

Some interelement relationships between lunar rocks and fines, and stony meteorites

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Abstract—The concentrations of 27 elements have been determined in three Apollo 12 rocks and two fines. Together with published analyses of Apollo 11 materials, these data are used to discuss elemental variations within and between Apollo 11 and Apollo 12 rocks and fines. The variations within the Apollo 12 rocks, and between Apollo 11 and Apollo 12 rocks are considered to be due mainly to differing degrees of partial melting. The Apollo 12 fines are enriched, relative to both Apollo 12 rocks and Apollo 11 fines, particularly in K, Rb, Ba, P, Zr, Nb, Y, La, Yb, and Be. These enrichments are considered to be due to admixture of foreign material analogous to KREEP and rock 12013, and estimates are made of the Zr, Nb, and Be contents of such materials. These calculations support previous conclusions that the lunar interior is enriched in refractory elements.

Emphasis has been placed on chemical relationships between stony meteorites and the lunar surface, and in these discussions we have paid particular attention to the relationships between Ca and Al, Sr and Eu, and Mg and Cr. The Ca/Al ratio in lunar fines is closely similar to that found in stony meteorites. The Sr–Eu relationship between stony meteorites and lunar rocks and fines is remarkably well-developed, whereas the Mg–Cr relationship in these materials further supports the similarity previously postulated for the lunar surface and basaltic achondrites.

INTRODUCTION

THE PURPOSES of this paper are five-fold: (1) presentation of our analytical techniques and data as determined either by X-ray fluorescence or optical emission spectroscopy in three Apollo 12 rocks (12002,113; 12053,24; 12063,52) and two Apollo 12 fines (12032,38 and 12070,88); (2) a general discussion of the compositional variations observed within and between lunar rocks and fines, with special reference to certain interelement relationships; (3) a critical evaluation of the Ca–Al relationship in stony meteorites and all types of lunar materials, particularly lunar fines; (4) a study of the relationship between geochemically closely coherent pairs of refractory elements, with particular reference to Sr and Eu, in stony meteorites and lunar materials; and (5) a comparison of Cr abundances between terrestrial and extra-terrestrial matter (stony meteorites and lunar rocks and fines); and a brief examination of Mg–Cr relationship between basaltic achondrites (howardites and eucrites) and lunar rocks and fines.

ANALYTICAL TECHNIQUES AND DATA

As this is the first time we are reporting data for lunar materials, brief details of our analytical techniques are set out below.

Sample preparation

The amounts of lunar material received varied between 2 g and 6 g. The samples were first crushed by hand in a carbon steel pestle and mortar to pass a 60 mesh nylon screen, and then ground in an automatic agate mortar to approximately 300 mesh size.

X-ray fluorescence

A Philips PW 1220 2 kW semiautomatic X-ray spectrometer was used for all determinations, except Ba, which was determined on a PW 1540 manual spectrometer (WILLIS *et al.*, 1969). The total sample, in powder form, was used for the determination of Rb, Sr, Y, Zr, and Nb, using techniques similar to those discussed by CHERRY *et al.* (1970). The mass absorption coefficient was also determined on the powder by the method of REYNOLDS (1963). 1 g of powder was then briquetted and used for the determination of Zn, Cu, Ni, Ba, La, S, and Na. Zn and S were determined first to minimize any possible contamination from the vacuum oil.

Another 1 g of powder was dried at 120°C overnight in a preheated Vitreosil crucible, and then heated at 1000°C to constant weight (~12 hours). Three 0.28 g portions of the heated material were fused with Johnson Matthey Spectroflux no. 105 using the method of NORRISH and HUTTON (1969) for the analysis of Fe, Mn, Cr, Ti, Ca, K, P, Si, Al, and Mg.

Optical emission spectroscopy

Of the remaining heated material, 0.1 g was mixed with specpure graphite powder, containing Pd as internal standard, in the ratio 1 part sample to 2 parts graphite, for the determination of Be, Sc, V, Co, and Yb. A Jarrell-Ash 3.4 m plane grating spectrograph (5 Å/mm dispersion in the first order) was used for the analyses, with a conventional DC arc and a modified Stallwood jet with an argon-oxygen mixture. Spectral lines used were Be 3131, Sc 3613, V 3276, Co 3453, Yb 3289, Pd 3258, and Pd 3065 Å. Background corrections were made on all lines.

Standards

For XRF determinations either G-1 or W-1 was used as reference standard for the trace elements. PCC-1 and DTS-1 were used for Cr₂O₃ and a departmental standard for S. The rock standards BR, T-1, S-1, GSP-1, AGV-1, PCC-1, and DTS-1 were used for major element analysis, together with artificial standards for Fe and Ti. For optical emission analysis a number of international rock standards were used to establish working curves.

Table 1. Major element data (%) for Apollo 12 rocks and fines by X-ray fluorescence spectrometry

	s.d.*	12002,113	Rocks 12053,24	12063,52	Average	12032,38	Fines 12070,88	Average
SiO ₂	0.30	43.56	46.21	43.48	44.42	46.58	45.74	46.16
TiO ₂	0.02	2.60	3.32	5.00	3.64	2.56	2.79	2.68
Al ₂ O ₃	0.12	7.87	10.14	9.27	9.09	13.59	12.67	13.13
FeO†	0.10	21.66	19.77	21.26	20.90	15.11	16.52	15.82
MnO	0.002	0.283	0.280	0.280	0.281	0.207	0.222	0.215
MgO	0.10	14.88	8.17	9.56	10.87	9.89	10.42	10.16
CaO	0.05	8.26	11.01	10.49	9.92	10.53	10.45	10.49
Na ₂ O	0.01	0.23	0.26	0.31	0.27	0.56	0.39	0.48
K ₂ O	0.003	0.051	0.065	0.061	0.059	0.363	0.241	0.302
P ₂ O ₅	0.01	0.11	0.14	0.14	0.13	0.38	0.30	0.34
Cr ₂ O ₃	0.01	0.96	0.49	0.44	0.63	0.37	0.42	0.40
S	0.001	0.062	0.078	0.090	0.077	0.069	0.075	0.072
Subtotal		100.526	99.933	100.381		100.209	100.238	
O = S		0.031	0.039	0.045		0.035	0.038	
Total		100.49	99.89	100.33		100.17	100.20	

* Average experimental standard deviation (1 σ)

† Total Fe as FeO

Table 2. Trace element data (ppm) for Apollo 12 rocks and fines

	s.d.*	Rocks				s.d.*	Fines		
		12002,113	12053,24	12063,52	Average		12032,38	12070,88	Average
<i>X-ray fluorescence spectrometry</i>									
S	8	622	785	905	771	8	688	752	720
K	30	420	540	510	490	30	3010	2000	2510
Cr	100	6570	3350	3010	4310	100	2530	2870	2700
Ni	1.2	64	10	20	31	1.4	117	202	~160
Cu	0.9	4.6	26†	8.0	13	0.9	29†	8.0	19
Zn	0.6	1.5	1.2	4.5	2.4	0.5	22†	9.7	16
Rb	0.2	1.25	1.1	0.8	1.05	0.2	8.9	6.4	7.7
Sr	1.4	86	111	145	114	1.3	154	136	145
Y	1.6	39	52	65	52	1.8	197	149	173
Zr	1.5	106	138	133	126	2.2	741	549	645
Nb	1.6	8.5	10.0	7.9	8.8	1.5	58	45	52
Ba	2	66	86	67	73	4	531	373	452
La		<6	<6	<6	<6	2.6	51	33	42
<i>Emission spectrography</i>									
Be	0.2	1.0	1.7	1.5	1.4	0.7	4.3	4.0	4.2
Sc	9	45	50	55	50	8	39	39	39.0
V	7	175	148	135	153	8	96	112	104
Co	5	62	30	36	43	5	31	40	36
Yb	0.6	4.3	3.8	5.7	4.6	1.5	16	12	14

* s.d. Average experimental standard deviation.
† Contamination?

A study of the data from the Second Lunar Science Conference (unpublished proceedings) indicates a probable systematic error for P₂O₅ in our lunar rock analyses. This error may also be present in our soil analyses. The samples had already been returned to NASA and could not be reanalyzed. However, a check on the Apollo 11 rock 10017,70 indicates that the rock analyses reported here may be high by ~0.09% P₂O₅, due to blank problems. A study of the Cr data in the unpublished proceedings, together with that for PCC-1 and DTS-1, (FLANAGAN, 1969), indicates an urgent need for the accurate standardization of Cr below the 1% level. Cl data presented at the Second Lunar Science Conference have been omitted from this paper, as the samples are thought to have been contaminated by the high local sea salt content of the air. All analytical data are presented in Tables 1 and 2, together with average experimental standard deviations which are derived from replicate determinations and take into account all sources of imprecision. Some interelement ratios are presented in Table 3.

GENERAL DISCUSSION ON LUNAR ROCKS AND FINES

Lunar rocks

As indicated by the preliminary data (LSPET 1970) the Apollo 12 rocks show a larger variation in major element composition than the Apollo 11 rocks and this is evident from the data given in Table 1, even though we have only analyzed three rocks. From the petrographic data available to us, and as shown by the variations in Mg and Ni, it might be inferred that these three rocks are members of a differentiated suite which has undergone olivine fractionation. However, detailed inspection of the data does not support this contention. For example, a substantial amount of olivine would have to be removed from rock 12002 (14.9% MgO) to produce rock 12063 (9.6% MgO), yet Ba, which is not readily accommodated in the olivine structure, is present in virtually identical amounts in the two samples. This would imply removal also of

Table 3. Some interelement ratios in lunar rocks and fines.

	Rocks				Fines		
	12002,113	12053,24	12063,52	Average	12032,38	12070,88	Average
K/Rb	336	491	638	467	338	313	327
K/Ba	6.36	6.28	7.61	6.71	5.67	5.36	5.54
Ba/Rb	53	78	84	72	60	58	59
Zr/Nb	12.5	13.8	16.8	14.4	12.7	12.3	12.5
Ba/Zr	0.62	0.62	0.50	0.58	0.72	0.68	0.70
K/Sr	4.9	4.9	3.5	4.3	19.5	14.7	17.3
K/Zr	3.96	3.91	3.83	3.88	4.06	3.64	3.88
Rb/Sr	0.014	0.010	0.006	0.010	0.058	0.047	0.052
Ba/Sr	0.77	0.77	0.46	0.66	3.45	2.74	3.09
Rb/Zr × 10 ²	1.18	0.80	0.60	0.86	1.20	1.17	1.19

interstitial material (mesostasis) and the existence of open system conditions. The variation of other elements (e.g., Sr, Y, and Nb) is also not in accord with that expected from olivine fractionation alone (or spinel or pyroxene fractionation) and hence we infer that varying degrees of partial melting must also be invoked to explain the observed compositional variation in the Apollo 12 rocks. Critical interelement ratios (Table 3) do not suggest that different source areas are involved in the production of the three rocks analyzed here. We have insufficient data and samples to further evaluate these possibilities.

Compared to the Apollo 11 low K (Rb) rock suite (COMPSTON *et al.*, 1970; GAST *et al.*, 1970), and allowing for compositional variations and analytical error, the Apollo 12 rocks are enriched in Si, Mg, Ni, V, Co, and Cr, and depleted in Ti, Zr, S, Sc, Y, Nb, La, Yb, and possibly Be, indicating the more mafic character of the Apollo 12 rocks. Considered collectively, the data suggest a greater degree of partial melting during the production of the liquids giving rise to the Apollo 12 rocks, in view of the relative similarity in major element composition when compared to the larger differences present for dispersed elements such as Nb and Zr in the Apollo 11 and Apollo 12 rocks. The case for varying degrees of partial melting giving rise to the observed compositions, as opposed to advanced near-surface crystal fractionation (O'HARA, *et al.*, 1970), has been cogently argued by RINGWOOD (1970) and GAST AND HUBBARD (1970). Different source areas may also be partly responsible as K/Rb ratios for example are lower in the Apollo 12 basalts than in the low K Apollo 11 basalts (Fig. 1). However, K/Ba ratios are indistinguishable in the two suites (Fig. 2).

Lunar fines

The two samples of fines analyzed (Tables 1 and 2) have fairly similar major element compositions, but differ appreciably for several trace elements, for example K, Ba, Rb, Zr, and Nb. This demonstrates that the regolith at Apollo 12 is not well-mixed. It may be noted however that several interelement ratios (e.g., Ba/Rb, Ba/Zr, Zr/Nb) are remarkably similar (Table 3) and this merits consideration in any mixing process which is proposed to account for the lunar fines.

Compared with data for the Apollo 11 fines 10084 (COMPSTON *et al.*, 1970; ANNELL and HELZ 1970; MORRISON *et al.*, 1970; SMALES *et al.*, 1970) the Apollo 12 fines are depleted in Ti and Sc (ilmenite?) and enriched in Mg and V (olivine from the more

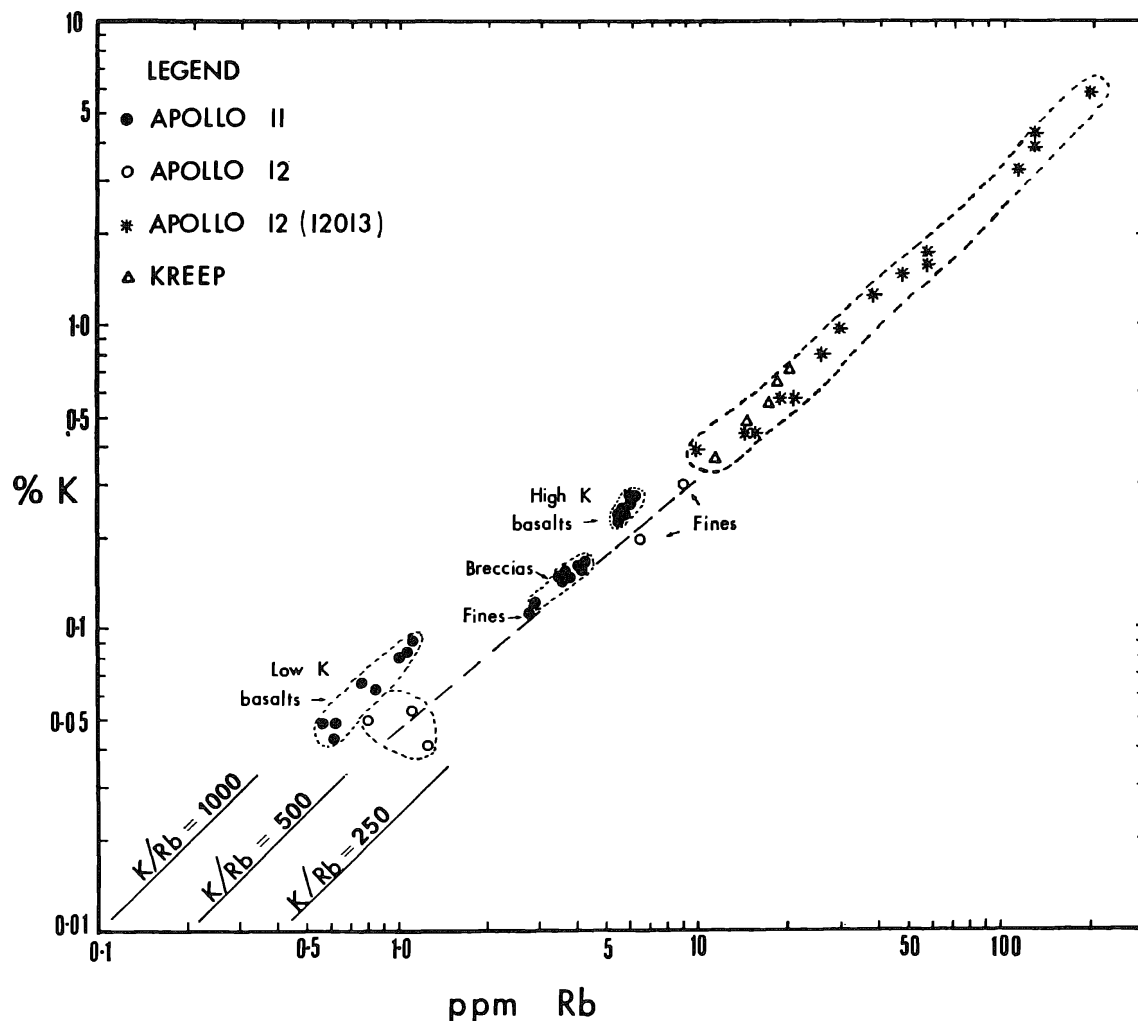


Fig. 1. The K-Rb relationship in lunar materials. Apollo 12 data for rocks and fines are from this paper. Apollo 11 rocks, breccia, and fines data are from COMPSTON *et al.* (1970), GOPALAN *et al.* (1970), MURTHY *et al.* (1970), GAST *et al.* (1970), PHILPOTTS and SCHNETZLER (1970), TERA *et al.* (1970), SMALES *et al.* (1970), and HUBBARD *et al.* (1970). Apollo 12 rock 12013 data from GAST *et al.* (1970) and SCHNETZLER *et al.* (1970). Apollo 12 KREEP data from HUBBARD *et al.* (1971b).

Mg rich Apollo 12 rocks?) and K, Rb, Ba, P, Zr, Nb, Y, La, Yb, (La > Yb), and possibly Be. Where reliable data are available it may be shown that some interelement ratios involving the last named elements also vary. For example it can be seen from Fig. 1 that the Apollo 12 fines have lower K/Rb ratios than Apollo 11 10084. These features reflect varying admixture of foreign material and this is discussed below.

Lunar rocks versus fines

Several authors have concluded that the Apollo 11 fines cannot be solely derived from the range of Apollo 11 rocks which have been analyzed. In particular, TERA *et al.* (1970) showed that an extra component, with lower K/Rb and K/Ba ratios than those observed in the rocks, was necessary to explain the composition of the fines. LSPET (1970) also demonstrated that the Apollo 12 fines cannot be directly derived from the

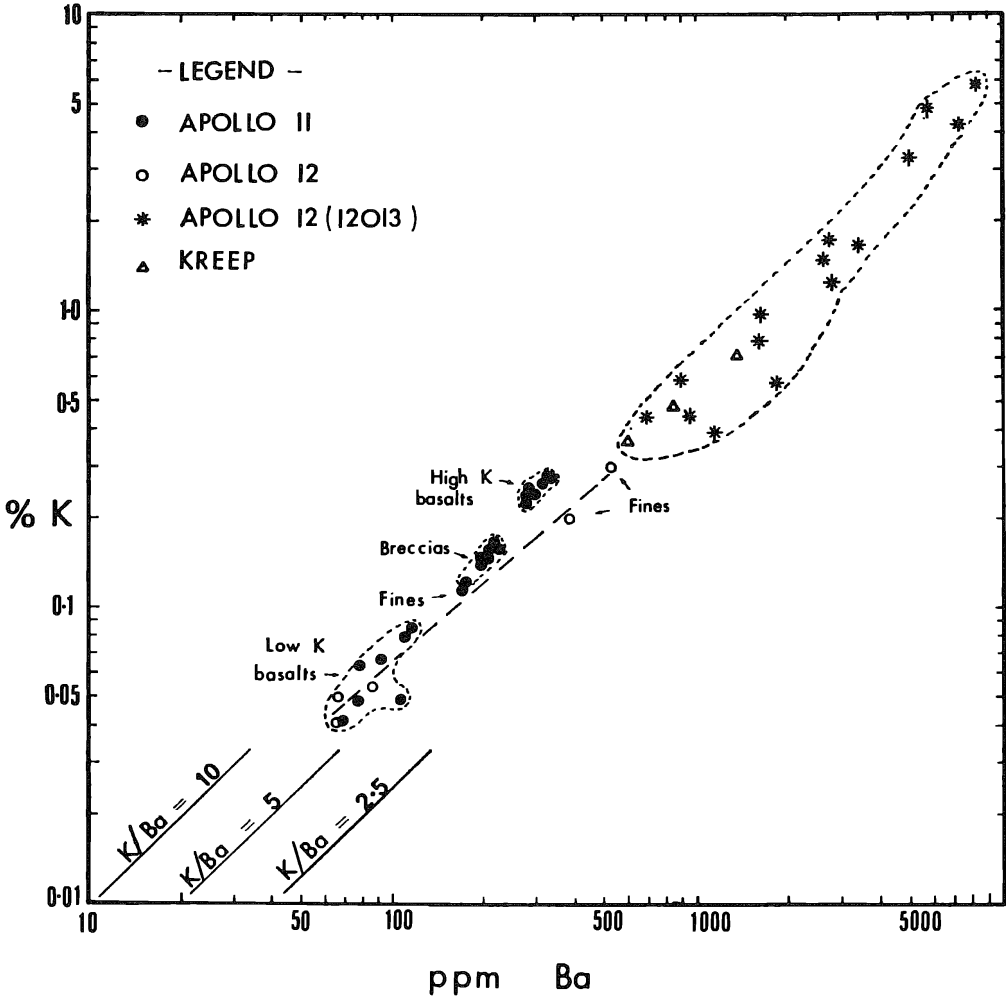


Fig. 2. The K-Ba relationship in lunar materials. Sources of data as for Fig. 1.

Apollo 12 rocks and this is confirmed by the data presented here. It is instructive to consider the ratio of fines/rocks for the averages given in Tables 1 and 2 for those elements where distinctions are reasonably clear-cut.

<i>Ratio Fines/Rocks</i>	<i>Elements</i>
0.6-0.9	Fe, Mn, Cr, V, Sc
1.0-2.0	Al, Na, Sr
> 2.0	K, Rb, Ba, P, Y, La, Yb, Zr, Nb, Be, Ni, Zn

The first group of elements (ratios < 1) shows that the fines have less ferromagnesian and opaque minerals than the rocks. The second group indicates the presence of more plagioclase or anorthosite in the fines. Of those elements greatly enriched in the fines, the increased abundance of Ni and Zn is considered to be due to small amounts of meteoritic infall; the others are all characteristically enriched in residual liquids (dispersed or incompatible elements) and hence their increased abundance must be due to admixture of more differentiated rock types, or rocks derived by smaller degrees of partial melting.

SCHNETZLER *et al.* (1970) and HUBBARD *et al.* (1970) have suggested that the dark (mafic) portions of the unique rock 12013 represent the “cryptic” or “magic” component of Apollo 12 fines. More recently HUBBARD *et al.* (1971a, b) have drawn attention to the presence of high K, REE, P glass (KREEP) in the Apollo 12 fines and demonstrated that these fines are quantitatively matched by mixtures of average Apollo 12 basalt and KREEP. K/Rb and K/Ba plots shown in Figs. 1 and 2 confirm that either the mafic portions of rock 12013 or KREEP may represent the missing cryptic component in the Apollo 12 soils, if they are derived from the Apollo 12 basalts. The mixing lines in these diagrams are drawn through the average of our three rock analyses and the average of our two analyses of fines. The K/Ba plot also shows that it is possible to derive the Apollo 11 fines from a mixture of either the Apollo 11 low K rocks on the one hand and the mafic portions of rock 12013 or KREEP on the other. However, the K/Rb plot demonstrates that rock 12013 or KREEP cannot be the precise missing component added to either of the Apollo 11 basalt types to produce the Apollo 11 fines; these can be derived from the Apollo 12 rocks. If the mafic portions of rock 12013 or KREEP are wide-spread components of the lunar surface (fines), the implication is that neither of the Apollo 11 rock types are major components (or are present) in the Apollo 11 soil. It is pertinent to recall that the Apollo 11 rocks are younger than the model age given for Apollo 11 fines (COMPSTON *et al.*, 1970) and it has yet to be established that the basal fragments in the Apollo 11 fines (WOOD *et al.*, 1970) are derived from either of the two Apollo 11 basalt types which have been analyzed.

The abundances of Zr and Nb are substantially higher (by a factor of about five) in the Apollo 12 fines when compared to the Apollo 12 rocks (Table 2). As no data are available for individual fragments of rock 12013 or KREEP glass it is of interest to calculate estimated abundances in these materials. This could be done singly for either element using the same approach and mixing proportions given for various Apollo 12 fines by HUBBARD *et al.*, (1971a, b), but this requires the mixing proportions to be correct and necessitates the use of an average composition for the rocks (Zr varies by about 30% in the three samples analyzed). A more sophisticated approach is possible because the K/Zr and Zr/Nb ratios given in Table 3 are relatively constant for both rocks and fines and it follows that the ratios in the missing components must be similar also, hence problems due to assumptions of average rock compositions and mixing proportions are avoided. The KREEP 1 glass used by HUBBARD *et al.* (1971a, b) in their mixing calculations contains 7030 ppm K. Using the ratios given in Table 3 for Apollo 12 fines ($K/Zr = 3.9$, $Zr/Nb = 12.5$), KREEP 1 glass should contain 1800 ppm Zr and 144 ppm Nb. A similar approach may be used for other KREEP glasses or rock 12013 fractions. It may be noted that a single sample of rock 12013 analyzed by LSPET (1970) yielded concentrations of 2200 ppm Zr and 170 ppm Nb ($Zr/Nb = 12.9$).

We emphasize that Zr and Nb concentrations of this order are, together with the rare-earth contents (HUBBARD *et al.*, 1971b), substantially higher than those observed in terrestrial basaltic rocks. A wide variety of oceanic island basalts analyzed in this laboratory (KABLE *et al.*, 1971) generally contain less than 400 ppm Zr and 80 ppm Nb (Zr/Nb 4–10). It is difficult to envisage the derivation of a basaltic liquid (HUBBARD

et al., 1971a give 48% SiO₂ for average KREEP glass) with the high contents of Zr and Nb estimated above for KREEP from a chondritic type parent (~ 10 ppm Zr, ≈ 1 ppm Nb, ERLANK and WILLIS, 1964). Even if all Zr and Nb partition into the melt during melting, it is necessary to assume about 0.5% partial melting which we consider to be unrealistic. The alternative is that these two refractory elements are enriched in lunar basalt source regions and this is in agreement with the conclusion reached by GAST and HUBBARD (1970) for other refractory elements.

The enrichment of Be in the Apollo 12 lunar fines (Table 2) is interesting as this has not been previously reported. No suggestion for this may be found in the Apollo 11 data presented by ANNELL and HELZ (1970) and MORRISON *et al.* (1970); however, their Be results show a fairly large scatter. We assume that the excess Be in the Apollo 12 fines is contributed by the KREEP component and using a K-Be plot we estimate that KREEP 1 glass will contain of the order of 10 ppm Be. This again attests to the differentiated nature of this component. It is also noteworthy that the Be concentration in eucrites Pasamonte and Sioux County is of the order of 0.3 ppm (SILL and WILLIS, 1962).

The features discussed above indicate that a small amount of meteoritic component and a "differentiated" component (related to rock 12013 and KREEP) are required to partly account for the composition of lunar fines. Mention has also been made of an anorthitic component as the Apollo 11 and Apollo 12 fines contain more Al than any rocks from these missions (Fig. 3) and as the Apollo 11 and Apollo 12 fines have also been shown to contain anorthositic fragments. The special significance of this observation is discussed under Ca-Al below.

The Ca-Al relationship in stony meteorites and lunar materials

The close relationship between Ca and Al in chondrites and basaltic achondrites is now well established (AHRENS and VON MICHAELIS, 1969; AHRENS, 1970a; AHRENS, 1971). The average Ca/Al ratio is 1.08 (mesosiderites have a characteristically lower ratio, average = 0.86). It should be noted (1) that most minerals which have Ca and Al as major constituents have ratios far removed from these values (see Fig. 3 for anorthite and clinopyroxene ratios); (2) that despite a large variation in the overall concentration of the principal host minerals for Ca and Al, clinopyroxene and plagioclase (anorthitic in basaltic achondrites and sodic maskelynite glass in chondrites) the ratio remains virtually the same; and (3) even if the mineralogy is unusual, e.g., the presence of many Ca and Al phases in Allende (C III chondrite) including gehlenite and Ca-Al rich glass (see Fig. 3), the ratio for the meteorite as a whole remains unchanged.

We have experienced some difficulty in compiling available Ca and Al data on Apollo 11 and Apollo 12 lunar rocks and fines, as the data are often not in satisfactory agreement (data for sample 12070 presented at the Second Annual Lunar Science Conference show a spread in the Ca/Al ratio of 0.89–1.13). For this reason we have used only the data of AGRELL *et al.* (1970), MAXWELL *et al.* (1970), MAXWELL and WILK (1971), COMPSTON *et al.* (1970, 1971), MASON *et al.* (1971), SCOON (1971), and our own data. This choice in no way implies that all other data are in error (inaccurate or imprecise), but we consider from our experience that the data from these

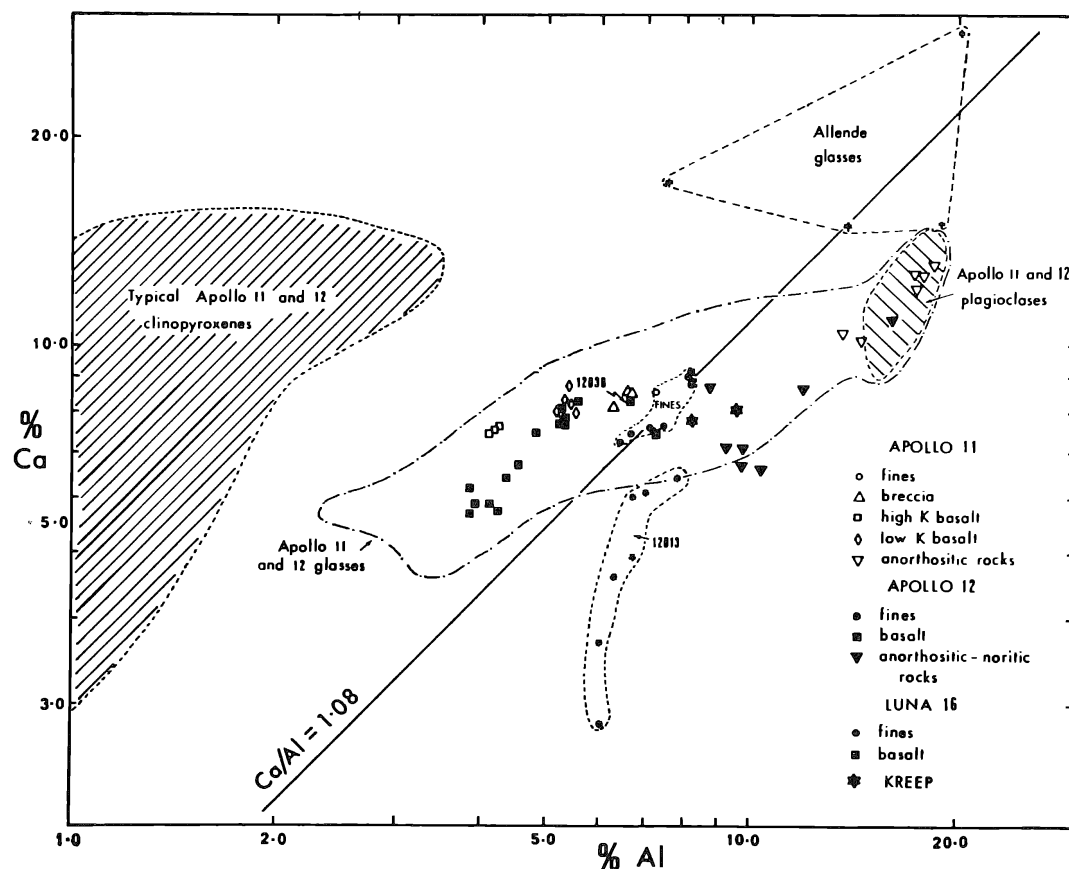


Fig. 3. The Ca-Al relationship in lunar materials. Note the clustering of the lunar fines about the stony meteorite trend line. Sources of data: DENCE *et al.* (1971), KEIL *et al.* (1971), GREENE *et al.* (1971), AGRELL *et al.* (1970), FRONDEL *et al.* (1970), WARE and LOVERING (1970), DOUGLAS *et al.* (1970), KEIL *et al.* (1970), DUKE *et al.* (1970), CHAO *et al.* (1970), ADLER *et al.* (1970), BROWN *et al.* (1970), HARGRAVES *et al.* (1970), DRAKE *et al.* (1970), CARTER *et al.* (1971), COMPSTON *et al.* (1970), MAXWELL *et al.* (1970), COMPSTON *et al.* (1971), MAXWELL and WIIK (1971), SCOON (1971), MASON *et al.* (1971), WOOD *et al.* (1970), BUNCH *et al.* (1970), WAKITA and SCHMITT (1970), HUBBARD *et al.* (1971a), WOOD *et al.* (1971), VINOGRADOV (1971), MARVIN *et al.* (1970), and this paper.

laboratories is internally consistent and reliable. The only available Luna 16 data are from VINOGRADOV (1971). Rock 12013 data are from WAKITA and SCHMITT (1970), KREEP glass data from HUBBARD *et al.* (1971a), and the anorthosite-norite data from WOOD *et al.* (1971). Our requirements for mineral and impact glass data are not so stringent and are derived from several authors. Allende glass data may be found in MARVIN *et al.* (1970). The assembled Ca-Al plot is shown in Fig. 3.

It is immediately apparent that, apart from a single sample of Luna 16 basalt, the only samples which cluster around the stony meteorite trend line are lunar fines. Ca/Al values are as follows:

Locality	Ca/Al
Apollo 11 (10084)	1.19
Apollo 12 (5 samples)	1.02-1.13
Luna 16 (4 samples)	1.08-1.12

Allowing for analytical error there is probably a real spread of at least 10% in the Ca/Al ratio showing that the lunar fines are not perfectly mixed (note also variation of Ca and Al absolute abundances in Fig. 3). Nevertheless, considering that these samples are from three separate localities and bearing in mind the overall consistency of the Ca/Al ratio, the similarity of the Ca/Al ratio in lunar fines and stony meteorites can hardly be fortuitous. In considering the significance of this feature, the following comments may be briefly considered.

(1) The lunar fines are mixtures of Apollo 11 and Apollo 12 basalts, anorthositic rocks (WOOD *et al.*, 1970, 1971; and KEIL *et al.*, 1970), KREEP (HUBBARD *et al.*, 1971a, b) and possibly material similar to the mafic portion of rock 12013 (note that KREEP has higher Ca and Al abundances than any of the fractions in rock 12013). The exact proportions of each are difficult to evaluate, but any reasonable combination implies a rather uniform mixing process.

(2) The lunar fines are derived from rocks with lower Ca/Al ratios, similar to the Luna 16 basalt, with smaller amounts of anorthosite or KREEP admixture. Such rocks have not been reported from the Apollo 11 or Apollo 12 sites (rock 12038 has the lowest Ca/Al observed), but many glasses have ratios close to the meteoritic value. Glasses comprise 50% of the < 1 mm fraction of the Apollo 11 fines (WOOD *et al.*, 1970), and it appears that the most abundant glass has a Ca/Al ratio of 1.16 (FRONDEL *et al.*, 1970). Further discussion on the mixing history of the lunar fines will not be attempted here, but we interpret the above observations to indicate that the lunar fines may, at least for the major elements, represent fairly well mixed averages of the lunar surface, and, by implication, may reveal the Ca/Al *ratio* of the lunar interior. If so, this places restrictions on the composition of the source regions of lunar basalts. RINGWOOD (1970) considers that these regions are comprised essentially of clinopyroxene and orthopyroxene, and gives analyses for synthetic clinopyroxene and orthopyroxene liquidus phases which have ratios of 2.5 and 1.3, respectively. Any mixture of these two minerals therefore cannot generate the required ratio. Hence the lunar interior must either be composed of pyroxenes which are more aluminous than inferred by Ringwood, or else another aluminous phase, such as plagioclase or spinel, must be present (the presence of plagioclase in the lunar interior is not supported by experimental evidence, see RINGWOOD, 1970).

The Ca/Al ratio in the earth's mantle, as estimated from kimberlitic garnet peridotites (CARSWELL and DAWSON, 1970), and the sun (ALLER, 1968) appear to be similar (Ca/Al \sim 1.0) and thus close to the stony meteorite average. One form of Allende glass has a ratio of 1.08 (Fig. 3) and we suggest that this ratio is characteristic of the solar system.

In order to account for the uniformity of the Ca/Al ratio and the trends of other refractory elements, it may be instructive to bear in mind that a variety of species exist, AlO, CaO, TiO, ZrO, and others, all of them spectrum emitters, at the high temperatures prevailing in hot nebulae (the vaporization experiments on lunar samples by DE MARIA *et al.* (1971) appear to be pertinent in this respect). If a given nebular mass is quenched or isolated in some way, the relative proportions of these elements (which may or may not be similar to so-called cosmic proportions) will presumably be independent of the mineralogy of the final condensed object (moon, meteorite etc.),

provided that all processes acting on this object subsequent to condensation are of an isochemical nature. Rather, the mineralogy in the first place is dependent on the relative proportions of elements in the condensate and subsequently on the post-condensation history. The pair Ca–Al provide a classic example in this respect. Thus the Ca/Al ratio of Allende is in fact determined by the relative proportions of Ca and Al in the condensate rather than by its present complex mineralogy. We consider that greater attention should be given to preaccretion chemistry in order to understand more fully the problems of lunar and solar system petrology and geochemistry.

The comments above on the Ca/Al ratio in condensing nebulae apply also to Sr and Eu, a pair of elements which we will now consider.

THE RELATIONSHIP BETWEEN CLOSELY COHERENT PAIRS OF REFRACTORY ELEMENTS

Although the chemistry of the refractory group of elements (Al, Ca, Sc, Ti, Sr, Y, Zr, Nb, Ba, rare earths, Hf, Ta, Th, and U) varies considerably when taken as a whole, some pairs or larger groups are chemically and geochemically very similar, e.g., Zr and Hf, trivalent rare earths, Nb and Ta, Th and U, and Sr and Eu^{II}. In our opinion, a critical and highly quantitative comparison of the relationships between such pairs or larger groups of these geochemically coherent refractory elements in stony meteorites and lunar materials would be highly significant for cosmochemistry. Much has been written on the rare earths, but data on the other geochemically coherent groups is scant or unsatisfactory, except for Sr and Eu^{II}, and our discussion here will be restricted to these two elements.

In order to reduce analytical uncertainty to a minimum, and as it is desirable to have both elements determined in the same meteorite or lunar specimen, the data of one laboratory only will be considered (PHILPOTTS and SCHNETZLER, 1970; SCHNETZLER and PHILPOTTS, 1968; and PHILPOTTS and SCHNETZLER, 1971). The Sr–Eu relationship (Fig. 4) is remarkably well developed, particularly with respect to the stony meteorites. (We have not plotted data for Serra de Mage and Moore County, as these eucrites are generally considered unusual). The slope of the fitted line is less than unity (rate of increase of Eu is slightly greater than that of Sr) and if substantiated by further data this relationship may be of particular significance with respect to small differences in bond type (Sr → O and Eu → O) in various compounds, whether we are emphasizing processes in cooling nebulae or in melts (partial melting or differentiation). The importance of *small* differences in bond type in geochemical processes has been stressed by AHRENS (1964).

The significance of the presence of high rare earth content glass (KREEP) in Apollo 12 soil has been discussed by HUBBARD *et al.* (1971b). Highly differentiated or unusual material such as KREEP and rock 12013 will, however, not be considered here.

Cr ABUNDANCES AND THE Mg–Cr RELATIONSHIP

The characteristically high Cr concentration in *all* stony meteorites and lunar rocks and fines relative to terrestrial rocks of approximately the same bulk chemistry has been stressed before (AHRENS and DANCHIN, 1970), and RINGWOOD (1970) has

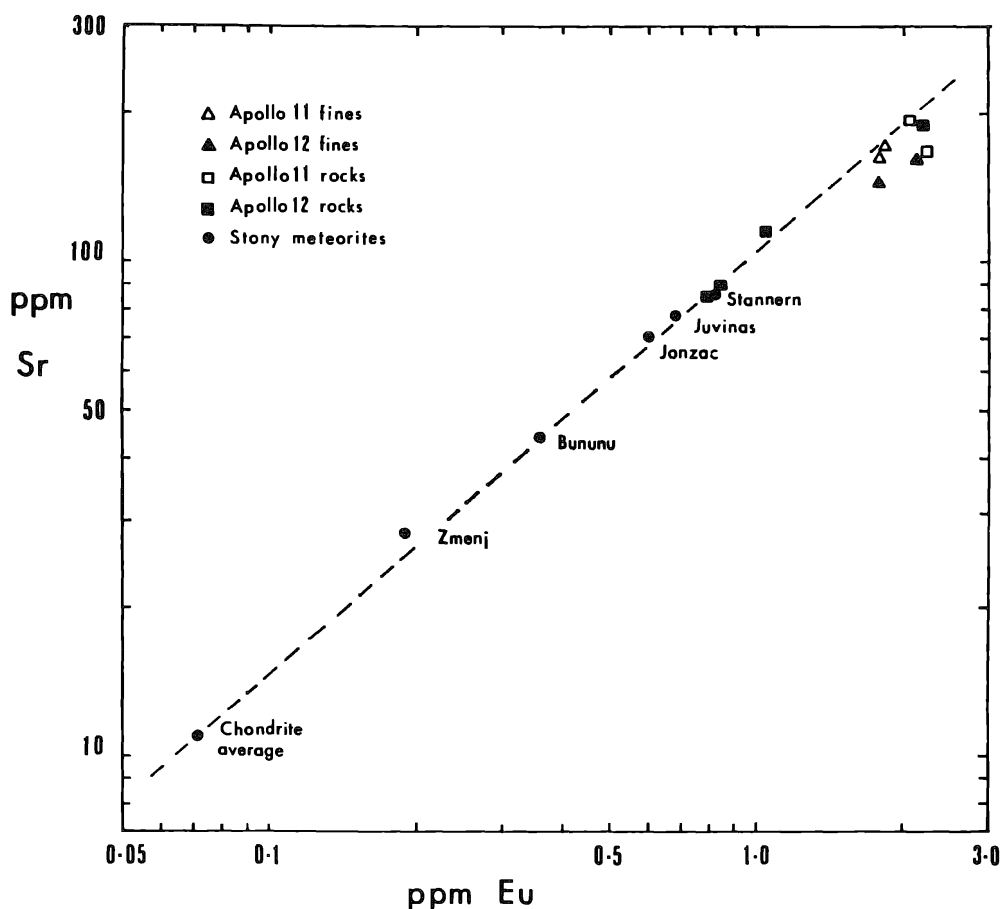


Fig. 4. The relationship between Sr and Eu in some stony meteorites and Apollo 11 and Apollo 12 rocks and fines. The regularity, particularly with respect to the meteorites, is well developed.

emphasized the importance of this element in lunar petrology. Here we wish, in the first place, to examine the Cr abundance relationship more fully and more quantitatively than before. On the basis of several hundred Cr determinations in terrestrial basalts (MANSON, 1967) a histogram (not shown) was constructed using a linear scale. This histogram displayed extreme positive skewness and is similar in appearance to that for Cr in Ontario diabases (Fig. 20 of AHRENS, 1954). Although the spread of the Cr concentration is very large, a striking characteristic of this element in most types of terrestrial rock, it is quite clear that the terrestrial levels are much lower than those typical of chondrites, basaltic achondrites, and lunar materials. It is noteworthy that the Cr level in rock 12013 is remarkably high (~ 1000 ppm or more; WAKITA and SCHMITT, 1970) for this type of material. In fact, Cr may be one of the most effective index elements for distinguishing terrestrial from much of extra-terrestrial matter in the solar system.

A sympathetic relationship between Mg and Cr in howardites, eucrites, and lunar rock 12038 has been noted (Fig. 1 of AHRENS 1970). The problem of a thorough quantitative study of such a relationship is complicated, mainly, it seems, because of considerable uncertainty in the analytical data. For example, Cr levels in fines 12070 range from ~ 2000 ppm to ~ 3000 ppm. Mg is far more uniform. As a result of this

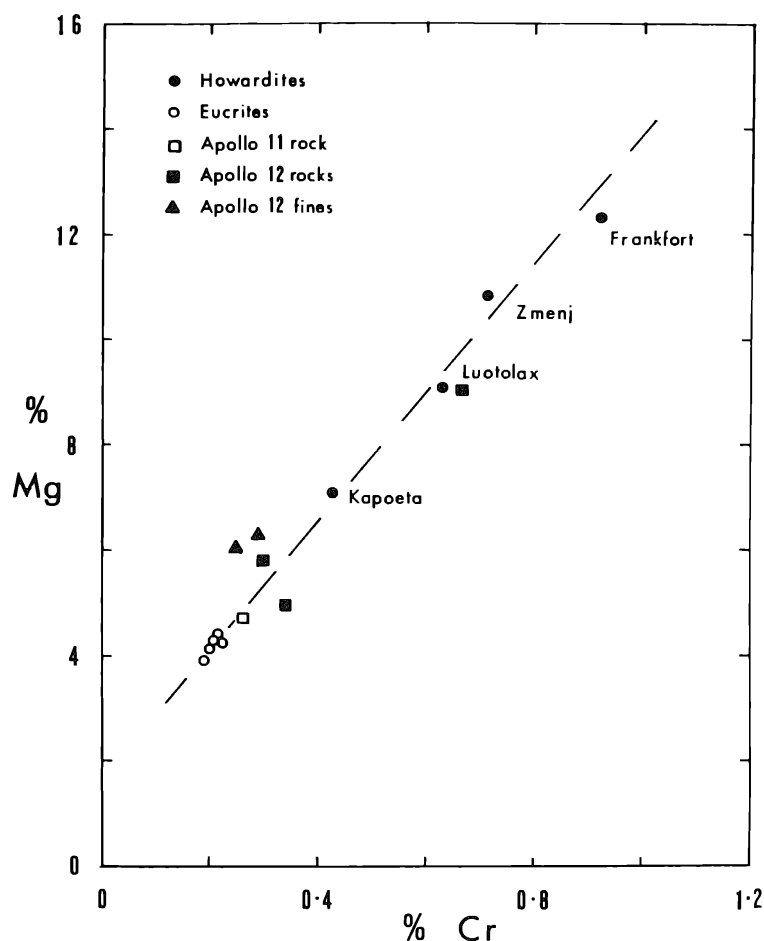


Fig. 5. The Mg-Cr relationship in basaltic achondrites and some lunar materials.

problem we have adopted a rather arbitrary procedure and for Mg and Cr in basaltic achondrites have used the data of AHRENS (1970b) and for lunar materials used only our own data. A graphical representation of the Mg-Cr relationship is shown in Fig. 5. In a general way, the lunar data fit the basaltic achondrite trend line. Lunar sample 12002 (high olivine) is of considerable interest as both Mg and Cr are very high. High Mg and Cr concentrations have also been observed in other samples.

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