Reports

Excess Lead in "Rusty Rock" 66095 and Implications for an Early Lunar Differentiation

Abstract. *Apollo 16 breccia 66095 contains a remarkably high amount of lead (15 parts per million), 85 percent of which is not supported by uranium and thorium in the rock. An acid leach experiment coupled with separate analyses of the whole rock and mineral fractions for uranium, thorium, and lead indicate that the excess lead has a lunar source and was apparently introduced about* 4.0×10^9 *years ago. The data also suggest that a major lunar crustal differentiation occurred about* 4.47×10^9 *years ago.*

Lunar studies have shown that the moon extensively differentiated very early in its history and that large quantities of volatile elements were lost then, at least from the outer portions of the moon. Wood *et al.* (*1*) were among the first to propose that the lunar highlands consisted of plagioclase-rich material formed by fractional crystallization during this early differentiation. Later, orbital x-ray fluorescence measurements supported this suggestion by proving that the highlands consist of aluminum-rich rocks (*2*). Physiographically, the highlands are older than the mare basalts which filled post-highland impact craters 3.2 to 3.9×10^9 years ago. Thus, the first pure anorthosite sample of any size to be collected from a highland region (sample 15415 from the Apennine mountain front) attracted considerable attention, because it was the best candidate to be a piece of the primitive lunar crust yet returned from the moon. Analyses of this rock for U, Th, and Pb by Tatsumoto *et al.* (*3*) and Tera *et al.* (*4*) and studies of its $^{40}Ar/^{39}Ar$ ratio by Husain *et al.* (*5*), Turner (*6*), and Eberhardt *et al.* (*7*) revealed an approximate age of 3.8 to 4.1×10^9 years. The workers on $^{40}Ar/^{39}Ar$ (*5, 6*) interpreted this age as the lower limit of the time of crystallization and considered sample 15415 to represent a fragment of primitive lunar crust. However, the groups studying U-Th-Pb (*3, 4*) independently concluded that the age of anorthosite 15415 gave no evidence for an ancient lunar crust, and they suggested that it may reflect an Imbrian excavation event. Indeed, the Apennine mountain front is blanketed with Imbrian ejecta, and finding a rock with U-Th-Pb and K-Ar systems that were not reset at Imbrian time might be unlikely.

Apollo 16 ventured farther into the lunar highlands with a landing in the Descartes mountain region. Many Apollo 16 samples exhibit unusually high concentrations of volatile elements. Of the 14 samples analyzed by Krähenbühl *et al.* (*8*), 66095 contains by far the most Zn, Cd, and particularly Tl. An analogously high Pb content for 66095 is reported here (about 15 ppm) and by El Goresy *et al.* (*9*), who found Pb concentrations of up to 4000 ppm in troilite-geothite boundaries. "Rusty rock" 66095 has been described as a fine-grained xenocryst-laden vesicular anorthositic rock with an igneous texture (*10*) and as a breccia with a dark matrix and light clasts (*11*). Particularly interesting is the presence of goethite (FeOOH) associated with FeNi metal grains in one case, and with troilite, sphalerite, and two sulfate phases in another case (*9*). Electron microprobe workers have suggested that the oxidation necessary to form the goethite may have occurred in the earth's atmosphere (*12*) or resulted from the impact of carbonaceous chondrites or a comet on the lunar surface (*9*). The opaque minerals have meteoritic compositions and are interpreted as extralunar by these workers. In this report, we present strong evidence that excess Pb in rock 66095 has a lunar origin, and not an extralunar one as proposed by El Goresy *et al.* (*9*).

Four small chunks of rock 66095 weighing about 80 mg each were pulverized together. Two samples of this powder were used for the first determination of the U-Th-Pb concentrations and the Pb isotopic composition of the whole rock. A third sample was dissolved and the solution was divided into two parts for the second such determination. A magnetic concentrate separated with a hand magnet, a hand-picked plagioclase concentrate and two samples of the whole rock sample minus these concentrates were also analyzed (Table 1). A sample of the whole rock weighing 704 mg was ground gently in a boron carbide mortar to a grain size of less than ½ mm for an acid-leaching experiment. The six leach steps were as follows:

1) a 10-minute wash with 5 ml of H_2O;

2) a 10-minute wash with 5 ml of $1N$ HNO_3 followed by a 2-ml H_2O rinse;

3) a 1-day wash with 4 ml of $1N$ HNO_3 followed by a 2-ml H_2O rinse;

4) a 1-day wash with 2 ml of $16N$ HNO_3 followed by a 3-ml H_2O rinse;

5) a 1-day wash with 2 ml of $16N$ HNO_3 plus 2 ml of 50 percent HF; and

6) transfer of the residue in the centrifuge tube to a beaker, where it was washed overnight with a warm solution consisting of 2 ml of $16N$ HNO_3 plus 2 ml of 50 percent HF.

Nitric acid leach steps 2 to 4 decomposed the accessory sulfur-bearing minerals (such as troilite), as evidenced by the release of H_2S, and likely dissolved most or all of the goethite. The bulk of the sample, however, was not visibly attacked until HF was used in step 5. The solids were separated by centrifuging from the leach solutions, which were then divided into portions and weighed for separate determinations of concentrations and Pb isotopic composition. A small residue (<20 mg) remaining after step 6 was not analyzed. Material balances (Table 2) indicate that essentially all the U and Pb were leached from the sample, although some Th apparently remained behind in the final

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Scoreboard for Reports: In the past few weeks the editors have received an average of 68 Reports per week and have accepted 12 (17 percent). We plan to accept about 12 reports per week for the next several weeks. In the selection of papers to be published we must deal with several factors: the number of good papers submitted, the number of accepted papers that have not yet been published, the balance of subjects, and length of individual papers.

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Table 1. Lead isotopic compositions and U, Th, and Pb concentrations of breccia 66095. The ^{208}Pb spike contribution has been subtracted from concentration data. The Pb enrichment age was calculated by using two-stage and three-stage U-Th-Pb evolution models (see text). The constants used are: $\lambda_{238} = 0.15369 \times 10^{-9}$ year^{-1}; $\lambda_{235} = 0.97216 \times 10^{-9}$ year^{-1}; $^{238}U/^{235}U = 137.8$. Total Pb blanks made with these analyses were: 3.4 ng (whole rock 1), 3.9 ng (whole rock 2), 2.0 ng (magnetic concentrate), 1.6 ng (plagioclase), and 1.4 ng (last two analyses). The abbreviations are P, composition; C, concentration. In the three-stage model $t_1 = 4.47 \times 10^9$ years.

Analysis	P, C	Weight (mg)	Concentration (ppm)			Atomic ratios								Pb enrichment age (× 10^9 years)	
						Observed			Corrected for blank						
			U	Th	Pb	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{232}Th/^{238}U$	$^{238}U/^{204}Pb$	Two-stage	Three-stage
Whole rock 1	P	11.0				143.5	183.0	139.6	155.8	199.7	150.0				
	C	112.0	1.026	3.815	16.26	181.0	232.8		183.6	236.3		3.84	35.6	3.76	4.00
Whole rock 2	P	94.0				180.7	232.4	169.9	185.1	238.4	173.8				
	C	26.4	1.004	3.746	13.75	179.6	231.1		192.1	247.8		3.85	37.7	3.78	4.01
Plagioclase concentrate	P	46.9				159.3	222.5	149.2	167.0	234.1	155.6				
	C	52.5	0.117	0.487	4.862	160.0	223.8		166.6	233.5		3.86	11.6	3.77	4.01
Magnetic concentrate	P	52.5				178.1	235.0	166.6	181.8	240.2	169.9				
	C	62.7	0.881	3.146	15.47	175.0	231.1		177.7	234.7		3.69	29.1	3.77	4.01
Whole rock-plagioclase-magnetics 1	P	80.3				184.2	235.4	172.7	186.4	238.3	174.9				
	C	61.3	1.029	3.874	13.13	186.4	238.5		188.8	241.6		3.89	40.5	3.79	4.03
Whole rock-plagioclase-magnetics 2	C	69.0	1.052	3.904	14.54	185.7	237.8		187.6	240.2		3.84	37.8	3.75	4.00

residue (compare the summed concentration data in Table 2 with the whole rock data in Table 1). Lead and uranium were both isolated by anion exchange techniques (*13*).

We may use U (a refractory element) and ^{204}Pb (a volatile, nonradiogenic lead isotope) in the ratio $^{238}U/^{204}Pb$ (μ) as a measure of volatile depletion. Values of μ for typical lunar basalts range from 400 to 600 and those for lunar KREEP range from 1000 to 3000 (*3, 14*). These values are very high compared to those for terrestrial basalts (about 10) and suggest that considerable volatile element depletion relative to the earth occurred at least in the outer layers of the moon. It was inferred previously [for example, see (*3, 14, 15*)] that typical lunar basalts and KREEP basalts were derived from sources with μ ranges of about 100 to 300 and 600 to 1000, respectively. Rock 66095 has a low μ (35 to 38) and an extremely high Pb content—the highest reported to date for any lunar sample except for the light portion of 12013 (*14*). The U and Th concentrations of the light portion of 12013 are large enough to account for all the accompanying radiogenic Pb, whereas the U and Th contents of 66095 are an order of magnitude lower and most of the Pb ("excess Pb") is not supported in situ U and Th.

In the following section we discuss evidence that this excess Pb probably evolved in a source environment similar to that for KREEP before its introduction into 66095. We estimate ages of 4.0 to 3.8×10^9 years for the Pb enrichment by using both two-stage and three-stage models for the evolution of Pb from U.

If we assume a simple two-stage evolution for the U-Th-Pb system of these rocks, and an age of 4.65×10^9 years (*15*) for the origin of the moon, we may use the following equations to calculate (i) the age of the end of the first stage of evolution, and (ii) the $^{238}U/^{204}Pb$ ratio in these samples during this first stage

$$^{206}Pb/^{204}Pb = (^{206}Pb/^{204}Pb)_0 + \mu_1(e^{\lambda_8 t_0} - e^{\lambda_8 t_1}) + \mu_2(e^{\lambda_8 t_1} - 1) \quad (1)$$

$$^{207}Pb/^{204}Pb = (^{207}Pb/^{204}Pb)_0 + \mu_1/137.8(e^{\lambda_5 t_0} - e^{\lambda_5 t_1}) + \mu_2/137.8(e^{\lambda_5 t_1} - 1) \quad (2)$$

where t_0 is primordial time (4.65×10^9 years); t_1 is the time of the change in μ; μ_1 is the $^{238}U/^{204}Pb$ ratio from t_0

Table 2. Lead isotopic compositions and U, Th, and Pb contents of acid leaches of rock 66095 and calculated initial Pb isotopic compositions. The total sample weight was 704.0 mg. The apparent concentrations are equal to micrograms removed from an acid wash (composition + concentration) divided by grams of total sample. The ^{208}Pb spike contribution has been subtracted from concentration data. Total Pb blanks were: 1.1 ng for steps 1 to 4 and 1.2 ng for steps 5 and 6. The Pb isotopic composition in step 1 (values in parentheses) is very uncertain due to the small amount of lead in the water leach. The abbreviations are P, composition; C, concentration. The initial Pb isotopic compositions were calculated with the U-Pb evolution models (see text) and the whole rock data from Table 1.

Step	P, C	Pb removed (corrected for blank) (ng)	Apparent concentrations (ppm)			Atomic ratios								
						Observed			Corrected for blank					
			U	Th	Pb	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{232}Th/^{238}U$	$^{238}U/^{204}Pb$
1) 10 minutes, H_2O	P	7.88				(72.4)	(96.9)	(81.2)	(110.6)	(154.6)	(112.2)	(0.715)		
	C	6.11	0.026	0.053	0.020	(27.9)	(29.0)		(30.3)	(32.3)		(1.07)	2.08	4.34
2) 10 minutes, 1*N* HNO_3	P	1594				160.1	226.9	159.4	161.1	228.7	160.7	0.7047		
	C	1532	.126	1.54	4.44	162.1	229.9		162.8	231.1		.7045	12.6	13.5
3) 1 day, 1*N* HNO_3	P	1088				163.1	229.8	161.4	164.5	232.1	163.0	.7088		
	C	916	.028	0.162	2.84	162.0	228.5		163.3	230.5		.7085	13.2	4.70
4) 1 day, 16*N* HNO_3	P	2133				164.1	230.1	161.7	165.0	231.4	162.8	.7132		
	C	1641	.030	.246	5.36	164.9	231.2		165.6	232.3		.7129	8.62	2.66
5) 1 day, 16*N* HNO_3 + 50% HF	P	658				402.4	323.6	296.5	413.6	332.6	304.7	1.2437		
	C	653	.660	.122	1.86	408.7	329.1		419.5	337.7		1.2422	0.19	322
6) Hot 16*N* HNO_3 + 50% HF	P	170				416.2	314.4	296.5	462.1	348.9	327.0	1.3245		
	C	139	.188	.402	0.438	427.8	323.5		487.1	368.1		1.3233	2.20	373
		Sums	1.06	2.53	15.0									
Calculated initial Pb isotopic composition:						Two-stage model			155.3	227.9		0.6814		
						Three-stage model			159.9	234.6		0.6816		

to t_1 calculated to the present-day value; μ_2 is the $^{238}\mathrm{U}/^{204}\mathrm{Pb}$ ratio from t_1 to the present (present-day value); $(^{206}\mathrm{Pb}/^{204}\mathrm{Pb})_0$ and $(^{207}\mathrm{Pb}/^{204}\mathrm{Pb})_0$ are primordial values (*16*); and λ_8 and λ_5 are the decay constants for $^{238}\mathrm{U}$ and $^{235}\mathrm{U}$ (see Table 1 heading).

Using this two-stage model, we calculate an age and a first-stage value of μ of $3.77 \pm 0.01 \times 10^9$ years and 570, respectively, for 66095 (Table 1). This age agrees very well with an internal U-Pb isochron age of $3.82 \pm 0.28 \times 10^9$ years [2 standard deviations (S.D.)] (Fig. 1). The rather high calculated μ_1 value of 570 suggests that the excess Pb was derived from a uranium-rich reservoir similar to the previously inferred source region for KREEP basalt. Therefore the significant KREEP-type component in 66095, deduced from U and Th concentrations, and the excess Pb were apparently both derived from the same uranium-rich source region or similar ones. By omitting the last term of Eqs. 1 and 2 we may calculate a first-stage ("initial") Pb isotopic composition for this rock. A calculated initial $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ ratio of 0.682 from whole rock data agrees excellently with the value of 0.684 ± 0.005 (2 S.D.) derived graphically from the internal U-Pb isochron (Fig. 1).

Table 2 contains the results of the acid-leach experiment. We stress the following points. (i) About 85 percent of the Pb and only 20 percent of the U present in rock 66095 were leached with $\mathrm{HNO_3}$ (steps 2 to 4). (ii) The remaining ("residual") Pb (15 percent) and U (80 percent) were removed only with more vigorous $\mathrm{HNO_3}$-HF acid leaches (steps 5 and 6). (iii) The isotopic compositions of the easily leached lead ($^{206}\mathrm{Pb}/^{204}\mathrm{Pb} \sim 164$; $^{206}\mathrm{Pb}/^{207}\mathrm{Pb} \sim 0.71$) and the residual Pb ($^{206}\mathrm{Pb}/^{204}\mathrm{Pb} \sim 415$; $^{206}\mathrm{Pb}/^{207}\mathrm{Pb} \sim 1.25$) are very distinct and appear to form two end members. (iv) The data on residual Pb and U, if plotted on a Pb-U evolution diagram, fall in the same field as Apollo 16 soils (*17*). (v) The apparent residual U and Pb concentrations, 0.85 and 2.3 ppm (summation of steps 5 and 6, Table 2), are close to the U and Pb concentrations of Apollo 16 soils from South Ray crater, 0.6 and 2.0 ppm (*17*). (vi) The isotopic composition of the easily leached (excess) Pb closely approaches the initial Pb isotopic composition of the whole rock, calculated by using the two-stage evolution model (Table 2). These observations indicate that we have a good separation of radiogenic Pb generated in situ (the residual portion) and excess Pb.

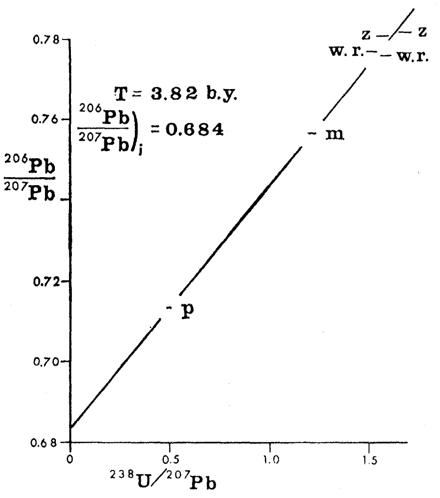

Fig. 1. Internal isochron for rock 66095; *w.r.*, whole rock; *m*, magnetic concentrate; *p*, plagioclase concentrate; *z*, whole rock minus plagioclase and magnetic separates; *b.y.*, 10^9 years; *i*, initial. A least-squares regression line fitted to the data (*31*) yields a slope of 0.60 ± 0.04 (2 S.D.) with an intercept of 0.684 ± 0.005 (2 S.D.). The slope corresponds to an age (*T*) of $3.82 \pm 0.28 \times 10^9$ years.

All the reported Pb isotopic data for 66095, plotted in Fig. 2, fall on a mixing line for initial Pb and radiogenic Pb generated in situ, with a slope corresponding to an apparent age of 4.01 ± 0.06 (2 S.D.) $\times 10^9$ years.

Origin of the excess Pb. Our values for the isotopic composition of excess Pb ($^{206}\mathrm{Pb}/^{204}\mathrm{Pb} \sim 164$) (Table 2, steps 2 to 4) are very different from the value in carbonaceous chondrites (~ 9). We cannot rule out isotopically the possibility that some of this excess Pb was derived from an extralunar source and mixed with a lunar Pb more radiogenic than the excess Pb we have measured. The uniformity of the Pb isotopic compositions in acid leach steps 2 to 4 (Table 2), however, suggests that we are dealing with a homogeneous Pb from a single source—that is, that all of the excess Pb in 66095 had a lunar source. Furthermore, it is difficult to imagine a mechanism by which an excess lunar Pb would mix with a carbonaceous chondrite Pb to form the apparently homogeneous initial Pb in 66095. Since meteorites other than carbonaceous chondrites generally have very low Pb contents, we do not consider them as plausible sources for the initial Pb in 66095. It has been suggested that many types of meteorites (especially carbonaceous chondrites) are derived from comets (*18*), and we speculate that cometary Pb might be similar to carbonaceous chondrite Pb, or even less radiogenic. If this is true, a cometary source for the initial Pb in 66095 may be as untenable as a meteorite source. This is extremely speculative, since no one has yet been able to study a cometary U-Pb system. We see no reason, however, to postulate such a far-fetched explanation for the source of initial Pb in 66095 when it is so easily explained as indigenous to the moon. We conclude that carbonaceous chondrite or cometary sources for the excess Pb in 66095 (*9*) are unsatisfactory. We do not understand how so much initial Pb and other volatiles (*8*) were highly enriched in 66095, but we think that trapping of thermally volatilized surface material as envisioned by Silver (*19*) and concentration of volatile volcanic emanations (from fumaroles?) are both reasonable hypotheses.

Age discussion. The slope of the mixing line in Fig. 2 corresponds to an age of $4.01 \pm 0.06 \times 10^9$ years. This age has strict significance only if the excess Pb in 66095 was introduced during a discrete time when the Pb in the rock was isotopically homogenized. Because the Pb in 66095 is physically heterogeneous, as shown by an electron microprobe study (*9*), one might expect isotopic homogenization during Pb enrichment 3.8 to 4.0×10^9 years ago to have been difficult to achieve. For two reasons, however, we stress that the vast bulk of the Pb present in 66095 about 4.0×10^9 years ago was probably isotopically homogeneous. First, the nearly uniform Pb isotopic compositions of $\mathrm{HNO_3}$ leach steps 2 to 4 (B in Fig. 2) suggest that one kind of Pb was introduced into 66095 at a discrete time. The physically admixed KREEP-type component in 66095 and the excess Pb were apparently both derived from a uranium-rich reservoir. This means that any initial Pb associated with the KREEP component had a Pb isotopic composition very similar to that of the excess Pb introduced about 4.0×10^9 years ago. Second, even if the non-KREEP components of 66095 contained an isotopically dissimilar Pb about 4.0×10^9 years ago, it was probably swamped by the excess Pb introduced about that time. This is reasonable since 66095 is about 60 percent plagioclase, and the Pb contents of lunar anorthosites are typically very small (~ 0.2 ppm) compared to the overall Pb concentration of 66095 (~ 15 ppm). Because the 66095 plagioclase concentrate contains so much Pb (~4.8 ppm), we believe that it and the other mineral concentrates with even greater Pb contents probably contained troilite-goethite inclusions with associated excess Pb. Indeed, the agreement of model ages calculated from both mineral concentrate and whole rock data (Table 1) argue that this is the case.

These observations explain why, within error, U-Pb isochrons from mineral concentrates (for example, Fig. 1) empirically yield an initial Pb isotopic composition the same as that calculated from whole rock data for 66095 by using a two-stage (or three-stage) U-Pb evolution model (Table 2). Therefore, although undetectable Pb isotopic heterogeneity may be present in 66095, we believe that the slope of the mixing line in Fig. 2 corresponds to an age (4.01×10^9 years) very close to that of Pb enrichment—whether or not this age is strictly correct.

This ^{207}Pb/^{206}Pb age of $4.01 \pm 0.06 \times 10^9$ years is significantly greater than the two-stage U-Pb evolution model age of $3.77 \pm 0.01 \times 10^9$ years (Table 1). The internal U-Pb isochron age (Fig. 1) of $3.82 \pm 0.28 \times 10^9$ years agrees within error with both these ages. Thus, if 4.01×10^9 years ago represents the time of Pb enrichment, the calculated age (3.77×10^9 years) may be slightly in error. This discrepancy can be resolved by using a three-stage U-Pb evolution model rather than a two-stage one to explain the Pb evolution in 66095. A three-stage model may be mathematically expressed with the following equation and an analogous one for ^{207}Pb/^{204}Pb

$$^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = (^{206}\mathrm{Pb}/^{204}\mathrm{Pb})_0 + \mu_1(e^{\lambda_8 t_0} - e^{\lambda_8 t_1}) + \mu_2(e^{\lambda_8 t_1} - e^{\lambda_8 t_2}) + \mu_3(e^{\lambda_8 t_2} - 1)$$

where μ_1, μ_2, and μ_3 are present-day ^{238}U/^{204}Pb ratios which characterized the first (t_0-t_1), second (t_1-t_2), and third (t_2-0) stages of U-Pb evolution. In order to calculate μ_2 and t_1, we make the following assumptions. (i) The lead enrichment age t_2 is 4.01×10^9 years, as inferred from Fig. 2. (ii) The moon is 4.65×10^9 years old ($t_0 = 4.65 \times 10^9$) (*15*). (iii) The moon's Pb isotopic composition at t_0 was the primordial value determined from meteorite data (*16*). (iv) The primordial ^{238}U/^{204}Pb value was about the same as that of carbonaceous chondrites ($\mu_1 = 1.5$) (*16*). Using this model and U-Pb data for the whole rock, we calculate an early differentiation age (t_1) of 4.47×10^9 years and a μ_2 of 1115 (about twice as high as the two-stage μ_1 of 570). If we assumed $\mu_1 = 34.5$—a value obtained from Apollo 17 orange soil (*20*)—instead of 1.5, calculated t_1 decreases from 4.47 to nearly 4.46×10^9 years, a difference of less than 0.01×10^9 years. Therefore, this calculation does not critically depend on the assumed μ_1 value. The inferred first stage of evolution lasted about 180×10^6 years and was presumably necessary for the moon's thermal regime to prepare for a major period of differentiation about 4.47×10^9 years ago, when μ_1 apparently increased from less than 50 to about 1100. This model suggests that the excess Pb in 66095 evolved in a U-rich reservoir (a high-μ reservoir) from about 4.47×10^9 years ago to about 4.01×10^9 years ago—presumably the time when Pb migrated from the U-rich reservoir to rock 66095.

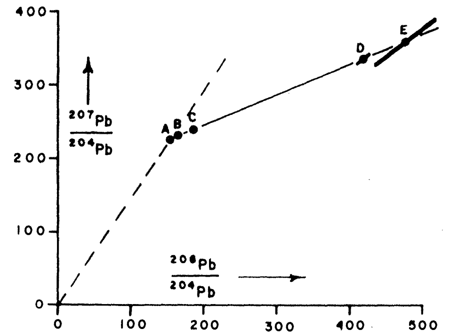

Fig. 2. (A) Initial Pb isotopic composition of rock 66095 calculated by using a two-stage U-Pb evolution model (see text). (B) Data for acid leach steps 2 to 4 (Table 2) and the plagioclase analysis in Table 1. (C) All Table 1 data except the plagioclase concentrate. (D) Data for acid leach step 5. (E) Data for acid leach step 6. A least-squares regression treatment (*32*) of all the acid leach data excluding step 1 yields a mixing line of slope 0.4127 ± 0.0144 (2 S.D.), which corresponds to an age of $4.01 \pm 0.06 \times 10^9$ years. Errors of individual analyses at points A, B, and C are smaller than the circles shown. Errors shown at points D and E are propagated errors computed by using twice the standard deviation of the mean for the mass spectrometry data and assuming a blank error of ± 50 percent. The dashed line drawn through the origin and the calculated initial Pb isotopic composition of 66095 corresponds to a ^{206}Pb/^{207}Pb ratio of 0.682, which agrees well with the ^{206}Pb/^{207}Pb initial ratio obtained from the mineral isochron (Fig. 1).

The credibility of this model is strongly enhanced by the fact that Apollo 16 metaclastic rocks 65015 (*13, 21*) and 60315 (*13*) have essentially concordant U-Pb ages of 3.99×10^9 years and igneous rock 68415 yields a U-Pb concordant age of 4.47×10^9 years (*13, 21*). The apparent production of a U-rich reservoir 4.47×10^9 years ago which accompanied a major period of lunar differentiation may have resulted in layers of different μ's, as discussed by Tatsumoto (*22*). Tera and Wasserburg (*23*) suggested a similar differentiation model from a consideration of initial Pb isotopic compositions of Apollo 14 rocks 14053 and 14310. The initial ^{206}Pb/^{207}Pb ratio they determined for these rocks agrees within error with the more precise initial ^{206}Pb/^{207}Pb value reported here for 66095. Papanastassiou and Wasserburg (*24*) also pursued such a model with Rb-Sr data for lunar soil. Perhaps it is not coincidence that Rb-Sr model ages of some Apollo 14 and Apollo 16 KREEP basalts are about 4.4×10^9 years (*25, 26*), or that the Xe implantation age of 14301 parent material is $4.41 \pm 0.05 \times 10^9$ years (*27*) and not more. Also, despite a Rb-Sr internal isochron age of 4.0×10^9 years probably associated with the Imbrian event for rock 12013 (*28*), Tatsumoto (*14*) presented U-Pb data which, when corrected for meteorite primordial Pb, yielded an age of 4.4×10^9 years—quite possibly the true crystallization age of this rock. Model Rb-Sr ages of 4.4 to 4.5×10^9 years for 12013 were also reported (*25, 28*).

A consequence of the 4.47×10^9 years differentiation model is that the moon as a whole may well not be very depleted in ^{204}Pb (and other volatiles?) relative to the earth as is so commonly believed, but only the outer layers may be so depleted. The important discovery of a relatively nonradiogenic Pb ($^{206}\mathrm{Pb}/^{204}\mathrm{Pb} \sim 23.4$) in the Apollo 17 "orange soil" (*20*) could be interpreted as supporting this inference. Recent evidence that KREEP and very high alumina rocks from different localities have distinct trace element contents (*29*) and possibly distinct pre-Imbrian formation ages (*26*) and the heterogeneous distribution of KREEP rocks on the lunar surfaces as inferred from gamma-ray studies (*30*) indicate to us that the inferred differentiation 4.47×10^9 years ago could be of major regional extent rather than on a global scale.

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Chondrules: An Origin by Impacts between Dust Grains

Abstract. *A barred chondrule in the Ngawi meteorite contains a magnetite spherule embedded in it. The collision between these two objects fractured and partially remelted the chondrule, an indication that the impact velocity was 10^5 to 10^6 centimeters per second. This observation supports Cameron's and Whipple's recent predictions that grains achieved high velocities in the nebula and that the resulting impacts provide a suitable chondrule-forming mechanism.*

Chondrules are millimeter-sized spherules that occur in abundance in primitive stony meteorites. They commonly contain glassy silicate material which, together with their spherical shape, indicates formation as rapidly cooled molten droplets dispersed in space (*1*). Their presence in primitive meteorites has led to the suggestion that they formed in the solar nebula, just prior to or during the accretion of planetary matter.

Modern theories on their origin may be divided into two broad categories: primary and secondary. According to primary theories, chondrules are thought to condense directly from the cooling nebular gas as stable (*2*) or metastable (*3*) liquid droplets. According to secondary theories, chondrules are thought to be produced by the flash heating and remelting of the original dust-like condensate. Various mechanisms for these secondary theories have been proposed: impact events (*4*) or quasi-volcanic activity (*5*) on the surfaces of protoplanets and lightning discharges (*6*) or high-velocity ($\gtrsim 10$ cm/sec) collisions between dust grains (*7, 8*) in the nebula.

There is a growing body of evidence in support of those secondary theories, for example, lightning or collisions, in which some fraction of the nebular dust is heated and melted just prior to accretion. Both lightning and collision models predict that the isotopic and elemental composition of chondrules should resemble the unaltered dust minus whatever volatile materials are lost during heating. Those dust particles which escaped reheating should retain their volatile components and presumably comprise the fine-grained, volatile-rich groundmass, or matrix, found in chondritic meteorites (*9*). Oxygen isotope ratios measured on separated chondrules and matrix are similar, an indication that both components ceased to exchange oxygen with the gas phase at about the same temperature. The temperatures inferred are rather low, 450° to 475°K, probably close to the temperature at which chondritic material accreted (*10*). Moreover, each family of chondritic meteorites has its own chemically distinct, characteristic type of chondrules and matrix, a finding that suggests a close genetic link between the two components. Both chondrules and matrix are depleted to the same degree in metallic elements, notably iron and nickel plus moderately volatile gallium and germanium. The simplest explanation is that a fraction of the metal grains was lost from the original condensate (= matrix) sometime after the condensation of gallium and germanium but before the conversion of dust into chondrules (*11*).

Several other clues support the collisional mechanism of chondrule formation over the lightning model. If chondrules were produced by lightning discharges, a correlation between mass and composition would be expected because the heat input depends on the surface area-mass ratio of the particles. Small chondrules would be heated to higher temperatures, and this would result in more efficient outgassing of certain elements, such as the alkali metals. But no correlation between mass and composition has been observed (*12*). In the collision model, where energy input depends upon both the mass and the relative velocity of the particles, a strict correlation is not expected. Moreover, it has been established for nearly a century that chondrules display numerous features indicative of impacts: fragmented chondrules, compound chondrules, fractures, veins, and crater-like indentations on their surfaces (*13*).

However, none of these features can unambiguously be interpreted as evidence that chondrules are produced by collisions; they merely imply that collisions were common. More definitive evidence would be a chondrule that froze in the process of formation or one that clearly displays evidence of a highly energetic impact between two low-temperature particles which led to a partial but not complete melting. It seems probable that at least a few such cases should be preserved if, as seems likely, grain size, velocity, and, hence, impact energies were variable. But, given the number of conditions that