

<sup>204</sup>Pb, Bi, Tl AND Zn IN APOLLO 16 SAMPLES AND INFERENCES ON THE LUNAR GEOCHEMISTRY OF <sup>204</sup>Pb BASED ON METEORITIC AND TERRESTRIAL SAMPLE STUDIES.\*

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The concentrations of primordial Pb as <sup>204</sup>Pb and of Bi, Tl and Zn have been measured in Apollo 16 samples and in Apollo 17 orange soil by neutron activation techniques. In addition, in order to gain some insights into the possible geochemistry of the heavy metals in lunar samples, selected meteoritic and terrestrial samples were studied. These included basaltic achondrites, metallic spherules from Meteorite Crater, Arizona; Disko Island basalt and metal from this basalt.

Apollo 16 samples from Stone Mountain (64501, 64801), from the North Ray crater ejecta blanket (63501) and from station 1 on the rim of Plum crater (61221) were measured. Breccias 61016 and 66095 which have unusually high halogen contents were studied - since labile <sup>204</sup>Pb and Bi fractions correlated with halogens were observed in Apollo 14 and 15 samples (Allen et al., 1973). Another high halogen containing sample, Apollo 17 orange soil 74220, was also measured. As in previous studies the samples were leached for ~10 minutes in a hot aqueous solution of HNO<sub>3</sub> at pH 5-6. The data are summarized in Table 1.

The <sup>204</sup>Pb contents of a few ppb in the Apollo 16 soils are similar to those in other lunar soil samples. Bi concentrations in soils are 1-2 ppb and Tl a few ppb. The orange soil is distinct in having an order of magnitude more <sup>204</sup>Pb and Bi and 3-4 times more Tl than any other soil measured. The fractions of leachable <sup>204</sup>Pb and Bi are similar to those of other soils. The breccia 66095 has a high <sup>204</sup>Pb and Bi content; however, it has an order of magnitude more Tl than the orange soil. Breccia 61016 has a <sup>204</sup>Pb content of ~5 ppb like most soil samples but it is enriched in Bi and Tl.

The correlations of <sup>204</sup>Pb<sub>r</sub> with metal, <sup>204</sup>Pb<sub>l</sub> and Bi<sub>l</sub> with Br<sub>l</sub> and Bi<sub>r</sub> with P<sub>2</sub>O<sub>5</sub> reported for samples from Apollo 14 and 15 do not appear to apply for most of the Apollo 16 samples measured. These samples may represent the early crust altered by events that mixed materials from various sources (depths?). The components of this mixture, never homogenized on a regional basis, may have been subjected to local alteration due to impact melting, shock brecciation and metamorphism. In comparison samples from the Apollo 14 and 15 sites appear to have undergone a less complicated evolution since they have preserved a more or less common record.

The lunar chemistry of <sup>204</sup>Pb in Apollo 14 and 15 samples involved extraction of some of this Pb into a metal related phase and the association of the remainder with halogens. A possible parallel in the geochemistry of lunar samples with the non-lunar systems listed above was explored. No leach data were acquired since leaching was done primarily to remove terrestrial contamination. The achondrites may be magmatic differentiates from which a metal

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phase has been separated. For comparison with lunar samples the heavy metals in two basaltic achondrites were measured. The results, Table 2, suggest that <sup>204</sup>Pb is highly partitioned into the silicate phase if the iron meteorites are representative of the metal phase. This is also true for Bi on the basis of its concentration in iron meteorite troilite and possibly also for Tl.

The metal in basalt from Disko Island was formed *in situ* by the reaction and equilibration of basaltic magma with carbonaceous shales (Melson and Switzer, 1966). This highly reduced basalt may be compared with lunar samples. The <sup>204</sup>Pb and Tl are enriched in the silicate relative to the metal and the Bi is enriched in the metal. On the basis of these results <sup>204</sup>Pb is not partitioned into Disko basalt metal as it appears to be in metal in lunar samples.

The impact of iron meteorites causes the ejection of spherules of metallic Fe containing eutectics with Fe, FeS and Fe<sub>3</sub>P components. The structures are similar to some found in lunar metal (Blau et al., 1973). We have separated the metal phase from associated oxides and silicates in spherules from Meteorite Crater, Arizona. The metal bearing phase constituted about 36% by weight of the spherule mass and after separation was 90-95% pure. The <sup>204</sup>Pb content in the metal phase is 122 ppb. The spherules themselves contain <62 ppb <sup>204</sup>Pb and this limit is consistent with most or all of the <sup>204</sup>Pb being in the metal. The high concentration of <sup>204</sup>Pb accommodated in this phase is probably due primarily to the presence of the eutectic. Troilite from the Canyon Diablo meteorite contains 73 ppb <sup>204</sup>Pb (Mason, 1971).

The <sup>204</sup>Pb contents of lunar samples are too high to be attributed to Pb in the metal only. The <sup>204</sup>Pb contents of iron meteorites (metal + troilite) are too low to account for the <sup>204</sup>Pb in lunar samples. A mechanism then has been operative on the moon that concentrates <sup>204</sup>Pb in a metal associated phase. The results discussed above suggest that the process of spherule formation is an efficient way to accomplish this. Most of the metal in lunar samples is endogenous according to a number of investigators. A constraint on the mechanism by which the metal is formed is that it must cause the extraction of <sup>204</sup>Pb into the metal or metal-related phase at least in basaltic samples. A Canyon Diablo spherule type process would require that S be involved. Lunar fines contain from 0.05-0.1 wt % S, which if associated with the 0.1-0.5 wt % metal could provide the troilite and/or eutectic. The amount of S and its isotopic composition varies with the apparent maturity of the soil (Thode and Rees, 1973). Whereas the metal can be formed *in situ*, the incremental S must be introduced from an external source. Since most of the <sup>204</sup>Pb is associated with the metal, increments of <sup>204</sup>Pb with increasing metal must also be supplied from an external source. Since the <sup>204</sup>Pb in metal of  $\sim 10^{-3}$  ppb is too high to be attributed even to meteoritic troilite another source is necessary. A lunar source would require transporting the <sup>204</sup>Pb and probably S to surfaces from which it may become incorporated into splatter material involved in agglutinate formation. According to McKay et al., (1972) agglutinates form in finer grained, more highly comminuted soils. These would supply both the surfaces for deposition of Pb and S and the heating and melting, caused by micrometeorite impacts, that could promote metal-

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eutectic formation and Pb extraction.

If such a mechanism can account for the behavior of  $^{204}\text{Pb}$  in Apollo 14 and 15 samples lack of conformity by Apollo 16 samples which contain similar amounts of  $^{204}\text{Pb}$  metal and sulfur may be due to lack of homogenization, as suggested earlier, or may be chemical. In these highly anorthositic samples an alternate site may compete with the metal-eutectic for the Pb.

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References: Allen, Jr., R. O., Jovanovic, S., and Reed, Jr., G. W. (1973), *Geochim. Cosmochim. Acta*, Suppl. 4, Vol. 2, 1169; Melson, W. G. and Switzer, G. (1973), *Am. Min.* 51, 664; Blau, P. J., Axon, H. J. and Goldstein, J. I., (1973), *J. Geophys. Res.*, 78, 363; Mason, B., (1971), *Handbook of Elemental Abundances in Meteorites*, Gordon/Breach; McKay, D. S., et al. (1972), *Geochim. Cosmochim. Acta*, Suppl. 3, Vol. 1, 983.

Table 1. Lead, Bismuth, Thallium and Zinc in Apollo 16 Samples and Apollo 17 Orange Soil.

Sample	$^{204}\text{Pb}$		Bi		Tl		Zn	
	r <sup>†</sup>	l <sup>†</sup>	r	l	r	l	r	l
	ppb		ppb		ppb		ppm	
61221,17	<2.6	<0.65	0.67	0.81				
63501,41	4.9±0.5	0.4 ±0.3	0.7	-	3.8	0.41	11	0.7
64501,18	3.2±0.5	0.5 ±0.2	0.62	1.1				
64801,41	1.9±0.9	0.4 ±0.1	0.93	0.24	5.3	0.68	36	1.0
61016,131	3.0±1.9	1.8 ±0.9	9.7	2.5	57	2.7	2.9	2.3
66095,23	41 ±6	4.8 ±0.9	12	0.6	197	79	18	0.99
74220,111	36 ±2	3.9 ±0.4	9.7	2.5	16	6.2		

<sup>†</sup> r = residue after leach. l = leach,  $\text{HNO}_3$  solution at pH 5-6.

Table 2. Distribution of Lead, Bismuth and Thallium in Shock Melted and Magmatic Meteoritic and Terrestrial Samples (in ppb).\*

Sample	$^{204}\text{Pb}$	Bi	Tl
Shergotty, eucrite	41 ± 6		13
Moore County, eucrite	58 ± 11	6.0	0.4
Canyon Diablo metal from spherules	122 ± 6	4.4	2.9
Canyon Diablo spherules (~36% metal)	<62**	-	-
Disko basalt metal	6.1 ± 1.9	15	23
Disko basalt silicate	138 ± 30	7.5	1.6
Canyon Diablo metal <sup>†</sup>	2.76	-	0.25
	4.33		
Canyon Diablo FeS <sup>†</sup>	72.8	40	7.8,13,1.5

\* All samples were leached at pH 5-6 primarily to remove assumed terrestrial contamination. The leach was discarded.

\*\*A limit only is set because of excessive decay of the sample after the end of the irradiation.

<sup>†</sup>The concentrations are from data compiled in Mason (1971).