

INDIGENOUS ABUNDANCES OF SIDEROPHILE ELEMENTS IN THE LUNAR HIGHLANDS: IMPLICATIONS FOR THE ORIGIN OF THE MOON*

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Abstract. Substantial indigenous abundances of siderophile elements have been found to be present in the lunar highlands. The abundances of 13 siderophile elements in the parental magma of the highlands crust were estimated by using a simple model whereby the Apollo 16 highlands were regarded as being a mixture of three components (i.e. cumulus plagioclase + intercumulus magma that was parented to the highlands crust + meteoritic contamination by ordinary chondrites). The parental magma of the highlands was found to possess abundances of siderophile elements that were generally similar to the abundances of the unequivocally indigenous siderophile elements in primitive, low-Ti mare basalts. This striking similarity implies that these estimated abundances in the parental highlands magma are truly indigenous, and also supports the basic validity of our simple model.

It is shown that metal/silicate fractionation within the Moon cannot have been the cause of the siderophile element abundances in the parental highlands magma and primitive, low-Ti mare basalts. The relative abundances of the indigenous siderophile elements in highland and mare samples seem, instead, to be the result of complex processes which operated *prior* to the Moon's accretion.

The abundances of the relatively involatile, siderophile elements in the parental highlands magma are strikingly similar to the abundances observed in terrestrial oceanic tholeiites. Furthermore, the abundances of the relatively volatile, siderophile elements in the parental highlands magma are also systematically related to the corresponding abundances in terrestrial oceanic tholeiites. In fact, the parental magma of the lunar highlands can be essentially regarded as having been a volatile-depleted, terrestrial oceanic tholeiite.

The complex, siderophile element fractionations in the Earth's upper mantle are thought to be the result of core segregation. However, it is well-known that the siderophile element abundances do not correspond to expectations based solely upon equilibration of metal/silicate at low-pressures, as evidenced by the over-abundances of Au, Re, Ni, Co and Cu. Ringwood (1977a) has suggested that the siderophile element abundances in the Earth's upper mantle are the product of equilibration at very high-pressures between the mantle and a segregating core that contained substantial quantities of an element with a low atomic weight, such as oxygen. Comparable processes cannot have operated within the Moon due to its small internal pressures and the very small size of its possible core. Therefore, the fact that the Moon exhibits a systematic resemblance to the Earth's upper mantle is highly significant.

The origin of the Moon is discussed in the context of these results. The possibility that depletion of siderophile elements occurred in an earlier generation of differentiated planetesimals similar to those which formed the basaltic achondrites, stony-irons, and irons is examined but can be dismissed on several grounds. It seems that the uniquely terrestrial "siderophile signature" within the Moon can be explained only if the Moon was derived from the Earth's mantle subsequent to core-formation.

1. Introduction

Analyses of soils and rocks from the lunar highlands have shown that most samples contain substantial abundances of siderophile elements. Two conflicting views have been

* Paper dedicated to Professor Hannes Alfvén on the occasion of his 70th birthday, 30 May, 1978.

expressed, however, concerning the origin of these siderophiles. Anders *et al.* (1973), Baedeker *et al.* (1972, 1973), Ganapathy *et al.* (1970, 1972, 1973), Hertogen *et al.* (1977), Morgan *et al.* (1972a, b, 1974, 1976) and Wasson *et al.* (1973) have maintained that the siderophile elements are overwhelmingly derived from the remnants of meteoritic projectiles which have impacted the Moon. Hence, these investigators regard the *indigenous* abundances of siderophile elements to be very small. In contrast to this view, Wänke *et al.* (1975, 1976, 1977) maintain that most of the Ni and W in the lunar highlands was accreted as part of a "primary component" and is therefore indigenous. Although the presence of a substantial meteoritic component is recognised, Wänke and co-workers imply that important indigenous abundances of additional siderophiles may also exist in the lunar highlands. Similarly, Jovanovic and Reed (1976, 1977) argue that significant indigenous abundances of Os and Ru exist in the lunar highlands. In the present study, we will provide further evidence supporting the latter view that substantial proportions of many siderophile elements in the lunar highlands belong to an indigenous component.

Morgan *et al.* (1974) and others have attempted to characterise the compositions of the meteoritic projectiles by examining the abundances of some siderophile elements (i.e. Ir, Au, Re, Sb, Ge) in highlands breccias. Although they claim to recognise 9 distinct projectiles (Gros *et al.*, 1976) by their siderophile element signatures, we are sceptical of their general approach to this problem. For example, an important assumption of their scheme for estimating the composition of the meteoritic contamination in lunar samples is that the meteoritic component did not experience substantial element fractionation during the time between the moment of impact and subsequent implantation into the rocks and soils of the lunar crust. However, it is now known that this requirement for a closed system on the scale of centimeters was generally violated by many elements including Rb, K, Na (Gibson and Hubbard, 1972; Nyquist *et al.*, 1974; Wänke *et al.*, 1974), Cd, Zn (Chou *et al.*, 1973), Ge (Gros *et al.*, 1976; Palme *et al.*, 1978), Fe and Si (Naney *et al.*, 1976; Ivanov and Florensky, 1975). The common occurrence of element-mobility during impact must necessarily introduce large uncertainties into any alleged identifications of distinct meteoritic components, particularly when based upon ratios of elements possessing widely varying volatilities (e.g., Ir/Au). Furthermore, when one considers the extremely limited sampling so far carried out on the Moon, it becomes difficult to accept the reality of the discrete groups of projectiles postulated by, for example, Morgan *et al.* (1974) and Gros *et al.* (1976). We suspect that with a greatly expanded data base, these groups would probably merge into a continuum.

There are additional objections to the rationale used by Morgan *et al.*, (1974) and Gros *et al.* (1976) to characterise the meteoritic projectiles. The validity of their approach is highly dependent upon their assumption that the abundances of indigenous siderophile elements in highlands samples is very much smaller than the meteoritic contamination. It is therefore of interest to examine the reasons which Morgan *et al.* (1974) advance to justify this key assumption.

Firstly, they point out that in the highlands rocks the siderophile elements are much more abundant in breccias than in "genuine igneous rocks". We suggest that this observation

would be simply explained if many of these "genuine igneous rocks" (e.g. KREEP basalt 15382) had been formed by impact melting of pre-existing soils and breccias. During crystallization of the impact melt, a metallic phase, which is present in most highlands rocks and breccias, would have separated out and extracted most of the siderophile elements. The low abundances of siderophile elements in some highlands "igneous" rocks would therefore be attributed to a simple secondary differentiation process on or near the lunar surface.

Secondly, Morgan *et al.* (1974) argue that experimentally determined, metal/silicate distribution coefficients (e.g., Kimura *et al.*, 1974) for siderophile elements, such as Au, are consistent with highland rocks possessing only extremely low indigenous abundances. Since most highland breccias contain abundances of Au and other siderophiles that exceed these equilibrium values by orders of magnitude, Morgan *et al.* (1974) maintain that the abundances must be attributed overwhelmingly to meteoritic contamination. We regard this argument as feeble since it tacitly assumes that the abundances of any *indigenous* siderophile elements in the lunar highlands would have been established by low-pressure equilibration between metallic iron and silicates. This view is known to be inapplicable to the Earth (Ringwood, 1977a) and no reason is offered as to why it should be true in the case of the Moon. Indeed, we shall explain in Section 5 that the assumption is invalid because the lunar highlands system was *not* saturated with respect to iron when it formed at 4.4 AE.

In our view, there is no justification for assuming that the indigenous abundances of many siderophile elements in the lunar highlands are as small as suggested by Gros *et al.* (1976). We shall demonstrate that there are stronger reasons for suggesting that an important, indigenous, siderophile component is present in most lunar highland samples. This conclusion, if verified, would not only invalidate any previous claims for identification of distinct meteoritic projectiles, but would also have important implications for the origin of the Moon.

2. Petrogenesis of the Lunar Highlands

The formation of the lunar crust is generally believed to have involved a large scale melting and differentiation process which affected an outer zone of the Moon, some hundreds of kilometers thick (e.g., Wood, 1970, 1972, 1975; Walker *et al.*, 1975). The energy source may have been supplied by partial conservation of the gravitational energy of accretion of the Moon (Ringwood, 1966, 1970). It is possible that an outer layer, perhaps 400 km thick, was totally melted, thereby forming an ultramafic parent magma (e.g. Walker *et al.*, 1975). However, consideration of available energy sources and heat balances and the large temperature interval between the liquidus and solidus (Ringwood, 1976) indicate a greater likelihood of producing extensive (e.g., 20–30%) partial melting of the outer regions of the Moon (see also Brett, 1977). This would produce a magma of basaltic bulk composition (parental to the lunar crust) overlying a thick zone of residual, refractory ferromagnesian minerals. Even in the event that total melting of the outer

TABLE I
Derivation of composition of basaltic magma multiply saturated with plagioclase and olivine, which may have been parental to the lunar crust (PLC magma)

	I Mean composition of upper crust (Taylor and Jakeš, 1974)	II Column I minus 57% of plagioclase An ₉₅ PLC magma
SiO ₂	44.8	47.3
TiO ₂	0.55	0.88
Al ₂ O ₃	24.6	18.4
Cr ₂ O ₃	0.1	0.13
FeO	6.6	9.4
MgO	8.6	12.3
CaO	14.2	11.3
Na ₂ O	0.45	0.16
<u>Mg</u>		
(Mg + Fe)	0.70	0.70

Moon occurred, thereby forming an ultra-mafic magma, extensive fractional crystallization of olivine + pyroxene would be necessary before the Al₂O₃ content of the residual magma was sufficiently high (17–19% Al₂O₃) to precipitate plagioclase (Ringwood, 1976). Thus, in this case also, by the time that the plagioclase-rich lunar upper crust began to form, the parental magma must have been of a mafic or basaltic composition.

Schonfeld (1975) has pointed out that the composition of the upper lunar crust can be interpreted in terms of a mush of cumulus plagioclase crystals plus trapped inter-cumulus parental gabbroic magma from which the plagioclase had crystallized. This is a simple and attractive concept. The high Mg/(Mg + Fe) ratio and Cr contents of the lunar crust suggest that the parental mafic liquid had not evolved extensively via fractional crystallization when it became trapped in the plagioclase cumulate.

Melting relationships of relevant lunar gabbroic anorthosite compositions at low pressures (<5kb) have shown that plagioclase crystallizes over a wide temperature interval before being joined at a cotectic by olivine and/or pyroxene (Kesson and Ringwood, 1976). The cotectic liquid is of an overall basaltic composition. In the case of the lunar crust, we obtain the composition of the parental basaltic composition by removing increasing amounts of liquidus plagioclase (An₉₅) from the mean upper crust composition (Table I), and determining the stage at which the residual liquid becomes multiply saturated at its liquidus by plagioclase and a ferromagnesian mineral (olivine and/or pyroxene). This composition has been experimentally determined (Table I, column 2). The liquidus phases at the cotectic at atmospheric pressure are plagioclase (An > 95) and olivine (Fo₈₈). This composition is believed to approximate that of the magma parental to the lunar crust, and, in terms of the previous discussion, to represent the bulk composition of the lunar crust. Thus, it may be of major volumetric and petrogenetic significance.

It is of interest to compare the composition of this magma with that of primitive

TABLE II

Comparison of composition of basaltic magma which could have been parental to the lunar crust, with composition of a typical primitive terrestrial oceanic tholeiite modified by partial loss of volatile components

	I Primitive terrestrial oceanic tholeiite ^a	II Parental lunar crust magma	III Column I minus (7% SiO ₂ + 1.8% Na ₂ O)
SiO ₂	50.3	47.3	47.5
TiO ₂	0.73	0.9	0.8
Al ₂ O ₃	16.6	18.4	18.2
FeO	7.99	9.4	8.8
MgO	10.2	12.3	11.2
CaO	13.2	11.3	14.5
Na ₂ O	2.00	0.2	0.2
<hr/>			
Mg			
(Mg + Fe)	0.69	0.70	0.69
<hr/>			
ΣREE ^b	~ 9	~ 10	~ 10
Chondrites			

^aSample DSDP 3-18 from Frey *et al.* (1974).

^bREE stands for rare-earth elements.

terrestrial oceanic tholeiites, which represent the most abundant rock type erupted at the Earth's surface. This comparison is made in Table II, in which sample 3-18 recovered from Leg 3 of the Deep Sea Drilling Project (Frey *et al.*, 1974) is chosen to represent a typical primitive oceanic tholeiite. It is well-known that lunar basalts are depleted in volatile elements relative to terrestrial basalts. Of the major elements shown in Table II, the most volatile are Na and Si (Grossman, 1972). In Table II, column 3, we have removed 7% of SiO₂ and 1.8% of Na₂O. We see that the composition of the residual modified terrestrial tholeiites is very similar to that of the parental lunar crustal (PLC) magma*.

The resemblance between the magma parental to the lunar crust and terrestrial oceanic tholeiites extends also to key trace elements such as the rare earths. Hubbard *et al.* (1971) calculated the REE abundances of the parental basaltic magma from which the anorthosite 15415 has crystallized, using plagioclase-liquid partition coefficients. The parental liquid was found to possess chondritic relative abundances of the REE elements at about 10 times the absolute chondritic abundances. It is similar in this respect to many primitive terrestrial tholeiites including the example chosen in Table II. Hubbard *et al.*, (1971) also showed that other low-K lunar anorthosites possessing positive Eu anomalies had likewise crystallized from parental liquids with generally similar REE abundances. Laul *et al.* (1974) demonstrated that lunar anorthosites possessing marked positive Eu

*The higher content of Cr₂O₃ in the PLC magma (0.13%) compared to the terrestrial tholeiite (0.05% Cr₂O₃) can be attributed to the effect of differing oxygen fugacity conditions upon the partition of chromium between magma and residual olivines and pyroxenes.

anomalies were derived from parental magmas containing 8 to 15 times the chondritic abundances. McCallum *et al.* (1975) found that the parent liquids in equilibrium with analogous lunar anorthosites contained 4 to 12 times the chondritic REE abundances.

The similarity in major element and REE abundances between the most abundant kind of primitive lunar basaltic magma and the most abundant class of primitive terrestrial basaltic magma, modified only by the partial loss of two of the most volatile components (Na_2O and SiO_2) is believed to be of considerable genetic significance.

The intent of the present study has been to increase our knowledge of the abundances of other elements in the PLC magma, especially the siderophile elements W, Ni, Co, P, Au, S, Se, As, Cu, Ga, Ag, Sb and Ge. The following section will discuss in detail the procedures used in determining the abundances of these additional elements.

3. Numerical Procedures

Elimination of Meteoritic Contamination

Since we recognise that lunar highlands samples contain meteoritic contamination in addition to any indigenous component, chemical information about this meteoritic component is required prior to any attempt at estimating the indigenous siderophile abundances in the PLC magma. Baedeker *et al.* (1973) and Gros *et al.* (1976) have concluded that, to a first approximation, the meteoritic component has a generally "chondritic" nature in the sense that it contains approximately primordial abundances of cosmochemically involatile elements but is systematically depleted to varying degrees for a wide range of volatile elements. The inference that the meteoritic component is depleted in volatile elements as compared to Type 1 carbonaceous (C1) chondrites is implied particularly by the Bi (Krähenbühl *et al.*, 1973; Morgan *et al.*, 1974; Higuchi and Morgan, 1975) and Te (Krähenbühl *et al.*, 1973; Ganapathy *et al.*, 1974) abundances in the Apollo 16 highlands. To obtain an *upper* limit on the volatile abundance pattern in the meteoritic component, we have assumed that *all* Ir, Bi and Te in the Apollo 16 highlands was contributed by meteorites. The result of this exercise is that the time-integrated, meteoritic component could not have contained more than $\sim 25\%$ of the C1 chondritic abundances of Bi and Te relative to Ir. These two elements are also depleted in ordinary chondrites, which contain $\sim 11\%$ of the C1 abundance of Te (Smith *et al.*, 1977) and $\leq 10\%$ of the C1 abundance of Bi (Lipschutz, 1971a). These constraints suggest that the time-integrated, meteoritic component might have generally resembled ordinary chondrites, which also happen to be the most abundant class of meteorites falling on the Earth today. Accordingly, we have made the fundamental assumption that the meteoritic component in the lunar highlands is equivalent to H-group ordinary chondrites. However, it must be emphasised that the general conclusions discussed in this study do not depend strongly on the assumption that the meteoritic component was precisely of H-group composition. We could equally well have selected a terrestrial

(i.e. whole Earth) abundance pattern, which is more strongly depleted in many volatile elements than H-group chondrites.

Since highlands rocks and soils contain variable quantities of meteoritic contamination, some direct indicator of that component is required. Ir was selected as that parameter because we had two reasons for concluding that the indigenous abundance of Ir was probably very low. Firstly, data from the Earth show that during partial melting Ir remains behind in the refractory residue so that its abundance in the basaltic liquid is very low. For example, in a summary of data by Ringwood and Kesson (1977), terrestrial oceanic tholeiites were found to contain an average of ~ 0.04 ppb Ir, whereas terrestrial ultramafics contained ~ 2.4 ppb Ir. This behaviour would suggest that the basaltic PLC magma was likely to have been low in Ir. The second reason for concluding that the Ir abundance was exceedingly low is its observed abundance in mare basalts, which are unequivocally of indigenous origin. Ganapathy *et al.* (1970), Morgan *et al.* (1972a, 1974) have reported Ir abundances in Apollo 11, 15 and 17 mare basalts of generally ≤ 0.02 ppb. Abundances in Apollo 12 mare basalts were somewhat greater at ~ 0.095 ppb (Anders *et al.*, 1971). Since an approximate upper limit of ~ 0.1 ppb on the indigenous Ir abundance is 10^{-4} of the value in H-group chondrites (730 ppb; Baedecker, 1971) it is clearly evident that Ir would serve satisfactorily as a direct indicator of meteoritic contamination. It should, however, be noted that to the extent that the indigenous Ir abundance in the PLC magma was non-zero, the assumption that all observed Ir is meteoritic provides an *upper* limit on the quantity of meteoritic contamination in a highlands sample. Accordingly, this upper limit on the mass fraction of H-group chondrite contamination in a sample was simply obtained by dividing the measured Ir abundance in the sample by the Ir abundance in a H-group chondrite. The meteoritic contribution for each element was then obtained simply through multiplying this mass fraction of contamination by the abundance of each particular element in an average H-group chondrite. To find the indigenous abundance of the particular element in the sample merely involved subtraction of the meteoritic contribution from the observed abundance in the sample. The indigenous abundances of Ni, Co, Au, Mn, As, Cu, Ga, Ag, Sb, Ge, Zn, S and Se in highland samples were thereby obtained using this simple procedure. The pertinent numbers used in the arithmetic determinations are provided in a later section of this report entitled "Data Base", where we discuss each element individually.

Adjustment for Plagioclase Dilution

The abundance of an element remaining after subtraction of the meteoritic contamination is the indigenous abundance of that element in a particular sample, whereas we require the abundance of the element in the PLC magma. The indigenous abundance in a sample must therefore be corrected for the dilution caused by the accumulation of plagioclase during formation of the highlands crust. As discussed previously in Section 2 of this report, the PLC magma was found to contain 18.4 weight % Al_2O_3 . Thus, any highland sample with an Al_2O_3 abundance greater than 18.4 wt.% must necessarily contain some cumulate plagioclase, in addition to intercumulus PLC magma. To compensate for this

effect of element-dilution by plagioclase accumulation, we have applied a simple correction based upon the Al_2O_3 content of the sample as compared to the Al_2O_3 content of the PLC magma. Samples containing more than 30 wt.% Al_2O_3 were not included in our array owing to the large ($> 3x$) corrections that are needed to compensate for the strong plagioclase enrichment. Large corrections would have introduced dispersions that were largely artifacts of the high Al_2O_3 in the sample.

Sample Heterogeneities

Lunar highlands rocks are generally polymict breccias having complex chemical histories. Therefore, when determining the abundance of an element in the PLC magma from analyses of breccias, we found it desirable, wherever possible, that both Ir and Al_2O_3 be reported on the same sample by the same investigators. However, since soil samples at Apollo 16 were homogeneous, the restraint applied to rocks would be relaxed for soils. This permitted the collection of element abundances for a specific soil from the published reports of many investigators.

Necessity for Averaging

In determining the abundance of each element in the PLC magma, a maximum number of soil and rock samples were used. This was considered imperative due to the fact that *individual samples cannot be regarded as having been closed chemical systems* during the energetic interactions of hypervelocity meteorites with the lunar materials. It has been demonstrated that Rb, K, Na (Gibson and Hubbard, 1972; Nyquist *et al.*, 1974; Wänke *et al.*, 1974), Cd, Zn (Chou *et al.*, 1973), Ge (Hertogen *et al.*, 1977; Gros *et al.*, 1976), Fe and Si (Naney *et al.*, 1976; Ivanov and Florensky, 1975) were mobile during impact events on the lunar surface. *Therefore, we selected as many Apollo 16 rock and soil samples as possible from the literature in order to maximise the size of our chemical system.* As expected from this process of impact mobilisation and fractionation, the calculated abundances of many elements in the PLC magma spanned a wide range. Therefore, the reported abundances in the PLC magma are averages from a large array of rocks and soils which we hope comprise a sufficiently large chemical system to have remained effectively closed throughout lunar history.

Apollo 16 Samples

Since we have been most concerned with obtaining siderophile – (and lithophile –) element abundances in the global PLC magma, it was desirable that we choose samples that would be most representative of the global highlands system. Inspection of landing site chemistries from Apollo and Luna missions clearly shows that the Apollo 16 highlands most closely resemble the average, near-surface composition of the highlands crust (Table III) derived by Taylor and Bence (1975). Furthermore, unlike the highlands at Apollo 14, 15 and 17, the Apollo 16 highlands are dominated by the anorthositic component, with other components such as KREEP, mare basalts, and granite, amounting to $\leq 20\%$ (Schonfeld, 1974). Therefore, Apollo 16 was the preferred choice due not only to its

TABLE III

Comparison between the global, average composition of the highlands surface and Apollo 16 soils (stations 1, 4, 5, 6, 8, 10).

	Average highlands ^a	Apollo 16 highlands ^b
SiO ₂	45.0	45.1
TiO ₂	0.56	0.59
Al ₂ O ₃	24.6	26.9
FeO	6.6	5.5
MgO	8.6	5.9
CaO	14.2	15.5
Na ₂ O	0.45	0.42
K ₂ O	0.075	0.11
Mg/(Mg + Fe)	0.70	0.66

^aTaylor and Bence (1975)

^bApollo 16 Prelim. Exam. Team (1973)

general similarity to the average, global composition of the highlands surface (Taylor and Bence, 1975) but also on its relative simplicity of components (Schonfeld, 1974).

The Apollo 14, 15 and 17 samples were used for determining the indigenous abundances of Ni and Co. However, as will be shown in Section 5, these results are plotted separately from the Apollo 16 data.

Comparisons with Terrestrial Oceanic Tholeiites

The elemental abundances derived for the global PLC magma will be compared with observed abundances in terrestrial oceanic tholeiites. Oceanic tholeiites have been preferred instead of other varieties of basalts, because they are the most widely occurring magma to be erupted on to the Earth's surface. It would seem therefore that they are being derived from a system of global dimension representing a significant portion of the Earth's upper mantle.

Ringwood (1977b) has demonstrated that the PLC magma displayed a close resemblance in major-element chemistry to terrestrial oceanic tholeiites. Furthermore, Hubbard *et al.* (1971) reported that, like terrestrial oceanic tholeiites, the PLC magma was uniformly enriched in the rare-earth elements by a factor of ~ 10 to 12 relative to primordial abundances. If these chemical similarities between oceanic tholeiites and the PLC magma can be expanded further to include many siderophile elements, then this information will have profound implications for theories of the Moon's origin.

DATA BASE

The simple numerical procedures that have been described in the previous section were used in determining the abundances of Ni, Co, Au, Mn, As, Cu, Ga, Ag, Sb, Ge, Zn, S and Se in the PLC magma. W, P, Li, Na and K abundances were obtained using well-established, inter-element correlations in highland samples. Procedural information pertaining individually to each of these elements will be discussed in this section.

TABLE IV
Element abundances in the PLC magma (this study), low-Ti mare basalts and terrestrial oceanic tholeiites (from summary by Ringwood and Kesson, 1977)

	PLC magma	Low-Ti mare basalts	Terrestrial oceanic tholeiites
(Siderophile elements)			
W	63 ppb	140 ppb	80 ppb
Ni	200 ppm	150 ppm	250 ppm
Co	30 ppm	45 ppm	41 ppm
P	220 ppm	380 ppm	300 ppm
Au	~ 0.7 ppb	0.03 ppb	~ 1 ppb
S	700 ppm	1150 ppm	900 ppm
Se	180 ppb	140 ppb	170 ppb
As	200 ppb	6 ppb	1000 ppb
Cu	10 ppm	12 ppm	70 ppm
Ga	4.6 ppm	4 ppm	20 ppm
Ag	4 ppb	1 ppb	30 ppb
Sb	2 ppb	0.06 ppb	29 ppb
Ge	400 ppb	7 ppb	1500 ppb
(Lithophile elements)			
Li	8 ppm	6 ppm	19 ppm
Mn	730 ppm	2090 ppm	1360 ppm
K	230 ppm	250 ppm	1500 ppm
Na	3100 ppm	1800 ppm	19440 ppm
Zn	11 ppm	1 ppm	100 ppm

The array of elements mentioned above has been divided into two sets (Table IV) according to whether they are siderophile or lithophile. In each set the elements have been arranged according to relative volatilities. The arithmetic procedures used in determining the abundances of these elements in the PLC magma will be discussed in the order in which the elements appear in Table IV.

SIDEROPHILE ELEMENTS

Tungsten

The abundance of W in the PLC magma has been estimated using the La vs. W systematics (Figure 1) observed in mare and highlands samples (Wänke *et al.*, 1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977). Figure 1 clearly demonstrates that the W/La ratio remains constant at a mean value of 0.019 through large (factor of 30) variations in La abundance. This behaviour of W in mare and highlands samples unequivocally demonstrates that W was present as an oxidised species in both the mare and highlands systems. Terrestrial samples BCR-1 and PCC1 (Wänke *et al.*, 1974) also have W/La ratios comparable to the lunar value. This similarity in W/La ratios between the Earth's upper mantle and the lunar interior implies that the W abundances in these two systems are comparably depleted relative to the primordial by a factor of 18 (Rammensee and Wänke, 1977).

Meteoritic contamination does *not* appreciably affect the abundances of either W or La in highlands samples. For example, 4% contamination of a sample, which is the mean level of contamination in Apollo 16 samples (Wasson *et al.*, 1975), by H-group chondrites (W ~ 0.16 ppm; Ehmman, 1971a:

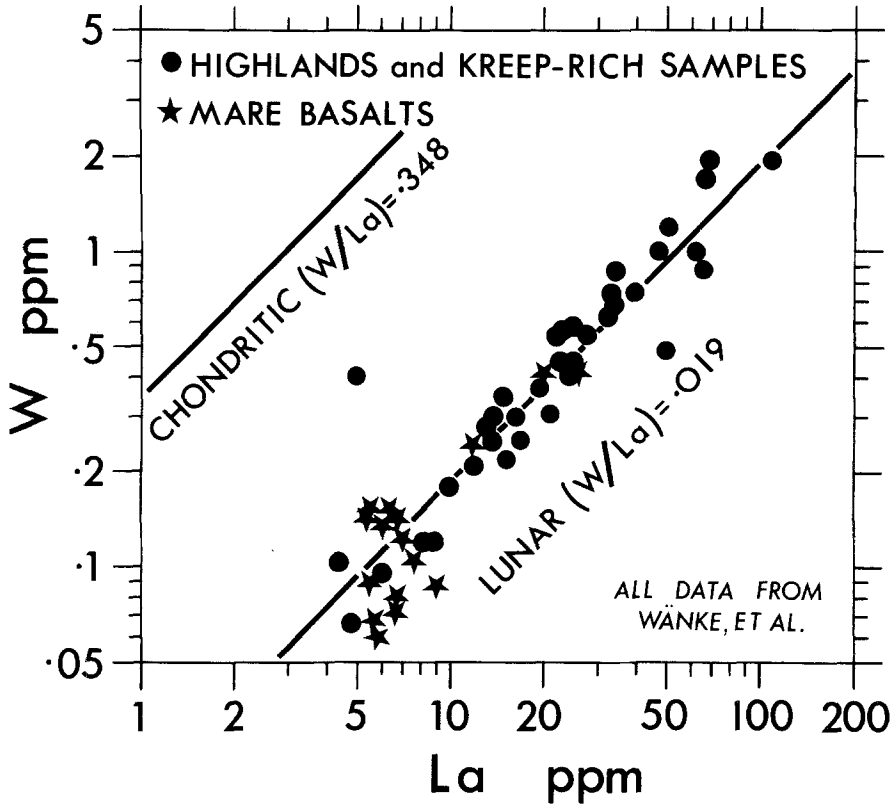


Fig. 1. W vs. La systematics in mare and highland samples. Data are from Wänke *et al.* (1970, 1971, 1972, 1973, 1974, 1975, 1976, 1977). Samples containing > 30 wt.% Al_2O_3 have not been included.

La ~ 0.329 ppm* (Nakamura, 1974) would contribute only ~ 0.006 ppm W and ~ 0.013 ppm La to a sample. Inspection of Figure 1 shows that all of the samples contain much higher ($> 10x$) abundances which must be indigenous to the Moon.

Since the PLC magma is known to have contained a La abundance that was $\sim 10x$ chondritic (Hubbard *et al.*, 1971), the W abundance can be determined for $W/La = 0.019$. A $10x$ chondritic La abundance (La abundance in ordinary chondrites ~ 0.329 ppm* (Nakamura, 1974) of 3.29 ppm yields a W value in the PLC magma of ~ 63 ppb (Table IV).

Terrestrial oceanic tholeiites have a reported range in W abundance from ~ 50 ppb to ~ 250 ppb (Helsen *et al.*, 1978). Since it is well-established that most oceanic tholeiites have experienced low-pressure, crystal/liquid fractionation causing incompatible elements such as P, rare-earth elements and W to increase in abundance with decreasing $Mg/(Mg + Fe)$, we have chosen the W abundance of 80 ppb which we consider may be appropriate for primitive oceanic tholeiites containing $10x$ chondritic abundances of rare-earth elements and a $Mg/(Mg + Fe) \sim 0.65$.

* Average of 10 ordinary chondrites: Brownfield, Bruderheim, Grady, Leedey, Modoc, Mount Browne, Peace River, Queen's Mercy, Takenouchi, Yonōzu.

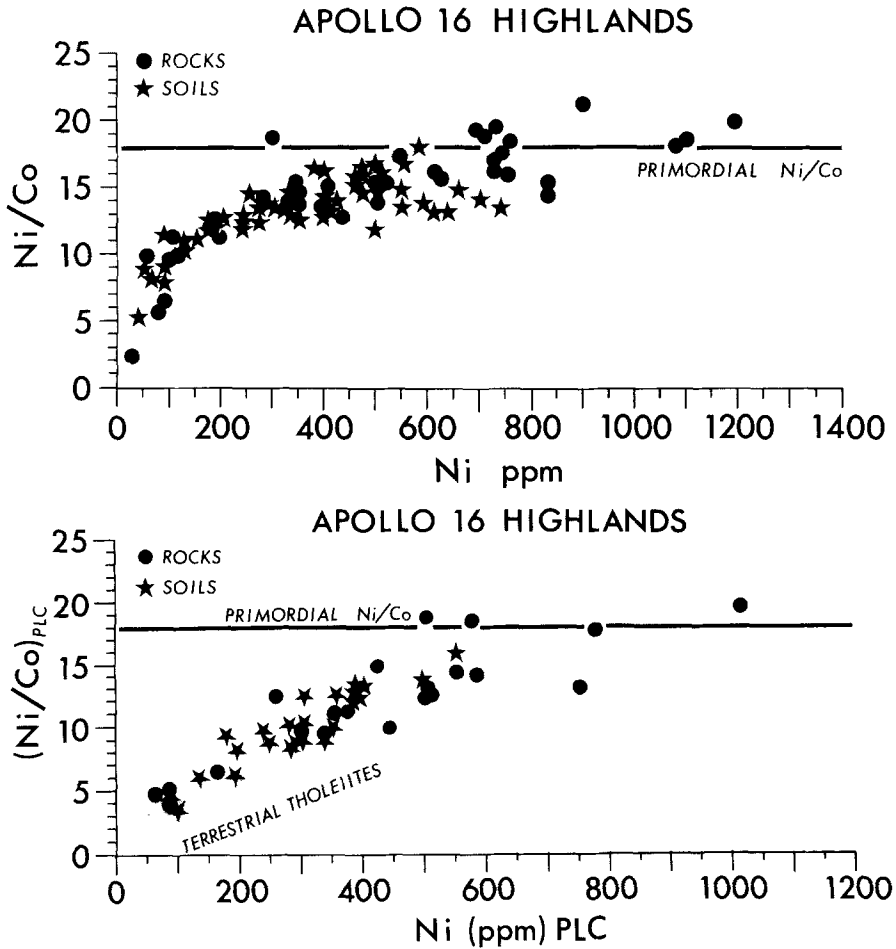


Fig. 2. (a) Ni/Co vs. Ni diagram shows evidence for mixing of two components in Apollo 16 samples. The meteoritic contamination has not been removed and the effect of plagioclase accumulation has not been compensated for. Data are from Boynton *et al.* (1975, 1976), Haskin *et al.* (1973), Laul and Schmitt (1973), Rhodes *et al.* (1975), Wänke *et al.* (1973, 1974, 1975, 1976), and Warner *et al.* (1976). (b) Ni/Co vs. Ni diagram for the PLC magma after removal of meteoritic contamination and compensation for dilution-effect by cumulus plagioclase from Apollo 16 samples. Fewer number of data points in (b) relative to (a) is due to the fact that not all the samples in (a) had been analysed for Ir and Al_2O_3 , which are required for subtraction of meteoritic contamination and compensation for cumulus plagioclase. Field for terrestrial oceanic tholeiites is from data by Engel *et al.* (1975), Frey *et al.* (1974), and Langmuir *et al.* (1977).

Nickel and Cobalt

49 analyses for Ni and Co in Apollo 16 rocks and soils were obtained from Boynton *et al.* (1975, 1976), Laul and Schmitt (1973), and Wänke *et al.* (1973, 1974, 1975, 1976). These authors also provided analyses of Ir and Al_2O_3 necessary for subtracting the meteoritic contamination ($\text{Ir}/\text{Ni} = 5.1 \times 10^{-5}$; $\text{Ir}/\text{Co} = 1.1 \times 10^{-3}$; Baedecker, 1971; Moore 1971a, b) and for compensating for cumulus plagioclase.

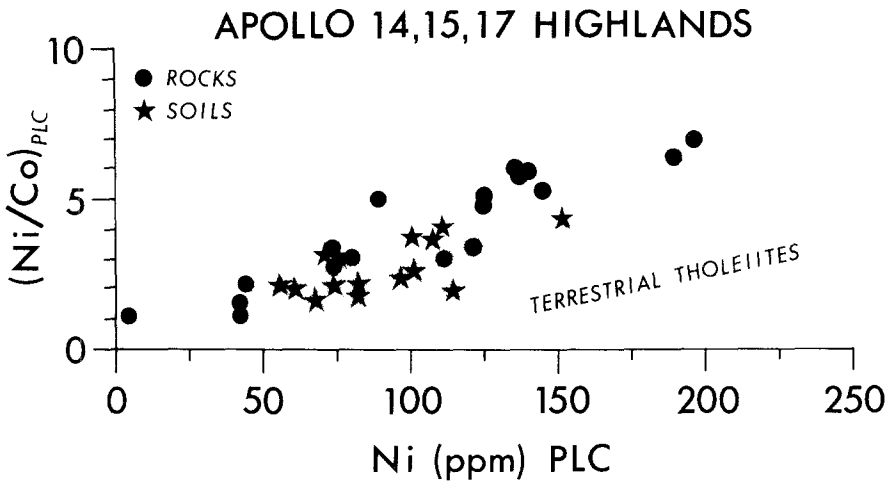
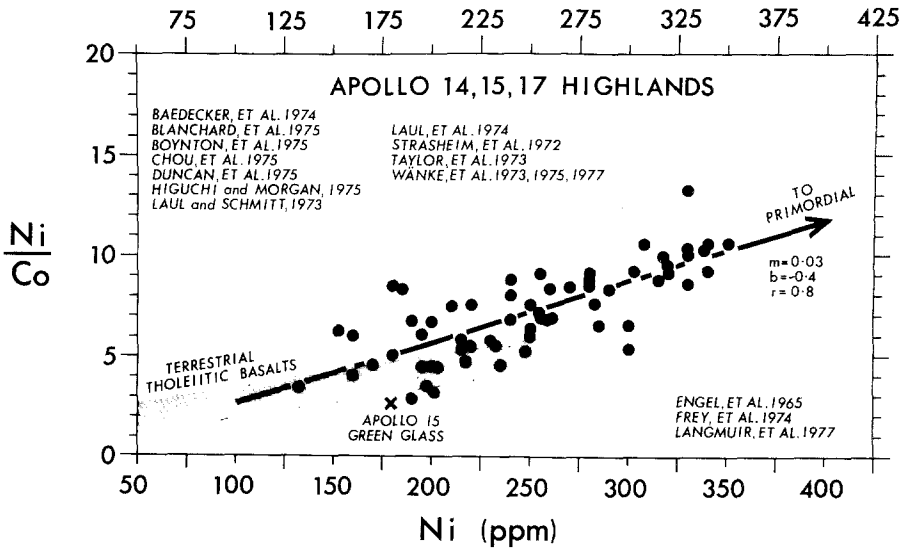


Fig. 3. (a) Ni/Co vs. Ni diagram shows evidence for mixing of two components in Apollo 14, 15 and 17 highlands samples. The meteoritic contamination has not been removed and the effect of plagioclase accumulation has not been compensated for. Data are from authors shown in upper portion of diagram. Apollo 15 green glass is from Taylor *et al.* (1973). Field for terrestrial oceanic tholeiites is from data by Engel *et al.* (1965), Frey *et al.* (1974), and Langmuir *et al.* (1977). (b) Ni/Co vs. Ni diagram for the PLC magma after removal of meteoritic contamination and compensation for dilution-effect by cumulus plagioclase in Apollo 14, 15 and 17 highland samples. Fewer number of data points in (b) relative to (a) is due to the fact that not all of the samples in (a) had been analysed for Ir and Al_2O_3 , which are required for subtraction of meteoritic contamination and compensation for cumulus plagioclase. Field for oceanic tholeiites is from data by Engle *et al.* (1965), Frey *et al.* (1974), and Langmuir *et al.* (1977).

These data provided mean abundances for Ni and Co in the PLC magma of ~ 200 ppm and ~ 30 ppm, respectively. Additional analyses from Haskin *et al.* (1973), Rhodes *et al.* (1975), and Warner *et al.* (1976) were used to construct Figure 2(a), in which neither meteoritic contamination nor cumulus plagioclase were required to be considered. Figure 2(a) demonstrates that substantial indigenous abundances of Ni and Co exist in the Apollo 16 samples because the Ni/Co ratio departs markedly from the primordial value at low Ni-values. At high levels of meteoritic contamination (i.e. high Ni-abundances) the Ni/Co ratio intersects the primordial value.

Following subtraction of the meteoritic contamination and compensation for plagioclase dilution, the individual samples from Boynton *et al.* (1975, 1976), Laul and Schmitt (1973), and Wänke *et al.* (1973, 1974, 1975, 1976) were plotted on a Ni/Co vs Ni diagram (Figure 2(b)). Comparison of the PLC trend was made with data for terrestrial ocean tholeiites obtained from Engel *et al.* (1965), Frey *et al.* (1974) and Langmuir *et al.* (1977).

62 analyses for Ni and Co in Apollo 14, 15, 17 and Luna 20 rocks and soils were obtained from Baedeker *et al.* (1974), Blanchard *et al.* (1975), Boynton *et al.* (1975), Chou *et al.* (1975), Duncan *et al.* (1975), Higuchi and Morgan (1975), Laul and Schmitt (1973), Laul *et al.* (1974), Strasheim *et al.* (1972), Taylor *et al.* (1973) and Wänke (1973, 1975, 1977). These raw data were used to construct Figure 3(a). Samples for which Ir and Al analyses had also been performed had their meteoritic contamination subtracted and the effect of cumulus plagioclase compensated. These data were used to construct Figure 3(b).

Mean Ni and Co abundances in primitive oceanic tholeiites (Table IV) of 200 ppm and 41 ppm were taken from a summary by Ringwood and Kesson (1977).

Phosphorous

The P abundance in the PLC magma was estimated by using the La vs. P systematics observed in lunar highlands samples ($\text{Al}_2\text{O}_3 < 30$ wt.%) from Apollo 14, 15, 16 and 17 (Hubbard *et al.*, 1974; Nakamura *et al.*, 1973; Rose *et al.*, 1972, 1974, 1975; Taylor *et al.*, 1972; Wänke *et al.*, 1973, 1974, 1975). Meteoritic contamination was not subtracted from the samples since it does *not* appreciably affect the La and P abundances in highlands samples. For example, 4% contamination of a sample, which is the mean level of contamination in Apollo 16 samples (Wasson *et al.*, 1975), by H-group chondrites (La ~ 0.329 ppm*; Nakamura, 1974: P ~ 0.097 wt.%; Moore, 1971c) would contribute only ~ 0.013 ppm La and ~ 0.004 wt.% P to a sample. Inspection of Figure 4 shows that all samples, except two, have La and P abundances more than a factor of 10 greater than can be accounted for by high levels (i.e. 4%) of meteoritic contamination. Therefore, the La vs. P systematics in highlands samples (Figure 4) are a product of indigenous La and P. The La/P remains between ~ 0.01 and ~ 0.03 through large (factor of 100) variations in La abundance.

The P abundance in the PLC magma of ~ 220 ppm was estimated for a La/P = 0.015 and a La abundance (Hubbard *et al.*, 1971) of 10x chondritic (i.e. La = 3.29 ppm).

The P abundance in primitive [i.e. $\text{Mg}/(\text{Fe} + \text{Mg}) \sim 0.65$] oceanic tholeiites of ~ 300 ppm was obtained using 135 analyses of abyssal volcanic glasses (Melson *et al.*, 1976). The main body of data terminated abruptly at a $[\text{Mg}/(\text{Mg} + \text{Fe})] \sim 0.65$, which corresponds to liquids being in equilibrium with olivine of composition Fo_{86} . That olivine chemistry closely resembles olivines in the upper mantle ($\sim \text{Fo}_{86}$) and thereby attests to the primitive composition of glasses having P ~ 300 ppm.

The field for alkali basalts (Figure 4) is from data of Sun and Hanson (1975).

The La vs. P systematics for low-Ti mare basalts (Rhodes and Hubbard, 1973) and terrestrial oceanic tholeiites (Langmuir *et al.*, 1977; Sun and Nesbitt, 1977) are somewhat more complicated than the other samples because they are depleted in La relative to the intermediate – and heavy-rare-earth elements. There is general agreement that the La depletion is the result of minor, post-accretionary partial melting events (e.g. Gast, 1968). Hence, the abundance of La in the bulk Earth and Moon is regarded as being in primordial proportions with the other rare-earth elements. To compensate for the geochemical depletion of La in low-Ti mare basalts and terrestrial oceanic tholeiites, we used the

* Average of 10 ordinary chondrites: Brownfield, Bruderheim, Grady, Leedey, Modoc, Mount Browne, Peace River, Queen's Mercy, Takenouchi, Yonōzu.

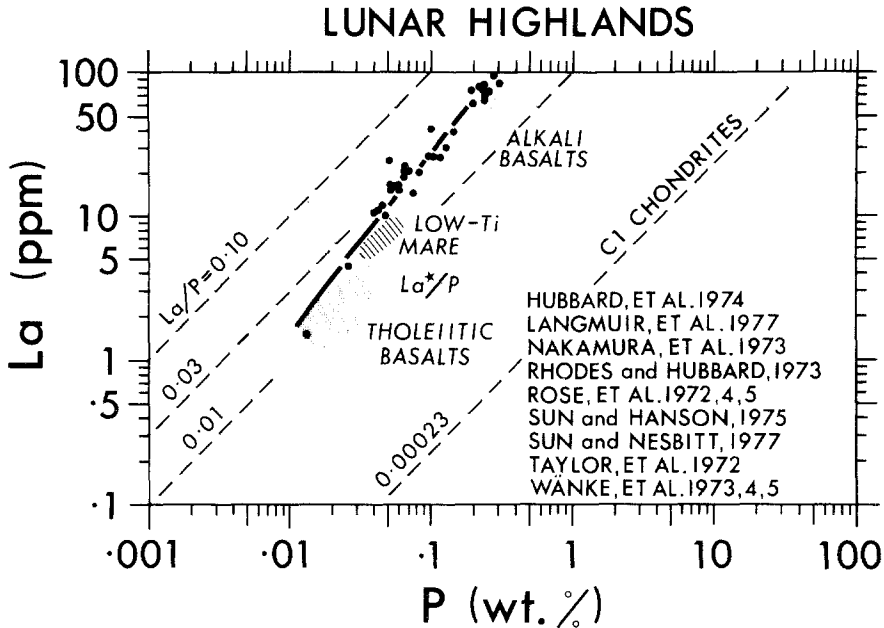


Fig. 4. P vs. La systematics in lunar highland samples containing less than 30 wt.% Al_2O_3 from Apollo 14, 15, 16 and 17. Field for terrestrial alkali basalts is from data by Sun and Hanson (1975). Field for low-Ti mare basalts is from Rhodes and Hubbard (1973). Field for terrestrial tholeiitic basalts is from Langmuir *et al.* (1977) and Sun and Nesbitt (1977). See text for explanation of La^* in Section 3.

abundance of Sm as a guide for determining the normal La abundance. For example, if an oceanic tholeiite with La depletion had a Sm abundance of 12x chondrites, then a 12x chondritic La abundance would be used. This modified La abundance is the La^* used in Figure 4 for light rare-earth element depleted, low-Ti mare basalts and terrestrial oceanic tholeiites.

Gold

Au abundances in 82 rocks and soils containing ≤ 10 ppb Ir from Apollo 16 were obtained from Boynton *et al.* (1976), Ganapathy *et al.* (1974), Krähenbühl *et al.* (1973) and Wänke *et al.* (1975). Meteoritic contamination was eliminated using $\text{Ir}/\text{Au} = 3.3$ (Baedecker, 1971; Ehmann, 1971b). Compensation for cumulus plagioclase was not necessary since results from the Skaergaard intrusion (Wager and Brown, 1968) indicate that Au does not markedly fractionate between silicate melt and plagioclase. This behaviour is probably due to Au being present in the neutral atomic state.

The mean indigenous Au abundance estimated from the Apollo 16 samples is ~ 0.7 ppb with considerable dispersion in the range from ~ 0.1 to 4 ppb. Although this estimated value is comparable to the mean Au abundance of ~ 1 to 2 ppb observed in terrestrial basalts (Crocket and Teruta, 1977; Ehmann *et al.*, 1970; Gottfried *et al.*, 1972; Wasson and Baedecker, 1970), we believe that the abundance of Au in the Apollo 16 highlands has been strongly affected by an additional mechanism (see discussion in Section 4). Hence, we do not at present have a good estimate for the indigenous Au abundance in the PLC magma.

Sulfur

24 analyses for S in rocks and soils from Apollo 16 were obtained from Apollo 16 P.E.T. (1973), Duncan *et al.* (1973), Hubbard *et al.* (1973), and Wänke *et al.* (1975). Since all analyses, except those from Wänke *et al.* (1975), did not include Ir, some Ir abundances were gathered from Krähenbühl

et al. (1973). Meteoritic contamination was removed using $\text{Ir/S} = 3.65 \times 10^{-5}$ (Baedecker, 1971; Moore, 1971d). Compensation for cumulus plagioclase was performed.

The mean abundance of S in the PLC magma was found to be ~ 700 ppm. The S abundance in terrestrial basalts is difficult to establish owing to the high volatility of S during basalt extrusion. A value of ~ 900 ppm (Ringwood and Kesson, 1977) was obtained from data on primitive oceanic tholeiites (Mathez, 1976).

Selenium

22 analyses for Se in Apollo 16 rocks were obtained from Ganapathy *et al.* (1974), Krähenbühl *et al.* (1973), and Wänke *et al.* (1975, 1976). Since all these investigators performed Ir analyses on their samples, meteoritic contamination was eliminated using $\text{Ir/Se} = 0.104$ (Baedecker, 1971; Pelly and Lipschutz, 1971). However, only those samples reported by Wänke *et al.* (1975, 1976) had been analysed for Al. Therefore, to compensate for the dilution caused by cumulus plagioclase, Al abundances for the other samples were extracted from additional sources (Apollo 16 P.E.T., 1973; Hubbard *et al.*, 1973, 1974). The mean abundance of Se in the PLC magma was found to be ~ 180 ppb.

The mean abundance of Se in terrestrial oceanic tholeiites is ~ 170 ppb (Ringwood and Kesson, 1977).

Arsenic

12 analyses for As in Apollo 16 rocks and soils were obtained from Wänke *et al.* (1973, 1974, 1975, 1976). Using Ir abundances reported by Wänke *et al.* for the same samples, meteoritic contamination was eliminated by $\text{Ir/As} = 0.348$ (Baedecker, 1971; Lipschutz, 1971b). Dilution by cumulus plagioclase was compensated for using the Al_2O_3 abundance in each sample from Wänke *et al.* (1973, 1974, 1975, 1976). The mean As abundance in the PLC magma was found to be ~ 200 ppb (see Section 4).

The abundance of As in terrestrial oceanic tholeiites is taken as ~ 1 ppm (Ringwood and Kesson, 1977).

Copper

13 analyses for Cu in Apollo 16 rocks were obtained from Wänke *et al.* (1973, 1974, 1975, 1976). Using Ir abundances reported by Wänke *et al.* for the same samples, meteoritic contamination was eliminated by $\text{Ir/Cu} = 8.1 \times 10^{-3}$ (Baedecker, 1971; Goles, 1971a). Dilution caused by cumulus plagioclase was compensated for by using the Al_2O_3 abundances obtained by Wänke *et al.* on the samples. The mean Cu abundance in the PLC magma was found to be 10 ppm.

Terrestrial oceanic tholeiites were found to display no clear correlation between Cu abundance and $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio. An average Cu abundance in oceanic tholeiites of 70 ppm was obtained for 17 samples having $\text{Cu} \leq 100$ ppm and $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios ranging from 0.71 to 0.46 (Dickey *et al.*, 1977; Frey *et al.*, 1974; Langmuir *et al.*, 1977).

Gallium

46 analyses for Ga in Apollo 16 rocks and soils were obtained from Boynton *et al.* (1976), Boynton and Wasson (1977), Wänke *et al.* (1973, 1974, 1976), and Wasson *et al.* (1975). Meteoritic contamination was removed using the Ir abundances determined on each sample by these authors and a Ir/Ga ratio of 1.41×10^{-1} (Baedecker, 1971; Baedecker and Wasson, 1971a) for the H-group chondrite component. No compensation for cumulus plagioclase was needed since Wänke *et al.* (1976) has shown that, with the possible exception of KREEP, plagioclase does not markedly fractionate Ga because of substitution of Ga^{3+} for Al^{3+} . The results indicate that the PLC magma contained 4.6 ppm Ga.

For comparison, the average Ga abundance in Hawaiian and oceanic tholeiites is 20 ppm, according to a summary by Ringwood and Kesson (1977).

Silver

27 analyses for Ag in Apollo 16 rocks were obtained from Ganapathy *et al.* (1974) and Krähenbühl

et al. (1973). Meteoritic contamination was removed using the Ir abundances reported by these authors and $\text{Ir}/\text{Ag} = 9.13$ (Baedecker, 1971; Buseck, 1971). Compensation for dilution by cumulus plagioclase was performed using Al_2O_3 values reported by Apollo 16 P.E.T. and Hubbard *et al.* (1973). The mean abundance of Ag in the PLC magma was found to be 4 ppb (see Section 4).

The abundance of Ag in terrestrial oceanic tholeiites is ~ 30 ppb, according to a summary of data by Ringwood and Kesson (1977).

Antimony

21 analyses for Sb in Apollo 16 rocks were obtained from Krähenbühl *et al.* (1973). Using the Ir abundances reported for these same samples by Krähenbühl *et al.* (1973), the meteoritic contamination was eliminated by $\text{Ir}/\text{Sb} = 8.11$ (Baedecker, 1971; Ehmann, 1971c). Compensation for dilution by cumulus plagioclase was performed using Al_2O_3 values reported by Apollo 16 P.E.T. and Hubbard *et al.* (1973). The mean abundance of Sb in the PLC magma was found to be ~ 2 ppb (see Section 4).

Terrestrial oceanic tholeiites have an abundance of Sb at ~ 29 ppb, according to a summary of data by Ringwood and Kesson (1977).

Germanium

50 analyses for Ge in Apollo 16 rocks and soils were obtained from Ganapathy *et al.* (1974), Krähenbühl *et al.* (1973), and Wänke *et al.* (1974, 1976). Meteoritic contamination was removed using the Ir abundances reported by these authors and the Ir/Ge ratio in H-group chondrites of 6.1×10^{-2} (Baedecker and Wasson, 1971b). Compensation for cumulus plagioclase was not applied since Ge does not markedly fractionate between plagioclase and co-existing mafic liquids due to ready substitution of Ge^{4+} for Si^{4+} (De Argollo and Schilling, 1978). The results indicate that the PLC magma contained ~ 400 ppb Ge.

The abundance of Ge in Hawaiian and oceanic tholeiites is 1.5 ppm, according to a summary of data by Ringwood and Kesson (1977).

LITHOPHILE ELEMENTS

Lithium

The Li abundance in the PLC magma has been estimated using the Li vs. Zr systematics in lunar and terrestrial samples. Dreibus *et al.* (1976) have reported that the Li/Zr ratio remains constant for variations in absolute abundance of a factor of 10. According to Dreibus *et al.* (1976), lunar samples have an average Li/Zr ratio of 0.04, while mafic, terrestrial samples have an average value of ~ 0.10 . This means that, for a given abundance of Zr, the Li abundance in lunar samples is $\sim 40\%$ of that in a terrestrial sample. Since the average Li abundance in unaltered, oceanic tholeiites is ~ 19 ppm (Frey *et al.*, 1974), the abundance of Li in the PLC magma is estimated to have been approximately 8 ppm.

Meteoritic contamination does *not* appreciably affect the abundances of either Li or Zr in highlands samples. For example, 4% contamination of a sample, which is the mean level of contamination in Apollo 16 samples (Wasson *et al.*, 1975), by H-group chondrites (Li ~ 1.7 ppm; Nichiporuk, 1971; Zr ~ 6.4 ppm; Ehmann and Rebagay, 1971) would contribute only 0.068 ppm Li and 0.26 ppm Zr. Inspection of the data from Dreibus *et al.* (1976) shows that all the samples on which the Li/Zr ratio is based, have Li and Zr abundances that are much greater ($> 100\times$) than the meteoritic contributions. Therefore, the Li and Zr abundances are overwhelmingly indigenous and entirely unaffected by reasonable levels of meteoritic contamination.

Manganese

38 analyses for Mn in Apollo 16 rocks and soils were obtained from Duncan *et al.* (1973), Laul and Schmitt (1973), Nakamura *et al.* (1973), Nava (1974), and Wänke *et al.* (1973, 1974, 1975). Since Ir abundances were not available for most of these samples, an average Ir value of 30 ppb (i.e. $\sim 4\%$ meteoritic contamination is average at Apollo 16; Wasson *et al.*, 1975) was assumed. Using an Ir/Mn

ratio of 2.9×10^{-4} (Baedecker, 1971; Goles, 1971b) for the meteoritic contamination, this exotic contribution amounted to ~ 100 ppm. This quantity was subtracted from the Mn abundance of each sample and the procedure for compensating for dilution by cumulus plagioclase was applied. The results indicated that the PLC magma contained 730 ppm Mn.

For comparison, terrestrial oceanic tholeiites have an average Mn abundance of ~ 1360 ppm, according to a summary by Ringwood and Kesson (1977).

Potassium

The abundance of K in the PLC magma was estimated using the K vs. La systematics observed in highland samples by Wänke *et al.* (1973). The K/La ratio was found to remain constant at a value of 70 through variations in absolute abundances of 3-orders of magnitude. Since the PLC magma is known to have had a La abundance of 10x chondrites (see Section 2; Hubbard *et al.* 1971), the K abundance in the PLC magma was estimated using $K/La = 70$ and $La = 3.29$ ppm (Nakamura, 1974; average La abundance in 10 ordinary chondrites* is 0.329 ppm). The results indicate that the K abundance in the PLC magma was 230 ppm.

Meteoritic contamination does *not* appreciably affect the abundances of either K or La in highlands samples. For example 4% contamination of a sample, which is the mean level of contamination in Apollo 16 samples (Wasson *et al.*, 1975), by H-group chondrites (K = 830 ppm; Goles, 1971c: La = 0.329 ppm; Nakamura, 1974) would contribute only 33 ppm K and 0.013 ppm La. Inspection of the data from Wänke *et al.* (1973) shows that all the samples on which the K/La ratio is based have K and La abundances that are much greater ($> 10x$) than the meteoritic contributions. Therefore, the K and La abundances are overwhelmingly indigenous and entirely unaffected by reasonable levels of meteoritic contamination.

For comparison, Wänke *et al.* (1973) have shown that terrestrial basaltic rocks have a K/La ratio of 450. Hence, an oceanic tholeiite with a La abundance of 10x chondrites (3.29 ppm) would contain ~ 1500 ppm K.

Sodium

The Na abundance in the PLC magma was estimated using the Na/K vs. K systematics observed in highlands rocks and soils (Figure 5). This relation has a continuous range from $Na/K = 1$ at $K = 10\,000$ ppm to $Na/K = 20$ at $K = 100$ ppm. For a K abundance of 230 ppm, as discussed in a previous section, the corresponding value for Na/K is ~ 13.5 . This provides an estimate for the Na abundance in the PLC magma of 3100 ppm, which is in close agreement with the value of 3300 ppm estimated by Taylor and Bence (1975).

Meteoritic contamination does not appreciably affect the Na/K vs. K systematics in the lunar highlands. For example, 4% contamination of a sample, which is the average level of contamination at the Apollo 16 landing site (Wasson *et al.*, 1975), by H-group chondrites (Na = 5700 ppm; K = 830 ppm; Goles, 1971c, d) would contribute 230 ppm Na and 33 ppm K. Since 99% of the samples used to define the Na/K vs. K systematics contain more than 7x these abundances of Na and K, it is clear that the systematics are being defined by the indigenous lunar abundances.

For comparison, the average abundance of Na in terrestrial oceanic tholeiites is 19440 ppm, according to a summary by Ringwood and Kesson (1977).

Zinc

46 analyses for Zn in Apollo 16 rocks were obtained from Ganapathy *et al.* (1974), Krähenbühl *et al.* (1973), and Wänke *et al.* (1975, 1976). The meteoritic contamination was removed using the Ir abundances reported for the same samples by these investigators and an Ir/Zn ratio of 1.4×10^{-2} (Baedecker, 1971; Moore, 1971e) for the H-group chondrite component. Since the samples reported

* Brownfield, Bruderheim, Grady, Leedey, Modoc, Mount Browne, Peace River, Queen's Mercy, Takenouchi, Yonōzu.

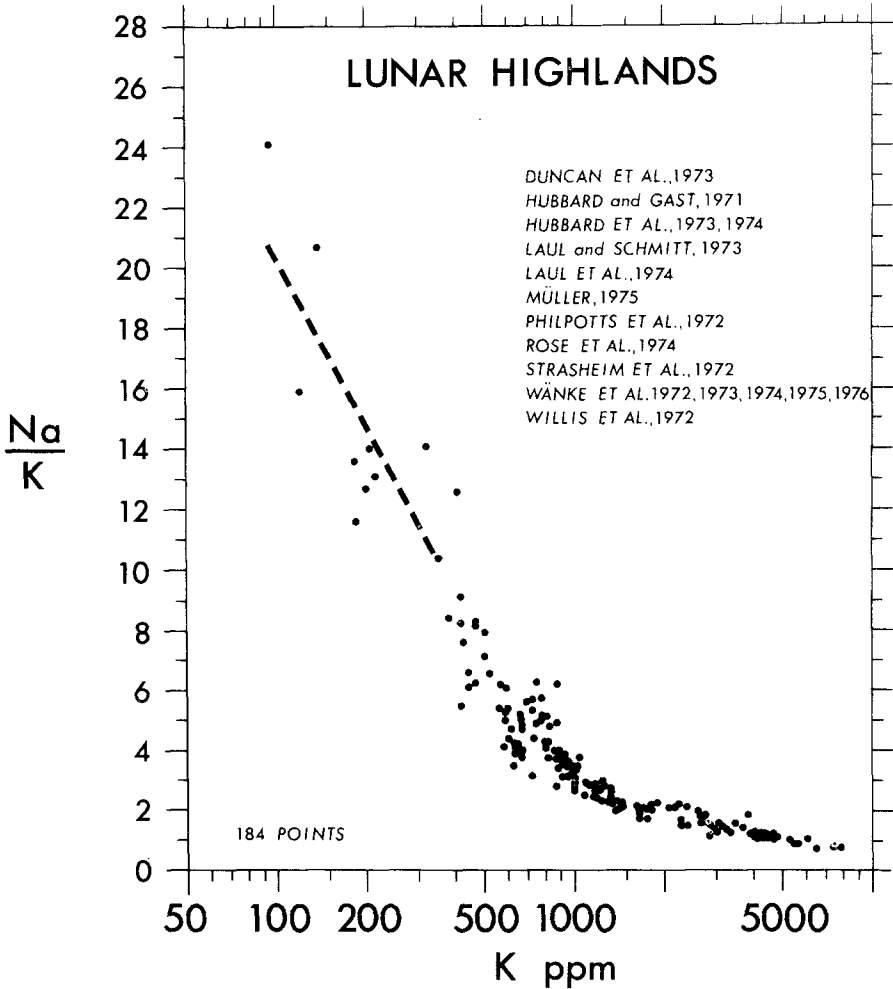


Fig. 5. Na/K vs. K systematics in highland samples from Apollo 14, 15, 16 and 17. Data are from authors shown in upper portion of diagram.

by Ganapathy *et al.* (1974) and Krähenbühl *et al.* (1973) had not been analysed for Al_2O_3 , an Al_2O_3 abundance of 27 wt.% was assumed for the sample array when compensating for the effect of dilution by cumulus plagioclase. This value of 27 wt.% is the average abundance of Al_2O_3 in the soils at the Apollo 16 landing site (Apollo 16 P.E.T., 1973). The result of this procedure provided a value of 11 ppm for the Zn abundance in the PLC magma (see Section 4).

For comparison, the abundance of Zn in terrestrial oceanic tholeiites is 100 ppm, according to a summary by Ringwood and Kesson (1977).

4. Indigenous Siderophile Element Abundances in the PLC Magma

As discussed in the previous section, the indigenous abundances of the siderophile elements (Table IV) have been obtained using a very simple model, which considered the Apollo 16

highlands to be comprised of cumulus plagioclase, intercumulus PLC magma, and variable quantities of ordinary chondrite-contamination. This section will examine various aspects of these calculated element abundances and will demonstrate that this simple approach has, in fact, yielded good estimates for the genuinely indigenous abundances of siderophile elements in the PLC magma.

Comparison with Mare Basalts: Similarities

Mare basalts were derived by partial melting of the lunar interior in the time-interval from ≥ 3.9 AE to ≤ 3.1 AE. Since this mode of origin involved no interaction with contaminating meteorites, the siderophile element abundances are generally regarded by lunar scientists as being wholly indigenous. It will, therefore, be of some interest to compare the indigenous abundances of the siderophile elements in low-Ti mare basalts with the abundances obtained in this study for the PLC magma. Low-Ti mare basalts were selected due to their less fractionated chemistries and less complicated mode of origin as compared to high-Ti mare basalts (Ringwood and Kesson, 1976).

Table IV and Figure 6 clearly demonstrate that abundances of the siderophile elements W, Ni, Co, P, S, Se, Cu and Ga are very similar in low-Ti mare basalts and the PLC magma. This observed similarity of siderophile abundances in the low-Ti mare basalts and the PLC magma has two exceedingly important implications: (1) *it strongly implies that our estimated abundances for the PLC magma are truly indigenous; and* (2) *it supports the general validity of our simple model.*

The similar abundances of the lithophile elements Li, Mn, K and Na (Table IV; Figure 6) between low-Ti mare basalts and the PLC magma provides additional support for these conclusions.

Comparisons with Mare Basalts: Disparities

Table IV and Figure 6 also show that Au, As, Ag, Sb, Ge and Zn are markedly deficient in the low-Ti mare basalts relative to the PLC magma. A possible reason for these significant disparities is suggested by some compositional characteristics of Apollo 15 green glass and the Apollo 17 orange glass. These two glasses, which are generally regarded as having been formed by volcanic fire-fountaining (Chou *et al.*, 1975; Meyer *et al.*, 1975; Reid *et al.*, 1973), have been found to be strongly enriched relative to mare basalts in these elements* (Allen *et al.*, 1974; Chou *et al.*, 1974, 1975; Duncan *et al.*, 1974; Jovanovic and Reed, 1974; Morgan *et al.*, 1974; Rhodes *et al.*, 1974; Wänke *et al.*, 1973). Because the enrichments have been found to be exclusively associated with the *surfaces* (Table V) of the green and orange glasses (e.g., Chou *et al.*, 1975; Meyer *et al.*, 1975; Silver, 1974; Tera and Wassenburg, 1976), these elements seem to have been part of a vapor-phase expelled during the volcanic eruptions at ~ 3.6 AE for the orange glass

* Information seems equivocal at present for As, although a comparison of Apollo 17 orange glass and Apollo 17 mare basalts (Chou *et al.*, 1975) suggest a probable enrichment in the former. However, the important point as to whether this As-enrichment is surface-correlated has yet to be established.

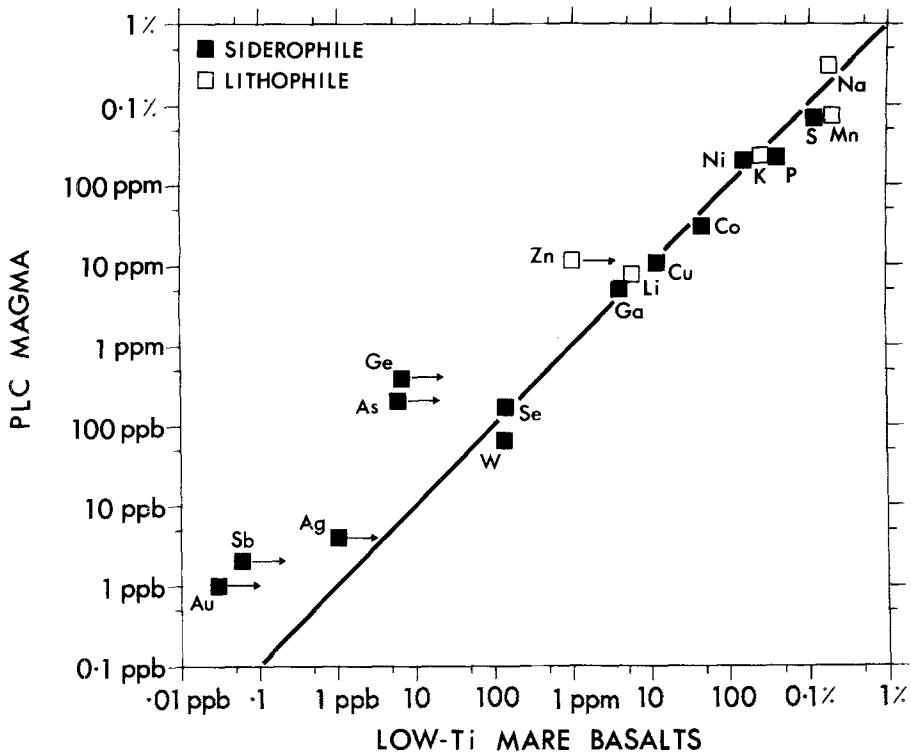


Fig. 6. Comparison of lithophile and siderophile element abundances in the PLC magma (this study) and low-Ti mare basalts (see summary by Ringwood and Kesson, 1977). The diagonal line is the line along which elements having identical abundances in the PLC magma and low-Ti mare basalts are located. Lithophile and siderophile elements are plotted as open and closed symbols, respectively. The arrows alongside Zn, Ge, As, Ag, Sb and Au signify that these are the elements that have been found to be enriched on the surfaces of the Apollo 15 green glass and Apollo 17 orange glass (see text for a discussion of this topic). Abundances in the PLC magma and low-Ti mare basalts are listed in Table IV.

TABLE V

Comparison between element abundances on the surface of and the interior of the Apollo 15 green glass and the Apollo 17 orange glass. Data from Chou *et al.* (1975). The indigenous abundances of these elements have been found to be considerably greater in the Apollo 16 highlands relative to low-Ti mare basalts (Figure 6).

	(surface/interior)
Zn	71
Ge	54
As	(no data)
Ag	> 30
Sb	> 100
Au	110

(Eberhardt *et al.*, 1973; Huneke *et al.*, 1973; Schaeffer and Husain, 1973; Tera and Wasserburg, 1976) and at ~ 3.3 AE for the green glass (Huneke *et al.*, 1974; Podosek and Huneke, 1973). Thermodynamic considerations suggest that these elements (Table V) were transported as volatile species in a fluorine and chlorine-rich vapor (Chou *et al.*, 1975; Meyer *et al.*, 1975). Therefore, the characteristic that Zn, Ge, Ag, Sb and Au (and As?) have in common, which distinguishes them from the other elements in Figure 6 is their high volatility under specialised conditions. Due to the likelihood that these elements have been enriched in the Apollo 16 highlands by volatile-transport, we are presently unable to estimate the indigenous abundances of Zn, Ge, As, Sb, Ag and Au in the PLC magma.

Ni/Co systematics

When plotted on a Ni/Co vs. Ni diagram, the Ni and Co abundances in Apollo 16 rocks and soils provide strong evidence for a mixing model involving two sources for these elements (Figure 2(a)). One component is characterised by high Ni (≥ 800 ppm) and a primordial Ni/Co ratio, whereas the second component has low Ni (≥ 100 ppm) and Ni/Co < 10 . We suggest that the first component is meteoritic in origin, but that the second clearly is not. The Ni/Co ratio in iron meteorites, pallasites, and chondrites is very close to the primordial value. This low dispersion is due to the fact that Ni and Co possess very similar volatilities, which has apparently prevented appreciable fractionation during condensation. The point is amply demonstrated in Table VI where the average Ni/Co ratios in all varieties of chondritic meteorities are listed (Moore, 1971a, b). Figures 7 and 8 serve to further illustrate the limited Ni/Co variations even within the pallasitic and iron meteorites that have experienced major chemical fractionations between the refractory and moderately volatile elements by crystal/liquid (e.g. Scott, 1972) and condensation/accretion processes. For example, even after fractionations between Ir and Ni by factors of up to 10^4 , the Ni/Co ratio deviates from the primordial value by less than 50% (Figure 8).

TABLE VI
Average value of the Ni/Co ratio in all varieties of chondritic meteorities (Moore, 1971a, b)

	(Ni/Co)
Carbonaceous Chondrites	
Type 1	21
Type 2	22
Type 3	22
Ordinary Chondrites	
H-group	20
L-group	21
LL-group	19
Enstatite Chondrites	19

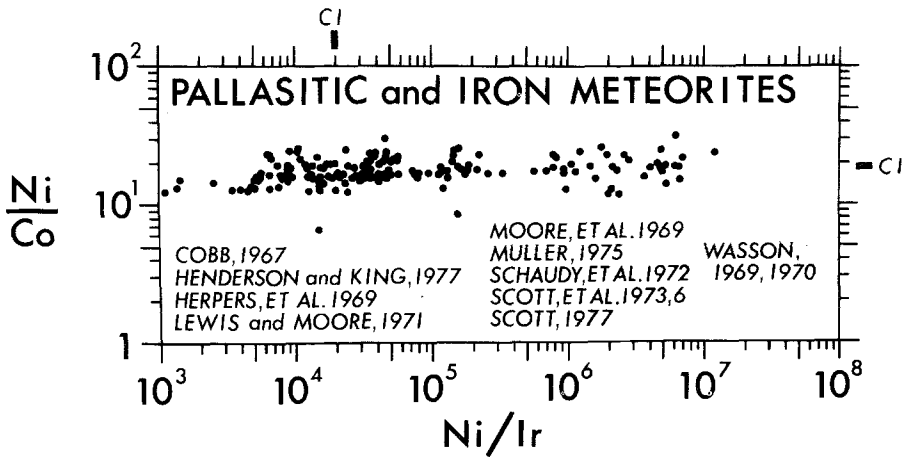


Fig. 7. Ni/Co vs. Ni/Ir data in 177 pallasitic and iron meteorites. Diagram shows the small ($\sim 50\%$) variation in Ni/Co ratio during fractionation of Ni and Ir by a factor of 10,000. Primordial value for each ratio is indicated by CI. Data are from authors shown in lower portion of diagram.

We conclude that the component at low Ni and low Ni/Co (Figure 2(b)) is not meteoritic and must therefore be indigenous. This conclusion is strongly supported by the indigenous Ni/Co systematics in primitive, low-Ti mare basalts, which are characterised by Ni ~ 150 ppm and Ni/Co ~ 3 . This furnishes, therefore, clear evidence that *substantial proportions of Ni* (as suggested by Wänke *et al.*, 1975, 1976, 1977) *and Co in the lunar highlands are truly indigenous.*

5. Oxidation State of the Lunar Interior, Indigenous Siderophiles and the Question of a Lunar Core

An important consideration for theories dealing not only with the petrogenesis of the mare and highland systems but also with the origin of the Moon, has been the oxidation state of the lunar interior. This has a key bearing on the existence of a lunar core and the question of whether the indigenous, siderophile element abundance patterns have been caused by the differentiation of a metallic phase within the Moon. This section will discuss these questions using evidence provided by the indigenous abundances of the siderophile elements W, P, Ni and Co in the PLC magma and primitive, low-Ti mare basalts.

Tungsten

Indigenous W is observed to co-vary with La in mare and highland samples (Figure 1; e.g., Wänke *et al.*, 1974). The constancy of the W/La ratio over a large (factor of 30) range in absolute abundance of La and W clearly demonstrates that no appreciable fractionation has occurred between these two elements at any time during diverse petrologic origins of

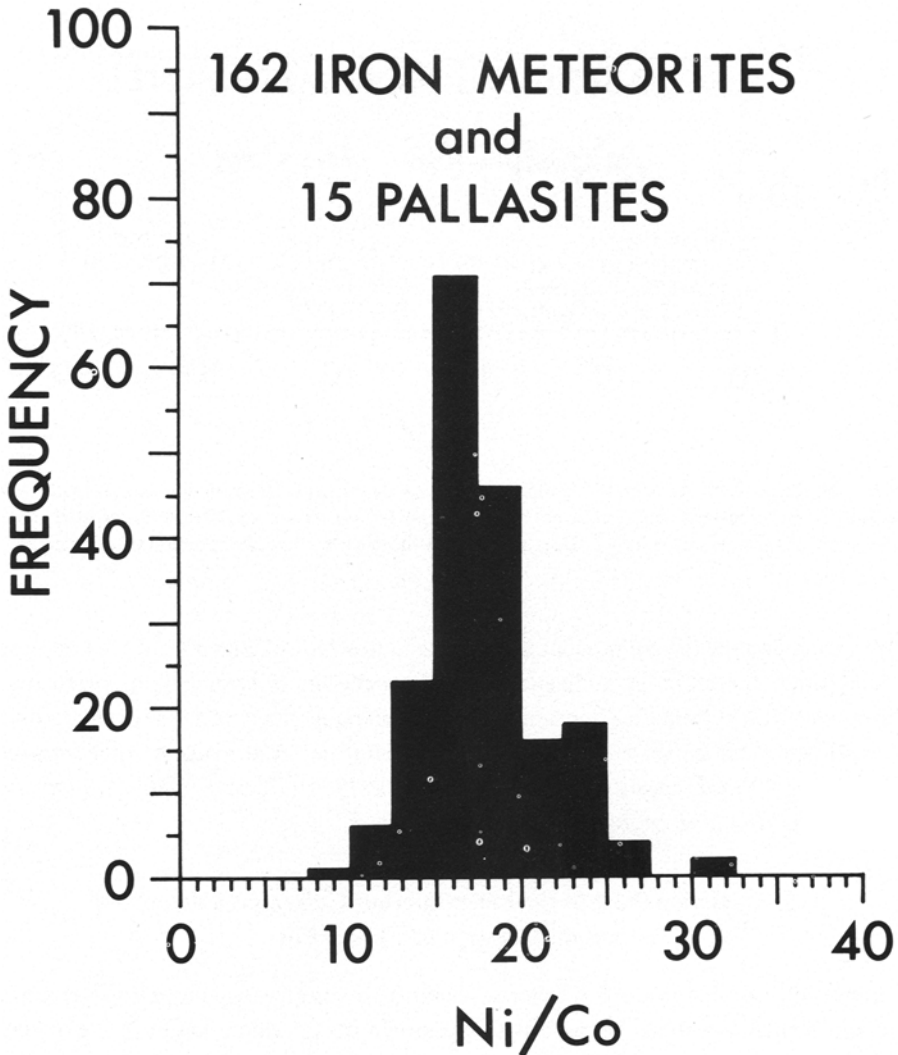


Fig. 8. Histogram of Ni/Co values in 177 pallasitic and iron meteorites. Mean value is 17.7 ± 3.6 (1σ). See Figure 7 for sources of data.

these systems (e.g. Wänke *et al.*, 1974). Since, therefore, W and La have had effectively similar distribution coefficients during the chemical evolution of the Moon, the indigenous W must be present in lunar samples as an oxidised species.

The constancy in the W/La ratio also precludes any possibility of equilibration with substantial quantities of an Fe-rich, metallic phase at any time during the petrogenesis of the mare and highland systems because even minute quantities (e.g. 0.5 wt.%) of metallic Fe would have buffered the W abundance causing the W/La ratio to strongly vary as a function of La abundance. The 19-fold depletion of W relative to La (e.g.

Wänke *et al.*, 1974) in lunar samples (relative to chondrites) cannot be explained by Fe-rich metal/silicate fractionation within the Moon, and would seem therefore to be a distinctive feature of matter that accreted to form the Moon. Rammensee and Wänke (1977) have previously reached an identical conclusion based on a parallel but separate argument.

Phosphorus

Figure 4 illustrates the systematic variation of P and La in mare and highland samples. The La/P ratio varies between 0.01 and 0.03 through a large (factor of 100) range in absolute abundance of La. It is readily apparent that no large fractionation between La and P has occurred even between mare and highland systems. Although P seems to have had a slightly larger (crystal/liquid) partition coefficient than La during the petrologic evolution of the mare and highlands, as evidenced by the increase in La/P with increasing La, the data indicate definitively that P was varying in the lunar samples as an oxidised species.

The near constancy of the La/P ratio would seem to preclude the possibility of equilibration with substantial quantities of an Fe-rich, metallic phase at any time during the petrogenesis of the mare and highland systems since equilibrium with ≥ 1 wt.% metallic iron (metal/silicate partition coeff. for $P \geq 20$; Ringwood *et al.*, 1978) would have buffered the P abundance, thereby causing the La/P ratio to strongly vary as a function of La abundance. The approximate 90-fold depletion of P relative to La (Figure 4) in mare and highland rocks cannot therefore be explained by equilibration with an Fe-rich, metallic phase in the Moon, and would appear to be a characteristic of the matter that accreted to form the Moon.

Ni and Co

In Section 4, we demonstrated that the sub-primordial Ni/Co ratio observed in many highland samples from Apollo 16 (Figure 2(a)) was strong evidence for substantial, indigenous abundances of Ni and Co. This has also been found to be applicable to the Apollo 14, 15 and 17 highlands (Figure 3(a)). When the meteoritic contamination is removed and the dilution effect by cumulus plagioclase is compensated (Figures 2(b) and 3(b)), additional information becomes available. Figures 2(b) and 3(b) illustrate that highlands samples possess not only substantial indigenous abundances of Ni and Co but also a prominent fractionation trend. This trend, which is similar to the one produced in terrestrial oceanic tholeiites by olivine fractionation, suggests that the indigenous Ni and Co were present as oxidised species during the petrogenesis of the lunar highlands at 4.4 AE*.

* The fact that most Ni and Co in lunar highlands samples today occurs in metallic form is due to reduction during impact metamorphism/melting subsequent to the 4.4 AE differentiation event. The high W/Ni ratio (i.e. about a factor of 80 greater than primordial) in metal grains in the highlands is strong evidence for this reduction process (Wlotzka *et al.*, 1973).

Detailed studies of olivine-metal relationships in low-Ti mare basalts by Reid *et al.* (1970) and Hewins and Goldstein (1974) have shown that; (a) liquidus olivines contain up to 500 ppm Ni and 250 ppm Co; and (b) the earliest liquidus olivines to crystallize do *not* co-precipitate with a metallic phase; and (c) the earliest metal to crystallize contains 30 to 50 wt.% Ni. These observations indicate that metallic iron was not a residual phase in the source regions of primitive low-Ti mare basalts and that Ni and Co were present as oxidised species in these magmas. This conclusion is further supported by the Ni vs. Mg/(Mg + Fe) correlation in low-Ti mare basalts (Ringwood and Kesson, 1977) and the Ni vs. Mg correlation in highland samples (Wänke *et al.*, 1976). This coherence of Mg and Ni, which is apparently the result of olivine fractionation, implies that Ni was present as an oxidised species during magmatic differentiation. The uniform distribution of Ni within the Apollo 15 green glass (Ringwood *et al.*, 1978) also implies that the nickel was present as NiO, instead of as a discrete metal phase.

Although present evidence implies that neither the PLC magma nor primitive, low-Ti mare basalts were saturated with an Fe-rich, metallic phase, the mean, indigenous Ni abundance of 200 ppm (Table IV) provides a constraint on the maximum quantity of Fe-rich metal that could have depleted Ni and other siderophiles by metal/silicate equilibration inside the Moon. Before this constraint can be determined, however, an estimate (probably an upper limit) of the Ni abundance in the Moon can be made by assuming that the Ni/(total Fe) ratio has the primordial value of 0.053 and total Fe is 9.0 ± 4.7 wt.% (Parkin *et al.*, 1974). This yields an estimate of 4800 ± 2500 ppm Ni in the Moon. The final quantity needed is the metal/silicate partition coefficient for Ni which is estimated to be 2000 from Buseck and Golstein (1969). The resulting constraint is that the PLC magma and primitive, low-Ti mare basalts with indigenous Ni abundances of about 200 ppm could have hypothetically equilibrated with only 1.3 ± 0.7 wt.% of an Fe-rich, metallic phase. While this small quantity of metal is sufficient to have caused the observed Ni depletions in the PLC magma and primitive, low-Ti mare basalts, it is wholly inadequate for explaining the depletion of other siderophile elements such as W, which according to Rammensee and Wänke (1977) has a depletion in lunar rocks equivalent to the effect produced by equilibration with 26% wt.% of metallic iron. Therefore, hypotheses invoking a simple process of metal/silicate fractionation *inside the Moon* (e.g., Ganapathy *et al.*, 1970) to account for the indigenous siderophile abundances in mare and highland systems are confronted with a staggering dilemma.

FeS Hypotheses

Based dominantly upon physical considerations such as moments of inertia, electrical conductivity, thermal evolution, and remanent magnetisation, the eutectic in the Fe-S system has been proposed as the composition of hypothetical pods at a depth of 250 km (Murthy *et al.*, 1971) and of a hypothetical core (Brett, 1973). Although Murthy *et al.* (1971) suggest that the depletions in siderophile elements may be at least partially attributable to FeS segregation, we point out that the depletions of W and P are entirely immune to this process, since these two elements are not chalcophile (e.g., Imamura and

Honda, 1976). We suggest, therefore, that the hypotheses of FeS segregation are not viable as comprehensive explanations of the siderophile depletions in the PLC magma and primitive, low-Ti mare basalts. The inability of FeS to account for these depletions would again suggest that the siderophile abundances were intrinsic to the matter that formed the Moon.

Furthermore, the fact that the PLC magma and primitive, low-Ti mare basalts were not saturated with FeS (Kesson and Ringwood, 1976) suggests that segregations of FeS or a core of FeS are either non-existent or never equilibrated with the mare and highland systems.

Summary

We regard the following points as strong evidence that the siderophile element depletions in the mare and highland systems were intrinsic to the matter that accreted to form the Moon, instead of being the result of differentiation processes within the Moon.

(1) Since primitive, low-Ti mare basalts are not saturated with Fe-rich metal, a residual, Fe-rich metallic phase in the source regions cannot have been present to cause the siderophile depletions in the melt.

(2) The near-constancy of the W/La and P/La ratios in mare and highland systems restricts the quantity of residual metal (hypothetical) that could have equilibrated with each of these systems at less than 1 wt.%. This, therefore, allows no chance of accounting for the W depletion, which requires 26 wt.% metal (Rammensee and Wänke, 1977), by simple equilibration between metal and silicate inside the Moon.

(3) The Ni-depletion in the PLC magma and primitive, low-Ti mare basalts could have hypothetically been produced by simple metal/silicate equilibrium involving less than 2 wt.% of metal. Since this is an *upper limit*, the W depletion, which requires 26 wt.% metal (Rammensee and Wänke, 1977), cannot be explained by processes internal to the Moon.

(4) FeS segregation is not a viable hypothesis for comprehensively explaining the siderophile element depletions since W and P, which have depletion factors of 19 and 90 respectively, would have been unaffected.

Finally, the absence of saturation with respect to Fe-rich metal and FeS in the PLC magma and primitive, low-Ti mare basalts suggests that a metallic or sulfide core is either nonexistent or never equilibrated with the mare and highland systems.

6. Comparison with Terrestrial Oceanic Tholeiites

The major element composition of the PLC magma is known to have been similar to that of primitive oceanic tholeiites, except for depletion of the two most volatile elements Na and Si (see Section 2). Furthermore, the abundances of the rare-earth elements were also similar in both cases. In this section, we shall expand the comparison through the use of elements listed in Table IV.

TABLE VII

Comparison of relatively involatile siderophile-element abundances of the PLC magmas and primitive, low-Ti mare basalts vs. terrestrial oceanic tholeiites and Type 1 carbonaceous (C1) chondrites

1		2	3
<u>PLC magma</u>		<u>Low-Ti mare basalt</u>	<u>PLC magma</u>
oceanic tholeiites		oceanic tholeiites	C1 chondrites
<i>Relatively Involatile</i>			
W	0.8	1.8	0.7
Ni	1.0	0.8	0.02
Co	0.7	1.1	0.06
P	0.7	1.3	0.2
S ^a	0.8	1.3	0.01
Se ^a	1.1	0.8	0.01

^aS and Se have been included among the relatively involatile elements because their condensation temperatures are sensitive to the ambient hydrogen fugacity. They are relatively involatile under conditions of low hydrogen fugacity which may have prevailed during the formation of the Moon (Ringwood and Kesson, 1977).

Relatively Involatile, Siderophile Elements

The PLC magma and terrestrial oceanic tholeiites contain similar abundances of the relatively involatile, siderophile elements, W, Ni, Co, P, S* and Se* (Table VII; column 1). This similarity probably also applies to the abundances of these elements in their respective source regions. In contrast, comparison of these elements in the PLC magma and in Type 1 carbonaceous (C1) chondrites (Table VII; column 3) clearly demonstrates that there are no obvious, systematic relationships between these two systems.

In view of our conclusion in Section 5 that the fractionated lunar siderophile abundances were an intrinsic feature of the matter that accreted to form the Moon, we consider it very significant that the PLC magma and terrestrial oceanic tholeiites possess similar, non-primordial abundances of these relatively involatile, siderophile elements.

Relatively Volatile, Siderophile Elements

We wish also to compare the abundances of some relatively volatile, siderophile elements in the PLC magma with those in terrestrial oceanic tholeiites. This is, however, complicated by the well-established observation that lunar rocks are depleted in volatile elements relative to corresponding terrestrial rocks, so that it is crucial to be able to discriminate the effects of differential volatility from possible fractionations due to siderophile behaviour. Accordingly, for our comparison we have included estimates for the abundances of several *lithophile* elements of varying volatility.

We have found that Na, K, Cu, and Ga, which have comparable volatilities, are all depleted by a factor of ~ 7 in the PLC magma and low-Ti mare basalts relative to terres-

* S and Se have been listed among the relatively involatile elements because their condensation temperatures are sensitive to the ambient hydrogen fugacity. They are relatively involatile under conditions of low hydrogen fugacity which may have prevailed during the formation of the Moon (Ringwood and Kesson, 1977).

trial oceanic tholeiites. That is, the depletion of the siderophile elements Cu and Ga in the PLC magma relative to terrestrial oceanic tholeiites corresponds to expectations based solely upon their respective volatilities and is independent of their siderophile character. Therefore, based upon the abundances of Cu, Ga, Li, Mn, Na, and K, the PLC magma can be essentially regarded as having been a volatile-depleted, terrestrial oceanic tholeiite.

In view of our conclusion in Section 5 that the fractionated lunar siderophile abundances were an intrinsic feature of the matter that accreted to form the Moon, we consider it very significant that the relatively volatile, siderophile – (and lithophile) element abundances display such a simple relationship to observed abundances in terrestrial oceanic tholeiites.

Significance of PLC and Terrestrial Similarities

Although the Earth's upper mantle is known to be depleted in siderophile elements due to the effects of core segregation, several of the siderophile elements (e.g. Au, Re, Ni, Co, Cu) are significantly more abundant in the upper mantle (factors varying from 10 to 1000) than would be expected if these elements had been partitioned under equilibrium conditions into an Fe-rich, metallic phase. Ringwood (1977b) has proposed that these siderophile abundances in the Earth's upper mantle are the product of at least two major processes.

(1) Large changes in metal/silicate partition coefficients caused by the high pressures deep within the Earth.

(2) The presence of large quantities of an element with a low atomic weight, such as oxygen (Ringwood, 1977b), within the segregating core, which caused large changes in metal/silicate partition coefficients.

The important point is that each of these processes is intrinsically terrestrial, and not the result of generalised cosmochemical fractionations within the solar nebula. Thus, *the relative abundances of siderophile elements in the Earth's upper mantle constitute a unique signature of terrestrial origin.*

In Section 5, we concluded that the indigenous, siderophile element abundances in the Moon could not simply be the result of equilibration between metal and silicate. In this Section, we have found that the siderophile abundances in the PLC magma are systematically related to the "siderophile signature" in terrestrial oceanic tholeiites, which is the result of processes unique to the Earth. *We, therefore, regard this similarity between the PLC magma and oceanic tholeiites as evidence that the Moon was derived from the Earth's mantle subsequent to core formation.*

Heterogeneous Accretion

An alternative suggestion for dealing with the siderophile-element abundances in the Earth's upper mantle has been heterogeneous accretion. Turekian and Clark (1969), Clark *et al.* (1972) and Kimura *et al.* (1974) have suggested that a primordial component was added to the upper mantle at a late stage of accretion. During condensation of the solar nebula, nickel would have been present in the condensate as a metal until tem-

TABLE VIII

Elements, which would have been fully condensed prior to oxidation of Ni in the solar nebula, are shown to occur in non-primordial proportions in the Earth's upper mantle

	Earth's upper mantle ^a	Primordial ^b
Ni/Ir	85×10^4	2.0×10^4
Ni/Au	42×10^4	6.5×10^4
P/Pd	8.5×10^3	2.2×10^3
Cu/Au	85×10^2	7.2×10^2
F/Ge	62	2.2
Ni/S	7.2	0.2
Ni/Se	240×10^2	5.0×10^2
Co/Ge	89	14
Ge/Ag	0.2×10^2	1.9×10^2
Ga/Au	15×10^2	0.6×10^2
Cu/Cd	9.7×10^2	1.7×10^2

^aElement abundances in pyrolite are from Ringwood and Kesson (1977).

^bType 1 carbonaceous chondrites.

peratures fell below about 400 K, when NiO would have become stable. If the NiO now present in the upper mantle had been introduced in the form of a low-temperature, metal-free condensate, then this condensate should also have introduced primordial ratios of all the elements which became fully condensed above approximately 400°K. Inspection of Table VIII demonstrates, however, that the ratios generally diverge from the primordial values.

We conclude that present evidence does not support hypotheses suggesting that the fractionated siderophile abundances in the Earth's upper mantle are the result of either heterogeneous accretion or cosmochemical processes. Instead, the element abundances appear to be the result of complex processes intrinsic to the Earth. Therefore, the fact that the Moon contains a siderophile signature that systematically resembles the Earth's upper mantle is strong evidence for the Moon having been derived from the Earth.

7. Comparison with Eucrites

In Section 6, we demonstrated a close similarity in the abundances of siderophile elements between the Moon and the Earth's upper mantle. We concluded in Sections 4 and 5 that the lunar siderophile abundances were not established by metal/silicate fractionation within the Moon, but were apparently produced within another body that had segregated a large, Fe-rich core amounting to about 26 wt.% of the planet (e.g., Rammensee and Wänke, 1977). We have suggested that the Earth was the parent body. However, Kaula (1974) proposed that the Moon was derived from differentiated planetesimals similar to the bodies on which some of the achondritic, stony-iron, and iron meteorites were formed. In this model, metal/silicate differentiation occurred within the bodies, causing extraction of the siderophile elements from the silicate-rich portions. Subsequently, in a complex scenario, the silicate-rich portions of these parent bodies became physically separated from the metallic cores and the former accreted in geocentric orbit to form the Moon.

TABLE IX

Comparison of some siderophile-element abundances in the PLC magma (this study), low-Ti mare basalts (from summary by Ringwood and Kesson, 1977), and eucrites

	PLC magma	Low-Ti mare basalt	Eucrites
Ni (ppm)	200	150	3.5 ^a
Co (ppm)	30	45	8 ^{a,b,c,d}
Cu (ppm)	10	12	4.7 ^b
Ga (ppm)	4.6	4	1.4 ^{b,c}
Ir (ppb)	unknown	0.07	0.004 ^{a*}
Os (ppb)	unknown	0.5	0.02 ^a

^aMorgan *et al.* (1978)

^bLaul *et al.* (1972)

^cWänke *et al.* (1977)

^dSchmitt *et al.* (1972)

* Large dispersion exists for Ir abundance in the eucrites. This value was chosen since it was from the vesicular, unbrecciated eucrite, Ibitira (Steele and Smith, 1976).

There are some intriguing chemical similarities between low-Ti mare basalts and eucrites, as well as some important differences. Eucrites possess generally similar abundances of the major elements and some siderophile elements (i.e. W, P, S, Se, Ge^{*}) relative to low-Ti mare basalts and were evidently formed by partial melting of a small parent body (or bodies), which was strongly depleted in volatile elements (e.g. Duke and Silver, 1967; Laul *et al.*, 1972; Stolper, 1977). While these similarities provide some support to Kaula's model of relating low-Ti mare basalts and eucrites, the profound chemical differences discussed next show that any implied genetic links between these two systems are more apparent than real.

The crucial difference between the eucrites and the low-Ti mare basalts is that the eucritic melts were saturated with respect to an Fe-rich, metallic phase (Stolper, 1977), whereas the low-Ti mare basalts (and PLC magma) were not (Hewins and Goldstein, 1974). This important distinction between these two systems is amply demonstrated through comparison of their Ni, Co, Cu, Ga, Ir and Os abundances (Table IX). These strong depletions in eucrites relative to low-Ti mare basalts is clear evidence that these basaltic melts were derived from fundamentally different systems. The eucrites equilibrated with 13 to 20 wt.% (Morgan *et al.*, 1978; Dreibus *et al.*, 1977; Rammensee and Wänke, 1977)

* Low-Ti mare basalts and eucrites contain similar abundances of Ge (i.e. about 6 ppb). We regard this similarity, however, as being coincidental because it must have resulted from *different* mechanisms within the two systems. The depletion of Ge due to its volatility is similar (a factor of 2: see discussion of this aspect in a later portion of this Section) in the Moon and the eucritic parent body. However, the superimposed depletion of Ge due to its siderophile behaviour is very different, as shown by a comparison of the Ge/Ni ratio in the low-Ti mare basalts (4.5×10^{-5}) and eucrites (1.7×10^{-3}). Since metal/silicate fractionation during planetary differentiation should *not* produce large fractionations between Ge and Ni (Wai *et al.*, 1968), the fact that massive differences in Ge/Ni ratios exist between the low-Ti mare basalts and eucrites is clear evidence that the chemical processes operating in these two systems were wholly dissimilar.

of an Fe-rich, metallic phase (Stolper, 1977) during differentiation of their parent body. The Fe-rich, metallic phase in equilibrium with the eucritic melts may have contained about 6 to 8 wt.% Ni (Stolper, 1977). This Ni abundance in the metal and combined with its low abundance of 3.5 ppm (Table IX) in the eucritic liquid indicates that the bulk of the parent body's Ni was present in the metallic phase. Therefore, if the eucritic parent body possessed a primordial Ni/Fe ratio of 0.053, then the Ni/Fe ratio of ≤ 0.08 for the metal in equilibrium with the eucritic liquid requires that $\geq 60\%$ of the parent body's abundance of total Fe was present as a metallic phase. If the parent body possessed an abundance of total Fe comparable to that in H-group ordinary chondrites (i.e. about 27 wt.%; Morgan *et al.*, 1978), then at least 23 wt.% of the parent body was composed of an Fe-rich, metallic phase ($\text{Fe}_{93}\text{Ni}_7$) that had segregated during the differentiation. In contrast, this process did not occur within the Moon.

A second important difference between the eucrite and low-Ti mare basalts involves their strong depletions in the volatile elements. Well-established ratios such as K/La (70 in the low-Ti mare basalts; 126 in eucrites: Dreibus *et al.*, 1977), K/U (about 2500 in the low-Ti mare basalts; about 5000 in eucrites: Eldridge *et al.*, 1975), Zn^*/U (5 in the low-Ti mare basalts; 14 in eucrites: Ringwood and Kesson, 1977; Morgan *et al.*, 1978), and F^*/U (200 in the low-Ti mare basalts; 500 in eucrites: Ringwood and Kesson, 1977; Reed, 1964; Reed and Jovanović, 1969; Allen and Clark, 1977) demonstrate that the Moon was more strongly depleted (by about a factor of 2) in volatiles than the eucritic parent body.

The third major difference between the eucrites and the Moon is their oxygen-isotopic composition. Although both materials lie on the terrestrial, mass-fractionation line, thereby indicating that the Earth, Moon, and eucrites came from a single, well-mixed reservoir, it is important to appreciate that the Moon and eucrites do not have the same oxygen-isotopic composition (Clayton and Mayeda, 1975). Whereas the Moon has a $\delta^{18}\text{O}^{**} = +5.5 \pm 0.2\text{‰}$ (Grossman *et al.*, 1974; Clayton and Mayeda, 1975), the eucrites have values typically in the range from +3.0 to +3.5‰ (Clayton *et al.*, 1976).[‡] Since this difference is too large to have resulted from igneous processes in either the Moon or the eucritic parent body, Clayton and Mayeda (1975) concluded that the eucrites observed today cannot be directly related to the Moon.

The differences, therefore, between the eucrites and low-Ti mare basalts in siderophile-element abundances (i.e. Ni, Co, Cu, Ga, Ir, Os), depletion of volatile elements (i.e. K/La, K/U, Zn/U, F/U), oxidation state (i.e. \pm metal saturation), and oxygen-isotopic composition indicate that the Moon's distinctive chemistry is not a consequence of an earlier evolution within an earlier generation of planetesimals similar to the eucritic parent body.

* F and Zn have volatilities similar to Ge.

** $\delta^{18}\text{O}(\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{SAMPLE}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right] \times 1000$

where SMOW is Standard Mean Ocean Water.

‡ The Earth has a value between +4.5 and +6.0 (Taylor, 1968; Anderson *et al.*, 1971; Onuma *et al.*, 1972), which is indistinguishable from the lunar value.

8. Summary

The indigenous, siderophile-element abundances in the PLC magma have been obtained using a very simple model, which considered the Apollo 16 highlands to be a mixture of cumulus plagioclase, intercumulus PLC magma and variable quantities of contamination by H-group, ordinary chondrites. Ordinary chondrites were selected as the meteoritic component because: (1) they are an abundant group of meteorite observed to fall on Earth today; (2) Bi and Te abundances in the Apollo 16 highlands are consistent with the time-integrated, meteoritic component being volatile-depleted, similar to ordinary chondrites; and (3) the results of Gros *et al.* (1976) suggest that the meteoritic component was of a generally "chondritic" nature. Our conclusions, however, do not strongly depend upon the actual contamination being precisely equivalent to H-group, ordinary chondrites.

Based upon the estimated abundances of siderophile elements in the PLC magma, the following conclusions have been made.

(1) The similarity of siderophile-element abundances (W, Ni, Co, P, S, Se, Cu, Ga) between the PLC magma and primitive, low-Ti mare basalts has two important implications: (a) it strongly suggests that our estimated abundances in the PLC magma are truly indigenous; and (b) it supports the basic validity of our simple, 3-component model for the Apollo 16 highlands.

(2) The Ni/Co vs. Ni systematics in highland samples provide strong evidence that substantial proportions of these two elements are indigenous.

(3) Based upon the indigenous Ni abundance and the low dispersion observed in the W/La and P/La ratios, the highland and mare systems cannot have equilibrated (hypothetically) with more than about 1 wt.% of an Fe-rich, metallic phase. However, the depletion of W in mare and highland systems is equivalent to the effect produced by metal/silicate equilibration involving about 26 wt.% of metallic iron. This dilemma suggests that the lunar "siderophile signature" cannot be the result of simple, low-pressure equilibration between metal and silicates within the Moon, but must instead be intrinsic to the matter which accreted to form the Moon.

(4) Since the PLC magma and primitive, low-Ti mare basalts were not saturated with respect to either an Fe-rich, metallic phase or FeS, the Moon either (a) does not possess a core or (b) the core did not equilibrate with the mare and highland systems.

(5) The disparities in abundance of Au, Ag, Sb, Ge, Zn, and possibly As between the PLC magma and low-Ti mare basalts is a consequence of the enrichment of these elements at the Apollo 16 landing site by processes arising from their volatility (e.g. fumarolic activity as suggested by Krähenbühl *et al.*, 1973; impact mobilization as suggested by H. Wänke in personal communication). Due to this complication, the indigenous abundances of these six elements in the PLC magma are presently uncertain.

(6) The PLC magma and terrestrial oceanic tholeiites contained similar abundances of the relatively involatile, siderophile elements (W, Ni, Co, P, S, Se).

(7) The PLC magma was systematically depleted (relative to oceanic tholeiites) in the relatively volatile, siderophile elements. The depletion of these elements was strictly related to their relative volatility, instead of their siderophile behaviour.

(8) The Earth's upper mantle possesses a unique "siderophile signature" that is a product of equilibration between mantle phases and an oxygen-bearing, Fe-rich core at very high pressures (Ringwood, 1977a). For the Moon to exhibit a comparable "siderophile signature" when it is incapable of having experienced similar processes, implies that the Moon was derived from the Earth's upper mantle after segregation of the core. Possible mechanisms by which material was removed from the Earth's upper mantle and reassembled in geocentric orbit have been discussed by Ringwood (1978).

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