

# The composition of the Earth<sup>1</sup>

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## Abstract

Compositional models of the Earth are critically dependent on three main sources of information: the seismic profile of the Earth and its interpretation, comparisons between primitive meteorites and the solar nebula composition, and chemical and petrological models of peridotite–basalt melting relationships. Whereas a family of compositional models for the Earth are permissible based on these methods, the model that is most consistent with the seismological and geodynamic structure of the Earth comprises an upper and lower mantle of similar composition, an Fe–Ni core having between 5% and 15% of a low-atomic-weight element, and a mantle which, when compared to CI carbonaceous chondrites, is depleted in Mg and Si relative to the refractory lithophile elements.

The absolute and relative abundances of the refractory elements in carbonaceous, ordinary, and enstatite chondritic meteorites are compared. The bulk composition of an average CI carbonaceous chondrite is defined from previous compilations and from the refractory element compositions of different groups of chondrites. The absolute uncertainties in their refractory element compositions are evaluated by comparing ratios of these elements. These data are then used to evaluate existing models of the composition of the Silicate Earth.

The systematic behavior of major and trace elements during differentiation of the mantle is used to constrain the Silicate Earth composition. Seemingly fertile peridotites have experienced a previous melting event that must be accounted for when developing these models. The approach taken here avoids unnecessary assumptions inherent in several existing models, and results in an internally consistent Silicate Earth composition having chondritic proportions of the refractory lithophile elements at  $\sim 2.75$  times that in CI carbonaceous chondrites. Element ratios in peridotites, komatiites, basalts and various crustal rocks are used to assess the abundances of both non-lithophile and non-refractory elements in the Silicate Earth. These data provide insights into the accretion processes of the Earth, the chemical evolution of the Earth's mantle, the effect of core formation, and indicate negligible exchange between the core and mantle throughout the geologic record (the last 3.5 Ga).

The composition of the Earth's core is poorly constrained beyond its major constituents (i.e. an Fe–Ni alloy). Density contrasts between the inner and outer core boundary are used to suggest the presence ( $\sim 10 \pm 5\%$ ) of a light element or a combination of elements (e.g., O, S, Si) in the outer core. The core is the dominant repository of siderophile elements in the Earth. The limits of our understanding of the core's composition (including the light-element component) depend on models of core formation and the class of chondritic meteorites we have chosen when constructing models of the bulk Earth's composition.

The Earth has a bulk Fe/Al of  $\sim 20 \pm 2$ , established by assuming that the Earth's budget of Al is stored entirely within the Silicate Earth and Fe is partitioned between the Silicate Earth ( $\sim 14\%$ ) and the core ( $\sim 86\%$ ). Chon-

<sup>1</sup> This paper is dedicated to Ted Ringwood, his ideas and his enthusiasm.

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chondritic meteorites display a range of Fe/Al ratios, with many having a value close to 20. A comparison of the bulk composition of the Earth and chondritic meteorites reveals both similarities and differences, with the Earth being more strongly depleted in the more volatile elements. There is no group of meteorites that has a bulk composition matching that of the Earth's.

## 1. Introduction

An accurate and precise model of the chemical and isotopic composition of the Earth can yield much information regarding its accretion processes, and global-scale differentiation processes, including: core segregation, possible mineral fractionation in a primordial magma ocean and crust–mantle differentiation. With such a model we can also constrain compositional estimates for present-day reservoirs in the Silicate Earth and thus provide insights into their evolution. (The terms Silicate Earth and Primitive Mantle are synonymous.) There are three main approaches which have been used to model the composition of the Earth: (1) using the seismic profile of the core and mantle and their interpretation; (2) comparing the compositional systematics of primitive meteorites and the solar photosphere to constrain the solar nebula composition and from this estimate the composition of the inner rocky planets; and (3) using chemical and petrological models of peridotite–basalt melting relations (i.e. the pyrolite model).

The seismic velocity structure of the Earth, in combination with mineral physics data for phases at the appropriate pressures and temperatures, provide important information about the average density and from this the bulk composition of the crust, mantle and core. These data yield basic insights into the gross compositional characteristics of these regions, but cannot be used to constrain the minor- and trace-element composition of the Earth.

Compositional models based on primitive meteorites relates elemental abundances in the bulk Earth to those observed in chondritic meteorites in general, but particularly the CI carbonaceous chondrites, the most primitive of the chondritic meteorites. These meteorites are free of chondrules, possess the highest abundances of the moderately-volatile and volatile elements rela-

tive to the refractory elements, and have a composition that closely matches that of the solar photosphere (Anders and Ebihara, 1982; Anders and Grevesse, 1989), thus providing a scale with which we can compare other meteorites. The question remains however, do the chondritic meteorites, which are believed to be fragments of primordial accretionary material that formed during the early development of the solar nebula (Wasson, 1985), reflect the degree of chemical and isotopic heterogeneity in the early solar nebula? Perhaps other material such as comets, with a higher volatile to refractory element component compared to CI chondrites, have more primary signatures (Ringwood, 1989). It is from this heterogeneous collection of meteoritic materials that we attempt to construct and constrain our models of planetary compositions, in particular the bulk Earth composition.

Establishing the composition of the Silicate Earth is critical to our understanding of the composition of the Earth. One method of doing this is by investigating mantle-derived samples such as peridotite xenoliths, massif peridotites and primitive high-temperature melts (e.g., basalts and komatiites). Studies of peridotites provide direct information on the nature and composition of the upper mantle. Primitive basalts and komatiites, ranging from Archean to modern, are large degree partial melts of the mantle that have not experienced significant fractional crystallization or crustal contamination. They can thus provide additional, although less direct, information about the initial composition of their source regions as early as ~3.8 Ga. Chemical and isotopic studies of these lavas and peridotites can be used to construct a time-integrated evolution model for the Earth's mantle. There have been many attempts to do this (Ringwood, 1966, 1975; Jagoutz et al., 1979; Sun, 1982; Anderson, 1983; Wänke et al., 1984; Palme and Nickel,

Table 1  
Classification of the elements

<i>Lithophile elements:</i>	
Refractory	Be, Al, Ca, Sc, Ti, V <sup>a</sup> , Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th U
Transitional	Mg, Si, Cr <sup>a</sup>
Moderately volatile	Li, B, Na, K, Mn <sup>a</sup> , Rb, Cs <sup>a</sup>
Highly volatile	F, Cl, Br, I, Zn
<i>Siderophile elements:</i>	
Refractory	Mo, Ru, Rh, W, Re, Os, Ir, Pt
Transitional	Fe, Co, Ni, Pd
Moderately volatile	P, Cu, Ga, Ge, As, Ag, Sb, Au
Highly volatile	Tl, Bi
<i>Chalcophile elements:</i>	
Highly volatile	S, Se, Cd, In, Sn, Te, Hg, Pb
<i>Atmophile elements:</i>	
Highly volatile	H, He, C, N, O, Ne, Ar, Kr, Xe
50% CONDENSATION TEMPERATURES (K) AT 10 <sup>-4</sup> atm:	
Refractory elements	≥ 1,400
Transitional elements	~ 1,350 and ~ 1,250
Moderately volatile	~ 1,250 and ~ 800
Highly volatile	< 800

<sup>a</sup>At high pressure these elements may develop siderophile behavior and thus partition into the core.

1985; Taylor and McLennan, 1985; Hart and Zindler, 1986). All models assume that the refractory lithophile elements (Table 1) are in chondritic proportions. Beyond this, however, the models diverge in approach and assumptions. There are in general two groups of models: (1) those that assume the Silicate Earth has a complement of Mg and Si equal to that in CI carbonaceous chondrites, or (2) those that model the Silicate Earth as being depleted in Mg and Si relative to the refractory lithophile elements. In addition, there is no consensus regarding the absolute abundances of the refractory lithophile elements in the Silicate Earth, and there is even less agreement regarding the relative and absolute abundances of the moderately-volatile (e.g., Na, K, Rb, As, Sb, Ge) and the volatile elements (e.g., S, Se, Cd, Pb, Bi, Tl) in the Silicate Earth.

None of the three approaches outlined above can be adopted unilaterally when establishing a compositional model for the Earth. Data from geophysical, geochemical and cosmological studies need to be integrated into a model in order to

make it consistent with our understanding of the present geodynamic structure of the Earth. Observations of the Earth's geodynamic cycle (e.g., fate of subducted oceanic lithosphere, inclusions in diamonds, origins of mantle plumes) can underpin our models for the composition of the lower mantle. Insights gained from these studies will be particularly useful when evaluating the material exchange between the upper mantle, transition zone and lower mantle. Moreover, a very real appreciation of the assumptions and uncertainties in the geophysical, geochemical and cosmological models is needed.

## 2. Physical properties of the Earth

The two major divisions of the Earth are the metallic and silicate portions, the core and mantle (including the crust), respectively. These regions are divided into subregions based on their

seismic velocity characteristics. The silicate portion of the Earth is subdivided into the crust, upper mantle, transition zone and lower mantle, with each region separated by a seismic discontinuity and having a distinct seismic velocity gradient. The core, or metallic Earth, is subdivided into an outer liquid shell and inner solid region that is dominantly composed of a mixture of Fe and Ni, which is assumed to be in chondritic proportions ( $\text{Fe/Ni} \approx 17$ ).

The physical properties of the three main regions of the mantle are distinct which, in principle, could be due to either compositional changes or phase changes with depth. There is considerable debate surrounding these issues. The upper mantle, that region beneath the Mohorovicic discontinuity and above the  $\sim 410$ -km-deep seismic discontinuity, is the most studied and best understood part of the mantle, and in this region there is considerable agreement between geochemists, petrologists and geophysicists. The upper mantle consists of olivine, 2 pyroxenes and garnet and has a pyrolitic composition (Ringwood, 1975). The transition zone, between the 410- and 660-km discontinuities, has a distinct mineralogy, a strong seismic velocity gradient and different physical characteristics from the upper mantle. It is believed to play an important role in the geodynamic evolution of the Earth (Ringwood, 1994). Our understanding of the lower mantle, beneath the 660-km seismic discontinuity, is generally restricted to information derived from seismology, mineral physics and fluid dynamic experiments.

Although we have fragments of the mantle from each of its three main regions, it is the upper mantle that provides the greatest amount of material. Samples of the upper mantle are most often brought up to the surface by magmas, as xenolith fragments, or through tectonic processes such as the emplacement of massif peridotite and ophiolite bodies. Samples of the transition zone and the lower mantle have been recognized as inclusions in diamonds and polyminerale fragments in kimberlites (Scott-Smith et al., 1984; R.O. Moore and Gurney, 1985; Haggerty, 1991; Kesson and Fitz Gerald, 1991; Harris and Harte, 1994).

There is a growing consensus in the seismological and mineral physics community that the bulk composition of the mantle above the 660-km discontinuity is similar to that of the lower mantle. There still remains, however, some doubt about this conclusion due to the uncertainties in the experimental data and their extrapolation to appropriate pressure and temperature conditions (Jackson, 1983; Weidner, 1986). These uncertainties allow for alternative model compositions (Anderson, 1989; Agee, 1993) which argue against bulk chemical homogeneity in the mantle. Importantly, Kesson and Fitz Gerald (1991) showed that the composition of mineral inclusions in diamonds that formed in the lower mantle were in equilibrium with a mantle having a similar bulk composition to that of the upper mantle. Moreover, seismic evidence of subducted slabs penetrating the 660-km discontinuity (Creager and Jordan, 1984, 1986; Van der Hilst et al., 1991), combined with observations on the geoid and constraints from fluid dynamics (Hager and Richards, 1989; Davies and Richards, 1992), indicate that there is considerable mass transfer between the upper and lower mantle. Thus, it follows that the bulk compositions of the upper and lower mantle are similar.

It has been recognized for some time that the seismically constrained density of the liquid outer core is lower than that of an Fe–Ni alloy. This has led to the suggestion that  $\sim 5$ – $15\%$  of a low-atomic-weight element is present in the outer core. There are few constraints on the nature of this light element in the outer core. A number of candidate elements, including O, Si, S, C, H, have been proposed and it is possible that more than one of these is present. We will discuss the composition of the Earth's core in Section 6.

### 3. Estimating the Earth's mantle composition

In this section the two classes of mantle model, the pyrolite model and CI carbonaceous chondrite model, are reviewed. One of the earliest estimates of the Earth's mantle composition is provided by Ringwood's (1962, 1966) pyrolite model. This model uses the complementary

melt–residuum relationship between basalts and peridotites as a basis for estimating the major- and minor-element composition of the Earth's upper mantle. Ringwood (1966) showed that this model was consistent with heat flow data, and found that the refractory lithophile element composition of the pyrolite model closely matched the composition of CI carbonaceous chondrites, minus the core components. Subsequent compositional estimates of the Earth's primitive mantle (Jagoutz et al., 1979; Sun, 1982; Wänke et al., 1984; Palme and Nickel, 1985; Hart and Zindler, 1986) have also used the compositions of fertile peridotites and/or high-temperature melts derived from peridotite to establish the composition of the Earth's primitive mantle. These models show remarkable similarity to one another and also to the original pyrolite model. This is most significant in view of the separate data sets and independent methods of derivation used in constructing these models. For the most part, the pyrolite class of models argue for compositional homogeneity between upper and lower mantle.

One of the principal objections to pyrolite-type models has been the use of peridotites and high-temperature melts to infer the composition of the deep mantle. Some have suggested that these materials are samples of only the upper mantle, and not the lower mantle. If the lower mantle is compositionally distinct from the upper mantle, then the usefulness of any model which is based on data from peridotites and their melts are limited.

The second class of models can generally be referred to as the CI chondrite-type, where the Earth is assumed to have a bulk “major-element” composition equal to that of CI chondrites. The reason for specifying “major element”, is because this class of models assumes the Earth has a major-element composition of CI chondrites, but is depleted in volatile trace elements relative to CI chondrites. For example, the Earth is considered to have K/U and Rb/Sr ratios which are much lower than those of CI chondrites (Gast, 1960; Clark and Ringwood, 1964).

Several workers (Ringwood, 1966; Ganapathy and Anders, 1974; Morgan and Anders, 1980; Anderson, 1983; Taylor and McLennan, 1985) have appealed to the CI chondrite-type model for various seismological and cosmochemical reasons. A requirement of this class of model is that the mantle experienced global-scale differentiation early in Earth history which was not subsequently erased by convective re-homogenization. It is necessary to invoke this differentiation processes in order to explain the depletion in Mg and Si relative to the refractory lithophile elements that is observed in the upper mantle. In this model the 660-km seismic discontinuity represents not only a major phase change, but also a boundary layer isolating convection in the mantle. Alternative models may appeal to sequestering of Si into the core. However, this still requires an explanation for the depletion of Mg relative to the refractory lithophile elements that is observed for the upper mantle.

In the CI chondrite-type models, the primitive mantle composition is enriched in the refractory lithophile elements by  $\sim 1.5$  times a CI chondrite composition (on a volatile-free basis). This enrichment factor is simply the result of core separation (i.e. separating out  $\sim 32.5\%$  by mass of the Earth).

A CI chondritic model is a good starting point from a historical perspective, but these models cannot predict the abundances of the moderately-volatile and volatile lithophile elements in the Earth's primitive mantle (Ringwood, 1975; Jagoutz et al., 1979; Sun, 1982). In addition, the O isotopic compositions (Clayton, 1977) and bulk O contents of carbonaceous chondrites are distinctly different from that of the Earth and Moon, suggesting their formation in a separate region of the solar nebula. The wide variation in Mg/Si ratios in chondritic meteorites reflects the degree of chemical heterogeneity in the nebula (Taylor, 1993). Therefore, considering the different evolutionary histories of the Earth and CI chondrites, there is no reason to assume a CI composition a priori for the Earth, in particular, the Mg/Si ratio.

#### 4. Recommended composition of CI carbonaceous chondrites

A primary purpose of this study is to evaluate the existing models for the composition of the Earth and to present a revised model of its composition. To do this and to compare this estimate to chondritic meteorites, it is necessary to ex-

amine in detail the average composition of CI carbonaceous chondrites. It is therefore necessary to evaluate and update the existing average CI chondrite composition (Palme et al., 1981; Anders and Ebihara, 1982; Palme, 1988; Wasson and Kallemeyn, 1988; Anders and Grevesse, 1989). Special emphasis is given to ensuring that an internally consistent data set is used for com-

Table 2  
Recommended composition for CI Carbonaceous chondrites

Element	This study	Anders & G	Palme	Wasson & K	Element	This study	Anders & G	Palme	Wasson & K
Li (ppm)	1.5	1.50	1.45	1.57	Pd ppb	550	560	530	560
Be	0.025	0.025	0.025	0.027	Ag	200	199	210	208
B	0.9	0.87	0.27	1.20	Cd	710	686	770	650
C (%)	3.50	3.45	3.50	3.20	In	80	80	80	80
N (ppm)	3,180	3,180	3,180	1,500	Sn	1,650	1,720	1,750	1,720
F	60	60.7	54	64	Sb	140	142	130	153
Na	5,100	5,000	5,020	4,900	Tc	2,330	2,320	2,340	2,400
Mg (%)	9.65	9.89	9.40	9.70	I	450	433	560	500
Al (%)	0.860	0.868	0.820	0.860	Cs	190	187	190	183
Si (%)	10.65	10.64	10.70	10.50	Ba	2,410	2,340	2,600	2,300
P (ppm)	1,080	1,220	1,010	1,020	La	237	234.7	245	236
S (%)	5.40	6.25	5.80	5.90	Ce	613	603.2	638	616
Cl (ppm)	680	704	678	680	Pr	92.8	89.1	96.0	92.9
K	550	558	517	560	Nd	457	452.4	474	457
Ca (%)	0.925	0.928	0.900	0.920	Sm	148	147.1	154	149
Sc (ppm)	5.92	5.82	5.90	5.80	Eu	56.3	56.0	58	56
Ti	440	436	440	420	Gd	199	196.6	204	197
V	56	56.5	56	55	Tb	36.1	36.3	37.0	35.5
Cr	2,650	2,660	2,670	2,650	Dy	246	242.7	254	245
Mn	1,920	1,990	1,820	1,900	Ho	54.6	55.6	57.0	54.7
Fe (%)	18.1	19.04	18.30	18.20	Er	160	158.9	166	160
Co (ppm)	500	502	501	508	Tm	24.7	24.2	26.0	24.7
Ni	10,500	11,000	10,800	10,700	Yb	161	162.5	165	159
Cu	120	126	108	121	Lu	24.6	24.3	25.0	24.5
Zn	310	312	347	312	Hf	103	104	106	120
Ga	9.2	10.0	9.1	9.8	Ta	13.6	14.2	14	16
Ge	31	32.7	31.3	33.0	W	93	92.6	93	100
As	1.85	1.86	1.85	1.84	Re	40	36.5	37	37
Se	21	18.6	18.9	19.6	Os	490	486	490	490
Br	3.57	3.57	3.56	3.60	Ir	455	481	480	460
Rb	2.30	2.30	2.06	2.22	Pt	1,010	990	1,050	990
Sr	7.25	7.80	8.60	7.90	Au	140	140	140	144
Y	1.57	1.56	1.57	1.44	Hg	300	258	5,300	390
Zr	3.82	3.94	3.87	3.8	Tl	140	142	140	142
Nb (ppb)	240	246	246	270	Pb	2,470	2,470	2,430	2,400
Mo	900	928	920	920	Bi	110	114	110	110
Ru	710	712	690	710	Th	29	29.4	29	29
Rh	130	134	130	134	U	7.4	8.1	8.2	8.2

From Li to Zr element concentrations are given in ppm; Nb to U are given in ppb; and C, Mg, Al, Si, S, Ca and Fe are in wt%. Anders & G = Anders and Grevesse (1989); Palme = Palme (1988); Wasson & K = Wasson and Kallemeyn (1988).

parison with the Silicate Earth's composition. Previous compilations and their source references are used as a foundation on which revisions were then made; these studies are the most recent and thorough evaluations of the existing data.

Table 2 presents our recommended values for the average composition of the CI carbonaceous chondrites. The table also provides a comparison with the previous compilations mentioned above. Our composition was developed from the available data, as cited in the earlier papers (Palme et al., 1981; Anders and Ebihara, 1982; Palme, 1988; Wasson and Kallemeyn, 1988; Anders and Grevesse, 1989), and from later work, particularly that which reports new, high-quality measurements of chondritic materials (Beer et al., 1984; Morgan, 1985; Walker and Morgan, 1989; Dreibus et al., 1993; Jochum et al., 1993; Rocholl and Jochum, 1993).

For establishing a best estimate composition for CI chondrites we considered that refractory element ratios are relatively constant in the chondritic meteorites. This constraint is particularly important given the limited major-element database for CI chondrites. There are only 5 specimens of CI carbonaceous chondrites; of these 5 specimens, there is only compositional data for 3 of them (Orgueil, Ivuna and Alais) that are reliable enough for making this compilation.

Table 3 lists some element ratios in carbonaceous chondrites and an estimate of their relative variation. Data for enstatite and ordinary chondrites are used to place some important constraints on refractory element ratios in carbonaceous chondrites. For example, as noted by Anders and Ebihara, there are no Rh data for the carbonaceous chondrites. The large data set of Kallemeyn, Wasson and coworkers (Kallemeyn and Wasson, 1981, 1982, 1985, 1986; Wasson, 1985; Wasson and Kallemeyn, 1988; Kallemeyn et al., 1989, 1991, 1994) provides a strong foundation with which to evaluate the chemical variation found in chondritic meteorites, because all of these data were determined at one, well-established (and dependable) laboratory, using a single technique (neutron activation analyses)

which has a standard deviation of replicate analyses for the Allende standard at  $\leq \pm 5\%$  for most of these elements. From this data set we have characterized the refractory element variations in CI carbonaceous chondrites.

An inspection of Table 3 shows that many refractory element ratios are fairly well established in the chondritic meteorites (i.e.  $\leq \pm 10\%$  variation at the  $1\sigma$  level). Thus, given sufficient justification for the Earth possessing a chondritic proportion of the refractory lithophile elements, ratios of these elements can be used to critically evaluate the internal consistency in the proposed Silicate Earth models.

## 5. Composition of the Silicate Earth (Primitive Mantle)

Geophysical data provide some compelling evidence for gross scale chemical homogeneity of the mantle, implying considerable mass transfer between the upper and lower mantle. Thus, samples of peridotites and mafic to ultramafic magmas can be used to examine the composition of the Silicate Earth in detail. The model presented here has several features in common with pyrolyte-type models discussed earlier, although we will present some contrasts between our and these models.

The 160 peridotites used in this study occur as either xenoliths ( $n=76$ ) or massifs ( $n=84$ ). Two selection criteria were used for choosing the samples used in this study, namely that all samples: (1) have  $\leq 40.5$  wt% MgO; and (2) show no evidence of metasomatic enrichment, for example, they have a chondrite-normalized rare-earth element (REE) pattern in which the  $[La/Yb]_N \leq 2$ . The first criterion eliminates samples which have experienced excessive loss of a basaltic component. The second criterion eliminates only a few additional samples, but its purpose was to reject samples which have been modified by secondary enrichment processes.

Fig. 1 is a plot of MgO vs. CaO,  $Al_2O_3$ , Ni and Yb for the xenolith and massif samples used in this study. The trends shown by these samples are typical of peridotites worldwide (Maaløe and

Table 3  
Element ratios in chondritic meteorites

	CI	Carbonaceous	Ordinary	Enstatite
Mg/Si	0.906	0.91 ± 0.04	0.81 ± 0.03	0.70 ± 0.07
Al/Mg	0.0891	0.105 ± 0.010	0.081 ± 0.002	0.075 ± 0.003
Ca/Al	1.076	1.07 ± 0.06	1.08 ± 0.04	1.01 ± 0.08
Al/Sc	0.145	0.150 ± 0.009	0.145 ± 0.005	0.145 ± 0.007
Al/Yb	5.34	5.44 ± 0.35	5.45 ± 0.24	5.50 ± 0.35
Al/Ti	19.5	19.9 ± 1.3	19.6 ± 0.9	18.5 ± 3.0
Ca/Sc	0.156	0.160 ± 0.009	0.156 ± 0.006	0.143 ± 0.014
Ca/Yb	5.75	5.86 ± 0.27	5.88 ± 0.30	5.46 ± 0.51
Ca/Ti	21.0	21.1 ± 1.1	21.0 ± 1.0	19.1 ± 2.2
Ti/Sc	74.3	75 ± 6	75 ± 3	74 ± 7
Sc/Yb	36.8	36.4 ± 1.8	37.7 ± 1.9	37.9 ± 3.1
Sm/Yb	0.919	0.89 ± 0.04	0.90 ± 0.04	0.86 ± 0.05
Fe/Al	21.0	16.2 ± 2.4	24 ± 1/17 ± 1	35 ± 3/21 ± 4
Fe/Mg	1.88	1.68 ± 0.12	1.9 ± 0.1/1.4 ± 0.1	2.6 ± 0.2/1.6 ± 0.2
Fe/Ni	17.2	18.1 ± 1.4	17.5 ± 1.1	16.5 ± 0.8
Fe/Cr	68.3	66 ± 5	74 ± 4/53 ± 4	72 ± 14/90 ± 6
Cr/V	47	40 ± 3	50 ± 1	55 ± 5
Mg/Cr	36.4	39 ± 2	39 ± 1	45 ± 8/35 ± 4
Cr/Mn	1.4	2.2 ± 0.5	1.51 ± 0.08	1.54 ± 0.13
Mg/V	0.172	0.157 ± 0.009	0.195 ± 0.006	0.204 ± 0.025
Os/Ir	1.077	1.07 ± 0.04	1.07 ± 0.03	1.15 ± 0.06
Na/K	9.3	10.7 ± 2.1	8.2 ± 0.6	8.4 ± 0.8

Average values are reported for the Carbonaceous chondrites (CI, CM, CO, CV and CK), the Ordinary chondrites (L, LL and H) and the Enstatite chondrites (EL and EH). Ratios of Mg, Si, Al, Ca, Ti (except Ti/Sc and Cr/V), Cr, Mn, Fe and Ni are in wt%, and for Na, K, Sc, V, Yb, Os and Ir are given in ppm. Where two values are given the first is the average for the high-Fe group/the second for the low-Fe group. Ratios and  $\pm 1$  standard deviations were determined on relatively unaltered chondritic meteorites.

Aoki, 1977; BVSP, 1981; McDonough, 1990b), suggesting that similar magmatic and metamorphic processes operated in all tectonic environments. There is a slight distinction in the trends for massif and xenolith peridotites in the  $Al_2O_3$  vs. MgO diagram. Although this difference is not statistically significant, this distinction may reflect different depths of melt separation. The isotopic and chemical data for these peridotites imply that none of these samples are pristine mantle. Some have had a melt component extracted, while others may have experienced a limited degree of secondary melt enrichment. However, our attempt is to establish their initial compositions by using a melt–residuum relationship to “see through” previous melting event(s).

Fig. 2 presents mantle-normalized plots for representative peridotites used in this study. A reference mantle composition was used for nor-

malization, which assumed chondritic proportions of the refractory lithophile elements. This diagram illustrates the systematic behavior of the major and trace elements in these peridotites. Elements are positioned according to their relative enrichment (or incompatibility) in basaltic melts, with increasing melt enrichment factors increasing from right to left. The Si contents of the melt and residue are similar (i.e. the bulk distribution coefficient for Si is  $\sim 1$ ), whereas the abundances of Mn, Ca and Al are higher (and Mg lower) in basalts relative to their source regions. Other elements (e.g., Fe, Ni, Co, Cr, V, Cu, Zn) can be added to this diagram; their position is determined by their relative distribution between melt and residue (i.e. their melt enrichment factor).

The data for these peridotites also define coherent trends in ratio–ratio plots in which the



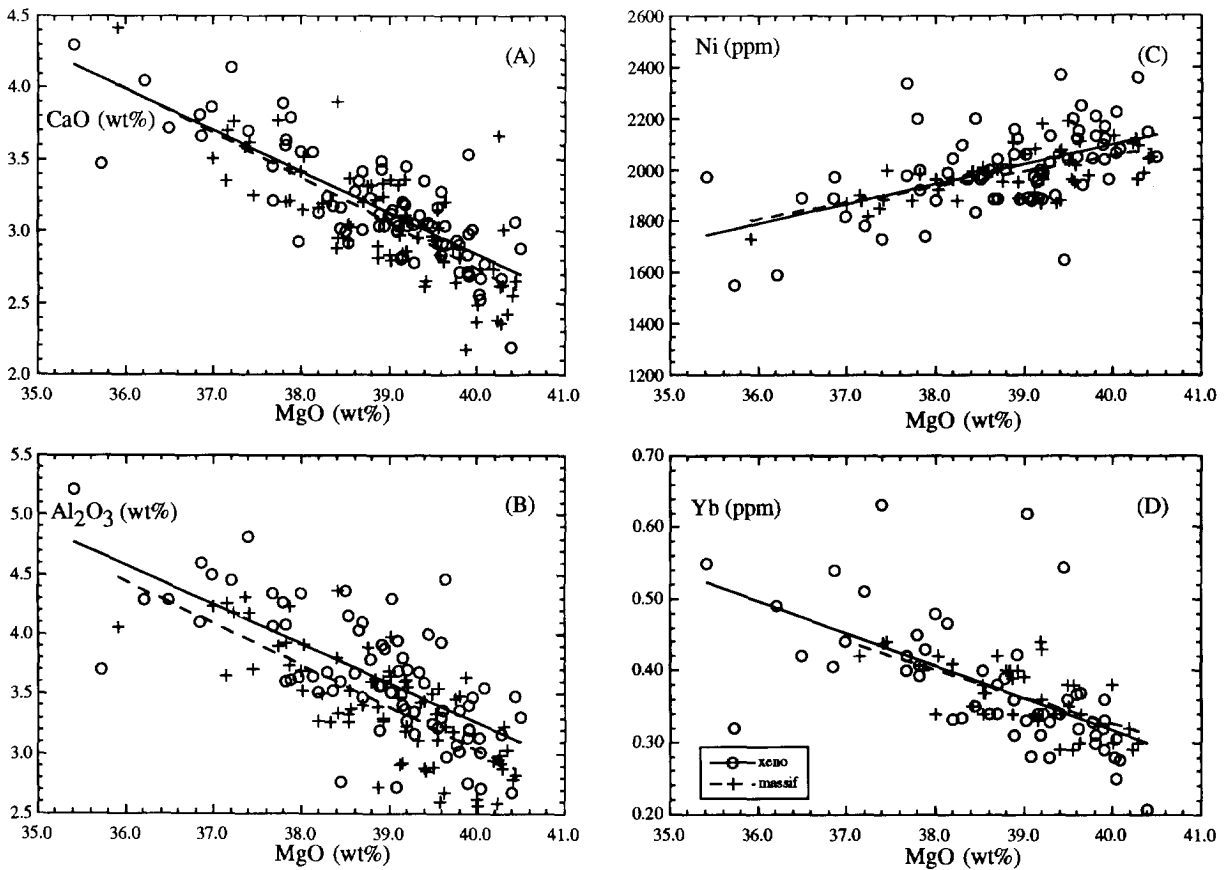


Fig. 1. MgO vs. CaO, Al<sub>2</sub>O<sub>3</sub>, Ni and Yb in peridotite massifs (*crosses*) and peridotite xenoliths (*open circles*). Linear regression lines are given for peridotite massifs (*dashed line*) and peridotite xenoliths (*solid line*); see text for further discussion. Data are shown for fertile peridotites with  $\leq 40.5$  wt% MgO; data from the literature and are available from the first author upon request.

trends pass through the uniquely defined chondritic values for refractory lithophile element ratios (Fig. 3). This is strong evidence that these peridotites originally possessed chondritic relative proportions of these elements and supports the assumption that the Silicate Earth has chondritic relative abundances of the refractory lithophile elements.

Several important observations regarding the compositions of peridotites arise from these diagrams. A dominant feature, seen in Fig. 2, is the positive slopes of the element patterns. Even for these peridotites, which are considered to be some of the most fertile samples, there is a depletion trend seen in the incompatible elements from Sm or Hf to Ca or Sc. This reflects the loss of a melt. The relative depletion and enrichment

of elements in these peridotites can be used to identify the character and amount of partial melt extracted, given the peridotite experienced a relatively simple history. These diagrams can also be used to identify enrichments or depletions in a specific mineral (e.g., clinopyroxene addition). Finally, in the light of mineral/melt partition coefficient data for the high-pressure phases, Ca-perovskite, Mg-perovskite and majorite garnet (Kato et al., 1988; Ohtani et al., 1989), the order of element depletion coupled with the smooth trends exhibited by these peridotites demonstrates that they have not experienced any high-pressure fractionation involving these phases. Consequently, these peridotites are not residues of a terrestrial magma ocean or its crystallized melt products.

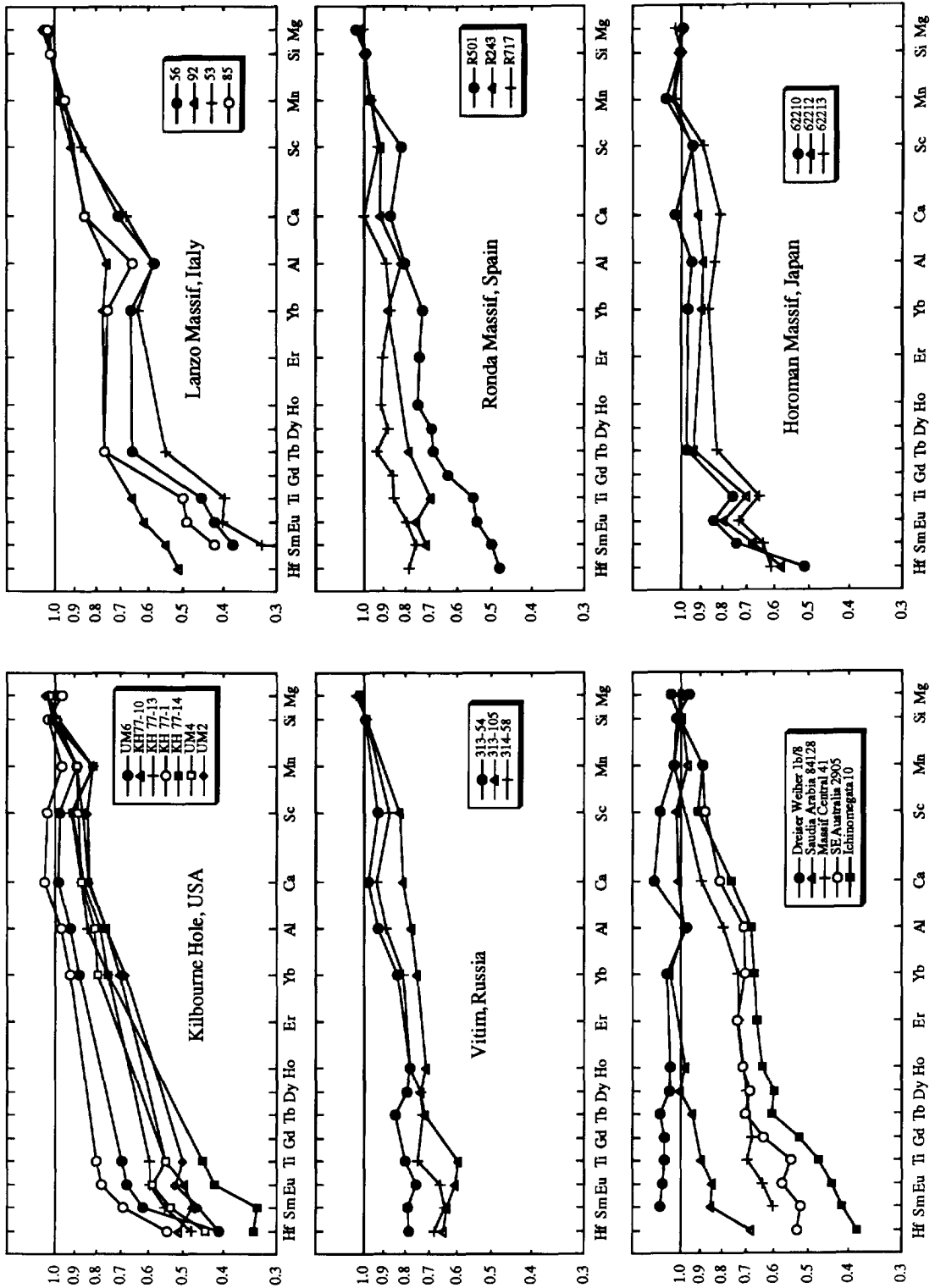


Fig. 2. Mantle-normalized diagrams for samples from various peridotite massifs (Lanzo, Ronda and Horoman) and peridotite xenoliths (Kilbourne Hole, Vitim and other localities). A reference mantle composition was used for normalization. Data sources include published (Stosch and Seck, 1980; Frey et al., 1985, 1991; Downes and Dupuy, 1987; Bodinier, 1988; Roden et al., 1988; Ionov et al., 1993) and some unpublished data (W.F. McDonough).

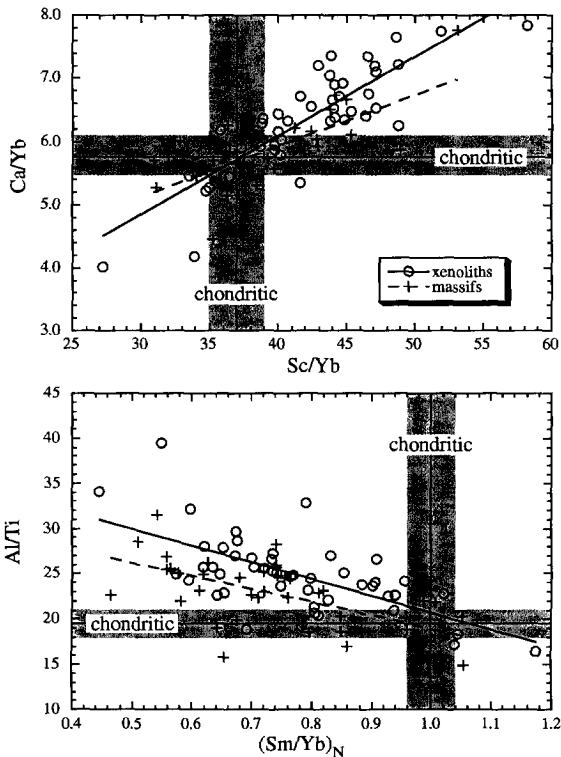


Fig. 3. Variation diagrams using refractory lithophile element ratios for peridotite massifs (crosses) and peridotite xenoliths (open circles). The chondritic values are given as a range (shaded region) and best estimate (fine line). Linear regression lines are given for peridotite massifs (dashed line) and peridotite xenoliths (solid line); see text for further discussion.

The relative positions of Ca and Al in Fig. 2 are of particular interest. In correcting for the effects of partial melting it is important to note that the proportional depletion of Al is greater than that of Ca. This in turn causes a residual peridotite (e.g., the upper mantle) to possess a Ca/Al ratio which is higher than its initial value.

Previous studies have suggested that this feature of fertile peridotites is due to selective enrichment of a particular mineral or majorite garnet fractionation (Palme and Nickel, 1985; Hart and Zindler, 1986). For reasons given above, there is no evidence of a global-scale signature of majorite garnet fractionation in the mantle. There are examples of peridotites with fractionated Ca/Al ratios that appear to be due to enrichments or depletions in a specific mineral as

suggested by Hart and Zindler (1986). Fertile peridotites with relatively flat patterns (Fig. 2) and an anomalous depletion in one or more elements are examples of this feature. Sample *Ib/8* from Dreiser Weiher, Germany (Stosch and Seck, 1980) has a flat unfractionated pattern for most elements, except Al and Cr (Fig. 4). The relative depletions in Al and Cr can be explained by a 1% depletion in spinel, which commonly contains ~50–60 wt%  $\text{Al}_2\text{O}_3$  and ~10 wt%  $\text{Cr}_2\text{O}_3$  in these samples. Likewise, the patterns for peridotites *KH1* (Fig. 4) and *Po1* (Jagoutz et al., 1979) show further evidence for spinel depletion, while peridotite *Ka 168* (Jagoutz et al., 1979) appears to have an excess of spinel. The loss or gain of a spinel component could be due to metamorphic or igneous processes or possibly mineral fractionation during sample processing and analyses. These element patterns point towards an anomaly in a spinel component and not a clinopyroxene component, indicating that the clinopyroxene correction of Hart and Zindler (1986) may not be valid for some samples. In summary, the high Ca/Al ratio observed in most fertile peridotites is likely to be caused by melt depletion processes and is not an original feature of the mantle.

Using the above observations the unmelted, initial compositions of these peridotites can be established, providing an estimate of the composition of the Silicate Earth. It is necessary to correct the compositions of these peridotites for the effects of partial melting (Fig. 5) in order to calculate their initial compositions. The removal of a partial melt will deplete the peridotites in elements more incompatible than Si and enrich those that are more compatible than Si. Using only refractory lithophile elements, trends of ratios vs. element abundances (Fig. 6) for fertile peridotites, establish the absolute proportion of these elements in the Silicate Earth at ~2.75 times that in the CI chondrites. Similarly, trends for  $\text{SiO}_2$ , MgO and FeO vs. ratios of the refractory lithophile elements are used to establish the absolute proportions of these major elements in the Silicate Earth. The minor-element abundances (Ni, Cr, Mn and Na) are determined using a combination of these trends and constant

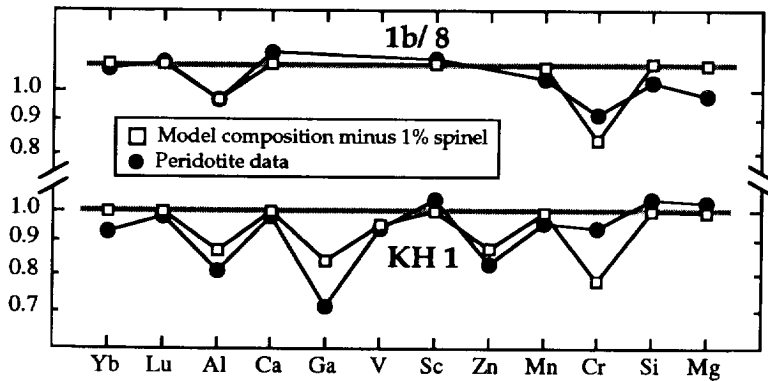


Fig. 4. A mantle-normalized diagram for peridotite xenoliths *1b/8* (Stosch and Seck, 1980) and *KH1* (Jagoutz et al., 1979). Also shown are model compositions (*grey line*) for these peridotites assuming a flat, undepleted pattern. From these model compositions a 1% spinel component was subtracted (*open boxes*), based on the composition of data for spinels from these peridotites (Blum, 1982; Stosch, 1982; McDonough et al., 1992a), demonstrating that the anomalous depletions seen in the bulk rock data can be accounted for by the loss of a spinel component, not by the loss of a clinopyroxene component.

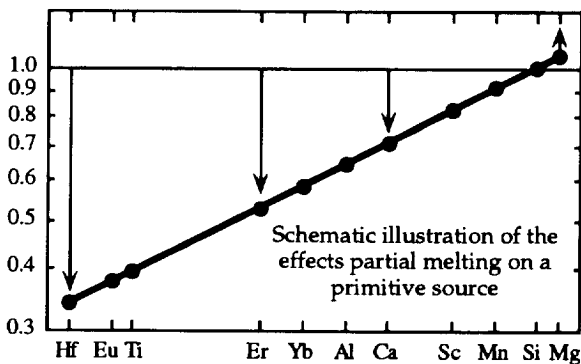


Fig. 5. An idealized mantle-normalized diagram illustrating the effect of melt extraction on the abundances of elements in the residual peridotite. Under most conditions Si will have a bulk distribution coefficient of  $\sim 1.0$  and thus it will be a neutral pivot point on the diagram.

element ratios with the major elements (Fig. 7). The bulk composition of the Silicate Earth estimated from this method is given in Table 4 and compared with some previously established model compositions.

Our model composition for the Silicate Earth has ratios of Mg/Al and Mg/Si which are fractionated relative to the CI chondrite values. Some of the Si depletion is potentially due to its partitioning into the core. It is unlikely, however, that this can explain all of the Si depletion, nor is it likely that Mg has been sequestered into the core (see discussion on the core in Section 6). Thus,

we suggest that cosmochemical processes have led to depletions in the moderately-volatile and volatile elements, including Si and Mg. Were other elements (e.g., V, Cr, Li and Mn) with condensation behavior similar to Mg and Si also partially depleted in the Earth due to volatilization? This is a difficult question to answer since V, Cr and Mn are likely to have been depleted by core formation (see Section 5.2.1). The relative and absolute abundances of these elements need to be examined in detail in order to better understand the accretionary processes and initial composition of nebula material in the collection zone of the growing Earth.

### 5.1. Refractory lithophile elements

The Silicate Earth is believed to possess chondritic relative abundances of the refractory lithophile elements. Since we have established the absolute concentration of Al, Ca and Ti (at  $\sim 2.75$  times CI chondritic abundances), we can calculate the absolute abundances for the rest of the refractory lithophile elements (Table 1) based on their chondritic proportions (Table 2). Table 5 presents our recommended composition of the Silicate Earth. When comparing the composition of the Silicate Earth to CI carbonaceous chondrites, which are water- and  $\text{CO}_2$ -rich meteorites, it is common to normalize the element

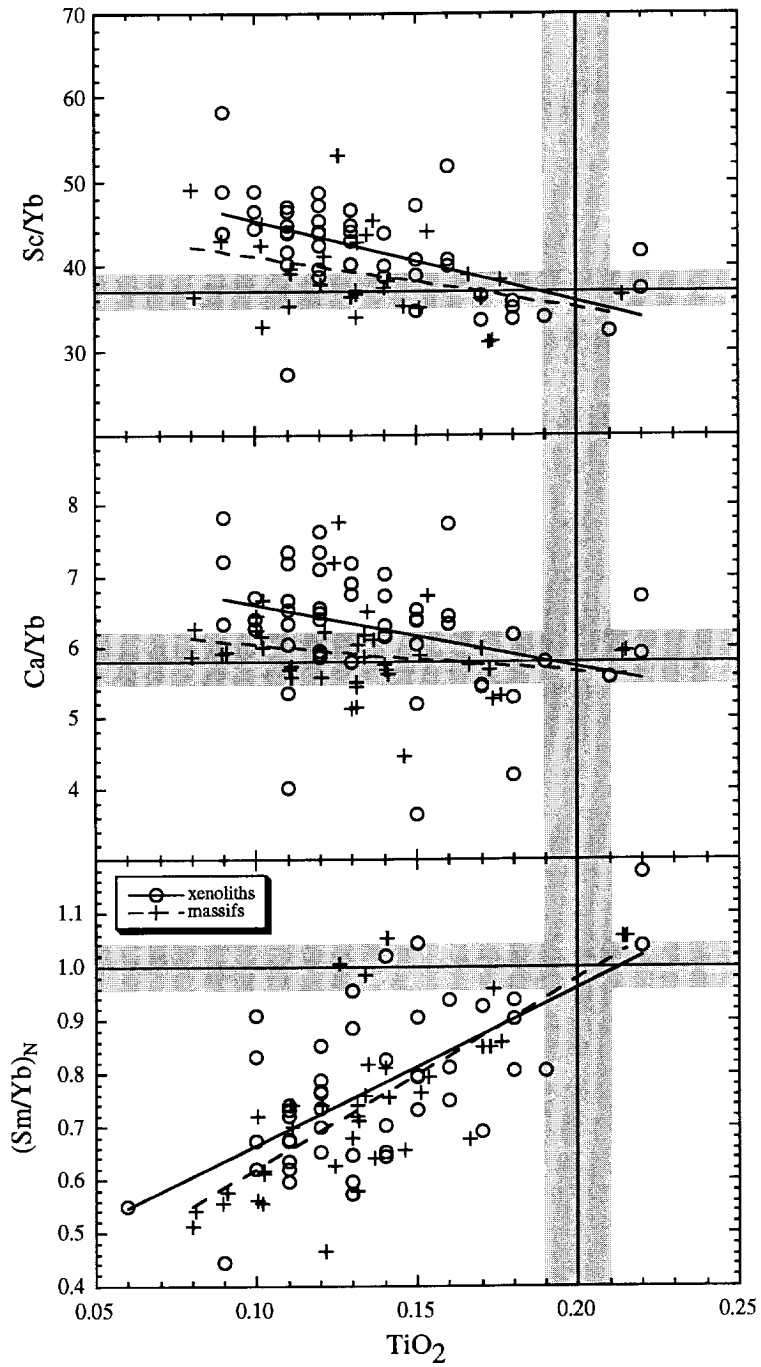


Fig. 6.  $TiO_2$  vs.  $Sc/Yb$ ,  $Ca/Yb$  and  $(Sm/Yb)_N$  in peridotite massifs (crosses) and peridotite xenoliths (open circles). The horizontal lines and shaded areas show the chondritic ratio and an estimate of its variation in chondritic meteorites, respectively. The vertical line and its shaded area is our estimate of the  $TiO_2$  content of the Silicate Earth and the precision of this estimate, respectively. Linear regression lines are given for peridotite massifs (dashed line) and peridotite xenoliths (solid line); see text for further discussion. Data are shown for fertile peridotites with  $\leq 40.5$  wt%  $MgO$ .

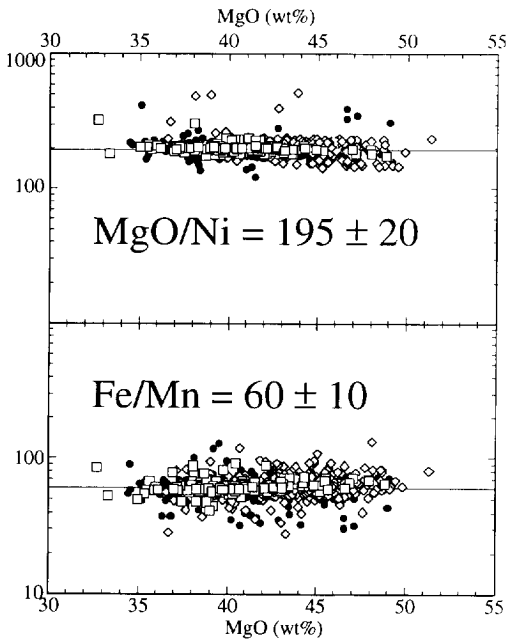


Fig. 7. A plot showing constant ratios of MgO/Ni (195) and Fe/Mn (60) in peridotites over a range of MgO contents. Samples (> 1300) include spinel-bearing peridotite xenoliths (filled circles), garnet-bearing peridotite xenoliths (open diamonds) and massif peridotites (open squares). Data from the literature. The average ratio and  $\pm 1$  standard deviation is given.

abundances to Mg or Si to remove the effects of this volatile component. Hence, the Mg-normalized abundances of the refractory lithophile elements in the Silicate Earth are  $\sim 1.16$  times that in CI carbonaceous chondrites (Table 5).

### 5.2. Non-refractory lithophile elements

There are significant differences in various estimates of the absolute and relative abundances of the moderately-volatile and volatile lithophile elements (Table 1) in the Silicate Earth. In addition, some elements appear to behave as either lithophile or siderophile elements in the Earth's mantle under different conditions (e.g., P, V, Cr, Mn, Cu, Zn, Tl, Ga, Ge, Mo, W and Pb). These elements have different relative and absolute abundances in various chondritic meteorites. For the Earth the relative depletion of the non-refractory elements is thought to have been produced prior to, or during, accretion. Here we dis-

cuss ratios of these elements which can be used to define their abundances in the Silicate Earth [see also Sun (1982) for additional discussion].

#### 5.2.1. V, Cr and Mn

Some controversy exists regarding the absolute and relative abundances of V, Cr and Mn in the bulk Earth and in the Silicate Earth (Drake et al., 1989; Ringwood et al., 1990). Ringwood (1966) first noted that these elements are depleted in the Earth's mantle relative to the CI chondrite composition. Dreibus and Wänke (1979) noted that the relative abundances of V, Cr and Mn in the Earth and Moon are similar. In contrast, Drake et al. (1989) found that the Eucrite Parent Body and the Shergottite Parent Body have near-chondritic proportions of these elements. Ratios involving Cr and V relative to some other elements in chondrites show limited variations (Table 3), while there is much larger variation ratios involving Mn [e.g., in the carbonaceous chondrites Cr/Mn ( $2.08 \pm 0.49$ ), Mn/V ( $20.8 \pm 6.2$ ) and Mg/Mn ( $81.1 \pm 18.2$ )]. Cr and Mn are moderately-volatile elements, whereas V is, based on chondritic meteorites, more refractory than Mg.

It has been suggested that V, Cr and Mn are depleted relative to Mg in the Silicate Earth due to either volatility, or their incorporation into the Earth's core, or both (Ringwood, 1966; Dreibus and Wänke, 1979; Drake et al., 1989; Ringwood et al., 1990; O'Neill, 1991b). There is experimental evidence suggesting that Cr, V, and Mn have siderophilic character at high temperatures and within the range of  $f_{O_2}$  in the Earth's mantle (Brey and Wänke, 1983; McCammon et al., 1983; Rammensee et al., 1983; Drake et al., 1989) and at high pressure (Ringwood et al., 1990). By and large, these data support the suggestion that core-mantle fractionation is an important factor (most particularly for V and Cr) contributing to the depletion of these elements. However, the possibility still exists that some volatilization of Cr and Mn may have occurred. The estimated abundance for V in the Silicate Earth come from the data of peridotites (Jagoutz et al., 1979; McDonough and Frey, 1989) and Archean komatiites (Sun, 1982); the corre-

Table 4  
Silicate Earth model compositions

	Pyrolite models			CI model
	1	2	3	4
SiO <sub>2</sub>	45.0	45.16	45.0	49.9
TiO <sub>2</sub>	0.201	0.217	0.17	0.16
Al <sub>2</sub> O <sub>3</sub>	4.45	3.97	4.4	3.65
Cr <sub>2</sub> O <sub>3</sub>	0.384	0.46	0.45	0.44
MnO	0.135	0.13	0.11	0.13
FeO	8.05	7.82	7.6	8.0
NiO	0.25	0.27	0.26	0.25
MgO	37.8	38.30	38.8	35.15
CaO	3.55	3.50	3.4	2.90
Na <sub>2</sub> O	0.36	0.33	0.4	0.34
K <sub>2</sub> O	0.029	0.031	0.003	0.022
P <sub>2</sub> O <sub>5</sub>	0.021	–	–	–
100Mg/(Mg+Fe)	89.3	89.7	90.1	88.7

1=pyrolite model based on peridotites, komatiites and basalts (this study); 2=least depleted ultramafic xenolith model (Jagoutz et al., 1979); 3=MORB-harzburgite model (Green et al., 1979); 4=Bulk Silicate Earth model based on CI carbonaceous chondrites (Talyor and McLennan, 1985).

lations with Ca, Sc and Yb vs. V give us a similar value of ~82 ppm V in the Silicate Earth (McDonough and Frey, 1989). The abundances of Cr and Mn in the Silicate Earth are estimated from melting models (Sun, 1982) and from using constant element ratios in peridotites (Fig. 7) (McDonough, 1994).

#### 5.2.2. Li, Na, K, Rb, Cs

Several ratios of refractory to moderately-volatile lithophile elements (e.g., Li/Dy, Na/Ti, K/U, Ba/Rb, Rb/Sr, Ba/Cs) are useful in establishing the Silicate Earth's inventory of the alkali metals. Several studies have examined the systematics of Li in various rocks in order to determine its abundance in the Silicate Earth (e.g., Dreibus et al., 1976; Bailey and Gwozdz, 1978; Jagoutz et al., 1979; Sun, 1982; Ryan and Langmuir, 1987). During basalt generation, Li has a residuum/melt distribution coefficient similar to Dy (Ryan and Langmuir, 1987) and is generally considered to be more compatible than Na or Ti during mid-ocean ridge basalt (MORB) genesis (Sun et al., 1979). When compared to the estimated abundances of Dy or Ho in the Silicate Earth the abundance of Li is depleted by 25–60%

relative to the refractory elements (Sun, 1982; Wänke et al., 1984). Li is likely to substitute into the Mg sites in peridotite minerals. There is a limited variation in the Li abundances ( $1.5 \pm 0.3$  ppm) in fertile peridotites (Jagoutz et al., 1979), which we interpret to reflect its mildly incompatible behavior during mantle melting.

In comparison to CI chondrites, Na is depleted in the Silicate Earth relative to the refractory elements. The chondritic Na<sub>2</sub>O/TiO<sub>2</sub> ratio is ~9, whereas in primitive, low-TiO<sub>2</sub> MORB and Archean komatiites it is ~1.8 (Sun and Nesbitt, 1977); similarly low values of Na<sub>2</sub>O/TiO<sub>2</sub> are found in melt inclusions hosted in unaltered olivines from Archean komatiites in Zimbabwe (McDonough and Ireland, 1993) and Alexo, Canada (W.F. McDonough, unpublished data). A Na<sub>2</sub>O/TiO<sub>2</sub> ratio of ~2.0 is also found in fertile spinel lherzolite xenoliths (Jagoutz et al., 1979; Preß et al., 1986; Ionov et al., 1993). Given a TiO<sub>2</sub> content of ~0.20 wt%, it follows that the Silicate Earth has ~0.36 wt% Na<sub>2</sub>O. Additionally, correlations of ratio vs. element (cf. Fig. 6) using Na and several refractory lithophile elements gave an estimated Na abundance for the Silicate Earth of ~2670 ppm.

Table 5  
Recommended chemical composition of the Silicate Earth—"Pyrolite"

Element	CI	Pyrolite	Pyrolite (normalized to Mg and CI)	±	Element	CI	Pyrolite	Pyrolite (normalized to Mg and CI)	±
Li (ppm)	1.5	1.6	0.45	30	Pd	550	3.9	0.003	80
Be	0.025	0.068	1.16	20	Ag	200	8	0.017	F3
B	0.9	0.30	0.14	F2	Cd	710	40	0.024	30
C	35,000	120	0.0015	F2	In	80	11	0.058	40
N	3,180	2	0.0003	F2	Sn	1,650	130	0.033	30
F	60	25	0.17	F2	Sb	140	5.5	0.017	50
Na	5,100	2,670	0.22	15	Te	2,330	12	0.002	F2
Mg (%)	9.65	22.8	1.00	10	I	450	10	0.009	F3
Al (%)	0.860	2.35	1.16	10	Cs	190	21	0.047	40
Si (%)	10.65	21.0	0.83	10	Ba	2,410	6600	1.16	10
P (ppm)	1,080	90	0.035	15	La	237	648	1.16	10
S	54,000	250	0.002	20	Ce	613	1,675	1.16	10
Cl	680	17	0.011	F2	Pr	92.8	254	1.16	10
K	550	240	0.18	20	Nd	457	1,250	1.16	10
Ca (%)	0.925	2.53	1.16	10	Sm	148	406	1.16	10
Sc	5.92	16.2	1.16	10	Eu	56.3	154	1.16	10
Ti	440	1,205	1.16	10	Gd	199	544	1.16	10
V	56	82	0.62	15	Tb	36.1	99	1.16	10
Cr	2,650	2,625	0.42	15	Dy	246	674	1.16	10
Mn	1,920	1,045	0.23	10	Ho	54.6	149	1.16	10
Fe (%)	18.1	6.26	0.15	10	Er	160	438	1.16	10
Co	500	105	0.089	10	Tm	24.7	68	1.16	10
Ni	10,500	1,960	0.079	10	Yb	161	441	1.16	10
Cu	120	30	0.11	15	Lu	24.6	67.5	1.16	10
Zn	310	55	0.075	15	Hf	103	283	1.16	10
Ga	9.2	4.0	0.18	10	Ta	13.6	37	1.16	15
Ge	31	1.1	0.015	15	W	93	29	0.13	F2
As	1.85	0.05	0.011	F2	Re	40	0.28	0.003	30
Se	21	0.075	0.002	70	Os	490	3.4	0.003	30
Br	3.57	0.050	0.006	F2	Ir	455	3.2	0.003	30
Rb	2.30	0.600	0.11	30	Pt	1,010	7.1	0.003	30
Sr	7.25	19.9	1.16	10	Au	140	1.0	0.003	F2
Y	1.57	4.30	1.16	10	Hg	300	10	0.014	F4
Zr	3.82	10.5	1.16	10	Tl	140	3.5	0.011	40
Nb (ppb)	240	658	1.16	15	Pb	2,470	150	0.026	20
Mo	900	50	0.024	40	Bi	110	2.5	0.010	30
Ru	710	5.0	0.003	30	Th	29	79.5	1.16	15
Rh	130	0.9	0.003	40	U	7.4	20.3	1.16	20

From Li to Zr element concentrations are given in ppm; Nb to U are given in ppb; and Mg, Al, Si, Ca and Fe are in wt%. The ± column is a subjective judgement of the uncertainty of this estimate. Uncertainties are expressed in %, unless otherwise stated; F = factor (F2 = we know this estimate to within a factor of 2). Most of the major and minor elements and a number of the refractory lithophile elements are known to within ± 10% or better.

The abundances of K, Rb and Cs have recently been examined by McDonough et al. (1992b); we use their estimate of the Silicate Earth for our values (Table 5). Limits on the K and Rb abundances in the Silicate Earth are derived from its

K/U ( $\sim 10^4$ ), K/Rb ( $\sim 400$ ), Rb/Sr ( $\sim 0.03$ ) and Ba/Rb ( $\sim 11$ ) ratios, as established from the data for crustal and mantle-derived rocks and by Sr, Nd and Hf isotope systematics. The continental crust and depleted mantle (MORB source



region) have similar K/U and Ba/Rb ratios, which indicates that these ratios are conserved during crust–mantle differentiation (Hofmann and White, 1983; Jochum et al., 1983). Thus, knowing the abundances of Ba and U in the Silicate Earth the K and Rb abundances can be estimated. The ratio of Na/K in the Silicate Earth is  $\sim 11$ , which is similar to or a little higher than in chondritic meteorites (Table 3); this value is consistent with the relative volatility of these elements and their abundance in CI chondrites. The Cs abundance of the Silicate Earth is constrained by estimates of the Rb abundance of the crust and mantle and values of their Rb/Cs ratio. We recognize that there are different views on the bulk Rb/Cs ratio of the Earth and Moon (Jones and Drake, 1994; McDonough et al., 1994).

#### 5.2.3. Boron

The abundance of B in the Silicate Earth has been estimated to be  $\sim 0.5$  ppm based on whole-rock data for fertile peridotites (Higgins and Shaw, 1984), or  $\sim 0.25$  ppm based on geochemical mass-balance arguments for the continental crust and mantle (Chaussidon and Jambon, 1994). The incompatibility of B during mantle melting is comparable to that of K (Ryan and Langmuir, 1993; Chaussidon and Jambon, 1994), which is a highly incompatible element. Chaussidon and Jambon (1994) argue that K/B is relatively constant at  $\sim 10^3$  in a spectrum of modern basalts and that this value is comparable to that in the bulk continental crust. By analogy with the K/U ratio, which is similar in the continental crust and mantle ( $\sim 10^4$ ), the K/B ratio is therefore believed to be conserved during crust–mantle differentiation. Examining the K/B variation in oceanic basalts, however, reveals considerable spread of values. K/B values are 1000–2000 in N- and E-type MORB, 2000–3000 in Hawaii, and  $< 500$  to 2000 in arc and back-arc basin basalts (Ryan and Langmuir, 1993; Chaussidon and Jambon, 1994). In addition, there is some variation in estimates of the K/B in the continental crust. Taylor and McLennan (1985) estimate the continental crust's K/B ratio to be  $\sim 900$ , whereas Shaw et al. (1986) propose a value of  $\sim 3000$ . Given the uncertainties

involved, we tentatively suggest a value of  $\sim 0.3$  ppm B for the Silicate Earth.

#### 5.2.4. Zinc

Zn can be considered either as an oxyphile–lithophile element or a chalcophile element. In chondritic meteorites Zn is dominantly concentrated in oxides and silicates (Nishimura and Sandell, 1964) and is therefore treated as a lithophile element. Sun (1982) estimated the abundance of Zn to be between 50 and 60 ppm in the Silicate Earth based on Zn's melting behavior and models of the source abundance of Zn for modern MORB and Archean komatiites. There is a limited range of Zn contents ( $55 \pm 7$ ) in the fertile peridotites. These observations indicate that a value of 55 ppm Zn for the Silicate Earth is reasonably well established.

#### 5.2.5. The halogens

Estimates of the abundances of the halogens in the Silicate Earth are constrained mainly from constant ratios of the halogens to refractory lithophile elements in basalts; data for the abundances of the halogens in peridotites are limited (Jagoutz et al., 1979; Dreibus et al., 1983). As established from basalts, the relative incompatibility of these elements are, from least to most incompatible,  $F < Cl \approx Br < I$  (Schilling et al., 1980; Déruelle et al., 1992), with I being one of the most incompatible elements known.

Schilling and coworkers (Rowe and Schilling, 1979; Schilling et al., 1980) found relatively constant F/P ( $\sim 0.3$ ) and F/Sr ( $\sim 2$ ) in basalts from ocean islands and mid-ocean ridges. Sun (1982) used these observations to suggest a value of  $\sim 26$  ppm F in the Silicate Earth. Jagoutz et al. (1979) report a range of F contents in fertile peridotite (7–16 ppm) and low F/Sr (0.7) in the three most fertile peridotites. From this, we obtain an estimate of  $\sim 15$  ppm F for the Silicate Earth. The largest unknown when estimating the Silicate Earth's F abundance is the continental crust, for which there is no good estimate.

Cl and Br are believed to behave similarly to Rb or Ba during MORB and ocean island basalt genesis (Schilling et al., 1980; Sun, 1982). Constant ratios of Cl/Ba ( $\sim 2.5$ ), Cl/Rb ( $\sim 28$ ) and

Cl/Br ( $\sim 350$ ) in these basalts reflect their source values (Schilling et al., 1980; Sun, 1982). An average Cl/Br for surface reservoirs (including the crust and oceans) is comparable to that of the mantle or slightly higher (350–450). The above mantle ratios are used to estimate the Cl and Br abundances in the Silicate Earth. The abundance of I in the Silicate Earth has recently been reviewed by Déruelle et al. (1992). They found that much of the I in the Earth is likely to be concentrated at the surface and suggest the Silicate Earth has between 9 to 24 ppb I. After comparing their estimate with the only values available for fertile peridotites (Wänke et al., 1984), Déruelle et al. (1992) proposed a value of 10 ppb I for the Silicate Earth. We adopt this value.

### 5.2.6. A depletion trend for the moderately-volatile lithophiles

The normalized abundances of lithophile elements in the Silicate Earth are plotted against their condensation temperatures for an assumed solar nebular condition (Wasson, 1985) in Fig. 8. The refractory lithophile elements are shown as a group at a factor of 1.16 above Mg. In general, there is a uniform decrease in the normalized abundances of the moderately-volatile lithophile elements with decreasing condensation temperature (Fig. 8). This trend may reflect the nature of the nebula material in the planetary feeding zone of the proto-Earth.

### 5.3. Siderophile and chalcophile elements

Depletion of siderophile and chalcophile elements in the Earth's mantle results from core formation, making estimates of their absolute and relative abundances difficult to obtain. Refractory siderophile elements are significantly depleted in the Earth's mantle compared to CI carbonaceous chondrites (about a factor of 10 for the siderophiles and  $> 100$  for the highly siderophile noble metals) (Fig. 8). Comparison of the relative and absolute abundances of these elements in Archean to modern, mafic to ultramafic lavas and peridotite samples provides insights into their absolute abundances in the mantle and the possibility of secular variation in

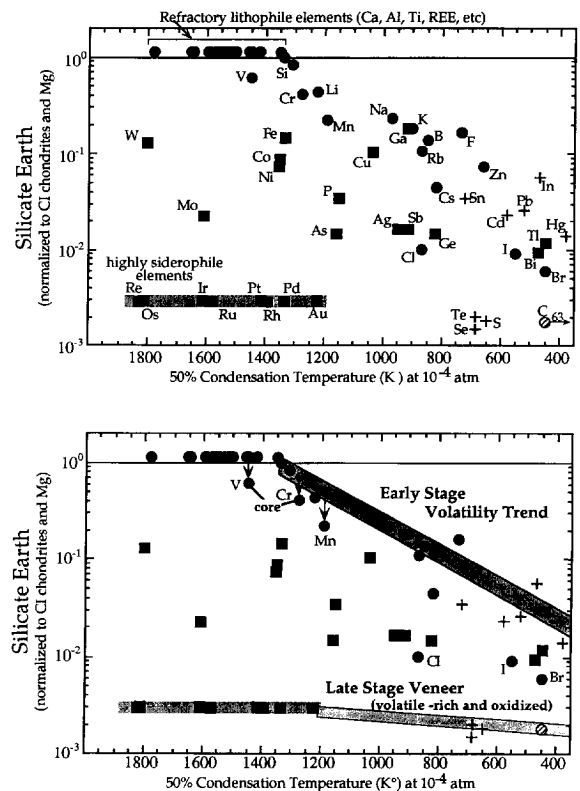


Fig. 8. A plot of the abundances of elements in the Silicate Earth (normalized to Mg and CI chondrites, Table 5) vs. their 50% condensation temperature at  $10^{-4}$  atm. The upper panel identifies the data points for the lithophile (filled circles), siderophile (filled squares) and chalcophile (crosses) elements. The lower panel schematically illustrates the Early Stage Volatility Trend as established by the moderately-volatile lithophile elements and the trend for a Late Stage Veneer component, believed to be added after the bulk of the planet was accreted, as established by the highly siderophile elements and S, Se, Te and C. The arrows for V, Cr and Mn indicate the further depletion of these elements in the Silicate Earth as a result of their partial subtraction into the

mantle. These data have in turn been used to understand the relative lithophile/siderophile behavior of the refractory siderophile elements during core–mantle fractionation.

#### 5.3.1. Refractory siderophile elements

These elements include Fe, Ni, Co, Mo and W. Constant Ba/W, Mo/Pr and Ce/Pb ratios in modern oceanic basalts that have a large range of Pb isotopic compositions demonstrate that there has been no significant fractionation of the

siderophile or chalcophile elements in the sources of these basalts over the last  $\sim 2.0$  Ga (Hofmann et al., 1986; Newsom et al., 1986). Sims et al. (1990) extended this type of analysis (using Mo/Ce) to include various crustal rocks of Archean and post-Archean age. They observed a limited variation in Mo/Ce (0.02–0.03) and greater variation in Ba/W (170–350) in mafic and ultramafic lavas and crustal rocks. Following Sims et al. (1990), we set the Mo/Ce and Ba/W ratios of the Silicate Earth to  $\sim 0.03$  and  $\sim 230$ , respectively.

An estimate of the abundances of Fe and Ni in the Silicate Earth was discussed in Section 5. We find that there is a Gaussian distribution of FeO and Ni contents in the fertile peridotites selected for this study. The average FeO content is  $8.06 \pm 0.34$  wt% and the average Ni content is  $1985 \pm 140$  ppm; these values are comparable to those determined using regression analyses. The Co abundance of the Silicate Earth is well constrained by a relatively constant Ni/Co ratio ( $18.7 \pm 1.5$ ) in the fertile peridotites and the systematic of this ratio with increasing melt depletion (McDonough, 1994). These estimates can be compared by examining Fe/Co ( $585 \pm 40$ ) and Fe/Ni ( $31.9 \pm 3.1$ ) ratios in the fertile peridotite suite. Ratios of these and other compatible elements in peridotites are unlikely to change greatly as a result of small amounts of melt extraction, and these ratios can be readily used to estimate their initial abundance in the Silicate Earth.

### 5.3.2. Highly siderophile elements

These elements include the platinum-group elements (PGE: Ru, Rh, Pd, Os, Ir, Pt), Re and Au. The relative abundance of these elements in peridotites and the Silicate Earth appear to be chondritic at  $\sim 0.3\%$  times an Mg- and CI-normalized abundance (Table 5; Fig. 8). Many workers have estimated the absolute and relative abundances of the highly siderophile elements in the Silicate Earth based on studies of primitive basalts and komatiites and fertile peridotite xenoliths (Chou, 1978; Jagoutz et al., 1979; BVSP, 1981; Sun, 1982; Chou et al., 1983; Morgan, 1986; Sun et al., 1991). The Re–Os isotopic sys-

tematics for peridotites and basalts from mid-ocean ridges (Martin, 1991; Pegram and Allègre, 1992) indicate that the upper mantle has chondritic proportions of these elements (Allègre and Luck, 1980; Luck and Allègre, 1983; Walker and Morgan, 1989). From this we argue that the Silicate Earth is likely to have a chondritic Re/Os ratio.

We accept the model that accounts for the abundances of highly siderophile elements in the Silicate Earth by the addition of a late-stage (e.g., post-95% growth of the planet) accretion of a veneer ( $< 1\%$  by mass) of chondritic material on to the Earth (Kimura et al., 1974; Chou et al., 1983; Morgan, 1986); the abundances of highly siderophile elements cannot be accounted for by core formation processes given their differences in metal/silicate and sulfide/silicate partition coefficients [see review in O'Neill (1991b)]. The compositions of peridotites and komatiites demonstrate that highly siderophile elements have been effectively re-homogenized in the Silicate Earth since the addition of this late-stage veneer. For example, a relatively uniform Ni/Ir ratio ( $610 \pm 140$ ) in peridotites (McDonough, 1994), with minor regional variation (Spettel et al., 1991) demonstrates the effectiveness of this re-homogenization process. It has also been shown that fertile peridotites and Archean to modern komatiites have a relatively constant Ti/Pd of  $\sim 3 \cdot 10^5$  (Keays, 1982; Brüggemann et al., 1987; Sun et al., 1991). In addition, there is a homogeneous distribution of the chalcophile elements, Cu, PGE and Au, with respect to the lithophile elements in the mantle, and by comparing lavas of different ages (Sun et al., 1991), it is further argued that this uniform siderophile and chalcophile signal from the mantle has been present throughout the geologic record.

### 5.3.3. Moderately-volatile siderophile elements

These elements include P, Cu, Ga, Ge, As, Ag and Sb. Their abundances in the Silicate Earth are constrained by ratios of these elements to refractory lithophile elements in modern oceanic basalts, komatiites and peridotites. The P content of the Silicate Earth is 90 ppm, estimated

from a relatively constant  $\text{TiO}_2/\text{P}_2\text{O}_5$  ratio ( $\sim 10$ ) in komatiites and modern MORB (Sun, 1982) and the constant P/Nd ratio ( $\sim 70$ ) in most modern basalts (McDonough et al., 1985; Langmuir et al., 1992) and unaltered Archean komatiites. An estimate of the Ga content of the Silicate Earth, established from the chemical systematic of Al, Sc and Ga in basalts and peridotites (McDonough, 1990a; and also from this study), is  $\sim 4$  ppm.

An estimate of the Cu content of  $\sim 30$  for the Silicate Earth given in Sun (1982) was based on data from komatiites and MORB. Using a regression analyses for fertile peridotites we have arrived at the same value, with  $\sim \pm 15\%$  uncertainty. The geochemistry of Ge during mantle melting is similar to that of Si and as such, its content in peridotites changes little with melt depletion (Ringwood, 1966). The average Ge content of fertile peridotites is  $\sim 1.0$  ppm and for all peridotites is  $\sim 0.95$  ppm. After correcting for the effects of melting, we estimate the Silicate Earth to have  $\sim 1.1$  ppm Ge.

Ag behaves as a moderately incompatible element during basalt genesis (Sun, 1982). The abundance of Ag in basalts (20–60 ppb) is  $\sim 3$ –10 times that in peridotites (Keays and Scott, 1978; Hertogen et al., 1980; BVSP, 1981). Only one Ag determination for a komatiite was found (Stone and Crockett, 1993) having  $\sim 5$  ppb. This may indicate that Ag is only slightly incompatible, and perhaps behaves comparably to Re or Se during mantle melting. An anomalously high Ag concentration (30–100 ppb) in fertile peridotites has been reported (Garuti et al., 1984) which might be due to melt enrichment processes. We concur with Sun's (1982) earlier assessment that the Ag content of the Silicate Earth is likely to be between 5 and 10 ppb.

The abundance of As and Sb in the Silicate Earth has recently been considered by Sims et al. (1990). They measured the abundances of these elements in basalts and various crustal rocks and found that As and Sb behave similarly to the light REE during melting; As/Ce and Sb/Ce ratios are not similar in mafic to ultramafic lavas compared to crustal rocks. After considering the proportion of these elements in the crust and mantle

they proposed that the Primitive Mantle had As/Ce and Sb/Ce values of  $\sim 0.036$  and  $\sim 0.003$ , respectively (Sims et al., 1990). We use these ratios to provide As and Sb abundances of the Silicate Earth.

#### 5.3.4. Volatile siderophile and chalcophile

These elements include S, Se, Te, Cd, In, Sn, Hg, Tl, Pb and Bi. It is difficult to estimate the proportion of these elements in the Earth's core and mantle because models for estimating their abundances in the Earth depend greatly on the nature and timing of accretion of the volatile material. Models of heterogeneous accretion of the Earth (Chou, 1978; Morgan and Anders, 1980; Wänke et al., 1984; Morgan, 1986; O'Neill, 1991a, b) call upon a range of volatile material (i.e. chondritic meteorites with various proportions of volatile elements) accreted on to the Earth during the latter stages of planet growth. As with the other volatile elements, the abundances of these elements in the Silicate Earth are constrained by ratioing them to refractory lithophile elements in basalts, komatiites and peridotites.

S is a mildly incompatible element (even during sulfide-saturated melting conditions), having an enrichment factor of  $\sim 4$  in mafic melts relative to their source regions. In peridotites S correlates with  $\text{Al}_2\text{O}_3$  (Lorand, 1991), and fertile peridotites have a relatively constant  $\text{Al}_2\text{O}_3/\text{S}$  of  $\sim 0.02$ . There is a wide range of S contents found in fertile peridotites, from low values of  $\lesssim 100$  ppm (Mitchell and Keays, 1981; Wänke et al., 1984; Ionov et al., 1992), to high values of 100–300 ppm (Garuti et al., 1984; Morgan, 1986; Lorand, 1990). This variation may in part be due to the poor preservation of sulfides, particularly in peridotite xenoliths during their transport from the mantle (Lorand, 1993). The source regions of MORB are suggested to have 200–300 ppm S (Mathez, 1976; Sun, 1982; O'Neill, 1991b; Sun et al., 1991). This estimate for the MORB source is comparable to the higher S contents commonly found in massif peridotites. Together, these studies indicate an upper-mantle S content of  $\sim 250 \pm 50$  ppm; a similar value for the whole of the Silicate Earth may be appropri-

ate, assuming that the crustal contribution, which is poorly constrained, represents a minor (<5%) proportion of the total.

Se and Te are two of the most chalcophile elements known. The geochemical behavior of Se and Te is similar to that of S and hence comparisons are often made between these three elements. In many instances, Se is used as a proxy for S because of the greater immobility of Se during hydrothermal alteration (Yamamoto, 1976; Howard, 1977; Hamlyn et al., 1985). Morgan and coworkers (Morgan and Anders, 1980; BVSP, 1981; Morgan, 1986) showed that S/Se ratios are close to chondritic ( $\sim 3000$ ) in peridotite xenoliths; similar ratios are also found for massif peridotites (Garuti et al., 1984). Morgan (1986) has also emphasized the relatively constant Se/Re ratios ( $\sim 260$ ) in fertile peridotites and MORB and used this to estimate the Silicate Earth's abundance of S and Se given a Re content established from and Re/Os isotope systematics. The S/Se ratio in MORB is estimated at 3000–4000 (Hertogen et al., 1980; Hamlyn et al., 1985; Morgan, 1986). Thus, the Silicate Earth is suggested to have an approximately chondritic S/Se value ( $\sim 2600$ ) (Dreibus et al., 1993). Te appears to be less incompatible than Se with basaltic melts having a slight ( $\sim 50\%$ ) enrichment in Te over their source abundance (Morgan, 1986). Fertile peridotites have relatively constant Te contents of  $\sim 12 \pm 3$  ppb (Morgan, 1986). There is very little Te data for peridotites and basalts; as a result, our estimate of the Silicate Earth's Te content is considerably tentative.

Cd and Hg, along with Zn, are group-IIB elements; these elements generally occur as 2+ cations with a size and range of ionic radii comparable to that of Mg to Ca. Because of its geochemically similar behavior to Zn, Cd is believed to be concentrated in oxides and silicates in carbonaceous chondrites (Nishimura and Sandell, 1964). In basalts, the Zn and Cd contents appear to be enriched by a factor of 2–3 over their source regions, suggesting that they are mildly incompatible elements during melting. Peridotites have relatively constant Zn/Cd ratios of  $\sim 1000$  and a limited range of Cd contents (30–60 ppb) (Baedecker et al., 1971; BVSP,

1981). From this we estimate the Silicate Earth to have  $\sim 40$  ppb Cd. There is a limited data base for Hg contents of basalts and peridotites (Flanagan et al., 1982; Garuti et al., 1984). Its larger ionic radius ( $\sim 1.1 \text{ \AA}$ ) indicates that it would behave more incompatibly during melting than Cd or Zn. However, there appears to be only a factor of 2–3 enrichment of Hg in basalts relative to ultramafic rocks. We suggest the Silicate Earth has  $\sim 10$  ppb Hg, but there is considerable uncertainty attached to this estimate.

The abundance of Sn in mantle-derived rocks and an estimate for the Silicate Earth have been reported recently (Jochum et al., 1993). Jochum et al. (1993) found that Sn/Sm appears to be constant in mantle-derived rocks for the last 3.4 Ga at a value of  $\sim 0.32$ . Based on this we estimate the Silicate Earth to have  $\sim 130$  ppb Sn.

The volatile elements In, Bi and Tl are moderately to highly incompatible elements during mantle melting (Sun, 1982). In the crust Tl behaves similarly to the alkali metals K and Rb, and during melting Tl is suggested to be highly incompatible (even during sulfide-saturated melting conditions), like Ba, Rb and Cs (Sun and McDonough, 1989). It is also suggested that Tl is a sensitive indicator of sulfide saturation in silicate melts (McGoldrick et al., 1979). There is a marked depletion of Tl in most peridotites. However, garnet harzburgites with strong re-enrichments of the highly incompatible elements have high Tl contents (BVSP, 1981). The Rb/Tl ratio in oceanic basalts is relatively constant at  $\sim 230$  (Laul et al., 1972; McGoldrick et al., 1979; Hertogen et al., 1980) and this value is at the high end of that estimated for the continental crust (100–200) (Sighinolfi and Santos, 1974; Taylor and McLennan, 1985; Shaw et al., 1986). As a result, we suggest the Silicate Earth has  $\sim 3.5$  ppb Tl. The concentration of Bi and In in the Silicate Earth is constrained by the data of oceanic basalts and peridotites. The Bi and In contents of oceanic basalts are  $\sim 7$  and 60–90 ppb, respectively, and of peridotites are 1–3 and 5–15 ppb, respectively (Baedecker et al., 1971; Laul et al., 1972; Hertogen et al., 1980; BVSP, 1981), indicating that these elements are moderately incompatible, with enrichment factors of  $\sim 2$ –6

during mantle melting. Based on these observations we estimate that the Silicate Earth has  $\sim 11$  ppb In and  $\sim 2.5$  ppb Bi.

The abundance of Pb in the Silicate Earth is estimated from U/Pb isotope systematics. There is a limited range of  $\mu$  ( $^{238}\text{U}/^{204}\text{Pb}$ ) values (8.0–9.0) for the Silicate Earth (Stacey and Kramers, 1975; Sun, 1982). Given an estimated U content of  $\sim 20$  ppb and this range of  $\mu$ -values for the crust–mantle system, we estimate that the Silicate Earth has a  $^{204}\text{Pb}$  abundance of  $\sim 2$  ppb and a Pb abundance of 144–156 ppb.

#### 5.4. The atmophile elements

The abundances of atmophile elements (H, C, N, noble gases) in the undegassed Silicate Earth can also be constrained by element ratios in mantle-derived rocks and the proportion of these elements in the mantle, atmosphere, ocean and crust. H is considered to be a highly incompatible element during mantle melting, behaving like K (J.G. Moore, 1970). Based on the water contents of basalts, the upper mantle is estimated to have 100–500 ppm  $\text{H}_2\text{O}$  (Byers et al., 1984; Michael, 1988). Data for the water contents of peridotitic minerals (Bell and Rossman, 1992) also indicates the upper mantle has  $\sim 100$ –300 ppm  $\text{H}_2\text{O}$ . An estimate for the water content of the degassed upper mantle is  $\sim 100$ –300 ppm, with considerable uncertainty in this estimate. Jambon and Zimmermann (1990) found a relatively constant  $\text{K}_2\text{O}/\text{H}_2\text{O}$  in oceanic basalts and similar values for this ratio in the oceanic mantle and exosphere (crust and ocean). They assumed that  $\text{K}_2\text{O}/\text{H}_2\text{O}$  behaved similar to the K/U (i.e. that it was conserved during crust–ocean–mantle differentiation), and from this estimated a water content for the Silicate Earth of 550–1900 ppm.

Estimates of the C content of the upper mantle vary widely ( $< 50$  to  $> 500$  ppm C) depending on whether the model is based on measurements of peridotite, basalts or recycling models (Wänke et al., 1984; Marty and Jambon, 1987; O’Nions and Oxburgh, 1988; Zhang and Zindler, 1993). The present-day upper mantle (MORB source region) is estimated to have a C content of 50–

250 ppm and relatively constant C/ $^3\text{He}$  [ $(2-7) \cdot 10^9$ ],  $\text{CO}_2/\text{H}_2\text{O}$  (1.07), and K/C ( $\sim 1$ ) (all given as molar ratios) (Des Marais, 1985; Marty and Jambon, 1987; O’Nions and Oxburgh, 1988; Javoy and Pineau, 1991; Trull et al., 1993). Using these observations and the estimates of K and  $^3\text{He}$  in the primitive mantle yields a Silicate Earth C abundance of  $\sim 100$  ppm (Des Marais, 1985; Marty and Jambon, 1987; O’Nions and Oxburgh, 1988; Trull et al., 1993; Zhang and Zindler, 1993). Nitrogen degassing of the mantle has been considered in terms of C/N ( $\sim 400$ ) and  $\text{N}_2/\text{Ar}$  ( $\sim 50$ ) (Javoy et al., 1986; Javoy and Pineau, 1991). The N abundance of the Silicate Earth is estimated at  $\sim 2$  ppm (Javoy et al., 1986; Javoy and Pineau, 1991; Zhang and Zindler, 1993).

In the above discussion we have determined the absolute abundances of the moderately-volatile and volatile elements from ratios of these elements to the refractory lithophile elements. A wide variety of element ratios were used to establish our estimates. However, there are some basic guidelines that we used. Importantly, we have attempted to ratio elements having similar behavior during mantle melting. In addition, for moderately to highly incompatible elements, we depend more heavily on the data for mantle-derived melts and crustal rocks, whereas for the mildly incompatible to compatible elements we have relied mainly on data from fertile peridotites. It follows then, that if one assumes different proportions of the refractory lithophile elements for the Silicate Earth (than that proposed here), there will be a similar proportional change in the abundances of the moderately-volatile and volatile elements.

## 6. The core

The mass of the core amounts to  $\sim 32.5\%$  of the Earth (Anderson and Kovach, 1967). The core is mainly an Fe–Ni alloy and is the dominant repository of siderophile elements in the Earth. A density increase at the outer core–inner core boundary of  $\sim 0.55 \text{ g cm}^{-3}$  (Shearer and Masters, 1990), combined with laboratory

compression data for a range of Fe–Ni alloys (Brown and McQueen, 1986; Mao et al., 1990), indicates the presence ( $\sim 10\% \pm 5$ ) of a low-atomic-weight component in the outer core (i.e. an element with a lower atomic number than Fe). The nature of this light element in the outer core has received considerable attention.

From Birch's (1952) early suggestion and from later proposals by many other workers H, C, N, O, Mg, Si, S (or a combination of some of these elements) are commonly considered to be the alloying light element in the outer core that will satisfy the density difference. Unfortunately, the exact proportion and character of the light element in the outer core cannot be constrained with our existing seismological and mineral physics data. It is recognized that the lighter the element, the less is needed to compensate for the density contrast. Thus, in order to characterize the light element in the outer core we need to understand the processes of core formation and compositional systematics of chondritic meteorites.

It is likely that there is a spectrum of processes which lead to core formation in the early Earth, ranging from metal–sulfide equilibrium at low pressures to high-pressure solubility of FeO in Fe. The physics of planetary accretion and core separation are presently insufficiently understood to effectively rule out some competing hypotheses. There is a vast amount of literature on this topic and we consider it beyond the scope of this paper to examine this question in detail. We have, however, estimated an upper and lower value for the composition of the core based on a (non-specified) light-element component of 5% and 15%, respectively (Table 6). The principal observation used to construct these estimates is the constant siderophile ratios in chondritic meteorites.

The Fe/Ni ratio in chondritic meteorites shows limited variation from a value of  $\sim 17$  (Table 3). Assuming the bulk Earth has a chondritic Fe/Ni ratio and the mantle has a ratio of 31.9, then the core should have an Fe/Ni ratio of  $\sim 16$  (Table 6). Likewise, the limited variation in Fe/Cr, Cr/V, Cr/Mn, Ni/Co and Ni/P in chondritic meteorites (Table 3 and the literature) provides an estimate for these minor to trace elements in the

core (Table 6). By setting an upper limit of  $\sim 15\%$  (and a lower limit of  $\sim 5\%$ ) for the light-element content of the core, the abundances of the major and minor siderophile elements are determined. In these end-member core compositions ( $\sim 5\%$  and  $\sim 15\%$  of a light-element component) there is  $\sim 5\%$  Ni,  $\leq 1\%$  Cr,  $\sim 0.5\%$  Mn and P and 0.25% Co along with trace abundances of other siderophile and chalcophile elements.

These two models place limits on the Fe content (78–88%) of the core and from this we determine that the bulk Earth has an Fe/Al of  $\sim 20 \pm 2$  (Table 6). [We use Al as a proxy for the refractory lithophile elements. It was chosen over other major elements (e.g., Si, Mg, O, Ca) since it is the element that is lighter than Fe, and is least likely to be incorporated as the light element in the core.] This is an important result; it provides us with a secure estimate of the composition of the planet which does not rely on knowing the nature of the light element in the core. Thus, we can use this ratio to evaluate the similarity of certain groups of chondritic meteorites to the bulk Earth. Chondritic meteorites display a range of Fe/Al ratios with many having a value close to 20. However, the high Fe/Al (35) of EH chondrites and the low values (13–15) for CV and CK chondrites make these meteorite groups unlikely building blocks for the bulk Earth.

The estimate of Si in the bulk Earth assumes no Si in the Earth's core. O'Neill (1991b) has recently suggested that a limited amount of Si ( $\leq 5\%$ ) may have entered the core, and considers it necessary to invoke additional components to satisfy the density requirements. The high abundances of V, Cr and Mn in the Earth's core (Table 6) can account for their depletions in the Silicate Earth (Fig. 8). Our estimate of the Mg/V ratio for the bulk Earth (0.163) is within the range for chondritic meteorites (0.15–0.24), assuming there is no Mg in the core. If we assumed there is no V in the Earth's core, the bulk Earth would have a Mg/V ratio (0.28) which is greater than that seen in all chondritic meteorites; thus we can conclude that there is a significant quantity of V in the Earth's core. This fact, in combi-

Table 6  
Limits on the composition of the core and bulk Earth

	15% Light element in core			5% Light element in core		
	mantle	core	bulk Earth	mantle	core	bulk Earth
Al (%)	2.35		1.59	Al (%)	2.35	1.59
Ca	2.53		1.71	Ca	2.53	1.71
Mg	22.8		15.4	Mg	22.8	15.4
Si <sup>a</sup>	21.0		14.2	Si <sup>a</sup>	21.0	14.2
Fe	6.26	78.0	29.6	Fe	6.26	87.5
Cr	0.263	0.80	0.44	Cr	0.263	0.95
Ni	0.196	4.90	1.72	Ni	0.196	5.40
Mn	0.105	0.45	0.22	Mn	0.105	0.50
Na (ppm)	2,670		1,800	Na (ppm)	2,670	1,800
V (ppm)	82	120	95	V (ppm)	82	120
Co	0.0105	0.24	0.085	Co	0.0105	0.26
P	0.009	0.50	0.17	P	0.009	0.50
Total		84.9		Total		95.1
Mg/Al	9.70		9.70	Mg/Al	9.70	9.70
Fe/Al	2.7		18.6	Fe/Al	2.7	20.6
Fe/Ni	31.9	16	17.1	Fe/Ni	31.9	16
Fe/Cr	23.8	98	68	Fe/Cr	23.8	92
Cr/V	32	67	46	Cr/V	32	79
Cr/Mn	2.5	1.8	~2.0	Cr/Mn	2.5	1.8
Ni/Co	18.7	20.8	20.7	Ni/Co	18.7	20.8
Ni/P	22	10	10	Ni/P	22	11

Element concentrations are given in wt%, except for Na and V which are given in ppm. The Cr/V ratio is expressed in terms of a ppm ratio. The composition of the mantle is from Table 5.

<sup>a</sup>This estimate assumes no Si in the Earth's core. Assuming 5% Si in the Earth's core (O'Neill, 1991a), then the bulk Earth would have 15.8% Si and a Mg/Si of 0.97.

nation with the experimental work of Ringwood et al. (1990), argues for high-pressure metal–silicate equilibration in the Earth's mantle during core formation. Under high pressure some amount of FeO is also dissolved in the metal, and thus, O is likely to be part of the light-element component in the outer core. There is circumstantial evidence that suggests that under high pressure, Cs and possibly other lighter alkali metals have been partially sequestered into the core. The marked depletions in the heavy halides (Cl, Br, I) may also be a result of their partial sequestering into the core. Thus, the relative depletions (beyond a volatility trend) of these elements in the Silicate Earth may be accounted for by a core component (Fig. 8).

Carbonaceous chondrites and the Earth have similar patterns of element abundances (Fig. 9), but the Earth is more strongly depleted in the more volatile elements. Similarities and differences are also found between the element abundance patterns of enstatite and ordinary chondrites with that of the Bulk Earth. We find no group of meteorites with an abundance pattern that matches that of the Bulk Earth's. Thus, chondritic meteorites can only provide us with a guide to understanding the composition of the Earth; these meteorites are not the main building blocks for the Earth.

Finally, we have discussed a number of element ratios which are considerably different between the core and the mantle (e.g., P/Nd, Ti/



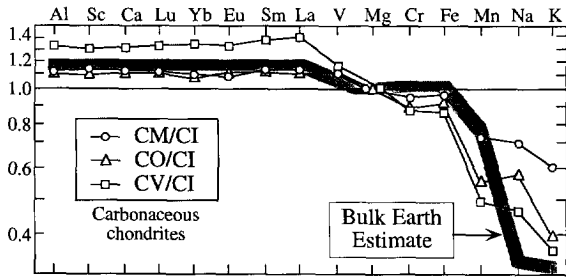


Fig. 9. Abundance patterns of elements in Carbonaceous chondrites and the Earth (bulk Earth estimate from Table 6) normalized to Mg and CI Carbonaceous chondrites. Data for the carbonaceous chondrites are from Wasson and Kallemeyn (1988).

P, Ti/Pd, Ba/W, Sn/Sm). Samples of mantle-derived material can thus be used to evaluate the degree of core–mantle interaction over geologic time. The relative constancy of these element ratios in peridotites, komatiites, and basalts of various ages (and also crustal rocks for some of these ratios) indicates that there has been negligible exchange between the core and mantle throughout the geologic record (the last  $\sim 3.5$  Ga).

## 7. Early evolution of the Earth

Constraints on the composition of the bulk Earth provide insights into the nature of accreting material in the inner nebula. This, combined with compositional models for the other inner planets (e.g., Morgan and Anders, 1980), places significant constraints on astronomical models of planet formation. The standard models of planet formation envisages the gravitational collapse of a rotating interstellar cloud which will form a star or star system, depending on the angular momentum of the collapsing system and planets (Safronov and Vitjazev, 1986; Wetherill, 1990). Wetherill's (1990) model for the early history of the Earth is one of coalescing planetesimals which form planetary embryos and subsequent collision of these embryos, with considerable physical consequences, to form Earth-size planets. In this model he considers it likely that there will be a significant degree of mixing of asteroidal material with proto-Earth material. The dynamics

of this type of mixing model for the Earth is consistent with models of heterogeneous accretion of the Earth (Wänke and Dreibus, 1988; O'Neill, 1991a, b).

It is beyond the scope of this paper to review and discuss models of accretion for the Earth. However, our results have direct bearing on three particular points: (1) the depletion trend of the moderately-volatile lithophile elements (Fig. 8); (2) the addition of a late-stage veneer to account for the mantle abundances of the PGE, S, Se, Te, C, and the heavy halides in the Silicate Earth; and (3) the idea of global-scale melting of the mantle.

Fig. 8 shows the normalized abundances of elements in the Silicate Earth relative to their condensation temperatures. The decreasing trend in the normalized abundances of the lithophile elements with decreasing condensation temperature may reflect the nature of the nebula material in the planetary feeding zone of the proto-Earth (see also the abundance patterns in Fig. 9). Alternatively, we can interpret this trend in terms of the result of a mixture of components, as envisaged in models of heterogeneous accretion of the Earth (Wänke and Dreibus, 1988; O'Neill, 1991a, b). In the first stage the accreted material was dominated by the refractory elements and contained little of the moderately-volatile and volatile components. In the second stage of accretion, refractory material continues to be accreted, but in addition there is the introduction of moderately-volatile material and lesser quantities of volatile material. These two distinct and early stages of accretions are invoked to account for the siderophile and chalcophile element signature of the Silicate Earth. This signature is the result of core formation, the conditions of which (i.e.  $P$ – $T$ – $f_{O_2}$ ) are still poorly understood. The third stage of accretion of the Earth is characterized by addition of the mantle abundances of the PGE, S, Se, Te and C; this is the latest stage of accretion and appears to involve the introduction of a small ( $<1\%$  by mass), oxidized chondritic body (see Section 5.3.2). It is likely that the abundances of the heavy halides in the Silicate Earth may have been controlled by a combination of this late-stage ad-

dition and some sequestering of these elements into the Earth's core.

We believe that the relatively chondritic proportions of the refractory lithophile elements in the fertile peridotites and the primitive Nd and Hf isotopic compositions of the early Archean komatiites from Barberton Mountain Land, South Africa (Jahn et al., 1982; Gruau et al., 1990) demonstrate that global-scale mineral-melt fractionation has not left an imprint on the mantle; we see no geochemical evidence for global-scale differentiation of the mantle. However, our data do not preclude the possibility that this has occurred in Hadean times and was subsequently erased by rapid, whole-mantle convection.

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