Lead and Thallium Isotopes in Mare Tranquillitatis Surface Material

Abstract: *Lead from Apollo 11 fines is more radiogenic than any meteoritic lead reported and older than any terrestrial radiogenic lead:* $^{204}Pb/^{206}Pb/^{207}Pb/^{208}Pb = 1/99_{.6}/69_{.0}/117_{.1}$. *Comparison with primordial lead from meteoritic troilite yields a* $^{207}Pb/^{206}Pb$ *age of* $4.7 \pm 0.1 \times 10^9$ *years. The* $^{238}U/^{204}Pb$ *ratio is* $\gtrsim 90$ *and the* $^{232}Th/^{238}U$ *ratio is* 3.9 ± 0.1. *The lead content is* $\gtrsim 1.7 \times 10^{-6}$. *Evidently Pb was strongly depleted and Th and U strongly enriched in the formation of this material. Thallium was too low* ($\lesssim 5 \times 10^{-9}$) *to yield mass spectra, but indications are favorable for eventual observation of extinct natural radioactivity of* ^{205}Pb.

We have made an isotopic analysis of lead from a sample of fines from the Apollo 11 site, from which an age of the lunar surface can be derived, and have initiated a search for isotopic anomalies due to certain extinct natural radionuclides, from which fine time-resolution of the earliest lunar history might be derived. In particular, we have undertaken to determine the abundance and isotopic composition of thallium, which might be altered by the electron-capture decay of ^{205}Pb (half-life $\sim 24 \times 10^6$ years) to ^{205}Tl. Previous searches for variations in the $^{205}Tl/^{203}Tl$ ratio in meteoritic thallium have given negative results (*1*). Lead and thallium are isolated by volatilization under vacuum at temperatures close to the melting point of the bulk rock. Anion exchange and electrodeposition are used for further purification. A single-filament mass-spectrometric technique modified from Cameron *et al.* (*2*) is used. Sub-microgram quantities of silica gel, the purified Tl and Pb in 1*M* HNO_3, and H_3PO_4 are successively loaded onto the filament; drying is effected by a combination of resistance and radiant heating in air. The mass spectrometer is a Nuclide Corporation Model SU 2.4 (90° deflection, 30-cm radius). Filament temperatures are monitored by an optical pyrometer. The Pb and Tl data are collected by repeated magnet-current switching between peak pairs; approximately 12 cycles are used for each ratio. The Tl is measured at ~740°C and Pb at ~1170°C.

Elemental abundances and yields of various parts of the procedure are determined by isotopic dilution with the use of enriched ^{203}Tl and ^{206}Pb. The ion-exchange purification yields were 95 to 100 percent for both Tl and Pb. The electrodeposition yields were 60 to 70 percent for Tl and 90 to 95 percent for Pb. Because isotopic mixing of spikes and elements in natural solids cannot be achieved, in actual runs with such materials the spikes are added to the solutions of the vapor condensates. Volatilization yields were estimated by comparison of recovered Tl and Pb from standard rocks AGV-1 and BCR-1 with published determinations (*3*) as 70 to 100 percent for Tl and 60 to 90 percent for Pb in heatings of 24 to 48 hours. Yields seem to be higher at temperatures just below the melting point than just above. The highest temperatures tried have been 1050°C.

The first lunar material used was a 3-g sample (A) of less than 1-mm fines from the Apollo 11 site (sample 10084,45) ground in a motor-shaken tungsten-carbide capsule-pestle to pass through a 200-mesh nylon screen. It was heated successively at 800°, 850°, and 900°C for 20 hours each. The vapor condensate solution was made up to 10 ml. Two 4-ml aliquots (**1** and **3**) were processed for isotope-abundance measurements and a 2-ml aliquot (**2**) was spiked for abundance determinations. In neither of the unspiked samples could Tl be seen in the mass spectrometer. In run **1**, Pb isotope ratios were obtained only with a chart recorder with ~2 percent accuracy; the signal appeared at a relatively low temperature (820°C) and disappeared before digital-voltmeter measurements could be made. In run **3** moderately stable ion beams of ~ 10^{-11} amp were obtained at 1170°C, and data were collected with the digital voltmeter. Digital-voltmeter data were obtained for both Tl and Pb in run **2**.

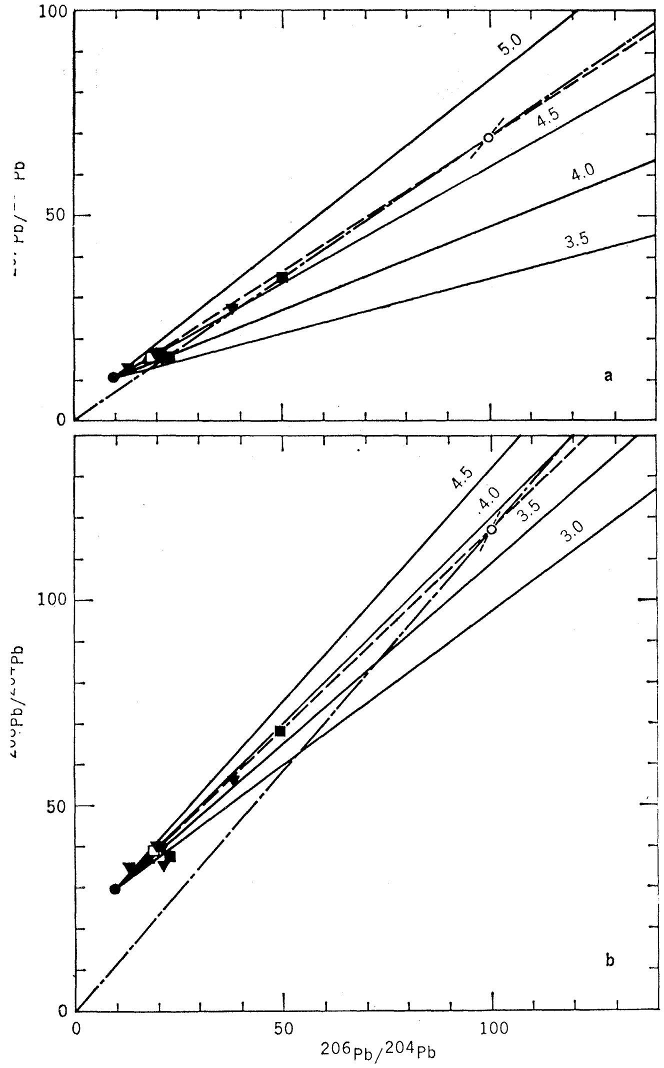
The results are given in Table 1. The results of run **3** were corrected for a typical blank of 0.07 μg of modern terrestrial Pb (*4*). Additional contamination during collection, handling, and grinding of the sample would not have been corrected for.

The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios are plotted along with similar data on meteoritic and common terrestrial lead in Fig. 1a. The troilite point represents the mean of several measurements selected by Murthy and Patterson (*4*), who adopt $^{204}Pb/^{206}Pb/^{207}Pb/^{208}Pb = 1/9.56/10.42/29.71$ for this and for primordial lead of the solar system. Subtraction of these ratios from the corresponding A-3 lunar values yields a radiogenic $^{207}Pb/^{206}Pb$ ratio of 0.65_1. With disintegration constants $\lambda(^{238}U) = 1.537 \times 10^{-10}$ year^{-1} and $\lambda(^{235}U) = 9.722 \times 10^{-10}$ year^{-1}, and $(^{238}U/^{235}U)_{now} = 137.8$ (*5*), the age of the lunar surface sample is calculated to be $T = 4.6_9 \times 10^9$ years. Isochrons corresponding to several ages are shown on the figure. The effects of possible corrections for error in the ^{204}Pb peak measurements, for contamination by modern terrestrial lead, and for isotope fractionation in the mass spectrometer are shown by dashed lines. Since the

Table 1. Mass-spectrometric data and calculations.

Quantity	Run A-1 (unspiked)	Run A-3 (unspiked) Data	Run A-3 (unspiked) Corrected	Run A-2 (spiked)
Effective sample mass	1.2 g	1.2 g		0.6 g
Mass Pb spike*				1.094 μg
Mass Tl spike†				221.0 ng
Measured $^{205}Tl/^{203}Tl$	Not seen	Not seen		0.093
Measured $^{206}Pb/^{204}Pb$	$71._2$‡	90.2 ± 0.3‡	$99._6$	
Measured $^{207}Pb/^{206}Pb$	0.70_6	$0.6965 \pm .0005$	0.69_4	
Measured $^{208}Pb/^{206}Pb$	1.25_6	$1.1978 \pm .0006$	1.17_8	0.333
Calculated $^{207}Pb/^{204}Pb$	$50._3$‡	62.8 ± 0.2‡	$69._0$	
Calculated $^{208}Pb/^{204}Pb$	$89._6$‡	108.0 ± 0.3‡	$117._1$	
Mass natural Tl				3.3 ng §
Mass natural Pb				1.01_7 μg
Tl abundance in sample				$<5._5 \times 10^{-9}$ ‖
Pb abundance in sample				$>1.7_0 \times 10^{-6}$ ¶

*$^{204}Pb/^{206}Pb/^{207}Pb/^{208}Pb = 1/2688/189.9/36.34$. †$^{205}Tl/^{203}Tl = 0.081_6$. ‡Probably lower limits because of possibility of lead contamination. Not corrected for possible isotope fractionation. §Calculated assuming for natural thallium $^{205}Tl/^{203} = 2.389$ as observed in this instrument (*1*). ‖ Probably an upper limit because of nonzero blank. ¶ Probably a lower limit because of incomplete volatilization.



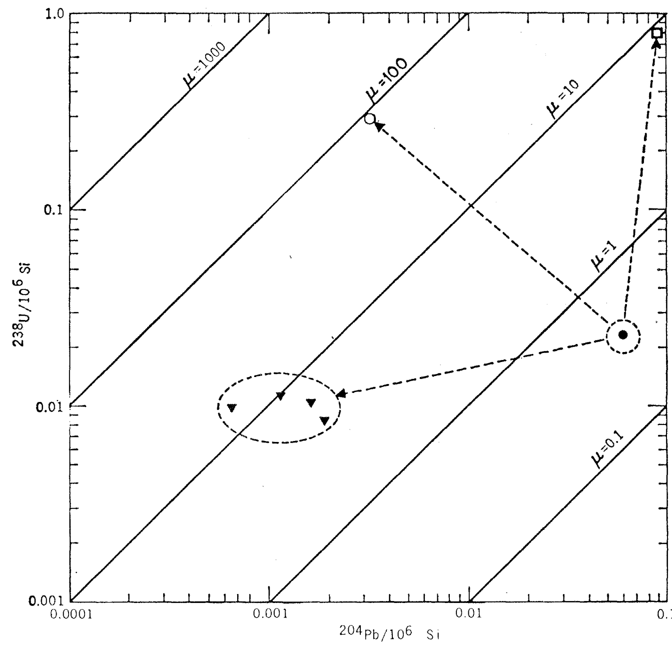


Fig. 1 (left). Comparison of isotopic composition of lead from Apollo 11 lunar surface fines with that of meteorites and the earth. (a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$. ——— Calculated isochrons for single-stage ages indicated in units of 10^9 years. (b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$. ——— Calculated locus lines for indicated values of $^{232}Th/^{238}U$ at the present time following 4.7 × 10^9 years of single-stage evolution. In both parts: (○) lunar fines sample 10084,45, A-3; (●) meteorite troilite; (▼) chondrite meteorite; (■) achondrite meteorite; (▲) iron meteorite; (□) typical modern terrestrial common lead; —·— common-lead contamination line; — — — ^{204}Pb error line; - - - isotope fractionation line. Fig. 2 (above). Comparison of ^{238}U and ^{204}Pb contents of Apollo 11 lunar surface fines (○) with those of type I carbonaceous chondrites (●), ordinary chondrites (▼), and the earth (□). μ = present atomic ratio $^{238}U/^{204}Pb$.

contamination line through the lunar point is almost identical with the isochron which it defines, and the other two corrections are not likely to be appreciable, the error in the age due to these effects should be small. For example, an uncertainty in the $^{207}Pb/^{206}Pb$ ratio of as much as 2 percent corresponds to an uncertainty of only $\sim 0.03 \times 10^9$ years in T. Considering all uncertainties we express our result as $4.7 \pm 0.1 \times 10^9$ years. This age is not substantially different from those derived from the meteorite Pb isochron, or for the earth by a similar calculation with mean oceanic lead, 4.55×10^9 years (*4*, *5*), or from meteoritic ^{87}Rb-^{87}Sr isochron ages. However, our radiogenic $^{207}Pb/^{206}Pb$ ratio, 0.65, seems significantly greater than that of chondrite and achondrite meteorites, 0.59 or 0.60, suggesting that the lunar surface may actually be the oldest sample of solar-system matter yet available. On the other hand, a growth model involving two or more stages could be consistent with a more recent formation of the Mare Tranquillitatis surface material.

The $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios are similarly plotted (Fig. 1b) along with iso-compositional lines corresponding to various $^{232}Th/^{238}U$ ratios, calculated for $T = 4.69 \times 10^9$ years with $\lambda(^{232}Th) = 4.99 \times 10^{-11}$ year^{-1} (*5*). The above-mentioned subtraction yields a radiogenic $^{208}Pb/^{206}Pb$ ratio of 0.97_1, which corresponds to an atomic $^{232}Th/^{238}U$ ratio of 3.8_9 and an elemental Th/U ratio of 3.7_6. Any uncertainty in the $^{208}Pb/^{206}Pb$ ratio corresponds to the same fractional uncertainty in these parent ratios. The effects of ^{204}Pb error, contamination, and fractionation are likewise shown in the figure; again these effects are very small. Considering all uncertainties, including that in the age, we express our result as $^{232}Th/^{238}U = 3.9 \pm 0.1$ and $Th/U = 3.8 \pm 0.1$.

Our lead isotopic composition and the assumption of a closed system aged 4.69×10^9 years corresponds to a present-day ratio $^{238}U/^{204}Pb$ (μ) ≈ 86. This is undoubtedly a minimum value, because a small amount of common-lead contamination could substantially increase the ^{204}Pb in the isolated sample. We conclude that $\mu \gtrsim 90$. The preliminary γ-ray measurement of similar Apollo 11 fines (*6*) indicated a U content of $\sim 0.46 \times 10^{-6}$. Combining this with $\mu = 86$ and our Pb isotopic composition yields a total Pb abundance of $\sim 1.3_3 \times 10^{-6}$, relatively insensitive to common-lead contamination. This is close to the value calculated from the isotope-dilution analysis of the vapor-condensate, $1.7_0 \times 10^{-6}$, which we regard as a lower limit because of probably incomplete volatilization. The γ-ray measurements (*6*) gave $\sim 1.6 \times 10^{-6}$ for the Th content, or ~ 3.5 for the Th/U ratio, consistent with our result.

Comparison of the ^{238}U and ^{204}Pb contents of the Apollo 11 fines, which, because of the natural mixing processes by which they were produced, may be fairly representative of the lunar surface, with the same values in type I carbonaceous chondrites (*7*) ($\mu \sim 0.4$), widely regarded as good samples of nonvolatile solar-system matter, is made in Fig. 2. Evidently U and Th were highly enriched and Pb highly depleted in the formation of the lunar surface. This process must have been distinctly different from that producing the characteristic elemental assemblages of the ordinary chondrites (*7*) ($\mu \sim 4$) and the earth ($\mu \approx 9$) (Fig. 2).

Unfortunately, too little Tl was present in the 1.2-g sample aliquots to yield mass spectra. The $3_{.3}$ ng of Tl calculated for the 0.6-g aliquote by isotope dilution is lower than that observed in any previous blank and probably still includes a residual blank. The Tl content of this composite lunar surface material, $< 5 \times 10^{-9}$, is at least tenfold lower than in type I carbonaceous chondrites, $\sim 74 \times 10^{-9}$ (*8*), and may be similar to that observed in some highly equilibrated ordinary chondrites, $\lesssim 1 \times 10^{-9}$ (*8*). The depletion of Tl seems to be greater than that of ^{204}Pb. This, combined with the extreme antiquity indicated for the lunar surface, indicates favorable conditions for the eventual detection of radiogenic ^{205}Tl from extinct natural radioactivity of ^{205}Pb (*1, 9*).

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