely reflects more accurate Nd isotope analyses obtained from the much larger sample sizes needed in the recent studies to obtain sufficiently precise  $^{142}\text{Nd}/^{144}\text{Nd}$  data. The larger sample sizes allowed Nd to be measured as a metal instead of oxide ion, thereby minimizing correction for oxide interferences and Ce and Sm interference that is difficult to extract from Nd-oxide beams. The larger samples also are less sensitive to uncertainties resulting from processing blanks. The Mg-suite samples have Sm/Nd ratios that are too similar to define a precise whole rock isochron. The marginally negative initial  $\epsilon\text{Nd}$  of the Mg-suite samples indicates their derivation from a





**Figure 7.** Measured Sm/Nd versus  $^{142}\text{Nd}/^{144}\text{Nd}$  data for lunar igneous rocks. The best fit line through all the data has a slope of 0.00198 that corresponds to an age of 4352 Ma (103 Ma  $^{146}\text{Sm}$  half-life) to 4416 Ma (68 Ma half-life). On this diagram, a slope of 0.0085 corresponds to the start of Solar System formation (4.567 Ga). Data from Rankenburg *et al.* [32], Boyet & Carlson [52], Brandon *et al.* [68], Borg *et al.* [14] and Borg *et al.* [61]. Two end member estimates are shown for the bulk-Moon composition, CHUR is the average of ordinary chondrites while EDR is the Early Depleted Reservoir, both defined in Boyet & Carlson [47]. The best fit line to the data passes 9 ppm below the EDR point in  $^{142}\text{Nd}/^{144}\text{Nd}$  and hence about 9 ppm higher than the CHUR value.

light-REE-enriched source, consistent with their extreme enrichment in incompatible elements. Assuming that the Mg-suite samples obtained their incompatible elements from KREEP and taking typical estimates of the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio for KREEP (0.168–0.177 [6,64]), the source model age for 77215 ranges from 4.38 to 4.42 Ga (figure 6a), ages that overlap the  $4347 \pm 29$  Ma whole rock Lu-Hf isochron for the Mg-suite rocks. Figure 6b,c shows that the starting point of the lunar data in  $^{142}\text{Nd}/^{144}\text{Nd}$  at *ca* 4.4 Ga appears to be of order 10 ppm lower than that of the accessible Earth, within the range measured for average enstatite chondrites [66]. This could reflect a nucleosynthetically induced offset in the initial  $^{142}\text{Nd}/^{144}\text{Nd}$  of the Earth and Moon compared to the average value in ordinary chondrites [51,67], but the limited variation in initial  $\epsilon^{143}\text{Nd}$  and  $\mu^{142}\text{Nd}$  of the lunar crustal samples also allow the Moon to have an early evolution characterized by a superchondritic Sm/Nd ratio (figure 6c,d [52]).

### (c) Simultaneous formation of ferroan anorthosite, Mg-suite, KREEP and mare basalt sources?

The many compositional distinctions between Mg-suite and FAN rocks show that their sources and/or petrogenetic processes clearly were distinct, but the initial Sr, Nd and Hf isotopic overlap at 4.35–4.40 Ga suggests that the distinct sources of the Mg-suite and FANs were not present in the lunar interior much before this time. This observation can be extended to other rock types on

**Table 3.** Age estimates for early lunar and terrestrial differentiation events.

observation	age (Ma)	references
Moon		
oldest concordant FAN ages	4360–4470	[14,18]
peak in lunar zircon age distribution	4320	[69]
oldest point on lunar zircon	4417	[70]
zircon Hf model ages	4380–4480	[71]
mare basalt $^{146}\text{Sm}$ – $^{142}\text{Nd}$ source age	4320–4420	[31,32,52,68]
Pb model age for lunar highlands	4420	[72]
KREEP Sm–Nd and Lu–Hf model ages	4360–4440	[34,35,64]
$^{182}\text{Hf}$ – $^{182}\text{W}$ lunar model age	<4500 Ma	[73]
Earth		
Hf–W age of core formation	4450–4540	[74–76]
U–Pb age of the Earth	~4450	[77,78]
I–Pu–Xe age of the Earth’s atmosphere	~4450	[79–81]
$^{146}\text{Sm}$ – $^{142}\text{Nd}$ model age for Isua	4350–4470	[82,83]
peak in oldest Hadean zircons	4350	[84]
$^{146}\text{Sm}$ – $^{142}\text{Nd}$ age for Nuvvuagittuq crust	4340–4400	[85]

the Moon by noting that the  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  slope ( $0.00193 \pm 0.00092$ ) defined by the 77215 mineral data overlaps the  $0.00153 \pm 0.00035$  slope defined by data for minerals from FAN 60025, and both of these overlap the slope of the Sm/Nd versus  $^{142}\text{Nd}/^{144}\text{Nd}$  correlation defined by both KREEP and mare basalts (figure 7 [31,32,52,68]). The overlapping slopes of all the Sm/Nd versus  $^{142}\text{Nd}/^{144}\text{Nd}$  data for this wide variety of lunar rock types suggest that their diverse sources formed over a relatively short time interval, as would be predicted by the magma ocean model for initial lunar differentiation. The slope of the best fit line through all the data shown in figure 7 is  $0.00198 \pm 0.00037$ , which corresponds to an age of 4416 (68 Ma half-life) to 4352 Ma (103 Ma half-life). The initial  $^{142}\text{Nd}/^{144}\text{Nd}$  indicated by this ‘planetary isochron’ is 9 ppm lower than the accessible Earth would have at this time, within uncertainty of the 7 ppm deficit suggested by Sprung *et al.* [35]. The statistical uncertainty on the line corresponds to an error in the age on the order of 20–30 Ma. This ‘planetary isochron’, however, includes magmatic rocks whose measured Sm/Nd ratios almost certainly are different from those of their source rocks due to fractionation accompanying partial melting. Various attempts have been made to correct for the effect of this fractionation [31,32,35,52,68]. These approaches tend to lessen the slope of the Sm/Nd versus  $^{142}\text{Nd}/^{144}\text{Nd}$  trend, making the inferred age younger by as much as 40 Ma. Given that this ‘planetary isochron’ consists of a wide variety of rock types formed over more than a billion years of lunar history, the true age uncertainty on this correlation is unclear. Nevertheless, the fact that all the data scatter along a similar trend is consistent with the idea that the source regions of all of these lunar rock types formed in a single event of limited duration. Although the absolute age is uncertain, the slope of this correlation clearly indicates that this event did not occur at Solar System formation, but was delayed by some 150–200 Ma.

A number of approaches to estimate the timing of the initial differentiation of the Moon return values closer to 4.4 Ga than above 4.5 Ga (table 3). This age could reflect a late formation for the Moon, a late start to magma ocean crystallization, or possibly that the Apollo lunar sample collection represents not the product of a global magma ocean, but instead a large impact melt ‘lake’ produced by a huge impact into the Moon, e.g. the proposed Procellarum basin [20,86].

An argument that this relatively young age may reflect the time of Moon formation is provided by the observation that a variety of approaches to estimate the age of early differentiation events on the Earth also provide ages approaching 4.4 Ga instead of more than 4.5 Ga (table 3). Concordance of early differentiation ages for the Earth and Moon is most simply explained if these ages are dating the time of the giant impact into the Earth that ejected the materials that now make up the Moon. Some of the terrestrial ages, for example, the Hf-W age of terrestrial core formation and the I-Pu-Xe age of the Earth's atmosphere are older than 4.5 Ga, but these conceivably could reflect memory of the Earth differentiation events that occurred prior to the giant impact and Moon formation [75,76,81,87]. Although all estimates of the time of Earth and Moon formation involve a good deal of interpretation, a number of approaches to estimate the time of earliest Earth and Moon differentiation point more towards ages less than 4.45 Ga than more than 4.5 Ga. The overlapping and relatively young age estimates for several early Earth/Moon differentiation events is compatible with Moon formation by a giant impact into the Earth some 150–200 Ma after the initiation of Solar System formation. This impact is the Moon forming event and likely the last major global differentiation event associated with the Earth accretion.

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