

## **Constitution of Terrestrial Planets [and Discussion]**

H. Wanke and T. Gold

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## Constitution of terrestrial planets

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Reliable estimates of the bulk composition are so far restricted to the three planetary objects from which we have samples for laboratory investigation, i.e. the Earth, the Moon and the eucrite parent asteroid. The last, the parent body of the eucritediogenite family of meteorites, an object that like Earth and Moon underwent magmatic differentiations, seems to have an almost chondritic composition except for a considerable depletion of all moderately volatile (Na, K, Rb, F, etc.) and highly volatile (Cl, Br, Cd, Pb, etc.) elements. The Moon is also depleted in moderately volatile and volatile elements compared to carbonaceous chondrites of type 1 (C1) and also compared to the Earth.

Again normalized to C1 and Si the Earth's mantle and the Moon are slightly enriched in refractory lithophile elements and in magnesium. It might be that this enrichment is fictitious and only due to the normalization to Si and that both Earth's mantle and Moon are depleted in Si, which partly entered the Earth's core in metallic form. The striking depletion of the Earth's mantle for the elements V, Cr and Mn can also be explained by their partial removal into the core. The similar abundances of V, Cr and Mn in the Moon and in the Earth's mantle indicate the strong genetic relationship of Earth and Moon.

Apart from their contents of metallic iron, all siderophile elements, moderately volatile and volatile elements, Earth and Moon are chemically very similar. It might well be that, with these exceptions and that of a varying degree of oxidation, all the inner planets have a similar chemistry.

The chemical composition of the Earth's mantle, for which reliable and accurate data have recently been obtained from the study of ultramafic nodules, yields important information about the accretion history of the Earth and that of the inner planets. It seems that accretion started with highly reduced material, with all Fe as metal and even Si and Cr, V and Mn partly in reduced state, followed by the accretion of more and more oxidized matter.

#### INTRODUCTION

The inner or terrestrial planets Mercury, Venus, Earth and Mars, and as a fifth object we can add the Earth's Moon (in context of this discussion), show considerable differences in their densities (table 1). These differences are generally explained by a varying degree of oxidation of iron and in addition by a variation of the total Fe/Si ratio.

The different amounts of water observed on these five objects clearly indicate that, compared to solar abundances or to the abundances of carbonaceous chondrites of type 1 (C1), the highly volatile elements and compounds are greatly depleted on the inner planets, but the depletion varies in a not yet fully understood manner. Today it is a major aim in cosmochemistry to increase our knowledge of the chemical composition of the inner planets as this knowledge might provide the key to the understanding of the formation of the Solar System.

Reliable estimates of the bulk composition of differentiated bodies of the Solar System

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planet	mean density observed	mean density at 10 kbar	percentage Ni–Fe phase	
Mercury	5.44	5.3	65	
Venus	5.24	3.96	28.8	
Earth	5.52	4.07	32.5	
Moon	3.34	3.40	5	
Mars	3.94	3.73	20	

#### TABLE 1. MEAN DENSITIES OF TERRESTRIAL PLANETS (RINGWOOD 1979)

exist only for those of which we have samples for laboratory analysis, apart from the Earth and the Moon, the parent asteroid of the eucrites and those other meteorites related to them, of which we have samples in form of basalts, pyroxenites, etc.

Eucrites are basaltic meteorites and two other groups of achondrites, the diogenites and howardites, are closely related to them. The howardites, which are in fact mechanical mixtures of eucrites and diogenites, were formed in the regolith of their parent asteroid. The reflectance spectra of the asteroid Vesta (diameter 500 km) is unique and matches exactly that of howardites (McCord *et al.* 1970). It might be that Vesta is indeed the parent body of the eucrite family (Hostetler & Drake 1978). With a Rb/Sr age of  $(4.60 \pm 0.07) \times 10^9$  a measured for the eucrite Juvinas (Allègre *et al.* 1975), the eucritic meteorites represent the oldest basalts of the Solar System known so far.

A number of people, including myself, have tried to use certain groups of elements related to each other by their condensation behaviour as building blocks for the planetary objects. However, it is only for the refractory elements that we have solid evidence of a good group behaviour; i.e. they appear relative to each other always in primordial abundance ratios (table 2).

The group of refractory elements was first observed as a pure phase, as so-called high temperature condensates or early condensates in form of white inclusions in the Allende meteorite (table 3).

TABLE 2. CONDENSATION BEHAVIOUR OF ELEMENTS

refractories	Al, Ca, Ti, Be, Sc, V, Sr, Y, Zr, Nb, Mo, Ru, Rh, Ba, r.e.e.†, Hf, Ta, W, Re, Os, Ir, Pt, Th, U
Mg-silicates	Mg, Fe(FeO), Si, (Cr), Li
metals (FeNi)	Fe, Ni, Co, Au, Pd, P, As, (Cr)
moderately volatiles	(Mn), Na, K, Rb, Cs, F, Cu, Zn, Ga, Ge, Ag, Sn, Sb, Te, S, Se
volatiles	Cl, Br, I, Cd, In, Hg, Tl, Pb, Bi, C, N, H₂O
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element	observed concentration†	abundance normalized to C1	element	observed concentration†	abundance normalized to C1
refractory la	ithophile elements		Lu	0.5	20.0
Al	17.5%	21.3	Hf	3.3	23.6
Ca	18.0%	20.0	Ta	0.25	14.7
Ti	0.91%	20.7	U	0.12	14.6
Sc	120	20.3	refractory n	uetals .	
V	620	11.2	W	1.84	20.7
Sr	130	15.1	Re	0.73	19.7
Y	33	22.9	Os	7.2	14.7
Zr	93	24.3	Ir	8.85	18.6
Nb	6.6	22.0	Ru	8.1	11.7
La	4.9	20.0	Pt	12.3	11.7
Ce	11.4	17.9	non-refracto	ry metals	
Pr	1.7	17.7	Fe	0.84 %	0.046
Sm	3.2	20.8	Cr	380	0.14
Eu	1.14	19.7	Co	44	0.088
Gd	2.8	14.0	Ni	900	0.084
Dy	4.7	18.5	Pd	0.082	0.15
Ho	0.86	15.1	Au	0.28	1.97
Er	3.3	19.9			
Yb	3.1	18.9			

# TABLE 3. ELEMENTAL ABUNDANCES IN A Ca, Al-RICH CHONDRULE OF ALLENDE METEORITE (WÄNKE et al. 1974)

<sup>†</sup> All observed concentrations are per 10<sup>6</sup> except where specified as percentages.

#### CORRELATED ELEMENTS.

It is clear that a rock sample from an object that underwent magmatic fractionations cannot give us a direct answer about the chemistry of its parent object. Very helpful in respect to the attempt to estimate the bulk chemistry of a planetary object are the so-called correlated elements (Laul *et al.* 1972; Wänke *et al.* 1973). Correlated elements are pairs of elements that, independent of their absolute concentrations, always appear in constant abundance ratios in samples of a given planet.

One example of such an element correlation is the pair FeO and MnO. As long as Fe is in the 2 + state only and metals or sulphides are absent, the ratio FeO/MnO remains constant because  $Mn^{2+}$  can easily replace Fe<sup>2+</sup> in the two major mafic minerals, olivine and pyroxene, because of their similar ionic radii. Hence, the FeO/MnO ratio observed in rocks of a given planet should come close to the bulk ratio of these two elements in the silicate phase of this planet.

Originally, it was generally assumed that the different FeO/MnO ratios observed for different planets mainly reflect the depletion of Mn. This assumption was based on the behaviour of Mn as a moderately volatile element in carbonaceous chondrites. However, it was found that Mn is not depleted on the eucrite parent asteroid in spite of a high depletion of Na and K (Dreibus & Wänke 1979). Eucrites have the highest Mn content (ca. 4200/10<sup>6</sup>) of all basalts known so far. Hence, it seems more likely that the FeO/MnO ratio depends on the oxygen fugacity of the object in question, i.e. on its Fe<sub>metal</sub>/FeO ratio. Under extreme reducing conditions, however, even Mn can be removed from the silicate phase in form of metal or sulphide.

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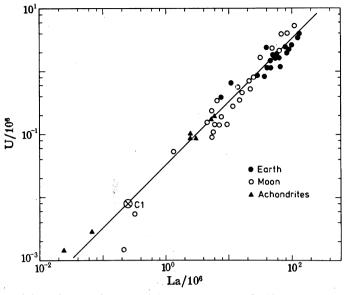


FIGURE 1. Correlation of the refractory incompatible elements La and U in Earth, Moon and eucritic meteorites (achondrites). Note the occurrence of La and U in strictly C1 abundance ratios on Earth, Moon and eucrite parent body. All data from the Mainz laboratory.

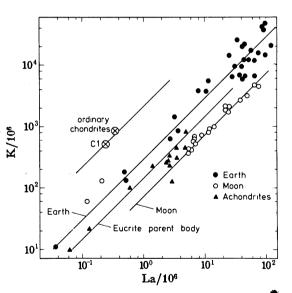


FIGURE 2. Correlation of the incompatible moderately volatile element K with the incompatible but refractory element La. Earth, Moon and eucrite parent body clearly have different K/La ratios considerably below that in C1 chondrites and in ordinary chondrites. All data from the Mainz laboratory.

Other examples of correlated elements are the pairs Ba-La, U-La, or Th-U (figure 1). These four elements are highly incompatible with major mineral phases and they have very low solid-liquid partition coefficients. Hence, they will concentrate in the liquid phase of either partial melting or fractional crystallization processes. They are also easily extracted by other fluid phases like  $CO_2$  or  $H_2O$ .

As La, Ba, U and Th belong to the group of refractory elements that do not easily fractionate from each other, it is understandable that they always appear in almost their exact C1

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abundance ratio (no fractionation during evaporation or condensation and no or only little fractionation by magmatic processes). However, the appearance of correlated refractory elements in their C1 abundance ratios on all planetary objects studied so far strongly suggests that all refractory elements have been added to each object of the Solar System in C1 abundance ratios.

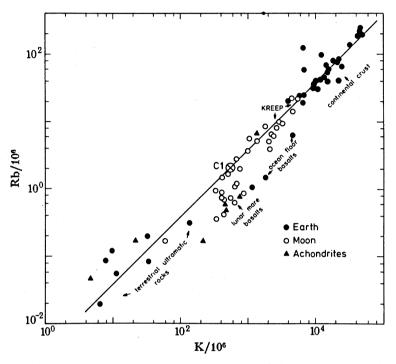


FIGURE 3. Correlation of the two moderately volatile and incompatible elements Rb and K. The Rb/K ratio seems equal to the C1 value for the Earth and Moon and perhaps slightly below the C1 value from the eucrite parent body (achondrites). All data from the Mainz laboratory.

Potassium is also a highly incompatible element and indeed the constancy of the K/U ratio in terrestrial rocks has been known for a long time. Even more constant seems the K/La or K/Ba ratio (figure 2). In all these pairs the moderately volatile element potassium is compared with a refractory element. As the depletion of volatile elements varies from planet to planet, the K/U or K/La ratios are also variable and in fact can be used to characterize the planets. K and Rb are two highly incompatible elements and both have moderately volatile character. Thus, it is not too surprising that we find them always close to their C1 abundance ratios in all planetary objects (figure 3).

The W/La correlation has considerable bearing on the genesis of planetary objects (figure 4). The correlation line for lunar samples lies below the chondritic ratio by a factor of 19. As can be seen from figure 6, data points from terrestrial rocks as well as those from achondrites fall close to the correlation line of lunar samples. W is a refractory element like La. The reason for the depletion of W in the silicate (oxide) phase of planets is the siderophile character of this element. About 95% of W seems to have been separated with a metal phase and only 5% went as oxide into the silicates and fractionated together with La in magmatic processes. Rammensee & Wänke (1977) have shown that under equilibrium conditions a metal phase of 26% by mass is required to account for the observed depletion of W. Such an amount of

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metallic iron is in line with the mass of the Earth's core but exceeds the upper limit for a possible lunar core by almost a factor of 10.

Besides the density and the coefficient of inertia the heat flux is a very valuable physical constraint for the determination of the chemistry of planets. It seems that potassium is considerably depleted relative to its C1 abundance on all inner planets as well as on the eucrite

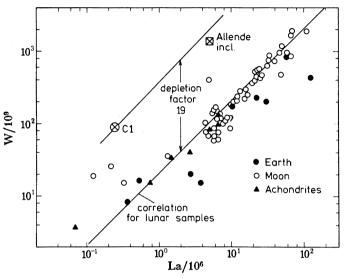


FIGURE 4. Correlation of the two incompatible refractory elements W and La. The W depletion of the Earth and Moon is due to the partly siderophile character of W of which up to about 95% must have been present in metallic form while the rest fractionated in oxide form together with the incompatible lithophile elements (Rammensee & Wänke 1977). All data from the Mainz laboratory.

parent body. As a consequence of this depletion the two refractory elements U and Th are the main contributors to the heat generation in planetary interiors except for the very early period of planetary evolution in which the decay energy of <sup>26</sup>Al, accretional or even chemical energy can be of importance.

If one assumes that thermal equilibrium, i.e. production of heat in the interior, is equal to the loss of heat through the surface, the heat flux that can be measured by the temperature gradient in the upper surface layers is a direct function of the planets' U and Th contents. We have seen above that the refractory elements do not fractionate from each other during planet formation. Thus, the value for the concentration of one refractory element yields immediately the concentration of all other refractory elements (Ganapathy & Anders 1974). Determination of the heat flux is especially easy for objects covered with a regolith layer and free of volatiles, as for the Moon and Mercury. The loose structure of the lunar regolith leads to values of its thermal conductivity almost three orders of magnitude smaller than those of igneous rocks (Langseth *et al.* 1976) and to correspondingly higher temperature gradients.

I shall return to a general discussion of the chemistry of the inner planets later and now concentrate on the planet of which we have the most reliable information, the Earth.

#### CHEMISTRY OF THE EARTH

The mantle amounts to about two-thirds of the mass of the Earth. Except for the most incompatible elements, for which the contribution of the crust (0.4% of the Earth's mass) becomes important, the mantle determines the chemistry of the Earth for all lithophile elements. Furthermore the concentrations of the siderophile elements in the mantle give us important clues as to the accretion sequence of the Earth. Today there is general agreement that the material of the crust is derived from the mantle mostly in form of partial melts.

The most common type of such partial melting products of the mantle are the basaltic magmas, which frequently carry with them, in violent volcanic eruptions, more or less unaltered solid mantle material, the so-called ultramafic nodules. The nodules of most interest to us here are the garnet-lherzolites and the spinel-lherzolites. The former are characterized by the presence of garnet, which is only stable below a depth of 70 km and hence reflects the chemistry of this depth, while the spinel-lherzolites come from more shallow depth of 20 to 70 km. These lherzolite nodules very frequently became severely contaminated by various processes before, during or after their eruption. We have therefore to apply various criteria to distinguish between nodules that represent true mantle material and those that contain alteration products. In fact unaltered samples have so far only been found among the spinel-lherzolites.

Jagoutz et al. (1979) have succeeded in selecting from several hundred nodules studied five spinel-lherzolites that were free of contamination except for small amounts of extremely incompatible elements. As the eruption process of ultramafic nodules is somehow related to the genesis of the magmas that carry them to the surface, it is no surprise that many of the nodules are depleted in those elements that in basalts are enriched relative to their mantle abundances.

Fortunately, we have clear cosmochemical constraints to distinguish those nodules, which really represent primitive or close to primitive mantle material. For a long time it was not clear at all that primitive mantle material could be found among the lherzolite nodules. To distinguish primitive mantle material we only have to remember that all the refractory lithophile elements must have been present in the primitive mantle in their C1 abundance ratios. Hence, nodules with a Ca/Al or an Al/Sc ratio more than 10 % from the C1 value cannot be primitive. Al, Ca and Sc are all rather compatible elements and of none of these elements can we expect more than 10 % of the original mantle concentration to have entered the crust.

Jagoutz et al. (1979) found five nodules that according to this criteria can be called primitive. On going to more and more incompatible refractory elements like Ti, Yb, Sm, Sr, or even La, Ba, U, we can actually not expect to find relative C1 abundances, as of the most incompatible elements the portions that reside in the crust may be of the order of 30 to 50 %. From the five nodules of Jagoutz et al. (1979) only one (SC 1 from San Carlos, Arizona, U.S.A.) had an almost flat rare-earth element pattern, i.e. it was only slightly depleted in La. Treatment with diluted HCl reduced the La concentration in SC 1 somewhat as well as the concentration of other highly incompatible elements, which was a clear indication of some contamination in the case of the most incompatible elements. However, we can be sure that, after removal of the contaminating material by acid treatment, the SC 1 nodule truly represents the chemistry of at least the upper mantle even for elements like La, Ba and K.

The chemistry of the Earth's mantle, as derived from the investigation on spinel-lherzolites

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Na Mg Al Si

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Cl

K Ca Sc Ti v Cr

Mn Fe Co Ni

Cu Zn Ga Ge As Se Br

Rb Sr Ag Cd Ba La Yb Lu W

Re Os Ir

Au U

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#### TABLE 4. COMPOSITION OF THE EARTH'S MANTLE

		Earth's mantle					Moon‡ e.p.b.§		
per	pyrolite*	Hutchison (1974)	Wedepohl (1975)	-	mantle + crust†	mantle + crust	(meta sulphu	l- and Ir-free)	
		· · ·	(-975/	(1979)		(normalized to Si and C1)			
106	·		2	2.07	2.17	0.76	—	0.92	
106		—	100	24¶	35	$5 \times 10^{-4}$			
106	68	—	97	16	24	0.22	—	0.044	
106	4167	2100	2230	2420	2700	0.27	0.054	0.082	
10 <sup>2</sup>	23.0	23.5	24.75	23.1	22.9	1.24	1.00	1.00	
10 <sup>2</sup>	2.1	1.85	1.43	2.10	2.19	1.35	1.56	1.04	
10 <sup>2</sup>	21.1	21.1	20.33	21.1	21.1	1.00	1.00	1.00	
106	102	· <u> </u>	220	61¶	74	0.037	—	0.048	
106	317	—	<b>400</b>	8¶	11	$1 \times 10^{-4}$		<u> </u>	
106	59		110	0.5¶	8.5	$6  imes 10^{-8}$		3 × 10-	
106	—	290	390	35¶	185	0.18	0.052	0.073	
10 <sup>2</sup>	2.2	2.32	2.72	2.50	2.53	1.42	1.57	1.01	
106	—	—	15	17	17.2	1.48	1.56	1.04	
106	1200	<b>54</b> 0	780	1300	1340	1.54	1.56	1.08	
106	—		50	77	78	0.71	0.76	0.81	
106	2524	2800	3090	3140	3100	0.59	0.51	1.11	
106	1095	850	1040	1010	1010	0.28	0.38	0.89	
10 <sup>2</sup>	6.1	6.22	6.48	6.08	6.08	0.17	0.28	0.31	
106	98	<u> </u>	110	105	104	0.11	0.079	0.013	
106	1694	1960	1450	2110	2080	0.10	0.074	$1.7 \times 10^{-1}$	
106	34	—	47	28	28	0.13	—		
106	50		56	50	50	0.072	_		
106	6		2.5	3.0	3.2	0.18	—	0.036	
106	1.1	· <u> </u>	1	1.2	1.2	0.019	—	—	
106	1	—	1	0.14	0.16	0.044		· —	
109	70		20	26¶	26	$7 \times 10^{-4}$	—	_	
109	—	—	240	<b>4.6</b> ¶	43	$8.4 \times 10^{-8}$		6.3 × 10	
106	—	—	1.2	0.28¶	0.77	0.16	—	_	
106	—	· <u> </u>	22		22	<b>1.30</b>	1.56	1.10	
10 <sup>9</sup>	50		50	2.5¶	3.3	$8 \times 10^{-3}$	—	—	
10 <sup>9</sup>	35	—	60	25.5	27.6	0.018	—	—	
106	—	—	20	—	5.7	1.30	1.56	1.34	
106		—	0.92	0.39	0.62	1.28	1.56	1.31	
106	—	—	0.38	0.42	0.44	1.35	1.56	1.29	
106		—	0.065	0.064	0.067	1.36	—		
109	—	—	300	16	16	0.090	0.089	0.078	
10 <sup>9</sup>	0.1		200	0.23¶	0.23	0.0031	—		
109	5	·	—	3.1¶	3.1	0.0032	_	·	
109	2	_	_	3.2	3.2	0.0034		_	
109	4	_	7	0.49¶	0.54	0.019	—	·	
10 <sup>9</sup>		_	25	· _ "	21	1.30	1.56	1.33	

\* Pyrolite: Ringwood (1977) and Ringwood & Kesson (1977).

† Data of the crust from Taylor (1964) and Taylor & McLennan (1981).

‡ Dreibus & Wänke (1980) and Wänke et al. (1979).

§ Eucrite parent body; Dreibus & Wänke (1980).

¶ Unpublished data from the Mainz laboratory on leached samples of SC1 (see Jagoutz et al. 1979).

|| Calculated assuming a normalized abundance of 1.30.

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by Jagoutz et al. (1979) is listed in table 4 together with other authors' data on lherzolite nodules and Ringwood's pyrolite model (Ringwood 1977; Ringwood & Kesson 1977). The element concentrations given by Hutchison (1974) and Wedepohl (1975) are mean values for several hundreds of nodules. This averaging over many nodules of quite different chemistry may be justified for compatible elements, but not for moderate or highly incompatible elements. In addition to the data from Jagoutz et al. (1979), table 4 contains new data derived from the acid-treated SC 1 nodule. Hutchison (1974) gives only data on a few trace elements but clearly his Ti value must be too low and his K value too high. The high Mg/Al ratio of 12.7 (Hutchison 1974) or of 17.3 (Wedepohl 1975) compared to the C1 value of 11.4 is also unreasonable. Similarly many other data given by Wedepohl (1975) cannot be representative for primitive mantle material. Here again the high K and low Ti values but also large deviations from the C1 ratios for refractory lithophile elements indicate that the data base is a mixture of depleted and contaminated nodules. The high Ca/Al ratio of 1.9, for example, compared to the C1 ratio of 1.1 proves that many of the nodules of this compilation must be residues after basalt extraction or originated from cumulates. A Ba concentration of 20/10<sup>6</sup> as given in the compilation would lead to an unbelievably high enrichment factor for this element of 4.8.

On the contrary, normalized to Si and C1 the new data from the Mainz group show very similar enrichment factors, between 1.29 and 1.49 for all except the most incompatible refractory elements. The lower values for the most incompatible refractory elements are understood as a depletion either of the whole or of a considerable part of the mantle as these elements have been extracted from the mantle to a large extent into the crust.

Measurements of Nd isotopes in SC 1 (Jagoutz et al. 1980) proved that its primitive, i.e. unfractionated, composition relative to C1 for the refractory elements is not the result of a chance mixture of various components but that SC 1 was clearly in an unfractionated reservoir from the accretion of the Earth until about 800 Ma ago and only then was subjected to a slight depletion of the most incompatible elements. On the other hand, from the Nd data it also became evident that the strong depletion of sample KH 1 (one of the four depleted nodules of Jagoutz et al. (1979)) occurred at the same time (see figure 5).

The possibility of a mantle inhomogeneous not only in the incompatible elements like La, Nd, K, Rb, U, but also in its major element composition has been discussed by various authors.

Anderson *et al.* (1971), for example, suggested a considerable difference in the FeO and  $SiO_2$  content between lower and upper mantle. Drastic differences in the major and compatible trace element composition seem, however, very unlikely. Any larger fractionation of these kind would lead to a considerable change of the ratios of compatible to less compatible elements or of the ratios of mafic to non-mafic elements (Ca/Sc, Al/Yb, etc.). But all these ratios in SC 1 are in fact within about 10% of the C1 values. According to Ringwood (1979) a drastic increase of FeO and SiO<sub>2</sub> in the lower mantle as suggested by Anderson *et al.* (1971) is in serious disagreement with the corresponding properties of the lower mantle derived by Davies & Dziewonski (1975). Ringwood (1979) strongly argues against any major radial zoning in the mantle except for the depleted peridotite layer in the uppermost mantle and for the lowermost layers overlying the mantle-core boundary.

However, it might well be that the small variations in the abundance of refractory elements (excluding the most incompatible elements), i.e. their slightly different enrichment factors

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relative to Si and C1 resulted from small fractionations between upper and lower mantle. For example, it could be that the lower enrichment factor observed for Mg than those of Al and all compatible refractory elements is the result of a somewhat higher pyroxene content of the lower mantle, which would, of course, also influence the abundance of Si.

Having assumed that SC 1 represents unfractionated primitive mantle material in respect to the group of refractory elements logically, we can use the SC 1 abundance of all other elements as the best available data set on the composition of the Earth's mantle.

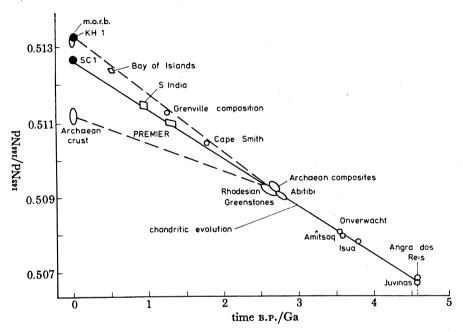


FIGURE 5. Nd-evolution diagram; after Jagoutz et al. (1980) and Jagoutz (1981).

The composition of the Earth's mantle as derived from the work of Jagoutz et al. (1979) is illustrated in figure 6 (see also table 4).

I shall not further discuss the abundances of the moderately volatile and volatile elements, but will concentrate on the abundances of siderophile elements and of V, Cr and Mn.

The depletion of Cr and Mn has been known for a long time but that of V was noticed only recently. Ringwood favoured a depletion mechanism based on the higher volatility of Cr and Mn than of Si. Certainly this mechanism cannot be excluded completely even though (Dreibus & Wänke 1979, 1980) Mn is not depleted on the eucrite parent asteroid, which is otherwise highly depleted in moderately volatile elements like Na, K. V, however, is a refractory element and hence should be enriched relative to Si and not depleted. Dreibus & Wänke (1979) have suggested that the amounts of Cr, V and Mn missing in the mantle went into the core in the form of sulphides or oxides. Segregation into the core in the form of sulphides had already been suggested by Hutchison (1974) to explain the low concentration of Cr and Ti. However, undepleted nodules contain Ti in C1 abundance relative to the other refractory lithophile elements.

The similar abundances of the moderately siderophile elements Ga, Cu, W, Ni and Co relative to chondritic abundances are also very informative. We especially note that Ni and Co are present in almost exact C1 abundance ratios, but we feel that the smaller abundance

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of Ni relative to Co is outside the experimental variance. The elements Ga, Cu, W, Co and Ni have very different metal-silicate partition coefficients (experimental values are given in figure 6), but it may be important that, with the exception of W, of which the true abundance is rather uncertain due to the incompatible character of this element, Ni, the most siderophile of these elements, has the lowest abundance.

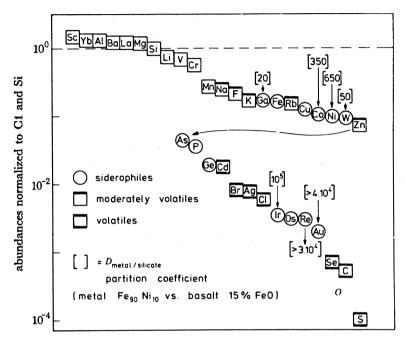


FIGURE 6. Composition of the Earth's mantle normalized to C1 and Si derived from analyses of primitive spinellherzolites (Jagoutz et al. 1979 and unpublished data of the Mainz laboratory).

The high concentration of Ni in the Earth's mantle has for a long time been the concern of many scientists. Assuming a Ni concentration of 10 % in the core, we should, for a metalsilicate partition coefficient of 650 expect  $150 \text{ Ni}/10^6$  in the mantle under equilibrium conditions. It has been argued that the partition coefficients have been lowered due to high pressure or due to the presence of sulphur. Neither of these possibilities can be ruled out; however, they seem unlikely. Because of the very similar abundances of the elements Ga, Cu, W, Co and Ni, we require conditions that not only lower the partition coefficient for Ni, but also make the partition coefficient of these five elements almost equal. Furthermore, a great abundance of S is unlikely for the Earth, which is highly depleted in a number of elements less volatile than S (Ringwood 1979).

We also should note that the moderately volatile elements K, Na, Rb and F are similar in abundance to the moderately siderophile elements. The highly siderophile elements are again very much more abundant than is expected from their partition coefficients. Although less abundant than the moderately siderophile elements by more than an order of magnitude, of the highly siderophile elements, Pd, Ir, Re, Os and Au appear again in almost chondritic abundances relative to each other.

The relative low abundance of Ge has not yet been completely understood. Germanium is certainly considerably less volatile than Cd or Zn; hence its low abundance can at most only partly be explained by volatility. Unfortunately, we do not have reliable laboratory data

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TABLE 5. ESTIMATED COMPOSITION (PERCENTAGE BY MASS) OF THE EARTH BASED ON C1 ELEMENTAL ABUNDANCES, WITHOUT ELEMENTS OF MODERATELY VOLATILE OR VOLATILE CHARACTER

core				mantle		
Fe	26.90	80.27	SiO <sub>2</sub>	29.78	44.78	
Ni	1.83	5.46	MgŌ	26.32	39.57	
Co	0.09	0.27	FeO	5.24	7.88	
Si	4.19	12.5	Al <sub>2</sub> O <sub>8</sub>	2.63	3.95	
Mn	0.25	0.75	CaO	2.14	3.22	
Cr	0.25	0.75	Cr <sub>2</sub> O <sub>3</sub>	0.31	0.47	
total	33.51	100.00	MnO	0.09	0.13	
			total	66.51	100.00	

on the metal-silicate partition coefficients of these elements. However, Ge may indeed be more siderophile than Ni, as Rambaldi *et al.* (1978, 1979) found in chondrites for Ge the highest metal-silicate concentration ratios of all elements.

In summary, we note the following trends in the elemental abundances in the mantle of the Earth.

(i) All refractory lithophile elements and Mg are enriched by a mean factor of  $1.3 \pm 0.1$ .

(ii) V, Cr and Mn are depleted by factors of between 2 and 4.

(iii) Fe and the moderately siderophile elements Ga, Cu, W, Co and Ni are depleted by factors of between 7 and 10. The abundances are nearly independent of their metal-silicate partition coefficients.

(iv) The moderately volatile elements K, Na, Rb and F have abundances similar to those of moderately siderophile elements.

(v) Highly siderophile elements (e.g. Ir, Os, Au) although more depleted than the moderately siderophiles are again overabundant in respect to their metal-silicate partition coefficients, but are found in approximately C1 abundance ratios.

(vi) The halogens Cl and Br are found in their C1 abundance ratios both in the mantle and in the oceans. Today they are concentrated to over 90% in the crust of which about two-thirds is found in the oceans.

The uniform enrichment of Mg and the refractory lithophile elements relative to Si could also be interpreted in terms of a Si deficiency (Ringwood 1958). It was suggested that the missing Si went into the core in metallic form, which would indicate gross chemical disequilibrium between mantle and core. The mean enrichment factor of 1.3 for Mg and the refractory lithophile elements could correspond to an identical depletion factor for Si, which leads to an absolute Si deficit of 6.3% in the mantle or a Si content of 12.5% in the core.

#### ACCRETION SEQUENCE OF THE EARTH

To explain these trends in the elemental abundance pattern of the Earth's mantle, I postulate the following inhomogeneous accretion model.

(a) Accretion started with highly reduced material free of volatile elements. Si was partly present in metallic form, Cr, Mn and V were present as metals or sulphides, and Fe, Co, Ni, Ga, W, etc., were in metal form only.

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(b) After the Earth had reached about two-thirds of its present mass and after the metals and sulphides (Fe, Ni, Si, Cr, V, Mn and all siderophile and chalcophile elements) had segregated to form a core, more and more oxidized material was added and the portion of reduced material decreased.

The last 20% of the accreting mass of the Earth consisted of highly oxidized material (Fe, Co, Ni, Ga, W, Zn, Ge as oxides), which also contained elements of moderately volatile character, such as Na, K, Rb, F, in C1 abundances. The admixture of small amounts of metallic iron (< 1%) and segregation of this metal was responsible for the extraction of highly siderophile elements (Ir, etc.) which were also present in this material into the core. This metal was probably also responsible for the extraction of S and chalcophile elements.

(c) The accreting material became richer in volatiles ( $H_2O$ ; halogens; C, partly in the form of organic compounds which on Earth were transformed into  $H_2O$  and  $CO_2$ ). Such a veneer hypothesis was first suggested by Anders (1968). Finally metallic Fe became unstable; hence the highly siderophile elements of the last 0.2% of the Earth's mass remained in the mantle in their chondritic abundance ratios.

I believe that, if we neglect the depletion of the moderately and volatile elements (including S), we can build an Earth from material with strictly C1 abundances of all elements including Fe, but with the assumption of a shift in the oxygen fugacity of the accreting material from highly reducing to fully oxidized during the accretion sequence.

The calculated composition of the Earth based on strictly C1 abundances is given in table 5. Contrary to other models there is no need to arbitrarily raise the total Fe content beyond the C1 abundance. We find a core of 33.5% (by mass) containing 12.5% metallic Si, which will reduce the density of the core by about 10%, as required according to current theories. The presence of Si in the core might result in the precipitation of Ni<sub>2</sub>Si to form the solid inner core, as suggested by Herndon (1979).

The required change in the oxygen fugacity of the accreting material can fit into several models of the solar nebula. In fact, it is easy to visualize a scenario in which loss of  $H_2$  from certain regions of the solar nebula might be highly preferential to that of  $H_2O$ , which could be held back in the form of ice grains.

A more severe constraint is the high depletion of all moderately volatile elements like Na and K on all the inner planets as well as on the eucrite parent body and, in fact, on all differentiated objects of the Solar System. To fractionate these elements from the more refractory ones requires temperatures of the order of 1000 K, which will not be reached in most parts of the solar nebula, if its temperature remains as low as is now claimed even by the earlier proponents of a hot solar nebula (Cameron 1978; Cameron et al. 1981).

It may be of importance in this connection that all the differentiated objects of our Solar System (planets and asteroids) studied so far are considerably depleted in moderately volatile and volatile elements, but they also have identical oxygen isotopes as they plot on the same oxygen isotope fractionation line.

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## CHEMISTRY OF THE MOON AND OF THE EUCRITE PARENT BODY IN COMPARISON WITH THAT OF THE EARTH AND THE OTHER TERRESTRIAL PLANETS

The normalized chemical compositions of the Moon and the eucrite parent body are also given in table 4. These data are taken from Dreibus & Wänke (1980); estimates from other authors do not differ drastically (see, for example: Ganapathy & Anders 1974; Ringwood 1977; Consolmagno & Drake 1977).

Normalized to Si the silicate portion of the endite parent body is almost identical in composition to C1 chondrites for all refractory lithophile elements, while both the Earth and the Moon show a small enrichment for these elements, which may, however, be due to a Si deficiency as was discussed in the preceding chapter. Of great importance is the almost identical depletion of V, Cr and Mn for both the Earth and the Moon, while these elements show normal abundances in the eucrite parent body.

Especially noticeable is also the relatively high abundance of Ni and Co in the Earth and the Moon compared to the very low abundance of these elements in the silicate phase of the eucrite parent body. In the preceding section I tried to explain the unexpected high abundances of moderately siderophile elements in the Earth's mantle by a special accretion sequence. Hence we have to conclude that the Earth and the Moon are genetically very closely related to each other. Either the Moon was formed out of the Earth's mantle after core formation by some kind of fission process (Ringwood 1960, 1970; O'Keefe 1969; Binder 1974) or the Earth and the Moon accreted close to each other in a mechanism that concentrated the metal on the larger body (Earth) (see, for example, Kaula 1977).

Various attempts have been made to estimate the composition of Mercury, Venus and Mars (see, for example, Morgan & Anders 1980). It seems to be the general consensus that, except for the more volatile elements, the terrestrial planets have rather similar composition equal to that of C1 chondrites at least in respect to lithophile elements. This statement is in fact underlined by the great similarity of the abundance of all these elements in the Earth, the Moon and the eucrite parent body, the three objects from which we have samples. What differs is the degree of oxidation, which is certainly highest for Mars and lowest for Mercury. To account for the high density of Mercury a high metal-silicate ratio is generally assumed for this planet. However, to fully match the observed density of Mercury requires an increase of Fe/Si to almost five times the C1 value.

It seems that the chemical composition of the Earth is explained best if we assume that chemically highly reduced matter was present in large quantities during the first and major stage of accretion. We may assume that matter from which Mercury accreted was even more reduced or that the ratio of reduced to oxidized matter was higher. We might speculate that not only one-fifth of all the Si was in metallic form as in the Earth, but that all the Si was in the reduced metallic state. A planet formed from such material would have a FeNiSi core of 62% of its mass and a bulk density of 4.9, not too far from the value of 5.3, estimated for Mercury. Consequently, only a moderate increase of the Fe/Si ratio above the C1 value would be required.

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### CONSTITUTION OF TERRESTRIAL PLANETS

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#### Discussion

T. GOLD, F.R.S. (Centre for Radiophysics and Space Physics, Cornell University, Ithaca, New York 14853, U.S.A.). The information that an outer layer was accreted on the Earth that was of substantially different chemical composition from the main body has a very strong basis in geochemical information. It is interesting to note that such an inhomogeneous accretion is to be expected in the usual model of the formation process. When most of the available mass of the inner Solar System was still in the disk as finely divided material, all orbits are constrained to be circular and coplanar. Any aberrant orbit is damped out very quickly by the large amount of orbiting material. It is only when as little as 2% or so of the material is left as grains in a disk, the rest being in the formed bodies, that strongly perturbed orbits can be

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set up; at this stage the presence of the massive bodies will cause large perturbations and the absence of a massive disk will allow such orbits to persist. Therefore the last stages of accretion on the terrestrial planets brings to them samples that condensed in quite different places. An excess of volatiles brought in from further out in the Solar System can then be expected, but also an excess of very refractory elements from closer in.

I would attribute the overabundance, in the outer layers of the Earth, of the radioactive elements uranium, thorium and potassium to this type of late addition rather than to an extremely efficient sorting process within the formed Earth as is generally believed. Uranium and thorium would have been brought in from orbits originally much closer to the Sun, while potassium would have come from much further out.

R. HUTCHISON (Mineralogy Department, British Museum (Natural History), Cromwell Road, London SW7 5BD, U.K.). While I agree that estimates of the bulk composition of the Earth, such as Professor Wänke's, are useful as a basis for geochemical calculations, two important drawbacks need to be stressed. First, we know only the values of inter-element ratios. To obtain the bulk chemical composition we must know (or be able to calculate) absolute abundances for one element in each of the geochemical/volatility classes. Secondly, geophysical constraints on the composition of the lower mantle are wide and we cannot be sure that the whole mantle is chemically homogeneous. In fact, because the Mg/Si ratio is higher in the upper mantle than in any group of stony meteorites, it may be necessary to assume mantle heterogeneity. The high ratio may have been achieved by the preferential partition of Si into the lower mantle. If this is the case, then the density requires that some heavy element (Fe?) is also enriched in the lower mantle. The calculation of the bulk mantle composition then begins to break down.

H. WÄNKE. The estimates of bulk composition of the Earth's mantle are not based on element ratios but on absolute concentrations observed in primitive mantle nodules which are distinguished by C1 abundance ratios of compatible refractory elements like Al/Sc. I agree that small compositional differences between upper and lower mantle may exist. However, as pointed out in the paper drastic differences in the major and compatible trace element compositions seem very unlikely as any larger fractionation of this kind would result in a deviation of the ratios of refractory major and compatible trace elements from the C1 value.