9.02 The Composition and Major Reservoirs of the Earth Around the Time of the Moon-Forming Giant Impact

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9.02.1 Introduction

A treatise on geophysics needs some summary explanation of the current thinking on how Earth achieved its current composition and formed its primary reservoirs. This subject has taken enormous strides in the past decades thanks to significant improvements in mass spectrometry in particular. However, additional discoveries are being fuelled by exciting developments in other areas and are leading to joint research at the interfaces between disciplines traditionally viewed as scientifically distinct. The most significant of these are as follows:

- *Accretion dynamics* – theoretical calculations of the behavior of gas and dust in the solar nebula; the construction of planetesimals, planetary embryos, and planets; and the fluid dynamics of primordial mixing and differentiation
- *Cosmochemistry* – the isotopic and chemical history of the solar system deduced from meteorites and lunar samples
- *Mineral physics and experimental petrology* – the simulation experimentally and theoretically of the phases present in the Earth's interior and their physical properties and behavior
- *Observations* – the observations of planets, stars, disks, and exosolar planetary systems

In this chapter, we summarize briefly these lines of evidence and present the current thinking on the formation and primordial differentiation of the Earth–Moon system. We focus on constraints from cosmochemistry and experimental petrology in particular because other chapters provide complementary information. In particular, the introductory chapter by Stevenson (Chapter 9.01) covers aspects of the accretion dynamics as does the chapter by Rubie et al. (Chapter 9.03). There are now observations of Earth-sized planets around other stars, and in the coming years, the search for Earth-*like* objects represents a major thrust in experimental astrophysics. Indeed, the links between Earth sciences and astrophysics have probably never been stronger.

9.02.2 Key Features of the Earth and Moon

Any theory for how the Earth formed and acquired its present composition and distribution of component reservoirs after the Moon-forming giant impact has to explain several things:

1. Rocky terrestrial planets grew from the same disk as the gas giants Jupiter and Saturn although plausibly at different stages in its development.
2. Terrestrial planets and differentiated asteroidal objects are depleted in moderately volatile elements relative to refractory elements.
3. The Moon is larger relative to the size of its host planet than any other moon in the solar system.
4. The Moon carries most of the angular momentum of the Earth–Moon system.
5. The oxygen, silicon, titanium, chromium, and tungsten isotopic compositions of the Earth and Moon are identical

despite their different chemical compositions and accretion histories.

6. The Earth has a larger core proportionally speaking than does the Moon, Mars, or asteroid Vesta.
7. The Earth has a more oxidized mantle than the Moon, Mars, or asteroid Vesta.
8. Highly siderophile (metal-loving) elements in the Earth's mantle are inconsistent with low-pressure core formation.
9. The Earth has significant water and a high H/N ratio.
10. The Earth, unlike the Moon, Mars, or asteroid Vesta, lacks a geologic record for the period prior to 4.0 Ga.
11. Time-integrated parent/daughter ratios determined from isotopic data provide evidence of changes in composition during the accretion history of the protoplanetary material that built the Earth and Moon.

Most of the above features are still a matter of study. To tackle these subjects, this chapter first provides a brief and elementary summary of how the Sun and solar system formed and what we know about terrestrial planet bulk compositions. We then give a synopsis of the range of dynamic and isotopic constraints on the formation of the Earth and Moon, following this with a summary of the huge field of experimental and theoretical petrology that provides insights into how Earth must have changed during its accretion history.

9.02.3   The Birth of the Solar System

The Hubble Space Telescope has provided us with fascinating images of numerous young solar mass stars forming in giant molecular clouds such as the Eagle and Orion Nebulae. It is thought likely that our Sun originated in a similar kind of environment. New evidence confirms a long-held suspicion that the Sun did not form spontaneously but that cloud collapse was triggered by a shock wave originating from a nearby star. Such shock waves might be produced, for example, from supernovas – the explosive finale to the short life of giant stars. This idea, developed by Al Cameron of Harvard (e.g., Cameron and Truran, 1977), among others, appeared to be consistent with the discovery of the daughter products of a range of short-lived nuclides in meteorites (Table 1). The half-lives of these nuclides (100 ky–100 Ma) are such that they must have been synthesized in stars shortly before the start of our solar system (Figure 1). The most important paper outlining the likely explanation for the synthesis of the various nuclides in stars is still the work of Burbidge et al. (1957). A variety of more recent papers explore the growing body of evidence from short-lived nuclides regarding the later inputs to the solar nebula (Busso et al., 2003; Huss et al., 2009; Meyer and Clayton, 2000; Meyer and Zinner, 2006; Truran and Cameron, 1978; Wasserburg et al., 1994, 1996, 1998). The early Sun may have been associated with relatively energetic irradiation (Feigelson et al., 2002a,b). It has been proposed (Shu et al., 1997) that the conveyor belt of material being swept in toward the Sun may have led to some light short-lived nuclides being generated locally and heterogeneously (Lee et al., 1998). These might then have been scattered across the disk in early-formed condensates by X-winds (Shu et al., 1997). Although local production in the early Sun is feasible for a range of nuclides

Table 1   Short-lived nuclides that have been demonstrated to have existed in the early solar system as a result of anomalies in the abundance of their daughter isotopes

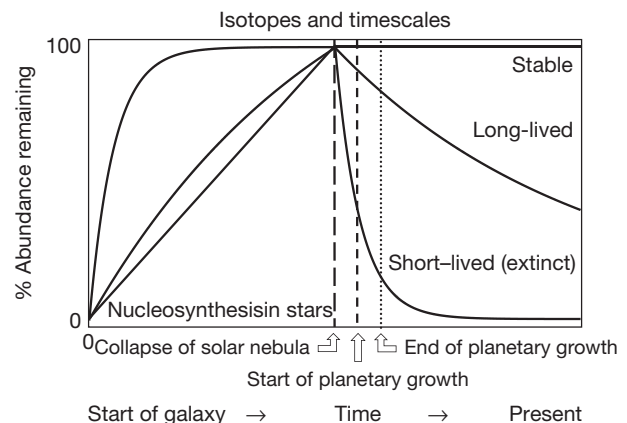| Radionuclide	Daughter	Half-life (million years)
^{10}Be	^{10}B	1.5
^{26}Al	^{26}Mg	0.71
^{36}Cl	^{36}S, ^{36}Ar	0.30
^{41}Ca	^{41}K	0.10
^{53}Mn	^{53}Cr	3.7
^{60}Fe	^{60}Ni	2.6
^{92}Nb	^{92}Zr	35
^{107}Pd	^{107}Ag	6.5
^{129}I	^{129}Xe	15.7
^{135}Cs	^{135}Ba	2.3
^{146}Sm	^{142}Nd	68
^{182}Hf	^{182}W	8.9
^{205}Pb	^{205}Tl	17
^{244}Pu	^{131,132,134,136}Xe	80
^{247}Cm	^{235}U	16

Figure 1   Most solar system nuclides heavier than hydrogen and helium were produced in stars over the history of our galaxy. This schematic figure shows the difference between nuclides that are stable, those that have very long half-lives (such as ^{238}U used for determining the ages of geologic events and the solar system itself), and those that have short half-lives of $<10^8$ years, assuming all were produced at a constant rate through the history of the galaxy. The short-lived nuclides decay very vast and provide crucial insights into the timescales of events, including planet formation, immediately following their incorporation into the solar nebula.

(Gounelle et al., 2001; Leya et al., 2003) for most, the abundances would be too low to be a match for those found in meteorites and this X wind model is not well accepted (Desch et al., 2010). Furthermore, some of these nuclides could only have been made in a large star that predated the solar system. They were then introduced to the gas and dust that ultimately became our Sun and planets. It is possible that this explosion actually triggered the collapse of the cloud material onto a core that became the solar nebula and nascent Sun.

Problems have arisen with this theory. First, a supernova is so powerful that rather than causing collapse, it may in fact

shred a molecular cloud unless located at sufficient distance that much of the energy and material have already dissipated (Foster and Boss, 1996, 1997; Stone and Norman, 1992; Vanhala and Cameron, 1998). The time taken to reach the location of the potential new star then becomes sufficiently long (hundreds of thousands of years) that it would be difficult, though not impossible, to detect the former presence of a nuclide such as ^{41}Ca with a half-life of just 100 ky, because most of it would have decayed.

The second problem is that the relative abundances of many of the short-lived nuclides are not well explained in terms of the production ratios expected in a supernova (Wasserburg et al., 1998). Therefore, attention has turned to other stellar sources, the most likely of which is an AGB (asymptotic giant branch) star. AGB stars are relatively common (<8 solar mass) stars that have been shown spectroscopically to be enriched in some heavy elements such as lead (Pb) supporting the idea that they represent the most likely 'factory' for s-process nuclides. This was confirmed by the discovery of technetium (Tc) in the spectrum of an AGB star (Merrill, 1952). With no stable nuclei, Tc can only be present if it is being synthesized. AGB stars shed material into space but are much less energetic than supernovas so could be located close to the site of the Sun's formation. The relative proportions of many of the former short-lived nuclides made better sense with an AGB star model. r-process nuclides such as ^{129}I, ^{182}Hf, and ^{244}Pu have to have been produced in a larger star but they possess relatively long half-lives (Table 1). The stars that produced them may therefore have been unrelated to the formation of the Sun. The principal problem with the AGB model is ^{60}Fe, which has a half-life of just 1.5 Ma. Although it is not an r-process nuclide, ^{60}Fe is difficult to make in large quantities in an AGB star. The AGB star model appeared to be consistent with the low initial solar system abundance of ^{60}Fe (Wasserburg et al., 1998) inferred from the first discoveries of this nuclide by Shukolyukov and Lugmair (1993). The initial abundance of ^{60}Fe is now known to have been higher than previously suspected, however (Mostefaoui et al., 2004). With this new discovery, plus the difficulty of finding a match for the initial abundance of ^{53}Mn, supernova contributions from two kinds of stars ($\leq$11 M$_\odot$ and 12–25 M$_\odot$) are recognized as potential candidates for a trigger (Huss et al., 2009).

The short-lived radionuclides discussed in the preceding text provide additional information relevant to the early solar system. First, they provide a method for determining timescales from isotopic measurements of the daughter isotopes. Second, they provide a source of heat that would have been available for melting the earliest planetesimals. Both of these are very relevant to understanding how Earth formed.

9.02.4   Meteorites

The Sun contains 99.9% of the mass of the solar system and spectroscopic measurements of its chemistry provide an indication of the composition of the circumsolar disk from which the planets grew. However, the compositions of the planets are highly variable and they have been left as a heterogeneous collection of parts of a small fractionated residue after much of the disk had dissipated or been consumed by the Sun. A better set of archives for studying the early solar system and its average composition is found in meteorites – solid extraterrestrial materials that have survived passage through the Earth's atmosphere. These have the added advantage that they can be studied in the lab at much higher precision than can the composition of the Sun. A detailed description of meteorites is beyond the scope of this chapter but two excellent reviews of the main undifferentiated and differentiated meteorite classes can be found elsewhere (Brearley and Jones, 1998; Mittlefehldt et al., 1998). In order to explain how we know certain things about the Earth's composition and origins, it is necessary to provide a brief explanation of this important archive.

The exact origins of meteorites are varied and the subject of some debate. The range and number of examples of each type has expanded significantly with the acquisition of Antarctic and Saharan meteorites. We refer to the body from which a meteorite came as its *parent body*. Meteorites are usually divided into three main types: *chondrites*, *achondrites*, and *irons*.

Chondrites are complicated mixtures of dust, glass and metal thought to represent accumulations of solar system debris that was floating in the circumstellar disk when the Sun formed. The average composition of chondrites is generally similar to that expected from unprocessed circumstellar solids, little affected by melting and loss of volatiles or metal. The most primitive are carbon-rich and are called *carbonaceous chondrites*. *Ordinary chondrites* are noncarbonaceous chondrites containing metal. *Enstatite chondrites* are a less common group of highly reduced chondrites. In some cases, a well-observed meteor trajectory has been linked to the meteorites found on the ground, and from these, it has been established that at least some ordinary chondrites come from the asteroid belt between Mars and Jupiter. Most chondrites contain calcium–aluminum *refractory inclusions* (*CAIs*) enriched in those elements expected to condense at very high temperatures from a hot nebular gas. These may have been ejected from the inner portions of the disk and are the oldest objects identified as having formed in the solar system. CAIs from the Efremovka chondrite have been dated by $^{235/238}$U–$^{207/206}$Pb at 4.5672 ± 0.0006 Ga (Amelin et al., 2002), which is close to all subsequent high-precision attempts to define the canonical start to the solar system (Figure 2). Most chondrites also contain *chondrules*, which are spheroidal objects with textures thought to reflect rapid heating, melting, and quenching of preexisting silicate material. Many of these formed as much as 2 million years after the start of the solar system (Bizzarro et al., 2004 2005; Kita et al., 2006; Russell et al., 1996).

Achondrites are silicate-rich mafic and rare ultramafic igneous rocks not too dissimilar from those formed on Earth but with different chemistry and isotopic compositions. They mainly represent basaltic rocks and cumulate from other planets and asteroids. It is possible to group these and distinguish which planet or asteroid they came from. This is done using their oxygen isotopic compositions. Oxygen is extremely heterogeneous isotopically in the solar system, and meteorites with similar chemistry and petrography seem to have specific compositions such that it is thought that they can be linked to parent bodies from different regions (Figure 3). This is one way in which *martian* meteorites are grouped although the more specific link to Mars is established through the dominance of young meteorite ages requiring a geologically active body and the similarity in volatile compositions to the martian
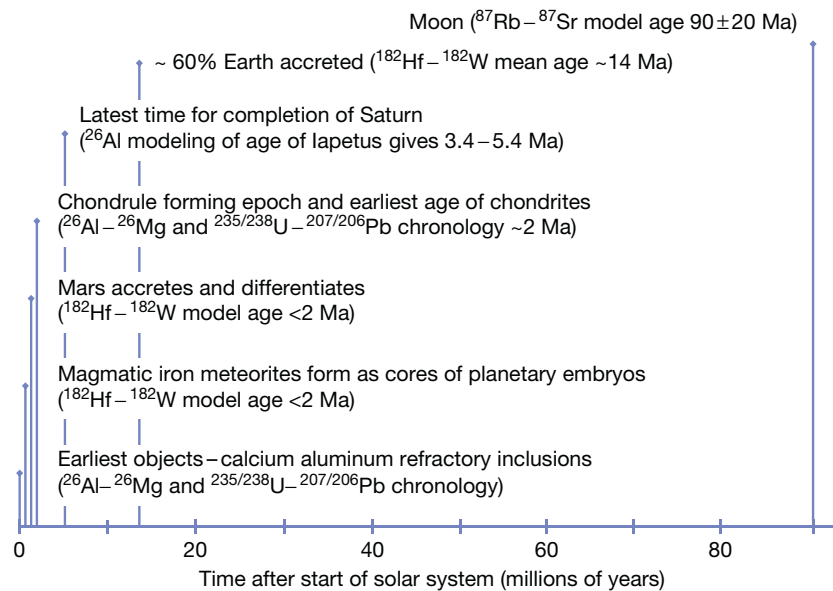
Moon ($^{87}Rb - {}^{87}Sr$ model age 90 ± 20 Ma)

~ 60% Earth accreted ($^{182}Hf - {}^{182}W$ mean age ~14 Ma)

Latest time for completion of Saturn
(^{26}Al modeling of age of Iapetus gives $3.4 - 5.4$ Ma)

Chondrule forming epoch and earliest age of chondrites
($^{26}Al - {}^{26}Mg$ and $^{235/238}U - {}^{207/206}Pb$ chronology ~2 Ma)

Mars accretes and differentiates
($^{182}Hf - {}^{182}W$ model age <2 Ma)

Magmatic iron meteorites form as cores of planetary embryos
($^{182}Hf - {}^{182}W$ model age <2 Ma)

Earliest objects – calcium aluminum refractory inclusions
($^{26}Al - {}^{26}Mg$ and $^{235/238}U - {}^{207/206}Pb$ chronology)

| 0 | 20 | 40 | 60 | 80 |

Time after start of solar system (millions of years)

Figure 2   The current best estimates for the timescales over which very early inner solar system objects and the terrestrial planets formed. The approximated mean life of accretion is the time taken to achieve 63% growth at exponentially decreasing rates of growth. Reproduced from Halliday AN and Kleine T (2006) Meteorites and the timing, mechanisms and conditions of terrestrial planet accretion and early differentiation. In: Lauretta D, Leshin L, and MacSween H (eds.) *Meteorites and the Early Solar System II*, pp. 775–801. Tucson, AZ: University of Arizona Press.

atmosphere, as sampled by Viking. The *eucrites*, *howardites*, and *diogenites* are all thought to come from the asteroid 4 Vesta. Other important groups are the *angrites*, which are extremely depleted in volatile elements (**Figure 4**), and the *ureilites*, which appear to have been produced by melting of a carbonaceous chondrite-like object that has not undergone core formation. Achondrites and lunar samples are immensely important for providing evidence for how differentiated planets other than Earth formed. An important feature of all of these samples of differentiated planetary bodies is that they indicate more extreme volatile depletion than is found in chondrites. The same is true of the Earth and Moon.

Irons are exactly what you would expect – metallic iron (Fe) with large amounts of nickel (Ni) and some blebs of iron sulfide. Most represent the remains of the metallic cores of early-formed small asteroidal bodies. Based on their cooling rates determined from Fe–Ni exsolution features, some ('nonmagmatic') types are thought to have formed at shallow depths from impact melting of asteroidal surfaces (Wasson, 1985). Magmatic group irons typically are more volatile-depleted and appear to be derived from the cores of objects of up to hundreds of kilometers in size. They provide evidence on the very earliest stages of core formation in the solar system.

The exposure age of a meteorite to cosmic rays can be determined from the nature of the cosmogenic nuclides it contains. Iron meteorites can have very long exposure ages – up to hundreds of millions of years – attesting to a long history of survival in space. Stony meteorites have much shorter exposure ages. They do not survive well, which explains why we have no examples of silicate mantle material that must have been complementary to the magmatic irons. All of the stony meteorites appear to have been knocked off their parent bodies from shallow depths in the relatively recent past. We do

however have some meteorites that contain metal mixed in with silicate that may have formed at some kind of core–mantle boundary in a small object. These are called *pallasites*. *Mesosiderites* are also metal–silicate mixtures but are thought to be the products of impact melting.

9.02.5   Meteorites and the Composition of the Earth and Its Primary Reservoirs

The Earth is depleted in those components that are expected to have partially resided in the gas phase of the solar nebula at low temperatures, such as H, N, O, and all of the noble gases. Although this is obvious, the magnitude of the depletion is in part gauged from comparing the Sun's composition with those of meteorites. The most primitive kind of chondrite is called a CI carbonaceous chondrite. If one compares compositional data for the Sun with those for CI carbonaceous chondrites, the agreement is very good for all but the most volatile elements. Thus, these primitive meteorites provide examples of the materials that went to produce the volatile-depleted terrestrial planets.

The estimated abundances of the elements in the solar system, dominated by the Sun (**Figure 5**), range through 13 orders of magnitude and are most easily compared by plotting on a log scale such that the number of atoms of Si is 10^6. Hydrogen and helium dominate over all other elements, reflecting production in the big bang and in first-generation stars. Other features reflect the processes of nucleosynthesis in stars, as first explained by Burbidge et al. (1957). The essential features are as follows.

First, the abundances of the elements decrease with increasing atomic number. This is because most of the elements are made from lighter elements. There is an anomalous peak in
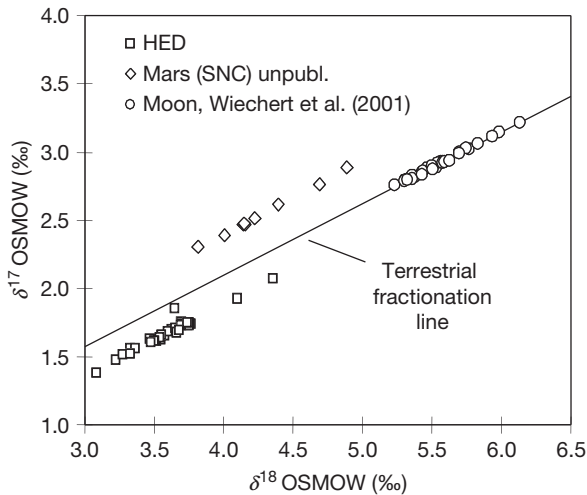
Figure 3 The oxygen isotopic composition of the components in chondrites, in particular CAIs, is highly heterogeneous for reasons that are unclear. The net result of this variability is that different planets possess distinct oxygen isotopic compositions that define an individual mass fractionation line as shown here for eucrites, howardites, and diogenites, which come from Vesta and martian (SNC) meteorites, thought to come from Mars. The Moon is thought to have formed from the debris produced in a giant impact between the proto-Earth when 90% formed and an impacting Mars-sized planet sometimes named 'Theia.' The fact that the data for lunar samples are collinear with the terrestrial fractionation line could mean that the Moon formed from the Earth, or the planet from which it was created was formed at the same heliocentric distance, or it could mean that the silicate reservoirs of the two planets homogenized during the impact process, for example, by mixing in a vapor cloud from which lunar material condensed. Reproduced from Halliday AN (2003) The origin and earliest history of the Earth. In: Davis AM (ed.) *Meteorites, Comets and Planets*, Holland HD and Turekian KK (eds.) *Treatise of Geochemistry*, vol. 1, pp. 509–557. Oxford: Elsevier-Pergamon.

abundance at Fe, which is about 1000 times more abundant than its neighbors, reflecting the maximum binding energy per nucleon at ^{56}Fe. There is a big dip in the abundance of Li, Be, and B because these elements are not stable in stellar interiors. There is also a saw-toothed variability that is superimposed on the overall curve, reflecting the relatively high stability of even numbered nuclides compared with odd numbered nuclides. Finally, all of the elements in the periodic table are present in the solar system except those with no long-lived or stable nuclides. Tc, promethium (Pm), and the transuranic elements fall into this category.

The four most abundant elements in the terrestrial planets are O, Mg, Si, and Fe. Broadly speaking, the density of the Earth and the size of its core provide a first-order indication that the ratio of Fe to Mg is at least similar to the values found in chondrites. In fact, it is slightly higher, as discussed later in the text, but to a first approximation, the Earth has chondritic proportions of elements that are refractory or only slightly volatile. Since carbonaceous chondrites appear to represent undifferentiated proto-planetary material, it seems likely that the bulk Earth contains the same relative proportions of all refractory elements as carbonaceous chondrites. This is the basis of the *chondritic reference model*. In detail, there are significant differences relative to chondrites, particularly with respect to the volatile elements.
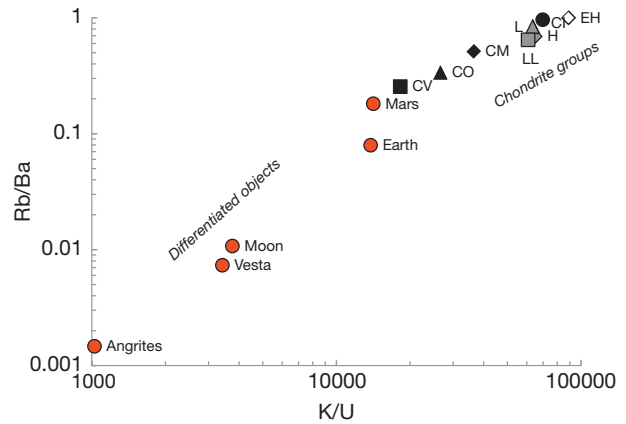

Figure 4 Comparison between the K/U and Rb/Bar ratios of the Earth and other differentiated objects compared with chondrites. The alkali elements K and Rb are both relatively volatile compared with U and Ba that are refractory. Therefore, these trace element ratios provide an indication of the degree of volatile element depletion in inner solar system-differentiated planets relative to chondrites, which are relatively primitive. It can be seen that the differentiated objects are more depleted in moderately volatile elements than are chondrites. Reproduced from Halliday AN (2014) The origin and earliest history of the Earth. In: Holland HD and Turekian KK (eds.) *Treatise on Geochemistry*, 2nd edn., vol. 2, pp. 149–211. Oxford: Elsevier.
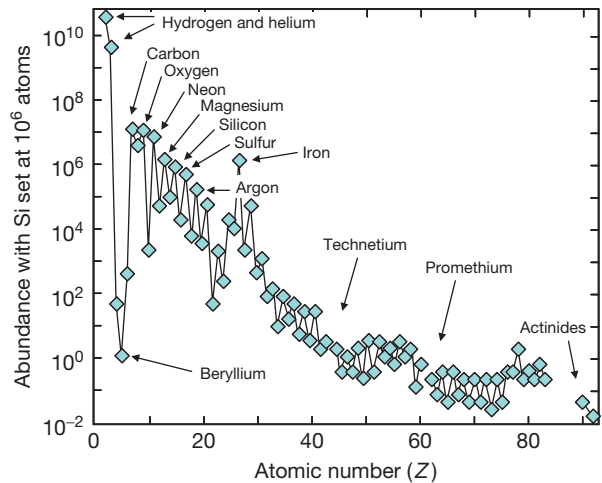

Figure 5 The abundances of elements in our Sun and the solar system are estimated from the spectroscopic determination of the composition of the Sun and the laboratory analysis of primitive meteorites called carbonaceous chondrites – thought to represent unprocessed dust and other solid debris from the circumsolar disk. To compare the abundances of different elements, it is customary to scale the elements relative to one million atoms of silicon. The pattern provides powerful clues to how the various elements were created. See text for details. Based on a figure in Broecker WS (1998) *How to Build a Habitable Planet*. Columbia University, New York: Eldigio Press with kind permission.

Furthermore, core formation has redistributed the Earth's elements internally. During and after growth of the Earth, *siderophile* (literally 'metal-loving') elements were partitioned into the metallic core, leaving *lithophile* (literally 'rock-loving') elements behind in the silicate mantle.

The composition of the *bulk silicate Earth* (BSE), otherwise known as the *primitive mantle* (PM), can be deduced in more detail by determining the compositions of a wide range of basalts and/or peridotite xenoliths and using these to identify specific features that are systematic. Determining BSE in this way requires that one makes an assumption of a homogeneous mantle. This assumption is still hotly debated by some, and for more detail, one can refer to companion volumes 2 (Mineral Physics) and 7 (Mantle Dynamics). However, two key observations lend confidence that the chemistry of the mantle is broadly speaking homogeneous, in striking contrast to Mars, for example (Lee and Halliday, 1997). First, no isotopic heterogeneity older than about 2 billion years has survived in the oceanic mantle, pointing to widespread efficient mixing processes over geologic time. Second, the ratios of the refractory lithophile elements Nb/U are relatively uniform but nonchondritic and fractionated by crust production (Hofmann et al., 1986). There is no reason why this ongoing fractionating process should have left the mantle so homogeneous unless the mantle is also relatively well mixed.

Assuming these features are representative of the total mantle, one can combine estimates of mantle composition with those of the average composition of the continental crust to define the composition of the PM (=BSE). For example, mantle peridotites are fractionated residues of partial melting but ratios of moderately or highly compatible elements such as Mg/Fe or concentrations such as of Ni or Mg can be compared to a wide range of samples and a representative estimate made for the composition of the BSE.

A different approach is adopted for the highly incompatible elements, which are lost from peridotite during partial melting. Basaltic magmas are the products of partial melting of broad regions of the peridotitic mantle. They fractionate compatible elements one from another but have lesser effects on highly incompatible elements such as the large ion lithophile elements. The latter are essentially completely extracted into the basaltic melt, yielding constant ratios one to another unless the degree of melting is very small. Element ratios that are not significantly fractionated by partial melting, as evidenced by little or no variation in ratio with change in concentration, are particularly useful for determining the BSE depletion in moderately volatile elements. The volatile element depletion can be determined from their ratio relative to a refractory element of similar incompatibility if both elements are lithophile and hence not partitioned into the core. Relevant examples include Rb/Ba (Hofmann and White, 1983), K/U (Jochum et al., 1983), and In/Y (Yi et al., 1995, 2000). A similar approach can be adopted for siderophile elements. Refractory siderophile/refractory lithophile element ratios for pairs of elements of similar incompatibility provide a clear indication of depletion caused by core formation, for example, Mo/Pr and W/Ba (Newsom et al., 1986). Finally, one can in the same way deduce the PM concentrations of some elements that are depleted because of both core formation and volatile loss, for example, [204]Pb/Ce (Hofmann et al., 1986), Sn/Sm (Jochum et al., 1993; Yi et al., 2000), and Cd/Dy (Yi et al., 2000). As with peridotite data, the budgets for the continental crust need to be added back in with those determined for the composition of the (depleted) mantle, to derive a value for the PM (which is the same as the BSE).

The conclusion reached from determining relative proportions of less incompatible lithophile elements in peridotites such as heavy rare earth elements (REEs), Ca, Sc, and Ti (e.g., Lee et al., 1996) is that, although the bulk Earth does not have an exactly CI composition (Drake and Righter, 2002), refractory lithophile elements are present in approximately the same relative proportions in the BSE as in the carbonaceous chondrites (Allègre, et al., 1995b; McDonough, 2003; McDonough and Sun, 1995). This view has been challenged because of the Earth's nonchondritic Fe/Mg and apparent Nd isotopic composition (discussed later in the text).

The moderately volatile elements such as potassium (K) are those predicted to have condensed 50% of their mass from a gas of solar composition at temperatures of 700–1100 K (Lodders, 2003). They are depleted in most chondrite groups when compared to solar or CI compositions (Figures 4 and 6). There has been much discussion in the literature of the cause of this, usually related to imperfect mixing of CAI, chondrule, and matrix fractions (e.g., Zanda et al., 2006). Moderately volatile elements are strongly depleted in the Earth and other differentiated objects, more so even than in chondrites (Figures 4 and 6). By plotting volatile siderophile/refractory lithophile element ratios (e.g., S/Sr) in the BSE and chondrites versus ratios of lithophile moderately volatile to refractory lithophile elements (e.g., Rb/Sr), one can estimate the likely partitioning of volatile elements into the core (Halliday and Porcelli, 2001) (Figure 6).

The very refractory lithophile elements are enriched relative to chondrites by a factor of ~3 (McDonough and Sun, 1995), more than can be explained by the separation of the core. A plot of concentrations of elements in the BSE divided by those in CI chondrites, normalized to $[Mg]_{Earth}/[Mg]_{CI} = 1.0$ in order to correct for the highly volatile contents of CI chondrites, is shown in Figure 7. These elemental ratios are plotted as a function of the temperature by which 50% of the element of interest would have condensed during the cooling of a gas of solar system composition (Lodders, 2003). Note that condensation may not be the mechanism of volatile loss.

If one compares the BSE composition, determined as described earlier in the text, with that of the Sun or CI chondrites (Figures 4 and 6–8), several features stand out:

1. There is an overall trend of decreasing chondrite-normalized abundance of lithophile elements as a function of decreasing half-mass condensation temperature (Figure 7). Losses of volatiles were important.
2. Some elements, for example, the halogens, are depleted (Figure 7) for reasons that are less clear. Even the alkalies do not display a clear relationship between depletion and volatility. Therefore, volatile losses may have involved additional controls beyond nebular condensation temperature.
3. The siderophile elements are depleted, even if they are refractory, presumably because they are partitioned into the Earth's core. The most depleted, hence presumably the most siderophile, are the platinum group elements (PGEs), rhenium (Re), sulfur (S), selenium (Se), and tellurium (Te) (Figure 7). They are present in roughly chondritic-relative proportions, a striking feature that relates to the history of accretion and core formation, discussed later in the text.
4. The Si/Mg ratio of the BSE is lower than is found in chondrites (Figure 8). A variety of reasons have been proposed
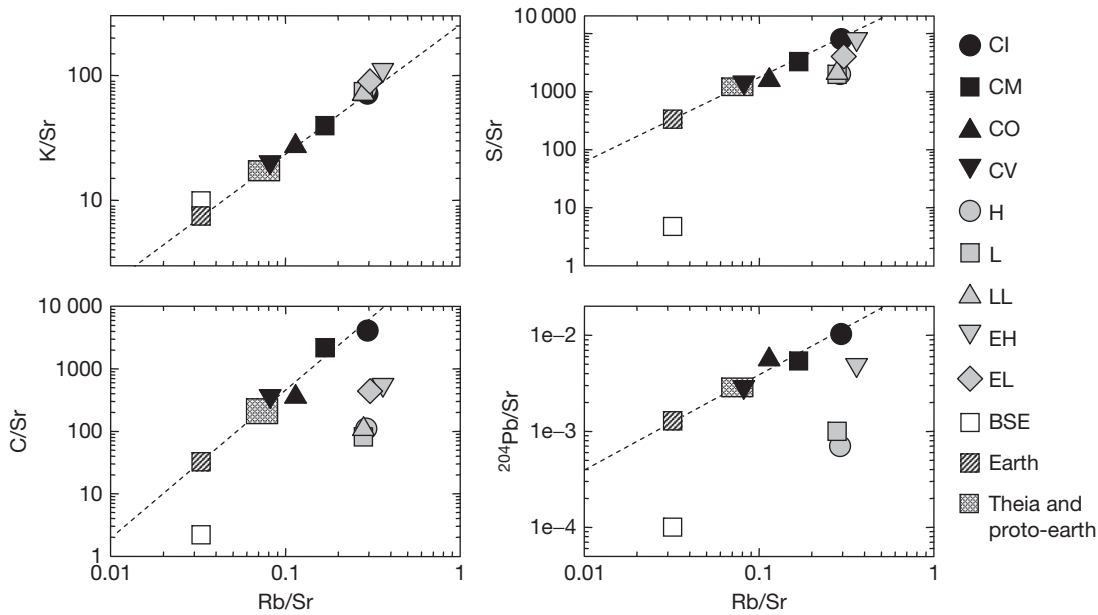
Figure 6 Volatile/refractory element ratio–ratio plots for chondrites and the silicate Earth. The correlations for carbonaceous chondrites can be used to define the composition of the Earth, the Rb/Sr ratio of which is well known because the Sr isotopic composition of the bulk silicate Earth (BSE) represents the time-integrated Rb/Sr. Data from Newsom HE (1995) Composition of the solar system, planets, meteorites, and major terrestrial reservoirs. In: *Global Earth Physics: A Handbook of Physical Constants*. Washington, DC: American Geophysical Union, AGU Reference Shelf, No. 1.
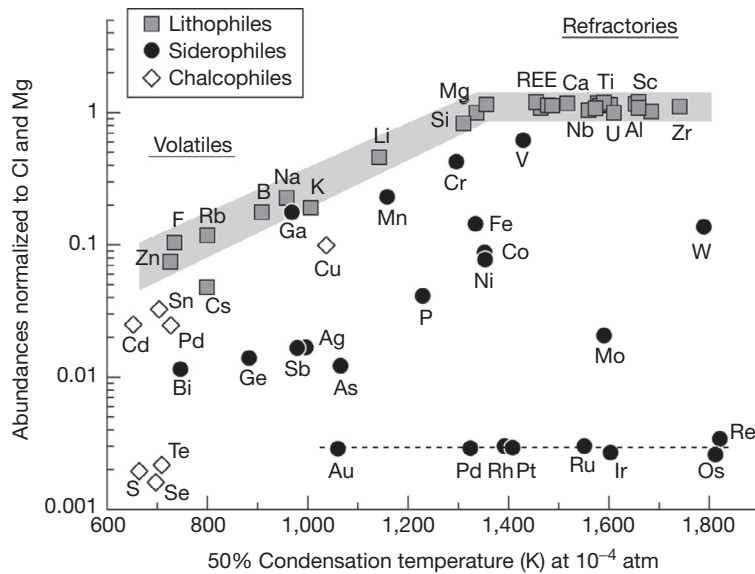

Figure 7 Elemental abundances in the silicate Earth (McDonough and Sun, 1995) ratioed to those in CI carbonaceous chondrites and normalized to $[Mg]_{Earth}/[Mg]_{CI} = 1.0$ are plotted on the ordinate. The abundances are plotted against the temperature by which 50% of the element of interest would have condensed from a gas of solar composition at a total pressure of 10^{-4} bar (Lodders, 2003). The silicate Earth is depleted in volatile elements (which condense at low temperatures) due to a combination of incomplete accretion and late volatile loss. Depletions of the silicate Earth in siderophile and some chalcophile elements are due to sequestration in the core.

to account for this, including partitioning of Si into the core (Gessmann et al., 2001; Takafuji et al., 2005; Wade and Wood, 2005), losses of Si to space (Ringwood, 1989a,b), and the idea that the Earth did not actually accrete from material that was the same as chondrites (Drake and Righter, 2002; Hewins and Herzberg, 1996).

5. The Mg/Fe ratio of the total Earth also appears to be slightly lower than is found in chondrites (Palme, 2000). The reason for this is also unclear. It could simply be that the Earth formed from nonchondritic material but it is also possible that this reflects some level of erosion of the outer part of the Earth during accretion (O'Neill and Palme, 2008), as
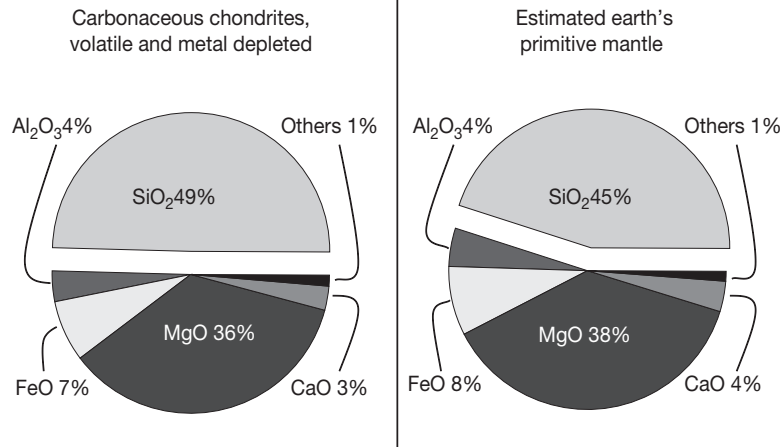
Carbonaceous chondrites,
volatile and metal depleted

Estimated earth's
primitive mantle

Figure 8 Pie chart showing the composition of the BSE compared with CI chondrites after correction for differences in volatiles and subtraction of a 'core' component. Note the depletion in Si that may be caused by partitioning into the core or a nonchondritic Earth.

has been proposed for Mercury, with its high density, hence proportionally bigger core (Benz et al., 1987).

The reasons for these patterns in composition of the Earth remain the focus of considerable debate. They provide evidence that the growth of the Earth was far from simple and may have changed with time, a view reinforced by isotopic data. However, a part of the composition probably relates to the Earth's location within the circumstellar disk from which the raw materials were obtained. This is therefore discussed first before moving on to other aspects related to the development of the Earth itself.

9.02.6 The Circumstellar Disk and the Composition of the Earth

About 200 years ago, Kant and Laplace considered that the most likely explanation for the formation of the solar system was planetary accretion from a swirling disk resulting from the angular momentum of the cloud of gas and dust that collapsed to form the Sun. A number of the previously mentioned compositional features of the Earth are thought to relate to early processes associated with such a circumstellar disk.

The general explanation for the depletion of the Earth in highly volatile elements such as H and He is that most of the growth of terrestrial planets, unlike the gas giants, post-dated the loss of nebular gases from the disk. However, this is far from certain. For example, a recent model for the origin of the Earth's water is that it was formed from nebular hydrogen trapped by the Earth as it grew (Ikoma and Genda, 2006). It is not possible to trap significant gas in this way until the Earth reaches >30% of its current mass, which given the short timescales for nebula dispersal is hard to reconcile with protracted accretion (see later text). Ikoma and Genda pointed out that the nebula can be much less dense than the nominal value, that is, captured gas is only logarithmically sensitive to nebula density, although the laws governing nebula dispersal and declining gas density are not well established.
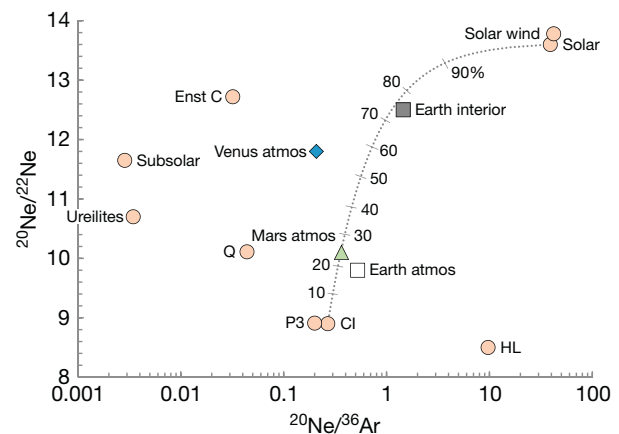

Figure 9 Neon isotopic compositions for the atmospheres of terrestrial planets are no different from the range of isotopic compositions in the solar system. There is no need to advocate fractionation caused by atmospheric loss. Indeed, the neon isotopic compositions of the terrestrial planets correlate negatively in a non-mass-dependent fashion with $^{20}Ne/^{36}Ar$. The variation is better explained in terms of admixing differing amounts of solar composition material with noble gases derived from CI chondrite-like material. On this basis, the mantle has a proportion of solar Ne of 75%, whereas in the atmosphere, this proportion is 20%. Reproduced from Halliday AN (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105: 146–171.

In support of the Ikoma and Genda model, there is clear isotopic evidence that some solar noble gases were trapped in the Earth (Porcelli et al., 2001) and Mars (Marty and Marti, 2002), possibly as a vestige of the nebula still present at the time of the Earth's accretion (Hayashi et al., 1979). Whether some is stored in the core is unclear (Porcelli and Halliday, 2001). The amount of solar Ne in the mantle appears to be ~75% (**Figure 9**) but is small compared with the far larger (×100) reservoir of atmospheric Ne, more than 80% of which is chondritic (Halliday, 2013). The relative size of the
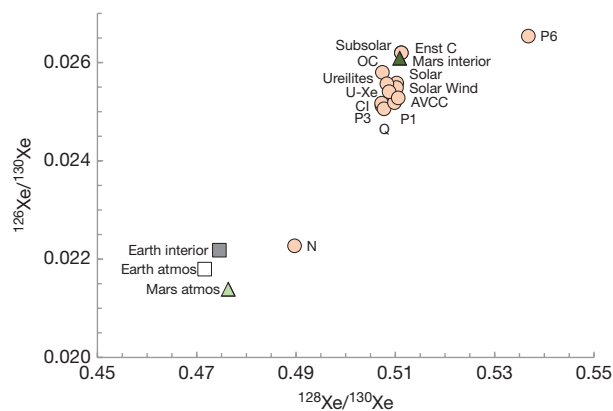
Figure 10 Xenon is isotopically fractionated in the Earth's atmosphere and mantle relative to the estimated composition of the material from which it formed. A similar heavy isotopic composition is found in the martian atmosphere. Reproduced from Halliday AN (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105: 146–171.

atmosphere versus interior budgets of noble gases is deduced from the decay of ^{40}K–^{40}Ar combined with the mantle $^{40}Ar/^{36}Ar$ and assuming that the mantle as sampled by ocean ridge basalts, ocean island basalts, and well gases is representative (Halliday, 2013). On this basis, <3% of the Earth's ^{36}Ar resides in the mantle. There is Xe isotopic evidence discussed later in the text that the majority (>99%) of the Earth's noble gases were lost at a late stage (Porcelli and Pepin, 2000) (**Figure 10**) possibly during the Moon-forming giant impact. This is consistent with the difference in noble gas budgets between the Earth and Venus (Halliday, 2013). However, the isotopic composition of the nonfissionogenic and nonradiogenic Xe in the Earth looks like neither fractionated Solar nor fractionated chondritic-relative abundances. Its origin is an enigma (Pepin, 2000). The dynamics and timescales for accretion are dependent on the presence or absence of nebular gas as discussed in the succeeding text.

As already pointed out, the moderately volatile elements are also depleted in the Earth (**Figures 4, 6**, and **7**) (Cassen, 1996; Gast, 1960; Wasserburg et al., 1964). The traditional explanation for this is that the inner 'terrestrial' planets accreted where it was hotter, within the so-called ice line (Cassen, 1996; Humayun and Cassen, 2000). It long was assumed for several reasons that the solar nebula in the terrestrial planet-forming region started as a very hot, well-mixed gas from which all of the solid and liquid Earth materials condensed. The geochemistry literature contains many references to this hot nebula and to major T-Tauri heating events that may have further depleted the inner solar system in moderately volatile elements (e.g., Lugmair and Galer, 1992). Some nebula models predict early temperatures that were sufficiently high to prevent condensation of moderately volatile elements (Humayun and Cassen, 2000) that somehow were lost subsequently.

Understanding how the volatile depletion of the inner solar system occurred can be greatly aided by comparisons with modern circumstellar disks. These were first detected using ground-based interferometry. Circumstellar protoplanetary disks (termed *proplyds*) now are plainly visible around young

stars in the Orion Nebula thanks to the Hubble Space Telescope (McCaughrean and O'Dell, 1996). With such refined observations combined with theoretical considerations, it is possible to trace the likely early stages of development of our own solar system (Ciesla and Charnley, 2006).

A solar T-Tauri stage during the development of the circumstellar disk could have had a profound effect on volatile depletions. T-Tauri stars are premain sequence stars. They are a few times 10^5 years to a few times 10^6 years in age and have many of the characteristics of our Sun but are much brighter. Many have disks. It has long been argued that the T-Tauri effect causes an early phase of heating of the inner portions of the disk. The T-Tauri stage may last a few million years and is often linked to the Earth's depletion in moderately volatile elements. Because it heats the disk surface however, it is unsure whether it would have a great effect on the composition of the gas and dust in the accretionary midplane of the disk where planetesimal accretion is dominant. Heating of inner solar system material in the midplane of the disk will, however, occur from compressional effects. The thermal response can be calculated for material in the disk being swept into an increasingly dense region during migration toward the Sun during the early stages of disk development. Boss (1990) included compressional heating and grain opacity in his modeling and showed that temperatures in excess of 1500 K could be expected in the terrestrial planet-forming region. The main heating takes place at the midplane, because that is where most of the mass is concentrated. The surface of the disk is much cooler. This process would certainly be very early but how it would have evolved with time and tie into the timescales for disk heating deduced from cosmochemistry is unclear.

Chondrules and CAIs provide us with the most important information about the processes of heating and melting in the disk that occurred within the first few million years of the solar system. The exact nature of these events has been hard to establish but chondrules are most likely produced by flash melting of the dusty disk (Kita et al., 2006). What role they played in the formation of planetesimals has been unclear, but some models predict that they might have accumulated preferentially in certain stagnant regions of the disk, facilitating planet formation (Cuzzi et al., 2001). Hewins and Herzberg (1996) had proposed that this is reflected in the Earth's nonchondritic Si/Mg (**Figure 8**).

9.02.7   Dynamics of Planet Formation

In broad terms, the rates of accretion of planets from disks are affected by the amounts of mass in the disks themselves. If there is considerable nebular gas present at the time of accretion, the rates are faster (e.g., Hayashi et al., 1985). If gas is present, then it is important to know what Jupiter is doing at the time of terrestrial planet accretion. At present, this is underconstrained and model-dependent. The absence of nebular gas is also calculated to lead to eccentric orbits (Agnor and Ward, 2002). Recently, however, it has been shown that accretion in the presence of swarms of planetesimals also decreases eccentricity (O'Brien et al., 2006).

The most widely accepted model of terrestrial planet formation is the planetesimal theory (Chambers, 2004). In the simplest terms, accretion of terrestrial planets is envisaged as taking place in four stages:

1. Settling of circumstellar dust to the midplane of the disk
2. Growth of planetesimals up to ~1 km in size
3. Runaway growth of planetary embryos up to ~10^3 km in size
4. Stochastic growth of larger objects through late-stage collisions

Stage 1 takes place over timescales of thousands of years if there is no turbulence but much longer otherwise. It provides a relatively dense plane of material from which the planets grow. The second stage is poorly understood but is necessary in order to build objects that are of sufficient mass for gravity to play a major role. Planetesimals would need to be about a kilometer in size in order for the gravitationally driven stage 3 to start. Although we do not know how stage 2 happens, somehow, it must be possible. Fluffy aggregates of dust have been made in the lab but these are typically less than a centimeter in size (Blum, 2000). Larger objects are more problematic. One obvious suggestion is that some kind of glue was involved. Volatiles would not have condensed in the inner solar system, however. Not only were the pressures too low, but also the temperatures were probably high because of heating as material was swept into the Sun (Boss, 1990). Organic material or molten droplets such as chondrules (Wiechert and Halliday, 2007) may have played an important role in cementing material together. An alternative to glues that has long been considered (Ward, 2000) is that within a disk of dust and gas, there are local separation and clumping of material as it is being swept around. This leads to gravitational instabilities whereby an entire section of the disk has relatively high gravity and accumulates into a zone of concentrated mass (Goldreich and Ward, 1973; Weidenschilling, 2006). This is a similar to some models envisaged by some for Jupiter formation (Boss, 1997).

Once stage 2 has occurred, runaway growth builds the 1 km-sized objects into 1000 km-sized objects. This mechanism exploits the facts that (1) larger objects exert stronger gravitational forces, (2) the velocity dispersion is small so the cross section for collision can be much larger than the physical cross section for the largest bodies in the swarm, (3) collisions resulting in growth are favored if the material is not on an inclined orbit, and (4) larger objects tend not to take inclined orbits. The net result is that the bigger the object, the larger it becomes until all of the material available within a given feeding zone or heliocentric distance is incorporated into planetary embryos. This is thought to take place within a few hundred thousand years (Chambers, 2004; Kortenkamp and Wetherill, 2000; Kortenkamp et al., 2000; Lissauer, 1987, 1993). The ultimate size depends on the amount of material available. Using models for the density of the solar nebula, it is possible that a body of the size of Mars (~$0.1M_E$) could originate in this fashion at its current heliocentric distance. However, in the vicinity of the Earth, the maximum size of object would be Moon-sized (~$0.01M_E$) or possibly even smaller.

Building objects that are as large as the Earth is thought to require a more protracted history of collisions between the 1000 km-sized planetary embryos (Wetherill, 1986). This is a

stochastic process that is hard to predict in a precise manner. The Russian theoretician Safronov (1954) proposed that, in the absence of a nebula, the growth of the terrestrial planets would be dominated by such a history of planetary collisions. Wetherill (1980, 1986) took this model and ran Monte Carlo simulations of terrestrial planetary growth. He showed that indeed, some runs generated planets of the right size and distribution to be matches for Mercury, Venus, the Earth, and Mars. He monitored the timescales involved in these 'successful' runs and found that most of the mass was accreted in the first 10 Ma but that significant accretion continued for much longer. Wetherill also tracked the provenance of material that built the terrestrial planets and showed that, in contrast to runaway growth, the feeding zone concept was flawed. The planetesimals and planetary embryos that built the Earth came from distances that extended over more than 2 AU. More recent calculations of solar system formation have yielded similar results (Canup and Agnor, 2000).

The latest 'Grand Tack' models for the solar system's accretion propose that *all* of the terrestrial planets and asteroids forming inboard of 1 AU in a relatively confined zone (Hansen, 2009). This helps to explain the small size of Mars. The new standard model of the inner solar system is that planetary embryos such as iron meteorite parent bodies accreted close into the Sun but then migrated outward subsequently (Bottke et al. (2006). The 1 AU edge of terrestrial planet accretion was set by an inward-migrating Jupiter that cleared or accreted everything in its path. However, Jupiter was then slowed and subsequently pulled back by the growth of Saturn. The terrestrial planets and asteroid belt spread out across the inner disk as these two giant planets migrated back outward (Hansen, 2009; Walsh et al., 2011).

Planetary collisions of the type that grew the terrestrial planets would have been catastrophic. The energy released would have been sufficient to raise the temperature of the Earth by thousands of degrees. The most widely held theory for the formation of the Moon is that there was such a catastrophic collision between a Mars-sized planet and the proto-Earth when it was approximately 90% of its current mass. The putative impactor planet sometimes named 'Theia' (the mother of 'Selene' who was the goddess of the Moon) struck the proto-Earth with a glancing blow generating the angular momentum of the Earth–Moon system.

These dynamic models can be tested with geochemistry and petrology, which provide 6 principal kinds of information relevant to the earliest history of the Earth:

1. Isotopic heterogeneity in the solar system can be used to trace the sources of the components that built the Earth and Moon.
2. Timescales for accretion, volatile loss, and core formation can be determined from short- and long-lived decay systems (Figure 1).
3. Conditions of core formation can be determined from metal–silicate partitioning behavior of indicative 'siderophile' elements.
4. Time-integrated parent/daughter ratios can be determined from isotopic compositions of the daughter elements yielding insights into the (paleo)chemistry of precursor materials.

5. Mass-dependent stable isotopic fractionations provide constraints on the prevalent processes and conditions.
6. Geochemistry and petrology provide our principal constraints on the state of the Earth at the end of accretion.

These represent a huge area of science and a continually evolving landscape as new and improved techniques are brought to bear on meteorites and lunar samples. The key aspects as they relate to the early Earth are as follows.

9.02.8 The Age of the Earth

Earth's antiquity is a problem that in many respects was solved when Clair Patterson published the results of Pb isotopic analyses of meteorites that lay on an isochron passing near the composition of the silicate Earth (Figure 11) and indicating an age of 4.5–4.6 Ga (Patterson, 1956). Following this work, many refinements to the Earth's age were suggested based on better estimates of the average Pb isotopic composition of the BSE (Galer and Goldstein, 1996) but the essential result remains unchanged. These further studies highlight the fact that there are a variety of inherent complications to take into account in determining an isotopic age or rate. These are very relevant to the issue of how well we know the exact timescales for the Earth's formation (Halliday, 2014).

In most isotopic dating, one has to make allowance for the initial daughter isotope that was present in the mineral, rock, or reservoir when it formed. This can be corrected for adequately or ignored in certain minerals with very high parent element/daughter element ratios. For example, the most accurate ages of ancient rocks in the continental crust are obtained by U–Pb dating of the common zirconium silicate mineral zircon. This mineral has high U/Pb ratio when it forms and is resistant to the effects of natural resetting via diffusion. Lead does not fit readily into the lattice when zircon grows so any initial Pb is minor and corrections can be made with sufficient confidence that the ages are extremely accurate. The oldest portion of a terrestrial zircon grain thus far found yields an age of 4.40 Ga (Wilde et al., 2001).

There are no rocks surviving from the first 500 Ma of the Earth's history and no zircons from the first 100 Ma. The age of the Earth and the solar system is determined using a different approach. Most minerals and rocks carry a significant proportion of initial Pb relative to that formed by radioactive decay. It is necessary to monitor the initial abundance of the daughter isotope precisely by measuring the parent and daughter isotopes relative to a nonradiogenic isotope of the same daughter element. This is commonly done using isochrons that allow one to determine an age without knowing the initial composition a priori. There are two isotopes of U that decay to two isotopes of Pb. By comparing the Pb isotopic ratios in reservoirs that all formed at the same time, it is even unnecessary to know the parent/daughter ratios, since the ratio $^{238}U/^{235}U$ is constant in nature (137.88). It was using these techniques that Clair Patterson determined that the age of iron and silicate meteorites, and the Earth, was between 4.5 and 4.6 billion years. This defines the time at which the major variations in U/Pb between U-depleted iron meteorites and (variably) Pb-depleted silicate reservoirs, such as the Earth's PM, were established by volatile loss and core formation (Figure 12).

Although Pb–Pb dating was at one time used for dating a wide variety of terrestrial samples, this method is all but obsolete except for studying extraterrestrial samples. Most chondrites contain CAIs, which, as previously explained, are enriched in elements expected to condense at very high temperatures from a hot nebular gas, such as U. These are the oldest objects yet identified that formed in the solar system. CAIs from the Efremovka chondrite have been dated by $^{235/238}U–^{207/206}Pb$ at 4.5672 ± 0.0006 Ga (Amelin et al., 2002), and although minor revisions have been proposed, this is still the best estimate of the age of the solar system (Figure 2) that defines a more precise slope to the meteorite isochron (called the 'Geochron') first established by Patterson (Figure 11).
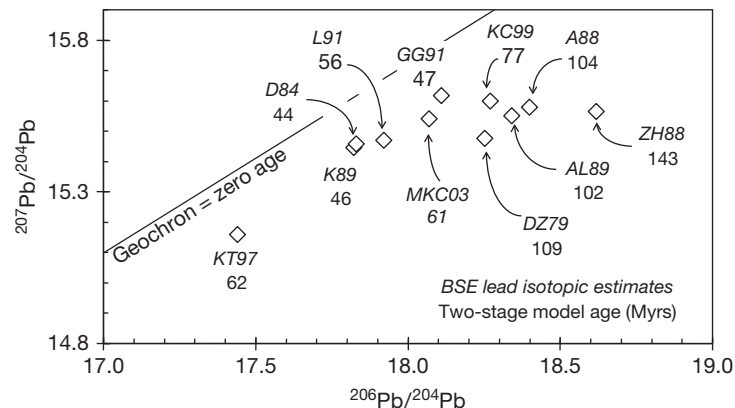

Figure 11 Estimates of the lead isotopic composition of the BSE plotted relative to the Geochron defined as the slope corresponding to the start of the solar system. All estimates plot to the right of this line, which, if correct, indicate protracted accretion and/or core formation. The times indicated in Ma are the two-stage model ages of core formation assuming the same values for bulk Earth parameters given in Halliday (2004) and Wood and Halliday (2005). Data from Doe and Zartman (1979), Davies (1984), Zartman and Haines (1988), Allègre et al. (1988), Allègre and Lewin (1989), Kwon et al. (1989), Liew et al. (1991), Galer and Goldstein (1991), Kramers and Tolstikhin (1997), Kamber and Collerson (1999), and Murphy et al. (2003). These Pb isotopic estimates are all significantly longer than the $^{182}Hf–^{182}W$ estimate of 30 Ma (Kleine et al., 2002; Yin et al., 2002).

^{180}Hf/^{184}W and ^{238}U/^{204}Pb fractionation in the Earth

Total Earth

Chondritic Hf/W but nonchondritic U/Pb (because Pb is moderately volatile)

^{180}Hf/^{184}W$_{total\ Earth}$ = ^{180}Hf/^{184}W$_{solar\ system}$ ~ 1.3

^{238}U/^{204}Pb$_{total\ Earth}$ ~ 0.7 > ^{238}U/^{204}Pb$_{solar\ system}$ ~ 0.14

Core
Rich in W and Pb
Poor in Hf and U

Silicate Earth
or primitive mantle
Rich in Hf and U
Poor in W and Pb

^{180}Hf/^{184}W$_{silicate\ Earth}$ = 30
^{180}Hf/^{184}W$_{core}$ = 0

^{238}U/^{204}Pb$_{silicate\ Earth}$ = 8–9
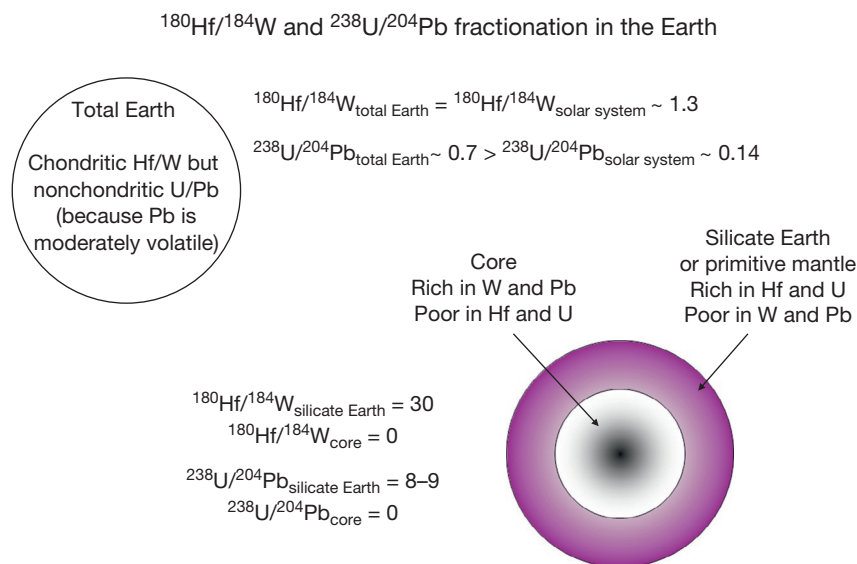^{238}U/^{204}Pb$_{core}$ = 0

Figure 12 Hafnium–tungsten chronometry provides insights into the rates and mechanisms of formation of the solar system, whereas U–Pb chronometry provides us with an absolute age of the solar system. In both cases, the radioactive parent/radiogenic daughter element ratio is fractionated by core formation, an early planetary process. It is this fractionation that is being dated. The Hf/W ratio of the total Earth is chondritic (average solar system) because Hf and W are both refractory elements. The U/Pb ratio of the Earth is enhanced relative to average solar system because approximately >80% of Pb was lost by volatilization or incomplete condensation mainly at an early stage of the development of the circumstellar disk. The fractionation within the Earth for Hf/W and U/Pb is similar. In both cases, the parent (Hf or U) prefers to reside in the silicate portion of the Earth. In both cases, the daughter (W or Pb) prefers to reside in the core.

Since Patterson published his work, various researchers have tried to estimate the average Pb isotopic composition of the bulk silicate portion of the Earth. This provides information on the timing of U/Pb fractionation caused by terrestrial core formation (Figure 12). The results of these various estimates are shown in Figure 11. It can be seen that none plot on the Geochron and this provide evidences that accretion of the Earth, or core formation, or both, was either late or protracted. These results need to be interpreted with caution for two reasons. Firstly, the average Pb isotopic composition of the bulk silicate portion of the Earth is very hard to estimate because the long-lived decay of U has resulted in considerable isotopic heterogeneity. All of the estimates could in principle be wrong. Secondly, converting these results into timescales is strongly model-dependent involving assumptions about how the Earth formed. The results of one simple model are shown in Figure 11. In this model, it is assumed that no U/Pb fractionation took place until a single point in time. So, for example, this could describe an Earth that formed its entire core in a single event (Figure 13(a)). The ages defined by the Pb isotopic compositions correspond to tens of millions of years after the start of the solar system (Figure 11). Although such data were at one time used to 'date' core formation, it is now recognized that the processes of accretion and core formation are more complex than can be described by such an approach. The data do, however, provide evidence of a protracted history of accretion and core formation. To sort out that history, it is necessary to use short-lived nuclides, dynamic simulations of planet formation, and petrologic constraints on likely core formation scenarios.

9.02.9   Short-Lived Nuclides and Early Processes

Since Patterson's study, it has become clear that one can resolve relatively small time differences between early solar system objects using more precise and different techniques (Figure 1). These provide us with fascinating information on accretion rates and permit the determination of which dynamic models of solar system formation are most probably correct. Progress in this field has been huge in the past 10 years. It is now becoming clear that different isotopic systems applied to the Earth most probably 'date' different processes. Volatile loss, metal segregation, sulfide segregation, mantle melting, atmosphere formation, and continental growth all affect particular elements in distinctive ways. As such, the isotopic geochemistry of an expanding range of elements is facilitating the first comprehensive view of the geochemical evolution of the early Earth.

The short-lived nuclides listed in Table 1 provide a set of powerful tools for unraveling a precise chronology of the early solar system. The advantage of these isotopic systems is that the changes in daughter isotope can only take place over a restricted early time window and there is no correction for the effects of decay over the past 4.5 billion years. They were present in the early solar system because of production in other stars, many of them massive, shortly before (within a few half-lives of) the formation of the Sun (Figure 1). Being extinct, the initial abundance can only be inferred. This is achieved by using differences in the atomic abundance of the daughter isotope in early objects (meteorites) of known absolute age.
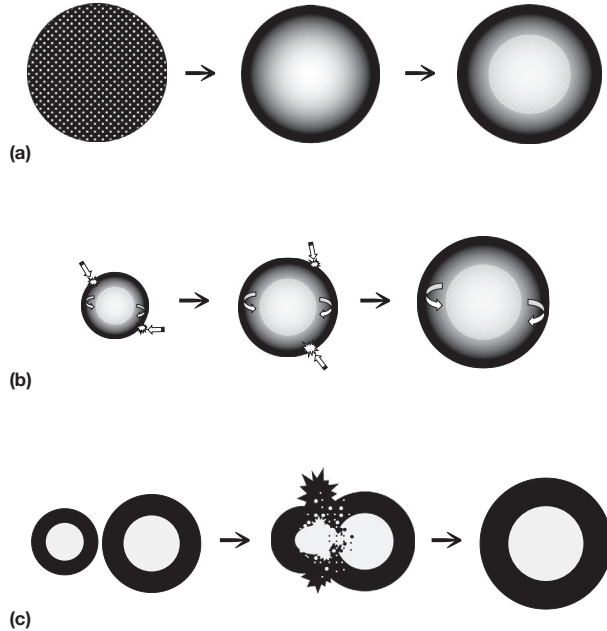
Figure 13 Schematic representation of core formation scenarios and how they translate into isotopic models and timescales.
(a) *Instantaneous core formation*. In this model, an age is calculated as the point in time that a fully formed planet segregated into core and silicate reservoirs. (b) *Continuous core formation*. The planet accretes from material with a chondritic Hf/W ratio and W isotopic composition. Newly accreted material is continuously mixed with W in the outer silicate portion prior to the segregation of new iron and siderophile elements (including W) into the core. Most models assume an exponentially decreasing rate of the overall growth for the planet and its core. (c) *Core–core mixing*. Terrestrial planets appear to have formed from material that was already differentiated into silicate and metal. How much equilibration between accreted metal and the planet's silicate reservoir occurs (an explicit requirement in calculating an age with model (b)) is not well understood at present. The net result if calculated with continuous core formation and equilibration as in model (b) is that the rate of growth of the planet appears faster than it really was. Reproduced from Halliday AN (2006) The origin of the Earth – What's new? *Elements* 2: 205–210.

To utilize any of the nuclides of Table 1 for deducing early solar system timescales, it is necessary to measure precisely the present-day isotopic composition of the daughter element. Therefore, the development of these chronometers is strongly linked to breakthroughs in mass spectrometry. In the simplest system, the present-day isotopic composition of the daughter element is a function of the initial abundance of the parent and daughter nuclide at the start of the solar system, the parent/daughter element ratio, and how much time elapsed. In effect, the isotopic composition of the daughter represents a time-integrated parent/daughter elemental ratio. If an object forms without a change in parent/daughter ratio, its time of formation will be undetectable with isotopic chronometry. It is the large change in parent/daughter ratio that accompanies certain processes associated with planetary accretion that renders some such isotopic systems useful. In fact, it is this change that is being dated. If there is no change that accompanies

accretion, there is no way to distinguish when an object formed relative to the start of the solar system.

The ^{182}Hf–^{182}W chronometer (Table 1) has been particularly useful in determining the timescales over which the planets formed. The principles are as follows: Excess ^{182}W comes from the radioactive decay of ^{182}Hf. Every atom of ^{182}Hf decays to a daughter atom of ^{182}W; therefore,

$$\left(^{182}\text{W}\right)_{\text{today}} = \left(^{182}\text{W}\right)_{\text{original}} + \left(^{182}\text{Hf}\right)_{\text{original}} \quad [1]$$

Because it is easier to measure these effects using isotopic ratios rather than absolute numbers of atoms, we divide by another isotope of W:

$$\left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{today}} = \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{original}} + \left(\frac{^{182}\text{Hf}}{^{184}\text{W}}\right)_{\text{original}} \quad [2]$$

However, the ^{182}Hf is no longer extant and so cannot be measured. For this reason, we convert eqn [2] to a form that includes a monitor of the amount of ^{182}Hf that would have been present as determined from the amount of Hf today. Hafnium has several stable nuclides and ^{180}Hf is usually deployed. Hence, eqn [2] becomes

$$\left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{today}} = \left(\frac{^{182}\text{W}}{^{184}\text{W}}\right)_{\text{original}} + \left\{\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{original}} \times \left(\frac{^{180}\text{Hf}}{^{184}\text{W}}\right)_{\text{today}}\right\}$$
$$[3]$$

which represents the equation for a straight line. A plot of ^{182}W/^{184}W against ^{180}Hf/^{184}W for a suite of cogenetic samples or minerals will define a straight line, the slope of which gives the ^{182}Hf/^{180}Hf at the time the object formed. This can be related in time to the start of the solar system with Soddy and Rutherford's equation for radioactive decay:

$$\left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{original}} = \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}}\right)_{\text{BSSI}} \times e^{-\lambda t} \quad [4]$$

in which *BSSI* is the bulk solar system initial ratio, λ is the decay constant (or probability of decay in unit time), and t is the time that elapsed since the start of the solar system. Using this method and the $\left(^{182}\text{Hf}/^{180}\text{Hf}\right)_{\text{BSSI}}$ of $\sim 1 \times 10^{-4}$ (Table 1), it has been possible to determine the age of a wide range of early solar system objects. Note that some early papers utilized a $\left(^{182}\text{Hf}/^{180}\text{Hf}\right)_{\text{BSSI}}$ of $\sim 1 \times 10^{-5}$ (Jacobsen and Harper, 1996). Later, papers used a value of $\sim 2 \times 10^{-4}$ (e.g., Lee and Halliday, 1997). Now, it is clear that the value must be $\sim 1 \times 10^{-4}$ (Kleine et al., 2002; Schönberg et al., 2002; Yin et al., 2002).

There have been several reviews of ^{182}Hf–^{182}W chronometry, none of which is complete because the field is changing fast. The most recent comprehensive modern review is that provided by Kleine et al. (2009). The principle of the technique is that Hf/W ratios are strongly fractionated by core formation because W normally is moderately siderophile, whereas Hf is lithophile (Figure 12). Therefore, in the simplest of models, the W isotopic composition of a silicate reservoir such as the Earth's PM is a function of the timing of core formation (Figure 13(a)). This could be determined from eqns [3] to [4] that together provide the time (usually referred to as a two-stage model age) when the Hf/W ratio was fractionated by core formation.

For the ^{182}Hf–^{182}W system, this time is given as

$$t_{\mathrm{CHUR}} = \frac{1}{\lambda} \ln \left[\left(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}} \right)_{\mathrm{BSSI}} \times \left(\frac{ \left(\frac{^{182}\mathrm{W}}{^{184}\mathrm{W}} \right)_{\mathrm{SAMPLE}} - \left(\frac{^{182}\mathrm{W}}{^{184}\mathrm{W}} \right)_{\mathrm{CHONDRITES}} }{ \left(\frac{^{180}\mathrm{Hf}}{^{184}\mathrm{W}} \right)_{\mathrm{SAMPLE}} - \left(\frac{^{180}\mathrm{Hf}}{^{184}\mathrm{W}} \right)_{\mathrm{CHONDRITES}} } \right) \right]$$

[5]

where t_{CHUR} is the time of separation from a CHondritic Uniform Reservoir. If, however, a planet grows over tens of millions of years and the core grows as the planet gets larger, as is nowadays assumed to be the case for the Earth (**Figure 13(b)**), the W isotopic composition of the PM is also a function of the rate of growth or the longevity of accretion and core formation. In this case, the equations need to be more complex (Jacobsen, 2005) or numerical models need to be established that calculate the W isotopic effects as a result of each stage of accretion or growth (Halliday, 2004).

As already stated, the earliest precisely dated objects that are believed to have formed within our solar system are the CAIs found in many chondrites (**Figure 2**). It would appear that at least some chondrules formed a few million years after the start of the solar system. Therefore, isotopic dating provides evidence that the disk from which the planets grew was still a dusty environment with rapid melting events, say, 2 million years after the start of the solar system (**Figure 2**). This means that chondrites must also have formed after this time.

Differentiated asteroids and their planetary cores and silicate reservoirs, as represented by some iron and basaltic achondrite meteorites formed *before* chondrites. A variety of chronometers have been used to demonstrate that iron meteorite parent bodies, the eucrite parent body, and the angrite parent body appear to have formed in the first few million years of the solar system (**Figure 2**) (Kleine et al., 2005a,b; Markowski et al., 2006; Scherstén et al., 2006). With extensive replication and better mass spectrometers, very high precision can now be achieved on the W isotopic compositions of iron meteorites. The latest data for iron meteorites provide evidence that accretion and core formation were very short-lived (Kleine et al., 2005a,b; Kruijer et al., 2012; Markowski et al., 2006; Qin et al., 2008; Scherstén et al., 2006). By correcting for cosmogenic effects, it can be demonstrated that some magmatic iron meteorites, thought to represent planetesimal cores, formed within 2 million years of the start of the solar system. Therefore, they appear to represent examples of early planetary embryos, as predicted from dynamic theory.

In a similar manner to differentiated asteroids, Mars also seems to have accreted quickly. The most recent compilations of data for martian meteorites (Foley et al., 2005; Halliday and Kleine, 2006; Kleine et al., 2004a,b; Lee and Halliday, 1997) provide a clear separation of W isotopic compositions between nakhlites and shergottites and confirm the view that accretion and core formation on Mars were fast. Some recent models (Dauphas and Pourmand, 2011; Halliday and Kleine, 2006) place the timescale for formation of Mars at less than one million years (**Figure 2**). If this is correct and the ages *are* based on assumptions about the model Hf/W of the martian mantle, Mars probably formed by a mechanism such as runaway growth, rather than by protracted collision-dominated growth. In other words, Mars may represent a unique example of a large primitive planetary embryo with a totally different accretion history from that of the Earth.

The conclusion from these studies of short-lived isotopic systems in meteorites is that chondrites, though widely considered the most primitive objects in the solar system and the building blocks for the planets, actually did not form for at least 2 million years, longer than the timescales for growth of planetary embryos determined theoretically. Where and how they formed are currently unclear. The chronometry is consistent with the chemistry in indicating that chondrites do not represent the actual building blocks of the Earth. In fact, it has long been thought that the Earth's growth was dominated by accretion of differentiated objects (Taylor and Norman, 1990). Chondrites almost certainly represent a good approximation of the average disk material but models that use chondrite variability to extrapolate to the bulk composition of the Earth, or attempt to build the Earth from chondritic components, need to be treated with some awareness of this issue.

9.02.10   Rates of the Earth's Accretion and Differentiation

Although Patterson determined the age of the Earth, there is in fact no such thing as a precise time when all of the constituents were amalgamated. It is more reasonable to instead assume a style of growth and use the isotopic data to define a rate of change of planetary growth from the integrated history of the chemical fractionation of the parent/daughter ratio. The latter is provided by the isotopic composition of the daughter.

The most powerful chronometers for estimating the growth rate of the Earth are $^{182}\mathrm{Hf}$–$^{182}\mathrm{W}$ and $^{235,238}\mathrm{U}$–$^{207,206}\mathrm{Pb}$ (Allègre et al., 1995a; Galer and Goldstein, 1996; Halliday, 2004, 2014). In both cases, the parent/daughter ratio is strongly fractionated during core formation (**Figure 12**). As such, the W and Pb isotopic compositions in the silicate portion of the planet reflect how fast it grew and internally fractionated by metal segregation. Although it was once thought that accretion was rapid (Hanks and Anderson, 1969) and formation of the core was protracted (Solomon, 1979), there exists strong evidence that the process of separating core material from mantle material and delivering it to the core after it arrives by impact is a faster one (Sasaki and Nakazawa, 1986) than the process of accretion itself; this is discussed in **Chapter 9.03** by Rubie et al. As such, the core grows proportionally, limited in size by the growth of the planet. On this basis, Pb and W isotopic data yield constraints on the rates of growth of the planet, provided certain assumptions are valid.

In practice, the $^{182}\mathrm{Hf}$–$^{182}\mathrm{W}$ system provides a more powerful constraint on how soon accretion and core formation started, whereas $^{235,238}\mathrm{U}$–$^{207,206}\mathrm{Pb}$ provides a better indication of how long it could have persisted. The $^{182}\mathrm{Hf}$–$^{182}\mathrm{W}$ system is better constrained in terms of the values of key parameters in Earth. To determine accretion rates, one needs to know the parent/daughter ratio in the total planet and in the reservoir, the formation of which is being dated. This is sometimes complex because we do not know independently how much resides in the inaccessible core. Some elements like Hf and W are refractory and were not affected by heating in the inner portions of the disk. Therefore, the Hf/W ratio of the total Earth is well known from independent measurements of chondrites (Newsom, 1995), even if the Earth is not exactly chondritic. However, Pb is moderately volatile and therefore variably depleted in the Earth, Moon, Vesta, and Mars and almost certainly in Venus and Mercury. Therefore, two distinct

processes have produced depletions of Pb in the silicate Earth – core formation and volatile loss. Two different methods are used to estimate the amount of Pb in the total Earth. The first is a comparison between the amount of Pb depletion in chondrites and that of other volatile elements that are not partitioned into planetary cores (Allègre et al., 1995a) (Figure 6). The second is based on estimates of the amount of volatile depletion expected given the average condensation temperature (Galer and Goldstein, 1996) (Figure 7). These two approaches are in broad agreement for Pb.

In addition to parent/daughter ratio, isotopic methods require a well-defined value for the isotopic composition of the silicate Earth relative to the rest of the solar system. The W isotopic composition of the silicate Earth is indeed extremely well defined because after 4.5 billions of convective mixing, the Earth's silicate reservoir has homogenized early isotopic variability. The W isotopic age of the Earth could in principle be determined from the composition of a tungsten carbide drill bit. However, with W, the problem has been to get the correct value for the average solar system. The earliest Hf–W papers assumed a certain value (Jacobsen and Harper, 1996). Early measurements of chondrites were variable (Lee and Halliday, 1996, 2000a,b). Although most of the early measurements for iron meteorites, achondrites, lunar samples, martian meteorites, and enstatite chondrites have reproduced well with more modern high-precision methodologies, it is now recognized that the early W isotopic measurements for carbonaceous chondrites in particular, reported in Lee and Halliday (1996), are incorrect and the timescales have had to be reassessed in the light of this (Halliday, 2004; Kleine et al., 2002; Schönberg et al., 2002; Yin et al., 2002). The problem for U–Pb is almost the opposite. The present-day value for the silicate Earth is very hard to constrain. The reason is that ^{235}U and ^{238}U are still alive in the Earth and capable of producing isotopic variations in $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$. Therefore, the Earth

is very heterogeneous in its Pb isotopic composition (Galer and Goldstein, 1996). This is shown in Figure 11 in which 11 estimates of the average Pb isotopic composition of the silicate Earth are presented. Each of these would imply a different timescale for the Earth's accretion, as discussed later in the text and shown in Figure 11.

The simplest kind of age calculation derives a time of fractionation or two-stage model age by assuming that the fractionating process was instantaneous (Figure 13(a)). This is the equivalent of assuming that the core formed instantaneously from a fully formed Earth. The $^{182}Hf-^{182}W$ model age so determined is ~30 Ma (Kleine et al., 2002; Schönberg et al., 2002; Yin et al., 2002), whereas the $^{235,238}U-^{207,206}Pb$ ages are more protracted (Figure 11). The possible reasons for this are discussed in more detail in the succeeding text. More complex models calculate an accretion rate (Halliday, 2000, 2004; Jacobsen and Harper, 1996; Kleine et al., 2009) by making assumptions about the style of growth. Generally speaking, this is an exponentially decreasing rate of growth that emulates what has arisen from dynamic simulations (Figure 14). This is consistent with the kinds of curves produced by George Wetherill who modeled the growth of the terrestrial planets using Monte Carlo simulations. To quantify the accretion timescale with an exponentially decreasing rate of growth requires the use of a time constant for accretion as follows:

$$F = 1 - e^{-(1/\tau) \times t} \qquad [6]$$

where F is the mass fraction of the Earth that has accumulated, τ is the mean life for accretion (or inverse of the time constant), and t is the time (in the same units). The mean life corresponds to the time taken to achieve 63% growth. The accretionary mean life for $^{182}Hf-^{182}W$ is ~11 Ma (Yin et al., 2002) but is again much longer for $^{235,238}U-^{207,206}Pb$ (Halliday, 2004, 2008, 2014) (Figure 15). Some of the most recent models
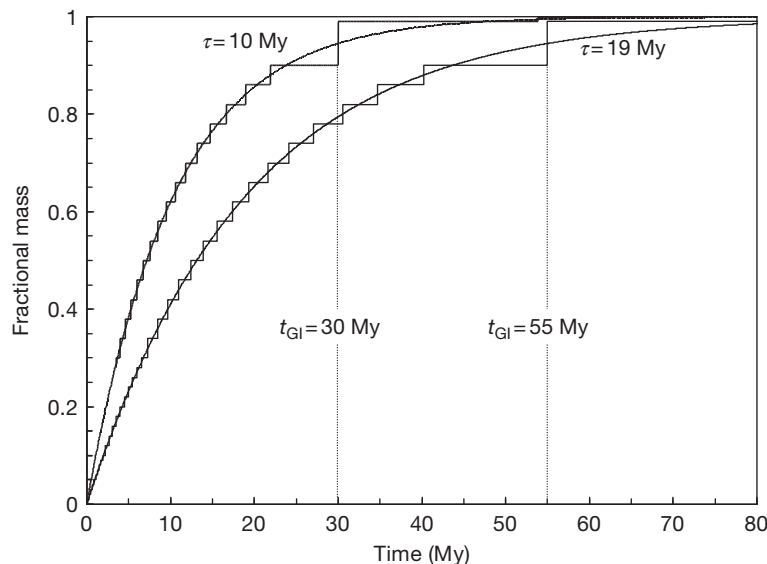

Figure 14 The mean life of accretion of the Earth (τ) is the inverse of the time constant for exponentially decreasing oligarchic growth from stochastic collisions between planetary embryos and planets. The growth curves corresponding to several such mean lives are shown including the one that most closely matches the calculation made by the late George Wetherill based on Monte Carlo simulations. The mean life determined from tungsten isotopes is in excellent agreement with Wetherill's predictions. Reproduced from Halliday AN (2004) Mixing, volatile loss and compositional change during impact-driven accretion of the Earth. *Nature* 427: 505–509.
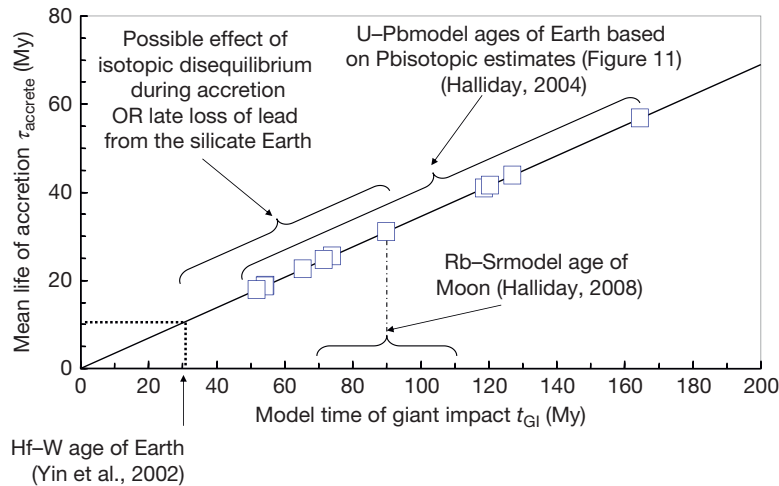
Figure 15   Calculated values for the Earth's mean life of accretion (τ) and time of the giant impact (t_{GI}) given in million years ago as deduced from the different estimates of the Pb isotopic composition of the BSE (**Figure 11**) using the type of accretion model shown in **Figure 14** (see Halliday, 2004). Note that while all calculations assume continuous core formation and total equilibration between accreted material and the BSE, the accretion is punctuated, as predicted from the planetesimal theory of planetary accretion. This generates more protracted calculated timescales than those that assume smooth accretion (Halliday, 2004). The $^{238}U/^{204}Pb$ values assumed for the Earth = 0.7 (Allègre et al., 1995a,b). Even the Hf–W timescales using the exact same style of model are significantly shorter.

(Halliday, 2004) also try to simulate the effect of a more stochastic style of accretion with growth from sporadic large (Moon- to Mars-sized) impactors (**Figure 14**). The staggered growth model shown in **Figure 14** assumes that the Earth grew from 90% to 99% of its current mass as a result of a collision with an impacting Mars-sized planet called 'Theia' that produced the Moon. The changes in the rate of accretion with time are calculated from the timing of this event. Therefore, the model time of the giant impact is directly related to the mean life of accretion in these models (**Figure 15**). Regardless of the details of the accretion processes, this last major impact would have had a dominant effect on the present-day W isotopic composition of the BSE. Therefore, predictions about the last major accretion event to affect the Earth, which are based on the W isotopic composition of the BSE, can in principle be tested by determining the age of the Moon. However, this has been less than straightforward.

9.02.11   The Age of the Moon

Despite considerable efforts using long-lived chronometers, the age of the Moon was for decades only known to be some time in the first 150 Ma of the solar system (Wasserburg et al., 1977). With the advent of Hf–W chronometry, it has been possible to determine that the Moon must have formed tens of millions of years after the start of the solar system. This is because the Moon has a high Hf/W of ~25 (König et al., 2011), and although it is thought to have formed in a single event, it has relatively unradiogenic W just like the Earth (Touboul et al., 2007). This means the Moon cannot have formed before about 37 Ma (Halliday, 2014). The first attempts to date the Moon with Hf–W (Lee et al., 1997) revealed some samples with relatively high ^{182}W in many lunar samples and the fact that these compositions were variable provided evidence that there was still live ^{182}Hf in the Moon during its earliest differentiation. Subsequently, it was shown that in some of these, a

portion of the effect was due to cosmogenic production of ^{182}Ta that decays to ^{182}W (Leya et al., 2000). This can be corrected in some cases by using exposure ages or internal mineral systematics (Lee et al., 2002). A novel and in many respects more straightforward and reliable approach was proposed by Kleine et al. (2005a,b) who used carefully separated metals with low Ta/W. All of these approaches yield similar timescales of between about 30 and 55 Ma after the start of the solar system. However, subsequent work by Touboul et al. (2007) showed that no effects from the decay of ^{182}Hf could be reliably resolved; all appeared to be cosmogenic. Since the publication of Touboul et al.'s paper, the best estimate of the Hf/W of lunar and terrestrial mantles has been shown to be remarkably similar at ~25 (König et al., 2011). The identical W isotopic composition and Hf/W provide powerful evidence that the Moon's atoms equilibrated with or were derived from those of the Earth. However, the age constraint is limited to ~37 Ma at the earliest (Halliday, 2014). This still provides strong support for the giant impact theory since such a late origin for an object of the size of the Moon is not readily explicable unless it is derived from a previously formed planet.

There are other isotopic systems that have been used to constrain the age of the Moon. In particular, the Rb–Sr system was deployed Carlson and Lugmair (1988) to define the age of the Moon assuming that its initial Sr isotopic composition was derived from the Earth, the Rb/Sr ratio (0.03) for which is well established. Initially, this approach appeared flawed because dynamic simulations of the giant impact derived most of the mass of the Moon from the impactor planet Theia (Canup and Asphaug, 2001). However, the average oxygen isotopic compositions of lunar samples cannot be resolved from the terrestrial fractionation line at the 5 ppm level (Wiechert et al., 2001). Other isotopic systems that are identical include Si (Armytage et al., 2012), Ti (Leya et al., 2008; Zhang et al., 2012), Cr (Lugmair and Shukolyukov, 1998), and W (Touboul et al., 2007). Whereas the O, Ti, and Cr isotopic effects could reflect formation from a similar inner solar system

provenance (Wiechert et al., 2001), the Si and W isotopic compositions reflect the history of core formation and are more likely to be planet-specific. Therefore, the atoms of the Moon either were derived from the Earth (Zhang et al., 2012) or reflect a process of large-scale equilibration between the Moon and Earth (Pahlevan and Stevenson, 2007; Pahlevan et al., 2011). Either way, the Rb/Sr of the Earth can be used in combination with the Moon's initial Sr isotopic composition to derive an age of 90 ± 20 Ma (Halliday, 2008). It has been proposed that the Earth's Rb/Sr is in fact lower because of impact erosion (O'Neill and Palme, 2008). In this case, the age is 125 ± 25 Ma (Halliday, 2014).

One other approach to defining the age of the Moon is to place a minimum age constraint from the ages of the oldest precisely dated lunar rocks. For a long time, this was given by the U–Pb age of 70 ± 10 Ma for lunar ferroan anorthosite 60025 (Hanan and Tilton, 1987). This ferroan anorthosite has been redated by Borg et al. (2011) and now appears to be much younger and closer to 200 Ma. Therefore, while 90 ± 20 Ma is shown as the Rb–Sr model age of the Moon in Figures 2 and 15, in reality, there is currently considerable uncertainty about the exact age. It does lie in the range 30–200 Ma and overlaps ages for the oldest terrestrial zircons (Wilde et al., 2001).

9.02.12   First Principles of Chemical Constraints on Core Formation

Having used the ^{182}Hf–^{182}W system to constrain the timing of core formation, the physical conditions of the core separation process can be estimated, provided chemical compositions of the BSE, the core, and the bulk Earth are known. As discussed earlier, the BSE exhibits a depletion in volatile elements with respect to the chondritic reference model. It also shows depletions in refractory siderophile elements such as W, Mo, Re, and Os. In these latter cases, the depletions cannot be due to volatility and must be the result of partial extraction into the core. The extent of extraction can be estimated by comparing silicate Earth concentrations (normalized to CI chondrites) to those of refractory lithophile elements such as the REE. This enables us to calculate, for each element, a core–mantle partition coefficient D_i defined as follows:

$$D_i = [i]_{\text{core}} / [i]_{\text{silicate Earth}} \qquad [7]$$

where [i] is the concentration of element i. Lithophile elements have D values close to zero. Table 2 shows that siderophile elements exhibit a very wide range of core–mantle partitioning behavior reflecting their different chemical properties and the conditions under which core segregation took place.

Core–mantle partitioning is best defined for those refractory elements that are weakly or moderately siderophile and that, like Ni and Co, are compatible in solid mantle silicates. The concentrations of these elements vary little in mantle samples, which means that D_i values based on the chondrite reference model have small uncertainties. Highly siderophile refractory elements such as the Pt group (Figure 7) are slightly less well constrained. The abundances of these elements in mantle samples are very low and rather variable. It is generally accepted, however, that their ratios one to another in the silicate Earth are, as shown in Figure 7, approximately chondritic.

Table 2   Core–mantle partition coefficients

Element	McDonough and Sun (1995) and McDonough (2003)	Allègre et al. (1995a,b)	Likely range	Low pressure / Experimental / D_i (Newsom, 1990; O'Neill and Palme, 1998)
D_{Fe}	13.66	13.65	13.65	13.65
D_{Ni}	26.5	24.4	23–27	4900
D_{Co}	23.8	24.7	23–27	680
D_{V}	1.83	–	1.5–2.2	0.02
D_{W}	16	–	15–22	3
D_{Pd}	800	–	600–1000	7×10^5
D_{Ir}	800	–	600–1000	10^{11}
D_{Pt}	800	–	600–1000	4×10^6
D_{Nb}	–	–	0.2–0.8	–
D_{Cr}	3.4	2.9	0.5–3.5[a]	0.2
D_{Mn}	0.29	5	0.2–2.0[a]	0.006
D_{Si}	0.29	0.34	0.1–0.35[a]	10^{-5}
D_{S}	76	–	50–100[a]	50
D_{Ga}	–	–	0–1.5[a]	15
D_{P}	22	45	20–50[a]	30

[a]Large uncertainty due to volatility.

There are a number of volatile siderophile elements such as S, Se, Te, P, and possibly Si whose core concentrations are difficult to estimate because their bulk Earth contents are not well constrained. This means, for example, that depletions in Mn, Si, and Cr (Figure 7) could be due to volatility or to sequestration in the core or both. The lack of constraint means that the uncertainties in D_i are large.

Segregation of the reduced core from the oxidized mantle took place at high temperatures, and since transfer from mantle to core involves reduction, element partitioning between the two must have depended on oxygen fugacity. From the current concentration of FeO in the mantle of about 8 wt% and of Fe in the core of 85% (Allègre et al., 1995b; McDonough, 2003; McDonough and Sun, 1995), it is fairly straightforward to estimate that core segregation took place at $\sim 2 \log f\text{O}_2$ units below Fe–FeO (IW) equilibrium (e.g., Li and Agee, 1996).

Table 2 shows a comparison of the calculated core(metal)–mantle(silicate) partition coefficients and those obtained experimentally at low pressures (0–2 GPa), high temperatures (~ 1800 K), and oxygen fugacity corresponding to 8 wt% FeO in the mantle (Newsom, 1990; O'Neill and Palme, 1998). As can be seen, the observed core–mantle partition coefficients are, for many of the siderophile elements, much (orders of magnitude) smaller than those determined experimentally. This manifests itself in the concentrations of many elements of concern (e.g., Ni, Co, and Pd) being much greater in the mantle than would be predicted from the experimental data, the so-called excess siderophile problem. Of equal importance are the weakly siderophile elements such as V and Cr for which the mantle concentrations are *lower* than predicted from the experimental data. Clearly, the mantle concentrations of these two groups of elements cannot be explained by equilibrium with metallic core at the fixed pressure, temperature, and oxygen fugacity conditions of Table 2. Early core segregation in small planetesimals

and planetary embryos, including proto-Earth, should, however, have resulted in siderophile element abundances generally consistent with the *D* values given in Table 2. The Earth, apparently, has inherited little of the geochemistry of these earlier events.

9.02.13   Explanations for the 'Excess Siderophile Problem'

Given that the 'excess siderophile problem' was not inherited, but arose from the manner of core formation on the Earth, several possible explanations have been proposed:

(1) *Inefficient core formation* (Arculus and Delano, 1981; Jones and Drake, 1986). In this model, some fraction of the core was left behind in the mantle, together with its siderophile element budget. Later, reoxidation and remixing of the metal led to the observed elevated mantle concentrations of siderophile elements. Principal objections to this model are that it can only explain the mantle abundances of some elements and that an enormous amount of water, about 15 times the current mass of the hydrosphere, would be required to reoxidize the 'retained' metal (O'Neill, 1991a,b).

(2) *Heterogeneous accretion* (Chou, 1978; O'Neill, 1991b; Wänke, 1981). In this model, it is suggested that the conditions of core segregation changed from reducing at the beginning of accretion to more oxidized toward the end. During the earliest, reduced, phase, highly and moderately siderophile elements (e.g., Ni, Co, and Pt group) would have been completely extracted to the core, together with some fraction of the weak siderophiles such as Si, V, and Cr. As conditions became more oxidizing, core extraction of siderophile elements would have ceased progressively, beginning with the weakest siderophiles and ending with more strongly metallic elements. The final phase, after core formation had ceased, was the addition of a 'late veneer' of about 0.5% of chondritic material. The latter raised the concentrations of highly siderophile elements in the mantle and, since core formation had ceased, ensured their chondritic proportions one to another (Figure 7). This model solves the 'excess siderophile problem,' but, being a disequilibrium model with multiple steps, is very difficult to test.

(3) *High-pressure core formation.* Murthy (1991) proposed that the partition coefficients for siderophile elements between metal and silicate should approach unity at high temperatures. This led to a variety of important new studies, and recent measurements of metal–silicate partitioning at high pressures and temperatures (Gessmann and Rubie, 1998; Li and Agee, 1996, 2001; Righter and Drake, 2000; Righter, et al., 1997) have shown that the partition coefficients of some siderophile elements change such that their mantle abundances, inexplicable by low-pressure equilibrium, may be explained by metal–silicate equilibrium at very high pressures and temperatures (e.g., Li and Agee, 1996; Righter and Drake, 1997). These observations led to the 'deep magma ocean' hypothesis to explain the 'excess siderophile' problem. As the Earth grew, it is argued (e.g., Righter and Drake, 1999) that droplets of metallic liquid descended through a 700–1200 km deep (28–40 GPa) magma ocean, ponding at its base in equilibrium with the magma ocean. The liquid metal subsequently descended in
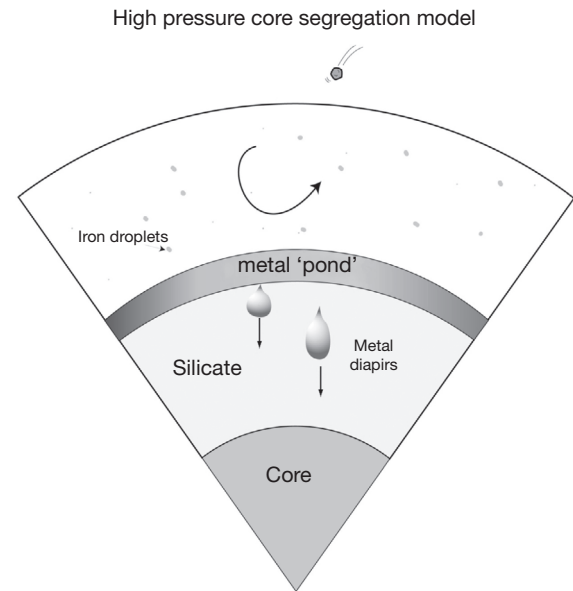
High pressure core segregation model

Figure 16   Core formation in the 'deep magma ocean' model. Impacting planetesimals disaggregate and their metallic cores break into small droplets due to Rayleigh–Taylor instabilities. These droplets descend slowly, reequilibrating with the silicate until they reach a region of high viscosity (solid), where they pond in a layer. The growing dense metal layer eventually becomes unstable and breaks into large blobs (diapirs) that descend to the core without further interaction with the silicate. The liquidus temperature of the silicate mantle should correspond to pressure and temperature conditions at a depth above the lower solid layer and plausibly within the metal layer.

large diapirs to the growing core without further reaction with the surrounding silicate (Figure 16). High-pressure core formation can explain, by metal–silicate equilibrium, the partitioning of many elements between the core and mantle. It does still require, however, the 'late veneer' of chondritic material to explain the concentrations and proportions of the highly siderophile elements in the silicate Earth.

9.02.14   The 'Deep Magma Ocean' Model of Core Formation

As the Earth grew, the gravitational energy deposited by accreting planetesimals would have increased, and at about 10% of its current size (Stevenson, 1981) was sufficient for significant melting to occur. After this point, the Earth would have periodically had an extensively molten outer layer (a magma ocean) of variable thickness. In some cases, the impact energy would have been sufficient to melt both the impactor and the proto-Earth (Cameron and Benz, 1991; Canup and Asphaug, 2001). From W isotopic evidence, it is clear that planetary cores segregated from their silicate mantles very early. As a result, most incoming planetesimals and planets are likely to have been already differentiated into silicate and metal like Vesta, Mars, and the Moon-forming planet Theia (Taylor and Norman, 1990; Yoshino et al., 2003). The fates of preexisting cores would have been dependent on the sizes of the Earth and impactor. Continuous core formation isotopic models normally assume that all of the metal

and silicate in the impactor mixes and equilibrates with the silicate portion of the Earth before further growth of the Earth's core (Kleine et al., 2002; Schönberg et al., 2002; Yin et al., 2002). However, the degree to which the impactor's core fragments depends on the angle of impact and relative size of the bodies (see discussion by Stevenson and in Rubie et al., this volume). Large fragments of metal could, under some circumstances, have mixed directly with the Earth's core (Dahl and Stevenson, 2010; Halliday, 2004; Karato and Rama Murthy, 1997) (Figure 13(c)). However, the size of those droplets depends on the fluid dynamics of the process.

Rubie et al. calculated the size of the droplets of liquid metal raining out of a magma ocean and concluded that these should have been about 1 cm diameter. Droplets of this small size would reequilibrate rapidly with the silicate melt as they fell (Rubie et al., 2003). Liquid metal and silicate would therefore have continued to reequilibrate until the former either reached the core–mantle boundary (if the mantle were completely molten) or collected at a level above a solid, high-viscosity lower layer (Figure 15). In the latter case, the metal layer would cease reequilibrating after it had reached about 5 km in thickness (Rubie et al., 2003) and because of the high viscosity of the lower layer would segregate as large diapirs to the core (Karato and Rama Murthy, 1997). The droplet model can apply in the case of small bodies accreting to the growing Earth, but may not apply after a giant impact such as the Moon-forming impact (see Chapter 9.03). In the latter case, isotopic and chemical equilibration of metal from the impactor with the silicate portion of the Earth depends on the extent to which the core of the impactor is fragmented.

The fact that the silicate Earth has a W isotopic composition that is so similar to average solar system (chondrites) means that in general terms, metal–silicate equilibration must have been the norm. However, the small difference that is now known to exist between the W isotopic compositions of chondrites and the BSE could reflect an event like the giant impact that involved particularly rapid amalgamation of large fragments of impactor metal with the Earth's core with little chance for equilibration with the silicate portion of the Earth (Halliday, 2004).

If we know the age of the Moon, we know the timing of the last accretion stage in the history of the Earth (Figures 2 and 15). From this, we can determine the extent to which the W isotopic composition of the silicate Earth reflects planetary-scale disequilibrium of added material during accretion. Preliminary attempts at calculating this (Halliday, 2004; Halliday and Kleine, 2006; Kleine et al., 2004b) showed that on average, the degree of equilibration between incoming metal and the Earth's silicate must have been high (70–90%). However, with a late (say 70–200 Ma) giant impact, the W isotopic compositions become harder to explain (Halliday, 2008). For example, with a 90 Ma giant impact and an exponentially decreasing stepped accretion rate (Halliday, 2004) (Figure 14), the W isotopic composition of the BSE is consistent with 55% of the cores of impactors merging directly with the Earth's core (Figure 13(c)). This might be more easily reconciled with dynamic simulations. However, it should be emphasized that greater resolution of the simulations and a more comprehensive understanding of the physics of metal–silicate mixing under such extreme conditions are needed before one can say which isotopic model is more consistent with the likely physical processes.

In the event that the energetics of impact and core segregation lead to a completely molten mantle, numerical simulations (Abe, 1997; Solomatov, 2000, Chapter 9.04) indicate that such a deep magma ocean would be short-lived and that the lower mantle would crystallize in a few thousand years. A shallower partially molten layer would crystallize much more slowly, however, and could remain as a mixture of crystals and melt for 100 Ma (Abe, 1997; Solomatov, 2000, Chapter 9.04). The energetics of impact, core segregation, and mantle crystallization leads to a dynamic view of the growing Earth in which the outer molten part deepened and shallowed many times after episodic impact. The pressures and temperatures recorded by core–mantle partitioning are therefore values averaged over numerous cycles of metal accumulation and segregation such as that depicted in Figure 16.

If one considers the magma ocean model of Figure 16 and takes account of the likelihood that the magma ocean shallowed and deepened many times during accretion and core segregation, several principles emerge. Firstly, accumulation of metal at the base of a completely or partially molten silicate layer, as shown in Figure 15, implies temperatures close to or slightly below the liquidus of the mantle peridotite. Secondly, average pressure should have increased as the planet grew. Thirdly, since the silicate liquidus has a positive pressure–temperature slope, average temperature of core segregation should also have increased as the planet grew. Having accepted these principles, we can use the dependences of D_i on pressure and temperature (Chabot and Agee, 2003; Li and Agee, 2001; Righter et al., 1997; Wade and Wood, 2005) to develop constraints on the core segregation process.

9.02.15   Core Segregation During the Growth of the Earth

If we consider the case of instantaneous core formation (Figure 13(a)), then current partitioning data for the elements of Table 2 yield average pressures and temperatures of ~40 GPa and ~3750 K, respectively (Wade and Wood, 2005). Given that the mantle has superchondritic Mg/Si, these conditions imply that a substantial amount of Si, more than required to give the bulk Earth a chondritic Mg/Si ratio, resides in the core (Wade and Wood, 2005). The reason is that Si partitioning into the metal is strongly temperature-dependent and the calculated temperature is very high, in fact 650° above the silicate liquidus. This seems unlikely because the base of the magma ocean should be at or below the mantle liquidus (Figure 16).

Continuous accretion and core formation models (Figure 13(b)) do not change the result, temperatures remaining above the silicate liquidus. Apart from invoking wholesale disequilibrium, the simplest solution (Wade and Wood, 2005), as illustrated in Figure 17, is to allow oxygen fugacity (as represented by the FeO content of the mantle) to increase as accretion and core segregation progress.

Figure 17 illustrates a continuous process of accretion and core segregation in 1% intervals. New material added to the Earth was assumed to be mixed with the preexisting mantle, but isolated from the protocore. The core was segregated in 1% steps, each aliquot being in equilibrium with the entire mantle at the time of segregation at pressures constrained by Ni and Co partitioning and temperatures on the peridotite liquidus
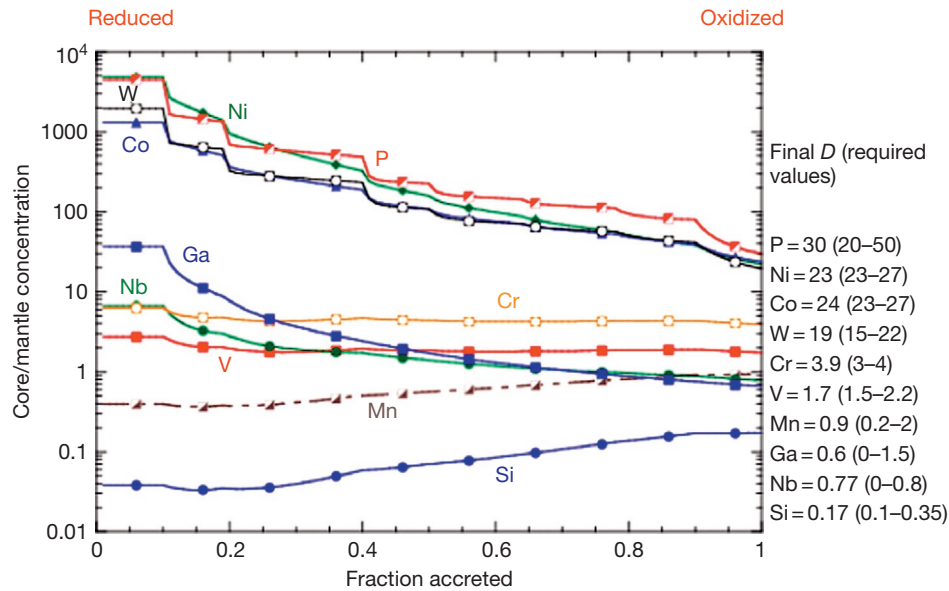
Figure 17 Figure showing one possible path of accretion and core segregation for the Earth. The Earth was accreted and the core segregated in 1% intervals. At each step, the silicate Earth was homogenized and the core segregated at the base of the magma ocean of **Figure 16**. At 100% accretion (right-hand side), the core/mantle partitioning of each element must match the 'required value' of **Table 2**. In order to achieve this and maintain temperatures on the silicate liquidus, the Earth must become more oxidized during accretion. In the example shown, the oxygen fugacity increases in small steps from about 3.5 log units below the Fe–FeO (IW) buffer to 2 log units below IW during accretion and the magma ocean depth corresponds to 30–40% of the depth to the core–mantle boundary in the growing planet.

(Wade and Wood, 2005). The latter were found to be consistent with magma oceans extending to 30–40% of the depth of the growing mantle. A large number of oxygen fugacity paths yield the partitioning of V, W, Nb, Ni, Co, Mn, Cr, Ga, P, and Si, which are consistent with the estimates of **Figure 17**. All require, however, that most of the Earth formed under conditions more reducing than those implied by the current FeO content of the mantle and that the Earth became more oxidized toward the end of accretion. The combined effects of increasing temperature and pressure during accretion lead to a progressive increase in core Si content (**Figure 17**) such that the final core contains about 4% Si. This brings the Mg/Si ratio of the bulk Earth much closer to chondritic than implied in **Figure 8**. As required by all accretion models, 0.5% of chondritic material must be added after cessation of core formation in order to generate the chondritic ratios of the highly siderophile elements such as Pd, Ir, and Pt (**Figure 17**). The current 'best explanation' is therefore an amalgam of 'deep magma ocean' and 'heterogeneous accretion' hypotheses, that is, core segregation at the base of a deepening magma ocean under progressively more oxidizing conditions (Wade and Wood, 2005).

The idea that the Earth became more oxidized during accretion has been proposed on a number of occasions (e.g., O'Neill, 1991a,b), but this leads to two other important questions. Firstly, the Earth has a substantially higher core/mantle mass ratio than Mars and is hence, as a planet, more reduced than this smaller body. What caused the Earth to be more reduced than smaller bodies? Was it due to part of the silicate Earth being removed during accretion (O'Neill and Palme, 2008) as proposed for Mercury (Benz et al., 1987)? If the Earth later became more oxidized, as evidenced by the relatively oxidized nature of terrestrial as opposed to lunar or martian basalts (Karner, et al.,

2006) and the constraints of core–mantle partitioning discussed earlier in the text, then what was the mechanism of oxidation and when did it operate?

### 9.02.16   Oxidation State of the Earth During and After Accretion

As planetesimals accreted during the first few million years of solar system history, they would have been surrounded by a hydrogen-rich nebular gas of solar composition. This gas would have had little effect on the chemical compositions of small bodies because the pressure was very low (10^{-4} bar). As protoplanets grew, however, their masses might have become high enough for them to capture a nebular gas atmosphere (Hayashi et al., 1979, 1985; Ikoma and Genda, 2006; Sasaki and Nakazawa, 1986) such that at a mass >20% of the current mass of Earth hydrogen pressures >1 bar are plausible.

There is a problem with these models because by the time a body that is sufficiently massive to retain a large hydrogen atmosphere has formed, the nebula may have already dissipated. Ikoma and Genda (2006) pointed out that the atmosphere thereby accreted is only logarithmically sensitive to the nebula density, which implies that a massive hydrogen atmosphere can be accreted even when the nebula has largely departed. However, the nebula may not decline exponentially with time; the favored process suggests it is highly superexponential. That is, the nebula declines to essentially zero pressure in finite time, perhaps a mere 5 Ma. Accretion rates based on W isotopes are agnostic on the earliest stage of the Earth's growth but are usually modeled with longer timescales (**Figure 14**). However, noble gas data do provide evidence of

solar components within the Earth that could have been acquired directly from the solar nebula (Porcelli et al., 2001).

So long as the nebula persisted, therefore, the episodic magma ocean at the Earth's surface would have reacted with hydrogen gas, raising the Fe/FeO ratio of the bulk Earth and increasing the mass fraction of its metallic core. After about 10^7 years, the nebula dissipated and the oxidation state of the mantle would have been free to increase, particularly if late-arriving planetesimals had higher FeO/Fe ratio than the early ones (O'Neill, 1991a,b). This mechanism, impossible to quantify, would have generated a gradual increase in FeO/Fe ratio of the Earth, but would not have produced any of the Fe^{3+} present in peridotite and MORB (Wood, et al., 1990). The latter can be explained if the Earth self-oxidized through crystallization of magnesium silicate perovskite (Frost, et al., 2004; Wade and Wood, 2005).

At depths deeper than 660 km in the present-day Earth, the stable phases are $(Mg,Fe)SiO_3$ (magnesium silicate perovskite) (79% by volume; Wood, 2000), $(Mg,Fe)O$ (magnesiowüstite) (16%), and $CaSiO_3$ perovskite (5%). An important property of magnesium silicate perovskite is that it accommodates the 5% Al_2O_3 that it dissolves in peridotite compositions by a coupled substitution with Fe^{3+} (McCammon, 1997; Wood and Rubie, 1996) as follows:

$$Mg^{2+}Si^{4+} \leftrightarrow Fe^{3+}Al^{3+}$$
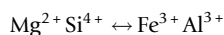
It has recently been discovered that this substitution mechanism is so stable that it forces ferrous iron to disproportionate to ferric iron plus iron metal (Frost et al., 2004)

$$3Fe^{2+} \leftrightarrow 2Fe^{3+} + Fe^0$$
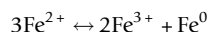
or, in terms of oxide components of the lower mantle,

$$3FeO + Al_2O_3 = 2FeAlO_3 + Fe^0$$
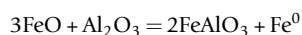
This means that, as perovskite began to crystallize in the extensively molten Earth, it dissolved ferric iron as $FeAlO_3$ component and produced Fe metal. Since the perovskite is stable throughout virtually the entire lower mantle, this process took place during most of accretion and core formation on Earth. The implications are that metal sinking through the lower mantle to the core would inevitably have dissolved some of this internally produced metallic iron, resulting in a perovskitic layer that was relatively oxidized. Given the gravitational instability of any metal layer (Figure 16), accretional energies, and heat loss, it is inevitable that the depth of the magma ocean fluctuated continuously, thereby generating fronts of dissolution and precipitation at the lower boundary. Perovskite dissolution and reprecipitation therefore released ferric iron to the magma ocean during dissolution and produced more during precipitation. This raised the oxygen fugacity of the mantle. Any later, droplets of metal falling through the magma ocean would have reacted with ferric iron, producing more Fe^{2+} that would then have dissolved in the silicate melt. Hence, the content of oxidized iron of the mantle (magma ocean) increased naturally as a consequence of perovskite crystallization. In the very final stages of the Earth's accretion, this mechanism may have caused sufficient oxidation to halt metal segregation, setting the stage for the 'late veneer' of chondritic or similar material to add the highly siderophile elements exclusively to the mantle. Note that the

oxidation-state change required by partitioning data is a simple consequence of the size of the Earth. Any planet in which magnesium silicate perovskite is an important crystallizing phase should undergo the same process. It could explain why terrestrial basalts are more oxidized than those of Mars (Herd, et al., 2002), a planet in which perovskite can only crystallize at depths close to the core–mantle boundary. Because of its small size, Mars cannot have undergone the same period of extensive perovskite crystallization and self-oxidation during accretion as did Earth.

9.02.17 Isotopic Evidence for Impact-Induced Losses During the Earth's Accretion

Geochemistry provides three kinds of information on the changes that may have affected a planet during growth. The first is chemical compositions that imply some process of modification to primordial materials such as chondrites. The second is mass-dependent stable isotopic fractionation, which can leave a marked imprint of processes that affected the Earth. The third is isotopic compositions that leave a record of time-integrated parent/daughter elemental ratios that are distinct from those found in the Earth today.

The most dramatic example of mass-dependent fractionation is provided by Xe isotopes. Heavy Xe isotopes are affected by early decay of formerly live ^{129}I ($T_{1/2} = 16$ Ma) and ^{244}Pu ($T_{1/2} = 82$ Ma) (Table 1). The lighter isotopes with a mass of 124 to 128 are not affected by decay but are markedly fractionated in a mass-dependent fashion to heavier overall proportions relative to meteoritic and solar values (Figure 10). Originally, it was thought that this provided key evidence that the noble gases were more abundant in the early Earth and that a major fraction has been lost, probably by shock-induced blow off of a large protoatmosphere by hydrodynamic escape (Hunten et al., 1987; Walker, 1986). However, it is now clear that this effect is also found in the Earth's interior (Caffee et al., 1999; Holland et al., 2009) and a remarkably similar composition is also found in the martian atmosphere (Halliday, 2013) (Figure 10) despite a very different accretion history. Furthermore, neon (Ne), a much lighter and more readily fractionated element, displays no such sign of fractionation; it resembles a simple mixture of solar and chondritic components (Figure 9). Therefore, other models need to be considered. It would be helpful to know the Xe isotopic composition of the Venusian atmosphere because the martian and terrestrial composition may be a particular feature of terrestrial planets that relates to a specific kind of accretion/loss process. Although a loss process has not yet been clearly identified, late-stage parent/daughter fractionation has clearly affected the Earth's noble gases. Put simply, the small difference between the isotopic composition of xenon in Earth and its initial starting composition is consistent with lower parent/daughter ratios than are found, thereby implying a major loss of Xe given that late additions of the parents would make no sense. Live ^{129}I and ^{244}Pu must have been relatively low in abundance at the time of Xe loss because there is a shortage (by two orders of magnitude) of the decay products of ^{129}I and ^{244}Pu. Given the known abundances of I and refractory lithophile elements (of which Pu is an extinct example), the radiogenic and

fissionogenic Xe atoms that should have formed in the first 100 Ma say are largely missing (Porcelli and Pepin, 2000; Pepin and Porcelli, 2006). Therefore, there must have been a major fractionation in parent/daughter ratio at a relatively late stage and large amounts of loss. Early estimates for the age of this loss are 50–80 Ma (Ozima and Podosek, 1999; Porcelli and Pepin, 2000). However, longer timescales are required to satisfy the ^{136}Xe constraint and provide evidence that the Earth's Xe was lost over the first few hundred million years. Pepin and Porcelli (2006) had proposed two episodes of atmospheric blow off related to giant impacts. It is also possible that other processes operated in the Earth's atmosphere that may have caused loss, the most likely involving ionization of Xe (Halliday, 2013; Zahnle et al., 2006). Pujol et al. (2011) presented evidence of progressive loss of atmospheric Xe in the Earth's early history.

Supporting evidence for such losses comes from the composition of the major volatiles H, C, and N (Dasgupta and Hirschmann, 2010; Halliday, 2013). It has long been considered likely that major volatiles were added after the Moon-forming giant impact, and a number of papers (Albarède, 2009; Morbidelli et al., 2000) have made a connection to a late veneer that is thought to have been responsible for the abundances of highly siderophile elements in the Earth's mantle (Chou, 1978). However, the relative abundances of H, C, and N bear no resemblance to those of chondrites or comets (Halliday, 2013) (Figure 18). Therefore, some fractionating process must be responsible for their present concentrations. The volatiles have been lost either to space or to the Earth's core (Dasgupta and Hirschmann, 2010; Halliday, 2013). Core formation would be unlikely to leave the silicate Earth more depleted in nitrogen than in carbon (Figure 19). The most likely scenario therefore is that N, C, and H were differentially lost to space, possibly as a result of ionization along with Xe by solar EUV irradiation (Figure 20) (Halliday, 2013).

In addition to losses of elements like the noble gases and major volatiles, the question has arisen as to what extent the depletions in moderately volatile elements also reflect accretion phenomena. Evidence for loss of moderately volatile elements during accretion was hard to reconcile with the uniform K isotopic compositions recorded by inner solar system objects (Humayun and Clayton, 1995). However, the precision on these K isotopic measurements was not at the kind of level that would resolve small evaporation effects. Furthermore, if K were atmophile because it was degassed from the mantle into a hot atmosphere nebular atmosphere that was blown off with Xe (O'Neill, 1991a,b), the losses would not necessarily record a major isotopic fractionation (Halliday, 2004). Pritchard and Stevenson (2000) showed that in any case, it is possible to have large volatile loss without large isotopic effects. They present an explicit calculation showing how the K-41 isotopic effect can be small even when the volatilization is large. The main point is that it is evaporation into a dense atmosphere not into vacuum.
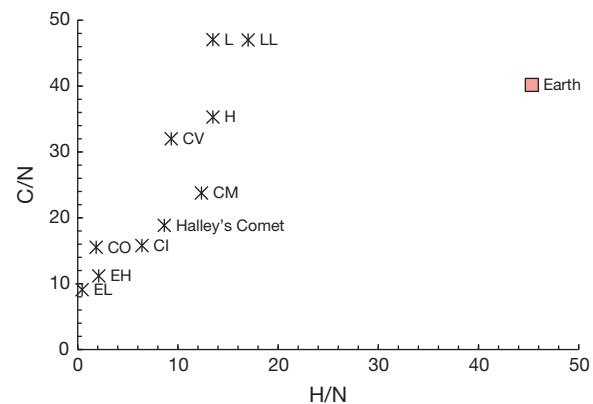

Figure 18   Weight ratios of C/N versus H/N in different classes of chondrites compared to the composition of the BSE. No combination of chondrites yields the composition of the Earth's major volatiles. Therefore, most H_2O (70%) predates the late veneer. Reproduced from Halliday AN (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105: 146–171.
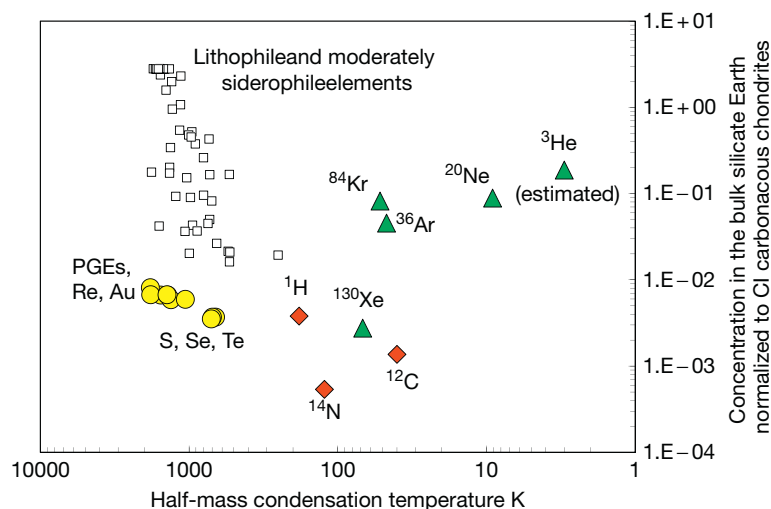

Figure 19   Concentrations of all elements in the BSE by weight normalized to CI carbonaceous chondrites, plotted against half-mass condensation temperatures given by Lodders (2003). Note the high concentrations of noble gases other than xenon and the strong depletion in carbon and nitrogen – more so than any other element in the BSE. Reproduced from Halliday AN (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105: 146–171.
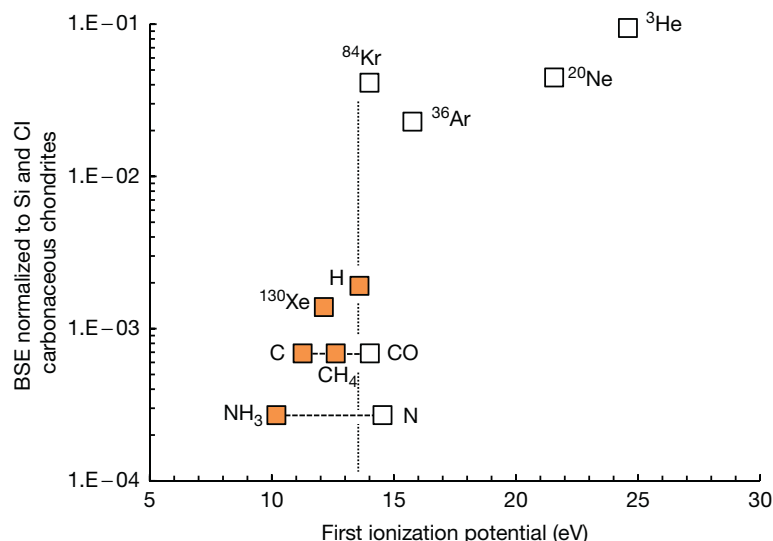
Figure 20 Concentrations of noble gases, hydrogen, carbon, and nitrogen in the BSE, normalized to silicon and CI and compared to the EUV first ionization potential. Differing ionization potentials are shown for differing molecular species of carbon and nitrogen, which would be a function of temperature (Lodders, 2003). Reproduced from Halliday AN (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105: 146–171.

It has been claimed that supporting evidence for accretionary losses of volatile elements is found in oxygen isotopic compositions (**Figure 3**). Oxygen isotopes provide a monitor of the degree of mixing of dust and gas in the disk (Clayton and Mayeda, 1975; Wiechert et al., 2001, 2004). The oxygen isotopic composition varies among different classes of meteorites and is therefore assumed to be highly heterogeneous in general among inner solar system objects (Clayton, 1986, 1993; Clayton et al., 1973). This is not a normal mass-dependent fractionation so much as a mass-independent effect, the origin of which is thought to be a self-shielding irradiation effect from the early Sun (Clayton, 2001). Regardless of the reason behind the heterogeneity, the oxygen isotopic composition provides a monitor of the origins of the material in a planetary object. The provenance of material in an object the size of the Earth may have been quite broad (Wetherill, 1994) although more recent accretion models define a more narrow feeding zone. As such, oxygen isotopes merely provide some average.

The Earth is distinct in oxygen isotopes from all classes of chondrites except enstatite chondrites, which may have formed in the more reducing inner regions of the solar system. Similarly, the provenance appears to be distinct from that of the material forming asteroid 4 Vesta or Mars, as judged from studies of meteorites thought to be derived from these objects (Clayton, 1986, 1993; Wiechert et al., 2004). The Moon, however, has an oxygen isotopic composition that is identical to that of the Earth (Clayton and Mayeda, 1975), demonstrated to persist to extremely high precision (Wiechert et al., 2001) (**Figure 3**). This has long provided a powerful line of evidence that the Moon formed from the Earth (Ringwood, 1989a,b; Wänke and Dreibus, 1986) or that the Earth and Moon formed from the same material (Wiechert et al., 2001), even though these two objects have demonstrably different chemical composition.

In simulations of the giant impact (Cameron and Benz, 1991), roughly 80% of the Moon forms from the debris
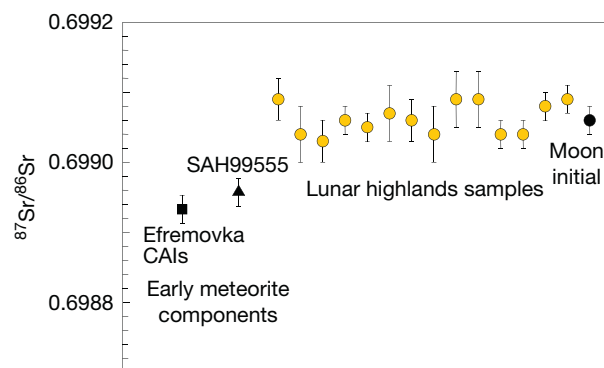

Figure 21 Initial Sr isotopic composition of early lunar highland rocks relative to other early solar system objects. From compilation in Halliday and Porcelli (2001). APB, angrite parent body; CEPB, cumulate eucrite parent body; BSSI, bulk solar system initial.

derived from Theia (Canup and Asphaug, 2001). If this is correct, the oxygen isotopic evidence provides evidence that Theia and the Earth had similar average provenance. Yet the Moon is far more depleted in volatile elements than the Earth (Taylor and Norman, 1990) (**Figure 4**). A possible explanation for this is that there were major reductions in volatile constituents during the Moon-forming giant impact (O'Neill, 1991b). Support for this is found in the initial ^{87}Sr/^{86}Sr of early lunar rocks from the highlands (Halliday and Porcelli, 2001). These yield an initial ^{87}Sr/^{86}Sr for the Moon that is clearly resolvable from the initial composition of the solar system (**Figure 21**), consistent with radiogenic growth in an environment with relatively high Rb/Sr.

It has been argued that it is very unlikely that the Earth and Theia had similar provenance. Pahlevan and Stevenson (2007) and Pahlevan et al. (2011) proposed that the identical oxygen isotopic compositions of the Earth and Moon more likely

represent equilibration of atoms between the hot proto-lunar disk and the Earth's magma ocean in the aftermath of the giant impact. As explained earlier in the text, it is now known that Si (Armytage et al., 2012), Ti (Leya et al., 2008; Zhang et al., 2012), Cr (Lugmair and Shukolyukov, 1998), and W (Touboul et al., 2007) are identical between the Earth and Moon but variable within the broader solar system. Therefore, the case for the Moon's atoms being largely derived from the Earth whether by direct impact or by equilibration is overwhelming.

Impact-driven chemical changes in the Earth are well supported by evidence that the planet Mercury lost a major fraction of its silicate by impact erosion (Benz et al., 1987). The Earth also has a Fe/Mg ratio of at least 2.11, which is 10% higher than the value of 1.90 for CI chondrites (Palme, 2000). A possible explanation for this is impact erosion of the outer portions of the Earth (Halliday et al., 2001; O'Neill and Palme, 2008). Impact erosion is likely to generate a Sm/Nd that is higher than chondritic through loss of low Sm/Nd crust, and with new high-precision isotopic data for meteorites, evidence for a subtle but important difference between chondrites and the Earth has been growing (Boyet and Carlson, 2005). This has spawned new questions about whether the Earth is simply nonchondritic (Drake and Righter, 2002) or whether there are hidden reservoirs inside the Earth that balance its composition (Boyet and Carlson, 2005) (see next section). The observed ^{142}Nd effect is explicable with just a 6% increase in Sm/Nd in the BSE relative to chondrites (Halliday, 2006).

O'Neill and Palme (2008) made the case that there have been selective losses of all incompatible elements from the outer portions of the Earth as a result of such impact erosion. If this is the case, the calculated budgets of refractory incompatible elements like Th and U have been overestimated and could be 40–50% lower. Potassium budgets are based on the K/U ratio of the mantle so would also be correspondingly reduced. Radiogenic heat production would be much less than currently accepted if, as argued, there has been impact erosion. The K budget affects the calculated budget for radiogenic ^{40}Ar in the Earth, which in turn provides a quantification of the ^{36}Ar budget so the small amount of primordial volatiles is even smaller if there has been impact erosion. The budgets for major volatiles are in turn determined by being ratioed to those of Ar isotopes (Marty, 2012) so the amount of water in the mantle, for example, could be as different as 1 or 9 ocean masses (Halliday, 2013) depending on impact erosion.

The mismatch between U–Pb chronometry and Hf–W chronometry may also be related to late volatile losses. The rates of accretion of the Earth based on the model of Figure 14 and the various estimates of the BSE Pb isotopic composition (Figure 11) are shown in Figure 15. Also shown are the results for W. It is clear that the kinds of timescales involved are on the order of 10^7–10^8 years, providing strong vindication of the Safronov–Wetherill style of protracted accretion via major impacts (Halliday, 2014). It is also immediately apparent however that a discrepancy exists between the W results and every estimate based on Pb isotopic data (Halliday, 2004). Either all of these Pb isotopic estimates are incorrect or there is some basic difference in the way these clocks operate. There are a number of parameters that play into these models that have a significant level of uncertainty associated.

When the ^{182}Hf–^{182}W and $^{235/238}$U–$^{207/206}$Pb chronometers are compared using the same style of model, a variable but unidirectional offset is found between the timing that is based on W and that based on any of the 11 estimates of the Pb isotopic composition of the silicate Earth (Figure 11). For example, the two-stage ^{182}Hf–^{182}W model age of the Earth is 30 Ma (Yin et al., 2002), whereas the same model applied to $^{235/238}$U–$^{207/206}$Pb yields ages ranging between >40 and >100 Ma (Figure 11). It is of course not unlikely that all the Pb isotopic estimates are wrong. Given the difficulties in defining meaningful average Pb isotopic ratios for the silicate Earth, this is certainly a possibility. In fact, some more recent estimates of Pb isotopic composition of the BSE have been made based on the results of W isotopes so there is circularity involved. Assuming, however, that some of the Pb isotopic estimates are close to correct, one can consider what kind of processes might result in a difference between W and Pb ages of the core.

One explanation (Wood and Halliday, 2005, 2010) is that the transfer of W and Pb to the core changed, but not together, during the accretion history of the Earth. Tungsten is moderately siderophile but not chalcophile, whereas Pb is thought to tend toward the opposite. Following the cooling and oxidation of the Earth after the giant impact, sulfide is likely to have formed. Removal of this sulfide to the core may have been responsible for a late-stage increase in U/Pb that defines the Pb isotopic compositions observed. This being the case, the Pb isotopic composition of the BSE provides information on the timescales over which the Earth cooled and core segregated following the giant impact. The timescales inferred depend on which Pb isotopic estimate is employed (Figures 11 and 15). However, they are all of the order of 100 Ma, which is close to the age of the giant impact.

There is another possible explanation for the apparent discrepancy between accretion rates determined from ^{182}Hf–^{182}W to $^{235/238}$U–$^{207/206}$Pb. Lead is moderately volatile, and as such, the younger ages could reflect loss of Pb from the Earth during accretion. Loss of such a heavy element from the Earth is dynamically difficult. However, if the surface of the Earth was very hot with a magma ocean, Pb might have been episodically atmophile rather than lithophile. The atmosphere may then have been blown off at a late stage (Walker, 1986). The depletion of the terrestrial planets in moderately volatile elements has long been considered to be a result of incomplete condensation because it was believed that the inner solar system formed from a hot solar nebular gas. Perhaps some of this depletion is, in fact, a late-stage phenomenon. Support for this model was found in results for the new ^{205}Pb–^{205}Tl chronometer (Nielsen et al., 2006) that are hard to explain without major losses of Tl from the Earth at a late stage.

With the advent of MC-ICPMS (Halliday et al., 1998), it has become possible to measure small mass-dependent isotopic differences between early solar system objects that may have been induced by the processes of accretion and evaporation of silicate and metal. Of particular interest are the less volatile but not highly refractory elements that would not have formed part of the Earth's protoatmosphere. Such elements include Li, Mg, Si, V, Cr, Fe, and Ni (Lodders, 2003). Precise stable isotopic compositions for mantle-derived samples from the Earth and meteorite groups have now been published for Li (Magna et al., 2006; Seitz et al., 2006), Mg (Pogge von Strandmann et al., 2011; Wiechert and Halliday, 2007), and Fe (Craddock et al., 2013; Poitrasson et al., 2004; Weyer et al., 2005; Williams

et al., 2004, 2006). The Fe isotopic data for 'normal' basalts from the Earth and Moon are slightly heavy (roughly 40 ppm per amu) relative to data for Mars and Vesta (Poitrasson et al., 2004; Weyer et al., 2005). This would be consistent with the loss of small amount of evaporated Fe during the giant impact. However, Williams et al. (2004) had shown that isotopic fractionations may also result from oxidation effects. Basalt melting may have generated different isotopic fractionations on the Earth, Moon, and other objects (Craddock et al., 2013; Schoenberg and von Blanckenburg, 2006). It has also been argued that the silicate Earth, being larger than Mars or Vesta, may have generated a heavy Fe isotopic composition during partitioning ferric iron into perovskite in equilibrium with metal that was transferred to the core, as discussed in the preceding text (Williams et al., 2006, 2012).

Silicon (Georg et al., 2007) and vanadium (Nielsen et al., 2014; Prytulak et al., 2013) display clear isotopic differences between the silicate Earth and meteorites although there have been counter claims for Si (Chakrabarti and Jacobsen, 2010; Fitoussi et al., 2009) that have not been replicated with more detailed work (Armytage et al., 2011; Savage et al., 2010). In the case of Si, the small (0.1‰ per amu) effect appears to relate to core formation and an isotopic fractionation between Si in metal and silicate (Figure 22). This is supported by experimental studies. In the case of V, the effect is very large (1‰ per amu) and no evidence for such a metal–silicate fractionation has yet been found (Nielsen et al., 2014). The explanation may relate to irradiation in the early circumstellar disk.

Evidence that the Moon does not carry a heavy isotopic composition as a result of boiling during the giant impact is found in the Li and Mg isotopic compositions (Magna et al., 2006; Seitz et al., 2006; Wiechert and Halliday, 2007), which provide no hint of a difference between any of the inner solar system-differentiated planetary objects.

9.02.18   Hidden Reservoirs and the Composition of the Earth

In all of the foregoing discussion, it is assumed that the composition of the BSE as deduced from basalts is representative of the entire silicate Earth. In fact, it may be different from chondrites or our best estimates of its true composition if there are *hidden reservoirs*. It has been argued that this is indeed the case, on the basis of oxygen isotopes. The oxygen isotopic heterogeneity of the solar system is not only of importance for defining meteorite parent bodies. It provides a fingerprint for the material that formed the Earth. The similarity between the Earth and Moon in terms of oxygen isotopes provides powerful evidence for a similar average provenance or equilibration. It is perhaps significant that the only chondrites with an oxygen isotopic composition like that of Earth are the enstatite chondrites. This has led to a variety of Earth models based on a total composition that is highly reduced and similar to that of the enstatite chondrites (e.g., Javoy, 1999). Because the mantle and crust of the Earth sampled by magmas and xenoliths are inconsistent with this composition, the 'enstatite chondrite Earth' has to have hidden reservoirs (customarily located in the lower mantle and hence not sampled) that are compositionally distinct from anything we can readily measure.

Hidden reservoir models are of little use scientifically because they are untestable. Further evidence of a link between the Earth and enstatite chondrites has, however, come from nitrogen (Marty et al., 2003) and chromium (Shukolyukov and Lugmair, 2004) isotopic measurements, adding support to the 'hidden reservoir' concept. Recently, a hidden reservoir of different composition has been proposed by Tolstikhin and Hofmann (2005) to explain noble gas isotope systematics. More compelling is the evidence that the BSE as sampled is slightly different from chondrites in terms of ^{142}Nd atomic abundance, possibly reflecting a different $^{146}Sm/^{142}Nd$ in the early solar system (Boyet and Carlson, 2005). One explanation given is that the Earth contains a hidden primordial reservoir with complementary lower $^{146}Sm/^{142}Nd$ balancing the higher $^{146}Sm/^{142}Nd$ of the silicate Earth as sampled by basalts and continents. The apparent model age of this reservoir is 30 Ma after the start of the solar system but this would have to predate the Moon-forming giant impact, which seems unlikely.

Melting as a result of the giant impact, followed by settling of majoritic garnet or silicate perovskites in the magma ocean, has been proposed as a mechanism for forming the primitive upper mantle with high, nonchondritic Mg/Si ratio (e.g., Herzberg et al., 1988; Ohtani et al., 1986; Ringwood, 1979)
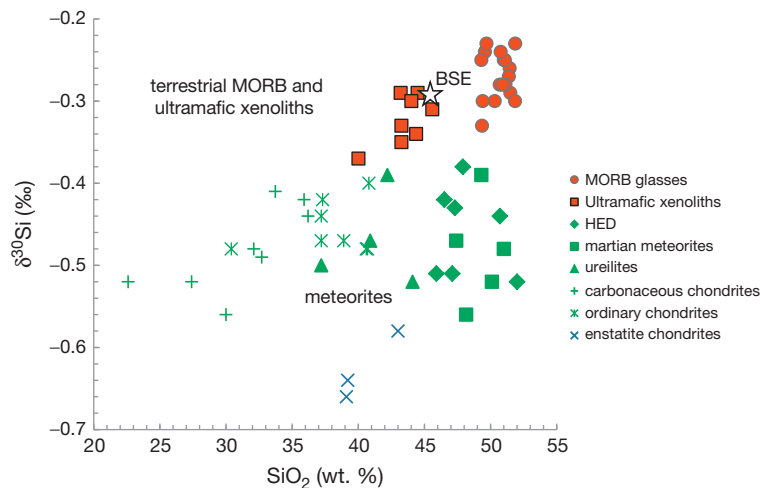

Figure 22   Silicon isotopic compositions of meteorites (Armytage et al., 2011) compared to average data defining the composition of the BSE (Savage et al., 2010).

and a complementary 'hidden' lower mantle reservoir. If substantial fractional crystallization of the magma ocean occurred, however, subsequent remixing must have removed most of the material segregated to the lower mantle because of the observation that the ratios of the refractory lithophile elements in the upper mantle are chondritic. The question is, however, could a small amount of undetected fractionation have shifted the Sm/Nd ratio of the silicate Earth sufficiently to generate the observed [142]Nd anomaly? Crystal–melt partition coefficients for majorite and for $CaSiO_3$ and $(Mg,Fe)SiO_3$ perovskites have been measured by Corgne and Wood (2004), Liebske et al. (2005), and Walter et al. (2004) and applied to calculate the maximum volumes of 'hidden' majorite or perovskite that could be present in the lower mantle, given the compositional constraints derived from the upper mantle. In the case of majorite, the maximum allowable hidden reservoir is 14% of the mantle volume (Corgne and Wood, 2004) while the maximum extent of combined calcium and magnesium silicate perovskite fractionation is about 10% (Liebske et al., 2005; Walter et al., 2004). In neither case is the 'hidden' amount sufficient to explain the nonchondritic Mg/Si ratio of the observable BSE (Figure 23).

Interestingly, the hidden reservoir would in both cases have a higher Sm/Nd ratio than the BSE, which is the wrong direction to explain the [142]Nd anomaly of the BSE. This leads, however, to the possibility that dense high-pressure melts (complementary to solid majorite and perovskite) could remain isolated at great depths and generate hidden reservoirs (e.g., Suzuki and Ohtani, 2003, and references therein). Recent molecular dynamics simulations in the $MgSiO_3$ system (Stixrude and Kirko, 2005) suggest that the density contrast between melt and crystals decreases with increasing pressure, such that a density crossover near the base of the mantle could occur. Hofmann et al. (2005) had proposed that downward migration of such dense melts formed in the deep mantle in equilibrium with Ca perovskite could have created a deep 'missing' reservoir unradiogenic in Pb (with a U/Pb ratio lower than that of PUM) as required to balance the Pb composition of the bulk MORB and OIB source reservoirs. It would

have high Nd/Sm ratio and could hence be the missing sub-chondritic [142]Nd/[144]Nd reservoir (Boyet and Carlson, 2005).

There are, however, problems preserving any distinct mantle reservoir from this early in the Earth's history. After the Moon formed, there would have been tidal interactions with the Earth that would have caused strong heating of the lower mantle in particular (Zahnle et al., 2006). Mantle overturn and melting should have been especially vigorous eliminating any early heterogeneity. Therefore, explanations for the Nd isotopic based on hidden reservoirs are at present very tentative.

9.02.19   Concluding Overview

1. The solar system formed because the angular momentum of the collapsing portion of a molecular cloud was transferred to a swirling disk of gas and debris left over from the proto-Sun. The disk experienced strong heating from the T-Tauri stage of irradiation and from frictional heating as material was being rapidly swept in toward the hot new Sun. This led to strong depletions in moderately volatile elements close in to the Sun.

2. The Earth was built from differentiated planetary embryos that formed from this volatile-depleted dust in the inner solar system. Such embryos and their metallic cores formed extremely early. The latest [82]Hf–[182]W chronometry provides evidence of timescales of <2 Ma for iron meteorite parent bodies. Mars may also have formed this quickly. These bodies almost certainly melted and differentiated as a result of the decay of short-lived nuclides in particular [26]Al and [60]Fe.

3. Chondrites are the most abundant form of meteorite that strikes the Earth. They have relative concentrations of nonvolatile elements that are broadly similar to those found in the Sun. They represent a convenient reference for the bulk composition of the Earth. However, though primitive, they are not early. They must have formed at least 1–3 Ma after the start of the solar system because the
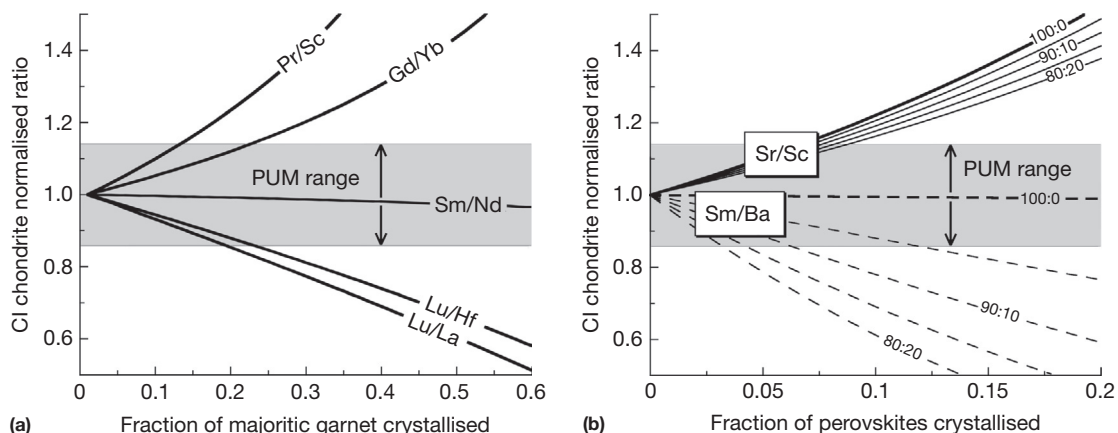

Figure 23   The effects of perovskite fractionation on Sm/Nd and Lu/Hf ratios.

chondrules they contain provide evidence of an epoch of formation in the dusty disk or solar nebula at this time.

4. The Earth accreted via a stochastic series of planetary collisions over tens of millions of years. The final major accretion stage was the Moon-forming giant impact currently estimated at between 70 and 110 Ma after the start of the solar system, when the last roughly 10% of the Earth was added.

5. The chemical composition of the solar system is defined using spectroscopic measurements of the Sun combined with laboratory measurements of chondritic meteorites. All of the stable elements and isotopes are present within our solar system and their relative abundance provides powerful evidence in support of the theories of nuclear stability in the stars and of stellar nucleosynthesis.

6. The density of the Earth combined with estimates of its core size leads to the conclusion that it must be approximately chondritic in its relative concentrations of refractory elements. Similarly, the chemical composition of the BSE, which is well constrained from measurements of mantle peridotites and basalts, exhibits ratios of refractory lithophile elements that are the same as in chondritic meteorites, the Moon, and the silicate portion of Mars.

7. The BSE is depleted in volatile elements relative to chondrites, and it has Mg/Si slightly greater and Mg/refractory lithophile elements slightly lower than chondritic. Depletions of the BSE in refractory siderophile elements are due to their sequestration in the core.

8. By using the chondritic reference model for refractory elements in the Earth, we can calculate the partitioning of siderophile elements between the core and the mantle. The results may then be used in conjunction with experimental liquid metal–liquid silicate partition coefficients to estimate the conditions of core segregation. This exercise requires the assumption that almost all of the core formed in equilibrium with the mantle. Partition coefficients depend on pressure and temperature, and the depletions of the BSE in siderophile elements can only be matched by very high pressures and temperatures.

9. Results imply segregation of the core at the base of a deep magma ocean that extended to 30–40% of the depth of the mantle in the growing earth. The bottom of the magma ocean was by definition below the peridotite liquidus temperature and the constraints this imposes leads to the requirement that the Earth became more oxidized during accretion. The BSE composition can only be matched if the oxidation state of the Earth changed as it grew. The resultant core contains about 4% Si, thus indicating that it contains substantial Si and is a major reason for the superchondritic Mg/Si of the BSE.

10. As the Earth accreted, it would, when it reached the current-day size of Mars, have begun to crystallize silicate perovskites close to the core–mantle boundary. The strong affinity of $(Mg,Fe)SiO_3$ perovskite for ferric iron means that crystallization of this phase forces disproportionation of Fe^{2+} into Fe^{3+} plus metal. This is one mechanism for oxidizing the Earth during accretion since progressive growth through impact would have led to the release of Fe^{3+} to the magma ocean and of metal to the core. This

mechanism also could explain the observation that the mantle of the Earth is at a higher oxygen fugacity than the mantles of Mars and the Moon.

11. The Moon-forming giant impact did not result in any significant losses of slightly volatile elements such as Li, Mg, and Fe.

12. The similarity between the O, Si, Ti, Cr, and W isotopic compositions of the Earth and Moon could have resulted from isotopic equilibration between the materials accreting to form the Moon with the proto-Earth. An alternative is that radically different giant impact scenarios need to be considered.

13. Major losses of volatiles affected Earth during its accretion, including losses of early-formed atmospheres. Such losses are apparent from Xe isotopic compositions and the strongly nonchondritic proportions of H/C/N in the silicate Earth ratios.

14. The late U–Pb age for the Earth is consistent with a giant impact at 70–110 Ma. The difference between Hf–W chronology and U–Pb chronology may reflect changes in partitioning during the final stages of core formation, or W isotopes reflect the effects of disequilibrium during accretion by core–core merging.

15. There is evidence that the Earth may be nonchondritic because of impact erosion of its outer portions during accretion. If this is the case, the budgets for incompatible elements including all heat-producing elements U, Th, and K have been overestimated, potentially by almost a factor of 2.

16. Budgets for hidden volatiles are closely related to those of U and K. Impact erosion models would lead to calculated mantle–water budgets of about 1 ocean mass, whereas standard chondritic models yield mantle–water budgets of nine ocean masses.

17. After the giant impact, crystallization of the Earth would have led to the production of majoritic garnet in the transition zone and of $(Mg,Fe)SiO_3$ and $CaSiO_3$ perovskites in the lower mantle. Crystal–liquid partition coefficients for these phases can be used to estimate the extent of any long-lived 'hidden' reservoir produced in the lower mantle after mantle crystallization. Results indicate a maximum extent of majorite crystallization of 14% of mantle volume and of perovskite fractionation of 10% could be hidden without perturbing the chondritic refractory lithophile element ratios of the BSE.

18. A 'hidden' reservoir with superchondritic Nd/Sm required to balance a putative chondritic BSE could not be perovskite or majorite since these phases all prefer Sm over Nd. One possibility would be isolation and freezing of dense high-pressure melts (complementary to perovskite) in the lower mantle. Such a low-volume reservoir would have appropriate Nd/Sm to generate superchondritic $^{142}Nd/^{144}Nd$ in the remaining BSE. However, the preservation of such a reservoir is hard to reconcile with the strong tidal melting anticipated for the deep Earth following Moon formation. Furthermore, the ^{142}Nd effects can be explained by small isotopic or elemental (Sm/Nd) differences between the Earth and chondrites, as exemplified by other lines of evidence.

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