

BASALTIC MAGMATISM AND THE BULK COMPOSITION OF THE MOON

II. *Siderophile and Volatile Elements in Moon, Earth and Chondrites: Implications for Lunar Origin*

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Abstract. Abundance patterns of siderophile and volatile elements imply that the Moon was derived from the Earth's mantle after the core had segregated. The relative abundances of siderophile and volatile elements in the Moon and in the Earth's mantle are obtained from a comparison of their abundances in terrestrial ocean-floor basalts and lunar low-Ti mare basalts. The abundances of a group of siderophile elements Ni, Co, W, Ir, Os, P, S and Se are found to be very similar in ocean-floor tholeiites and low-Ti mare basalts and this similarity is believed to extend to their respective source regions in the Earth's mantle and lunar interior. The abundances of the above siderophile elements in the Earth's mantle have been determined by the interaction of several complex processes *unique to the Earth*, which relate to core formation and non-equilibrium distribution of elements between metallic and silicate phases. Since these factors could not possibly have operated separately within the Moon, the similarity in siderophile element abundances therefore implies that *the Moon was derived from the Earth's mantle after the Earth's core was formed*.

Abundance patterns of volatile elements in the Moon differ dramatically from those in ordinary chondrites and from those to be expected from condensation of a nebula of solar composition. These differences imply that the Moon was not formed from components which themselves had condensed directly from the solar nebula. For these reasons, current versions of the capture and binary planet hypotheses of lunar origin, which maintain that the Moon formed independently by accretion in the solar nebula, can be rejected. The drastic depletion of many volatile elements in the Moon compared to the Earth implies that the separation of material from the Earth's mantle to form the Moon occurred at very high temperatures. Depletions of this magnitude are best explained by the hypothesis that material from the Earth's mantle was totally evaporated, and then selectively recondensed, whilst the more volatile components were lost. The Moon then formed in Earth orbit by accretion from this volatile-depleted, mantle-derived condensate.

1. Introduction

The compositions of basaltic magmas formed ultimately by partial melting in the Earth's mantle or in the lunar interior, are capable of providing invaluable information about the chemical and mineralogical characteristics of their respective source regions. In the accompanying paper (Part I), the observed compositions of lunar basalts were employed to deduce the bulk major element composition of the Moon. This composition was shown to be quite close to that of the Earth's mantle. Moreover, the abundances of certain involatile, lithophile trace elements (U, Th, REE) were also found to be similar in the Moon and the Earth's mantle.

In the present communication, we extend our approach to selected groups of volatile and siderophile minor and trace elements, with the objective of comparing the abundances of these elements in the Moon with those in the Earth's mantle and with the primordial

abundances as obtained from Type 1 (Cl) carbonaceous chondrites. The abundance patterns of volatile elements can provide key evidence concerning the relative accretion temperatures of Earth and Moon and also the chemical environment during accretion. Siderophile element abundance patterns, on the other hand, provide information on the conditions of core-formation in the Earth and may clarify the problem of comparative iron-depletion in the Moon.

In order to establish the chemical characteristics of the sources for lunar and terrestrial basalts, it is necessary to select classes of basalts which carry the most direct chemical 'memory' of their respective primordial source regions. This characteristic is best met by primitive basalts – i.e., magmas which have experienced relatively little crystal fractionation since leaving their source regions and therefore have relatively high MgO, Cr and Ni contents. Moreover, the accomplishment of our objective is simplified by considering only basaltic magma types which have been derived by relatively large degrees of partial melting ($\geq 15\%$). In the case of the Earth, these criteria are best met by ocean-floor tholeiites. However, we recognise that the source region of these basalts has been affected by pre-eruptive fractionation processes which have caused marked depletions of elements such as La, Ce, Ba, Rb, which possess relatively large ionic radii and/or charges (Gast, 1968), and appropriate corrections must be applied to allow for these effects. For the Moon, we have selected low-Ti basalts since these are believed to have been produced by similar degrees of partial melting to ocean-floor tholeiites (Ringwood, 1976). Furthermore, their source regions are believed to be essentially primordial, having experienced only relatively minor preeruptive chemical disturbances (Ringwood and Kesson, 1976). In contrast, high-Ti mare basalts are believed to have been derived from source regions which had been subjected to complex assimilation processes prior to partial melting (Ringwood and Kesson, 1976). High-Ti basalts would therefore be unsatisfactory for the purpose of deducing the nature of the primordial lunar interior.

Several other authors have previously employed the compositions of lunar and terrestrial basalts in an attempt to compare the compositions of their respective source regions (e.g., Wasson, 1971; Ganapathy and Anders, 1974; Anders, 1976). Some of the conclusions reached, particularly by Ganapathy and Anders, differ from ours in several vital respects. These differences derive partly from these authors' practice of combining compositional data both for low-Ti and high-Ti basalts, and of ignoring the effects of crystal fractionation. Moreover, the specific partition behaviour of various trace elements between the basaltic magmas and their source regions was treated inadequately.

2. Treatment of Analytical Data

Given an appropriate compositional data base for terrestrial and lunar basalts which are believed to have formed by similar (and substantial) degrees of partial melting, the comparative abundances of many elements in their source regions can be obtained simply from the ratios of their mean abundances in the respective basalts. Many *incompatible elements* are compared in this manner because their ionic radii and/or charges inhibit

their retention by residual olivine and pyroxene. Accordingly, they are strongly partitioned into basaltic magmas during partial melting. Incompatible elements which we have treated in this way include P, F, Na, Cl, S, Cu, Se, As, Sb, In, W, Bi. Another class of elements which can be compared simply by taking the ratio of lunar/terrestrial basaltic abundances are those *compatible elements* which possess ionic radii and charges which permit them to substitute readily for major elements in the principal mantle minerals. Most of these compatible elements are approximately equally partitioned between basaltic magma and residual olivines and pyroxenes during partial melting. The abundances of these elements in basalts therefore provide a good guide to their abundances in the source region. Compatible elements possessing crystal/liquid partition coefficients sufficiently close to unity include Mn, Co, Zn, Ga, Ge, Ag, and Au.* Thus, for the above-mentioned incompatible and compatible elements, we have simply compared averages of their mean abundances in terrestrial ocean-floor tholeiites to those in low-Ti mare basalts. We believe that ratios of these means provide adequate estimates of the corresponding abundance ratios of these elements in the terrestrial and lunar interiors.

There are some elements (e.g., Cr and Ni) which are preferentially concentrated in the residual olivine and pyroxenes during partial melting. Estimates of the relative abundances of these elements in the lunar and terrestrial interiors require a knowledge of their likely partition behaviour, which is complicated in the case of Cr by changes of valence state as a result of lower oxygen fugacities in the lunar interior. The treatment of these particular elements is considered later in this section.

An important group of incompatible elements including K, Rb, Cs, Tl, U and Pb cannot be treated in this manner. The source region of terrestrial ocean-floor tholeiites is believed to have been fractionated prior to magma generation, and as a result, marked depletions (mostly twofold to fivefold) of the lightest rare earths (especially La) are observed (Gast, 1968). Barium may display even larger depletions (Kay *et al.*, 1970). The elements affected by this fractionation are all highly incompatible, possessing either exceptionally large ionic radii, e.g., La^{3+} , Ce^{3+} , Ba^{2+} , Pb^{2+} , K^{+} , Rb^{+} , Cs^{+} , Tl^{+} or a combination of fairly large radii (U^{4+} , Th^{4+}) combined with high ionic charges. Because of these prior depletions, corresponding errors of $\times 2$ to $\times 10$ could be introduced into Earth/Moon ratios if we were simply to compare abundances in ocean-floor tholeiites with those in lunar low-Ti basalts.

The elements in this category in which we are most interested are relatively volatile and our objective is to examine the effect of differential volatility upon their relative abundances in Earth and Moon. Accordingly, we have normalized the abundances of these elements to that of a relatively *involatile* element possessing generally similar incompatible crystal chemical properties and known to be geochemically coherent with the group of volatile elements. We have chosen uranium for this exercise since (a) in Part I of this series, it was shown that the mean abundance of uranium in the Moon was similar to that in the Earth's mantle and (b) uranium is known to demonstrate a strong

* Au behaves as a compatible element, apparently because it occurs in crystals and magmas in the uncharged atomic state (Vincent and Crockett, 1960).

geochemical coherence with several volatile incompatible elements such as potassium (e.g., Wasserburg *et al.*, 1964). Moreover, because of the much wider availability of appropriate data and also because of the substantial prior fractionations of these elements in the source regions of ocean-floor tholeiites, the terrestrial K/U, Rb/U, Cs/U and Tl/U ratios have been obtained not from ocean-floor tholeiites but from other sources, such as estimated mean crustal abundances, as discussed later in this section. This procedure seems reasonable since it is believed that a large proportion of the Earth's total uranium (and presumably K, Rb, Cs, Tl) now resides in the crust (Gast, 1960, 1972; Taylor, 1964). The lunar/terrestrial ratios for K, Rb, Cs and Tl have thereby been obtained by dividing the given ratio (e.g., K/U) for the Moon (from low-Ti mare basalts) by the corresponding ratio for the Earth as obtained by the above methods. An analogous procedure was used in the case of lead, but here the Pb/U values for Moon and Earth were more readily (and precisely) estimated from isotopic measurements giving the respective μ ($^{238}\text{U}/^{204}\text{Pb}$) values for large scale reservoirs.

In the present paper, we also wish to compare the abundances of many volatile and siderophile elements in the Earth's mantle with their primordial abundances as obtained from Cl carbonaceous chondrites. For this, it is not sufficient to compare abundances in ocean-floor basalts directly with those in Cl chondrites. The latter basalts are partial melts of the Earth's mantle and it is this latter composition which is required. The bulk composition of the Earth's mantle is believed to be that of pyrolite, following the extensive discussion given by Ringwood (1975). The composition of pyrolite is estimated in the preceding reference (p. 188) to be represented approximately by a mixture of 1 part of ocean-floor tholeiite to 5 parts of residual refractory peridotite (harzburgite). Cl carbonaceous chondrites contain over 30% of water and complex organic compounds, whilst all of the iron and nickel are oxidized. For the present purposes we are interested in comparing the mantle pyrolite composition with the composition of the lithophile component of Cl chondrites: namely, that which would result if the volatiles were removed and sufficient oxidized iron and nickel reduced to metal so that the residual composition of the silicate component possessed a 100 MgO/(MgO + FeO) similar to that of pyrolite (88–89), e.g., Ringwood (1966a). Although it has become traditional to normalise to 10^6 silicon atoms, this procedure was not followed in the present case because we suspect that a significant proportion of silicon may have been lost from the Earth by volatilization prior to, or during accretion (Section 3). Accordingly, we have normalized all elemental abundances to be compared in pyrolite and Cl chondrites to 10^6 magnesium atoms. The relative abundances of elements in the Earth's mantle and in the model 'primordial mantle' derived from Cl chondrites, are compared as ratios in Table III.

The above procedure could not be followed in the cases of K, Rb, Cs, Tl and U because of their prior fractionation in the source regions of ocean-floor tholeiites as discussed earlier. We followed the previous procedure of comparing K/U, Rb/U, Cs/U, Tl/U and Pb/U ratios in the Earth's mantle and crust with the corresponding ratios in Cl carbonaceous chondrites.

Finally, in order to compare abundances in the Moon with the lithophile or primordial

mantle component of Cl chondrites, we have simply multiplied the ratios obtained previously for a given element (e.g., Zn): thus

$$\frac{\text{Zn (Moon)}}{\text{Zn (primordial)}} = \frac{\text{Zn (Moon)}}{\text{Zn (Earth's mantle)}} \times \frac{\text{Zn (Earth's mantle)}}{\text{Zn (primordial)}}$$

Detailed discussions of individual elements together with references are given below. The elements which we have selected are those for which, in our judgment, the analytical data are sufficient to justify meaningful discussions. New elemental abundance data on many key elements on appropriate lunar and terrestrial materials are urgently required.

DATA BASE

The data sources for terrestrial basalts and ultramafics and for lunar basalts are listed under the appropriate elements. All data for Cl chondrites have been taken from the relevant chapters in Mason (1971).^{*} Where data for more than one meteorite were available, the median value was used.

FLUORINE

Terrestrial basalts: our estimate based on Wedepohl (1974).

Terrestrial ultramafics: data from Stueber *et al.* (1968).

Lunar basalts: mean for Apollo 12 and 15 basalts, data from Reed and Jovanovic (1971), Wänke *et al.* (1972) and Jovanovic and Reed (1973).

SODIUM

Terrestrial basalts: mean of 101 ocean-floor basalts (Melson *et al.*, 1975).

Terrestrial ultramafics: data from Stueber and Goles (1967).

Lunar basalts: mean for Apollo 12 and 15 (Rhodes and Hubbard, 1973).

PHOSPHORUS

Terrestrial basalts: mean of 101 ocean-floor basalts (Melson *et al.*, 1975).

Terrestrial ultramafics: mean of DTS-1, PCC-1 (Flanagan, 1969).

Lunar basalts: mean of 12 Apollo 12 basalts and 20 Apollo 15 basalts (Papike *et al.*, 1976 and Rhodes, 1975).

SULPHUR

Terrestrial basalts: Mathez (1976) has estimated that unaltered, primitive ocean-floor tholeiites contain around 900 ppm S.

Terrestrial ultramafics: our estimate based on data of Goles (1976).

Lunar basalts: data for low-Ti basalts from Gibson *et al.* (1975).

CHLORINE

Terrestrial basalts: Anderson (1974) has shown that the abundances of Cl in glasses trapped in phenocrysts are 5-20x higher than those of the vesicular rock. Since Cl would be readily lost during eruption, the high values obtained by Anderson (1974) are believed to better represent the initial Cl contents of magmas. We have taken the average Cl content for 5 glass inclusions in phenocrysts from Hawaiian tholeiites (Anderson, 1974).

Terrestrial ultramafics: from Steuber *et al.* (1968).

Lunar basalts: low-Ti basalt averages from Jovanovic and Reed (1973).

CHROMIUM

The partition behaviour of Cr between a basaltic partial melt and its crystalline residuum is mainly determined by the ambient oxygen fugacity conditions. In terrestrial magma genesis, Cr is strongly

^{*} References are given at the end of this section, not at the end of the article.

partitioned into the residuum (as Cr^{3+}) in pyroxenes and spinel, as evidenced by abundance data for terrestrial basalts and ultramafics. However, experimental studies show that under the low oxygen fugacity conditions prevailing in the lunar interior where much of the Cr is reduced to Cr^{2+} , its partition behaviour is considerably different. Experimentally-determined coefficients for Cr partition between olivine and basalt, and between orthopyroxene and basalt are approximately unity (Ringwood, 1970 and unpublished results). This compatible-element behaviour for Cr means that the abundances in lunar basalts approximate those in their source region. However, 'terrestrial' abundances can only be obtained by combining appropriate proportions of basalt with its residuum (see Table III). Thus, in order to compare lunar with terrestrial abundances, we have taken the ratio of the mean abundance in lunar basalts to the calculated abundance in pyrolite.

Terrestrial basalts: mean of 10 ocean-floor basalts (Engel *et al.*, 1965).

Terrestrial ultramafics: data from Stueber and Goles (1967).

Lunar basalts: mean for Apollo 12 and 15 (Rhodes and Hubbard, 1973).

MANGANESE

A comparison of MnO in lunar basalts relative to terrestrial basalts leads to the conclusion that the Moon is modestly enriched in MnO. However, an alternative approach would have been to compare FeO/MnO ratios between terrestrial and lunar basalts, using data from the same sources. In this case, the lunar/terrestrial ratio of 76/64 implies a modest depletion in the Moon. See further discussion in Section 4.

Terrestrial basalts: mean value from Frey *et al.* (1974) and Cann (1971).

Terrestrial ultramafics: from Stueber and Goles (1967).

Lunar basalts: data from Rhodes (1975) and Papike *et al.* (1976). Mean for average of Apollo 12 basalts and Apollo 15 basalts.

COBALT

Terrestrial basalts: mean for 21 ocean-floor basalts (Frey *et al.*, 1974) and 10 ocean-floor basalts (Engel *et al.*, 1965).

Terrestrial ultramafics: from Stueber and Goles (1967).

Lunar basalts: mean for average Apollo 12 and average Apollo 15 basalts (Wänke *et al.*, 1971, 1975). Data consistent with all other neutron activation analyses.

NICKEL

Terrestrial basalts: Kay *et al.* (1970) demonstrated that Ni decreased with decreasing MgO content in ocean-floor basalts, and attributed the pattern to olivine fractionation. They interpreted the 200 ppm Ni cut-off at high MgO contents as representing the Ni content of the most primitive magmas. Their interpretation is also supported by the data of Bence *et al.* (1975). Our estimate of 200 ppm Ni in primitive ocean-floor basalts is based on these data sources.*

Terrestrial ultramafics: our estimate based on Goles (1967).

Lunar basalts: we have attempted to minimise the effects of olivine fractionation by considering only the more primitive low-Ti basalts. Our estimate is based on the data of Compston *et al.* (1971), Wänke *et al.* (1971), Taylor *et al.* (1971), Cuttitta *et al.* (1973) and Rhodes and Hubbard (1973). See further discussion in Section 6.

COPPER

Terrestrial basalts: mean of 21 ocean-floor basalts (Frey *et al.*, 1974).

Terrestrial ultramafics: our estimate based on data in Wedepohl (1974). Wide dispersion (10–60 ppm) amongst data; we take 20 ppm.

Lunar basalts: from Cuttitta *et al.* (1973).

ZINC

Terrestrial basalts: our estimate for ocean-floor basalts based on data of Rader (1973), Baedeker (1971) and Wedepohl (1974). Data show narrow dispersion.

* Recent data for DSDP ocean floor basalt glasses suggest that the cut-off for nickel in primitive basalts may be closer to 250 ppm (Blanchard *et al.*, 1976).

Terrestrial ultramafics: our estimate based on Gurney and Ahrens (1973). Data show very narrow dispersion.

Lunar basalts: mean of average for Apollo 12 (Anders *et al.*, 1971) and Apollo 15 (Ganapathy *et al.*, 1973).

GALLIUM

Terrestrial basalts: our estimate is based on neutron activation data for 19 Hawaiian tholeiites and 36 ocean-floor basalts (Argollo, 1974) together with data for 6 Hawaiian tholeiites and 2 ocean-floor basalts (Baedecker *et al.*, 1971). All data show narrow dispersion.

Terrestrial ultramafics: our estimate based on data of Goles (1967).

Lunar basalts: mean for Apollo 12 and 15 basalts (Cuttitta *et al.*, 1973).

GERMANIUM

Terrestrial basalts: Argollo (1974) provides neutron activation data for 19 Hawaiian tholeiites and 36 ocean-floor basalts. Our estimate is based on these data, which show very narrow dispersion.

Terrestrial ultramafics: our estimate is based on data contained in Wedepohl (1974).

Lunar basalts: Wänke (pers. comm.) believes his determinations on Apollo 12 basalts are too high. Accordingly, we have taken the mean for Apollo 15 basalts only (Ganapathy *et al.*, 1973), and disregarded the data of Baedecker *et al.* (1971), which may also be somewhat high because of the possibility of contamination (Wasson, pers. comm.).

ARSENIC

Terrestrial basalts: mean for 4 ocean-floor basalts (Bartel *et al.*, 1963).

Terrestrial ultramafics: data from Onishi and Sandell (1955).

Lunar basalts: average of data from Wänke *et al.* (1971) taking lowest values only (Wänke, pers. comm.) plus Wänke *et al.* (1975). Brunfelt *et al.* (1971) have determined As in several Apollo 12 basalts but their values were much higher than those of Wänke *et al.* (1971). We have not used Brunfelt *et al.*'s data because of the possibility of contamination. On the basis of more recent analyses, Wänke (pers. comm.) believes that the As content of low-Ti mare basalts may be about a factor of 6 smaller than we have estimated. If correct this strengthens the conclusions which are reached subsequently in this paper.

SELENIUM

Terrestrial basalts: mean of 3 ocean-floor basalts (Laul *et al.*, 1973). These data are consistent with data for all classes of basalts (Wedepohl, 1974).

Terrestrial ultramafics: data from Goles (1967).

Lunar basalts: mean for average of 8 Apollo 12 basalts and 5 Apollo 15 basalts from Anders *et al.* (1971) and Ganapathy *et al.* (1973). These data are consistent with those of Brunfelt *et al.* (1971).

PALLADIUM

Terrestrial basalts: data show considerable dispersion, due to rock alteration. Our estimate is based on Crocket and Teruta (1976), Crocket (1971).

Terrestrial ultramafics: our estimate based on data of Crocket and Chyi (1972) and Crocket (1971).

Lunar basalts: upper limit from Wänke *et al.* (1971).

SILVER

Terrestrial basalts: mean of 9 ocean-floor basalts (Laul *et al.*, 1973; Keays and Scott, 1976).

Terrestrial ultramafics: average value from Wedepohl (1974). Data show wide dispersion.

Lunar basalts: mean of average of 8 Apollo 12 basalts (Anders, *et al.*, 1971) plus 5 Apollo 15 basalts (Ganapathy *et al.*, 1973).

CADMIUM

Terrestrial basalts: data from Baedecker *et al.* (1971) for 6 Hawaiian tholeiites, 2 ocean-floor basalts and 1 intrusion (Skaergaard).

Terrestrial ultramafics: mean of DTS-1, PCC-1 (Baedecker *et al.*, 1971).

Lunar basalts: mean of average for Apollo 12 from Baedecker *et al.* (1971) and for 4 Apollo 15 basalts from Ganapathy *et al.* (1973).

INDIUM

Terrestrial basalts: average of 8 terrestrial basalts (Baedecker *et al.*, 1971).

Terrestrial ultramafics: average of DTS-1, PCC-1 (Baedecker *et al.*, 1971).

Lunar basalts: mean of average for Apollo 12 (Baedecker *et al.*, 1971) and Apollo 15 (Ganapathy *et al.*, 1973).

ANTIMONY

Terrestrial basalts: mean of 4 ocean-floor basalts (Tanner and Ehmann, 1967).

Lunar basalts: mean for average of 5 Apollo 12 basalts (Morrison *et al.*, 1971) and average of 5 Apollo 15 basalts (Ganapathy *et al.*, 1973). The data of Brunfelt *et al.*, (1971) would be in good agreement with the above sources if the units were ppb instead of ppm as quoted.

TUNGSTEN

Terrestrial basalts: mean of 15 ocean-floor basalts; data show narrow dispersion (Helsen, 1975).

Lunar basalts: mean of average Apollo 12 basalts (Wänke *et al.*, 1971) and average Apollo 15 basalt (Wänke *et al.*, 1975). These data are consistent with Brunfelt *et al.* (1971, 1972).

RHENIUM

Terrestrial basalts: estimate based on data of Ganapathy *et al.* (1973) and Morgan and Lovering (1967).

Terrestrial ultramafics: estimate based on above sources.

Lunar basalts: mean for average Apollo 12 basalt (Lovering and Hughes, 1971) and average Apollo 15 basalt (Ganapathy *et al.*, 1973).

OSMIUM

Terrestrial basalts: our estimate based on data of Morgan and Lovering (1967) and Crocket (1971).

Terrestrial ultramafics: estimate based on data of Crocket and Chyi (1972) and Crocket (1971).

Lunar basalts: average Apollo 12 basalt (Lovering and Hughes, 1971). Data consistent with those of Reed and Jovanovic (1971).

IRIDIUM

Terrestrial basalts: mean of 22 ocean-floor basalts (11 lithologic units drilled by DSDP plus 11 dredge samples) from Crocket and Teruta (1976), Baedecker *et al.* (1971), Laul *et al.* (1972) and Keays and Scott (1976). Data show considerable dispersion.

Terrestrial ultramafics: mean of 5 whole-rock fresh peridotites (Crocket and Chyi, 1972).

Lunar basalts: average of 15 Apollo 12 basalts (Anders *et al.*, 1971; Baedecker *et al.*, 1971) and average of 9 Apollo 15 basalts (Baedecker *et al.*, 1973). We take mean for Apollo 12 plus Apollo 15 (see discussion in Section 6).

PLATINUM

Terrestrial: our estimate for ultramafics (and pyrolite) based on Crocket and Teruta (1976) and Crocket (unpublished data).

GOLD

Terrestrial basalts: data show wide dispersion, so we have selected neutron-activation data (for tholeiites) from Wedepohl (1974) and taken the median value.

Terrestrial ultramafics: data selection from Wedepohl (1974) as above.

Lunar basalts: after disregarding anomalously high values, we took the mean for Apollo 12 average basalts (Anders *et al.*, 1971) and for Apollo 15 average basalt (Ganapathy *et al.*, 1973).

BISMUTH

Terrestrial basalts: these show wide dispersion, e.g., ~ 50 ppb for continental tholeiites (Greenland *et*

al., 1973) but only ~ 6 ppb for ocean-floor basalts (Laul *et al.*, 1973). The crystal-chemical properties of Bi^{3+} are such that it should behave as an incompatible element and partition into the liquid during partial melting. We have, therefore, estimated a value of 20 ppb.

Terrestrial ultramafics: mean for DTS-1, PCC-1 (Greenland *et al.*, 1973).

Lunar basalts: mean of average for 8 Apollo 12 basalts, 5 Apollo 15 basalts (Anders *et al.*, 1971; Ganapathy *et al.*, 1973).

K/U

Terrestrial: whole-earth estimate of Wasserburg *et al.* (1964).

Lunar basalts: mean of average Apollo 12 basalt (O'Kelley *et al.*, 1971) and average Apollo 15 basalt (O'Kelley *et al.*, 1972).

Rb/U

Terrestrial: the Rb/U ratio was obtained by dividing the whole-earth K/U ratio (see above) by the terrestrial K/Rb value obtained by Hurley *et al.* (1968a, b).

Lunar basalts: this ratio was likewise obtained by taking $\text{K/U} \div \text{K/Rb}$. K/U data as above, K/Rb ratios for average Apollo 12 and 15 basalts taken from Rhodes and Hubbard (1973).

Cs/U

Terrestrial: most of the earth's K, Rb, Cs, Tl and U is believed to be contained in the crust (e.g., Gast, 1960, 1968; Taylor, 1964). The comparatively high concentration of this geochemically coherent group elements in crustal rocks allow a high degree of analytical precision, and thus, the Cs/U and Tl/U ratios for the continental crust should closely approximate those of the earth's mantle. Average abundances for the continental crust were obtained from Taylor (1964).

Lunar basalts: mean Cs contents were obtained from average Apollo 12 basalts (Anders *et al.*, 1971) and average Apollo 15 basalts (Ganapathy *et al.*, 1973), with mean U contents taken from O'Kelley *et al.*, (1971, 1972).

Tl/U

Terrestrial: Tl/U ratio is obtained from Taylor (1964) continental crust averages (see discussion for Cs/U).

Lunar basalts: Cs from mean of Apollo 12 average (Anders *et al.*, 1971) and Apollo 15 average (Ganapathy *et al.*, 1973). U values from O'Kelley *et al.* (1971, 1972).

μ ($^{238}\text{U}/^{204}\text{Pb}$)

Terrestrial: our estimate based on Cumming and Richards (1975).

Lunar basalts: our estimate for Apollo 12 and 15 basalts based on data of Tatsumoto *et al.* (1971, 1972).

Abundances in terrestrial basalts and ultramafics, and lunar basalts derived from the above sources are listed in Table I. Uranium-normalised abundances for K, Rb, Cs, Tl and Pb are presented in Table II. Calculated element abundances in pyrolite and CI chondrites, normalised to 10^6 Mg atoms, are given in Table III.

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TABLE I

Mean abundances (ppm) of some volatile and siderophile trace elements in terrestrial basalts and ultramafics, and in lunar low-Ti mare basalts.

	Terrestrial basalt	Terrestrial ultramafics	Lunar basalts
F	300	21	39
Na	19 439	1040	1800
P	567	7	380
S	900	100	1147
Cl	190	32	4
Cr	297	2980	3555
Mn	1362	1040	2091
Co	41	110	45
Ni	200	2000	150
Cu	103	20	12
Zn	100	40	1
Ga	20	3	4
Ge	1.5	1	0.0067
As	1	1	0.006
Se	0.17	0.05	0.14
Pd	0.006	0.013	< 0.006
Ag	0.03	0.05	0.001
Cd	0.14	0.014	0.002
In	0.073	0.003	0.0009
Sb	0.029	—	0.06 ppb
W	0.15	—	0.14
Re	0.8 ppb	0.1 ppb	0.01 ppb
Os	0.3 ppb	5 ppb	0.5 ppb
Ir	0.04 ppb	2.4 ppb	0.07 ppb
Pt	—	~ 0.02	—
Au	2.4 ppb	4.2 ppb	0.03 ppb
Bi	0.02	0.006	0.24 ppb

TABLE II
Volatile element abundances normalised to uranium for terrestrial mantle, lunar basalts and CI chondrites (= primordial).

	CI	Terrestrial	Lunar
K/U	39 307	10 000	2456
Rb/U	176	29.2	4.9
Cs/U	14.1	1.1	0.21
Tl/U	7	0.17	0.002
$^{204}\text{Pb}/^{238}\text{U}$	5	0.13	0.001

TABLE III
Calculated element abundances in pyrolite and CI chondrites relative to 10^6 Mg atoms.

	Pyrolite ^a ppm	Pyrolite/ 10^6 Mg	CI/ 10^6 Mg
F	68	386	3382
Na	4167	1.9×10^4	5.7×10^4
P	102	354	9067
S	236	789	4.7×10^5
Cl	59	178	3511
Cr	2524	5024	1.2×10^4
Mn	1095	2137	8582
Co	98	179	2168
Ni	1694	3094	4.5×10^4
Cu	34	57	509
Zn	50	82	1508
Ga	6	9	44
Ge	1.1	1.6	126
As	1	1.4	6.2
Se	0.07	0.10	65
Pd	0.012	0.012	1.8
Ag	0.05	0.05	0.91
Cd	0.035	0.033	2.3
In	0.015	0.014	0.21
Re	0.0001	0.000 06	0.049
Os	0.005	0.003	0.68
Ir	0.002	0.001	0.58
Pt	0.020	0.011	1.13
Au	0.004	0.002	0.18
Bi	0.008	0.004	0.15

^a Pyrolite = 17% terrestrial basalt + 83% ultramafic.

3. Abundance Patterns of Volatile Elements in Chondritic Meteorites and in the Earth

A. INTERPRETATION OF CHONDRITIC ABUNDANCE PATTERNS

Abundances of many elements in ordinary chondrites are shown in relation to their primordial abundances (as displayed by CI chondrites) in Figure 1. * This may be compared

* Whereas our compositional data for ordinary chondrites are based upon averages for all classes of these meteorites, Wasson (personal communication) suggests that it would have been more appropriate to select compositional data exclusively from the unequilibrated chondrite class. This procedure may well be preferable but would not alter any of the conclusions reached in the present paper.

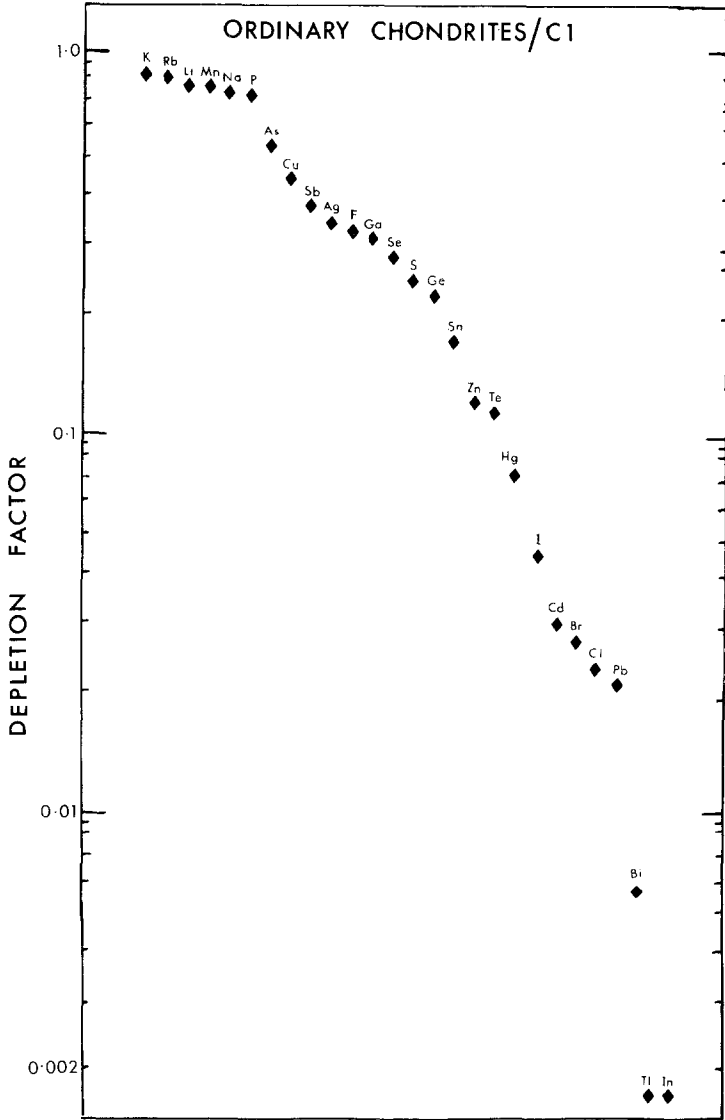


Fig. 1. Comparison of abundances of volatile elements in ordinary chondrites with corresponding abundances in C1 chondrites. Based on Wasson and Chou (1974) and Anders (1968).

with condensation temperatures of elements and compounds from a gas phase of solar composition at 10^{-4} atmospheres, as given in Table IV. The latter provides a measure of relative volatility of the relevant elements and compounds. There is seen to be a very strong correlation between the degree of depletion of a given element in ordinary chondrites and its relative volatility in the environment of the solar nebula. The exceptions are minor and may well be caused by errors in thermodynamic data used to construct the condensation sequence. There can be little doubt that the differing degrees of

TABLE IV

Condensation temperatures and sequence of phases and elements separating from gas of solar composition at 10^{-4} atmospheres total pressure. Temperatures correspond to 50% condensation of a given element. (Based on Grossman and Larimer, 1974, Figure 2; Grossman, 1972; Anders, 1968, Figure 5; Wasson and Wai, 1976; and Wai and Wasson, 1977)^a

Element or compound	°K
Ca, Al, Ti oxides and silicates	> 1400
Platinum metals, W, Mo, Ta, Zr, REE	> 1400
Mg ₂ SiO ₄	~ 1360
Fe-Ni metal	~ 1360
Remaining SiO ₂ (as MgSiO ₃)	1200-1350
Cr ₂ O ₃	—
P	1290
Au	1230
Li	1225
Mn ₂ SiO ₄	1190
As	1135
Cu	1118
Ga	1075
(K, Na)AlSi ₃ O ₈	~ 1000
Ag	952
Sb	910
F	855
Ge	812
Sn	720
Zn	660-760
Se	684
Te	680
Cd	680
S (as FeS)	648
FeO (10% ss. as (Mg _{0.9} Fe _{0.1}) ₂ SiO ₄)	~ 600
Pb	520
Bi	470
In	460
Tl	440
Fe ₃ O ₄	400
NiO	—
H ₂ O (as hydrated silicates)	~ 300

^a Significant differences appear in calculations by the authors cited. We have selected what appear to be the most reliable estimates based upon recent thermodynamic data.

depletion of elements in ordinary chondrites are caused by their differing volatilities with a general trend that the more volatile the element, the greater the degree of depletion.

Detailed interpretations of these relationships have been proposed by Larimer and Anders (1970), Anders (1968, 1971, 1976), Ganapathy and Anders (1974), Wasson (1972, 1974) and Wasson and Chou (1974). It is argued by Ganapathy and Anders (1974) and Anders (1976) that chondrites are mixtures of 7 distinct components, each of which

formed in the solar nebula under differing thermal conditions and were then mixed in appropriate proportions to reproduce the observed chondritic abundance patterns (Figure 1). These components comprise (1) high temperature condensates, e.g., Ca, Al, Ti, Os, Re, W, Mo, Ta, Zr, U, Th, REE, as oxides, silicates or metals, (2) Mg silicates which may contain some FeO, (3) metallic nickel-iron, (4) sulphide phase, FeS, (5) low temperature condensate – iron-magnesium silicates together with large amounts of magnetite and volatile components, e.g., Pb, In, Tl, Bi, H₂O, S and (6), (7) remelted portions of components (2) and (3) above, partially depleted in volatiles.

These authors have extended their interpretation of chondritic abundance patterns based upon the following philosophy (Ganapathy and Anders, 1974): “The fundamental assumption is that the inner planets were made by exactly the same processes as the chondrites. For the chondrites, it has been obvious for some time that they are mixtures of about half a dozen components that formed in a cooling solar nebula. We assume that the Earth and Moon were made from the same components, but in different proportions. The problem then reduces to estimating those proportions from appropriate geochemical constraints.”

There is little doubt that Anders and his colleagues have demonstrated the key roles played by selective condensation/volatility processes and fractionations of components in producing the chemical compositions of chondrites. However, because of the great flexibility of this model with its seven degrees of freedom,* we are unimpressed by the significance of the apparent agreement between the model and the observed compositions of chondrites. We doubt whether the extent of this agreement necessarily constitutes proof of their hypothesis. Indeed, Wasson and Chou (1974), Wasson (1972, 1974) and Dodd (1969, 1974) have pointed out several specific mineralogical, chemical and thermal difficulties encountered by the model. It appears premature to apply this 7-component model to other planets until independent evidence for the nature of each of these components and the reality of the processes which produced them becomes available. Moreover, it is by no means clear that the highly-localized fractionation processes responsible for the ultimate compositions of the very small parent bodies of chondrites played major roles in producing planets, which are many orders of magnitude larger in mass.

Wasson (1972, 1974) has proposed a much simpler model for explaining chondrite compositions. This invokes selective condensation/volatilization processes in the solar nebula under conditions of continuous separation of solids from the gas phase. When combined with chemical fractionations which can be attributed to metamorphism and recrystallization within meteorite parent bodies – processes supported by convincing empirical evidence (Dodd, 1969; Wasson, 1972, 1974) – an acceptable interpretation can be achieved. It should be noted however, that the proposition that fractionation occurred within a gas phase of solar composition (= solar nebula) is only an *assumption*, and not, as all too frequently stated, a *conclusion* resulting from these studies. Similar

* The model actually contains more than 7 degrees of freedom because it is possible to vary the temperatures at which equilibration occurred between the magnesium silicates and volatiles and at which the lowest temperature condensate separated from the nebula.

fractionations could well have occurred, not in the primordial solar nebula, but in localized gas clouds of non-solar composition under pressures far higher than could be achieved in the primordial nebula. An alternative environment might be provided by high velocity impacts of primordial icy planetesimals similar to comet nuclei upon the surfaces of large asteroids. We believe that many chemical and mineralogical characteristics of Allende inclusions, for example, might be explained more plausibly by condensation within rapidly cooling gas spheres derived in this manner, rather than within the solar nebula proper.

B. COMPOSITION OF EARTH'S MANTLE AND ITS RELATIONSHIP TO PRIMORDIAL COMPOSITION

A detailed review of evidence bearing upon the major element composition of the Earth's mantle is given in Ringwood (1975). It was concluded that the pyrolite model composition as derived from the upper mantle was most probably applicable to the entire mantle. An important property of this composition is its relationship to the primordial abundances of major elements as believed to be provided by Type 1 carbonaceous (CI) chondrites. The pyrolite major element composition can be obtained simply from this primordial composition by the following steps (Ringwood, 1966a, b; Larimer, 1971):

- (1) loss of volatiles, principally H_2O , carbonaceous material and some sulphur
- (2) reduction of FeO and NiO to metal phase until residual silicate phase possesses a $100MgO/(MgO + FeO)$ ratio of 88. Metallic iron and nickel thereby produced, together with remaining sulphur, enter the core
- (3) loss by volatilization of 67% of the original sodium and 16% of the total silicon originally present in the primordial material.

In connection with this last step, it should be noted that of the major elements (Mg, Fe, Si, Ca, Al, Ni and Na) under consideration, sodium and silicon are the most volatile under appropriate cosmochemical conditions, sodium being much more volatile than silicon (Grossman, 1972). Moreover, the abundances of involatile lithophile minor elements (e.g., REE, Sc, Zr, U, Th, Ti, Nb, Y) are consistent with derivation from the CI chondrite bulk composition as outlined in steps 1, 2 and 3 above. It has been concluded elsewhere that the abundances of these elements in the mantle on a weight for weight basis are about twice (2.0 ± 0.5) those in *ordinary* chondrites (Ringwood, 1975, 1976; Frey and Green, 1974; Loubet *et al.*, 1975; Sun and Nesbitt, 1976). At first sight, there might appear to be a contradiction between the statement that the abundances in the Earth's mantle can be derived directly from CI chondrites, and the following statement that the absolute abundances of these elements are present at about twice the ordinary chondrite levels, but this is not the case. When we derive the pyrolite composition from CI chondrites via steps 1, 2 and 3, the abundances of all lithophile elements are increased by a factor of 1.6 in the mantle, mainly owing to segregation of the core. Moreover, on a weight for weight basis, CI chondrites are enriched in these 'refractory' lithophile elements (Ca, Al, Ti, Zr, Sc, REE, U, Th, etc.) by an average factor of 1.4 compared to ordinary chondrites (Larimer and Anders, 1970; Larimer, 1971). Thus, a model mantle composition derived from CI chondrites via steps 1, 2 and 3 above would contain about

TABLE V

Comparison of (mainly) volatile element abundances between the Moon, the Earth's mantle and CI chondrites (= primordial).

	Earth/CI	Moon/CI	Moon/Earth
Mg	1	1	1
Al	1	1	1
Ca	1	1	1
U	1	1	1
Si	0.84	0.84	1
F	0.11	0.014	0.13
Na	0.33	0.030	0.09
S	0.0017	0.0019	1.27
Cl	0.051	0.0011	0.021
Cr	0.42	0.59	1.41
Mn	0.25	0.38	1.53
Cu	0.11	0.013	0.12
Zn	0.054	0.0054	0.01
Ga	0.20	0.040	0.2
Ge	0.013	0.000 059	0.0045
As	0.23	0.0014	0.0060
Se	0.0015	0.0012	0.80
Ag	0.055	0.0018	0.033
Cd	0.014	0.0002	0.014
In	0.067	0.0008	0.012
Sb	—	—	0.0021
Au	0.011	0.000 14	0.013
Bi	0.027	0.000 32	0.012
K/U	0.25	0.063	0.25
Rb/U	0.17	0.029	0.17
Cs/U	0.078	0.015	0.19
Tl/u	0.024	0.000 29	0.012
²⁰⁴ Pb/ ²³⁸ U	0.025	0.000 20	0.0080

2.2 times the ordinary chondritic abundances of these elements, in agreement with the estimates for the Earth's mantle cited above.

C. VOLATILE ELEMENTS IN THE EARTH'S MANTLE

Depletions of volatile elements in the Earth compared to primordial abundances have been discussed by Gast (1960, 1972) and Ringwood (1960, 1962, 1966a, b). In the latter (1966a, b) studies, it was concluded that the Earth is markedly to strongly depleted in Na, Zn, Cd, Hg, Pb, In, Bi, Ge, Cl, S and F. The depletion factors estimated in the present paper (Table V and Figure 2) using more recent and abundant compositional data, confirm and extend these results.

The general sequence of increasing depletion factors (Table V and Figure 2) corresponds quite well to the condensation sequence in Table IV and leaves little doubt that the terrestrial depletions are primarily a consequence of selective condensation/volatilization processes. In some cases (e.g., Cu, Ag, Ge, S, Se), depletions in the mantle are also

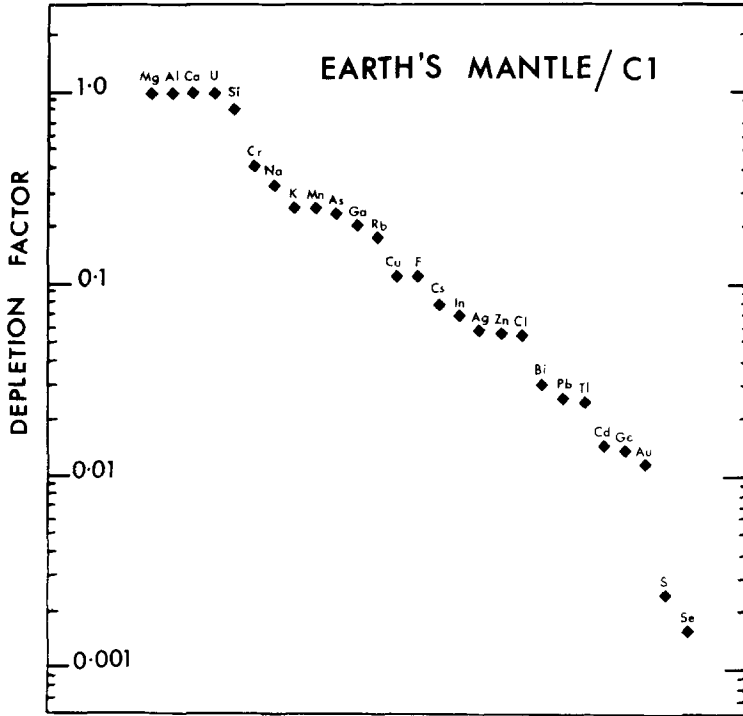


Fig. 2. Abundances of elements in the Earth's mantle compared to primordial abundances as given by CI chondrites.

caused in part by their siderophile nature which has resulted in preferential entry into the Earth's core. If we consider the elements with depletion factors between 1.0 and 0.05, there is a strong correlation between condensation temperature and degree of depletion. Copper and silver would doubtless have come higher in the sequence if allowance had been made for the amount of these elements which entered the core.

There is a jump from chlorine and zinc (depletion factors = 0.05) to Tl, Bi, Pb, Cd, Ge (depletion factors 0.027–0.013). In the case of Ge, this is certainly attributable to its strongly siderophile behaviour (Chou *et al.*, 1973). Experiments on the partition of Pb between metal and silicate phases (Oversby and Ringwood, 1971) show marked siderophile tendencies, particularly if the metal contains some sulphur. Likewise, the Cd contents of iron meteorites (Mason, 1971) suggest significant siderophile tendencies for this element. It seems likely, therefore, that substantial amounts of these elements have entered the core. However, the observed depletions are much too high to be caused solely by siderophile behaviour. Elements which are much less volatile and much more strongly siderophile (e.g., Ni, Co, Cu), have not been depleted in the mantle to the same extent as Bi, Pb, Cd, Tl and Ge (Tables III, V and VI). It seems clear, therefore, that the depletions of these elements in the mantle are dominantly caused by volatility but have been enhanced by their partly siderophile nature which has caused variable degrees of entry into the Earth's

core. The overall abundances of these elements in the Earth may be similar to those of other volatile, non-siderophile elements such as In, Cl and Zn, which possess depletion factors of about 0.05 (Table V). Nishimura and Sandell (1964) demonstrated that zinc is an oxyphile element possessing negligible siderophile or chalcophile tendencies at the redox states characteristic of ordinary chondrites. Thus, the inferred mantle depletions of Zn (and Cl) are likely to be a measure of their net Earth depletions.

It is widely believed that the Earth's core may contain about 10% of sulphur (e.g., Mason, 1966; Brett, 1976b). Thus, the depletion factor for sulphur in Table V is not representative of the bulk Earth. The appropriate depletion factor for this element in the bulk Earth is therefore 0.45. Selenium probably also possesses a similar net earth depletion factor.

D. COMPARISON OF DEPLETION PATTERNS IN ORDINARY CHONDRITES AND IN THE EARTH

The overall depletion pattern of volatile elements in the Earth thus displays some interesting differences in comparison with that of ordinary chondrites (Figure 1). The least volatile element to be significantly depleted in the Earth (by 16%) is silicon. The degrees of depletion generally increase with increasing volatility as Cr, Na, Mn, S, Se, the remaining alkali metals (except Li) and fluorine become progressively more depleted, until a plateau is reached consisting of In, Zn, Cl, possessing depletion factors of about 0.05. As noted earlier, we believe that Cd, Bi, Pb, Tl and Ge would also possess net Earth depletion factors of about 0.05 after allowances had been made for the amounts of these elements which entered the core.

The ordinary chondrites display zero depletions for Si and Cr, and only small or negligible depletions for Mn, Na, K and Rb. On the other hand, highly volatile elements such as Tl, Pb, In and Bi are depleted by much larger factors than the Earth (Figure 1) ranging up to 1000 (i.e., depletion factor = 0.001).

The depletion pattern exhibited by the Earth is remarkably simple. The present bulk composition of the Earth can be derived from that of primordial Cl chondrites simply by a process of chemical reduction to form a metal phase, combined with depletion of elements more volatile than silicon in accordance with their relative volatilities. The abundances (Tables III, V, Figure 2) of highly volatile elements such as Zn, Cl, In, Pb, Bi, Cd and Tl (depletion factor ~ 0.05) suggest that the Earth incorporated about 5% of a primordial low-temperature ($< 500^\circ\text{K}$) condensate. The remainder of the Earth accreted at sufficiently high temperatures so that these elements failed to condense, or were removed by volatilization. Elements of intermediate volatility (e.g., K, Rb, Cs, Mn, Ga, As, F) were depleted by intermediate factors of 0.1 to 0.25, whilst the three least volatile elements Na, Cr and Si were also the least depleted. Moreover, the depletion factors of these last three elements correspond with their relative volatilities. The entire terrestrial compositional pattern can be readily explained by the single-stage model of the formation of the Earth proposed by Ringwood (1960, 1966a, b, 1975). In this model, accretion temperatures are controlled by the gravitational potential energy (which increases as R^2)

liberated as planetesimals fall upon the growing Earth. A small cool nucleus ($\sim 5\%$ of the mass) forms first. Material accreting subsequently, is subjected to increasing temperatures accompanied by loss of elements which are volatile at these temperatures. The model leads to a direct correlation between the degree of depletion of elements in the bulk Earth and their relative volatilities.

The simplicity of the terrestrial fractionation pattern renders it quite unnecessary to introduce Anders' 7-component model aimed at explaining the compositions of chondrites. The attractions of this model are further reduced by the existence of major differences between chondritic and terrestrial fractionation patterns. A notable problem is posed by the high sulphur content believed to be present in the Earth's core. The condensation temperature of sulphur in the solar nebula is seen to be below those of Mn, alkali metals, Ge and Zn (Table IV). The conditions under which the Earth can become depleted by large factors (0.3–0.05) in these elements of lesser volatility whilst retaining 45% of the primordial sulphur abundance are extremely restrictive and can be satisfied only if the Earth accreted in an environment in which, compared to the solar nebula, hydrogen was strongly depleted relatively to sulphur and water vapour (Ringwood, 1975). This is *not* the environment in which ordinary chondrites accreted, according to Anders (1968, 1971).

The preceding discussion helps to place in perspective the conjectures of Lewis (1971) and Hall and Murthy (1971) that most of the Earth's potassium has entered the core because of its allegedly chalcophile* properties. These authors therefore claim that potassium is *not* depleted in the bulk Earth compared to chondrites. The data in Table V and Figure 2 show, however, that a large number of elements possessing highly diverse chemical properties are depleted in the Earth's mantle and that many of these (e.g., Si, Cr, Mn, Na, F, Cl, Zn) are *not* chalcophile at the redox condition pertaining in the Earth's mantle. The common property linking the depletions of these elements is volatility; and it is this factor, doubtless, which is also responsible for the depletion in potassium. It is shown in Section 4 that this explanation applies even more dramatically in the case of the Moon.

4. Abundance Patterns of Volatile Elements in the Moon

A. COMPARISON WITH PRIMORDIAL ABUNDANCES

Abundances of volatile elements in the Moon are compared with the primordial abundances in Table V and Figure 3. The magnitude of the depletions of many elements is most spectacular. There can be little doubt that volatility is the property responsible for most of these depletions. However, the overall pattern differs drastically from that

* In connection with the alleged chalcophile nature of potassium, it should be mentioned that Oversby and Ringwood (1972) measured the partition coefficient of potassium between relevant silicate systems and Fe–FeS melts and demonstrated that less than 1% of the total potassium in the system had entered the Fe–S phase. Goettel (1975) performed corresponding experiments and found that the partition coefficient for potassium in the sulphide phase was on the order of a few parts in a thousand. Clearly, potassium cannot be described in any sense as a chalcophile element.

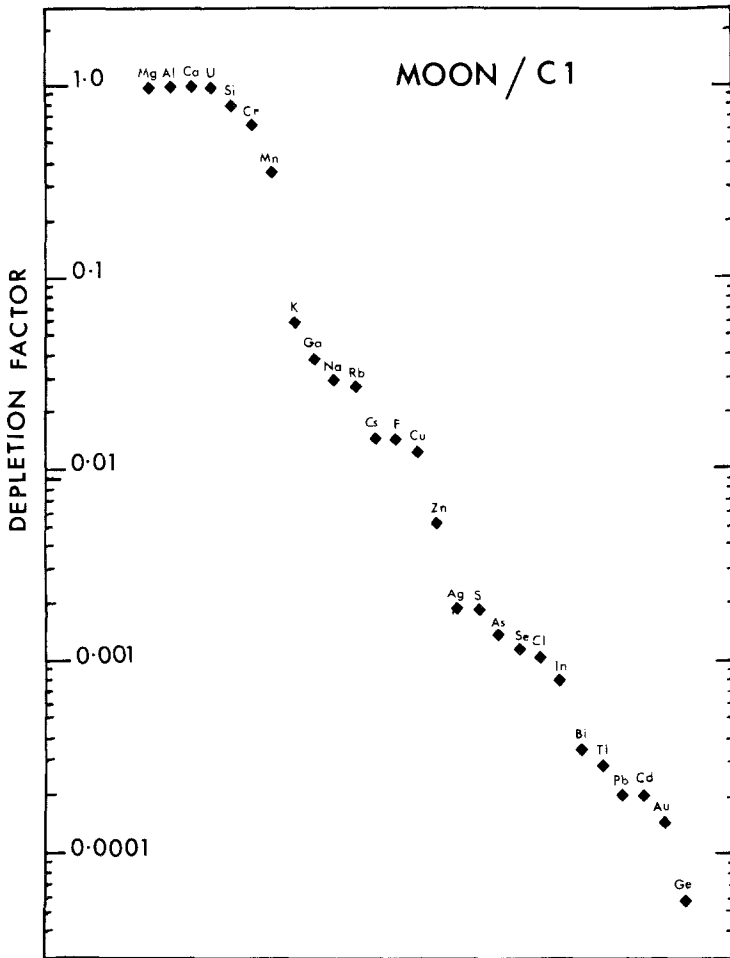


Fig. 3. Comparison of abundances of volatile elements in the Moon with corresponding abundances in CI chondrites.

displayed by ordinary chondrites (Figure 1) and implies that the Moon formed in a chemical and thermal environment very different to that which prevailed during the formation of chondrites. Moreover, the depletion patterns cannot readily be interpreted in terms of the solar nebula condensation sequence of Table I, or of various nebula fractionation models based on this sequence (e.g., Ganapathy and Anders, 1974). The following contrasts and inconsistencies should be noted.

(1) The elements As, Cu, F, Ag, Se, Ge, S and Zn are depleted in ordinary chondrites relative to CI chondrites by small factors in the limited range 0.3 ± 0.2 (Figure 1). Anders (1968, 1971) attributes the similarity in these depletion factors to the small range of temperatures over which these elements condense in the solar nebula (mostly 680–1000 °K, Table IV). However, these elements are depleted in the Moon by much greater factors

(0.04 for Ga to 0.00006 for Ge). The enormous *range* of these latter depletion factors should be emphasized in view of Anders' conclusion that condensation of the above elements in a nebula of solar composition would result in a high degree of coherence of the entire group.

(2) For elements more depleted in the Moon than potassium (Table V, Figure 3), there is little or no correlation of the order of depletion factors with the order of condensation temperatures in the solar nebula (Table IV) or with the order of depletion factors for these elements in ordinary chondrites.

Consider a particular example of the above statement. The condensation temperature of germanium in a nebula of solar composition is higher than those of Zn, S, Cd, Pb, Bi, In and Tl. Yet Ge is depleted in the Moon by large factors (up to 100-fold) compared to these elements. (See also Sections 5 and 6.)

(3) In a cooling solar nebula, significant quantities of FeO being to enter Mg_2SiO_4 and $MgSiO_3$ at about 800 °K and the lunar 100 MgO/(MgO + FeO) of about 80 is reached when the temperature has fallen to 520 °K (Grossman, 1972). At this temperature, all the elements in Table IV except Bi, Pb, Tl and In would be fully condensed. In models wherein the Moon is formed from material ultimately condensed from the solar nebula, oxidized iron is introduced by a component which has either cooled in equilibrium with nebula gases to 520 °K, thereby producing $(Mg_{0.8}Fe_{0.2})_2SiO_4$ and $(Mg_{0.8}Fe_{0.2})SiO_3$, or to an even lower temperature (400 °K), at which magnetite becomes stable. The Moon must contain a large proportion of the low temperature oxidized component, ranging from 20% (if all FeO was introduced as magnetite) to > 50%, if FeO was introduced in solid solution with magnesium silicates. As shown in Table IV, this low-temperature component should contain the primordial abundances of Na, Rb, Cs, Ge, Zn, Cd, S, Se and Pb. The maximum depletion factor of these elements in the Moon should thus be about 0.2, as compared to the observed range of depletion factors which range from 0.03 to 0.00006.

We conclude that the processes responsible for the present composition of the Moon did not resemble those involved in the formation of ordinary chondrites and furthermore, that the Moon was not formed from material which condensed directly from the solar nebula.

B. COMPARISON WITH TERRESTRIAL MANTLE ABUNDANCES

Abundances of (mainly) volatile elements in the Moon and in the Earth's mantle are compared in Figure 4 and Table V. As noted previously (Ringwood, 1976), the abundances of the major lithophile elements Mg, Si, Ca and Al, which are relatively involatile, are similar in both cases. Two elements, Cr and Mn, are found to be appreciably more abundant in the Moon than in the Earth's mantle by factors of 1.4 and 1.5, respectively. We doubt whether the discrepancy is significant in the case of Cr, in view of assumptions and approximations made in estimating the differing partition behaviour of Cr as between lunar and terrestrial basalts and their respective refractory residua (Section 2). The implied small overabundance of Mn may be real in terms of the model adopted in this paper, and is probably related to the higher FeO abundance inferred for the source region of mare

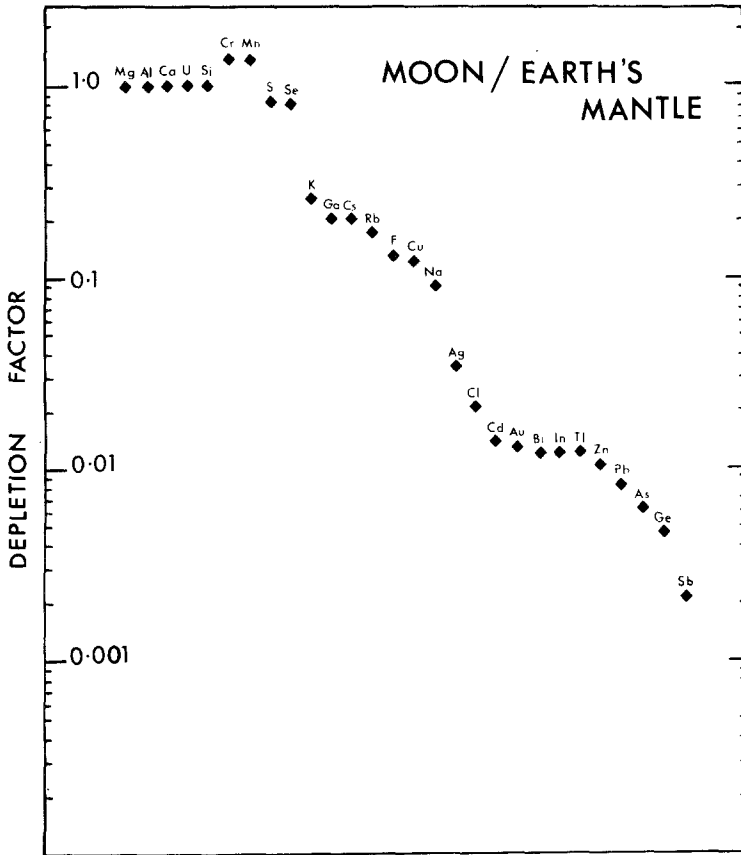


Fig. 4. Comparison of abundances of volatile elements in the Moon compared with corresponding abundances in the Earth's mantle.

basalts, as compared to terrestrial basalts (Ringwood, 1976). On the other hand, if the Mn content of the differentiated outer 400 km of the Moon is derived from the observed FeO/MnO ratio for this region (Section 2) combined with estimates of its FeO content (Ringwood, 1976), the Mn content is found to be significantly smaller than that of the Earth's mantle. It seems that if the Mn content of the bulk Moon were obtained by averaging that of mare basalt source regions below 400 km with that of the differentiated region above 400 km, the mean value obtained would be similar to that in the Earth's mantle.

Table V and Figure 4 show that the Moon is depleted in most volatile elements compared to the Earth's mantle, and, although important exceptions exist, there is a trend for the depletion factors to correspond to differing degrees of volatility. For example, fluorine (depletion factor 0.13) is less depleted than the more volatile chlorine (depletion factor 0.021). Likewise, the alkali metals and gallium (depletion factors 0.09–0.25) are less depleted than Zn, Ag, Cd, In, Bi and Tl (depletion factors 0.01–0.03), as would be expected from the relative volatilities shown in Table IV.

On the other hand, Ge, As and Sb (depletion factors 0.002–0.006) are more depleted in the Moon than the above group of elements, whereas the opposite trend would be expected for condensation/volatilization processes in a nebula of solar composition (Table IV). Calculations by Wai and Wasson (1977) show that the condensation of As, Sb and Ge in the solar nebula is strongly influenced by compound formation and solid solution with previously-condensed metallic iron. The condensation of these elements would occur at lower temperatures in an environment where metallic iron was absent. The strong depletion of these elements in the Moon thus suggest condensation in an environment very different from the solar nebula.

Two elements which are normally relatively volatile (S and Se) display similar abundances in the Earth's mantle and in the Moon (Table V). This is most remarkable in view of the strong relative depletions of all other volatile elements in the Moon. Most of the elements so strongly depleted in the Moon (Table V) are much less volatile in the solar nebula than S or Se (Table IV). The volatilities of S and Se are strongly affected by the abundance of hydrogen since the volatile species are H_2S and H_2Se . Volatilization of alkali metals and Ge whilst S and Se remain condensed can only occur in an environment in which the H_2/S and H_2/Se ratios are much smaller than those in the solar nebula (Ringwood, 1975). It seems, therefore, that the extremely strong fractionation of most volatile elements between Moon and Earth occurred in an environment in which hydrogen was strongly depleted as compared to the solar nebula.

Wasson (1971) has also discussed the comparative abundances of volatile elements in the Moon, Earth and ordinary chondrites, using as his data base the compositions of lunar mare basalts and terrestrial ocean-floor tholeiites. He concluded that Zn, Ag, Cd, Pb, Tl, Bi and In had been depleted by approximately similar factors as compared to the primordial abundances of these elements. This suggested that these volatile elements had been supplied to the Moon in the form of a small proportion of low-temperature condensate of primordial composition. According to our estimates (Table V), the relative abundances of these elements vary by more than a factor of 10 when normalized to primordial CI chondrite abundances. However, the uncertainties could be such that this may not be real, and Wasson's interpretation cannot, therefore, be firmly rejected. It does not, however, account for our estimate of the relative depletion of germanium within the Moon.

5. Siderophile Elements in the Earth's Mantle

Siderophile elements are those which become preferentially partitioned in the metal phase when metallic iron (or iron-nickel) and silicates are equilibrated. Generally speaking, the free energies of formation of the oxides of siderophile elements are comparable or smaller in magnitude than that of ferrous oxide. Such elements are spoken of as being more 'noble' than iron. Some, including Ni, Co, Ir, Pt, Re, possess low volatilities, either as metals or oxides, so that they are likely to be present in the earth in their primordial abundances. Others, such as Cu, Ag, Au, Ge, As, P are moderately volatile (Table V) so that they are likely to be depleted in the Earth compared to the primordial abundances.

TABLE VI

Abundances of some siderophile elements in pyrolite compared to Cl abundances together with relevant silicate/metal distribution coefficients.

Element	Pyrolite abundance ^[1] Cl abundance	K (silicate/metallic Fe)	Ref.
<i>Involatile</i>			
Co	0.08	0.005	[2]
Ni	0.07	0.0006	[3]
Re	0.001	5×10^{-4} – 10^{-6}	[4]
Os	0.004		
Ir	0.002	Probably similar	
Pt	0.01	to Au and Re	
<i>Volatile</i>			
P	0.04		
S	0.0017		
Cu	0.11	0.02–0.003	[2, 6]
Ge	0.013	0.001	[5]
As	0.23	< 0.01	[7]
Se	0.0015		
Pd	0.007		
Ag	0.055		
Au	0.01	$< 3 \times 10^{-5}$	[4]

[1] From Table III.

[2] Lovering, J. F.: 1957, *Geochim. Cosmochim. Acta* **12**, 253–261 (olivine-metal equilibrium).

[3] Buseck, P. and Goldstein, J.: 1969, *Bull. Geol. Soc. Am.* **80**, 2141–2158 (olivine-metal equilibrium).

[4] Kimura, K., Lewis, R., and Anders, E.: 1974, *Geochim. Cosmochim. Acta* **38**, 603–702 (basalt-metal equilibria; smaller part of quoted range for Re may be preferable because of more relevant redox conditions).

[5] Chou, C., Baedecker, L., and Wasson, J.: 1973, *Geochim. Cosmochim. Acta* **37**, 2159–2171 (chondritic silicate-metal equilibria).

[6] Allen, R. O. and Mason, B.: 1973, *Geochim. Cosmochim. Acta* **37**, 1435–1456 (chondritic silicate-metal equilibria).

[7] Fouche, K. and Smales, A.: 1967, *Chem. Geol.* **2**, 105–133 (chondritic silicate-metal equilibria).

In Table VI, we have compared the abundances of some siderophile elements in pyrolite with their primordial abundances (from Table V). These elements are all depleted in the upper mantle and it may confidently be assumed that they have become dominantly segregated into the core. Also shown are some relevant metal/silicate partition coefficients, mostly estimated from meteoritic data, for some of these elements. The remarkable feature (Ringwood, 1966a, b) is that the elements for which partition coefficients are available are much more abundant in the upper mantle by factors varying from 10 to 1000, than would be expected if these elements had been partitioned under equilibrium conditions into a metallic iron-nickel phase which had then become segregated into the Earth's core. From what is known of the general thermodynamic properties of Ir, Os, Pt, Pd and Ag compounds, the same conclusion almost certainly applies to these elements. The discrepancies in the cases of Cu, Au, Pd, Ag, Ge and As are probably greater than

indicated in Table VI since these elements are moderately volatile and may well have been intrinsically depleted in the bulk Earth by factors of 3 to 10 (so that the ratios in column 1 should be multiplied by these factors). Phosphorus, sulphur and selenium are also moderately volatile so that appropriate correction factors should again be introduced.

It is clear that these relationships must have a vital bearing upon the conditions under which core-formation occurred in the Earth. Ringwood (1959) suggested that a large increase in the distribution coefficient of nickel between silicates and metal caused by high pressures was responsible for the entry of nickel into the silicates of the deep mantle. However, he abandoned this explanation when it became clear that several other siderophile elements were similarly overabundant in the upper mantle (Ringwood, 1966a, b, 1971), since it would have been highly coincidental for pressure to change all of these partition coefficients in the same sense. Accordingly, he proposed a model of core-formation under disequilibrium conditions, in which material of primordial composition incorporated at an early stage of accretion was rapidly mixed into the mantle under conditions whereby equilibration with metallic iron did not occur. An analogous model, in which the primordial component was added to the earth at a late stage of accretion, and thereby became incorporated into the upper mantle only, was advocated by Turekian and Clark (1969), Clark *et al.* (1972) and Kimura *et al.* (1974).

Brett (1971) examined data on the distribution of siderophile elements in the mantle in the light of partition coefficient data available at that time and concluded that the abundances of most of these elements could be explained by low-pressure equilibrium partitioning between metal and silicate.

However, he agreed that nickel and cobalt were definitely overabundant and suggested that this could be explained in terms of large pressure effects upon the distribution coefficients for these elements. Ringwood (1971) pointed out that the partition coefficients for elements (other than Co and Ni) chosen by Brett were probably seriously in error because of contamination effects. Subsequent partition coefficient studies (refs. in Table VI) showed that this was indeed the case. Nevertheless, two additional sources of evidence now persuade us that there is room for compromise between the differing interpretations proposed by Ringwood and Brett.

(1) The dispersion of abundances of some siderophile elements, e.g., Ni, Co and Ge, in the rocks of the upper mantle is remarkably low. In fresh mantle-type ultramafic rocks, the vast majority of nickel and cobalt abundances are within $\pm 50\%$ of the mean values (Goles, 1967; Stueber and Goles, 1967); likewise, for cobalt and germanium in ocean-floor tholeiites and hence also in their mantle source regions (Frey *et al.*, 1974; Argollo, 1974; Wedepohl, 1974). It would be very difficult to explain these small dispersions by processes which involve *physical mixing* of two components of very different compositions as in the models of Ringwood and Clark *et al.* The uniformity may be better explained by the effects of high pressures on the partition coefficients at considerable depths in the mantle, followed by convective redistribution, as advocated by Brett.

On the other hand, the abundances of some siderophile elements (e.g., Au, Ir, Re, Os, Pt) show extremely wide dispersions among mantle rocks and basalts (references – Section

TABLE VII

Relative abundances of some siderophile elements in the Moon, the Earth's mantle and in CCI chondrites. Based on data from Tables I, III and V.

	I Mantle Moon	II CCI Chondrite Moon	III CCI Chondrite Earth's Mantle
<i>Involatile Group</i>			
Fe	0.6		
Ni	1.3	20	15
Co	0.9	8	12
W	1.0		
Re	80		
Os	0.6		
Ir	0.6		
<i>Intermediate Group</i>			
P	1.5	39	26
S	0.8	533	522
Se	1.2	853	650
<i>Volatile Group</i>			
Cu	9	72	9
Ga	5	25	5
Ge	224	17 700	79
As	167	668	4
Pd	≥ 1		
Ag	30	540	18
Sb	500		
Au	80		

2) and may be better explained by inhomogeneous mixing of a primordial component comparatively rich in these elements, with mantle material previously equilibrated with metal. According to this model (Ringwood, 1960, 1966a, b; Clark *et al.*, 1972), other volatiles such as H₂O, carbonaceous compounds, N₂ and the inert gases were likewise introduced into the mantle in varying proportions associated with this primordial component.

(2) If the oxidised nickel now present in the mantle has been introduced in the form of a low-temperature, metal-free condensate, as in the models of Ringwood and Clark *et al.*, then this condensate should also introduce primordial abundances of all elements (Table IV) which are fully condensed above 400 °K. (At temperatures higher than this, nickel would be present entirely in a metallic phase.) Thus, for example, germanium, which condenses at 820 °K should be present in the low-temperature condensate in an amount equal to the primordial Ni/Ge ratio of 357. However, the observed Ni/Ge ratio in the upper mantle is 2059 (Table III). Because of the small dispersions of Ge and Ni in mantle rocks, this ratio is firmly established. Moreover, on the basis of this model, the mantle should also contain the primordial Ni/Ir ratio of 7.8×10^4 , whereas the observed ratio is 3.3×10^6 (Table III).

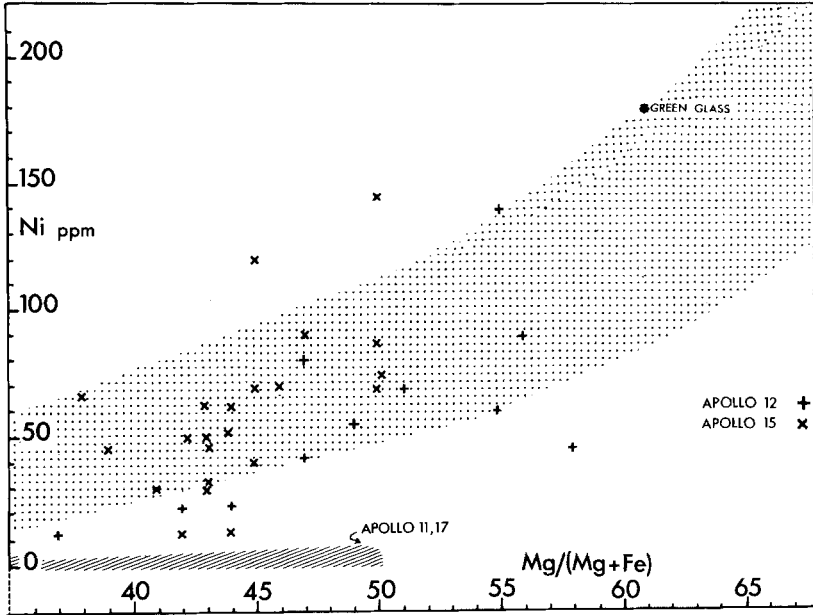


Fig. 5. Nickel contents versus $100 \text{ Mg}/(\text{Mg} + \text{Fe})$ ratios in low-Ti and high-Ti basalts compared with corresponding field (stippled) defined by Ni and $100 \text{ Mg}/(\text{Mg} + \text{Fe})$ ratios in terrestrial ocean-floor tholeiites. The latter field is based upon the data of Kay *et al.* (1970).

A. DISCUSSION

An adequate understanding of the abundance patterns displayed by siderophile elements in the mantle is likely to require a considerable amount of further data on the occurrences of these elements (particularly the platinum group) in ultramafic rocks and basalts, combined with extensive experimental determinations of relevant partition coefficients as functions of pressure and temperature. At present, there can be little doubt that most of these elements are considerably overabundant in the upper mantle compared to expectations based upon iron-silicate partition equilibria at low pressures. The observed patterns appear to reflect the operation of at least three processes.

(1) Incorporation of primordial low-temperature material in the mantle under conditions where equilibrium with metal was not achieved during core formation.

(2) Large displacements in metal/silicate partition equilibria caused by the effects of high pressures deep in the Earth's mantle, combined with convective mixing of material from the deep mantle into the upper mantle.

(3) Varying degrees of depletion of relatively volatile siderophile elements (e.g., Au, Ge, As, Cu, Ag) in the bulk Earth.

The important point is that each of these processes is intrinsically *terrestrial*, and not the result of generalized 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.*

6. Siderophile Elements in the Moon

Estimated abundance ratios of siderophile elements in the Moon and Earth's mantle are given in Table VII, column 1. One group which is characterized by low to intermediate volatility, displays similar relative abundances in both bodies. * On the other hand, those siderophile elements which are also volatile display substantial to strong depletions in the Moon by factors varying from 5 to 500. From the contrasting behaviour of the two groups, it is clear that the depletions are the result of volatility, not siderophile characteristics, as has sometimes been stated (e.g., Ringwood, 1970).

The inferred similarity in abundances of the involatile and intermediate groups of siderophile elements (Table VII) in the Moon and Earth's mantle is of profound genetic significance, as was recognized in the cases of W and P, by Wänke *et al.* (1976) and Dreibus *et al.* (1976). O'Keefe and Urey (1976) have also emphasized the significance of siderophile element abundance patterns and their bearing upon the relationship between Earth and Moon, although their detailed arguments differ in principle from the ones which we shall develop. Before commencing a general discussion, we shall consider the behaviour of some of these elements individually.

A. NICKEL

The relationship between nickel abundances and $100 \text{ Mg}/(\text{Mg} + \text{Fe})$ ratios for low-Ti and high-Ti mare basalts and also for terrestrial ocean-floor tholeiites is shown in Figure 5. An explanation for the low Ni contents of high-Ti basalts was provided by Ringwood and Kesson (1976). Because of their complex origins, high-Ti basalts are not believed to provide relevant information concerning the nickel content of the primordial, deep lunar interior. It is the low-Ti basalt suite which is of decisive importance in this connection (Ringwood and Kesson, 1976).

Low-Ti mare basalts appear to have been saturated with metal at eruption (Reid *et al.*, 1970). However, from a study of the nickel contents of metal grains precipitated at differing stages of crystallization, Reid *et al.* demonstrated that the metal had been produced by a reduction process in the near-surface environment. This is supported also by Sato *et al.*'s (1973) demonstration that in 12009, early-crystallized phenocrystic olivine shows $\log f_{\text{O}_2}$ values up to 0.4 units higher than those for the ground mass. It was concluded by Brett (1976a) that the reduction process was due to loss by volatilization of sulphur, probably occurring after eruption of the lava at the lunar surface. Accordingly, it followed that most or all of the nickel occurring in the magma at depth was originally present in the oxidized state as a NiO component. This interpretation is supported by the analysed NiO contents of early-formed olivine in some Apollo 12 basalts, ranging up to 400 ppm (Brett *et al.*, 1971).

Many Apollo 12 and 15 magmas are known to have experienced substantial degrees of near-surface olivine fractionation (e.g., Compston *et al.*, 1971; Chappell and Green, 1973).

* Excepting Re.

The effects of this fractionation upon the nickel contents of low-Ti basalt magmas are shown in Figure 5. The corresponding relationship between nickel contents of terrestrial ocean-floor tholeiites and their $100 \text{ Mg}/(\text{Mg} + \text{Fe})$ values, arising from near-surface fractionation of olivine (Kay *et al.*, 1970), is also shown. A large degree of overlap exists between lunar and terrestrial trends. Some of the scatter in the lunar rocks probably results from near-surface reduction and limited degrees of metal segregation.

The relationships shown in Figure 5 lead to several important conclusions.

(1) As in the case of terrestrial basalts, the variations in nickel contents of low-Ti basalts have been mainly controlled by olivine fractionation.

(2) In view of (1) above, and also in the light of evidence discussed previously, nickel was present in primitive low-Ti basalt magmas dominantly or exclusively in the *oxidized state*.

(3) Terrestrial ocean-floor tholeiites containing more than 200 ppm Ni are relatively rare. The abundances of nickel in ocean-floor tholeiites tend to level off at about 200 ppm, corresponding to $100 \text{ Mg}/(\text{Mg} + \text{Fe})$ values of 68–70 (Kay *et al.*, 1970). Liquids of this composition would be in equilibrium with residual peridotite (2000 ppm Ni, $100 \text{ Mg}/(\text{Mg} + \text{Fe}) = 90\text{--}92$). The most primitive low-Ti basalts contain 150–170 ppm of nickel (Figure 5) and these may well have undergone limited pre-eruptive olivine fractionation, so that the nickel content of the parental magmas could have been appreciably higher. We conclude that the nickel abundances in parental low-Ti basalt magmas and primitive terrestrial ocean-floor basalts were generally similar, implying similar abundances of nickel in the corresponding olivine and pyroxene components of their source regions.

(4) Following from (2) and (3) above, and also from evidence discussed earlier in this section, and from metal-silicate partition coefficient data described in Section 5, we conclude that primary low-Ti basalts have never been in equilibrium with metallic iron or with iron-rich metallic alloys. This conclusion applies equally to the source regions of low-Ti basalts.

B. COBALT

The mean cobalt content of terrestrial ocean-floor tholeiites (41 ppm) is similar to that of low-Ti mare basalts (45 ppm – Table I). Dispersions are low because cobalt is not nearly as effectively removed by olivine fractionation as is nickel (because of a much smaller olivine/liquid partition coefficient). We conclude that the abundance of cobalt is approximately the same in the source regions both of low-Ti mare basalts and terrestrial ocean-floor tholeiites. In Section 5, we showed that the abundance of cobalt in the Earth's mantle was much higher than could be explained if the mantle had once been equilibrated with metallic iron, which had subsequently been segregated into the core. As in the case of nickel, the lunar abundance of cobalt shows also that low-Ti basalt source regions are characterized by an oxygen fugacity which is too high to have permitted equilibration with metallic iron.

C. TUNGSTEN

Wänke *et al.* (1976) and Dreibus *et al.* (1976) pointed out that tungsten correlates closely with another involatile element, lanthanum, in all lunar samples, but that the W/La ratio is a factor of 12 smaller than the chondritic ratio. They also pointed out that some terrestrial rocks possess an approximately similar W/La ratio to the lunar ratio. The depletion of tungsten in terrestrial rocks may be attributed to its entry into the Earth's core, since tungsten is dominantly siderophile.

The Moon's core, if present, is very small compared to that of the Earth. The similarity of W/La ratios in terrestrial and lunar basalts is of considerable genetic significance as discussed later (Wänke *et al.*, 1976). Moreover it was shown earlier that the source regions of low-Ti mare basalts are not saturated with metallic iron and, therefore, could not have participated in core formation within the Moon.

The data in Table I confirm and extend Wänke's observation. Tungsten contents of low-Ti mare basalts and ocean-floor tholeiites show only limited dispersions and the means for both groups are almost identical. Since tungsten should behave as an incompatible element (W^{4+}) during magma genesis, it is likely that tungsten abundances in the respective source regions are similar.

D. IRIDIUM AND OSMIUM

The mean abundance of iridium in low-Ti mare basalts and terrestrial ocean-floor tholeiites are generally similar (Table I) although there is considerable dispersion. The strong depletion of iridium in 4 of the Apollo 15 basalts could have been caused by a very small degree of fractionation of metallic iron in the near-surface environment. The similarity in the mean Ir contents of terrestrial ocean-floor and low-Ti mare basalts is believed to be reflected by their respective source regions.

Although data are much more limited, the same conclusion appears to apply in the case of osmium.

By analogy with the discussion in Section 5, the abundances of these elements in both source regions are probably much too high for them to have been in equilibrium with metallic iron.

E. RHENIUM

Of the involatile siderophile elements, rhenium is the only one which appears (on the basis of rather limited data) to be strongly depleted (by about a factor of 80) in low-Ti mare basalts as compared to terrestrial basalts.

Explanations of the possible causes of this behaviour must necessarily be highly speculative. It is notable that in contrast to Os, Ir, and Pt, which are preferentially concentrated in refractory residua during the partial melting processes by which terrestrial basalts are formed, rhenium (probably present as Re^{4+}) appears to be preferentially concentrated in the basaltic magma (refs. in Data Base, Section 2). It is possible that under the more reducing conditions of the low-Ti basalt source regions in the lunar interior, rhenium is present in a lower valence state, Re^{3+} . In this valence state, rhenium is known to possess

unusual bonding and complexing characteristics and it is possible that these are responsible for its retention in the lunar interior. Another possibility warranting exploration is crystal field stabilization of Re^{3+} in octahedral sites in lunar mantle minerals.

Note that although we have previously concluded that neither the low-Ti mare basalt nor terrestrial basalt source regions possessed redox states appropriate to saturation by metallic iron, we are not suggesting that both source regions possessed similar oxygen fugacities. The presence of reduced species such as Cr^{2+} , V^{2+} , Ti^{3+} in mare basalts, combined with the near-absence of Fe^{3+} , show clearly that the mare basalt source region possessed a much lower ambient oxygen fugacity than the Earth's mantle. However, this was not sufficiently low to correspond to metallic iron-saturation.

F. PHOSPHORUS

Ordinary chondrites contain about 60% of the phosphorus present in CI chondrites and so this element can presumably be classed as moderately volatile (in the particular environment in which ordinary chondrites were formed). In the Earth's mantle, phosphorus is depleted by a factor of about 26 compared to CI chondrites. Part of this depletion could be caused by volatilization – we have seen that the Earth is substantially depleted relative to ordinary chondrites in several elements probably possessing comparable volatilities – e.g. Si, Cr, Na, Mn, K (Table V).

On the other hand, at the redox state of ordinary chondrites, phosphorus possesses both siderophile and lithophile tendencies, with appreciable proportions present both in silicate and metal phases. The depletion of phosphorus in the Earth's mantle is thus ascribed to a combination of volatile and siderophile behaviour. We suspect that the latter dominated, as in the case of cobalt and nickel.

The abundance of phosphorus in low-Ti mare basalts is seen to be very similar to that in terrestrial ocean-floor tholeiites (Tables I, VI and VII), and, because phosphorus (P^{5+}) is an incompatible element, this is likely to be true of their respective source regions. Dreibus *et al.* (1976) also obtained evidence suggesting similar phosphorus abundances in the Earth's mantle and in the Moon.

G. SULPHUR AND SELENIUM

Sulphur and selenium have become greatly depleted in the Earth's mantle as compared to CI chondrites as consequences of their combined volatile and siderophile properties. These elements are extremely volatile in the presence of hydrogen and in a nebula of solar composition, sulphur does not condense until 680 °K. We have noted already that the conditions under which a large proportion of the total primordial sulphur can be condensed in the bulk Earth, whilst most of the Mn, Na, K, and some Si are lost by volatilization, are extremely restrictive, and can only occur in an environment in which the $\text{H}_2/\text{H}_2\text{S}$ and $\text{H}_2/\text{H}_2\text{O}$ ratios are much smaller than are present in the solar nebula.

It has been suggested e.g. Moore and Fabbi (1971); Moore and Calk (1971) that terrestrial ocean-floor tholeiites are essentially sulphur-saturated on eruption. Our unpublished experimental data show that a primitive ocean-floor basalt liquid (8% FeO) requires

around 1200 ppm S for saturation at 5–10kb, 1240–1300 °C i.e. under the P.T. and f_{O_2} conditions equivalent to those pertaining during magma genesis in the earth's mantle. However Mathez (1976) has concluded that the sulphur content of many fresh, primitive (~ 7% FeO) ocean-floor basalts is only around 900 ppm. In view of our experimental results, we conclude that primitive ocean-floor tholeiites are not sulphur-saturated in their source regions, and that a sulphide phase does not remain in the residuum after partial melting. This conclusion is further supported by the very low sulphur contents observed in many unaltered harzburgite xenoliths (Wedepohl, 1974) which are believed to represent the material remaining after extensive partial melting in the Earth's mantle.

Primitive low-Ti basalts contain about 1150 ppm S and are believed to be undersaturated with sulphur (Brett, 1976). This conclusion is confirmed by Mathez' (1976) observation that the amount of sulphur required for saturation increases strongly with increasing FeO content of the liquid. The lunar basalts have FeO contents two to three times higher than those of primitive terrestrial ocean-floor tholeiites and yet their sulphur contents are very similar to those required for saturation of the terrestrial basalts. Because the low-Ti basalts were not sulphur-saturated, then it follows that there could not have been any sulphide phase remaining in the residuum after partial melting in the lunar interior.

Since the amount of sulphur remaining in either the lunar or terrestrial mantles after magma genesis was very small, sulphur would have behaved as an incompatible element during partial melting. Accordingly, the relative abundances of sulphur in the two basalt suites are believed to reflect those of their respective source regions. The same conclusion probably applies to selenium.

From Table I, we see that the abundances of sulphur and selenium are very similar in low-Ti mare basalts and in terrestrial basalts and conclude, therefore, that the abundances of S and Se in the Moon are very similar to those in the Earth's mantle. This is a remarkable observation, in view of the combined volatile and siderophile behaviour of these elements, and the very restrictive conditions (discussed above) which governed the condensation of sulphur in the Earth.

H. SIDEROPHILE ELEMENTS IN EUCRITES

There are some intriguing similarities between low-Ti mare basalts and eucritic meteorites, as well as some profound differences. Apart from having lower Ti and higher Al contents, eucrites possess generally similar bulk chemical compositions to low-Ti mare basalts and evidently were formed by partial melting on a small parent body which had experienced strong depletions of volatile elements. These depletions are qualitatively very similar (although not identical) to those exhibited by lunar mare basalts (e.g. Wänke *et al.*, 1976). Moreover, unlike most classes of meteorites, the eucrites formed from a reservoir possessing identical or very similar oxygen isotopic compositions to that from which the Earth and Moon were formed. For these reasons, close genetic relationships between Earth, Moon and eucrites have been postulated (e.g. Clayton and Mayeda, 1975).

However, several basic differences between eucrites and mare basalts should be recalled.

Firstly, the chemical (e.g. REE) and isotropic evolution of mare basalts has been much more complex, involving at least two stages of fractionations separated by a large time interval. Secondly, the ages of mare basalts and eucrites are very different. Finally, whilst Earth, Moon and the eucritic parent body were ultimately derived from a similar oxygen isotopic reservoir, there subsequently occurred a *chemical* isotopic fractionation which now differentiates eucrites on the one hand, from lunar and terrestrial basalts on the other (Taylor *et al.*, 1965; Clayton and Mayeda, 1975).

In the context of the present paper, an important difference is that eucrites were saturated (or almost so) with metallic iron (Stolper, 1976) whereas we have previously concluded that low-Ti mare basalts were substantially undersaturated with iron. It is, therefore, possible that eucrites formed in a differentiated parent body in which a metallic core segregated. Indeed, a survey of recent literature shows that the siderophile elements Ni, Co, Cu, Ga and W are substantially to significantly less abundant in eucrites as compared to low-Ti mare basalts. Other siderophile elements including Os, Re, Ag, Au and Ir show high dispersions in eucrites, their abundances overlapping those in low-Ti mare basalts. These elements are present at the parts per billion level and would be extremely susceptible to contamination, especially in meteorite samples which have been sitting for years in museums. For this reason, we do not believe that the measured abundances of Os, Re, etc. in eucrites are necessarily significant. On the other hand, Ni, Co, Cu, Ga and W are present at levels ranging from 10 000 to 100 ppb and are much less subject to contamination errors. The lower abundances of these elements in eucrites, as compared to low-Ti lunar basalts are, therefore, believed to be real, particularly in the cases of Ni and Co. However, the abundance of P appears to be similar in eucrites and low-Ti mare basalts and S abundances seem to overlap in both groups.

The trace-element relationships are evidently complicated and far from being understood. Nevertheless, the iron-saturated nature of eucrites combined with their relative depletions in key siderophile elements such as Ni and Co do not favour the derivation of the eucrite parent body from the Earth's mantle subsequent to core-formation as we have proposed in the case of the Moon.

7. Conclusions

In Part I of this series (Ringwood, 1977) we demonstrated that the major element composition of the bulk Moon was similar to that of the Earth's mantle, the principal difference being that the Moon was relatively depleted in volatile elements (sodium and potassium) and appeared to contain more FeO than the Earth's mantle. It was shown also that the abundances of U, Th and the REE in the bulk Moon and in the Earth's mantle were generally similar. Moreover, the oxygen isotope composition of the Moon is known to be identical to that of the Earth, in contrast to the differences displayed by nearly all groups of meteorites. These similarities point to a common genetic relationship between Earth and Moon.

In this paper, we have shown that the Earth's mantle and Moon possess similar abundances of the siderophile elements Ni, Co, W, Ir, Os, P, S, Se. The abundances of these

elements in the mantle have been determined by the interaction of several complex processes *unique to the Earth*, which relate to core formation and the distribution of siderophile elements between the metallic phase and silicates during this process. The abundances of these elements in the Earth's upper mantle are much higher than would be expected if the mantle had equilibrated with metallic iron, which had then segregated into the core. These 'overabundances' in the mantle are believed to reflect two main processes: (1) segregation of the core under highly specific conditions such that chemical equilibrium was not achieved between metal and silicate, and (2) large changes in metal/silicate partition coefficients for siderophile elements caused by the high pressure (and temperature) existing deep in the Earth's mantle.

These factors could not possibly have operated within the Moon, a body in which the core, *if present*, amounts to less than 10% of the proportional size of the Earth's core, and which, if present, must have formed under very different conditions from the Earth's core, and in a pressure field extending to a maximum of only 47 kilobars, as compared to 3.6 megabars for the Earth. The similarity in siderophile elements between the Moon and Earth's mantle therefore implies that *the Moon was derived from the Earth's mantle after the Earth's core had segregated*. See also Dreibus *et al.* (1976) and O'Keefe and Urey (1976).

There does not appear to be any other viable hypothesis to explain this 'terrestrial' siderophile element abundance pattern in the Moon. Clark *et al.* (1972) and others suggested that siderophile elements were added to the Earth's outer mantle (together with volatile elements) by the late accretion of a low temperature oxidized condensate from the solar nebula. Anders (1971, 1976) and Wasson (1971) have also suggested that volatile elements were added to Earth and Moon by such a process. However, in order for nickel to be incorporated in such a condensate as NiO, the temperatures in the nebula would need to be below 400°K. All the volatile elements and siderophile elements should be fully condensed at this temperature and present in their primordial proportions (Wasson, 1971). The following observations dispose of this interpretation.

(1) The relative abundances of many siderophile elements, e.g., Ir/Ni, Ge/Ni (Table V) in Earth and Moon depart grossly from the corresponding primordial ratios.

(2) The relative abundances of many volatile elements (e.g., Zn/Ge) (Table V) are very different between Moon and Earth and are also very different from the primordial (CI chondrites) relative abundances which should characterize any such low temperature condensate.

(3) The extreme depletion of volatile elements (by a factor of up to 200) in the Moon relative to the Earth (Table V) is not accompanied by corresponding relative depletions of many siderophile elements – a pattern inconsistent with the hypothesis invoking a late-stage condensate.

(4) The problems involved in incorporating any late-stage condensate deep in the planetary interior and of mixing this condensate *extremely uniformly* at the centimeter scale have been ignored. The very low dispersion of Co, Ni, Zn and Ge abundances in terrestrial ultramafic rocks are inconsistent with mechanical mixing.

We reiterate our conclusion that the involatile siderophile element abundances in the Moon and Earth cannot be explained by processes occurring in the solar nebula prior to accretion of both bodies. They are uniquely of terrestrial origin.

A. VOLATILE ELEMENTS

In Section 4, it was concluded that the abundance pattern of volatile elements in the Moon differed dramatically from the corresponding abundance patterns in ordinary chondrites and thus from patterns to be expected during condensation of a nebula of solar composition. These differences strongly suggested that the Moon did not form from components which themselves had condensed from a nebula of solar composition.

The drastic depletions of many volatile elements in the Moon compared to the Earth imply that the separation of material from the Earth's mantle to form the Moon occurred at very high temperatures. Depletions of this magnitude are best explained by the hypothesis that material from the Earth's mantle was totally evaporated, and then selectively recondensed, whilst the more volatile components were lost. It does not appear possible to explain the near-complete loss of many volatiles by surface evaporation from large volumes of solid or liquid material. Such processes are intrinsically inefficient.

Sulphur and selenium, two elements of high volatility in the solar nebula, are present in similar abundances in the Earth's mantle and Moon, whilst many other elements which are much less volatile in the nebula (e.g., Mn, Na, Ge) are greatly depleted in the Moon. This important relationship implies that the Moon fractionated from the Earth's mantle under conditions of low hydrogen fugacity, since S and Se (as H_2S and H_2Se) are considerably less volatile under these conditions.

Germanium is a key element because it is both volatile and siderophile and also because of its close geochemical coherence with Si^{4+} , it is very uniformly distributed within terrestrial basalts and ultramafics (Argollo, 1974; Wedepohl, 1974).

It is seen from Table V, that germanium is abnormally depleted in the Earth's mantle (depletion factor, $DF = 0.013$) compared to many other elements of comparable or greater volatility such as Zn ($DF = 0.05$ and Ga $DF = 0.2$). The additional depletion is caused by the siderophile nature of germanium which has largely entered the Earth's core. In the Moon, germanium is also abnormally depleted relative to other elements of greater volatility (e.g., Zn). The abundance of germanium in the Moon thus reflects the effect of the general depletion of volatiles in the Moon superimposed on a terrestrial fractionation pattern caused jointly by volatility and siderophile behaviour. It does not appear possible to explain the extremely low abundance of germanium in the Moon by any plausible cosmochemical fractionation processes occurring within the solar nebula. Similar considerations probably also apply in the cases of arsenic and antimony.

The above conclusions lend strong support to the hypothesis (Ringwood, 1960, 1966a, b, 1970a, b, 1972, 1975) that the Moon was ultimately derived from material evaporated from the Earth's outer mantle and selectively recondensed at some distance from the Earth under unique conditions which permitted further loss of volatile components. The volatile and siderophile element abundance patterns in the Moon cannot be explained in

terms of mixing of components which had condensed directly from the solar nebula. Thus, hypotheses requiring the Moon to have formed as an independent body by direct accretion in the solar nebula are not acceptable. For these and other reasons, the binary planet and capture hypotheses are rejected.

Our preferred working hypothesis is capable of being tested rigorously by new analytical data for the abundances of many volatile and siderophile elements in lunar and terrestrial rocks. For many of the elements discussed in previous sections, we have been obliged to use sparse and sometimes inadequate data. There are many other elements which could not be discussed because of the paucity or poor quality of the data, but which are vital to our arguments. The following data are especially required on as many samples as possible:

- (1) Abundances of all siderophile and volatile elements in glassy selvages of ocean-floor basalts, particularly those possessing high $\text{MgO}/(\text{MgO} + \text{FeO})$ ratios and Ni contents.
- (2) Abundances of these elements in fresh alpine ultramafic rocks and fresh peridotite inclusions in alkali basalts.
- (3) Abundances of these elements in low-Ti mare basalts possessing relatively high $\text{MgO}/(\text{MgO} + \text{FeO})$ ratios and Ni contents.
- (4) Satisfactory resolution of discrepancies presently existing between laboratories for analytical data on key elements such as Ge, Sb and As.

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