Age Measurements

Age of the Moon: An Isotopic Study of Uranium-Thorium-Lead Systematics of Lunar Samples

Abstract. *Concentrations of U, Th, and Pb in Apollo 11 samples studied are low (U, 0.16 to 0.87; Th, 0.53 to 3.4; Pb, 0.29 to 1.7, in ppm) but the extremely radiogenic lead in samples allows radiometric dating. The fine dust and the breccia have a concordant age of 4.66 billion years on the basis of $^{207}Pb/^{206}Pb$, $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$, and $^{208}Pb/^{232}Th$ ratios. This age is comparable with the age of meteorites and with the age generally accepted for the earth. Six crystalline and vesicular samples are distinctly younger than the dust and breccia. The $^{238}U/^{235}U$ ratio is the same as that in earth rocks, and ^{234}U is in radioactive equilibrium with parent ^{238}U.*

Patterson and others *(1)* first applied isotopic lead data to determine the age of meteorites and the earth as 4.55 ± 0.07 billion years, assuming that lead in stone meteorites and modern terrestrial lead have evolved from a primordial lead compositionally like the lead in iron meteorites. We have used this method to determine the age of lunar samples and to obtain insight into the chemical differentiation history of lunar surface material. The abundance ratios of lead isotopes and uranium isotopes (^{238}U, ^{235}U, and ^{234}U) were determined by mass spectrometry, and the radioactivity ratios of the uranium isotopes and the thorium isotopes (^{232}Th, ^{230}Th, and ^{228}Th) by α spectrometry.

Details of analytical procedures will be discussed in a later report. Lead was first separated by barium coprecipitation *(2)* and dithizone extraction after HF-$HClO_4$ sample decomposition. Uranium and thorium were separated by Dowex-1 resin from 6*N* HCl. Uranium was further purified by hexone extraction, and thorium was separated by Dowex-1 resin from 7*N* HNO_3 media *(2)* for isotopic ratio measurement.

The concentrations of lead, uranium, and thorium were determined by isotope dilution *(2)*. Owing to the importance of blank corrections, each set of analyses for the determination of both the isotopic composition and the concentration was accompanied by a blank analysis. Blanks yielded 0.015 to 0.032 μg for Pb concentration and composition separations; 0.0001 and 0.00015 μg for U and Th concentrations, respectively. Blanks for U and Th composition are about 10 times the blanks of the concentration runs. Lead was run by mass spectrometer with phosphoric acid–silica gel *(3)* with some modification. The standard deviations of the lead isotope ratios are $^{206}Pb/^{204}Pb$ (±1 percent, except sample 10050 which has ±3 percent uncertainty), $^{206}Pb/^{207}Pb$ (±0.2 percent), $^{206}Pb/^{208}Pb$ (±0.3 percent). However, because of the low concentration of lead in samples, the procedure for making blank correction of the data introduces relatively large overall uncertainties. The blank correction has the most effect on ^{204}Pb abundance; and, because corrections essentially change the location of points along isochrons (Fig. 1), no serious difficulty seems to arise for the age measurements.

Results are summarized in Table 1. The uranium and thorium concentrations are in good agreement with those reported by the Preliminary Examination Team *(4)*. The average values of uranium and thorium concentrations are higher than those in stone meteorites *(5)*; however, the lowest value of uranium and thorium observed for sample 10050 is similar to values of the Nuevo Laredo achondrite. Lead contents of the lunar samples are in the range of stone meteorites *(5)*. The uranium and thorium concentration is 2 to 4 times higher than that of terrestrial oceanic basalts and Hawaiian tholeiites, and it is similar to the concentration in oceanic alkali basalts *(6)*. Th/U ratios are about 3.9 with some variation. The uranium isotopic ratio ($^{238}U/^{235}U$) in five different lunar rocks that were measured is the same as for terrestrial rocks, within the experimental error (137.8 ± 0.4). The ^{234}U daughter is in radioactive equilibrium with parent ^{238}U within experimental error of ±1.5 percent.

The lead isotopic composition in all Apollo 11 samples examined is very

Table 1. Concentrations of lead, uranium, and thorium and isotopic compositions of lead in Apollo 11 samples.

Sample No.	Type	Concentration*			Atomic ratios				
		Pb (ppm)	U (ppm)	Th (ppm)	$^{206}Pb/^{201}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{238}U/^{204}Pb$	$^{232}Th/^{238}U$
10003	Crystalline	0.51	0.268	1.029	423.9 (311.9)†	198.0 (147.6)	448.9 (333.3)	491.3	3.96
10017	Crystalline	1.56	0.854	3.363	410.0 (367.7)	191.9 (173.7)	435.0 (390.2)	492.8	4.07
10020	Vesicular	0.37	0.202	0.694	288.7 (238.9)	139.0 (116.3)	289.7 (243.5)	338.3	3.55
10050	Crystalline	0.29	0.156	0.531	295.8 (187.7)	147.0 (95.8)	287.3 (190.2)	397.2	3.53
10057	Vesicular	1.68	0.865	3.415	1241.5 (938.6)	590.1 (447.9)	1281.3 (973.6)	1392	4.08
10071	Vesicular	1.71	0.873	3.434	199.7 (191.2)	95.8 (92.0)	206.7 (198.7)	222.5	4.06
10061	Breccia	1.74	0.674	2.572	249.1 (238.8)	163.2 (152.8)	258.2 (242.7)	255.6	3.94
10084	Fine material	1.39	0.544	2.092	261.9 (237.4)	171.0 (155.3)	270.1 (246.7)	239.6	3.97

*Estimated errors for the concentrations are better than 2 percent for Pb and 1 percent for U and Th.
†Values in parentheses are measured ratios before blank correction.
Erratum: The lead isotopic composition (corrected for blank) of sample 10071 was recalculated to be $^{206}Pb/^{204}Pb = 735.4$, $^{207}Pb/^{204}Pb = 361.2$, $^{208}Pb/^{204}Pb = 779.5$, and $^{238}U/^{204}Pb = 839.2$.

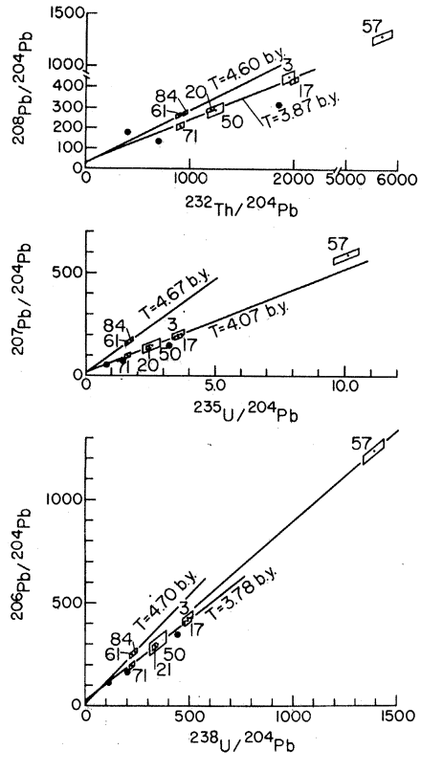


Fig. 1. The ^{206}Pb-^{238}U, ^{207}Pb-^{235}U, and ^{208}Pb-^{232}Th isochrons for Apollo 11 samples. Indicated errors (boxes) include blank corrections (see Table 1). Solid circles are for the mineral composite fraction of sample 10071. The errors in the data on the fractions are not indicated. Numbers are final digits of sample numbers.

radiogenic, which makes radiometric dating possible. The present $^{238}U/^{204}Pb$ is in the range of 200 to 1400. Patterson *(1)*, in his lead isotope study of meteorites, calculated the uranium and thorium concentrations required to produce the lead concentration and isotopic composition. However, these calculated values of uranium and thorium were an order of magnitude higher than those actually determined later in stony meteorites *(5)*. On the other hand, almost all lead that exists in the measured lunar samples is supported by its uranium and thorium parents, as is shown by the nearly concordant ages in Table 2.

The results are plotted in three ways in Fig. 1. By this plotting technique we may be able to obtain the initial $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, as well as isochron ages, on the assumption that some samples are coeval and were formed from sources of uniform lead isotopic composition. The dust (sample 10084) and breccia (sample 10061) have clearly older ages than crystalline rocks. The tie lines between these data points and primordial lead *(7)* correspond to 4.70, 4.67, and 4.60 billion years, respectively, in plots of ^{238}U-^{206}Pb, ^{235}U-^{207}Pb, and ^{232}Th-^{208}Pb. The data points of the crystalline rocks, except sample 10057, fall in a group and indicate, respectively, isochrons of 3.78, 4.07, and 3.87 billion years in the three-way plot. The initial lead ratios are obtained from the intercepts on the *Y* axes in Fig. 1. The initial values obtained by least-squares method *(8)* and based on these six crystalline rocks, if coeval, are 23.6 ± 5.4 for $^{206}Pb/^{204}Pb$, 13.3 ± 4.0 for $^{207}Pb/^{204}Pb$, and 11.9 ± 17.4 for $^{208}Pb/^{204}Pb$. These ratios are, however, highly uncertain. The $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ values appear to be too small, compared with those of the primordial lead of meteorites.

The $^{206}Pb/^{204}Pb$ intercept value is higher compared with that of primordial lead but seems reasonable if the $(^{238}U/^{204}Pb)_0$ value on the moon surface is high as seen in these Apollo 11 samples. The $(^{238}U/^{204}Pb)_0$ is calculated to be about 70 based on the observed intercept value. Of course the common lead correction does not introduce a large effect in the age, owing to the large sample age and to the very radiogenic nature of the lead.

Table 2. Apparent ages of Apollo 11 samples (in million years). Constants used were

$\lambda_{^{238}U} = 1.5369 \times 10^{-10}y^{-1}$

$\lambda_{^{235}U} = 9.7216 \times 10^{-10}y^{-1}$

$\lambda_{^{232}Th} = 4.990 \times 10^{-11}y^{-1}$

$^{238}U/^{235}U = 137.8$

Sample No.	$\frac{^{206}Pb}{^{238}U}$	$\frac{^{207}Pb}{^{235}U}$	$\frac{^{207}Pb}{^{206}Pb}$	$\frac{^{208}Pb}{^{232}Th}$
10003*	3878	3976	4025	3812
10017*	3767	3935	4022	3598
10020*	3765	3903	3996	3773
10050*	3760	3952	4051	3680
10057*	4089	4146	4173	3959
10071*	3794	3815	3826	3374
10061†	4710	4678	4663	4594
10084†	4685	4668	4659	4525

*Assumed isotopic composition for common lead: $^{206}Pb/^{204}Pb$, 23.6; $^{207}Pb/^{204}Pb$, 31.5; $^{208}Pb/^{204}Pb$ = 40.9. †Assumed initial lead for common lead: $^{206}Pb/^{204}Pb$, 9.346; $^{207}Pb/^{204}Pb$, 10.218; $^{208}Pb/^{204}Pb$, 28.96.

Crystalline sample 10017 and dust sample 10084 were separated into "mineral composites," and the fractions were analyzed for lead isotopes and for lead, uranium, and thorium content. The isochrons from mineral fractions are slightly younger than isochrons of total rocks. The reason for the difference is not well understood, but it may be due to a large lead contamination, to leaching out of daughters during the mineral separation, or to the rocks not being coeval. However, it should be mentioned that the intercepts for the initial $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ obtained from sample 10017 fractions are the same, within the experimental error, as the intercept of the six crystalline rocks (see Fig. 1). Therefore, we chose the following values, as a maximum, to correct common lead for the crystalline

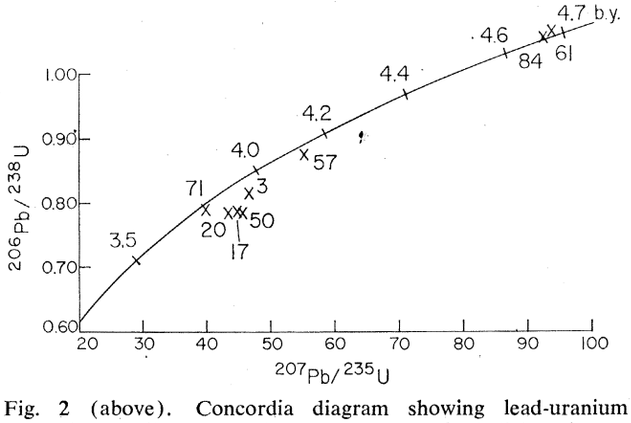
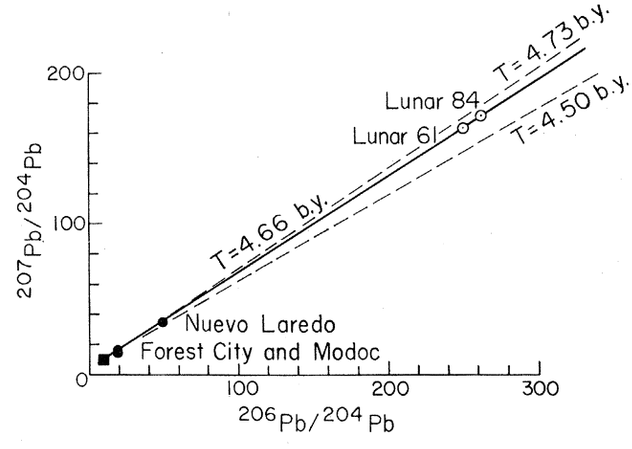


Fig. 2 (above). Concordia diagram showing lead-uranium ratios for Apollo 11 samples. Numbers are final digits of sample numbers. Fig. 3 (right). The ^{207}Pb-^{206}Pb evolution diagram for moon and meteorites.



rocks: $^{206}Pb/^{204}Pb$ = 23.6, $^{207}Pb/^{204}Pb$ = 31.5 and $^{208}Pb/^{204}Pb$ = 40.9. These values were calculated from the $^{206}Pb/^{204}Pb$ intercept and on the assumption that lead had evolved from 4.7 to 3.7 billion years prior to crystalline rock formation. The intercepts obtained from 10084 fractions are the same within experimental error as the value obtained from meteorite lead.

The apparent ages are shown in Table 2. The initial leads used for correction are primeval lead of meteorite (*7*) for samples 10061 and 10084 and common lead (given above) for crystalline rocks. The ages indicate that sample 10071 may be younger and 10057 older than the other four crystalline rocks. Thus it might be conceivable that the common lead used for age calculation remains small because the isochrons in Fig. 1 are strongly controlled by the position of sample 10071.

The results corrected for initial lead are plotted in the Pb-U evolution diagram (Fig. 2). The points of the dust and breccia are above the concordia line, but those of crystalline rocks are below the concordia line. The apparent ages of 3.8 to 4.1 billion years for crystallized rocks indicate that they solidified several hundred million years after the formation of the moon. The dust apparently contains only minor amounts of fine fragments of the younger rocks that were analyzed. The most feasible interpretation is that dust and breccia probably were formed at an early stage in the history of the moon.

In Fig. 3, $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ for lunar dust and breccia are plotted with Patterson's data (*1*) on stone meteorite and Oversby's measurement (*7*) of primordial lead on the Canyon Diablo troilite. These data indicate that the system, of which earth, moon, and meteorites are parts, probably was formed about 4.66 $^{+0.07}_{-0.16}$ billion years ago. We set the upper limit from our experimental error, which amounts to about 1.5 percent, and the lower limit to include Patterson's meteorite data. It might be argued that the obtained age for the moon is from breccia and dust—not the lunar crystalline rock—and there may be doubt that those two samples represent the oldest rock of the moon. However, inasmuch as (i) the observed data fit into the extension of the meteorite lead array, (ii) the data lie near the U-Pb evolution curve, and (iii) the obtained age is very similar to the "older" meteorite ages measured by the Rb-Sr method (*10*), the age may be correct.

Thorium-232, with a 4.0-Mev α particle emission, has been used as a natural yield tracer for the determination of the state of radioactive equilibrium between ^{230}Th and parent ^{238}U in crustal silicate rocks from the earth (*11*). This technique of using ^{232}Th, of known concentration in a sample, as the yield tracer for ^{230}Th was used on several samples from Apollo 11. Although, within experimental error, ^{234}U is in radioactive equilibrium with ^{238}U, preliminary data indicate a value for the $^{230}Th/^{238}U$ activity ratio that is greater than unity in three of the samples analyzed (10017, 10020, 10057). A $^{228}Th/^{232}Th$ activity ratio of unity would indicate that ^{228}Th is in radioactive equilibrium with parent ^{232}Th. In two of the rocks (10020, 10057) the ^{228}Th α activity was measured to be about 10 percent greater than the 4.0-Mev α activity of ^{232}Th. The reasons for these variations are not understood at this time.

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Ages, Irradiation History, and Chemical Composition of Lunar Rocks from the Sea of Tranquillity

Abstract. *The ^{87}Rb-^{87}Sr internal isochrons for five rocks yield an age of 3.65 ± 0.05 × 10^9 years which presumably dates the formation of the Sea of Tranquillity. Potassium-argon ages are consistent with this result. The soil has a model age of 4.5 × 10^9 years, which is best regarded as the time of initial differentiation of the lunar crust. A peculiar rock fragment from the soil gave a model age of 4.44 × 10^9 years. Relative abundances of alkalis do not suggest differential volatilization. The irradiation history of lunar rocks is inferred from isotopic measurements of gadolinium, vanadium, and cosmogenic rare gases. Spallation xenon spectra exhibit a high and variable $^{131}Xe/^{126}Xe$ ratio. No evidence for ^{129}I was found. The isotopic composition of solar-wind xenon is distinct from that of the atmosphere and of the average for carbonaceous chondrites, but the krypton composition appears similar to average carbonaceous chondrite krypton.*

Samples investigated were 10017, 10044, 10050, 10057, 10059, 10069, 10071, soil (10084), coarse fines (10085), and core 2 (referred to by Nos. 17, 44, etc.). Contamination levels were negligible. Standards were regularly run to control precision *to the levels reported.*

Rubidium-strontium analyses on total rocks and minerals were obtained. The Sr is concentrated in plagioclase and the K in a fine-grained or glassy interstitial phase, containing up to 12 percent K. Maximum Rb/Sr was obtained in cristobalite and ilmenite separates due to the interstitial high-K phase. Precise internal isochrons on five rocks give the same age of 3.65 × 10^9 years (Fig. 1). All $(^{87}Sr/^{86}Sr)_I$ are distinctly above BABI (*1*). The $(^{87}Sr/^{86}Sr)_I$ for No. 44 is distinct from that of other samples, indicating that the samples represent at least two different rock bodies (Fig. 2). The possibility that the isochrons are two-phase mixing lines cannot be excluded, considering the distribution of alkalis, but the coincidence of ages for rocks of different $(^{87}Sr/Sr^{86})_I$ and texture argues that 3.65 × 10^9 years is the time of crystallization.

The possibility that the age of 3.65 × 10^9 years represents closed-system meta-