

Collisional erosion and the non-chondritic composition of the terrestrial planets

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The compositional variations among the chondrites inform us about cosmochemical fractionation processes during condensation and aggregation of solid matter from the solar nebula. These fractionations include: (i) variable Mg–Si–RLE ratios (RLE: refractory lithophile element), (ii) depletions in elements more volatile than Mg, (iii) a cosmochemical metal–silicate fractionation, and (iv) variations in oxidation state. Moon- to Mars-sized planetary bodies, formed by rapid accretion of chondrite-like planetesimals in local feeding zones within 10^6 years, may exhibit some of these chemical variations. However, the next stage of planetary accretion is the growth of the terrestrial planets from approximately 10^2 embryos sourced across wide heliocentric distances, involving energetic collisions, in which material may be lost from a growing planet as well as gained. While this may result in averaging out of the ‘chondritic’ fractionations, it introduces two non-chondritic chemical fractionation processes: post-nebular volatilization and preferential collisional erosion. In the latter, geochemically enriched crust formed previously is preferentially lost. That post-nebular volatilization was widespread is demonstrated by the non-chondritic Mn/Na ratio in all the small, differentiated, rocky bodies for which we have basaltic samples, including the Moon and Mars. The bulk silicate Earth (BSE) has chondritic Mn/Na, but shows several other compositional features in its pattern of depletion of volatile elements suggestive of non-chondritic fractionation. The whole-Earth Fe/Mg ratio is 2.1 ± 0.1 , significantly greater than the solar ratio of 1.9 ± 0.1 , implying net collisional erosion of approximately 10 per cent silicate relative to metal during the Earth’s accretion. If this collisional erosion preferentially removed differentiated crust, the assumption of chondritic ratios among all RLEs in the BSE would not be valid, with the BSE depleted in elements according to their geochemical incompatibility. In the extreme case, the Earth would only have half the chondritic abundances of the highly incompatible, heat-producing elements Th, U and K. Such an Earth model resolves several geochemical paradoxes: the depleted mantle occupies the whole mantle, is completely outgassed in ^{40}Ar and produces the observed ^4He flux through the ocean basins. But the lower radiogenic heat production exacerbates the discrepancy with heat loss.

Keywords: composition of the Earth; collisional erosion; terrestrial planets

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One contribution of 14 to a Discussion Meeting Issue ‘Origin and differentiation of the Earth: past to present’.

1. Introduction

The gross structure of the Solar System consists of an inner Solar System of rocky planets and the gas-rich outer planets with their icy satellites, reflecting an overall increase in volatile components with distance from the Sun. Objects in the asteroid belt between Mars (1.52 AU) and Jupiter (5.2 AU) mark the transition between the two regimes. Reflectance spectroscopy of asteroids shows bright silicate-rich, metal-containing objects in the inner belt and a prevalence of dark, icy asteroids in the outer parts (Bell *et al.* 1989). In detail, there is, however, no continuous increase in volatile components with heliocentric distance. Basalts from Mars have lower Na contents than terrestrial and Venusian basalts, and the ^{36}Ar contents in the atmospheres of the inner planets decrease strongly with increasing heliocentric distance. The extremely volatile-poor Moon does not fit into any sequence.

Current theories of terrestrial planet formation can account for this irregularity by postulating significant mixing of bodies formed at various heliocentric distances. In these models, the formation of the terrestrial planets from the solar nebula begins with *planetesimal formation*, in which the gravitationally induced collapse of the gas and dust of the solar nebula results in the aggregation of the tiny dust grains into centimetre-sized objects, following settling to the mid-plane of the nebula. Collisional coagulation of the centimetre-sized objects by gas drag then leads to metre- and kilometre-sized blocks, the 'planetesimals'. Dynamic modelling suggests that the growth of terrestrial planets then proceeds through three stages (e.g. Wetherill 1994; Canup & Agnor 2000; Weidenschilling 2000; Chambers 2001, 2004; Morbidelli 2007), as follows.

Stage 1: *runaway growth*. Once the diameters of the planetesimals have reached 1–10 km, gravitational forces determine further growth. Owing to gravitational focusing, the growth rate of a body at this stage is proportional to its mass raised to the power of 4/3 ($dM/dt \propto M^{4/3}$), hence large bodies grow faster than smaller ones—the conditions for runaway growth.

Stage 2: *oligarchic growth*. When the larger bodies, which we can call *planetary embryos*, reach a certain size, gravitational stirring (also termed viscous drag) slows their growth, allowing the smaller bodies to catch up (Ida & Makino 1993). This occurs mainly by accretion of planetesimals. The computer simulations show that this process will produce a system of closely spaced planetary embryos, separated by approximately 0.01 AU, of some 10^{23} – 10^{24} kg (i.e. about Moon to Mars sized; cf. the Earth is 6×10^{24} kg), within *ca* 10^6 years. Up to this stage, the material of the growing bodies is predominantly derived from local feeding zones.

Stage 3: *giant impacts*. The system of planetary embryos is dynamically unstable, with orbits becoming increasingly elliptical and inclined; crossing orbits result in energetic collisions, and further growth of what may now be termed *proto-planets*. The computer simulations show that this process generally ends by yielding two to four terrestrial planets in the inner solar system (e.g. in our Solar System, Earth and Venus), and eliminating the planetary embryos originally in the asteroid belt (2–5 AU), due to gravitational excitations from Jupiter and Saturn. The models emphasize that the terrestrial planets are formed from material sourced throughout the inner Solar System, with perhaps approximately 10 per cent of material forming the Earth coming from beyond the 'snow line' at greater than 3 AU, (Morbidelli *et al.* 2000; Morbidelli 2007). This volatile-rich

material may be identified with the ‘oxidizing component’ in earlier heterogeneous accretion models of the Earth’s composition (Wänke 1981; Wänke & Dreibus 1988; O’Neill 1991*a,b*; O’Neill & Palme 1998). This stage may take 10^7 – 10^8 years, and in the case of the Earth seems to have concluded with the giant impact that formed the Moon (e.g. Canup 2004).

During this stage, the significant radial mixing should tend to erase any primary chemical differences that may have been present in the original structure of the inner Solar System. The large energetic collisions will have supplied sufficient energy to cause extensive melting, producing magma oceans and leading to differentiation by formation of dense metallic cores, and light basaltic crusts, rich in incompatible elements. During collisions of Moon- to Mars-sized bodies, large fractions of material may be lost (e.g. Agnor *et al.* 1999; Agnor & Asphaug 2004). Present theories of planet formation consider neither the fate nor the composition of the ‘lost’ material.

The chemical composition of the Earth and the compositional variations among the other rocky bodies of the inner Solar System have traditionally been explained in terms of the chemical fractionations inherited from the early stages of this evolutionary sequence, as recorded in the chondritic meteorites. The term ‘chondrite’ refers to all meteorites originating from parent bodies that never melted and therefore never differentiated to form a crust or metallic core. According to Meibom & Clark (1999), there are 27 chemically distinct types of chondritic meteorite, potentially sampling 27 chemically distinct undifferentiated bodies. Comparison of the chemical compositions of various types of chondrites has revealed several cosmochemical fractionation trends (e.g. O’Neill & Palme 1998). The most important of these may be summarized as follows.

Firstly, with the exception of the CI carbonaceous chondrites, all chondrites are depleted relative to the solar composition in moderately volatile elements. Volatile elements are defined as those elements that condense from the solar nebula at temperatures lower than that of the common terrestrial planet-forming elements, Mg, Si and Fe; ‘moderately volatile’ will be used here for all such elements other than the ‘ice-forming’ elements H, C, N and O, and the noble gases. The pattern of depletion varies in detail from one kind of chondrite to another (e.g. Palme *et al.* 1988), but in all patterns the extent of depletion approximately follows the sequence predicted by thermodynamic calculation for condensation from the solar nebula.

Secondly, chondritic meteorites have variable ratios of refractory elements to the common elements (Mg, Si and Fe), including variable Mg–Si–RLE ratios (RLE: refractory lithophile element). Refractory elements are defined as those that condense at higher temperatures than the common elements.

Thirdly, a cosmochemical metal–silicate fractionation may alter the ratio of magnesium silicates to Fe metal, and correspondingly the proportions of lithophile to siderophile minor and trace elements (Larimer & Anders 1970; O’Neill & Palme 1998). The bulk Fe/Mg ratios of chondrites thus mostly differ from the solar ratio, with both metal-rich and metal-poor compositions being found (e.g. O’Neill & Palme 1998, their fig. 1.8). Note that this cosmochemical metal–silicate fractionation has nothing to do with core formation.

Fourthly, there are large variations in the average oxidation state of chondrites, with the oxidation state of Fe ranging from entirely metallic to completely oxidized. The oxidation states of chondrites post-date the cosmochemical metal–silicate fractionation (O’Neill & Palme 1998).

The observation that RLEs are not fractionated from each other in any bulk chondritic composition, and the consequent assumption that RLEs are never fractionated in Solar System objects larger than a few milligrams, has been of central importance in deriving bulk silicate Earth (BSE) compositions (e.g. O'Neill & Palme 1998; Palme & O'Neill 2003). Although with improved accuracy in analytical procedures it has recently become apparent that ratios among refractory elements may show variations of several per cent between chondrite groups (e.g. Walker *et al.* 2002; Pack *et al.* 2007), for the purpose of our arguments these small variations are not significant. Although the Earth's composition is unlike that of any specific chondrite, all of these different kinds of 'chondritic' fractionations have been thought to contribute to making the Earth's composition, taking the composition of the solar nebula as the starting point. In keeping with other usages of the term, we use 'chondritic' in this paper for any composition that could be derived from the solar composition with only those chemical fractionation processes indicated by the spread of compositions of the chondritic meteorites. The unwary are warned that sometimes the term 'chondritic' has been applied in the literature specifically to the composition of the CI chondrites (which approach the solar composition most closely), but this usage has the defect of conveying an erroneous impression that chondritic meteorites define a single composition, rather than forming a family of compositions linked by several different fractionation processes, as discussed above.

By focusing only on the evidence from undifferentiated bodies (i.e. as sampled by chondrites), the discussion of the chemical processes responsible for setting the bulk composition of the terrestrial planets has explicitly excluded any processes that arise from the later stages of accretion. We propose that three such 'non-chondritic' processes have been important in determining the composition of the Earth and other terrestrial planets.

Firstly, the mixing of planetary embryos and proto-planets from different heliocentric distances should tend to average out the chondritic fractionations, insofar as these are produced at local scales during the initial growth of the planetesimals. As discussed in Palme (2000), there is almost no evidence from the accessible samples of Solar System objects to support the 'common-sense' prejudice that the inner Solar System ought to be zoned heliocentrically in chemical composition.

An example of the effects of averaging by mixing is provided by oxygen isotopes, which famously show different extents of mass-independent fractionation (usually expressed as $\Delta^{17}\text{O}$) relative to terrestrial ratios (defined as $\Delta^{17}\text{O}=0$) in the components of texturally primitive chondrites, in bulk chondrites and in samples from small, differentiated planetary bodies ('achondrites'). But, as pointed out by Palme & O'Neill (2003), 'The larger the object the smaller the variations in oxygen isotopes. The Earth and the Moon, the largest and the third largest body in the inner solar system for which oxygen isotopes are known, and which comprise more than 50% of the mass of the inner solar system, have exactly the same oxygen isotopic composition (Wiechert *et al.* 2001).' Recently Ozima *et al.* (2007) have also argued that the average oxygen isotopic composition of the minor bodies of the solar system is that of the Earth, with the diversity of oxygen isotopes in components of chondrites, bulk chondrites and other small planetary bodies attributed to 'statistical fluctuation'. They conclude that 'The average values for both achondrites and chondrites show roughly a normal distribution

around $\Delta^{17}\text{O}=0$, and the standard deviation of $\Delta^{17}\text{O}$ of achondrite groups is about one seventh of that for chondrite groups. We interpret these statistical trends to primarily reflect progressive growth of planetary objects by random sampling of planetesimals.' It has recently become apparent, however, that this planetary oxygen isotopic composition differs from the solar wind as sampled by the GENESIS mission (McKeegan *et al.* 2008), the results of which agree with the earlier measurements on lunar metals exposed to the solar wind (Hashizume & Chaussidon 2005). Thus an effective mechanism has to be found for fractionating average Solar System oxygen isotopes to produce the oxygen isotopic compositions of the terrestrial planets and meteorite parent bodies. Clayton (2002) has proposed self-shielding.

Secondly, the highly energetic collisions during the 'giant-impact' stage of planetary accretion are widely thought to have caused partial vaporization, which may result in the loss of volatile elements. This process should be recognizable by depletion patterns of moderately volatile elements that differ from the chondritic patterns established by the diversity of chondrites. We shall demonstrate the prevalence of post-nebular volatilization in the inner Solar System by examining bulk Mn/Na ratios, which are preserved in chondrites at the solar ratio, but elevated in all the small, differentiated planetary bodies for which we have suitable samples. The Mn/Na ratio shows that post-nebula fractionation of moderately volatile elements is not confined to bodies of proto-planet size such as Mars, but is common in the basaltic achondrite meteorites that are presumed to sample small (approx. 10^2 km radius) bodies such as 4 Vesta, which, from the point of view of both size and age, may be identified with the planetary embryos of the intermediate steps of the accretion process. Rb/Sr ratios and Sr isotope systematics, which constrain the timing of the volatile loss, support these conclusions (e.g. Halliday & Porcelli 2001).

Thirdly, the high-energy collisions of the last stages of planetary accretion may result in fragmentation and considerable loss of material (Agnor *et al.* 1999; Agnor & Asphaug 2004). In a differentiated planet, crustal material, enriched in incompatible elements, may be preferentially removed, which will lead to bulk planetary compositions that are non-chondritic in incompatible elements, including refractory ones such as the rare-earth elements (REEs). For the Earth and other terrestrial planets, it has been an almost axiomatic assumption that the RLEs are present in the BSE in strictly chondritic ratios (e.g. Palme & O'Neill 2003), because these elements had not been observed to fractionate from each other in any type of chondrite (although improved analytical accuracy may now be revealing small variations). The RLEs include Ca, Al, REEs, the radioactive heat-producing elements U and Th, and many others that are used in geochemical modelling. Because the assumption of chondritic RLE ratios is used to estimate the abundances of many volatile and siderophile elements in the BSE (e.g. O'Neill & Palme 1998; Palme & O'Neill 2003), it has a particular significance for models of the accretion and early differentiation of the Earth, including core formation.

The chondritic assumption has gone almost unchallenged for several reasons. Firstly, the assumption dates from well before our present understanding of planet building developed, in particular before the role of high-energy collisions during the later stages of the process was well appreciated. It has therefore been claimed, wrongly, that no mechanisms were known that could fractionate

chemical compositions of terrestrial planetary bodies apart from those mechanisms whose effects could be seen among the chondritic meteorites. Secondly, the pattern of chemical fractionations expected from preferential collisional erosion of early formed crust is just that which is expected anyway in the residues of crust formation. The process is therefore difficult to disentangle from the expected effects of the Earth's geological differentiation, except when the geochemical modelling involves summing over the whole planet. It is this latter difficulty that has enabled the paradigm of a chondritic Earth to persist despite the accumulation of several strands of contrary evidence, which are traditionally explained away by postulating never-sampled hidden reservoirs within the mantle. (For an excellent summary of the lack of evidence for a chondritic BSE from the long-lived radiogenic isotope systems featuring only RLEs, namely Sm/Nd and Lu/Hf, see [Kostitsyn \(2004\)](#).) The signature of post-nebular volatile loss, by contrast, should produce patterns of volatile element abundances that are unmistakably non-chondritic; therefore, this process will be addressed first, with the aim of demonstrating the inadequacy of the chondritic assumption unambiguously.

2. Post-nebular volatilization

(a) Mn/Na ratio systematics as a monitor of post-nebular loss of moderately volatile elements

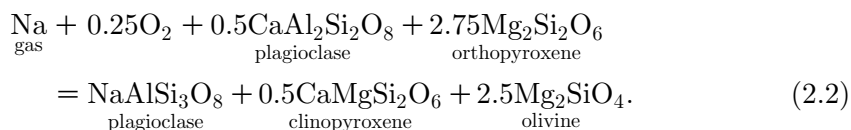
Manganese and sodium are two moderately volatile elements with similar condensation temperatures that show a remarkable correlation in their degree of depletion in all the chondritic meteorites ([table 1](#)). In constructing this compilation, only fresh meteorites were considered, because Na abundances are easily disturbed by weathering. The Mn/Na ratios of all classes of chondritic meteorites are nearly constant, almost within analytical error at the solar value of 0.39 ± 0.02 , as derived from CI meteorites ([Palme & Jones 2003](#)), despite the degree of depletion of both these moderately volatile elements, as monitored, for example, by the Mn/Mg ratio, varying by a factor of 3 ([figure 1](#)). The depletions in more volatile elements such as Zn are much more variable ([table 1](#)). Possibly, small deviations from the solar (CI) Mn/Na ratio may occur in the EL enstatite chondrites, with a slightly lower ratio, but Na is more susceptible to both parent-body and terrestrial alteration than Mn, and the low ratio in the EL chondrites might be due to the loss of some of the Mn held in sulphides, which are easily attacked by aqueous alteration. The most volatile-depleted carbonaceous, chondrites, the CV and CK groups, have a slightly higher ratio (0.45 ± 0.02), and two ungrouped, even more volatile-fractionated, carbonaceous chondrites, Coolidge and Loongana 001 ([Kallemeyn & Rubin 1995](#)), may have Mn/Na as high as 0.6, but both are weathered. But even accepting this value, the general conclusion is that no group of chondritic meteorites has a Mn/Na ratio elevated much above the CI value.

The significance of the chondritic Mn/Na ratio is that Mn and Na can only share similar volatility at a unique oxygen fugacity (f_{O_2}), for a given temperature and gas-phase pressure. The main gaseous species of both Mn and Na involved in cosmochemical condensation–fractionation processes are monatomic Mn(g) and Na(g). Both gas species are dominant over a wide range of oxygen fugacities,

Table 1. Mn/Na systematics in chondrites. (Sources of data: Davis *et al.* (1977), Graham *et al.* (1977), Kallemeyn & Wasson (1981, 1984), Palme *et al.* (1981), Kallemeyn *et al.* (1989, 1994, 1996), Wasson & Kallemeyn (1990), Bischoff *et al.* (1993), Weisberg *et al.* (1996), Brown *et al.* (2000) and Patzer *et al.* (2004).)

	no. of meteorites	Mn/Na	Mn/Mg ($\times 10^3$)	Zn/Mg ($\times 10^3$)
<i>carbonaceous chondrites</i>				
CI (Lodders)	3	0.381 ± 0.008	19.9 ± 0.4	3.23 ± 0.13
CI (Palme)	3	0.388 ± 0.023	20.1 ± 0.8	3.36 ± 0.35
CM	9	0.418 ± 0.022	14.5 ± 0.4	1.57 ± 0.05
CR	1	0.52	12.1	0.50
CR (Al Rais)	1	0.49	13.6	1.31
CO	5	0.398 ± 0.006	11.4 ± 0.1	0.69 ± 0.02
CV	4	0.455 ± 0.030	10.1 ± 0.5	0.80 ± 0.01
CK	7	0.457 ± 0.013	9.8 ± 0.3	0.67 ± 0.05
CH		0.6	8.8	0.3
<i>ordinary chondrites</i>				
all	66	0.370 ± 0.010	17.0 ± 0.6	0.325 ± 0.030
H	22	0.370 ± 0.006	16.3 ± 0.3	0.32 ± 0.03
L	20	0.368 ± 0.012	17.2 ± 0.4	0.34 ± 0.03
LL	16	0.372 ± 0.013	17.3 ± 0.5	0.31 ± 0.03
<i>enstatite chondrites</i>				
EH	12	0.35 ± 0.04	19.0 ± 1.9	2.05 ± 0.86 ($n=10$)
EL	5	0.28 ± 0.06	11.8 ± 2.8	0.13 ± 0.02
<i>others</i>				
R	6	0.354 ± 0.010	17.8 ± 0.2	1.13 ± 0.05
Kakangari	1	0.38	17	0.98
Cumberland Falls (ch)	1	0.35	21	0.09
Enon	1	0.37	14	0.05
Udei Station	1	0.36	13	1.43

from the reducing nebular environment to the relatively oxidizing conditions prevailing during the evaporation of silicates. But in condensed phases, Mn occurs as the MnO component, i.e. as divalent Mn^{2+} , e.g. as Mn_2SiO_4 in olivine and $MnSiO_3$ in pyroxene, whereas Na is monovalent and accordingly occurs as the $NaO_{0.5}$ oxide component, e.g. as $NaAlSi_3O_8$ in plagioclase. Consequently, their condensation–volatilization behaviours can be described by the following reactions:



The stoichiometries of these two reactions are such that the ratio of vapour pressures (p_{Mn}/p_{Na}) is proportional to $(f_{O_2})^{1/4}$. Mn will be relatively less volatile than Na at higher f_{O_2} and vice versa at lower f_{O_2} (which may, incidentally,

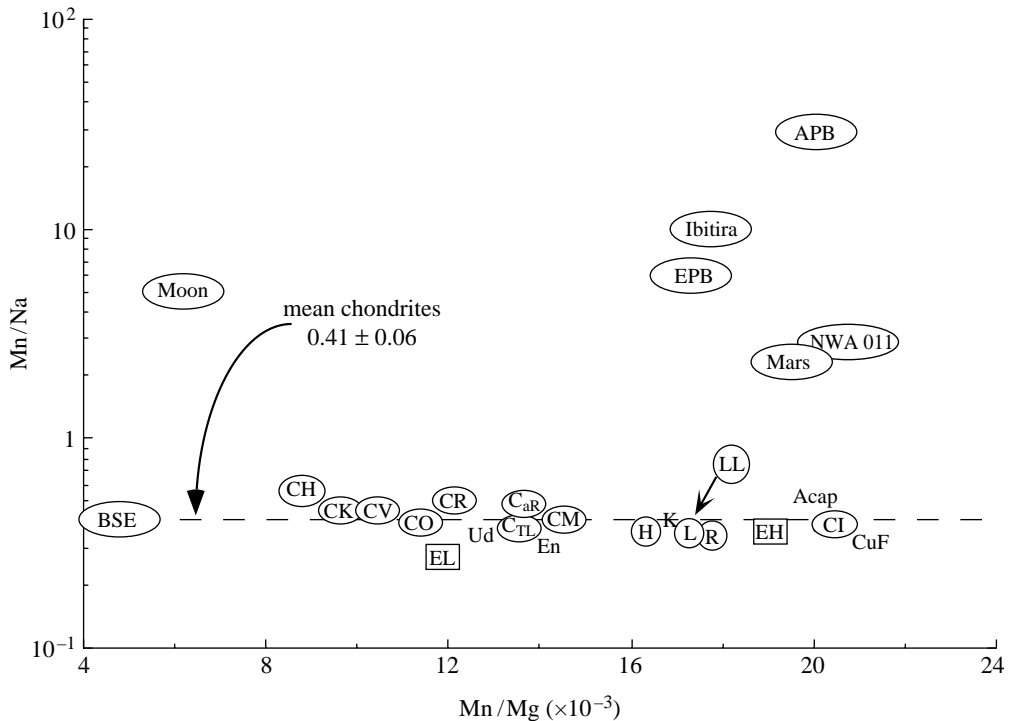


Figure 1. Mn/Na in chondrites, in small telluric bodies (STBs; Mars, Moon, eucrite parent body (EPB), angrite parent body (APB) and the parent bodies of Ibitira and NWA 011), and in the BSE. Chondrite groups (carbonaceous: CI, CM, CR, CO, CV, CK, CB and CH plus Tagish Lake and the anomalous CR Al Rais; ordinary: H, L and LL; enstatite EH and EL; rumurutiites, R) and anomalous chondrites (Kakangari, Enon, Udei Station and Cumberland Falls silicate portion) as well as the primitive achondrite Acapulco all cluster around the CI ratio of 0.39 ± 0.03 despite showing a variation of a factor of 3 in Mn/Mg, but all the STBs plot at markedly higher Mn/Na, indicating loss of Na under more oxidizing conditions than that of the solar nebula. The STBs can be derived from the CI Na–Mn/Mg ratios by loss of Na, conserving Mn/Mg, except the Moon, which has Mn/Mg similar to the Earth. For data sources, see [tables 1 and 2](#).

account for the slightly lower ratio in the highly reduced EL enstatite chondrites, if this is not an artefact of alteration). Otherwise, the constant Mn/Na ratio in chondrites is consistent with their Mn and Na abundances being set while the redox regime was that of the solar nebula, which buffers oxygen potential through the nebular H_2/CO and $\text{H}_2/\text{H}_2\text{O}$ ratios. Consequently, non-chondritic Mn/Na provides a means of distinguishing volatile depletion produced in planetary collisions after the solar nebula has dispersed from that occurring as a result of incomplete condensation of the solar nebula.

The 50 per cent condensation temperatures from the solar nebula at 10^{-4} bar calculated by [Lodders \(2003\)](#) are 1158 K for Mn and 958 K for Na. We suspect that the present difference in calculated condensation temperatures may be exaggerated by deficiencies in the thermodynamic data required to calculate the condensation temperatures. In particular, the calculated 50 per cent condensation temperature for Na is lower than that given by [Lodders \(2003\)](#) for K (1006 K), which is contrary to the experimentally observed difference in volatility among the

alkali metals (e.g. [Kreutzberger *et al.* 1986](#)). Note that because all the alkali metals vaporize as the monatomic gas, their relative volatilities are not dependent on f_{O_2} , so that varying ratios among the alkali metals (Li, Na, K, Rb and Cs) are potentially indicative of physicochemical variables other than redox conditions during volatile element fractionation.

(b) *Mn/Na ratios in small telluric bodies*

Non-chondritic Mn/Na is therefore an indicator of volatilization in a redox environment different from that set by the high hydrogen fugacity (f_{H_2}) of the solar nebula. In this section, we show that the Mn/Na ratio of every small, differentiated, rocky planetary body from which basaltic samples are known is greatly elevated above the chondritic ratio. The set of such bodies (we suggest the name ‘small telluric bodies’ or STBs) comprises the Moon and Mars, and the parent bodies of the non-primitive achondrites, namely of the angrites and the mainstream howardite–eucrite–diogenite (HED) association (APB and EPB, respectively), as well as of Ibitira, an anomalous eucrite (with vesicles) recently shown to have a resolvably different $\Delta^{17}\text{O}$ from the mainstream eucrites ([Wiechert *et al.* 2004](#); [Mittlefehldt 2005](#)), and of NWA 011, a newly discovered achondrite with distinctive $\Delta^{17}\text{O}$ ([Yamaguchi *et al.* 2002](#)).

The Mn/Na ratio of the terrestrial mantle is well known from samples representative of the upper mantle of the Earth. Such samples are not available for STBs. Deducing the bulk Mn/Na ratios of STBs is therefore not straightforward. Manganese and sodium have rather different geochemical properties, so they are fractionated by igneous differentiation. However, a robust estimate may be made using the empirical observations that Fe/Mn is very constant in basalts from a given planetary body and Na/Ti reasonably so. Using the Earth as the test case, it can then be shown that Fe/Mn is the same in a basalt as in its source while Na/Ti is almost so, especially at low pressure (see appendix A). The parent-body Mn/Na ratio is then obtained from

$$(\text{Mn/Na})_{\text{STB}} = [(\text{Fe/Mg})_{\text{STB}}/(\text{Fe/Mn})]/[(\text{Na/Ti})/(\text{Mg/Ti})_{\text{STB}}], \quad (2.3)$$

where $(\text{Fe/Mg})_{\text{STB}}$ is the planetary ratio (derived from petrologic modelling and, for the Moon and Mars, density constraints), and $(\text{Mg/Ti})_{\text{STB}}$ is obtained from the planetary Mg/RLE ratio (assumed to be solar, i.e. 210, in the absence of information to the contrary). In [table 2](#), we list the mean magmatic Na/Ti and Fe/Mn ratios needed to calculate planetary Mn/Na for all the STBs for which data exist (Moon, Mars, eucrite and angrite parent bodies, plus the parent bodies of Ibitira and NWA 011). The data for Mars are from 13 basaltic and olivine-phyric shergottites listed in [Lodders \(1998\)](#) or [Meyer \(2006\)](#), using the former’s selected values where available. The mean Na/Ti and K/U ratios of this dataset are both indistinguishable, within uncertainty, from their counterparts in terrestrial basalts ([table 2](#)); earlier estimates of Martian K/U, based on only the few Martian meteorites available at the time, gave somewhat higher values (e.g. [Wänke & Dreibus 1988](#)). The mean crustal Martian K/Th determined by the Mars Odyssey Gamma Ray Spectrometer is 5330 ± 220 ([Taylor *et al.* 2006](#)), implying that $\text{K/U} = 20 \times 10^3$, also higher than the magmatic ratio derived here, but not sufficiently so as to invalidate the arguments presented below.

Table 2. Mean magmatic Na/Ti, K/U and Fe/Mn ratios, planetary Mg# values and inferred planetary Mn/Na ratios (see equation (2.3) in text) in STBs.

	(Na/Ti) _{basalt}	K/U ($\times 10^{-3}$)	Fe/Mn	100 Mg# (atomic) ^a	Mn/Na
Moon	0.23 (O'Neill 1991 <i>a</i> ; Warren 2005)	1.5 \pm 0.5 (O'Neill 1991 <i>a</i>)	70 (O'Neill 1991 <i>a</i>)	84 \pm 3 (O'Neill 1991 <i>a</i> ; Warren 2005)	5
Mars	1.8 \pm 0.4 (Lodders 1998; Meyer 2006)	12 \pm 5 (Lodders 1998; Meyer 2006)	39 \pm 2 (Lodders 1998; Meyer 2006)	75 (Wänke & Dreibus 1988)	2.3
Eucrite PB	0.79 \pm 0.16 (Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	3.9 \pm 1.6 (Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	34 \pm 2 (Dreibus & Wänke 1980; Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	66 (Yamaguchi <i>et al.</i> 2002)	6
Ibitira PB	0.27 (Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	2.0 (Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	36 (Kitts & Lodders 1998; Barrat <i>et al.</i> 2000)	66 ^b	18
NWA 011 PB	0.93 (Yamaguchi <i>et al.</i> 2002)	11 (Yamaguchi <i>et al.</i> 2002)	75 (Yamaguchi <i>et al.</i> 2002)	~60 (Yamaguchi <i>et al.</i> 2002)	3
Angrite PB	0.028 \pm 0.010 (Mittlefehldt <i>et al.</i> 2002)	0.3 \pm 0.1 (Tera <i>et al.</i> 1970; Ma <i>et al.</i> 1977)	95 \pm 13 (Mittlefehldt <i>et al.</i> 2002)	71 \pm 4 (Longhi 1999)	30
BSE	2.0 \pm 0.2 (see table 3)	12 \pm 2	60 \pm 6	89.0 \pm 0.3	0.41 \pm 0.04
CI	(10.9 \pm 0.7) ^c	69.7 \pm 7	95	54.5 \pm 1.0	0.38 \pm 0.01

^a(Fe/Mg) = 2.297(1 - Mg#)/Mg#.^bAssumed to be the same as the EPB.^cWhole rock.

The derived planetary Mn/Na ratios are compared with the Mn/Na ratio in chondrites in figure 1. In every STB for which we have the necessary ‘basaltic’ samples, the calculated planetary Mn/Na is greatly elevated above the chondritic range. Even Mars, the most volatile-rich STB, has Mn/Na of 2.3, a factor of 6 above the solar value. However, the BSE has a ratio similar to the chondritic range, an important point to be discussed further below. As the Mn/Mg ratios show (figure 1), the elevated Mn/Na in all STBs apart from the Moon seems to be due to the loss of Na starting from Na–Mn–Mg abundances near the solar (CI) values. Only the Moon differs from this, being consistent with the loss of Na starting from the Na–Mn–Mg values of the BSE (yet another curious coincidence between the chemistry of the BSE and the Moon). The elevated Mn/Na ratios are confined to STBs that have undergone a sufficiently large degree of partial melting to produce basaltic samples. Primitive achondrites, such as the acapulcoites, and also, more interestingly, the near-primitive lodranites and brachinites, which show only minor degrees of silicate anatexis but partial loss of metal–sulphide (indicating incipient core formation), have chondritic Mn/Na or nearly so (e.g. *Palme et al.* 1981; *Nehru et al.* 1983; *Kallemeyn & Wasson* 1984; *Mittlefehldt* 2003; *Mittlefehldt et al.* 2003).

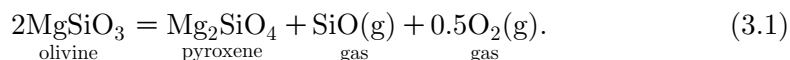
3. Mechanisms of volatile element depletion

(a) *Incomplete condensation versus evaporation*

In discussing the mechanisms of volatile element loss, we need to distinguish between fractionation by incomplete condensation from the solar nebula and that by subsequent evaporation. Under conditions of thermodynamic equilibrium between solids and gas of fixed bulk composition, condensation cannot be distinguished from evaporation. However, there is a large difference in redox state between the H₂-rich solar nebula and the H₂-poor vapour produced by the volatilization of silicates from planetary embryos or proto-planets after dispersal of the solar nebula, which should result in very different patterns of volatile element fractionation.

As originally set out by *Wasson & Chou* (1974), there are several arguments that suggest incomplete condensation, i.e. dissipation of volatile elements before condensation from the solar nebula, as the most likely process for the depletion of volatile elements in chondritic meteorites (*Palme et al.* 1988). Volatile element depletions are ubiquitous in primitive-textured, unmetamorphosed chondritic meteorites that could not have experienced temperatures high enough to lose volatile elements by evaporation. Most volatile element depletion patterns indicate a more-or-less smooth decrease of abundances with thermodynamically calculated condensation temperatures from the solar nebula. It is only depletions of volatiles that are found in Solar System materials, enrichments being extremely rare and only occurring at the intergranular scale. Thus, as we have pointed out, the constant (nearly) Mn/Na ratio in chondrites tells us that their depletion in Mn and Na was a nebular process.

Evaporation induced by heating or by impacts will reflect the relatively oxidizing conditions created by vaporization of planetary silicates, after the H₂-rich nebula has dissipated, according to the following reaction:



Thermodynamic calculations show that $\text{O}_2(\text{g})$ and $\text{SiO}(\text{g})$ are the main species in the gas phase in equilibrium with planetary silicate compositions at temperatures of approximately 3000 K (the approximate temperature that may be reached following a giant impact according to [Canup \(2004\)](#) or [Machida & Abe \(2004\)](#)); the stoichiometry of reaction (3.1) is such that $f_{\text{O}_2} = 0.5p_{\text{SiO}}$, hence $f_{\text{O}_2} \approx (1/3)p_{\text{total}}$, the total gas pressure.

Even at considerably lower temperature where magnesium silicates are not notably volatile, heating experiments have demonstrated that Na and K are much more volatile than Mn under conditions that are more oxidizing than the solar nebula. [Wulf *et al.* \(1995\)](#) heated Allende chunks at various oxygen fugacities. Severe losses of Na and K were found at temperatures from 1150 to 1300°C and heating times of up to 4 days, but no losses of Mn. The alkali losses were much stronger under reducing than oxidizing conditions. These findings are supported by the studies of alkali losses during chondrule formation. Experiments show rapid loss of alkalis, enhanced evaporation in the presence of H_2 gas and K isotope fractionation during loss of K (e.g. [Yu *et al.* 2003](#)). There are no reports of Mn evaporation during chondrule formation. [Floss *et al.* \(1996\)](#) heated Allende to very high temperatures and found minor Mn losses comparable with those of Fe, whereas alkalis were completely lost from the system.

These experiments also demonstrated that evaporation of alkalis led to isotope fractionation of K, which, however, is not observed in the alkali-poor, Mn-rich STBs or the Earth ([Humayun & Clayton 1995](#)). [Davis & Richter \(2003\)](#) pointed out that the lack of isotopic fractionation should not be taken as evidence for the absence of volatilization, as fractionated isotopes ‘are more a measure of the degree to which the system maintained thermodynamic equilibrium than a diagnostic of whether the path involved condensation or evaporation’. If the low abundances of Na and K in the Moon, eucrites and other STBs were caused by evaporation, some fractions are required to have lost all their inventory of alkalis (and other volatiles), while other parts were not affected at all. Later mixing of volatile-free with unvolatilized material may then produce the lower uniform concentration levels observed in the Moon, for example ([O’Neill 1991a](#)).

(b) Timing of moderately volatile element depletions

The decay of ^{53}Mn to ^{53}Cr (3.7 Myr half-life) and of ^{87}Rb to ^{87}Sr (48 Gyr half-life) can be used to obtain information about the time of Mn–Cr and Rb–Sr fractionations. The Mn–Cr system allows direct dating of the separation of systems with variable Mn/Cr ratios, provided that the Mn/Cr is scaled to a long-lived chronometer. The information provided by the Sr isotopes is more complex. If the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a planet before differentiation can be deduced, this contains information on the average Rb/Sr of the reservoir in which the parental material of the planet had evolved.

The slope of the $^{53}\text{Cr}/^{52}\text{Cr}$ versus $^{55}\text{Mn}/^{52}\text{Cr}$ correlation for bulk carbonaceous chondrites gives an age of $4568.1^{+0.8}_{-1.1}$ Ma ([Shukolyukov & Lugmair 2006](#)). This age is indistinguishable from the age of the oldest dated objects in the Solar System, calcium–aluminium-rich inclusions (CAIs) in CV chondrites with ages as old as 4567.2 ± 0.8 Ma ([Amelin *et al.* 2002](#)). Since increasing depletion of the moderately volatile element Mn is responsible for variations in Mn/Cr ratios of carbonaceous chondrites, this supports the primary nebular fractionation of Mn

by incomplete condensation. The Mn–Cr systematics in the HED parent body and in angrites are consistent with a CI-chondritic Mn/Cr ratio in their bulk parent bodies (Carlson & Lugmair 2000). There is presently no evidence for the vaporization of Mn from bulk meteorites or planets at a time later than *ca* 1 Myr after Solar System formation.

The Rb/Sr ratios of differentiated planetary bodies are very low when compared with the solar ratio, in accordance with the general depletion of volatile elements. The low Rb/Sr causes a slow increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios over time, which makes absolute dating with the Rb/Sr method for these objects impossible, but constrains initial $^{87}\text{Sr}/^{86}\text{Sr}$ accurately, especially if the age of formation of the object can be independently deduced. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ever measured in any Solar System material were found in CAIs of CV carbonaceous chondrites (see Podosek *et al.* 1991). The low Rb/Sr ratios and the old Pb–Pb ages of these objects indicate very early depletion of Rb, which is consistent with incomplete condensation. However, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Moon, angrites and eucrites are slightly elevated above the initial ratio of CAIs, reflecting an early stage of accelerated growth of ^{87}Sr under a higher Rb/Sr ratio than that presently observed in the object. For example, the material parental to the Moon could have evolved in a reservoir with a solar Rb/Sr ratio for 12 Myr before reaching the lunar initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. A younger age of the Moon would imply a correspondingly lower average Rb/Sr ratio (Carlson & Lugmair 2000). Post-nebular volatile loss of Rb from the material that makes up the Moon has been widely accepted (Nyquist *et al.* 1973; Carlson & Lugmair 1988; Alibert *et al.* 1994). Halliday & Porcelli (2001) have argued that secondary Rb loss is also observable in other STBs, occurring at *ca* 3 Myr after t_0 in the angrite parent body and slightly later in the eucrite parent body (or bodies). This is sufficiently late in the history of the Solar System that it should post-date the planetesimal stage of Solar System evolution and occur during the epoch of high-energy collisions between planetary embryos. The loss of Rb by degassing of alkalis from rapidly cooling magmas on the surface of STBs was considered unlikely by Halliday & Porcelli (2001). The evidence for this is the constancy of the ratios of the incompatible volatile alkali metals (K, Rb and Cs) with suitable RLEs of similar incompatibility (e.g. K/La, Rb/Sm and Cs/Nb) in cogenetic suites of basalts from STBs, which shows that the ratios in the basalts are inherited from their sources (e.g. Jochum & Palme 1990). Halliday & Porcelli (2001) accordingly concluded that ‘In the absence of better alternatives ... very energetic collisions between planets or sizeable planetesimals would seem the most like explanation.’ The Mn/Na evidence presented in this paper supports loss of alkali elements by post-nebular processes, with little or no loss of Mn (due to relatively high f_{O_2}), and with no isotopic fractionation of K.

A two-stage model for the Rb–Sr systematics of the Earth has been proposed by McCulloch (1994) based on his measurements of initial $^{87}\text{Sr}/^{86}\text{Sr}$ in a well-dated Archaean barite. This will be discussed further below.

(c) *Other chemical indicators of the physical conditions of post-nebular volatilization in STBs*

Not only is the depletion of Na in STBs as measured by Na/Ti well correlated with K/U (data in table 2), but also the correlation falls on the 1:1 line (figure 2a). This correlation shows that the depletions are related to the volatile

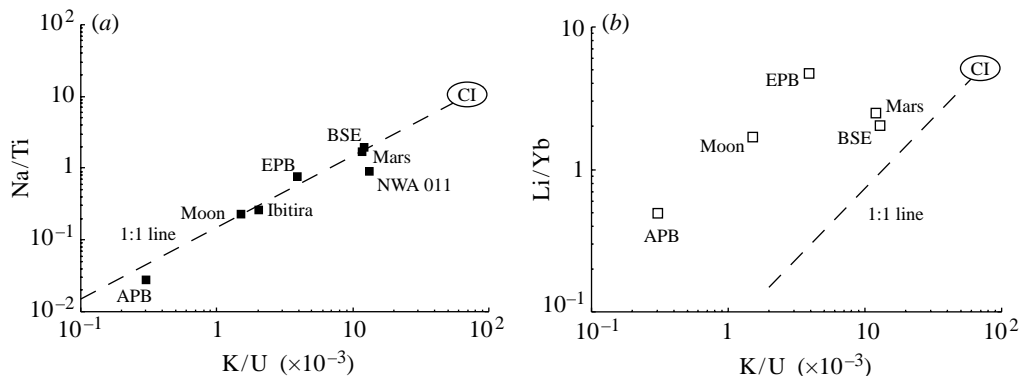


Figure 2. (a) Na/Ti versus K/U in the BSE and in STBs. There is an excellent correlation falling along the 1 : 1 line (dashed line) passing through the solar composition (marked CI), which is consistent with the volatilization of Na and K. The only datum falling off this trend, NWA 011, has similar Na, Ti and K to basaltic eucrites but much lower U, perhaps owing to the heterogeneous distribution of phosphate (Yamaguchi *et al.* 2002). (b) Average basaltic Li/Yb ratios from the Earth and STBs versus K/U. For a meaningful comparison between these basaltic Li/Yb ratios and the CI value, the latter has been divided by 1.7, to allow for the fractionation of Li from Yb during partial melting (see text). There is a poor correlation and all STBs and the BSE fall well off the 1 : 1 line.

properties of Na and K, which are similar, rather than to their incompatibilities, which are very different. A similar correlation between Rb/Sr and K/U has been shown by Halliday & Porcelli (2001); hence Na/Ti correlates with Rb/Sr, validating the use of Sr isotope systematics to date the post-nebular Na loss indicated by the superchondritic Mn/Na ratios in STBs.

Lithium is the least volatile of the alkali metals, but is still depleted in most chondrites relative to Mg and solar (CI) abundances, so its significance lies in constraining the conditions of volatile loss. It is also one of the least incompatible of the incompatible trace elements, such that its BSE abundance can be estimated directly from peridotite data, which gives 1.6 ± 0.3 ppm (Palme & O'Neill 2003), and a depletion factor in the BSE, normalized to Mg and CI, of 60 per cent. Thus Li, as expected from its lower volatility, is considerably less depleted than the other alkali metals in the BSE. Ryan & Langmuir (1987) showed that the Li/Yb ratio is reasonably constant in terrestrial basalts; they found $\text{Li/Yb} = 1.7$. An update using data in the PETDB database (Lehnert *et al.* 2000) for fresh oceanic basalts gives $\text{Li/Yb} = 2.0 \pm 0.7$, $n = 333$, and these data confirm that Li is better correlated with Yb than alternative choices of RLEs such as Sc, Ti or Zr. However, the BSE Li/Yb ratio as calculated from the peridotite data is 3.4 (Palme & O'Neill 2003), indicating some fractionation of Li from Yb during partial melting. This is not unexpected because Li is shared among olivine and pyroxenes in peridotites whereas nearly all of the Yb is in the pyroxenes. We therefore propose to correct Li/Yb in basalts by a factor of 1.7 to derive planetary values. The solar (CI) ratio is 9.0 ± 1.0 (Palme & Jones 2003).

The Li/Yb ratio in non-cumulate eucrites is 4.8 ± 0.7 ($n = 15$, data from Kitts & Lodders (1998) and Barrat *et al.* (2000)), which, when multiplied by 1.7, gives a eucrite parent-body Li/Yb of 8.2 ± 1.2 , the same as CI within uncertainty. The eucrite parent body is thus not depleted in Li despite its great depletion in the heavier alkalis. A similar exercise for Martian basalts (i.e. basaltic and

olivine-phyric shergottites) gives $\text{Li}/\text{Yb}=2.5\pm 0.9$ ($n=10$, data from Meyer (2006)), in between the EPB and BSE values. The Li/Yb ratio in the Moon is the same as that in the BSE (O'Neill 1991a). Remarkably, even Angra dos Reis, so very depleted in the other alkalis, contains 2 ppm Li (Tera *et al.* 1970), implying that $\text{Li}/\text{Yb}=0.5$ (Yb from Ma *et al.* 1977). Correlation of Li/Yb with Na/Ti or K/U is poor (figure 2b), indicating that it is little affected by post-nebular volatilization. Because the stoichiometry of the volatilization–condensation reactions controlling the volatility of Li is the same as those for the other alkalis, this cannot be ascribed to a difference in redox conditions, but, as pointed out by O'Neill (1991a, appendix 2), the relative volatilities of Li and Na appear to be sensitive to temperature. For the Moon, O'Neill (1991a) calculated that to condense Li but lose Na would require vapour temperatures below approximately 1400 K, surprisingly low in view of the 2000–4000 K indicated for the giant impact (Canup 2004; Machida & Abe 2004). The Li data will be potentially important in modelling volatile loss after giant impacts.

So far we have discussed only volatile element depletions in the silicate portions of STBs. Volatility-related fractionations are seen among the magmatic iron meteorites representing the metallic cores of planetesimals or STBs, as exhibited, for example, by Ge/Ni and Ga/Ni trends (Davis 2005). Good examples are the continuous depletion sequences of siderophile trace elements with decreasing condensation temperatures in IIAB and in IVB iron meteorites (Palme *et al.* 1988). The pattern in IIAB strongly resembles the H-chondrite pattern, while IVB meteorites have a much steeper depletion pattern. That these depletions are nebular in origin (i.e. due to incomplete condensation) is also indicated by the very early ages of most groups of iron meteorites from $^{182}\text{W}/^{184}\text{W}$ ratios (Kleine *et al.* 2005), which show that they formed before chondrites. There is no evidence to suggest any late-stage volatile loss from the cores of differentiated bodies.

(d) *Evidence for post-nebular volatile loss from the BSE*

The BSE abundances of the moderately volatile elements as given by Palme & O'Neill (2003) are plotted, normalized to Mg and CI abundances, against their calculated 50 per cent condensation temperatures from the solar nebula at 10^{-4} bar (from Lodders 2003) in figure 3a. For comparison, the same elements in CV carbonaceous chondrites, one of the groups of chondrites most depleted in volatile elements, are also plotted. The elements form a characteristic pattern of a smooth curve that flattens out at lower condensation temperatures, which is characteristic of carbonaceous chondrites and has been explained by continuous removal of material during condensation from the solar nebula (Wasson & Chou 1974; Wai & Wasson 1977; Cassen 1996, 2001). Any pattern in the depletions of the moderately volatile elements in the BSE is obscured by core formation, because many of the moderately volatile elements are also siderophile and/or chalcophile. To try to see through this effect, we have replotted these data after removing: one siderophile element, P; five siderophile–chalcophile elements, Cu, Ge, As, Sb and Ag, whose abundances plot significantly below the others; and three chalcophile elements, S, Se and Te. The remaining elements form a rough trend of decreasing normalized abundance with decreasing condensation temperature (figure 3b) that differs from the chondritic trend in not flattening out at lower temperatures.

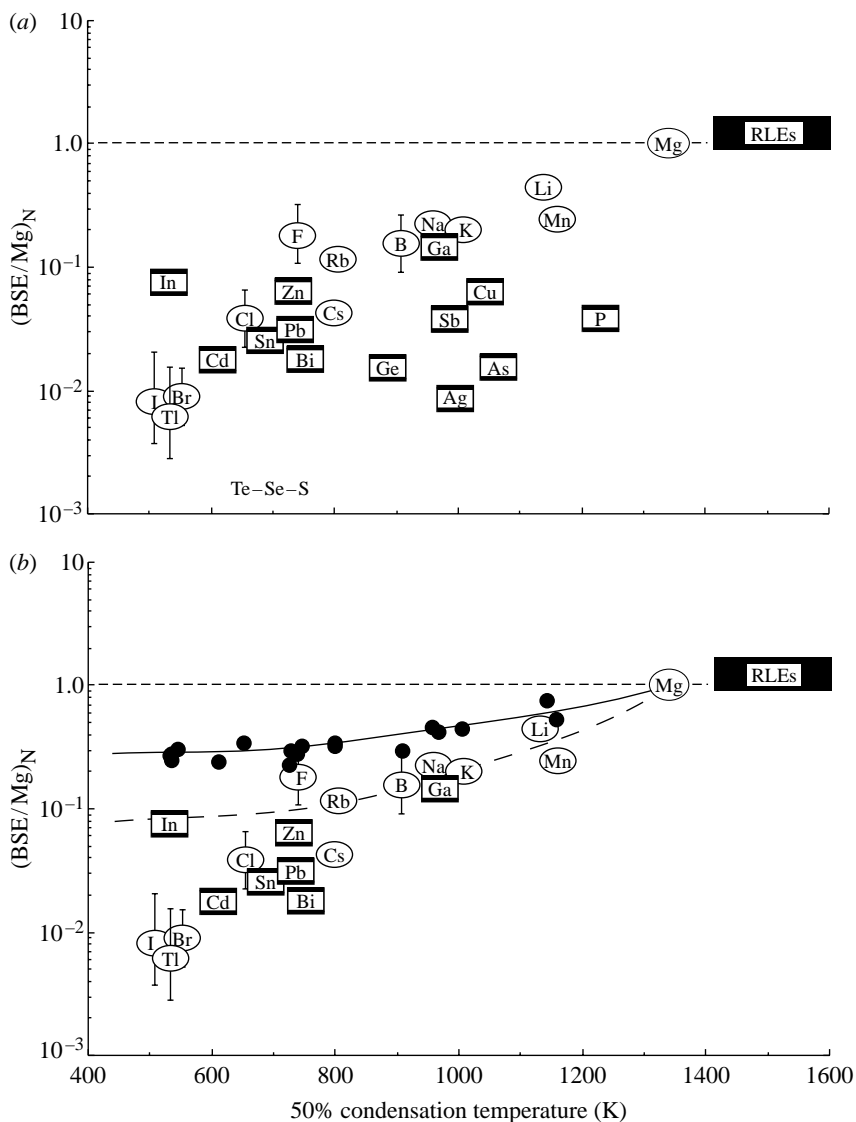


Figure 3. The pattern of volatile element depletion in the BSE. (a) Abundances from [Palme & O'Neill \(2003\)](#) normalized to Mg and CI against the calculated 50 per cent condensation temperature from the solar nebula at 10^{-4} bar from [Lodders \(2003\)](#). Siderophile and siderophile-chalcophile volatile elements are shown in rectangles and others in circles. (b) Arbitrary removal of six siderophile elements (P, Cu, As, Ag, Sb and Ge) plus the S-Se-Te group (to take account of siderophile removal by core formation) reveals a trend of depletion versus condensation temperature that is different from that shown in carbonaceous chondrites (the trend for CV carbonaceous chondrites is plotted for comparison as filled circles). In the BSE, the heavy halides (Cl, Br and I) plus Cs are much more depleted than elements of similar cosmochemical volatility such as Ga, Zn and In, even though some of these (e.g. particularly Ga) are also siderophile. A suggested pattern of depletion if the Earth were depleted in volatiles by the processes recorded in carbonaceous chondrites is indicated by the dashed curve, drawn parallel to the CV trend to pass through In.

A closer look at the data shows some other intriguing anomalies. The heavier halides (Cl, Br and I) show greatly enhanced depletions compared with Zn and In in the BSE compared with chondrites, despite the possibility that Zn and In, being siderophile–chalcophile, may be additionally depleted by core formation. The BSE abundances of both Zn and In are among the best determined of all trace elements (O'Neill & Palme 1998; Witt-Eickschen *et al.* 2007) and their BSE abundances do not depend on the 'chondritic assumption', whereas the BSE abundances of Cl, Br and I used in this plot (from Palme & O'Neill 2003) may be systematically overestimated by a factor of 2 by this assumption, as will be discussed below. This would increase the discrepancy. The heavy halides differ chemically from Zn and In in two ways relevant to their excess depletions. Firstly, their volatility, relative to other volatile elements, increases with increasing f_{O_2} (Fegley & Lewis 1980) whereas the volatilities of Zn and In decrease with increasing f_{O_2} (e.g. for Zn, see Wulf *et al.* 1995). Secondly, they are highly incompatible, and therefore may have been lost preferentially by collisional erosion (see below), whereas Zn and In are relatively compatible. Note that it is the pattern of depletion of the Zn–In grouplet rather than that of the halides that mimics best the pattern of depletion seen in chondrites (figure 3*b*), implying that it is the depletion of the heavy halides that is non-chondritic. The heavy halides are far more heavily depleted in the BSE than in any type of chondritic meteorite.

Siderophile elements whose volatility increases with increasing f_{O_2} also appear rather more depleted than their fellows (e.g. P, As, Sb; figure 3*a*). Elements such as Pb and Cd that can volatilize either as the monatomic species or as oxide species show intermediate depletions. In the case of Pb, the distinction is important, as the separation of radiogenic Pb from the RLE parents U and Th is conventionally taken to record 'the age of the Earth' (e.g. Galer & Goldstein 1996). If Pb is lost to the core, then this age records the age of core formation. On the other hand, if Pb is lost by reason of its volatility, this age may date post-nebular volatilization from planetary embryos or proto-planets added during the final stages of accretion.

It is a striking feature of the BSE composition that its Mn/Na ratio is chondritic, at 0.41 ± 0.03 (see appendix A). We have previously used this observation as indicating that the pattern of depletion of the moderately volatile elements in the BSE was chondritic, being set in the solar nebula (O'Neill & Palme 1998). However, Mn is more severely depleted relative to Mg in the BSE than any other planetary bodies (figure 1). In fact, the chondritic Mn/Na ratio is rather curious. Chondrules, bulk carbonaceous chondrites and the Earth fall, within error limits, on the same ^{53}Mn – ^{53}Cr isochron (see Palme & O'Neill 2003, their fig. 17; Shukolyukov & Lugmair 2006), suggesting that the Mn–Cr fractionation in all these objects occurred at about the same time, at the beginning of the Solar System. This was interpreted to support the early (i.e. nebular) loss of all the moderately volatile elements, which is not consistent with the BSE's Rb–Sr systematics (McCulloch 1994). But an alternative explanation consistent with the Rb–Sr evidence would involve decoupling of the secondary Mn and Na depletions, with part of the Mn depletion being due to early partitioning into the core under very reducing conditions (O'Neill 1991*b*), whereas the alkali metals are lost at a different time by volatility. That the BSE Mn/Na ratio ends up as chondritic would thus be coincidental.

Nitrogen is another element that is enormously depleted in the BSE relative to its abundance in any chondrite group, indicating that it may also have been depleted greatly by post-nebular volatilization. Loss of an early atmosphere has become the standard explanation for rare-gas abundances, especially the Xe isotopic pattern (e.g. [Ozima & Podosek 1999](#)).

In summary, the Earth and all small differentiated rocky bodies ('STBs') in the Solar System for which we have samples have non-chondritic patterns of the moderately volatile elements, caused by post-nebular volatilization. We cannot say definitively from the chemistry how this volatilization happens, but clearly it must involve not only very high temperatures but also a high degree of fragmentation to allow the volatile elements to vaporize. Both these factors may be achieved following a collision between planetary embryos or between an embryo and the growing Earth, in which simulations predict ejection of material as a mixture of vapour and molten silicate (e.g. [Canup 2004](#)). In many cases, a substantial fraction of the unvaporized material may also escape, and we now explore the implication of this 'collisional erosion' as the second non-chondritic means of modifying a planet's composition.

4. Collisional erosion

Empirically there is much evidence for collisional erosion among differentiated bodies of all sizes in the inner Solar System. The huge impact crater near the south pole of Vesta, which was discovered by the Hubble Space Telescope, is a directly observable example of the removal of silicates from a planetesimal-sized body. The volume of this crater corresponds to approximately 1 per cent of the mass of Vesta, and most of the excavated material appears to have been lost completely from the asteroid. [Binzel & Xu \(1993\)](#) found 20 small asteroids in the vicinity of Vesta with diameters of 10 km or less that have the same spectral reflectivity as Vesta, implying derivation from this asteroid. The HED group of meteorites is thought to derive from Vesta, implying other episodes of loss of material from that body. The Martian meteorites demonstrate in principle that material can be eroded by impact from Mars-sized bodies. The existence of magmatic iron meteorites, thought to be the cores of planetary embryos ([Scott 1972](#)), of which specimens from as many as 70 different parent bodies are known ([Wasson 1995](#)), attests to the frequency with which silicate mantles were stripped from differentiated bodies in the early Solar System. At a larger scale, a giant collision that removed approximately 80 per cent of the silicate mantle of Mercury has been proposed to explain the anomalously high density of this planet ([Benz *et al.* 1988](#)). Of course, the Moon itself is an example of the product of a collisional erosion event involving the Earth during the final stages of its accretion. The mass of the Moon is 1.8 per cent of the mass of the Earth's mantle. We now argue that substantially more silicate than this may have been lost, relative to metal, to the growing Earth during its accretion.

(a) *The Earth's superchondritic Fe/Mg ratio*

The amount of silicate material preferentially lost during the accretion of the Earth relative to its core may be estimated as follows ([Palme *et al.* 2003](#)). The Fe/Mg ratio of the Solar System as estimated from carbonaceous chondrites is

1.92 ± 0.08 (Palme & Jones 2003). The solar Fe/Mg ratio measured directly in the solar photosphere is 1.87 ± 0.4 , and is therefore the same as the CI ratio, but the uncertainty is too large to be useful. The Fe/Mg ratio of the Earth may be derived from a mass balance between the inferred composition of the Earth's core and mantle as follows:

$$(\text{Fe/Mg})_{\text{WE}} = [\text{Fe}]_{\text{core}} m_{\text{core}} + [\text{Fe}]_{\text{BSE}}(1 - m_{\text{core}}) / ([\text{Mg}]_{\text{BSE}}(1 - m_{\text{core}})), \quad (4.1)$$

where the square brackets denote concentrations; $m_{\text{core}} = 0.323$ is the mass fraction of the Earth's core; and the bulk silicate Earth (BSE) includes the mantle plus crust. The Earth's core may confidently be assumed to contain no Mg, because not only is the reduction potential of MgO to Mg metal so very large, but also Mg metal is nearly completely immiscible in Fe even in the liquid state at ambient pressure (Nayeb-Hashemi *et al.* 1985), and shows only slight miscibility at 2000°C and 20 GPa (Dubrovinskaia *et al.* 2004). The Earth's core is then made up of Fe, Ni and unspecified other elements known as the 'light component' (LC), such that $[\text{Fe}]_{\text{core}} = 1 - m_{\text{LC}} - [\text{Ni}]_{\text{core}}$, where m_{LC} is the mass fraction of this light component. The values $[\text{Mg}]_{\text{BSE}}$ and $[\text{Fe}]_{\text{BSE}}$ are estimated at 22.2 ± 0.2 and 6.3 ± 0.1 wt%, respectively (Palme & O'Neill 2003). With $[\text{Ni}]_{\text{BSE}} = 1860$ ppm and the assumption of a chondritic Fe/Ni ratio of 17.1 in the whole Earth, $[\text{Ni}]_{\text{core}} = 5.9 - 5.5 m_{\text{LC}}$ (in wt%). The whole-Earth Fe/Mg ratio, $(\text{Fe/Mg})_{\text{WE}}$, is $2.31 - 2.0 m_{\text{LC}}$ (± 0.03). Taking $m_{\text{LC}} = 0.1$ (Poirier 1994), we find $(\text{Fe/Mg})_{\text{WE}} = 2.11$. The fraction of the light component in the Earth's core is uncertain, but increasing m_{LC} to 0.15 only decreases $(\text{Fe/Mg})_{\text{WE}}$ to 2.01. It thus appears that the Earth is significantly enriched in Fe relative to Mg.

The MgO content of the upper mantle (36.3 ± 0.4 wt%) calculated by Palme & O'Neill (2003) is based on the observed Mg# (molar Mg/(Mg+Fe)) of 0.89 for least-depleted peridotite samples, and the surprisingly uniform $\text{FeO}_{\text{total}}$ content of mantle peridotite of 8.1 ± 0.1 wt%. Earlier estimates of mantle MgO contents have sometimes been slightly higher (see Palme & O'Neill 2003); for example, McDonough & Sun (1995) have estimated 37.8 wt% MgO, leading to $(\text{Fe/Mg})_{\text{WE}} = 2.05$, but this is still well above the chondritic value. A more critical issue is the question of whether the entire Earth's mantle has the same Mg and Fe contents as the upper mantle; that is, whether the mantle has, to a reasonable approximation, constant major-element composition from top to bottom.

The major support for a mantle that is chemically homogeneous in major elements comes from geophysical constraints on whole-mantle convection (e.g. Davies 1998, 1999). Radial differences in MgO and/or FeO would imply density differences that are unlikely to have been preserved in a globally convecting mantle over the age of the Earth. In particular, mantle with anomalously low Fe/Mg would be compositionally buoyant and should thus be relatively accessible to sampling at the Earth's surface. The absence of evidence for any such reservoir is therefore significant. While high FeO regions in the lower mantle have been suggested as a mechanism to allow for long-term chemical isolation (Kellogg *et al.* 1999), such Fe enrichment would only further increase $(\text{Fe/Mg})_{\text{WE}}$ above chondritic. It seems plausible that the value of $(\text{Fe/Mg})_{\text{WE}}$ is indeed approximately 10 per cent above the solar ratio.

There is no obvious reason why the material that condensed to form the inner Solar System should have had as much as 10 per cent more Fe than the solar composition. Volatility-related fractionation in the condensation of material

from the solar nebula would not lead to an abnormally high terrestrial Fe content, because Mg and Fe have similar nebular volatilities (Lodders 2003). Although chondrites demonstrate a nebular metal–silicate fractionation (e.g. Larimer & Anders 1970; O'Neill & Palme 1998), this is not correlated with other chemical fractionations and seems likely to be a local-scale phenomenon of the type that should be averaged out during the later stages of accretion. We postulate instead that the Earth's elevated $(\text{Fe}/\text{Mg})_{\text{WE}}$ may be caused by the loss of silicate due to collisional erosion. About a fifth of the presumed 10 per cent of silicate lost from the Earth is accounted for by the Moon (i.e. the mass of the Moon is 1.8 per cent of that mass of the Earth's mantle), with the rest having been lost throughout the giant-impact phase of chaotic collisions between proto-planets (stage 3) but perhaps also, based on the evidence of the small STBs like Vesta, during the evolution of planetary embryos from planetesimals (stages 1 and 2).

5. Possible consequences of preferential collisional erosion for the composition of the BSE

To illustrate the consequences of this possibility for producing a non-chondritic composition for the BSE, we construct a mass balance for a two-stage model, which gives the gist of the geochemical consequences of preferential collisional erosion in the simplest way possible. In the first stage, the planetary embryos in the population that will eventually form the Earth are assumed to differentiate into an incompatible-element-enriched proto-crust, making up a mass fraction $f_{\text{p-c}}^1$ of the final Earth's mass. In the second stage, collisional erosion removes some of this proto-crust (mass fraction, $f_{\text{p-c}}^2$, where $f_{\text{p-c}}^2 < f_{\text{p-c}}^1$), plus a mass fraction f_{res}^2 of the residue from crust formation. The concentration of a trace element M in the proto-crust of the first stage, relative to its chondritic abundance, c_{M}^{o} , is given by the batch melting equation:

$$\frac{c_{\text{M}}^{\text{p-c}}}{c_{\text{M}}^{\text{o}}} = \frac{1}{D_{\text{M}} + f_{\text{p-c}}^1(1 - D_{\text{M}})}, \quad (5.1)$$

where D_{M} is the partition coefficient of M between proto-crust and residue. The resulting depletion factor of M in the BSE after the second stage is then given by

$$\frac{c_{\text{M}}^{\text{BSE}}}{c_{\text{M}}^{\text{o}}} = \frac{f_{\text{p-c}}^1(1 - D_{\text{M}}) + D_{\text{M}}(1 - f_{\text{res}}^2) - f_{\text{p-c}}^2}{(D_{\text{M}} + f_{\text{p-c}}^1(1 - D_{\text{M}}))(1 - f_{\text{res}}^2 - f_{\text{p-c}}^2)}, \quad (5.2)$$

where $c_{\text{M}}^{\text{BSE}}$ is the calculated concentration of M. This two-stage calculation is analogous in spirit to that used by Hofmann (1988, 2003) to model the trace-element composition of the oceanic crust, which is thought to derive from the depleted mantle as the second stage following a first stage in which the continental crust was extracted from a primitive mantle composition. For illustrative purposes, we adopt a set of internally consistent values of D_{M} for incompatible elements deduced from the process of forming the basaltic oceanic crust, namely that of Workman & Hart (2005).

With an internally consistent set of values of D_{M} , there remain the three unknowns, $f_{\text{p-c}}^1$, $f_{\text{p-c}}^2$ and f_{res}^2 , requiring three independent constraints, which may be supplied as follows.

- (i) From the Earth's Fe/Mg ratio, we put $(f_{p-c}^2 + f_{res}^2) = 10$ per cent.
- (ii) As a limit to the loss of the most incompatible elements, we use the observation that the amount of ^{40}Ar in the atmosphere corresponds to the radioactive decay of 120 ppm K over the age of the Earth (4.5×10^9 years). Potassium is a cosmochemically moderately volatile element, whose abundance in the BSE has traditionally been estimated using the chondritic axiom, from the average of K/La and K/U ratios in crust- and mantle-derived rocks, because empirically K is intermediate in incompatibility between these two RLEs (O'Neill 1991*b*). The amount of K in the BSE estimated in this way was 260 ± 40 ppm, under the traditional assumption of chondritic relative abundances of U and La to the refractory major elements Ca and Al (Palme & O'Neill 2003). The comparison of this value with that implied by the ^{40}Ar argument (i.e. 120 ppm) has traditionally been taken to imply that the mantle is only approximately half degassed. Instead, we use this observation to provide a lower limit on the ratio c_M^{BSE}/c_M^o of 0.5 at $D_M = 0$.
- (iii) For the third constraint, we use a recent discovery that the BSE appears to be non-chondritic in its Sm/Nd ratio, as deduced from the $^{146}\text{Sm}/^{142}\text{Nd}$ isotope system (half-life 103 Myr). New high-precision measurements of the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio in chondritic meteorites and in various terrestrial rocks have shown that all the terrestrial samples have $^{142}\text{Nd}/^{144}\text{Nd}$ that is 20 ppm higher than that in the chondritic meteorites (Boyet & Carlson 2005, 2006). The implication is that all terrestrial samples are derived from a source that was depleted in the more incompatible Nd relative to Sm early in the history of the Earth. The calculated degree of depletion depends on its timing, but for early depletion within the time frame for a giant impact (*ca* 30 Myr), the depletion in Nd relative to Sm should be approximately 6 per cent (i.e. $^{147}\text{Sm}/^{144}\text{Nd} = 0.21$, versus the chondritic value of 0.1966). Therefore, we take $(c_{\text{Sm}}^{\text{BSE}}/c_{\text{Sm}}^o)/(c_{\text{Nd}}^{\text{BSE}}/c_{\text{Nd}}^o) = 1.06$. This degree of depletion is compatible with the secular evolution of $^{143}\text{Nd}/^{144}\text{Nd}$ in the mid-ocean ridge basalts (MORB) reservoir, and a present-day mass balance of Sm and Nd with the continental crust, assuming that the MORB reservoir comprises virtually the whole mantle (Boyet & Carlson 2005, 2006).

These three constraints allow the solution of equation (5.2) for all trace elements as a function of their incompatibility (i.e. D_M), as shown in figure 4. This solution has $f_{p-c}^1 = 0.026$ and $f_{p-c}^2 = 0.014$, i.e. differentiation of the planetary embryos and proto-planets that will eventually form the Earth produces crusts comprising 2.6 per cent of their silicate portions (the first stage, equation (5.1)). For comparison, the lunar crust with a thickness of 30–60 km would make up 5–10 per cent of the mass of the Moon, but the present Earth's oceanic crust comprises approximately 0.2 per cent of the mass of the mantle. In the subsequent collisional erosion events, 0.014/0.026 (i.e. 54% of this crust) is preferentially lost. All highly incompatible elements ($D_M < 0.001$) have $c_M^{\text{BSE}}/c_M^o \cong 0.5$ (our assumed limit) and are thus not significantly fractionated from each other; accordingly, the chondritic Th/U ratio is conserved, as required by the Th–U–Pb isotope systematics. Nd and Sm fall in the mid-range of incompatibility (here we

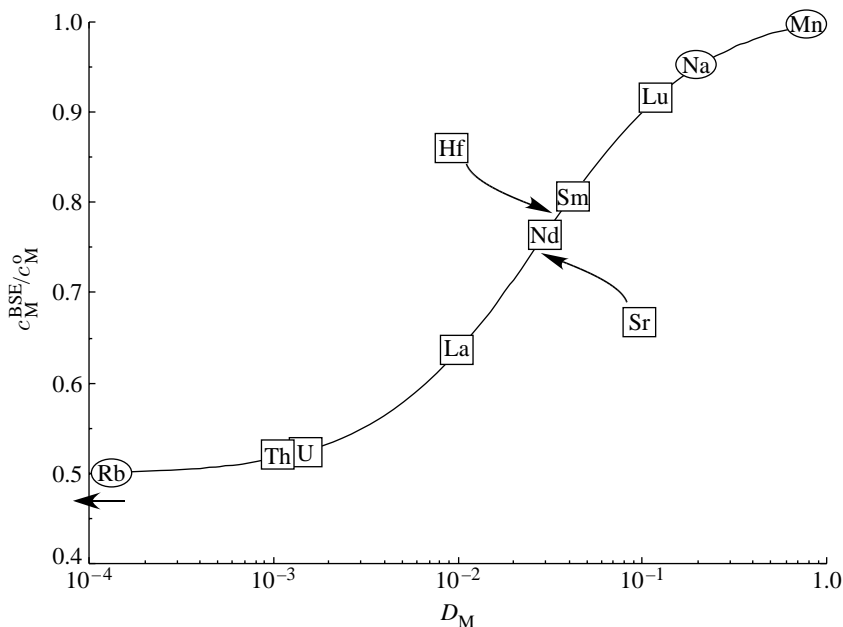


Figure 4. Hypothetical effects of preferential collisional erosion of early formed crust: calculated values of $c_M^{\text{BSE}}/c_M^{\text{O}}$ from a two-stage differentiation–erosion model (see equation (5.2)) for incompatible trace elements, M, as a function of their incompatibility, here quantified using the average melt–residue partition coefficients (D_M) from Workman & Hart (2005) for the production of MORB. As discussed in the text, the total fraction of early formed crust, f_{p-c}^1 , is taken as 0.026, and the fraction of collisionally eroded crust f_{p-c}^2 , is 0.014 (i.e. 54 per cent of f_{p-c}^1). c_M^{BSE} is the calculated concentration of M in the BSE after preferential collisional erosion, and is normalized to the concentration that M would have in a chondritic BSE, c_M^{O} . For volatile elements Na, Rb and Mn, c_M^{O} is assumed to include any depletion due to ‘chondritic’ processes (e.g. failure to condense completely). Although the model is overly simplistic, the shape of the curve is robustly constrained by the assumptions that $c_M^{\text{BSE}}/c_M^{\text{O}}$ would be 0.5 for a completely incompatible element ($D_M=0$) and Sm/Nd is 1.06 times chondritic.

used $D_{\text{Nd}}=0.031$ and $D_{\text{Sm}}=0.045$ from Workman & Hart (2005)), hence the assumed non-chondritic Sm/Nd constrains the position of the middle part of the curve. Major elements (Mg, Si, Ca, Al and Fe) and mildly incompatible elements (such as Mn and Na) are barely affected. More complex models, for example involving fractional melting or several stages, may considerably change the values of f_{p-c}^1 and f_{p-c}^2 , which therefore have little significance, but the basic shape of the curve shown in figure 4 would not change much because this shape reflects our three constraints. Our calculation gives Lu/Hf=1.17 times chondritic and La/Lu=0.69 times chondritic.

Because the fundamental cause of the chemical fractionation that results from preferential collisional erosion is crust formation, its signature is difficult to identify beneath the effects of ordinary crust formation in the Earth. This is especially the case because in the Earth crust formation occurs in two modes—the long-lasting highly differentiated continental crust and the basaltic oceanic crust with a much shorter lifespan (*ca* 10^8 years). The difficulty is well illustrated by considering the implications of our heuristic model for the Sr/Ba ratio in the BSE in some detail.

The significance of this ratio is that Sr and Ba are two RLEs, both of whose abundances may be related through their relationship to Rb, but in different ways (Hofmann & White 1983): Ba has the same geochemical incompatibility as Rb, and an isotope of Sr (^{87}Sr) is the daughter of parent ^{87}Rb . Ba is a highly incompatible trace element but Sr is less incompatible, with bulk distribution coefficients for MORB genesis given by Workman & Hart (2005) of 10^{-5} and 0.025, respectively. Therefore, according to the model of figure 4, Sr/Ba in the non-chondritic BSE should be approximately 45 per cent larger than the chondritic ratio. The solar (CI) ratio, $(\text{Sr}/\text{Ba})_{\text{CI}}$, is 3.0 ± 0.3 from Palme & Jones (2003), but Lodders (2003) gives 3.35 and the averages for the three ordinary chondrite groups given by Wasson & Kallemeyn (1988) are 2.4, 3.0 and 2.3 (the variation may be due to the fact that neither element, but especially Ba, has been among those determined routinely in the chemical analyses of meteorites). In the Earth, the Rb/Ba ratio was empirically found to be constant at 0.09 ± 0.02 in oceanic basalts (Hofmann & White 1983). The PETDB database (Lehnert *et al.* 2000) at present gives 0.094 ± 0.036 , $n=666$ (using basaltic samples described as ‘fresh’ only). But such a large fraction of Rb and Ba is in the continental crust that it is this reservoir that dominates BSE abundances. For the average continental crust, Rudnick & Gao (2003) give Rb/Ba=0.11. Most previous estimates, reviewed in Rudnick & Gao (2003), are even higher. The Rb/Sr of the BSE is constrained by $^{87}\text{Rb}/^{87}\text{Sr}$ systematics (i.e. the time-integrated value of $^{87}\text{Sr}/^{86}\text{Sr}$ compared with chondritic). For the mantle, this is usually done (following DePaolo & Wasserburg 1976) by plotting initial $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ (i.e. ϵSr versus $\epsilon^{143}\text{Nd}$) for all oceanic basalts and noting the $^{87}\text{Sr}/^{86}\text{Sr}$ at which this negatively correlated array passes through the chondritic $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (i.e. $\epsilon^{142}\text{Nd}=0$). This gives Rb/Sr=0.029, but with a high initial $^{87}\text{Sr}/^{86}\text{Sr}$ at 4.56 Gyr, and such an estimate should also logically be corrected within the preferential collisional erosion paradigm for non-chondritic Sm/Nd. By contrast, for his two-stage model, McCulloch (1994) gave Rb/Sr=0.023. With Rb/Ba=0.10 (average of crust and mantle), this latter implies $(\text{Sr}/\text{Ba})_{\text{BSE}}=4.3$, which is indeed 45 per cent larger than the preferred chondritic ratio, but clearly the uncertainties are so great that this apparent agreement with our scenario could be merely fortuitous. A more promising test comes from the heat- ^4He paradox.

(a) *Implications of a non-chondritic BSE for the ^4He -heat paradox*

Radioactive decay of U and Th produces both heat and ^4He . The good coherence in geochemical behaviour between U, Th and also K (Jochum *et al.* 1983) therefore means that there should be a simple relationship between the radiogenic heat and the ^4He coming out of the mantle (e.g. O’Nions & Oxburgh 1983; van Keken *et al.* 2001).

The flux of ^4He out of the ocean basins is estimated from the global ^3He flux into the oceans of 10^3 moles yr^{-1} (Craig *et al.* 1975; Farley *et al.* 1995). Although this flux is averaged over a short time scale (*ca* 10^3 years), it is consistent with the estimated ^3He abundances in undegassed MORB and probably has an uncertainty of a factor of 2 (Ozima & Podosek 2002). Assuming a mean $^3\text{He}/^4\text{He}$ of $8R_A$, where R_A , the atmospheric ratio, is 1.38×10^{-6} , this gives a ^4He flux of 1.7×10^{24} atoms s^{-1} . The production of ^4He from ^{238}U and ^{235}U is 1.0×10^8 atoms $\text{kg}^{-1} \text{s}^{-1}$, and that from ^{232}Th is 2.4×10^7 atoms $\text{kg}^{-1} \text{s}^{-1}$ (Stacey 1992). Assuming Th/U=3.8, the

chondritic ratio, the ^4He flux through the ocean floor corresponds to ^4He production from 9×10^{15} kg U^{ThK} , where we use the symbol U^{ThK} to denote U (by mass or concentration), but including the ^4He from the Th, or the heat from the Th and K, which is expected geochemically to be associated with that U. The mass of the mantle is 4×10^{24} kg, hence the ^4He flux corresponds to mantle with an average U^{ThK} content of 2.3 ppb. If the present-day ratio of Th/U of 2.5 as inferred for the depleted mantle (O'Nions & McKenzie 1993) is assumed instead, the U^{ThK} concentration needed to support the ^4He flux increases to 2.7 ppb. This is close to the lower limit of the concentration of U inferred to be present in the MORB source mantle, estimates of which range from approximately 3 to 8 ppb (Jochum *et al.* 1983; Workman & Hart 2005), and may be considered to be in agreement given the factor of 2 uncertainty in the ^4He flux. Moreover, U abundances deduced from abundances in MORB may be higher than the average depleted mantle, because basalts preferentially sample the more fertile parts of their source. Specifically, harzburgite from previous episodes of melt extraction might comprise some fraction of the mantle but would not contribute much basalt (nor heat nor ^4He) to modern partial melting, so behaving as an inert filler (e.g. Liu *et al.* 2008). The inference from the ^4He flux is that the present Earth's convecting mantle is thoroughly depleted from top to bottom.

A large fraction of the U^{ThK} in the BSE is in the continental crust. The average U concentration of the continental crust (which is constrained by heat flow arguments) has most recently been estimated at 1.3 ppm U (Rudnick & Gao 2003). Taking the mass of the continental crust at 0.54 per cent of the mantle (Taylor & McLennan 1995), with 3 ppb for the mantle, gives a total BSE U abundance of 10 ppb. This value is half of the 22 ppb that would be estimated using the chondritic assumption (Palme & O'Neill 2003), but agrees with our hypothesis that the BSE could be depleted by as much as 50 per cent in U by preferential collisional erosion.

The problem with such a low BSE abundance of U^{ThK} is, of course, the concomitant low radiogenic heat production in the mantle. The heat produced by 3 ppb U^{ThK} (assuming Th/U=3.8 and K/U= 1.2×10^4 , from Jochum *et al.* 1983) is 3 TW, which is only a small fraction (approx. 10%) of the heat flow from the ocean basins of 31 TW (Pollack *et al.* 1993). Although well known, this result has seemed so extraordinary, when viewed from the perspective of chondritic U and Th in the BSE being an unchallengeable axiom, that it has led to models of a layered mantle separated by a boundary impermeable to ^4He but not to heat, although how this might be accomplished is not apparent. An alternative explanation is simply that the BSE is not chondritic due to collisional erosion. There is a possibility that the Earth's U and Th contents may eventually be independently determined from geoneutrinos (Fiorentini *et al.* 2006).

(b) Implications of collisional erosion for the BSE composition

The composition of the BSE (otherwise known as primitive mantle) derived by Palme & O'Neill (2003) obtains the concentrations of the five most abundant oxide components MgO, SiO₂, FeO, Al₂O₃ and CaO from the data of mantle peridotites, assuming just one cosmochemical constraint, which is that the RLEs Ca and Al occur in the chondritic ratio. This constraint is not affected by collisional erosion, firstly because Ca and Al are only mildly incompatible, and secondly because the chondritic ratio is preserved during partial melting of peridotite at low pressures—the average CaO/Al₂O₃ ratio of 17 829 fresh

basalts, *sensu lato*, in the PETDB database (Lehnert *et al.* 2000) is 0.76, with a standard deviation of only 0.07, which compares with chondritic CaO/Al₂O₃ of 0.81 (Palme & O'Neill 2003). The abundances of Ca or Al and Mg so derived then yield a BSE RLE/Mg ratio, which determines the abundances of all RLEs under the chondritic assumption that RLEs are not fractionated when obtained from each other. The abundances of the siderophile and volatile elements were then determined mostly using the following three methods (O'Neill & Palme 1998).

- (i) Compatible or mildly incompatible elements (Li, Na, V, Cr, Mn, Co, Ni, Zn, Ge, Ga, Cd and In) and also S were obtained from data of mantle peridotites. The data plot as linear arrays on diagrams versus MgO, so that extrapolation to the BSE MgO gives their BSE value. The results of this method will not be affected by abandoning the constant RLE ratio axiom.
- (ii) More incompatible elements were obtained by ratioing to a suitable RLE, e.g. P/Nd, Rb/Ba, Sn/Sm and W/Th, so these abundances could be overestimated by factors that depend on the incompatibility of the selected RLE, according to equation (5.2), up to a factor of 2 (figure 4).
- (iii) Even more incompatible elements such as H (as H₂O), Cl, Br, I and N and the noble gases were estimated from their observed abundances in the Earth's exosphere (atmosphere and oceans), together with an estimate of the extent of degassing of the mantle, which was taken as 50 per cent from the ⁴⁰Ar–⁴⁰K argument, with K from K/U and K/La, again assuming U and La from the constant RLE ratio argument. A slight adjustment was made for the abundance still in the depleted mantle, as sampled by MORB. However, if the K abundance were to be only half of that given by the chondritic model, these BSE abundances would be overestimated by a factor of approximately 2.

6. Conclusions

The arguments presented in this paper show that a chondritic Earth composition is not necessarily expected given a modern understanding of how terrestrial planets accrete. Indeed, the pattern of the BSE's depletion in non-siderophile volatile elements shows evidence for volatile loss by non-chondritic processes, which presumably involve not only high temperatures but also fragmentation, as predicted by dynamic modelling of energetic collisions (e.g. Agnor & Asphaug 2004). The evidence for post-nebular volatile loss in STBs (Mars, the Moon, eucrite parent body, etc.) is even more conspicuous in the form of well-constrained non-chondritic Mn/Na, and the timing of this loss, which may be inferred from Rb/Sr isotope systematics. The loss of non-volatile material could lead to further non-chondritic bulk compositions if more material is lost from the outer crust of a differentiated planetary embryo or proto-planet, a process we call 'preferential collisional erosion'. That this may have been a common process in the inner Solar System is now indicated by apparently non-chondritic Sm/Nd in Mars as well as the Earth and Moon (Caro *et al.* 2008).

Based on the excess Fe/Mg of the whole Earth compared with the solar ratio, it seems likely that post-nebular volatile loss during the Earth's accretion was accompanied by collisional erosion of approximately 10 per cent of silicate relative to Fe-rich metal. We emphasize that this loss is a net one, operating throughout the later stages of the Earth's accretion, certainly during the giant-impact stage as the Earth is built up through collisions between proto-planets, starting from Moon- to Mars-sized planetary embryos sourced from throughout the inner Solar System, but perhaps also during the earlier stages as the planetary embryos themselves grow from planetesimals (e.g. [Weidenschilling *et al.* 2001](#)). Some 1.8 per cent of this approximately 10 per cent net loss is the Moon. It is then a small step to speculate that early formed, differentiated crust may have been lost preferentially, depleting the BSE in incompatible elements according to their geochemical incompatibilities. Such a pattern of fractionation is difficult to discern owing to the subsequent formation of both the continental crust and the oceanic crust, which processes also fractionate elements according to their geochemical incompatibilities.

Once the possibility of non-chondritic RLE ratios in the BSE is accepted, solutions to a variety of geochemical paradoxes emerge (other than ad hoc 'hidden reservoirs'). The current dominant paradigm in mantle geochemistry is that the continental crust is complementary to the depleted mantle, which is the source of ocean floor basalt (see [Hofmann \(2003\)](#) and [Kostitsyn \(2004\)](#) for recent reviews). However, attempts to mass-balance the continental crust with the depleted mantle assuming chondritic RLE ratios for the BSE show that the amount of depleted mantle that is complementary to the crust comprises only a fraction of the whole BSE, e.g. approximately 30 per cent from $^{143}\text{Nd}/^{144}\text{Nd}$ isotopes (e.g. [Zindler & Hart 1986](#)), or approximately 50 per cent from highly incompatible trace elements such as Rb (e.g. [Hofmann 2003](#)). The remaining 70 or 50 per cent is assumed to be primitive mantle, which has not had crust extracted from it, and should thus preserve chondritic proportions of RLEs, give rise to basalts with chondritic $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ (i.e. $\epsilon^{143}\text{Nd}=0$ and $\epsilon\text{Hf}=0$ by definition) and contain a large fraction of the BSE's heat-producing elements (U, Th and K). But it has become apparent that this paradigm is beset by several problems, one of the most obvious being that there is no empirical evidence from any rocks that primitive mantle exists, anywhere. [Kostitsyn \(2004\)](#) shows that, out of many hundreds of basalts analysed for $^{143}\text{Nd}/^{144}\text{Nd}$, none have $\epsilon^{143}\text{Nd}=0$ at chondritic Sm/Nd and similarly none have $\epsilon^{176}\text{Hf}=0$ at chondritic Lu/Hf, although nearly all basalts are produced by sufficiently high degrees of melting for neither Sm/Nd nor Lu/Hf to be fractionated by the melting process. Given that the hypothetical primitive mantle would be fertile, producing much more radiogenic heat than the depleted mantle, making it thermally buoyant, the lack of basalts from this hypothetical source is surely significant. The simple explanation is that the depleted mantle comprises the whole mantle, primitive mantle does not exist and the BSE has non-chondritic RLEs due to preferential collisional erosion during its accretion. That both Sm/Nd and Lu/Hf are superchondritic in the BSE, as advocated by [Kostitsyn \(2004\)](#), argues against the BSE $\epsilon^{142}\text{Nd}$ anomaly being due to nebular isotopic inhomogeneity. Accepting a non-chondritic BSE would vitiate geochemical arguments for a layered mantle and against whole-mantle convection. Models of the growth of the continental crust based on Sm/Nd and Lu/Hf systematics (e.g. as

reviewed by Bennett 2003) should be revisited. The formation of the Earth may be a bit more complicated than assumed by the current geochemical paradigm, but how the Earth works (e.g. patterns of mantle convection) may be simpler.

Appendix A. Estimating Mn/Na planetary ratios from basaltic data

The Mn/Na ratio of the Earth's upper mantle has been obtained independently of basalt data from actual mantle peridotites as 0.405 ± 0.044 (Palme & O'Neill 2003). This result may be used to test the accuracy with which the Mn/Na ratio of a source may be recovered from the observed concentrations of Mn and Na in basalts, which is necessary because no mantle samples are available for any of the other differentiated planetary bodies of the Solar System.

The proposed algorithm is:

$$(\text{Mn}/\text{Na})_{\text{source}} = [(\text{Fe}/\text{Mg})_{\text{source}}/(\text{Fe}/\text{Mn})_{\text{basalt}}]/[(\text{Na}/\text{Ti})_{\text{basalt}}/(\text{Mg}/\text{Ti})_{\text{source}}], \quad (\text{A } 1)$$

where, for the BSE, $(\text{Fe}/\text{Mg})_{\text{source}}$ is 0.054 from the molar Mg# of the BSE of 89.0 ± 0.3 , and $(\text{Mg}/\text{Ti})_{\text{source}}$ is 170 from the solar (CI) Mg/Ti ratio of 210 divided by the BSE $(\text{RLE}/\text{Mg})_{\text{N}}$ ratio of 1.21 (Palme & O'Neill 2003). We generally do not know the value of $(\text{RLE}/\text{Mg})_{\text{N}}$ for extraterrestrial planetary bodies because mantle samples are lacking; so when applying the algorithm to other bodies, this ratio will be assumed to be unity. Abundances of trace-element ratios from a large number of samples generally follow a lognormal distribution (Ahrens 1954), so that the optimum estimate of the ratio's value is its geometric mean (i.e. from the mean of the logarithm of the ratios), and the uncertainty attached to this value is the geometric standard deviation (from the standard deviation of the logarithm of the ratios). This has been used in calculating trace-element ratios and their standard deviations throughout this paper. Note that we report standard deviations, not standard errors of the mean.

Means and standard deviations for basalts arranged according to the type of basalt and to the tectonic setting are given in table 3. There is a discernible difference in Na/Ti and Fe/Mn between basalts produced at low and high pressures, e.g. between MORB and ocean island basalts (OIB). In the case of Na/Ti, the cause is well understood from many experimental partitioning studies: Na becomes more compatible with increasing pressure due to the increasing stability of the $\text{NaAlSi}_2\text{O}_6$ component in clinopyroxene while Ti becomes less compatible. However, the difference is not huge and tends to cancel with the increase in Fe/Mn, which is probably due to the preferential retention of Mn in the garnet in the source of OIB. Conversely, basalts produced in 'wet' environments (e.g. back-arc basin and island arc basalts) have higher than average Na/Ti and lower Fe/Mn. Extensive degrees of melting at low pressure as in ocean floor basalts recover the mantle Mn/Na to within ± 10 per cent. Because basalts from STBs will be neither of high-pressure origin nor wet (with the possible exception of Martian basalts), Mn/Na ratios should also be recovered quite accurately. As the Mn/Na ratios in STBs differ by several times at least from the solar ratio, an error as high as ± 50 per cent would not be problematic.

Table 3. Fe/Mn and Na/Ti in terrestrial basalts, and calculated Mn/Na in their sources using equation (A 1).

	Fe/Mn	s(Fe/Mn)	<i>n</i>	Na/Ti	s(Na/Ti)	<i>n</i>	Mn/Na calculated
oceanic basalts ^a	57.3	10.3	9378	2.22	0.54	17 658	0.38
<i>Basalts by tectonic setting and geography (GEOROC)</i>							
ocean floor (MORB)							
MAR 55S-52N	58.0	8.7	309	2.37	0.49	390	0.35
EPR 23S-23N	56.8	9.5	226	2.08	0.40	254	0.41
Indian Ocean	56.0	10.7	115	2.57	0.61	152	0.34
ocean floor (BAB)							
back-arc basins	54.6	8.3	417	2.80	0.67	490	0.32
oceanic flood basalt							
Ontong Java	58.1	9.3	204	2.35	0.95	204	0.35
continental flood basalt							
N. Atlantic Province	62.3	10.6	1798	1.92	0.93	1782	0.40
Deccan Traps	69.7	18.3	1131	1.58	1.02	1308	0.44
Siberian Traps	61.5	9.1	331	2.11	0.84	283	0.37
ocean island basalt							
Kilauea	66.4	6.1	480	1.07	0.14	520	0.68
St. Helena	70.5	19.5	44	1.25	0.72	44	0.55
island arc basalt							
Tonga arc	55.5	7.9	664	2.91	0.91	679	0.30
<i>basalts by type (GEOROC)</i>							
tholeiite (1)	62.4	10.6	3798	1.61	0.73	3726	0.48
tholeiite (2)	62.4	9.3	4588	1.48	0.60	4640	0.52
tholeiitic basalts	59.5	10.7	1689	2.15	1.07	1646	0.38
alkaline basalts	63.9	10.9	3507	1.57	0.58	3302	0.48
olivine basalts	61.1	14.9	1321	2.12	1.10	1312	0.37
komatiites	58.6	13.5	1412	2.79	1.97	427	0.30
calc-alkaline basalts	54.9	8.5	241	3.74	1.09	243	0.24

^aPETDB database, filtered for 'fresh'.

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