

The chemical composition of the Earth

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Abstract

The bulk composition of the Earth and the composition of the mantle and core are calculated using the ratios of major and trace elements.

The ratios of elements which do not enter the core (lithophile) are the same in the bulk Earth as in the mantle. Bulk earth ratios involving an element that does enter the core (siderophile) are therefore determined from meteorite correlation diagrams of siderophile–lithophile ratios vs. lithophile–lithophile ratios and from primitive mantle composition in elements which do not enter the core (e.g., Al). The composition of the core is determined by difference, without resorting to assumptions about core formation processes.

It is found that the core contains about 7.3 wt% silicon and 2.3 wt% sulphur. To account for the seismologically determined density deficit of the core, about 4 wt% oxygen must be added.

The present results are compatible with the idea that the core material equilibrated at low pressure, in reducing conditions. Furthermore, we propose that the Earth is closer to CM rather than to C1 for non-volatile element ratios.

1. Introduction

The determination of the chemical composition of the Earth and its principal units, the mantle and core, is one of the major goals in the Earth Sciences. Knowledge of this composition will constrain many geophysical and geochemical problems. From a chemical point of view, a knowledge of the bulk earth chemical composition will constrain models of continental crust differentiation and the structure of mantle convection through isotopic and chemical mass balance considerations. Geophysical evidence points to the core containing light elements that

decrease its density below that of pure iron [1]. Knowledge of the nature and proportion of these elements would constrain models of core formation.

Pioneering work on these questions was done by Goldschmidt [2] and, later, by Ringwood [3–8], to whom we dedicate this paper.

The classical contributions to this problem were based on guesses which identified the Earth with a specific type of chondrite or as a mixture of different types of chondrites. A different approach, based on data from terrestrial as well as meteoritic materials, has been used in more recent years to compute the composition of the Earth. This combines the use of

the major elements with that of trace elements. In a first attempt in this direction, Loubet et al. [9] used the fact that REE patterns are similar for all types of meteorites and looked for peridotites with similar primitive compositions. Subsequently, Jagoutz et al. [10] achieved a major breakthrough by using the intersection of a chondritic trend with a mantle trend in Mg–Si–Al space. This approach has since been slightly refined by Hart and Zindler [11].

Our approach differs from that of Jagoutz et al. [10] in that we assume that the intersection of the meteoritic trend with the mantle trend in Mg–Si–Al space does not represent a priori ‘true’ primitive mantle, because Si may enter the core, so that the silicon content of the mantle is reduced by core formation. Our present calculations specifically take this possibility into account, whereas the method of Jagoutz et al. [10] eliminated it a priori.

2. Basic assumptions

We use the following assumptions, which are also implicit in most previous treatments of the subject, although they have usually not been specifically stated.

(1) For concentration ratios of elements that are not highly volatile, we assume that the Earth follows the compositional trends of chondrites, or, as may happen, carbonaceous chondrites.

(2) For major elements, we assume that the mantle is chemically homogeneous (i.e., that the lower mantle has the same composition as the upper mantle). The estimate of the composition of the primitive upper mantle is therefore valid for the bulk mantle.

(3) We accept the seismological and laboratory evidence which indicates that the Earth’s core is made of 80–90% Fe–Ni alloy and of light elements that lower its density by 10–15% with respect to that of pure iron in the same conditions.

Each of these assumptions can be challenged, but not with an infinite degree of freedom. The hypothesis that different classes of chondrites represent the complete set of primitive planetary materials existing in the early solar system from which the Earth was made has never been proven and probably never will be. Nevertheless, certain concentration ratios are approximately uniform in most mantle-derived and

crustal rocks, and these uniform ratios do conform to chondritic ratios [12]. This ‘coincidence’ constitutes substantial independent confirmation of the chondritic hypothesis. The assumption of an essentially chondritic Earth has been implicitly or explicitly made by all authors who have estimated the chemical composition of the Earth.

We will follow the common approach but with a slightly different philosophy. We do not a priori identify the Earth with any specific class of meteorites (such as CI chondrites). We only assume that the composition of the Earth follows the meteoritic chemical trends in a manner similar to the postulates of Jagoutz et al. [10] and Hart and Zindler [11]. It must be noted that for ratios of highly refractory non-siderophile elements the chondritic trend includes both carbonaceous and ordinary chondrites but that for other elements there is one trend for the carbonaceous chondrites and another for the ordinary chondrites. This is particularly clear for ratios involving Fe or Ni, which clearly separate L, LL and EL chondrites from other meteorites, as well as for ratios involving sulphur and the Nd/Ca ratio [11].

The idea that the mantle is homogeneous in terms of major elements is based on two simple considerations. The first of these is straightforward. The continental crust, which is clearly different from the mantle, constitutes such a small mass fraction of the total silicate portion of the Earth (about 0.5%) that extraction of the crust does not significantly alter the concentration of the major elements of the residual mantle, even if this residual reservoir is restricted in volume to the upper mantle. This is a consequence of simple mass balance considerations which need not be elaborated upon here. The Earth’s mantle was undoubtedly well mixed in the beginning, as core differentiation implies a large turnover. It is difficult to imagine a later process that could have altered this early homogenization of major elements. Recent seismological observations [13] and geochemical modelling [14] suggest that a fair amount of exchange takes place between the upper and lower mantle, which also favours homogenization.

The second consideration is more controversial, although in our opinion unduly so. Claims that the lower mantle is enriched in iron or silicon with respect to the upper mantle, based on comparison of density or seismic velocity profiles with profiles

derived from mineral physics experiments, are certainly not universally accepted (e.g., [15]). The most recent efforts to determine the pressure–temperature–density relationships of mantle mineral assemblages are consistent with a compositionally uniform pyrolite model for the entire mantle [16]. Chemical heterogeneity of the mantle, although not impossible, is clearly not required by seismological and mineral physics data. The strongest geochemical constraints against a major element chemical stratification of the mantle resulting from the crystallization of a magma ocean have been provided by the combined weight of analytical data on upper mantle peridotites and their basaltic derivatives and the partitioning experiments of Kato et al. [17]. Although the literature is still somewhat divided on this issue, it appears that the defenders of the chemically stratified mantle for major elements must resort to ever more elaborate models in order to evade the obvious conclusion, namely that this is an idea whose time has come and gone [18].

There is a third assumption that is not very controversial. The meteorite model for the Earth virtually requires a major terrestrial repository for iron and nickel, and the core is the only place on Earth where such quantities of these metals could be stored. Furthermore Birch [19,20], using sound velocity–density systematics obtained from shock-wave experiments for various elements, conclusively showed that iron is the only element compatible with the density and pressure of the core. Since that time, the idea that the core consists mainly of Fe–Ni alloys has not been seriously challenged. However, from comparison of the seismologically determined density with equations of state for pure iron, it appears that the core is about 10–15% less dense than pure iron at the same conditions. This density deficit can be accounted for by the presence of light elements. The nature and proportions of these light elements have been, and still are, the subject of an active debate [1], and specifically are the subject of the present paper.

Our strategy is as follows: First we determine the bulk composition of the Earth from meteorite correlations and from the mantle rock composition in terms of *elements which do not enter the core*. We then use these bulk earth values and the composition of the silicate portion of the Earth (i.e., the ‘primi-

tive’ mantle) to determine the chemical composition of the core by difference.

3. Chemical composition of the primitive mantle (PRIMA)

The chemical composition of what is called ‘primitive’ mantle, i.e., the average mantle before extraction of the continental crust, is obtained from a set of samples from the upper mantle, even though these samples have already been processed by the complex chemical machine of plate tectonics, which involves extraction and re-injection of partially melted material as well as recycling of oceanic and continental crust.

We use the same approach as employed by Loubet et al. [9], Jagoutz et al. [10] and Hart and Zindler [11]: we consider the intersection of the chemical trend of peridotitic materials with the meteorite trend. The major—and fundamental—difference compared to the methods of Jagoutz et al. [10] and Hart and Zindler [11] is that we eliminate in this construction all elements which are suspected of entering the core (namely Fe and Ni) but also the light element ‘core candidates’ (S, O and Si). We will thus retain only the purely lithophile major elements Mg, Al and Ca. The Mg/Al vs. Nd/Ca diagram used by Hart and Zindler [11] yields a value of 10.5 ($Al/Mg = 0.095$) for the Mg/Al of the primitive earth mantle. This is considerably lower than the pyrolite value of 13.11 [6], although Jagoutz et al. [10] have obtained a similar result ($Mg/Al = 11.0$).

The Si/Mg ratio in the primitive mantle is a key ratio for estimating the composition of the Earth. We use the (Si/Mg, Al/Mg) diagram from the compilations for xenoliths and orogenic lherzolites of Jagoutz et al. [10] and Hart and Zindler [11] (Fig. 1). Assuming PRIMA corresponds to the least differentiated sample (and not to the intersection with the meteorite line) and disregarding an extreme orogenic sample, we obtain $Al/Mg = 0.095$ and $Si/Mg = 0.945$, corresponding to $Mg/Al = 10.50$. We then have $(Si/Al)_{PRIMA} = 9.682$.

Because meteorites have uniform Ca/Al ratios of 1.07 ± 0.04 , we will use this value for PRIMA, even though most terrestrial peridotites have values closer to 1.24 [24,25].

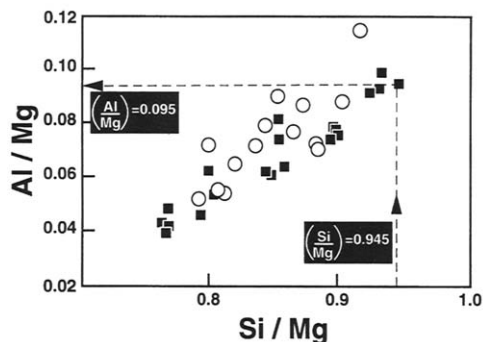


Fig. 1. (Si/Mg) vs. (Al/Mg) ratios for a suite of xenoliths and orogenic lherzolites [10,11]. Assuming that PRIMA corresponds to the least differentiated sample, we obtain $Al/Mg = 0.095$ and $Si/Mg = 0.945$. ■ = Xenoliths; ○ = orogenic lherzolites.

For $(Mg/Fe)_{PRIMA}$, we will use the value of 3.92 ± 0.03 derived from the value of the atomic ratio $(Mg/(Fe + Mg) = 0.9)$ determined by many workers, including Ringwood [6]. This immediately gives $(Fe/Al)_{PRIMA} = 2.683 \pm 0.011$.

Assuming a total of the minor oxides of $MnO + TiO_2 + Na_2O + K_2O + P_2O_5 + Cr_2O_3 + NiO = 1.38$ wt%, we can calculate the absolute values of each element by normalizing to 100%. The resulting val-

Table 1
Composition of PRIMA and pyrolite [6]

Ratios (Wt%)	Elements (Wt%)	Oxides (Wt%)	Pyrolites Oxide (Wt%)
$Mg/Al = 10.52 \pm 0.1$	O = 44.79	$SiO_2 = 46.117$	$SiO_2 = 45.1$
$Si/Al = 9.947 \pm 0.05$	Si = 21.521	$Al_2O_3 = 4.09$	$Al_2O_3 = 3.3$
$Ca/Al = 1.07 \pm 0.001$	Al = 2.164	$MgO = 37.77$	$MgO = 38.1$
$Fe/Al = 2.683 \pm 0.01$	Mg = 22.784	$FeO = 7.485$	$FeO = 8$
$Si/Mg = 0.945 \pm 0.002$	Fe = 5.818	$CaO = 3.232$	$CaO = 3.1$
$Fe/Mg = 0.255 \pm 0.005$	Ca = 2.308		
	K = 0.0280	$K_2O = 0.0337$	
	Na = 0.264	$Na_2O = 0.360$	
	Mn = 0.116	$MnO = 0.149$	
	Ti = 0.112	$TiO_2 = 0.180$	
	Ni = 0.200	$NiO = 0.25$	
	Cr = 0.270	$Cr_2O_3 = 0.38$	

ues for PRIMA are compared with Ringwood's [6] pyrolite results, and with those of McDonough and Sun [18] and Hart and Zindler, in Table 1.

We should point out here that, although obtained by a completely different method, our results are curiously quite close to those of Hart and Zindler [11]. Indeed, we have only used their Mg/Al vs. Nd/Ca diagram, which is not very sensitive to the choice of a meteoritic trend, and we have used none of their plots involving Si. Since the Earth's mantle is anomalously depleted in silicon, as we will discuss later, the Jagoutz et al. [10] construction should yield an unrealistic value of the ratio Mg/Si. However, they obtain an approximately correct result, because they arbitrarily chose to fit their meteoritic line to ordinary chondrites only. If the carbonaceous chondrites had been included, the results should have been entirely different (this may be more than a coincidence, as ordinary chondrites have some affinity with the Earth's mantle).

4. Critical ratios for the composition of the bulk earth (BE)

The idea is simple: *The ratios of elements which do not enter the core (lithophile), are the same in the bulk earth (BE) as in the mantle.* Bulk earth ratios involving an element that does enter the core (siderophile) are therefore determined from meteorite correlation diagrams of siderophile–lithophile ratios vs. lithophile–lithophile ratios.

Using Wasson and Kalleyman's [23] compilations, we can derive excellent correlations between Mg/Al, Fe/Al and Si/Al ratios and between Al/Mg, Fe/Mg and Si/Mg ratios. This applies to most meteorites, with the exception of the L, LL and EL chondrites, which are deficient in Fe and plot off any trend involving iron. EH chondrites, which are enriched in iron, also plot off such trends, which may suggest a balance of iron between the EL and EH chondrites.

We can estimate $(Fe/Al)_{BE}$ by two methods:

(i) We can use the Mg/Al–Fe/Al correlation in meteorites (Fig. 2) as explained above. Using the previously derived value $Mg/Al = 10.50$, we obtain $(Fe/Al)_{BE} = 18.8$.

(ii) We can also derive $(Fe/Al)_{BE}$ from the man-

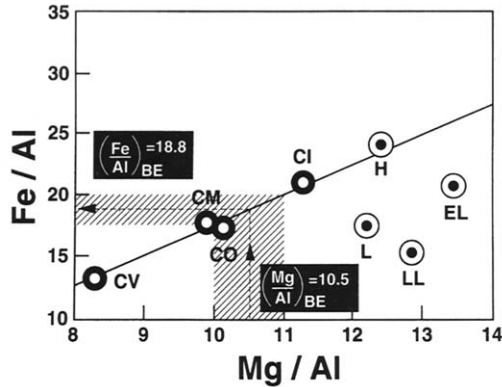


Fig. 2. (Mg/Al) vs. (Fe/Al) ratios for a suite of chondrites [20]. Black-edged and white-edged symbols are carbonaceous and ordinary chondrites respectively. The regression line passes through the carbonaceous chondrite points. Using the derived value $(Mg/Al)_{BE} = 10.50$, we obtain $(Fe/Al)_{BE} = 18.80$.

tle ratio $(Fe/Al)_{PRIMA}$ by an iterative method, assuming that Al does not enter the core:

$$(Fe/Al)_{BE} = \frac{(Fe/Al)_{PRIMA}}{\phi_M} \quad (1)$$

where ϕ_M , the ratio of the mass of Fe in the mantle to the total mass of Fe in the Earth, is given by:

$$\phi_M = \frac{(Fe)_M m_M}{[(Fe)_M m_M + (Fe)_C m_C]} \quad (2)$$

where m_M and m_C are the mass of the mantle and the core and $(Fe)_M$ and $(Fe)_C$ are the mass fractions of iron in the mantle and core. We take the mass of the primitive mantle as equal to $4.09 \cdot 10^{24}$ kg, rather than $4.07 \cdot 10^{24}$ kg, because we have to include the mass of the crust, which is not yet formed. The mass of the core is taken as equal to $1.967 \cdot 10^{24}$ kg. Taking as an initial approximation a value of $(Fe)_C = 80$ wt% Fe in the core and $(Fe)_M = 5.81$ wt% Fe in the mantle, Eq. (2) yields $\phi_M = 0.129$. With the value $(Fe/Al)_{PRIMA} = 2.687$ given in Table 1, we obtain $(Fe/Al)_{BE} = 19.4$. This value will subsequently be refined by iteration once estimates of the light element content of the core are made. As a good compromise, we use the average of two values: $(Fe/Al)_{BE} = 19 \pm 0.2$.

Similarly, we can estimate $(Fe/Mg)_{BE}$ by two methods:

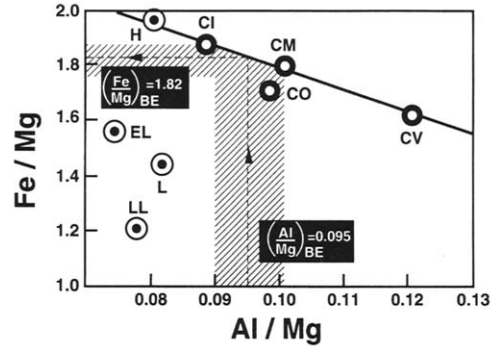


Fig. 3. (Al/Mg) vs. (Fe/Mg) ratios for a suite of chondrites (references and symbols are the same as in Fig. 2). We deduced the $(Fe/Mg)_{BE}$ value from the linear array based on $(Al/Mg)_{BE} = 0.095$.

(i) Using the $(Fe/Mg, Al/Mg)$ correlation, we obtain $(Fe/Mg)_{BE} = 1.82$ (Fig. 3).

(ii) Using the (Fe/Mg) value of the Earth's mantle and an Earth budget, we obtain, for 80% Fe in the core, $(Fe/Al)_{BE} = 1.83$, in excellent agreement with meteorite estimates. This suggests that the iron content of the core is closer to 80% than 85%.

Using the $(Si/Mg, Al/Mg)$ correlation, we can estimate $(Si/Mg)_{BE} = 1.10$, since this ratio is almost constant in carbonaceous chondrites (Fig. 4). The correlation $(Si/Al, Fe/Al)$ gives the estimate $(Si/Al)_{BE} = 12$.

In the same way, the correlations $(Ni/Al, Fe/Al)$

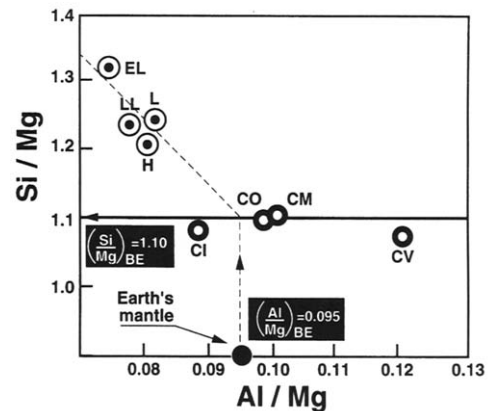


Fig. 4. (Al/Mg) vs. (Si/Mg) ratios for a suite of chondrites (references and symbols are the same as in Fig. 2). Carbonaceous and ordinary chondrites form an excellent trend. Assuming $(Al/Mg)_{BE} = 0.095$, we obtain $(Si/Mg)_{BE} = 1.10$.

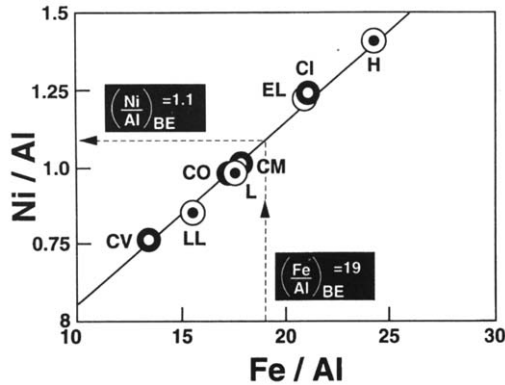


Fig. 5. (Fe/Al) vs. (Ni/Al) ratios of a suite of chondrites (references and symbols are the same as in Fig. 2). Assuming $(\text{Fe}/\text{Al})_{\text{BE}} = 19$ gives $(\text{Ni}/\text{Al}) = 1.1$.

and $(\text{Ni}/\text{Mg}, \text{Fe}/\text{Mg})$ give the estimates $(\text{Ni}/\text{Al})_{\text{BE}} = 1.1$ and $(\text{Ni}/\text{Mg})_{\text{BE}} = 0.104$. (Fig. 5).

We cannot compute directly the absolute composition of the bulk earth because we must know the composition of the core to make the calculation.

5. Chemical composition of the core

We will again use the fact that Mg, Al and Ca do not enter the core.

Iron content: We can write the simple budget equation:

$$\begin{aligned} \left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{BE}} &= \frac{m_{\text{M}}(\text{Fe})_{\text{PRIMA}} + m_{\text{C}}(\text{Fe})_{\text{C}}}{m_{\text{M}}(\text{Mg})_{\text{PRIMA}}} \\ &= \left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{PRIMA}} + \frac{m_{\text{C}}(\text{Fe})_{\text{C}}}{m_{\text{M}}(\text{Mg})_{\text{PRIMA}}} \end{aligned} \quad (3)$$

where $m_{\text{M}}(\text{Fe})_{\text{PRIMA}}$ and $m_{\text{M}}(\text{Mg})_{\text{PRIMA}}$ are the masses of Fe and Mg in the primitive mantle, and $m_{\text{C}}(\text{Fe})_{\text{C}}$ is the mass of Fe in the core. The mass fraction (concentration) of Fe in the core, $(\text{Fe})_{\text{C}}$, is related to the mass fraction (concentration) of Mg in the primitive mantle, $(\text{Mg})_{\text{PRIMA}}$, by:

$$\begin{aligned} (\text{Fe})_{\text{C}} &= \left[\left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{BE}} - \left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{PRIMA}} \right] (\text{Mg})_{\text{PRIMA}} \\ &\times \frac{m_{\text{M}}}{m_{\text{C}}} \end{aligned} \quad (4)$$

with the previously determined values, we obtain:

$$(\text{Fe})_{\text{C}} = 77.4\%$$

Silicon content: We have similarly:

$$\begin{aligned} (\text{Si})_{\text{C}} &= \left[\left(\frac{\text{Si}}{\text{Mg}}\right)_{\text{BE}} - \left(\frac{\text{Si}}{\text{Mg}}\right)_{\text{PRIMA}} \right] (\text{Mg})_{\text{PRIMA}} \\ &\times \frac{m_{\text{M}}}{m_{\text{C}}} \end{aligned} \quad (5)$$

and:

$$(\text{Si})_{\text{C}} = 7.17\%$$

Nickel content: In the same way, taking the value of the Ni content of the mantle as equal to 2000 ppm, we obtain:

$$(\text{Ni})_{\text{C}} = 4.75\%$$

The same computations have been carried out using Al instead of Mg as the reference element that does not enter the core. These computations give the same results.

The mass fractions of Fe, Ni and Si do not add up to 1, and we must therefore look for other light elements. The two other main candidates are oxygen and sulphur. Sulphur could in principle be treated like nickel or silicon but unfortunately the meteorite correlations involving sulphur with refractory elements are poor. In addition, the sulphur concentration in the mantle is clearly too low to be comparable with any meteorite materials. Estimates range from 350 ppm for recent peridotites [12,26] to 1000 ppm for komatiites [27], although recent estimates are closer to 240 ppm (Sun, pers. commun.). However, the crustal deposits of sulphates are far from being a quantitatively significant reservoir. The behaviour of sulphur during the cosmochemical stage, where volatility is a key parameter, is difficult to determine, because although as an element it is volatile the behaviour of sulphur is strongly dependent on its chemical state (it can form both highly refractory (CaS) or very volatile (SO_2 , SH_2) compounds).

To estimate the content of sulphur in the Earth, we will consider this element as volatile and examine the correlation of volatiles in meteorite families.

The K/Ca vs. S/Ca diagram for meteorites (Fig. 6) defines two trends, one for ordinary chondrites and one for carbonaceous chondrites.

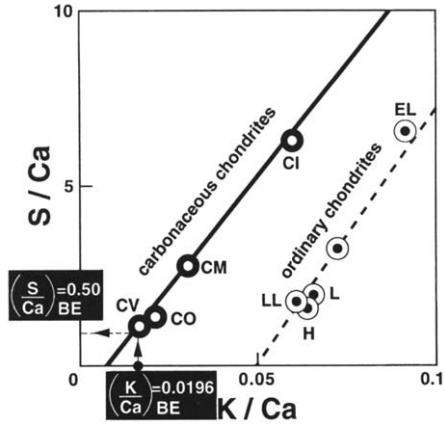


Fig. 6. (K/Ca) vs. (S/Ca) ratios for a suite of chondrites (references and symbols are the same as in Fig. 2). Carbonaceous and ordinary chondrites form two distinct trends. Using the carbonaceous trend, we calculated the $(S/Ca)_{BE}$ ratio from the $(K/Ca)_{BE}$ value.

Using the correlation for carbonaceous chondrites and the terrestrial K/Ca value of $1.96 \cdot 10^{-2}$ [28] we obtain a terrestrial S/Ca ratio of 0.50 and a bulk earth sulphur content of 0.7128%. This in turn corresponds to 2.25% S in the core. This is in accord with the recent estimate of Dreibus and Palme [29] based on Se/S ratios.

To calculate the oxygen content of the core, we will assume that the 10% density deficit of the core is completely accounted for by silicon, sulphur and

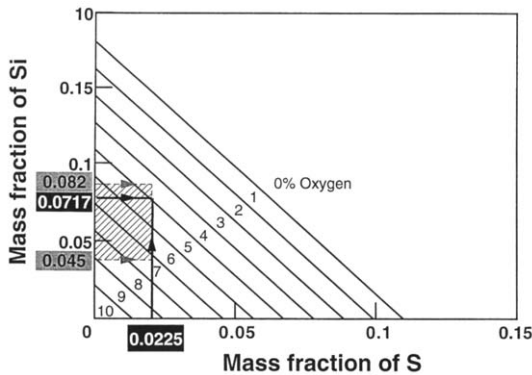


Fig. 7. Mass fraction of silicon vs. mass fraction of sulphur. The lines represent the value of mass fraction of oxygen necessary to account for a core density deficit of 10%. We find that for 7.17% Si and 2.25% S, about 4% oxygen is needed. For the extreme values of Si = 4.3% and 8.2% with 2.25%, the oxygen content is 4.5% and 7.5% respectively.

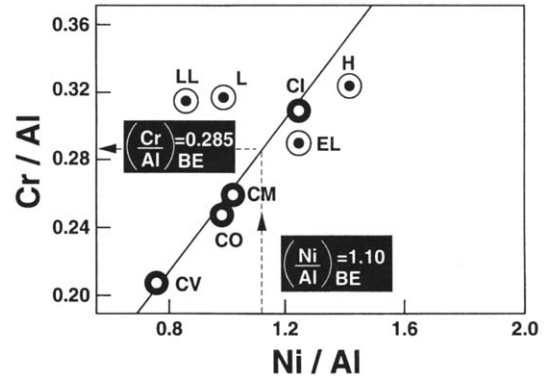


Fig. 8. (Ni/Al) vs. (Cr/Al) ratios (references and symbols are the same as in Fig. 2). EH chondrites fall on the trend but are not reported on the diagram because of the scale used. We calculated the (Cr/Al) ratios for the bulk earth based on the $(Ni/Al)_{BE}$ value following the procedure explained in the text.

oxygen. The composition of the alloys giving a core density deficit of 10% can be found [1] from the equation:

$$\sum f_x \left(\frac{\rho_{Fe}}{\rho_x} - 1 \right) = 0.11 \quad (6)$$

where f_x and ρ_x are the mass fraction and density at core conditions of element x and ρ_{Fe} is the density of iron at core conditions. Instead of the light elements O, S and Si, it is more convenient to consider the light-element-rich end members FeO, FeS and Fe₂O wt% Si, whose equations of state are known.

Using the equations of state for ϵ -Fe [30], FeO

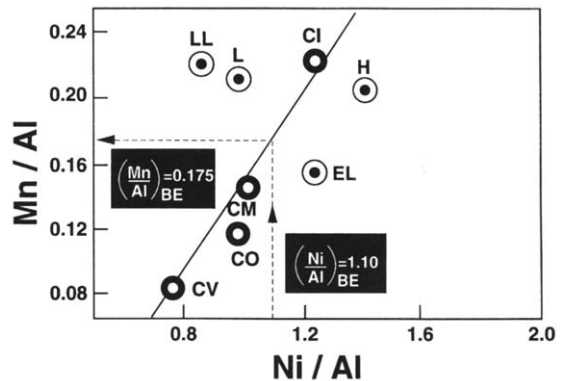


Fig. 9. (Ni/Al) vs. (Mn/Al) ratios. For calculation of the ratio on the vertical axis and further explanation, see Fig. 8.

[31], FeS [32] and Fe₂O wt% Si [33], we obtain for a given mass fraction of silicon and sulphur the approximate value of the mass fraction of oxygen necessary to account for a core density deficit of 10% (Fig. 7). We find that for 7.17% Si and 2.25% S about 4% oxygen is needed.

We can continue our investigation of core composition with other possible major elements (e.g., Ti, Cr, Mn, Co and P, which have been shown to have siderophile tendencies at high pressures [6,34,35]); the approach is the same as for Ni and Si. Titanium is not a siderophile element in meteorites and Ti/Ca is almost constant in meteorites (Ti/Ca = 0.0475). We therefore obtain (Ti)_{BE} = 0.073% and (Ti/Fe)_{BE} = 0.0243. Using the value TiO₂ = 0.18% in the pristine mantle [36], we obtain (Ti)_{PRIMA} = 1020 ppm (close to the result of Ebihira and Anders [37]) and (Ti/Fe)_{PRIMA} = 0.0212. The titanium content of the core is therefore almost zero: *Titanium is a non-siderophile element in the Earth as well as in meteorites.*

Using the Ni/Al vs. Cr/Al diagram, we can determine the ratio (Cr/Al)_{BE} = 0.285 which, with (Cr)_{PRIMA} = 2700 ppm, gives (Cr)_{BE} = 4290 ppm and (Cr)_C = 7600 ppm (Fig. 8). Similarly, from the Ni/Al vs. Mn/Al diagram, we obtain (Mn)_{BE} = 2600 ppm and (Mn)_{PRIMA} = 1160 ppm gives (Mn)_C = 5680 ppm (Fig. 9). The Ni/Al vs. Co/Al diagram gives (Co)_{BE} = 870 ppm and (Co)_{PRIMA} = 100 ppm gives (Co)_C = 2470 ppm (Fig. 10). Finally, in the Fe/Ca vs. P/Ca diagram, (P)_{BE} = 1240 ppm and (P)_{PRIMA} = 80 ppm gives (P)_C = 3600 ppm (Fig. 11).

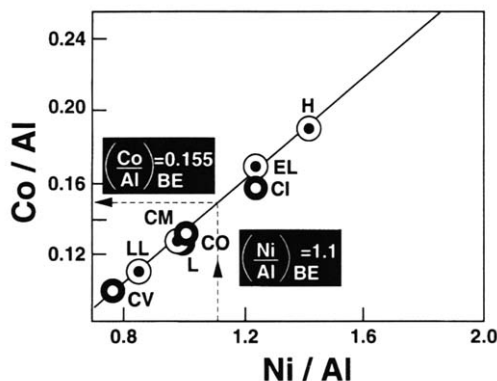


Fig. 10. (Ni/Al) vs. (Co/Al) ratios. For calculation of the ratio on the vertical axis and further explanation, see Fig. 8.

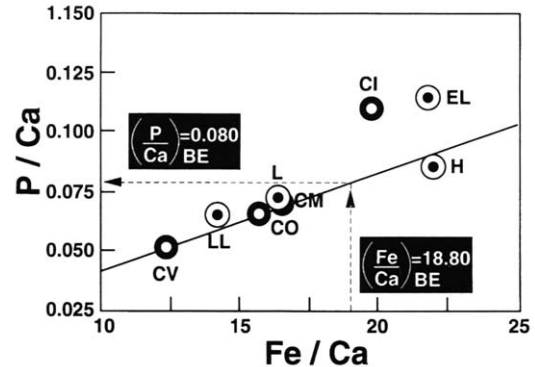


Fig. 11. (Fe/Ca) vs. (P/Ca) ratios for a suite of chondrites (references and symbols are the same as in Fig. 2). We calculated the (P/Ca)_{BE} ratio from the (Fe/Ca)_{BE} value.

The concentration of other elements (e.g., C or Cu), for which the meteorite correlations are poor, could not be evaluated.

Adding the above additional components to the core gives a total of 97.50%. To obtain 100% we renormalized multiplying by 1.025 and finally we obtain the core composition given in Table 2.

Table 2
Composition of the core and the bulk earth

CORE (Wt%)	BULK EARTH (Wt%)
Fe = 79.39 ± 2	O = 32.436
Ni = 4.87 ± 0.3	Si = 17.221
Si = 7.35	Al = 1.507
S = 2.30 ± 0.2	Mg = 15.866
O = 4.10 ± 0.5	Fe = 28.176
	Ca = 1.607
	K = 0.0192
	S = 0.7010
	Na = 0.249
	Ti = 0.0710
	Ni = 1.6147
In ppm	In ppm
Mn = 5 820	Mn = 2 600
Cr = 7 790	Cr = 4 290
Co = 2 530	Co = 870
P = 3 690	P = 1 240

6. Discussion

Let us first assess the accuracy of our estimates. For the mantle, which is assumed to be homogeneous, it is remarkable that two recent estimates [11,18] agree very well with the present work. It is now clear that further improvement will depend on better quality analyses of peridotites having undergone a minimum number of melting episodes. Therefore, we will not discuss this question further, except insofar as it concerns the composition of the core. Two important points must be addressed, the Fe content and the Si content in the core (the oxygen content will automatically follow) (see Fig. 7).

The Fe content of the core depends on the (Fe/Mg) ratios of the bulk earth and of the mantle, and on the Mg concentration of the mantle. The (Fe/Mg) ratio of the bulk earth compatible with the (Mg/Al) ratio observed in peridotites varies, at most, from 1.85 to 1.75 (Fig. 1). The Mg concentration and the (Fe/Mg) ratio of the mantle are relatively well known. The ratio m_M/m_C varies from 2.17 to 2.07 depending on the author [18–38]. This corresponds to an Fe content of the core varying from 79 to 70%. A lower mantle enriched in iron would lower the Fe content of the core and lead to an uncomfortably high concentration of light elements.

The Si content of the core depends sensitively (Fig. 12) on the somewhat inaccurate estimates of

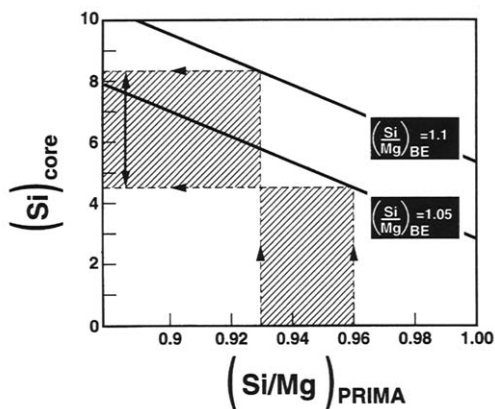


Fig. 12. $(\text{Si}/\text{Mg})_{\text{PRIMA}}$ vs. $(\text{Si})_{\text{core}}$ (%). Two extreme values are taken for $(\text{Si}/\text{Mg})_{\text{BE}}$ on the basis of various carbonaceous chondrites.

(Si/Mg) in the bulk earth and in the mantle. The value of $(\text{Si}/\text{Mg})_{\text{BE}}$ varies between 1.1 and 1.05, depending on whether it is calculated from carbonaceous or CI chondrites. The value of $(\text{Si}/\text{Mg})_{\text{PRIMA}}$ varies from 0.93 to 0.96. A simple calculation then shows that the most extreme possible values for $(\text{Si})_{\text{C}}$ are 8.2% and 4.3%. The corresponding $(\text{O})_{\text{C}}$ contents are 4.5 and 7.5% respectively (Fig. 7).

The proposition of putting silicon into the core is not a new one. It was initially proposed by Ringwood [4]. This proposition was abandoned for the reason that silicon can enter metallic iron only under very reducing conditions. Several experiments have shown that it is indeed difficult to reconcile the presence of silicon in the core with the FeO content of the mantle (e.g., [39,40]). The constant Ni/Co ratio in the mantle as discussed by Palme and Nickel [22] presents a similar problem. Because nickel and cobalt have extremely high partition coefficients (which, nevertheless, differ by a factor of ten), favouring iron in reducing conditions, the fact that the Ni/Co ratio is only slightly less than 'chondritic' in the mantle is puzzling. Palme and Nickel [22] assume a change in oxidation state of the mantle at a late stage, which inhibits the incorporation of Ni and Co in the core and fixes their ratio in the residual mantle. With this scenario, there is no difficulty in introducing silicon into the core during a reducing episode (FeO appearing later, as a late oxidation product), as did Wänke [12]. Wänke, however, did not include sulphur and oxygen in the light elements of the core.

O'Neill [40] claims that 5% Si in the core of the proto-Earth would release enough O to oxidize 12% Fe to FeO in the proto-mantle. If this were true, the 7.7% Si we find for the core would entail more FeO in the mantle than acceptable. However, O'Neill considers that all of the silicon in the core entered during differentiation of the Earth, which is far from being proven. If the Earth was formed in very reducing conditions in the beginning, as were the E chondrites, about 4% Si would have been already present in the metal inventory. Only 3.7% Si would have to be obtained by reduction of silicates, which would yield about 8% FeO, very close to the proportion of $\text{FeO} + \text{TiO}_2 + \text{MnO} + \text{NiO}$ observed in PRIMA. The fact that the conditions of the primitive Earth were very reducing was argued on many occasions by

Wänke [12,26], and Javoy [41] insisted that, insofar as stable isotope fractionation is concerned, the Earth was closer to E chondrites than to any other meteorites. Furthermore, nothing guarantees that the core differentiation was an equilibrium process as assumed by O'Neill [40].

It must also be pointed out that although the change in redox conditions from reducing to oxidizing during differentiation of the core can be accounted for by heterogeneous accretion, this process is also compatible with homogeneous accretion. The evolution of the oxidation state of the mantle would then be a consequence of the differentiation of the core: the oxygen evolved during reduction of silicates to elemental silicon could migrate upward and progressively modify the oxidation state of the mantle [40]. The late stages of accretion would then have occurred in oxidizing conditions, as argued by Palme and Nickel [19] and Wänke [26].

We have, admittedly, not considered the possibility of carbon in the core because of the lack of good constraints for meteorites. A small amount of carbon, of the order of 1%, could indeed be present in the core, as proposed by Wood [42].

If our composition of the core is correct it places some constraints on scenarios of core formation—the presence of Si, Cr and Mn, little O and no Ti places limits on the oxidation state and pressure at which the core was differentiated. The present, albeit preliminary, results support the idea that the core material equilibrated at low to intermediate pressure in reducing conditions.

This accords with Ahrens's observation [43] that core formation could not have occurred at a very high pressure. On the other hand, the idea that iron metal segregation occurred at low pressure in the Earth is apparently not supported by the data because Mn and Cr are lithophile elements at low pressure, whereas we find them to be siderophile. However, the meteorite correlations show that they can be siderophile in very reducing conditions, as is the case for EL chondrites.

One difficulty remains: At low pressure, the Fe–Si–S phase diagram exhibits a large immiscibility gap in the liquid state [44]. For our calculated core composition to correspond to a single-phase solution of light elements in liquid iron, we must assume that at higher pressure (and/or temperature) the gap

closes up. This is usually the case if temperature increases [8], but the evolution of the miscibility gap for high pressures and temperatures should be experimentally investigated.

The idea that the composition of the Earth is close to that of C1 chondrites for refractory elements (although not for all elements) was proposed by Anders [45], Wänke [12] and Ringwood [5,6], among others. However, examination of meteorite correlation diagrams leads us to a new claim that as far as *refractory elements* are considered, the Earth is closer to CM than to C1. Our approach also shows that the bulk earth is very different from ordinary chondrites, which, rather than being primitive, appear to have been differentiated by planetesimal fractionation.

The complex scenarios often used to explain the so-called 'silicon problem' become unnecessary: the Earth has accreted all refractory elements in solar proportion, and it lost the most volatile elements (Na, K, S and P) above a rather sharply defined temperature (about 1200 K in the condensation scheme of Larimer [46]). This will be the object of a more detailed discussion in the future.

The present computations, which are based on mass balance calculations with minimal assumptions, provide a consistent model for the chemical composition of the Earth, the primitive mantle and the core. This model is entirely based on the assumptions stated above and uses no hypotheses for Earth accretion or core formation scenarios. The composition of the core derived here by mass balance is the most complete to date. Without engaging in premature speculation, we would like to point out that to discard this model it would be necessary to discard one of the three basic assumptions.

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