

Fractionation of siderophile elements in the earth's upper mantle

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Abstract—Abundances of 20 siderophile elements in the upper mantle of the earth have been estimated using available data on basalts and ultramafic rocks. The CI chondrite-normalized siderophile element/Ir ratios in the upper mantle show a large range of variation, and can be divided into two groups. The first group, consisting of eight noble metals (Ru, Rh, Pd, Re, Os, Ir, Pt, and Au), has nearly chondritic ratios (within a factor of 4). The noble metal group is interpreted as derived from meteoritic influx during late heavy bombardment after the formation of the core. Their concentrations can be explained by about 1% of CI-like material in the upper mantle. The second group, consisting of Ni, Co, Ge and others, has high element/Ir ratios (8–120× chondrites). The abundances of the Ni-Co-Ge group in the upper mantle appear to be related to the indigenous mechanisms invoking high oxygen fugacity and effects of high temperature and pressure at the core-mantle boundary region. The influx of meteoritic material could have increased the indigenous abundance by 30% for Ge and less than 10% for other elements of this group.

INTRODUCTION

Siderophile elements (Pt, Os, Ir, Pd, Ru, Rh, Ni, Re, Co, Ge, etc.) are those which are highly concentrated in the metallic phases of meteorites. These elements would either have condensed in the metal phases during nebular condensation stage or preferentially partitioned into the metal phases during metal-silicate equilibration in planetary bodies, as the siderophiles are thermochemically easily reduced to the metallic state. The knowledge of siderophile abundances in the earth's upper mantle is of great interest because these data are closely related to several fundamental planetary problems.

Ringwood (1966) and Ringwood and Kesson (1977) have shown that the abundances of siderophile elements in the upper mantle are remarkably higher than the values indicated by low-pressure partitioning experiments of these elements between metal and silicate phases. Several hypotheses have been proposed to explain the phenomenon (Ringwood, 1966, 1975; Turekian and Clark, 1969; Brett, 1971; Mao, 1974). Two most viable mechanisms are: 1) *Effects of pressure and temperature*. It is suggested that distribution coefficients of some elements between metal and silicate phases can be changed under high temperature and pressure conditions in the lower mantle (Brett, 1971; Mao, 1974; Ringwood, 1977). Therefore the silicate material in the lower mantle may contain an appreciable amount of siderophiles. Convection in the mantle after core formation may have brought the siderophile-rich material up to the upper

mantle. 2) *Meteoritic influx after core formation*. This hypothesis is supported by recent studies of lunar highland rocks of impact origin. Pristine crustal rocks contain very low concentrations of siderophiles. Lunar highlands breccias contain an excess amount of siderophile elements, which have been attributed to meteoritic influx after the formation of lunar crust (e.g., Hertogen *et al.*, 1977; Wasson *et al.*, 1975). On the earth, geochemical evidence for a similar bombardment during the early history of the earth is obscured in crustal rocks because of geological fractionation processes. However, excess siderophile contents may be preserved in the upper mantle, reflecting the extraterrestrial influx after the core formation that failed to equilibrate with the core because of the mantle barrier (e.g., Kimura *et al.*, 1974).

The relative effects of these processes can be assessed using siderophile abundance patterns. The high T and P mechanism in the lower mantle predicts a planetary pattern because of different crystallo-chemical properties of the elements. The meteoritic bombardment mechanism produces a chondritic pattern, assuming the projectiles are chondritic in composition. In this paper siderophile abundance pattern in the upper mantle is compiled following critical evaluation of all available data. The siderophile element/Ir ratios relative to CI chondrites are used to measure the enrichment of these elements, which may have bearings on the earth's upper mantle. Iridium is used for normalization because it is an immobile refractory siderophile element and has been accurately determined.

SIDEROPHILE ABUNDANCES IN THE EARTH'S UPPER MANTLE

There is no direct sample from the upper mantle. However, geophysical and geochemical evidence indicates that it is ultramafic in composition, perhaps close to garnet peridotite. Since basalt is derived from ultramafic rocks in the upper mantle by partial melting, the composition of the undepleted upper mantle can be estimated using a simple mixing model with basalts and ultramafic rocks as two components.

Table 1 shows concentrations of 20 elements in CI chondrites, basalts, ultramafic rocks and a model upper mantle. The sources for data and criteria for obtaining the mean values are listed in footnote of Table 1. In estimating the mean abundances in basalts, preference has been given to ocean floor tholeiites when data on these samples are available, since they are the least contaminated partial melt from the mantle. Palladium, Ir and Au show a remarkable difference between ocean floor and ocean island basalts; mean abundances in both types are listed.

Abundances in the ultramafic rocks can be estimated from various kinds of peridotites, including Alpine-type bodies, komatiites and inclusions in alkali basalts. Peridotitic komatiites are particularly important because they were formed by a large degree of partial melting of the mantle (e.g., Green, 1975). Possibly all phases except olivine have been melted. Abundances of Co, Ni, Pd, Pt, Au and Ir in komatiites have been determined by a number of authors (Arndt *et al.*, 1977; Nesbitt and Sun, 1976; MacRae and Crocket, 1977; Villaume and

Rose, 1977; Kuo and Wilson, 1976). Mean concentrations are listed in Table 1. The siderophile element/Ir ratios normalized to CI chondrites are Co, 97; Ni, 58; Pd, 7.7; Pt, 3.9; and Au, 3.5. These data indicate two interesting features of peridotitic komatiites: (1) Pt: Pd: Au ratios in komatiites are quite close to chondrites. However, Ir is low. Probably Ir is partly retained in the residual phases during partial melting; and (2) Co and Ni contents are higher by an order of magnitude than noble metals. This is discussed in later sections as such features appear to hold for ultramafic rocks and the upper mantle.

Alpine-type peridotites from the Mount Albert pluton have been analyzed for Pd, Os, Au and Ir by Crocket and Chyi (1972). Some noble metal data of Alpine-peridotites from Urals also have been reported by Fominykh and Khvostova (1970). The CI-normalized Pd/Ir, Os/Ir, and Au/Ir ratios for Alpine-type peridotites from Mount Albert are 3.1, 2.6, and 1.1, respectively. Yushko-Zakarova and Ilupin (1973) reported Pt and Pd contents in some garnet peridotite inclusions in kimberlite pipes. The CI-normalized Pd/Pt ratio has a range of 0.2 to 2.2 and averages 0.65.

Comparison of basalts with peridotites shows that some elements such as Ge, As and Ag have similar abundances in both types of rocks, whereas other elements are either enriched or depleted in basalts relative to peridotites. Hence, when the upper mantle undergoes partial melting, its abundances of siderophile elements are fractionated. The upper mantle abundances listed in Table 1 are calculated using 5:1 mix of ultramafic rocks and basalts based on a pyrolite model of Ringwood (1975).

In order to investigate the fractionation of siderophile elements I have calculated the siderophile element/Ir ratios, normalized to CI chondrites. These values are listed as $(SE/Ir)_{CI}$ in Table 1, and are plotted in Fig. 1. The CI-normalized siderophile element/Ir ratios vary over two orders of magnitude, indicating the siderophile element ratios in the upper mantle of the earth are highly fractionated. It shows an important feature that siderophile elements in the upper mantle can be classified into two groups. The first group has siderophile element ratios within a factor of 4 of that in chondrites. This group, comprising eight noble metals (Ru, Rh, Pd, Re, Os, Ir, Pt and Au), has the highest siderophile affinity. The remaining elements in Fig. 1, having siderophile element/Ir ratios much higher than that of CI chondrites, are generally only moderately siderophile. This pattern can be interpreted by a model involving two steps in the early history of the earth (Table 2):

- 1) During the core formation, highly siderophile elements were efficiently extracted into the core and severely depleted in the mantle; however, the efficiency of extraction of moderately siderophile elements was significantly lower and maintained approximately present levels in the mantle.

- 2) The meteoritic influx during the late heavy bombardment enhanced the concentrations of highly siderophile noble metals in the upper mantle, but caused insignificant changes on the moderately siderophile elements because of high indigenous background concentrations.

These mechanisms are discussed in the following sections.

Table 1. Abundances of 20 siderophile elements in CI chondrites, basalts, ultramafic rocks and the pyroclitic upper mantle of the earth, as well as the siderophile element/Ir ratios in the upper mantle relative to CI chondrites. Data on PCC-1, the most frequently analyzed peridotite, are also listed. Means are calculated following critical evaluation of all published results. Concentrations are in ng/g except Co, Ni, Cu, Ga and Ge in $\mu\text{g/g}$, and Fe in %.*

Ele m.	CI	Basalt	PCC-1	Komatiite	Alpine peridotite	Mean ultramafic	Upper mantle	(SE/Ir) _{CI} ‡
Fe	18.4	—	—	8.37	—	—	6.1	75.1
Co	480	41	112	104	—	110	98	46
Ni	11800	200	2500	1530	—	2000	1700	33
Cu	127	100	11.3	—	—	30	42	74
Ga	10.5	20	0.68	—	—	2.5	5.5	120
Ge	32.7	1.6	1.0	—	—	1.0	1.1	7.6
As	1800	1000	54	—	—	1000	1000	100
Mo	1400	1000	25	—	—	25	190	31
Ru	690	1	9.5	—	—	9.5	8.1	2.7
Rh	240	0.2	1.0	—	—	2.0	1.7	1.6
Pd	490	0.6* 1.9+	5.4	8.4	7.9	8.2	7.0	3.2
Ag	390	30	9.7	—	—	50	47	27
Sn	1600	1600	840	—	—	350	560	79
Sb	170	29	1500	—	—	100	88	120
W	140	150	60	—	—	60	75	120
Re	35.2	1.0	0.05	—	—	0.1	0.2	1.3
Os	510	0.1	7.2	—	6.7	6.0	5.0	2.2
Ir	450	0.05* 0.34+	5.1	1.0	2.5	2.4	2.0	1.0
Pt	1060	2.3	8	9.3	—	10	8.7	1.8
Au	180	0.3* 2.5+	0.77	2.0	1.1	3.0	2.7	3.5

*Ocean floor basalts. +Ocean island tholeiites.

‡Siderophile element/Ir ratios relative to CI chondrites.

†The sources of data and some criteria in compiling Table 1 are as follows.

CI chondrites: Chou *et al.* (1976a), Krähenbühl *et al.* (1973) and Mason (1971).

PCC-1: Flanagan (1976).

Basalts and peridotites:

Fe: Upper mantle abundance from Ringwood (1975). Peridotitic komatiite abundance from Arndt *et al.* (1977) and Nesbitt and Sun (1976).

Co: Arndt *et al.* (1977), Engel *et al.* (1965), Frey *et al.* (1974), and Nesbitt and Sun (1976).

Ni: Arndt *et al.* (1977), Fisher *et al.* (1969), Kay *et al.* (1970) and Nesbitt and Sun (1976). High Ni values in basalts with the least olivine fractionation were chosen.

Cu: Frey *et al.* (1974) and Goles (1967).

Ga: Baedeker *et al.* (1971) and Rhodes and Dawson (1975).

Ge: Baedeker *et al.* (1971) and Wedepohl (1974).

As: Onishi (1974).

Mo: Kuroda and Sandell (1954).

Ru: BCR-1 and PCC-1 values compiled by Flanagan (1976).

Rh: BCR-1 and PCC-1 values compiled by Flanagan (1976).

Pd: Ocean floor basalts from Crocket and Teruta (1977), ocean island tholeiites from Crocket and Skippen (1966), and peridotites from Crocket and Chyi (1972), MacRae and Crocket (1977), Fominykh and Khvostova (1970) and Yushko-Zakarova and Ilupin (1973).

Ag: Keays and Scott (1976), Laul *et al.* (1972) and Wedepohl (1974).

Sn: Hamaguchi *et al.* (1964), and data on standard basalts compiled by Flanagan (1973).

Sb: Tanner and Ehmann (1967) and Onishi and Sandell (1955).

W: Helsen and Shaw (1973) and Vinogradov (1962).

Re: BCR-1 from Morgan and Lovering (1967), Ganapathy *et al.* (1973), and data on two ocean ridge basalts cited by Kay and Hubbard (1978), and PCC-1 data by Lovering and Hughes (1971) and Morgan and Lovering (1967).

Os: W-1 and BCR-1 data by Crocket *et al.* (1968), Morgan (1965), and Bate and Huizenga (1963), PCC-1 by Lovering and Hughes (1971) and Morgan and Lovering (1967) and ultramafic rocks by Crocket and Chyi (1972) and Fominykh and Khvostova (1970).

Ir: Ocean floor basalts and Hawaiian tholeiites have different Ir contents. Thirty-four ocean floor basalts analyzed by Baedecker *et al.* (1971), Keays and Scott (1976) and Crocket and Teruta (1977) have 0.05 ± 0.08 ng/g Ir (1σ). Mean concentration of Ir in Hawaiian tholeiites is 0.34 ± 0.14 (1σ) ng/g based on data of 16 samples analyzed by Baedecker *et al.* (1971) and Gottfried and Greenland (1972), about a factor of 7 higher than ocean floor basalts. The Ir contents in ultramafic rocks were obtained using data on komatiites (MacRae and Crocket, 1977), alpine peridotites from Mount Albert pluton (Crocket and Chyi, 1972) and Urals (Fominykh and Khvostova, 1970) as well as those analyzed by Crocket and Teruta (1977) and Baedecker *et al.* (1971).

Pt: Basalt BCR-1 has 2.3 ng/g Pt (Rowe and Simon, 1971). Data on ultramafic rocks is estimated from komatiites (MacRae and Crocket, 1977), PCC-1 (Flanagan, 1976) and ultramafic rocks analyzed by Das Sarma *et al.* (1966).

Au: Gottfried *et al.* (1972) showed that ocean floor basalts are lower in Au than ocean island tholeiites. Their data along with Laul *et al.* (1972), Wasson and Baedecker (1970) and Ehmann *et al.* (1970) give 0.3 ng/g Au in ocean floor basalts and 2.5 ng/g Au in ocean ridge tholeiites. Data of Crocket and Teruta (1977) on DSDP Leg 37 are significantly higher in Au than other ocean ridge basalts. It is likely that their samples have been enriched in Au by secondary processes, since anomalies as high as 30–70 ng/g Au are found in some samples among the suite. Au in ultramafic rocks is estimated from Komatiites (MacRae and Crocket, 1977; Villaume and Rose, 1977; Kuo and Wilson, 1976; Anhaeusser *et al.*, 1975), and peridotites (Crocket and Chyi, 1972; Crocket, 1974).

ORIGIN OF HIGHLY SIDEROPHILE ELEMENTS (NOBLE METALS) IN THE UPPER MANTLE

This group consisting of eight noble metals is characterized by (1) much lower CI-normalized abundances in the upper mantle than the moderately siderophiles (e.g. Ni, Co, Ge); and (2) chondritic compositions. Noble metals have a strong siderophile affinity. Kimura *et al.* (1974) suggested that Au would be more siderophile under higher P and T based on limited thermodynamic data. Therefore it is very likely that noble metals were efficiently scavenged by the sinking metal phase during core formation. Core formation probably occurred very early in the earth's history. Oversby and Ringwood (1971) indicated that formation of the core occurred within 10^8 years following rapid accretion. After the accretion of terrestrial planets the intensive meteoritic bombardment continued for hundreds of million years (Wetherill, 1975). On the moon, there is ample evidence that this "late heavy bombardment" had occurred until 3.9 Ga ago and may well be episodic (Tera *et al.*, 1974). It is proposed here that the noble metal abundances in the upper mantle are related to the meteoritic influx associated with the late heavy bombardment.

Concentration. Let us first consider the amount of chondritic material required for explaining the abundances of noble metals. Fig. 1(A) shows that the concentrations are equivalent to 1.0 ± 0.4 % CI chondrite component (error of 1

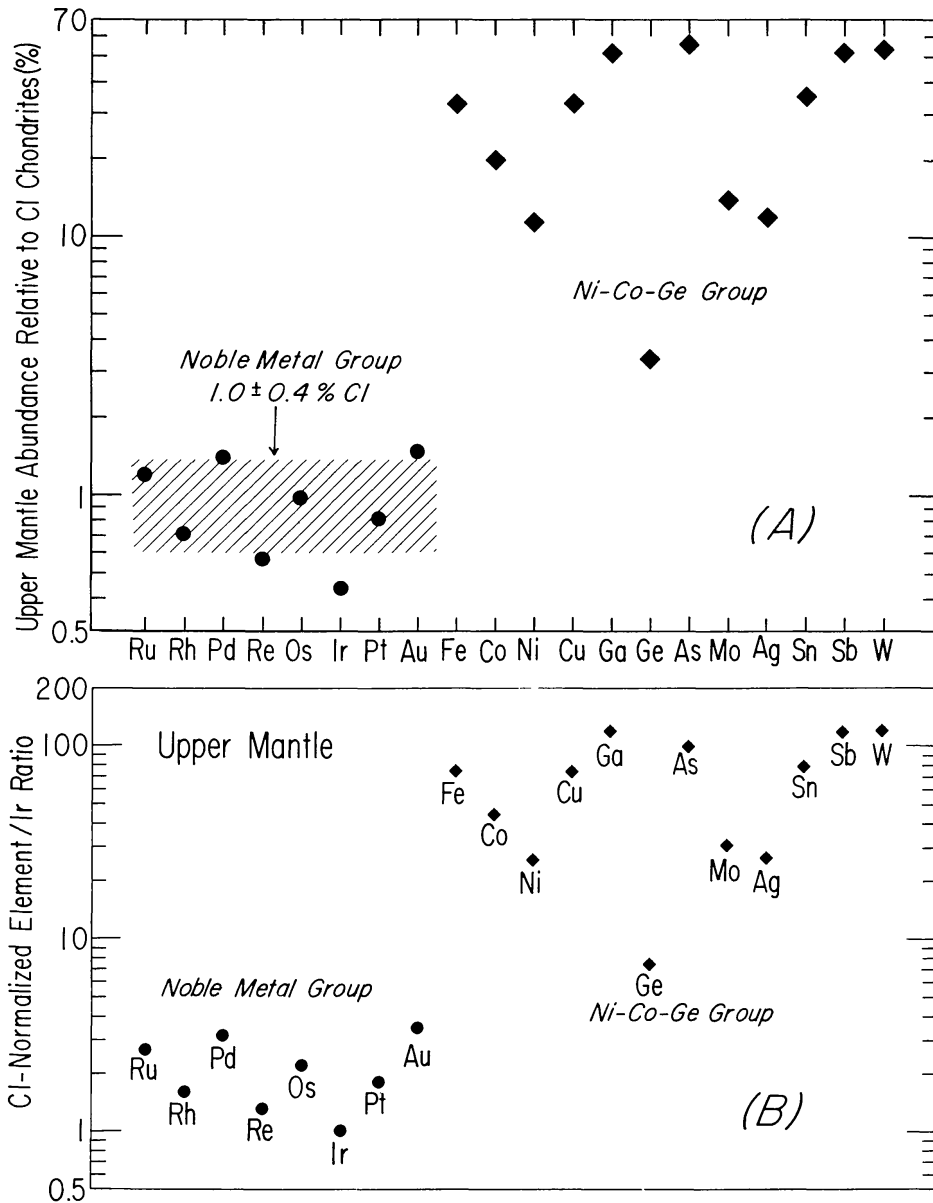


Fig. 1. (A) Abundances of siderophile elements in the upper mantle are normalized to CI chondrites, clearly indicating two groups—the noble metal group and the Ni-Co-Ge group. The abundances of noble metals can be interpreted by $1.0 \pm 0.4\%$ CI component in the upper mantle. The abundances of the Ni-Co-Ge group are related to the oxygen fugacity and effects of temperature and pressure in the core-mantle boundary region. Data are from Table 1. (B) CI-normalized siderophile element/Ir ratios in the upper mantle, indicating the noble metal group has ratios within a factor of 4 of CI chondrites, remarkably uniform considering the large sampling error. It is therefore suggested that noble metals in the upper mantle were acquired during the late heavy bombardment (until about 3.9 Ga) after the formation of the core (about 4.5 Ga). The ratios of the Ni-Co-Ge group are too high to be explained by meteoritic influx, but are indigenous to processes during formation of the mantle.

Table 2. Fractionation of siderophile elements in the upper mantle.

Group	Highly siderophile (Noble metals)	Moderately siderophile (Ni-Co-Ge group)
Elements	Ru, Rh, Pd, Re, Os, Ir, Pt, Au	Co, Ni, Cu, Ga, Ge, As, Mo, Ag, Sn, Sb, W
Element/Ir ratio relative to CI chondrites	1-4	8-120
Explanation	Chondritic composition indicating a meteoritic source during the late heavy bombardment follow- ing the core formation.	Low efficiency of extraction by the core, controlled by the oxygen fugacity in the mantle, and high pressure and temper- ature equilibration between the lower mantle and the core.

standard deviation). This value is close to the amount of the extralunar component in lunar mare regoliths, such as 1.18% at the Apollo 12 site and 1.33% at the Apollo 11 site, but lower than that at lunar highlands regoliths, 2.69% at the Apollo 14 site and 3.69% at the Apollo 16 site (Wasson *et al.*, 1975). The accretion rate per unit area is higher by a factor of 22 on the earth than on the moon (Ganapathy *et al.*, 1970; Singer and Bandermann, 1970), but the siderophile-rich layer on the earth is probably much thicker, implying that the concentration of the chondritic component doesn't have to be much higher in the earth's upper mantle than the lunar regolith.

Composition. The strongest evidence for the chondritic origin of noble metals in the upper mantle is their chondritic composition. No chondritic ratios are found in fractionated meteorites, such as eucrites (Morgan *et al.*, 1978; Chou *et al.*, 1976b) or silicate portions of ordinary chondrites (Chou *et al.*, 1973).

The siderophile element ratios could also reflect the mean composition of impacting planetesimals. It is of interest to compare these ratios to those of the lunar regolith. Some of the ratios in the upper mantle are compared to lunar highlands breccias (Table 3). It is found that the Au/Ir and Re/Ir ratios of the upper mantle are within the ranges of highlands breccias, and are close to group 1H, the most populated group of meteoritic components at the Apollo 16 site (Hertogen *et al.*, 1977). The Ge/Ir and Ni/Ir ratios in the upper mantle are considerably higher than highlands breccias. High Ge and Ni contents in the

 Table 3. Comparison of some CI chondrite-normalized siderophile element ratios in highlands breccias with the upper mantle of the earth. Lunar data were taken from Hertogen *et al.* (1977) and Wasson *et al.* (1975).

	Au/Ir	Re/Ir	Ge/Ir	Ni/Ir
Highlands breccias	0.2-6.6	0.6-1.5	0.1-2.4	0.7-2.6
Upper mantle	3.5	1.3	7.6	26

upper mantle are probably related to the oxygen fugacity and high T and P in the mantle as explained below.

ORIGIN OF MODERATELY SIDEROPHILE ELEMENTS (Ni-Co-Ge GROUP) IN THE UPPER MANTLE

Nickel, Co, and Ge, and a few other elements, are traditionally regarded as siderophile elements because of their partitioning into the metal phases in meteorites (Goldschmidt, 1954). Yet their concentrations in the upper mantle are rather high (Table 1). Figure 1 shows that the element/Ir ratios of this group of elements are 8–120× those of chondrites. I propose that this group of siderophile elements should be considered separately from the noble metals because their abundances are related to indigenous processes rather than meteoritic influx. This group of elements is called moderately siderophile elements or Ni-Co-Ge group since these three elements are the most frequently investigated. Their abundances are most likely to be related to oxygen fugacity in the mantle and high pressure and temperature effects in the lower mantle. Dubretsev and Pankov (1972) indicated that FeO would transform to the metallic state under high pressure, and the metallic FeO could be an important constituent of the outer core. Ringwood (1977) pointed out the significance of solubility of FeO in the metal, which may be accompanied by a large increase of oxygen fugacity in the core-mantle boundary region. Mao (1974), on the basis of his high-pressure experiments, suggested that FeO disproportionates into Fe⁰ and Fe³⁺. This explains the presence of a considerable amount of Fe³⁺ in the mantle. The oxygen fugacity, as a function of the amount of Fe³⁺, would accordingly increase in the lower mantle by this mechanism. Therefore some siderophile elements can be favorably incorporated in the silicate part of the earth because of oxygen fugacity. Thermodynamic calculations indicate that high pressure favors the incorporation of Ni in the silicate phase in the metal-silicate partition reaction (e.g. Brett, 1971). There are not enough thermodynamic data to show that all elements in the Ni-Co-Ge group behave similarly under high pressure and temperature conditions, but the possibility remains.

If the abundances of the Ni-Co-Ge group in the upper mantle are controlled by high T and P and maintained moderately high abundances during core-mantle segregation and thereafter, addition of 1% chondritic material during late heavy bombardment will only change the abundances of these elements to a limited extent. The chondritic influx after core formation would have enhanced indigenous abundances by 30% for Ge, 8.6% for Ni, and about 2–8% for all other elements of this group.

DISCUSSION OF THE MODEL

The model outlined in this paper differs from the inhomogeneous-accretion model of Turekian and Clark (1969) and Anders (1971) in using high P and T

planetary processes to explain the abundances of the Ni-Co-Ge group in the upper mantle while maintaining that noble metals were derived from meteoritic influx. Hence, the question of Ringwood and Kesson (1977) regarding the non-chondritic ratios of Ni/Ge and Ni/Au in the upper mantle can be explained.

Ringwood and Kesson (1977) pointed out an interesting question about the nature of uniform distribution of some siderophile elements (e.g., Ni, Co, and Ge) in the upper mantle as indicated by experimental results. The answer may be related to global mechanisms in the upper mantle, such as strong convection in the early history of the earth. However, noble metals do show large dispersions. For example, Pd, Ir and Au contents show a remarkable difference between ocean floor and ocean island tholeiites (Table 1), possibly indicating the heterogeneous nature of their source regions.

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