CHEMICAL STUDIES OF THE LUNAR REGOLITH WITH EMPHASIS ON ZIRCONIUM AND HAFNIUM, W. D. Ehmann, L. L. Chyi, B. R. Hawke, M-S. Ma, M. D. Miller and R. A. Pacer, Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506.

New data for Zr and Hf abundances in Apollo 16 and 17 samples have been obtained by NAA. The new data support our suggestion of a homogeneous accretion of the moon, followed by a two stage crustal evolution (1,2). The new data are presented in Table 1 along with abundances of five other elements determined simultaneously.

Precise data for Zr and Hf in lunar anorthosite are reported for the first time. The mean anorthosite Zr/Hf mass ratio of 30.5 is the lowest we have observed for lunar materials and further confirms our earlier suggestion of a Zr-Hf fractionation in the formation of the lunar crust. Figure 1 presents all the Zr-Hf data obtained in our laboratory to date. The majority of the rocks and soils define a trend extending from anorthosite through the KREEP basalts. The Apollo 11 and 12 basalts and the Apollo 17 soils which are rich in orange glass depart from this primary trend and constitute a secondary trend of presently ill-defined slope with a Zr/Hf mass ratio centered around 33. Rocks produced from an early stage melting and their resultant soils appear to lie along the primary trend. Rocks derived from partial melting of deep lying primitive condensates and subsequently contaminated by passage upward through a pyroxene-rich layer constitute the secondary trend and, hence, suggest a two stage evolution of the lunar crust.

Breccia 73215 clearly contains two types of gray matrix material pointing to a complex history. While the Zr/Hf ratios for all splits of 73215 are similar, subsample 73215,172 clearly has a unique composition with abundances of all seven elements we determined being approximately 1/10 those in the other subsamples. It is suggested that 73215,172 might be a mixture of approximately 10% Apollo 17 basalt with anorthosite, but further analyses are required for confirmation. However, our suggestion is consistent with the preliminary examination of 73215,172 as given in the Apollo 17 Sample Catalog. It is reported that this matrix sample is darker than typical and contains abundant crystals of plagioclase and olivine.

Studies of Zr/Hf ratios in terrestrial materials are also underway. Figure 2 illustrates new Zr and Hf data for the gravitationally differentiated Palisades Sill. Variation of the Zr/Hf mass ratio is within the narrow limits of 38 to 42 and a further experimental correction may additionally reduce the upper limit. The average for the chilled margins is 38.9. This slight ratio variation contrasts with a greater than 4 variation in the individual abundances. Other studies (3) on the Littleton metamorphic pelitic rock series in New Hampshire indicate a virtually invarient Zr/Hf mean mass ratio of 47.3±0.8, while individual abundances vary by a factor of 2. We feel these new data support our suggestion that Zr^{3+} may play a part in the Zr-Hf fractionation of highly reduced lunar magmas. The 100 to 1 atomic abundance difference between Zr and Hf and the small terrestrial Zr/Hf ratio variations suggest that solidus-liquidus partitions invoked by Laul, *et al*. (4) to explain the fractionation of certain REE pairs may not be sufficient to explain the observed lunar Zr-Hf fractionation.

Table 2 presents new major and minor abundance data for several samples whose analyses were completed subsequent to submittal of our Fifth Lunar Science Conference paper.

REFERENCES

(1) CHYI L. L. and EHMANN W. D., 1973, Proc. Lunar Sci. Conf. 4th, p. 1219-1226.

(2) EHMANN W. D. and CHYI L. L., 1974, Proc. Lunar Sci. Conf. 5th, p. 1015-1024.

(3) CHYI L. L., EHMANN W. D. and SHAW D. M., Paper in preparation.

(4) LAUL J. C., HILL D. W. and SCHMITT R. A., 1974, Proc. Lunar Sci. Conf. 5th, p. 1047-1066.

(5) WALKER K. R. (1969) The Palisades Sill, New Jersey: A Reinvestigation. G.S.A. Special Paper 111, 178 p.

Table 1. New trace element and iron determinations in lunar rocks and fines.

Sample	Description	Zr (ppm)	Hf (ppm)	Zr/Hf (weight)	Fe (%)	Co (ppm)	Sc (ppm)	Cr (ppm)	Eu (ppm)
60025,72	anorthosite	0.48 0.54	0.015 0.018	30.5	0.23	0.7	0.4	-	1.1
72141,8B	fines	325 237	7.76 6.22	40.2	10.3	39	36	2540	1.3
73215,66	gray matrix	370	8.64	42.8	4.7	25	12	1370	1.3
73215,68	gray matrix	419	9.24	45.3	5.0	30	13	1410	1.4
73215,160	black matrix	874	19.7	44.4	6.2	28	15	1440	2.1
73215,163	black matrix	621	14.1	44.0	5.5	25	13	1310	1.6
73215,166	black matrix	751	17.1	43.9	5.8	25	14	1370	1.6
73215,172	gray matrix	49.4	1.11	44.5	0.6	3.4	1.5	160	0.1
73215,176	gray matrix	571	12.4	46.0	6.6	33	17	1710	1.6
78421,23B	fines	197 196	5.30 5.99	34.8	8.2	32	30	2080	1.2
78461,7B	fines	201 249	5.33 6.61	37.7	8.8	34	33	2220	1.2

Table 2. New major and minor abundance data for lunar samples.

Element	12001,47 fines	12070,69 fines	14003,13* fines	14259,65* fines	15465,16 breccia	73215,176 gray breccia matrix	77035,53 green-gray breccia
O	42.0%	42.0	43.2	44.8	44.5	47.2	42.8
Si	21.4	22.1	23.2	23.1	22.7	22.8	21.0
Al	6.5	6.7	9.2	9.3	8.6	11.3	8.4
Mg	6.2	5.5	4.6	5.6	11.5	10.9	12.0
Fe	13.8	13.4	8.4	8.4	9.0	7.0	7.2
Ca	6.6	6.1	7.0	6.6	<4	<1	7.5
Ti	1.8	1.3	1.2	~0.5	n.d.	n.d.	n.d.
Mn	0.159	0.166	0.104	0.103	0.125	0.079	0.088
Na	0.34	0.35	0.47	0.54	0.42	0.38	0.050
Σ	98.8	97.6	97.4	98.9	-	-	99.0

* Data for some elements have been reported earlier by our group.

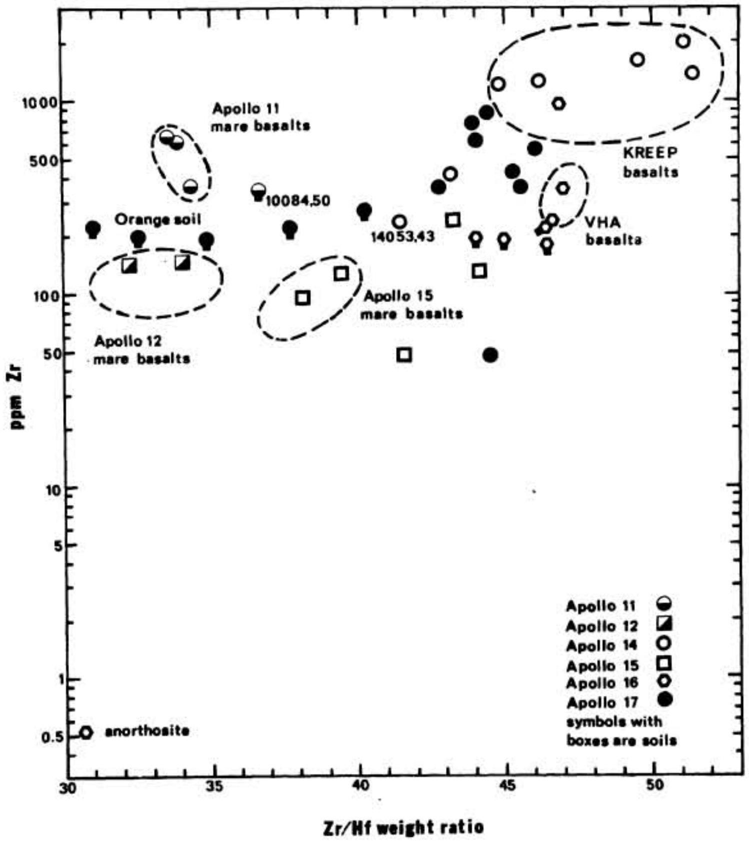

Figure 1. Zr and Hf in lunar samples. Note: log scale used compresses the primary trend from anorthosite through the KREEP basalts.

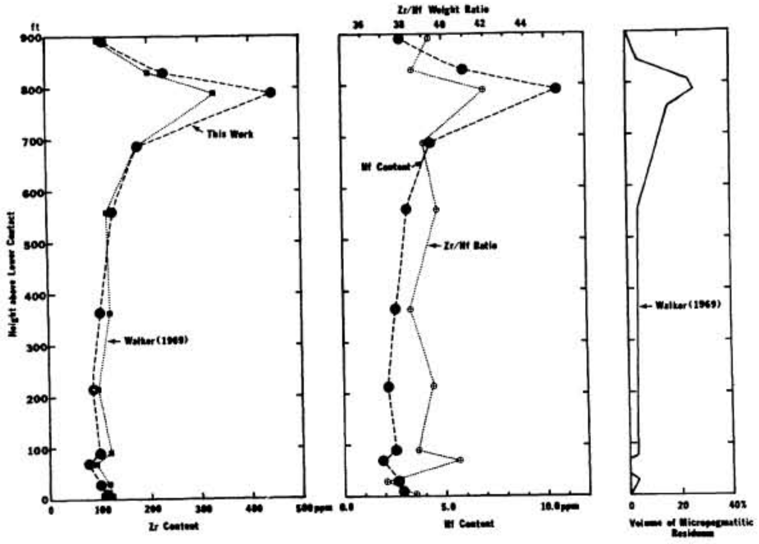

Figure 2. Zr and Hf in the Palisades Sill. Earlier Zr data from Walker (5) are also plotted.