LUNAR BALL GAMES AND OTHER SPORTS

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A study was conducted on glass balls and total soil samples from the orange soil 74220 collected at the Apollo 17 site. Other workers have shown this soil to be rich in volatiles (1) and to contain Pb with a remarkably high abundance of ^{204}Pb as compared with other lunar samples (2). Previous work has shown the volatiles to be readily leachable, and studies with the ion microprobe (3) and by ultramicroanalytical chemical and mass spectrometric procedures (4) has shown the leachable lead to be sited on the surface of the glass balls. The time of formation of the glass balls is determined as 3.5-3.7 AE by the ^{40}Ar-^{39}Ar method [3.71 $\pm$0.06 AE (5); 3.67 $\pm$0.04 AE (6); and 3.54 $\pm$0.05 AE (7)]. The disagreement between these values is largely a reflection of the variable trapped Ar composition. While the antiquity of the balls is established, the age is much too uncertain to aid in refined models pertaining to the origin of the balls or the detailed early time scale of the moon. As pointed out by Tatsumoto *et al.* (2), the extremely low values of ^{206}Pb/^{204}Pb for the leachable Pb require a low $\mu \sim 35$ for the source region that is distinctive from that of the mare basalts or KREEPUTh rocks. Further, the residual Pb was highly radiogenic in contrast to the leachable Pb. Silver (8) pointed out that a low temperature volatile Pb from the orange soil is even more primitive than found by Tatsumoto *et al.* (2) for the leachable Pb and indicated the multicomponent nature of Pb in the soil including a radiogenic contribution.

While the total soil is dominated in its bulk chemistry by glass balls and shards, the soil is nonetheless an aggregate of different materials so that the Pb isotopic values of the bulk soil and for leaches of the bulk do not define the lead directly associated with the glass surfaces. If the lead on the surface of the glass particles represents the condensate of an isotopically homogeneous gas in a single event, then the surface Pb should have a unique isotopic composition. If the surface Pb represents the initial Pb in a lava and the glass balls are samples of the same lava, then it should be possible to determine a self-consistent isochron and determine the age of the extrusion. From the initial Pb and the age, it is also possible to calculate a single-stage model age for the moon and ^{238}U/^{204}Pb ($\equiv \mu$) in the source reservoir from which the glass and surface Pb were derived. Various origins of the glass balls have been proposed, but the most plausible mechanism is that they are volcanic in origin and produced in lava fountains (9) although strong opposing arguments favoring impact formation have been proposed (10).

To more accurately identify the various types of Pb, we analyzed individual glass balls (4) by repeated leaching; large masses of glass balls of different sizes by leaching and analyzing the residues; a total soil sample and the -60μm fraction of bulk soil. The results are given in Table 1 and the Pb isotopic data shown in Fig. 1. Individual balls ($\sim$250μm) were picked from the soil, rinsed in H_2O with ultrasonic agitation to remove any adhering fine material and then leached in a drop of 1N HNO_3. The balls typically contain $\sim 4 \times 10^{10}$ Pb atoms each. About 80% of the Pb was removed by the first leach. The second leach contains very little Pb and is dominated by the loading blank (see Ball 1, 1st and 2nd leach). The trend between the loading blank and the pure surface Pb is evident. Repeated mild leaching of individual balls does not indicate the removal of any radiogenic Pb from the interior.

To minimize the effect of the blank, ten balls were picked and subjected to similar treatment. The data point is shown in Fig. 1 and should represent the lunar Pb on the surface of a ball. We then took 383 balls (200 to 300 μm), carefully selected to be free of all exotic materials and washed in H_2O with ultrasonics to remove any fines. The data are in excellent agreement with the 10 ball experiment for all isotopes. We tentatively conclude that these values of very primitive lunar lead define the surface Pb *on* the glass spheres.

The values reported here for the surface Pb are α=18.74, β=23.28, γ=36.62. It should be noted that there is reasonable agreement (to$\sim$5%) between these precise data and the limited semiquantitative data from ion microprobe measurements for $^{208,\ 207,\ 206}$Pb as reported by Meyer *et al.* (3).

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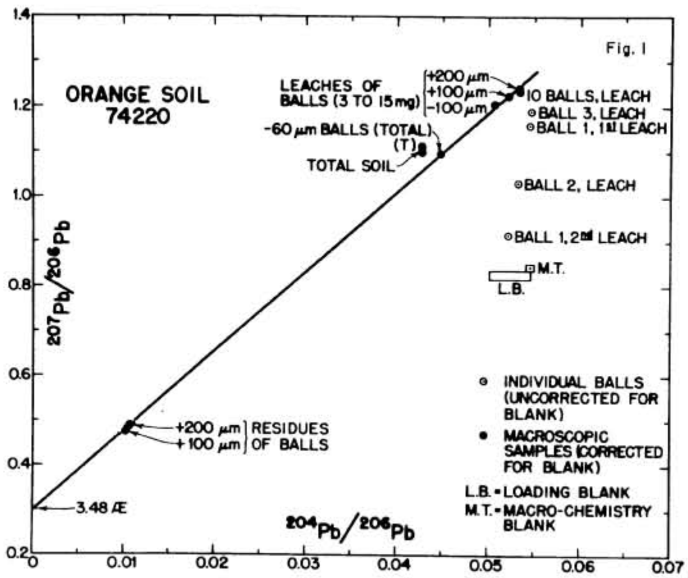
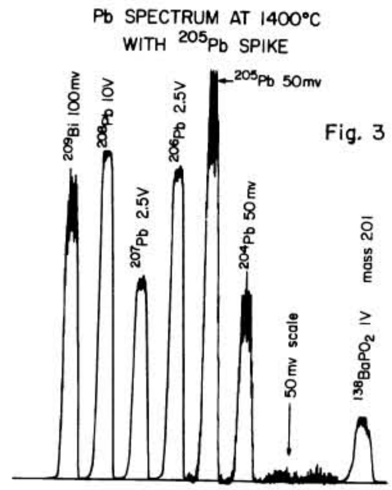
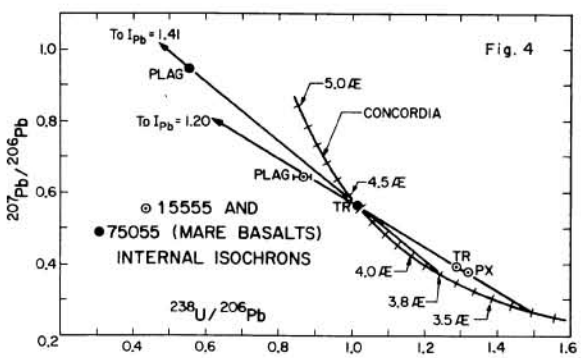
Some of the data reported here were taken with a ^{205}Pb spike which permits determination of composition and concentration in a single run. This tracer permits spiking of microsamples of unknown weight and concentration without risk to the experiment and can readily be measured to good precision with $5x10^9$ atoms.







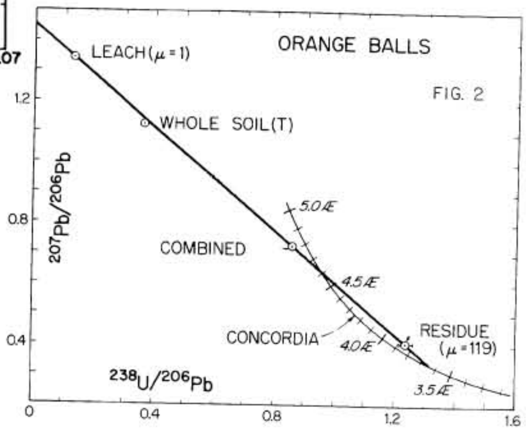


Fig. 1. Isotopic composition of Pb in total soil, in acid leaches of pure balls, in not so pure balls and in their residues. Total soil (T) from ref. (2). Ten ball point is offset from ultrapure +200 μm balls leach for visibility. Displacement of total soil shows large contribution of exotic radiogenic component in total soil. Mild leaching of ultrapure balls (individual and bulk) appears to point to a unique composition.

Fig. 2. Pb-U evolution diagram showing leach and residue with PAT lead removed. This "internal-external" isochron is affected by small but significant contribution of radiogenic Pb from an exotic source which displaces the lower intersection from 3.48 AE to 3.62 AE.

Fig. 3. Typical analog spectrum using a large ^{205}Pb tracer of $30x10^9$ atoms following ultramicrochemistry for a large sample ($2x10^{-4}$g with 14ppm of Pb). Ion current for ^{205}Pb is $2x10^{-15}$A. U and Th determined on the same sample. Note background at masses 203 and 202. Mass 203 is not Tl.

Fig. 4. Internal isochrons for two mare basalts of different ages and different initial Pb. Note the isochrons both intersect concordia at 4.42 AE.

References: (1) Wänke, H. *et al.* (1973) 1461; Jovanovic, S. *et al.* (1973) 1313; Proc. Fourth Lunar Sci. Conf.; (2) Tatsumoto, M. *et al.* (1973) *54*, 614, EOS; (3) Meyer, C. *et al.* (1975) 1673, Proc. Sixth Lunar Sci. Conf.; (4) Tera, F., and Wasserburg, G. J. (1975) 2214, Anal. Chem.; ((5) Schaeffer, O. A. and Husain, L. (1973) *180*, 1358, Science; (6) Eberhardt P., *et al.* (1973) *8*, 360, Meteoritics; (7) Huneke, J. C. *et al.* (1973) 1725, Proc. Fourth Lunar Sci. Conf.; (8) Silver, L. T. (1974) *55*, 681, EOS; (9) Prinz, M. *et al.* (1973) *54*, 605; Reid, A. M. *et al.* (1973) *54*, 606, EOS; (10) Roeder, E. and Weiblen, P. W. (1973) *54*, 612, EOS; (11) Tera, F. and Wasserburg, G. J. (1975) 807, Sixth Lunar Sci. Conf. (Abstract); (12) Tera, F. and Wasserburg, G. J. (1974) 1571, Proc. Fifth Lunar Sci. Conf.

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The leached ultraclean +200μm balls (called residue) were then dissolved and analyzed. The Pb in the residue is highly radiogenic, confirming the general observation of Tatsumoto *et al.* (2). In contrast to their results, which give an age of 3.83 AE, we find that the tie line through the leach and the residue has an intercept of $(^{207}Pb/^{206}Pb)^*=0.2996 \pm 0.0061$ corresponding to an age of 3.48 ±0.03 AE. The presence of initial Pb in our residues is interpreted as due to residual surface Pb not removed by the mild leaching.

A clean sample of -100 + 60μm balls was prepared but some exotics were present. After the sample was washed in H_2O, it was leached and the leach was analyzed. The data lie very close to the tie line for the ultrapure +200 μm balls but diverge slightly in the direction of the total soil. A bulk analysis of the -60 μm soil was found to lie on the tie line as shown in Fig. 1. A sample of +100 μm balls (not ultrapure) with rough surfaces was prepared and the leach and residue analyzed for Pb and U. The Pb isotopic data lie very close to the tie line, but the leach shows small radiogenic excess. The radiogenic Pb-U relationships are shown in Fig. 2 and define a tie line with a lower intersection with concordia at 3.62 AE. The residue is close to concordia. To first order the Pb isotopic data are in accord, but there is a clear discrepancy in the apparent age as determined by the Pb-U data (Fig. 2) and the Pb isotopic data alone (Fig. 1). The existing data prove the presence of at least three components of Pb in the orange soil: 1) on the balls, 2) in the balls, 3) exotic, easily soluble radiogenic highland Pb in the bulk of the soil.

From the ultrapure samples we infer a distinctly younger age for the orange glass balls of 3.48 AE in accord with the Ouija board of Huneke *et al.* (7). The orange glass balls thus appear to be a young event distinct from the time neighborhood of the terminal lunar cataclysm and are most plausibly produced in the last stage of volcanism in the Taurus Littrow valley, manteling the much older lava floods of the valley floor.

Assuming that the Pb on the surface of the glass balls is the product of a single stage evolution, we calculate an age of the parent reservoir of 4.59 AE. This age is much greater than the value of 4.45 AE first reported by us for two mare basalts as illustrated in Fig. 4 (11) and also for several terra rocks (12). The simplest explanation of these data are that: A) the moon formed at ~4.59 AE with a low value of $\mu(<29)$; B) the moon differentiated down to at least 200 km at ~4.45 AE forming the crust and outer mantle (basalt magma reservoirs) with major volatile loss from the moon; C) the deep interior was either undifferentiated or else was enriched in Pb during the late crust and mantle formation; D) this primary or Pb/U enriched secondary material is represented by the A-17 orange glass.

Table 1

Sample	Weight mg.	Lunar Lead[1,2] ^{208}Pb	^{207}Pb	^{206}Pb	^{204}Pb	α[3] Comp	Conc	^{204}Pb[1] Blank	$\Delta(^{204}Pb)$[1] Blank	^{238}U[1]
75055 Plag	58.91	5.284	4.759	4.972	0.03854	68.94	68.80	0.02656	0.0002	2.575
15382,114	2.346	26.43	14.63	26.30	0.02700	629.5	695.7	0.01109	0.0037	——
Orange soil 74220, 113										
Total soil	3.842	(19.98	12.61	11.47	0.4913)[4]	23.25	——[5]	0.00895	——	——
Balls +200μm	15.5									
Residue		(7.574	3.324	6.796	0.07286)[4]	85.59	——[5]	0.00830	——	——
Leach		(15.87	10.09	8.116	0.4334)[6]	18.72	——[5]	0.00199	——	——
Balls -100 +60μm	4.55									
Leach		(4.524	2.896	2.393	0.1211)[6]	19.74	——[5]	0.00132	——	——
Soil -60μm	0.70	(1.297	0.8109	0.7325	0.03250)[7]	22.30	——[5]	0.00199	——	——
Orange soil 74220, 13										
Balls +100μm	2.77									
Residue		1.738	0.7433	1.586	0.01502	81.85	86.84	0.00412	0.0015	1.782
Leach		2.760	1.789	1.457	0.07596	19.16	19.15	0.00332	0.0004	0.0978
10 Balls 250-300μm										
Leach		(0.3278	0.2092	0.1677	0.008954)[8]	18.72	——[5]	0.000133	——	——

[1]In picomoles. [2]Corrected for blank with α=18.30, β=15.46 and γ=38.01. [3]Uncorrected for blank, α values of concentration runs are corrected for cross contamination from spikes. [4]Based on a yield determination on 10% of the composition aliquot. [5]No concentration run was made. [6]An estimate based on the Pb concentration in the leach of +100μm balls. [7]Estimate based on the Pb in the leach plus the residue of +100μm balls. [8]An estimate based on the Pb on the surface of one ball (Tera and Wasserburg, Anal. Chem. 47, 2214 (1975).

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