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BULK, RARE EARTH AND OTHER TRACE ELEMENTS
IN APOLLO 14 AND 15 AND LUNA 16 SAMPLES

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Abstract--The chemical abundances of 24 and 34 bulk, minor and trace elements have been measured by instrumental (INAA) and radiochemical (RNAA) neutron activation analysis, respectively, in a variety of lunar specimens. Apollo 14 soils are characterized by significant enrichments of Al_2O_3 , Na_2O and K_2O and depletions of TiO_2 , FeO , MnO and Cr_2O_3 relative to Apollo 11 and to most of Apollo 12 soils. The uniform abundances in 14230 core tube soils and three other Apollo 14 soils indicate that the regolith is uniform to at least 22 cm depth and within ~200 m from the lunar module. The chondritic normalized REE distribution patterns of Apollo 14 soils resemble those of KREEP-norite and Apollo 12 soils. A Sm/Eu ratio of 11.6 observed in the average Apollo 14 soil is compared to 7.4, 9.7 and 3.9 in Apollo 11, 12 and Luna 16 soils, respectively. This indicates a larger KREEP-noritic component in Apollo 14 soils. Elemental abundances in the igneous rock 14073 are quite similar to igneous rock 14310 and to clastic rocks such

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as 14318. Apollo 14 soils may be produced by pulverizing ~80% rocks like igneous 14073 or breccia 14318 and ~20% KREEP. Clastic rock 14047 is indistinguishable in composition from Apollo 14 soils and, therefore, 14047 is merely a compacted soil. Elemental abundances in four clastic rocks, 14063 and 14083 (STA C1), 14318 (STA H) and 14066 (STA F) reveal a large variety of KREEP and variable quantities (25-100%) of KREEP components in individual clasts as well as in the overall rock composition. Two Luna 16 breccias are similar in composition to Luna 16 soils. Four Apollo 15 soils (LM, STA 4, 9 and 9a) have variable compositions. The REE abundances reveal ~6-14% KREEP components in these soils compared to ~25-80% KREEP in Apollo 12 and 14 soils. Although the Apollo 15 site is in the ESE edge of Mare Imbrium, the presumed source of ejected KREEP-norite matter, the mare lavas at Palus Putredinis (3.2 AE) have flowed to tens of meters in depths over the older (3.9 AE) Mare Imbrium event. Interelement correlations between MnO-FeO, Sc-FeO, V-Cr₂O₃ and K₂O-Hf negate the hypothesis that howardite achondrites may be primitive lunar matter, argue against the fission hypothesis for the origin of the moon, and precludes any selective large scale volatilization of alkalies during lunar magmatic events.

EXPERIMENTAL

The detailed analytical procedure used here has been described by SCHMITT et al. (1970), REY et al. (1970) and WAKITA et al. (1970). In our sequential INAA procedure for 24 elements, sample weights ranged from 1 to 500 mg. To increase the sensitivity of elemental detection, samples were grouped into four batches

depending on their weights, i.e., <20 mg, 20-80 mg, 80-200 mg and 200-500 mg weight groups. A duplicate set of U.S.G.S. standards BCR-1 and one sample of GSP-1 were also analyzed with each batch. Aliquants of two soils, 14003 and 14163, were also subjected to RNAA.

RESULTS AND DISCUSSION

Results are shown in Tables 1 and 2. In general, the elemental abundance data of this work agree well with those obtained by BRUNFELT et al. (1971), SCHNETZLER and NAVA (1971), TAYLOR et al. (1971), HELMKE and HASKIN (1972), HUBBARD and GAST (1972), SCHNETZLER et al. (1972), and ROSE et al. (1972). The overall reproducibility of our procedure was tested from replicate analyses of BCR-1. Only the average value of eight replicates of BCR-1 is listed in Table 2.

Apollo 14 Soils

Apollo 14 soils are characterized by significant enrichment of Al_2O_3 , Na_2O and K_2O and depletions of TiO_2 , FeO , MnO and Cr_2O_3 , relative to Apollo 11 and to most of Apollo 12 soils. Chemical compositions, including trace elements, of these three Apollo 14 soils are essentially the same. (Table 1) This suggests that the regolith seems to be uniform for distances of ~ 100 meters both east and west of North Crater. Abundances of Hf, Th, Ba and the REE greatly exceed those observed in Apollo 11 soil [WAKITA et al. 1970] and Luna 16 soil [GILLUM et al. 1972] by a factor of ~ 5 , and exceed those in some Apollo 12 soils by a factor of ~ 2 [WAKITA et al. 1971]. However, abundances of bulk, minor and trace elements in

Apollo 14 soils are nearly equal to those measured in Apollo 12 soil 12033 and breccia rocks 12010 and 12034 [GOLES et al. 1971 and WAKITA et al. 1971]. Total REE + Y abundances in Apollo 14 soils with an average value of 770 ppm are higher by factors of ~ 2.5 and ~ 4 , compared to Apollo 11 and Luna 16 soils and are slightly higher than REE + Y abundances of Apollo 12 soil, 12033. These observations are consistent with the suggestion of SCHNETZLER and NAVA (1971) that breccia rocks, such as 12010 and 12034, may have been ejected from cratering events on the Fra Mauro formation onto the Apollo 12 mare site followed by comminution to Apollo 12 soils such as 12033.

The chondritic normalized REE distribution patterns of Apollo 14 soils (Fig. 1) resemble those of Apollo 12 soils and these distribution patterns are quite different from those of Apollo 11 and Luna 16 soils. Apollo 14 soils have the greatest negative Eu anomalies. Apparent positive Ce anomalies ($\sim 15\%$) are observed in all Apollo 14 soils, one clastic and on igneous rocks that we analyzed. The Ce abundance in soil 14163 agrees with those reported by BRUNFELT et al. (1971) and TAYLOR et al. (1971) and these Ce values are $\approx 20\%$ higher than those obtained by SCHNETZLER and NAVA (1971) and HUBBARD and GAST (1971). MASUDA et al. (1972) also found the same degree of the positive Ce anomalies using isotope dilution technique. However, since we did not observe positive Ce anomalies in 14230 core tube soils, the alleged Ce anomaly may not be real.

The Rb/Cs ratio is fairly constant for Apollo 11, 12, 14 and Luna 16 soils. The Rb/Cs ratio of 26 observed in the average Apollo 14 soils is compared with 27 [TERA et al. 1970], 15-29

[WAKITA et al. 1971] and 23 [MORGAN et al. 1972] found in Apollo 11, 12 and Luna 16 soils, respectively. A Sm/Eu ratio of 11.6 observed in the average Apollo 14 soils is compared to those of 7.4, 9.7 and 3.9 in Apollo 11, 12 and Luna 16 soils, respectively. This indicates a larger KREEP or noritic component in Apollo 14 soils. For KREEP-norite, the average Sm/Eu is 15.3. (Table 2)

Core Samples 14230, STA G

Abundances of 24 elements are essentially identical for the three layers and for soil 14240 (STA G), scooped at ~2 cm depth near the core tube and other soils 14003 and 14163. (Tables 1 and 2) In Apollo 12 double core LAUL et al. (1971) reported a peculiar layer 12028,66 (13.2 cm) which was spectacularly enriched in Bi, Cd and relatively less abundant in other trace elements with respect to neighboring layers. This led them to conclude that little mixing had occurred and that the turnover rate was of the order of magnitude slower than previously estimated. Based on our trace data, we see no evidence for vertical or horizontal non-mixing and we predict similar behavior for other trace elements. If such a chemical homogeneity is typical of the Fra Mauro site, the regolith has been well-mixed with a turnover rate of few m.y./cm.

Derivation of these soils can be explained by a simple two-component mixing model of KREEP and crystalline rock [SCHNETZLER et al. 1970 and HUBBARD and GAST, 1971]. About 20% KREEP-noritic like component and 80% comminuted basaltic rocks like 14073 are required to account for the mass-balance of the soil composition. In addition, about 2% type C1 carbonaceous chondrites are needed

to explain the enrichment of trace elements [LAUL et al. 1971]; anorthosite, considered to be an highland material, and micro-breccia are additional components [DUNCAN et al. 1972].

Igneous Rock 14073, STA G

Elemental abundances of one igneous rock 14073 are similar to those observed in Apollo 14 soils, with some exceptions such as ~10-15% higher Al_2O_3 , CaO and Na_2O and 20-30% lower TiO_2 and FeO and ~50% lower Co abundances in 14073 relative to the soils. The REE abundances in 14073 are about 90% of those in Apollo 14 soils; the same degree of the negative Eu anomaly was observed. These REE abundances are significantly higher than those of Apollo 11, 12 and Luna 16 igneous rocks. The chondritic normalized REE distribution pattern of 14073 is quite different from those of Apollo 11 and 12 and Luna 16 igneous rocks; the 14073 pattern is very similar to those observed in KREEP or noritic fragments. The chemical compositions and ages of the alkali rich rocks 14073 and 14310 are the same [LSPET, 1971; HELMKE and HASKIN, 1972; WASSERBURG et al. 1972]. This suggests a common lava flow. On the other hand, MORGAN et al. (1972) showed that the trace elemental abundances in 14310 are similar to soil and breccia and concluded that the so-called igneous 14310 may actually be a melted breccia rock. Our data for clastic rock 14318 (Table 2) whose overall chemical composition can be represented by the sawdust [SHOWALTER et al. 1972] matches closely to 14310. This infers some genetic relationship between them.

Rock 14047

This rock has been reported to be a fine-grained gas rich, clastic rock and has a glass coating [LSPET 1971]. Our analyses for bulk and trace elemental composition and the Sm/Eu ratio of this work are identical to those of Apollo 14 soils (Table 1), except for slightly lower Na₂O and K₂O abundances in the clastic rock. Such a close chemical similarity suggests that the rock 14047 is merely a compacted soil sample. Similarities in noble gas contents [LSPET 1971] between 14047 and 14259 soil support this conclusion. Our conclusion is further strengthened by the close correspondence for siderophilic and volatile trace data in 14047 and soils [MORGAN et al. 1972].

Clastic Rocks

Clastic rocks are more prevalent than crystalline rocks on the Apollo 14 area [LSPET 1971]. Petrographic and stratigraphic studies of these clastic rocks are complex. Presumably, KREEP-norite is associated with these clasts. The average KREEP-norite composition and its range are listed in the last column of Table 2. We have also tabulated ratios of Sm/Eu, K/U and K/Ba as KREEP-norite indicators. Sm/Eu is an indicator for Eu depletion and Sm, for the total REE abundance. The ratio of Th/U in the bottom row (Table 2) merely reflects a typical ratio of two highly refractory elements in high temperature lunar minerals.

Clastic Rock 14063, STA C1 (Tatsumoto Consortium)

This rock is a thermally metamorphosed microbreccia F3 [JACKSON and WILSHIRE, 1972]. Its parent rock is 14065, an

alkali rich rock collected from the continuous Cone Crater ejecta blanket. Five samples of 59-81 mg each were analyzed by us before they were analyzed via RNAA by MORGAN et al. (1972). We could not report Zr, Hf, Th, Tb and Ta because of insufficient time for decay of short-lived radionuclides.

These samples have in general high plagioclase content. Overall, our data suggests that the composition of all five Al_2O_3 rich ($\sim 20\%$) clasts generally are rather similar in composition, especially BS and B11-3 which are quite similar. However, detailed inspection shows some differences in their REE content (Fig. 2). Coarse matrix A11 has the highest REE content and Sm/Eu ratio of 6.5, and therefore, the largest fraction of KREEP. The upper limit of KREEP in this clast is $\sim 30\%$. The distribution patterns of other REE are identical except that they have lower KREEP components. The compositions of the clasts from 14083, also picked up from STA C1, vary markedly (see below for discussion). The average value of K/U is 1390 and K/Ba, 3.6 for 14063. Potassium correlates linearly with U but not with Ba.

Clastic Rock 14083, STA C1 (Wasserburg Consortium)

This rock is also a thermally metamorphosed microbreccia like 14063 [JACKSON and WILSHIRE, 1972] and has been dated via Rb-Sr at 3.95 AE [WASSERBURG et al. 1972]. This rock was a piece of 14082 rock, which was chipped from the top surface of the "White" rock, ~ 20 m near Cone Crater rim. Abundances in a black and white fragment and in a pure dark interior sample are quite similar to the composition of KREEP or noritic matter for all elements, except for the high Cr_2O_3 abundance in the pure dark matter

which we attribute to a mineral grain of chromite. The higher CaO and Al₂O₃ contents and lower FeO, Na₂O, MnO, V and TiO₂ suggest higher anorthitic plagioclase and lower pyroxene and ilmenite contents in the pure white matter. REE distribution patterns (Fig. 3) are similar for the three clasts. The black-white fragment 2,1 and pure dark matter 2,4 match the average composition of KREEP. The close correspondence between these two clasts suggests that the pure dark matter dominates the black-white fragment. The pure white matter is relatively depleted in KREEP; i.e., <40% maximum KREEP. The Sm/Eu for the black-white fragment, pure dark and pure white matter are 14, 13, and 9 respectively. The mean K/U is 830 and K/Ba is 3.5. Potassium correlates linearly with Ba but not with U whereas 14063 shows the reverse correlations.

Since the clastic rocks 14063 and 14083 are Cone Crater ejecta, the chemical dissimilarity between these two rocks suggest a very complex and heterogeneous stratigraphy for the Fra Mauro formation. The same conclusion was reached by LSPET (1971), who analyzed two rocks, 14321 and 14065, both of which were on the Cone Crater ejecta blanket and which also yielded quite dissimilar chemical compositions.

Clastic Rock 14318, STA H (Tatsumoto Consortium)

This rock, although picked up ~100 m NW of the LM, was also in the Cone Crater ejecta blanket [SWANN et al. 1971]. We analyzed four clasts (5-15 mg) and two sawdust samples. No specific petrographic information for these four analyzed clasts is available at this writing. In general the overall rock composition for 24 elements of 14318 (as exemplified by the well-mixed 31 mg

sawdust sample [SHOWALTER et al. 1972]) match the composition of igneous rock 14073 with the exception of slightly lower Al_2O_3 and higher FeO content for the sawdust. This suggests a genetic relationship between igneous and microbreccia rocks at the Apollo 14 site. Also the similarity in composition between 14318 and the average Apollo 14 soil suggests that either the soil is pulverized from breccia rocks such as 14318 or that 14318 was compacted from the soil in a meteoritic impact event. The latter suggestion may be valid since 14318 rock is a shocked compressed microbreccia [JACKSON and WILSHIRE, 1972]. If ejected from Cone Crater, the chemical composition of 14318 underscores the complexity of the Fra Mauro formation as noted in the 14083 discussion. The REE distribution is shown in Fig. 4. Clasts 26A and 26B are largely KREEP-noritic matter, while 27B contains ~80-90% KREEP and a large content of orthoclase. Although clast 26C has ~3.5 times more orthoclase and ~2.5 times more Ba than average KREEP-norite, 26C appears to contain <50% KREEP. Normal KREEP abundances of U were found in these two clasts. Sm/Eu ratios of 17, 20 and 18 for 26A, 26B and 27B seem to be the highest values obtained so far for any lunar sample. If we compare the average composition of 14318 and the Apollo 12 samples, 12034 breccia, 12033 and 12032 soils, which contain about 80%, 70% and 60% KREEP [WÄNKE, 1971], respectively, we find no close correspondence. The mean K/U is 2300 for clasts; K/Ba is 7.3. These high average values are attributed to high K abundances of the clasts 26C and 27B. Potassium and Ba correlate fairly well, while K and U show no correlation at all.

Clastic Rock 14066, STA F (Reynolds Consortium)

This rock was picked up from smooth terrain, ~100 m SSE of Weird Crater. The rock is a thermally metamorphosed microbreccia [JACKSON and WILSHIRE 1972] and contains cosmogenic and extremely low solar wind content [KAISER, 1972]. Its Rb-Sr age is 4.0 AE [CLIFF et al., 1972]. We analyzed one sawdust and four different clasts.

The compositions of the sawdust and four clasts are all different. The overall rock (sawdust) composition is slightly lower in Al_2O_3 and higher in K_2O and REE compared to the average in Apollo 14 soil. On the other hand, the whole rock (sawdust) composition of 14318 is higher in plagioclase, lower in orthoclase, the REE, Zr, Hf, Th, U and Ta abundances, relative to rock 14066. Among the clasts, "matrix small clasts" and the "white igneous clast" have high K_2O abundance of 1.3 and 1.4% respectively. An enrichment of anorthitic plagioclase is noted in the "many clasts" relative to the other fragments.

REE patterns for the five specimens are shown in Fig. 5. The matrix has $\leq 75\%$ KREEP component; the remaining fragments cluster at $\leq 50\%$ KREEP. The KREEP component in clastic rock 14066 is higher than that observed in clastic rock 14318. K_2O abundances of 1.3 and 1.4% are not correlated with the REE, Ba and U abundances. Six fragments in rock 12013 also had high K_2O abundances ranging from 0.7 to 3.6% and low REE abundances that were $\leq 50\%$ KREEP composition [WAKITA and SCHMITT, 1970]. We may conclude that high orthoclase contents ($>1.1\% K_2O$) are not always associated with REE abundances and distribution patterns that are indicative of average KREEP-norite. This underscores the

complexity of lunar crustal matter as would be expected for chemical differentiation of a large planetary body. The mean K/U is 1990 and K/Ba is 7. Potassium shows no correlation with U and Ba.

The REE patterns and the tabulated Sm/Eu ratios in different clasts clearly demonstrate that KREEP is not a homogeneous component, i.e., large variety of KREEP exists [HUBBARD and GAST, 1971, and MEYER, et al. 1971]. Our work supports this conclusion and further suggests that KREEP is associated to variable degrees, i.e., from 25-100%, in clasts from the Apollo 14 clastic rocks. Our analyses show high enrichments of the refractory and large ionic elements Zr, Hf, Ta, Th, and U elements in these clasts. This suggests that the crust of the moon is rich in refractory elements. KREEP is considered to be derived from an exotic source by impact [HUBBARD and GAST, 1971; MEYER et al., 1971; MARVIN et al., 1972]. GANAPATHY et al. (1972) suggested that an impact event on the Mare Imbrium (3.9 AE) was caused by a cyprus-size body (190 km) with low velocity (5 km/s) and that the associated ejecta thrown onto the Apollo 14 area is now the Fra Mauro formation. If valid, the average composition of its counterpart (Mare Imbrium) should possess similar KREEP components; i.e., the Imbrium basin should be rich in refractories.

Luna 16 Breccias

The chemical compositions of these small 1-2 mg breccia samples (Table 2) are similar to the Luna 16 soil composition with the exceptions of the alkalies; i.e., the feldspar contents are higher in these breccias by factors of two or greater. This is

attributed to sample heterogeneity. The basic conclusion reached here is the same as was reported for the soil, i.e., the overall Luna 16 composition matches more closely to Apollo 11 soil than to any other lunar soil [GILLUM et al. 1972; LAUL et al. 1972a].

Apollo 15 Soils, 15021,21 (LM), 15471,49 (STA 4), 15501,40 (STA 9) and 15531,52 (STA 9a):

These soils are <1 mm fines and represent a wide sampling area. Our major elemental results (Table 2) agree well with x-ray fluorescence data of LSPET (1972). Their 15601 soil matches closely to our 15531, both from the same Rille site. Our REE data for 15531 are in agreement with isotopic dilution data of SCHNETZLER et al. (1972). In general, elemental abundances of all four soils are different. Soils 15531 (STA 9a) and 15501 (STA 9) are only 0.3 km apart, yet the bulk compositions are widely different. Comparing Apollo 11 and 14 soils, we note that none of the soils match in their major elemental content. Among Apollo 12 soils, 12032 comes close to 15021 in FeO, Al₂O₃, CaO, Cr₂O₃ and MnO contents; however, the alkalis, REE and refractories are depleted in 15021, indicating much less KREEP matter. Likewise, soil 12070 comes closer to 15501 (STA 9) in bulk composition but 12070 soil is more abundant for many other elements.

The REE abundance patterns (Fig. 1) for the four soils vary considerably, e.g., soil 15021 (LM) has the highest REE content while 15531 (STA 9a) has the lowest REE abundances of all lunar soils measured to date. These REE abundances are lower than those measured in Apollo 11, 12 and 14 soils. The REE abundances in 15531 soil are also less than the REE abundances in Luna 16

soil. The chondritic normalized REE patterns of the Apollo 15 soils parallel the observed distribution in 12070 soil. The Sm/Eu ratios though low, are quite variable 6-13 and do not correlate with the KREEP content as expected. The ratio Th/U = 3.4 is constant for the soils.

It is apparent from Figure 1 that the KREEP component in Apollo 15 soils is much less than observed in Apollo 12 and 14 soils. SCHNETZLER et al. (1972) studied separated minerals and whole rock 15555 (STA 9a) and estimated 6% KREEP, 88% contribution of 15555 basalt, and 6% anorthositic components for the composition of 15531 soil. Our upper limit, neglecting the basaltic rock contribution, for KREEP is 10%, which is close to their value of 6%. If we use 6% as the KREEP component value for 15531 and assume that the average REE abundances in all Apollo 15 basalts are similar to that observed in 15555, then we calculate that the KREEP components for the soils 15021, 15471, and 15501 are about 14%, 8% and 11%, respectively, all of which are very low compared to KREEP in Apollo 12 and 14 soils. Even though the Apollo 15 site is on the eastern edge of Mare Imbrium, the presumed source of ejected KREEP matter, the low KREEP content in Apollo 15 soils indicates that basaltic components dominate the soil constituency. This suggests that the Palus Putredinis mare basalts (3.2 AE), perhaps derived by melting processes at depths >200 km, have covered the older (3.9 AE) Mare Imbrium basin with many lava flows of considerable thicknesses.

Inter-Element Correlations

We have attempted to establish a few inter-element correlations with the wealth of data from five lunar missions. In our

Inter-Element Correlations

We have attempted to establish a few inter-element correlations with the wealth of data from five lunar missions. In our comparison, we have included primitive carbonaceous chondrite type 1 (C1), meteoritic "basalts" (Ca-rich achondrites: eucrites and howardites) and terrestrial basalts (continental and oceanic ridge). The unique breccia rock 12013 and dominant component KREEP-norite are included as well. Symbols in the Figures 6-9 are unified.

Figure 6 shows a correlation between MnO versus FeO. Such a strong correlation suggests that FeO and MnO are associated together in pyroxenes. Extrapolation of FeO and MnO through zero implies that Fe and Mn did not fractionate significantly during lunar differentiation processes. MARVIN et al. (1972) noted howardite-like composition for lunar green glasses and suggested howardites may have been some of the raw material for planetary accretion of the Moon. The howardite data for Fe and Mn are narrow in range [SCHMITT et al. 1972]. It is evident from Fig. 6 that howardites and eucrites both fall far away from the lunar correlation line. MORGAN et al. (1972) also reported that the abundances of 15 trace elements in lunar green glass do not approximate the corresponding abundances observed in six howardites by LAUL et al. (1972b). Both evidences support our conclusion that no genetic relationship exists between howardites and primitive lunar composition.

Figure 7 indicates that Sc is approximately correlated with FeO and resides mainly in pyroxenes [GOLES et al. 1970]. However, we note considerable Sc enrichments in Apollo 11 low and high

alkali rocks and to a lesser degree in Apollo 12 (Mg-poor) rocks. Mass balance calculations indicate that ilmenite in Apollo 11 rocks [GOLES et al. 1970] is not responsible for the high Sc content in Apollo 11 rocks. Apparently either the magmatic processes or the primitive matter responsible for generation of Apollo 11 basalts differed considerably from the corresponding factors that produced other lunar basalts.

In Fig. 8, we note that V and Cr₂O₃ correlate strongly over a factor of six in abundances. It seems that V and Cr are tied together in spinels. Extrapolation to zero V content yields ~800 ppm Cr₂O₃ in the whole rock; this quantity of Cr₂O₃ may be attributed to the Cr content in pyroxenes. Howardites and Cl chondrites lie below the correlation line and eucrites tend to approach the line. The average value for oceanic ridge basalts is spectacularly high. Spinels are high temperature minerals and should reflect early condensates from a hot cooling nebular gas. Such a hiatus between lunar and terrestrial correlations for V and Cr₂O₃ argues against the fission hypothesis for the origin of the Moon. [WISE, 1963; O'KEEFE, 1969].

Siderophile and volatile trace patterns by GANAPATHY et al. (1970), LAUL et al. (1971) and MORGAN et al. (1972) have been used to characterize the nature of impacting meteoritic bodies on the lunar surface, but this work has not escaped criticism of relative volatilization. The authors argued against selective volatilization on the constancy of Rb/Cs, Cs/U and Tl/U ratios in all lunar rocks and soils. HUBBARD and GAST (1972) from laboratory experiments presented evidence for alkali loss from basaltic rocks that were differentially volatilized to temperatures of

850-1050°C at 10^{-3} atm. However, ERLANK et al. (1972) reported a relative constant ratio for K/Zr (4.5) for lunar matter. This observation in lunar magmatic processes argues against any large-scale volatilization of the alkalis from lunar lavas or by exotic impact processes. To test it further, we have plotted K₂O (volatile) versus Hf, a refractory element-like Zr, in Fig. 9. A good correlation exists. Only the clasts from Apollo 14 clastic rocks fall off the line. These clastic deviations may be ascribed to a large variety of KREEP. Therefore high or low K (in KREEP) values in clasts may account for the observed dispersion. The sawdusts, which represent the overall rock composition of clastic rocks, fall on the line. Our data precludes selective large-scale volatilization of alkalis during lunar magmatic events.

Table III

Correlation Coefficients for 11 Elemental Pairs in Lunar Samples^a

	Na ₂ O K ₂ O	MnO FeO	V Cr ₂ O ₃	Sc FeO	K ₂ O Hf	Zr Hf	Nb Ta	Ba La	CaO Na ₂ O	CaO Al ₂ O ₃	FeO TiO ₂
C.C. for igneous _b basalts ⁻	.93 (9)	.76 (8)	.98 (6)	.60 (6)	.88 (6)	.95 (5)	1.00 (4)	.98 (7)	.74 (8)	.66 (8)	.30 (7)
C.C. for ign. plus clastic plus soils ^c	.94 (15)	.95 (35)	.97 (21)	.81 (37)	.96 (20)	.97 (11)	.98 (7)	.98 (14)	.52 (11)	.67 (12)	.58 (11)

^aBest average data of our work and that available from the literature for Apollo 11, 12, 14 and 15 and Luna 16 samples.

^bNumbers in parenthesis represent the number of points used for C.C. computations. Normally, one best average value each for Ap. 11 high and Ap. 11 low alkali rocks, Ap. 12 Mg rich and Mg poor rocks, Ap. 14 igneous, Ap. 15 igneous and Luna 16 igneous basalts.

^cNumbers in parenthesis represents the number of points used for computations. In addition to numbers in ^a, the best average values each for Ap. 11, 12, 14 and 15 and Luna 16 soils and the average value for Ap. 14 clastic rocks are included. In MnO-FeO, V-Cr₂O₃, Sc-FeO, and K₂O-Hf correlations, individual clasts and rock sawdust abundances were also included.

In Table 3, we have tabulated correlation coefficients for 11 pairs of elements from data obtained from sample analyses of five different lunar sites. The first eight pairs Na₂O-K₂O to Ba-La (Table 3) except Sc-FeO show strong linear relationships within the 95% confidence level in both basalts and basalts plus soils and clastic rocks. This suggests that these genetically related pairs do not fractionate appreciably during magmatic events. The last three pairs, CaO-Na₂O, CaO-Al₂O₃, and FeO-TiO₂ are poorly correlated. This may be attributed to the fact that Ca does not always reside in plagioclase; because of the variable ilmenite content in lunar basalts, FeO and TiO₂ are not well correlated. Average abundance ratios of Zr and Hf are 28±6 and 31±4 for Apollo 11 igneous rocks and soils; likewise, 36±6 and 40±4 were obtained for Apollo 12 igneous rocks and soils [WAKITA et al. 1971]. In general, the Zr/Hf ratio for Apollo 12 samples were 20-30% higher than for Apollo 11 samples. This was attributed to different chemical fractionizations at the two sites. Zr/Hf ratios at the Apollo 14 site are 33±3 for the soils, 31 for igneous rock 14073 and 31±2 for the clastic rocks. These ratios indicate no evidence for significant fractionization for this geochemically coherent pair in Apollo 11, 12 and 14 igneous basalts.

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Table I

Elemental Abundances in Three Apollo 14 Soils, One Clastic and One Igneous Rock^a

Element	Soils						Clastic rock		Igneous rock
	14003-31		14163-55		14240-10 (SESC)		14047-30		14073-3 0.0308g powdered aliquant ^d
	^b .528g	^c .478g	^b .537g	^c .392g	^b .227g	^b .187g	^b .402g	^b 0.553g	
TiO ₂ (%)	1.8		1.9		1.8	2.0	1.8	1.9	1.2
Al ₂ O ₃ (%)	18.3		18.4		19.4	18.5	18.5	18.8	20.0
FeO(%)	11.0		10.4		10.9		10.9		8.9
CaO(%)	11		11		12	12	12	11	13
Na ₂ O(%)	0.689		0.711		0.717	0.745	0.670	0.662	0.76
K ₂ O(%)	0.57	0.60	0.52	0.54	0.57	0.60	0.48	0.47	0.48
MnO(%)	0.128		0.124		0.125	0.130	0.125	0.123	0.120
Cr ₂ O ₃ (%)	0.214		0.197		0.209		0.204		0.196
Rb(ppm)	13		13						
Cs(ppm)	0.5		0.5						
Sc(ppm)	23		21		22		22		21
V(ppm)	53		57		55	40	40	50	45
Co(ppm)	39		38		36		38		18
Cd(ppb)	(139)		(189)						
In(ppb)	(104)		(85)						
Zr(ppm)	780		900		790		880		810
Hf(ppm)	20		20		20		20		17
Th(ppm)	14		13		14		14		8
Ba(ppm)	810		730		790		730		660
La(ppm)	68	66	69	68	70		69		60
Ce(ppm)	200	193	200	200	214		204		196
Pr(ppm)	20.5		24.4						
Nd(ppm)	103		103						
Sm(ppm)	30	31.2	29	32.2	31		29		26.4
Eu(ppm)	2.60	2.56	2.70	2.78	2.65		2.70		2.2
Gd(ppm)	36		37						
Tb(ppm)	6.1		6.4						
Dy(ppm)	41		41						
Ho(ppm)	9.7		10.2						
Er(ppm)	23.9		24.5						
Tm(ppm)	4.0		4.1						
Yb(ppm)	23	22	22	24	24		22		21
Lu(ppm)	3.2	3.3	3.1	3.6	3.2		3.0		2.9
Y(ppm)	192		204						
Σ REE+Y(ppm)	754		784						
Sm/Eu	11.5	12.2	10.7	11.6	11.7		10.7		12.0

^a One standard deviation due to counting statistics and other errors for single determinations are approximately ±2-3% for Al, Na, Mn and Cr; ±5% for Ti, Fe, Mg, Ca, Sc, Co, Cd, In, 14 rare earth elements and Y; ±10% for K, Rb, Cs and Hf; ±15% for V, Zr, Th and Ba, and ±10% for Ce and Eu in 14073 analysis. Cd and In abundances are probably high due to LRL contamination.

^b Abundances were obtained via instrumental neutron activation analysis.

^c Abundances were obtained via radiochemical neutron activation analysis.

^d This sample was prepared by D. S. Burnett as a member of the G. J. Wasserburg consortium for analysis of the 14073 rock.

Table II

Elemental Abundances in One Igneous and Four Apollo 14 Clastic Rocks, Three Apollo 14 Core Tube Soils, Two Luna 16 Breccias and Four Apollo 15 Soils^a

Element	14073,3A (STA G)	14063,37 Clastic (STA C1)					14083 Clastic (STA C1)			14318 Clastic (STA H)					14066 Clastic (STA F)					
	Igneous 269mg	Al0 Finest matrix 81mg	Al1 Coarse matrix int. 59mg	Al2 Black clasts 61mg	BS Scrap. frag. int. 80mg	B11-3 Coarse matrix int. 72mg	2,1 Black and white frag. 73mg	2,White A, 1/16 Pure white matter 31mg	2,4 Int. Dark 1/8 Pure Dark matter 28mg	40 Sawdust ^b 56mg	Sawdust ^c 31mg	26-A clast 14.2mg	26-B clast 5.2mg	26-C clast 12.8mg	27-B clast 7.6mg	31,3 Sawdust 269mg	21,2.02 Many clasts like 2.03 226mg	21,1.01 Matrix small clasts 33mg	21,2.01 Breccia clast 27mg	21,2.04,2 White igneous clast 10.6mg
TiO ₂ (%)	1.3	1.5	1.4	1.3	1.8	1.6	1.6	0.72	1.7	1.6	1.2	1.8	1.7	1.0	1.1	1.8	1.0	1.6	2.0	1.0
Al ₂ O ₃ (%)	20.8	22.0	21.5	20.4	22.8	23.5	16.4	21.8	17.0	16.3	16.1	17.8	18.9	15.9	19.3	15.3	23.1	16.3	16.6	17.9
FeO(%)	8.2	7.0	6.8	7.7	6.5	6.4	10.4	6.8	9.1	9.9	10.7	9.8	11.5	7.7	7.5	9.5	6.2	8.4	11.7	8.4
CaO(%)	12.8	13.1	13.2	11.6	13.3	14.6	10.4	14.1	12.4	10.0	11.3	10.8	10.3	9.4	10.3	9.5	12.8	11.0	8.9	9.1
Na ₂ O(%)	0.737	0.835	0.782	0.755	0.782	0.795	0.984	0.657	0.973	0.728	0.728	0.821	0.976	0.852	0.837	0.764	1.07	0.864	0.935	0.759
K ₂ O(%)	0.49	0.17	---	0.11	0.12	0.13	0.36	0.21	0.44	0.58	0.53	0.63	0.61	3.3	2.1	0.77	0.33	1.3	0.30	1.4
MnO(%)	0.108	0.081	0.081	0.085	0.079	0.076	0.116	0.076	0.110	0.105	0.109	0.113	0.107	0.099	0.101	0.112	0.073	0.111	0.115	0.107
Cr ₂ O ₃ (%)	0.150	0.180	0.171	0.233	0.160	0.147	0.180	0.100	0.700	0.193	0.180	0.143	0.148	0.121	0.097	0.165	0.128	0.150	0.240	0.124
Sc (ppm)	18.7	13.6	12.4	13.5	14.7	14.1	21.5	10.1	19.2	17.9	17.1	18.6	17.5	16.6	15.3	17.7	9.8	17.6	16.1	15.3
V	29	29	27	31	17±6	18±6	45	25	48	46	30	46	45	24	25	33	21	59	55	68
Co	18	20	18	27	17	17	34	17	26	31	28	26	86	28	12	28	20	23	38	17
Zr	660	---	---	---	---	---	830	450	1100	800	600	1400	950	600	1300	950	640	970	550	800
Hf	21	---	---	---	---	---	31	13.0	31	20	21	42	32	23	27	28	19	33	23	33
Th	11	---	---	---	---	---	19	6.1	19	12	13	24	18	24	17	15	10	16	15	13
U	2.6	1.1	1.8	0.5	0.9	0.8	5.0	1.6	4.5	4.1	2.1	6.1	6.0	6.3	5.4	4.0	2.1	4.1	2.7	3.3
Ba	600	360	550	280	310	260	900	450	1100	700	600	1100	1000	2600	1700	920	770	1000	800	1350
La	61	26.5	34.2	18.6	22.6	21.8	109	41	92	66	65	129	110	58	95	79	58	78	61	57
Ce	142	---	---	---	---	---	253	94	249	151	170	290	255	115	215	178	130	200	180	140
Sm	27	10.6	15.6	8.7	10.6	10.1	44	18.0	42	26	26	51	53	22	40	34	24	40	32	28
Eu	2.1	2.4	2.4	2.4	2.4	2.5	3.2	2.1	3.2	2.0	2.0	3.0	2.7	2.7	2.2	2.6	4.5	2.5	3.0	2.3
Tb	4.8	---	---	---	---	---	9.4	3.6	8.6	5.8	5.9	11	9.6	5.7	8.1	6.3	4.2	7.8	6.3	5.4
Yb	22	10	12	7.0	8.6	8.0	36	13.4	32	23	22	37	30	24	30	22	14.2	28	21	17
Lu	2.9	1.4	1.7	1.0	1.2	1.1	5.0	2.0	4.4	3.1	3.1	5.6	4.2	4.3	4.5	3.8	2.4	4.0	2.7	3.2
Ta	2.4	---	---	---	---	---	3.7	1.3	3.5	2.3	2.4	5.1	4.6	5.0	3.7	3.2	2.0	3.4	3.4	3.2
Sm/Eu	11.3	4.4	6.5	3.6	4.4	4.0	13.8	8.6	13.1	13.0	13.0	17.0	19.6	8.1	18.1	13.1	5.3	16.0	10.7	12.2
K/U	1560	1280	---	1830	1110	1350	600	1090	810	1170	2100	860	840	4350	3230	1600	1300	2630	920	3520
K/Ba	6.8	3.9	---	3.3	3.2	4.2	3.3	3.9	3.3	6.9	7.3	4.8	5.1	10.5	10.3	6.9	3.6	10.8	3.1	8.6
Th/U	4.2	---	---	---	---	---	3.8	3.8	4.2	2.9	6.2	3.9	3.0	3.8	3.1	3.8	4.8	3.9	5.6	3.9

a. Abundances were determined by INAA. Estimated errors due to counting statistics are: TiO₂, ±7%; Eu, Ta and Th, ±5-10%; V, Zr, Ba, Ce, Tb and U ±10-30%. Standards and duplicate BCR-1 samples were activated with all samples. Whenever BCR-1 values differed from published values, sample abundances from a given activation analysis were recalculated using BCR-1 values in last column. Abundances of Zr and Th were determined relative to 540 and 110ppm, respectively, in GSP-1.

b. This sawdust sample, obtained by the LRL in sawing 14318, was scooped from the container before the sample was split into two aliquants that were analyzed independently. Average of two analyses are given.

c. This sample was obtained from well-mixed sawdust and, therefore, should be representative of the whole rock composition after correcting for sawing contamination.

d. Sample was split into two aliquants that were analyzed independently. Average of two analyses are given.

e. F. R. basalt is an Oregon coastal mountain basalt, picked up near the east boundary of the range on the Fred B. Ramsey property (123° 19' x 44° 39').

f. Overall average and range values for TiO₂, Al₂O₃, FeO, CaO, Na₂O and K₂O are taken from HUBBARD and GAST (1971). Values for anorthositic basalt are not included in range. All other values from MnO to Lu are taken from HUBBARD and GAST (1971) for five KREEP fragments from 12003 and dark 12013, 10, 15, and 8 matrix and from WAKITA and SCHMITT (1970) for 12013-06. BROWN et al. (1971) determined MnO and Cr₂O₃ in noritic glass. Assuming 12034 breccia rock is ~80% KREEP of these three elements in 12034 (GOLES et al. 1971 and WAKITA et al. 1971).

Al₂O₃, Na₂O, MnO, Cr₂O₃, Sc, La and Sm, ±1-3%; FeO, K₂O, Co, Yb, Lu and Hf, ±5%; CaO of this table. Average values in Apollo 14 soils were taken from WAKITA et al. (1971).

sawdust was mixed; therefore, this sample is not representative of the rock sawdust.

given.

the Fred B. Ramsey property (123° 19' x 44° 39').

GAST (1971). Values for anorthositic basalt are not included in range. All other 12033 and the dark material from 12013, 10-5 and also from SCHNETZLER et al. (1970) for determined MnO and Cr₂O₃ in noritic glass. Assuming 12034 breccia rock is ~80% KREEP of these three elements in 12034 (GOLES et al. 1971 and WAKITA et al. 1971).

Table II (continued)

Element	14230 core tube (STA G)			Average in 3 Ap. 14 soils, 3,163,240	Luna 16 Breccias		15021,24 soil, <1mm LM cont. 261mg	15471,49 soil, <1mm STA 4 Dune c. 500mg	15501,40 soil, <1mm STA 9 Scraplet c. 497mg	15531,52 soil, <1mm STA 9a Rillig 498mg	BCR-1 Basalt	F.R.2 Basalt	KREEP or Moritic matter avg. (range)
	110 13- 14.3cm 56mg	116 18- 19.8cm 74mg	127 21.5- 22.6cm 74mg		A-36	G-41							
TiO ₂ (%)	1.7	1.6	1.7	1.9	3.7	3.8	1.8	1.6	1.6	2.1	2.23	1.5	1.6(1.3-2.9)
Al ₂ O ₃ (%)	18.1	18.0	18.7	18.6	16.8	16.8	14.1	13.3	12.7	10.0	13.7	14.8	19(15-21)
FeO(%)	9.3	10.1	9.7	10.8	16.5	16.4	15.0	15.9	16.5	19.5	12.3	10.3	9(9-12)
CaO(%)	11.2	12.5	11.6	11.3	14.0	9.0	10.8	10.9	10.0	10.5	7.0	11.3	10.5(10-11)
Na ₂ O(%)	0.714	0.741	0.714	0.74	0.99	0.76	0.434	0.364	0.377	0.301	3.32	2.15	1.0(0.8-1.0)
K ₂ O(%)	0.60	0.48	0.55	0.56	0.21	0.20	0.22	0.12	0.17	0.09	1.71	0.65	0.9(0.5-1.1)
MnO(%)	0.122	0.125	0.129	0.127	0.215	0.213	0.190	0.204	0.207	0.248	0.174	0.171	0.18(0.16-.22)
Cr ₂ O ₃ (%)	0.180	0.200	0.190	0.207	0.314	0.314	0.400	0.430	0.430	0.490	0.0022	0.290	0.19(0.17-.21)
Sc (ppm)	18.8	20	20	22	49	49	28	31	31	36	32	39	25
V	50±7	64±9	34±7	52	106	70	114	147	139	182	430	280	50
Co	32	33	34	38	33	32	40	44	43	50	36	45	35
Ni	550	600	700	---	---	---	350	160	370	130	---	170	800
Nb	21	21	22	20	6.5	8.8	9.9	6.3	7.1	4.4	4.7	2.9	36
Tb	13	12	14	---	---	---	4.9	2.4	3.4	1.8	---	0.5	19
U	3.5	3.0	3.4	---	---	---	1.5	0.7	1.0	---	1.4	---	6
Ba	850	800	800	780	---	---	320	200	120	110	700	90	1100(600-1600)
Zn	64	66	68	68	14	13	26	15.0	20	10.9	26	6.7	108(93-134)
Ce	162	160	170	203	30	23	73	42	53	35±	53	15±	297(243-374)
Sm	29	32	30	31	8.4	7.6	12.9	7.4	9.7	5.7	7.0	3.2	49(38-62)
Eu	2.7	2.5	2.6	2.7	2.9	3.6	1.4	0.64	0.77	1.0	2.0	1.2	3.2(2.6-3.7)
Tb	6.0	5.8	6.4	6.2	1.6	1.3	2.3	1.5	1.8	1.0	0.96	0.62	10
Yb	22	23	24	23	6.2	6.0	9.5	5.7	6.2	4.8	3.6	2.1	39(34-47)
Lu	3.2	3.2	3.3	3.3	.91	.90	1.3	0.81	1.1	0.66	0.55	0.43	5.7(4.7-7.0)
Ta	2.8	2.5	2.8	---	1.5	1.3	1.2	0.75	0.83	0.60	0.74	0.43	3.9
Sm/Eu	10.7	12.8	11.5	11.5	2.9	2.1	9.2	11.5	12.6	5.7	3.5	2.7	15.3
K/U	1420	1330	1340	---	---	---	1220	1420	1410	---	10100	18000	1250
K/Ba	5.9	5.0	5.7	6.0	---	---	5.7	5.0	11.8	6.8	20	60	6.8
Th/U	3.7	4.0	4.1	---	---	---	3.3	3.4	3.4	---	---	---	3.2

Figure Captions

Fig. 1. Abundances of REE (La, Ce, Sm, Eu, Tb, Yb and Lu) in soils normalized to chondritic abundances (La 0.34, Ce 0.91, Sm 0.195, Eu 0.073, Tb 0.047, Yb 0.22, Lu 0.034, Ba 3.6). Values of Apollo 11 and 12 and Luna 16 soils are taken from WAKITA et al. (1970, 1971) and GILLUM et al. (1972). Apollo 15 soils are 15021 (LM), 15471 (STA 4), 15501 (STA 9) and 15531 (STA 9a). Average values for KREEP (K) are listed in Table 2.

Fig. 2. Chondritic normalized abundances of 7 REE and Ba in clastic rock 14063 (STA C1). Clasts are A10 finest matrix, A11 coarse matrix, A12 black clasts, BS scrappings and B11-3 coarse matrix.

Fig. 3. Chondritic normalized values of 7 REE and Ba in clastic rock 14083 (STA C1). Clasts are 2,1 black and white; 2, white-A, 1/16 pure white matter, and 2,4 interior dark 1/8 pure dark matter.

Fig. 4. Chondritic normalized abundances of 7 REE and Ba in clastic rock 14318 (STA H). Data for sawdust (31 mg) is plotted.

Fig. 5. Chondritic normalized abundances of 7 REE and Ba in clastic rock 14066 (STA F). Clasts are 21,2.02 many clasts, 21,1.01 matrix, 21,2.01 breccia, and 21.2.04,2 white igneous rock. Rock sawdust is for overall rock composition.

Fig. 6. Abundances of FeO and MnO in lunar, meteoritic and terrestrial matter. Sources for these data are WAKITA et al. (1970), WAKITA and SCHMITT (1971), this work, GILLUM et al. (1972), SCHMITT et al. (1972) and CORLISS (1970). For KREEP, see references in Table 2. The correlation coefficient is 0.95 (>99% confidence level) for all lunar values.

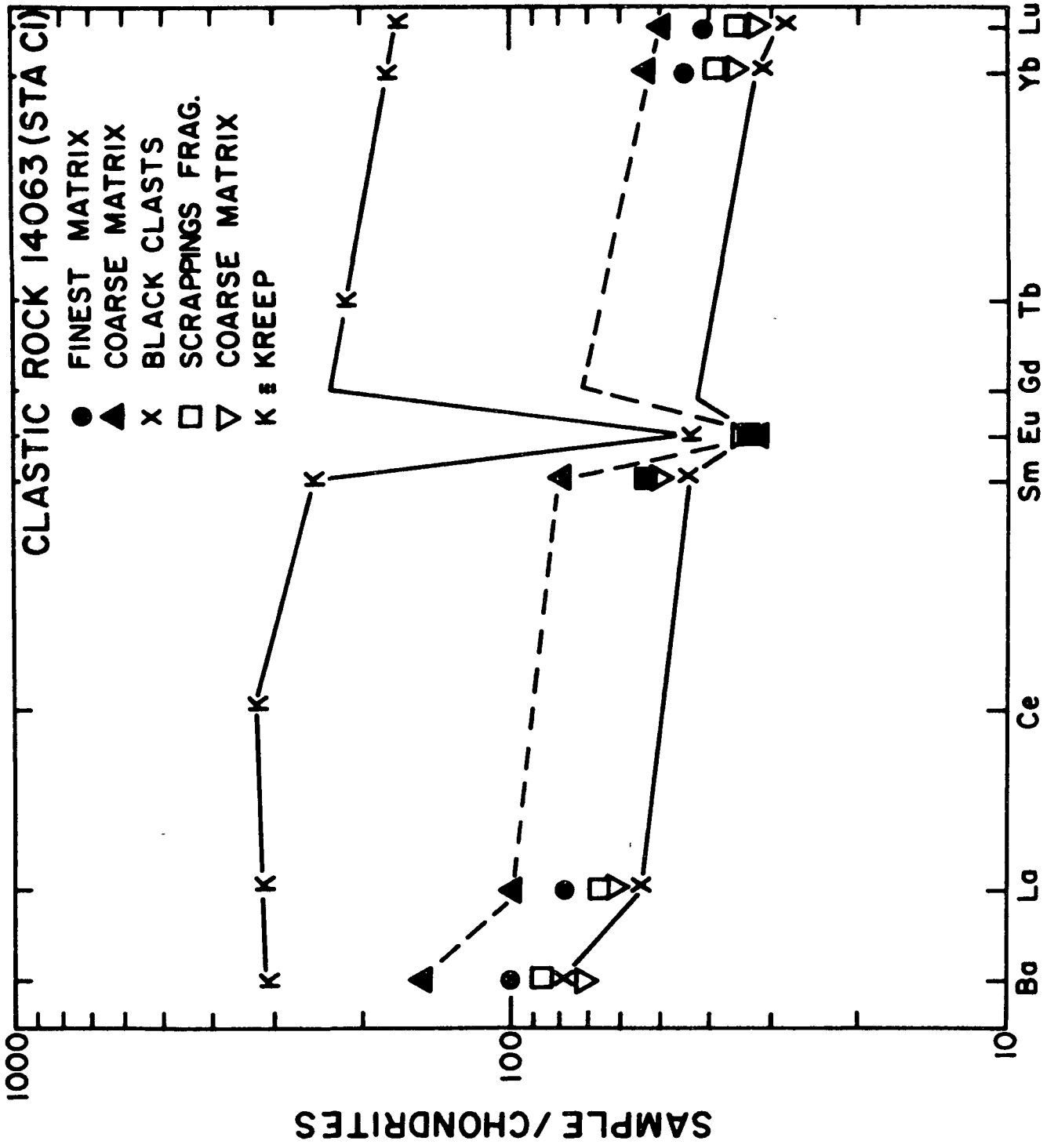
Fig. 7. Sc-Fe correlation in lunar, meteoritic and terrestrial matter. Symbols are identical to those found in Fig. 6. The correlation coefficient is 0.81 (>99% confidence level) for all lunar values and 0.93 for lunar values excluding Ap. 11 soils and rocks and Ap. 12 low Mg rocks.

Fig. 8. Correlation of V-Cr₂O₃. Same symbols as found in Fig. 6. The correlation coefficient is 0.97 (>99% confidence level) for all lunar values.

Fig. 9. Correlation of K₂O-Hf. Same symbols as found in Fig. 6. The correlation coefficient is 0.48 and 0.96 (both >99% confidence level) for all lunar values and for lunar values excluding the individual clasts, respectively.

CLASTIC ROCK 14063 (STA CI)

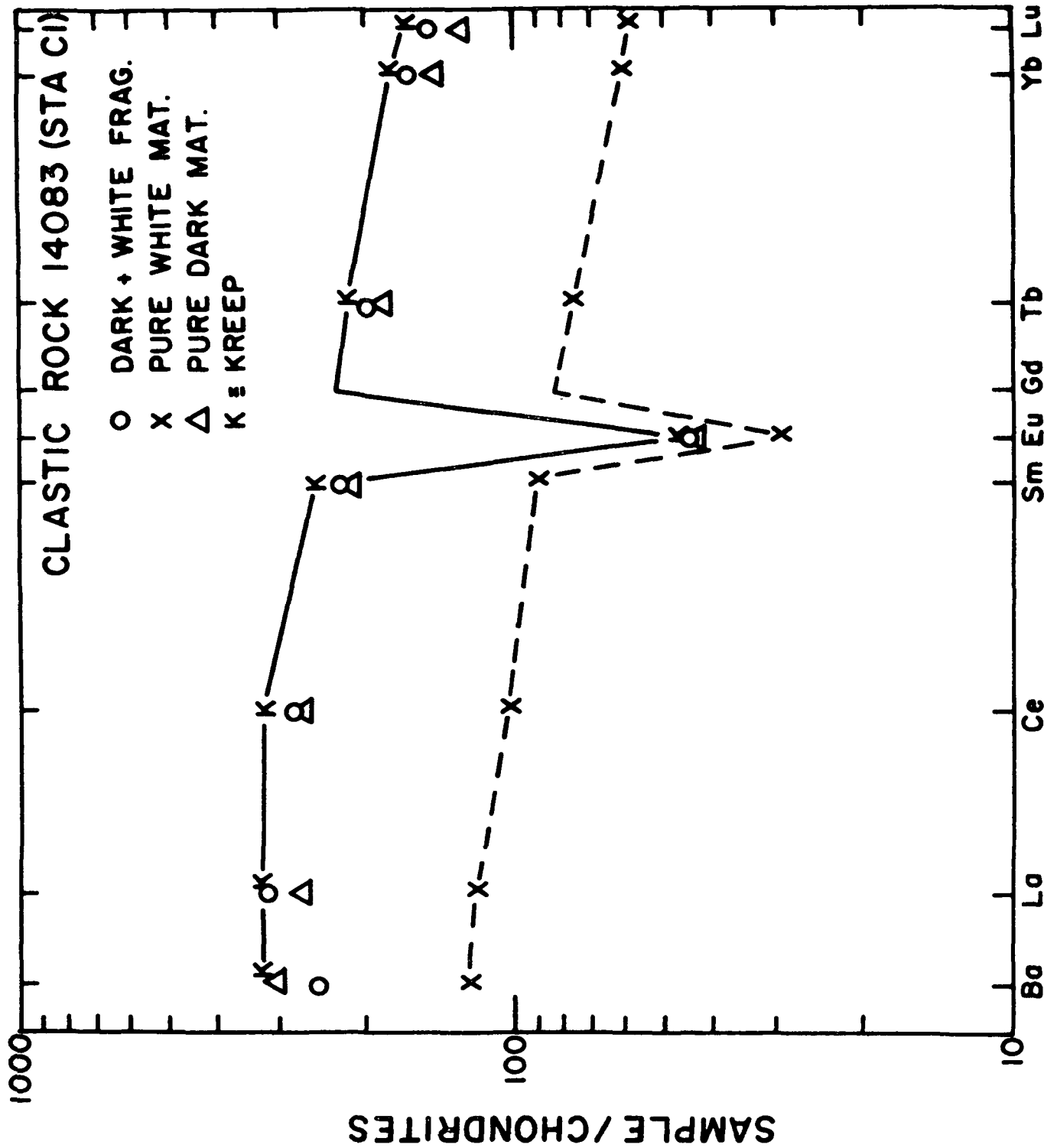
- FINEST MATRIX
- ▲ COARSE MATRIX
- X BLACK CLASTS
- SCRAPPINGS FRAG.
- ▽ COARSE MATRIX
- K ≡ KREEP



REE IONIC RADII

CLASTIC ROCK 14083 (STA CI)

- DARK + WHITE FRAG.
- × PURE WHITE MAT.
- △ PURE DARK MAT.
- K = KREEP



REE IONIC RADII

