

1.20

The Origin and Earliest History of the Earth

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1.20.1 INTRODUCTION

The purpose of this chapter is to explain the various lines of geochemical evidence relating to the origin and earliest development of the Earth, while at the same time clarifying current limitations on these constraints. The Earth's origins are to some extent shrouded in greater uncertainty than those of Mars or the Moon because, while vastly more accessible and extensively studied, the geological record of the first 500 Myr is almost entirely missing. This means that we have to rely heavily on theoretical modeling and geochemistry to determine the mechanisms and timescales involved. Both of these approaches have yielded a series of, sometimes strikingly different, views about Earth's origin and early evolution that have seen significant change every few years. There has been a great deal of discussion and debate in the past few years in particular, fueled by new kinds of data and more powerful computational codes.

The major issues to address in discussing the origin and early development of the Earth are as follows:

- (i) What is the theoretical basis for our understanding of the mechanisms by which the Earth accreted?
- (ii) What do the isotopic and bulk chemical compositions of the Earth tell us about the Earth's accretion?
- (iii) How are the chemical compositions of the early Earth and the Moon linked? Did the formation of the Moon affect the Earth's composition?
- (iv) Did magma oceans exist on Earth and how can we constrain this from geochemistry?
- (v) How did the Earth's core form?
- (vi) How did the Earth acquire its atmosphere and hydrosphere and how have these changed?
- (vii) What kind of crust might have formed in the earliest stages of the Earth's development?
- (viii) How do we think life first developed and how might geochemical signatures be used in the future to identify early biological processes?

Although these issues could, in principle, all be covered in this chapter, some are dealt with in more detail in other chapters and, therefore, are given only cursory treatment here. Furthermore, there are major gaps in our knowledge that render a comprehensive overview unworkable. The nature of the early crust (item (vii)) is poorly constrained, although some lines of evidence will be mentioned. The nature of the earliest life forms

(item (viii)) is so loaded with projections into underconstrained hypothetical environments that not a great deal can be described as providing a factual basis suitable for inclusion in a reference volume at this time. Even in those areas in which geochemical constraints are more plentiful, it is essential to integrate them with astronomical observations and dynamic (physical) models of planetary growth and primary differentiation. In some cases, the various theoretical dynamic models can be tested with isotopic and geochemical methods. In other cases, it is the Earth's composition itself that has been used to erect specific accretion paradigms. Therefore, much of this background is provided in this chapter.

All these models and interpretations of geochemical data involve some level of assumption in scaling the results to the big picture of the Earth. Without this, one cannot erect useful concepts that address the above issues. It is one of the main goals of this chapter to explain what these underlying assumptions are. As a consequence, this chapter focuses on the range of interpretations and uncertainties, leaving many issues "open." The chapter finishes by indicating where the main sources of uncertainty remain and what might be done about these in the future.

1.20.2 OBSERVATIONAL EVIDENCE AND THEORETICAL CONSTRAINTS PERTAINING TO THE NEBULAR ENVIRONMENT FROM WHICH EARTH ORIGINATED

1.20.2.1 Introduction

The starting place for all accretion modeling is the circumstellar disk of gas and dust that formed during the collapse of the solar nebula. It has been theorized for a long time that a disk of rotating circumstellar material will form as a normal consequence of transferring angular momentum during cloud collapse and star formation. Such disks now are plainly visible around young stars in the Orion nebula, thanks to the Hubble Space Telescope (McCaughrean and O'Dell, 1996). However, circumstellar disks became clearly detectable before this by using ground-based interferometry. If the light of the star is canceled out, excess infrared can be seen being emitted from the dust around the disk. This probably is caused by radiation from the star itself heating the disk.

Most astronomers consider nebular timescales to be of the order of a few million years (Podosek and Cassen, 1994). However, this is poorly constrained because unlike dust, gas is very difficult to detect around other stars. It may be acceptable to assume that gas and dust stay together for a portion of nebular history. However, the dust in some of these disks is assumed to be the secondary product of planetary accretion. Colliding planetesimals and planets are predicted to form at an early stage, embedded in the midplane of such optically thick disks (Wetherill and Stewart, 1993; Weidenschilling, 2000). The age of Beta Pictoris (Artymowicz, 1997; Vidal-Madjar *et al.*, 1998) is rather unclear but it is probably more than ~20 Myr old (Hartmann, 2000) and the dust in this case probably is secondary, produced as a consequence of collisions. Some disks around younger (<10 Myr) stars like HR 4796A appear to show evidence of large inner regions entirely swept clear of dust. It has been proposed that in these regions the dust already may be incorporated into planetary objects (Schneider *et al.*, 1999). The Earth probably formed by aggregating planetesimals and small planets that had formed in the midplane within such a dusty disk.

1.20.2.2 Nebular Gases and Earth-like versus Jupiter-like Planets

What features of Earth's composition provide information on this early circumstellar disk of dust that formed after the collapse of the solar nebula? The first and foremost feature of the Earth that relates to its composition and accretion is its size and density. Without any other information, this immediately raises questions about how Earth could have formed from the same disk as Jupiter and Saturn. The uncompressed density of the terrestrial planets is far higher than that of the outer gas and ice giant planets. The four most abundant elements making up ~90% of the Earth are oxygen, magnesium, silicon, and iron. Any model of the Earth's accretion has to account for this. The general explanation is that most of the growth of terrestrial planets postdated the loss of nebular gases from the disk. However, this is far from certain. Some solar-like noble gases were trapped in the Earth and although other explanations are considered (Tieloff *et al.*, 2000; Podosek *et al.*, 2003), the one that is most widely accepted is that the nebula was still present at the time of Earth's accretion (Harper and Jacobsen, 1996a). How much nebular gas was originally present is unclear. There is xenon-isotopic evidence that the vast majority (>99%) of Earth's noble gases were lost subsequently (Ozima and Podosek, 1999; Porcelli and Pepin, 2000). A detailed discussion of this is provided in Chapter 4.11. The dynamics and

timescales for accretion will be very different in the presence or absence of nebular gas. In fact, one needs to consider the possibility that even Jupiter-sized gas giant planets may have formed in the terrestrial planet-forming region and were subsequently lost by being ejected from the solar system or by migrating into the Sun (Lin *et al.*, 1996). More than half the extrasolar planets detected are within the terrestrial planet-forming region of their stars, and these all are, broadly speaking, Jupiter-sized objects (Mayor and Queloz, 1995; Boss, 1998; Lissauer, 1999). There is, of course, a strong observational bias: we are unable to detect Earth-sized planets, which are not massive enough to induce a periodicity in the observed Doppler movement of the associated star or large enough to significantly occult the associated star (Boss, 1998; Seager, 2003).

For many years, it had been assumed that gas dissipation is a predictable response to radiative effects from an energetic young Sun. For example, it was theorized that the solar wind would have been ~100 times stronger than today and this, together with powerful ultraviolet radiation and magnetic fields, would have driven gases away from the disk (e.g., Hayashi *et al.*, 1985). However, we now view disks more as dynamic "conveyor belts" that transport mass *into* the star. The radiative effects on the materials that form the terrestrial planets may in fact be smaller than previously considered. Far from being "blown off" or "dissipated," the gas may well have been lost largely by being swept into the Sun or incorporated into planetary objects—some of which were themselves consumed by the Sun or ejected (Murray *et al.*, 1998; Murray and Chaboyer, 2001). Regardless of how the solar nebula was lost, its former presence, its mass, and the timing of Earth's accretion relative to that of gas loss from the disk will have a profound effect on the rate of accretion, as well as the composition and physical environment of the early Earth.

1.20.2.3 Depletion in Moderately Volatile Elements

Not only is there a shortage of nebular gas in the Earth and terrestrial planets today but the moderately volatile elements also are depleted (Figure 1) (Gast, 1960; Wasserburg *et al.*, 1964; Cassen, 1996). As can be seen from Figure 2, the depletion in the moderately volatile alkali elements, potassium and rubidium in particular, is far greater than that found in any class of chondritic meteorites (Taylor and Norman, 1990; Humayun and Clayton, 1995; Halliday and Porcelli, 2001; Drake and Righter, 2002). The traditional explanation is that the inner "terrestrial" planets accreted where it was hotter,

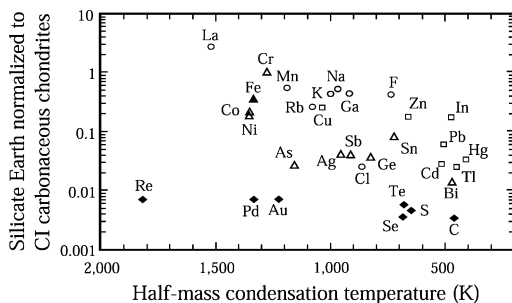


Figure 1 The estimated composition of the silicate portion of the Earth as a function of condensation temperature normalized to CI values in [Anders and Grevesse \(1989\)](#). Open circles: lithophile elements; shaded squares: chalcophile elements; shaded triangles: moderately siderophile elements; solid diamonds: highly siderophile elements. The spread in concentration for a given temperature is thought to be due to core formation. The highly siderophile element abundances may reflect a volatile depleted late veneer. Condensation temperatures are from [Newsom \(1995\)](#).

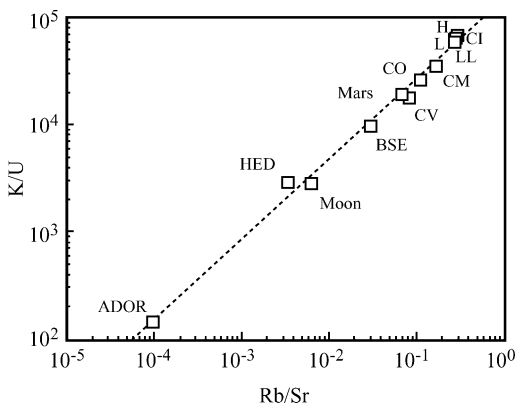


Figure 2 Comparison between the K/U and Rb/Sr ratios of the silicate Earth compared with other solar system objects. ADOR: Angra dos Reis; HED: howardite-eucrite-diogenite parent body; BSE: bulk silicate Earth; CI, CM, CV, CO, H, L, and LL are all classes of chondrites (source [Halliday and Porcelli, 2001](#)).

within the so-called “ice line” ([Cassen, 1996](#); [Humayun and Cassen, 2000](#)). For several reasons, it has long been assumed 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, as well 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](#)), which somehow were lost subsequently. To what extent these volatile elements

condensed on grains that are now in the outer solar system and may be represented by interplanetary dust particles ([Jessberger et al., 1992](#)) is unclear.

Nowadays, inner solar system models are undergoing major rethinking because of new observations of stars, theoretical models, and data from meteorites. It is important to keep track of the models and observational evidence on stars and disks as this continuously changes with greater resolution and detectability. The new data provide important insights into how our solar system may have developed. As of early 2000s, the linkage between temperature in the disk and accretion dynamics is anything but clear. There is no question that transient heating was important on some scale. But a large-scale hot nebula now is more difficult to accommodate. The depletion in volatile elements in the Earth is probably the result of several different processes and the latest astronomical evidence for these is summarized below. To understand these processes one has to have some idea of how solar mass stars and their disks are thought to “work.”

1.20.2.4 Solar Mass Stars and Heating of the Inner Disk

Solar mass stars are thought to accrete rapidly. The pre-main-sequence solar mass *protostar* probably forms from collapse of a portion of a molecular cloud onto a “cloud core” in something like 10^5 yr ([Hartmann, 2000](#)). Strong outflows and jets are sometimes observable. Within a few hundred thousand years such protostars have developed into class I young stellar objects, as can be seen in the Orion nebula. These objects already have disks and are called *proplyds*. Remaining material from the cloud will accrete onto both the disk and onto the star itself. The disk also accretes onto the star and, as it does so, astronomers can track the accretion rate from the radiation produced at the innermost margin of the disk. In general terms, the accretion rate shows a very rough decrease with age of the star. From this, it can be shown that the mass of material being accreted from the disk onto the star is about the same as the minimum mass solar nebula estimated for our solar system ([Hartmann, 2000](#)).

This “minimum mass solar nebula” is defined to be the minimum amount of hydrogen-helium gas with dust, in bulk solar system proportions, that is needed in order to form our solar system’s planets ([Hoyle, 1960](#); [Weidenschilling, 1977a](#)). It is calculated by summing the assumed amount of metal (in the astronomical sense, i.e., elements heavier than hydrogen and helium) in all planets and adding enough hydrogen and helium to bring it up to solar composition. Usually, a value of 0.01 solar masses is taken to be the “minimum mass” ([Boss, 1990](#)). The strongest constraint on

the value is the abundance of heavy elements in Jupiter and Saturn. This is at least partially independent of the uncertainty of whether these elements are hosted in planetary cores. Such estimates for the minimum mass solar nebula indicate that the disk was at least a factor of 10 more massive than the total mass of the current planets. However, the mass may have been much higher and because of this the loss of metals during the planet-forming process sometimes is factored in. There certainly is no doubt that some solids were consumed by the protosun or ejected into interstellar space. This may well have included entire planets. Therefore, a range of estimates for the minimum mass of 0.01–0.1 solar masses can be found. The range reflects uncertainties that can include the bulk compositions of the gas and ice giant planets (Boss, 2002), and the amount of mass loss from, for example, the asteroid belt (Chambers and Wetherill, 2001).

Some very young stars show enormous rapid changes in luminosity with time. These are called *FU Orionis* objects. They are young Sun-like stars that probably are temporarily accreting material at rapid rates from their surrounding disks of gas and dust; they might be consuming planets, for example (Murray and Chaboyer, 2001). Over a year to a decade, they brighten by a hundred times, then stay bright for a century or so before fading again (Hartmann and Kenyon, 1996). A protostar may go through this sequence many times before the accretion disk and surrounding cloud are dispersed. Radiation from the star on to the disk during this intense stage of activity could be partially responsible for volatile depletions in the inner solar system (Bell *et al.*, 2000), but the relative importance of this versus other heating processes has not been evaluated. Nor is it known if our Sun experienced such dramatic behavior.

T-Tauri stars also are pre-main-sequence stars. They are a few times 10^5 yr to a few million years in age and the *T-Tauri* effect appears to develop after the stages described above. They have many of the characteristics of our Sun but are much brighter. Some have outflows and produce strong stellar winds. Many have disks. The *T-Tauri* effect itself is poorly understood. It has long been argued that this is an early phase of heating of the inner portions of the disk. However, such disks are generally thought to have inclined surfaces that dip in toward the star (Chiang and Goldreich, 1997, 1999). It is these surfaces that receive direct radiation from the star and produce the infrared excess observed from the dust. The *T-Tauri* stage may last a few million years. Because it heats the disk surface it may not have any 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* be produced from

compressional effects. The thermal effects 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 1,500 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. More recent modeling includes the detailed studies by Nelson *et al.* (1998, 2000), which provide a very similar overall picture. Of course, if the material is being swept into the Sun, one has to ask how much of the gas and dust would be retained from this portion of the disk. This process would certainly be very early. The timescales for subsequent cooling at 1 AU would have been very short (10^5 yr). Boss (1990), Cassen (2001), and Chiang *et al.* (2001) have independently modeled the thermal evolution of such a disk and conclude that in the midplane, where planetesimals are likely to accrete, temperatures will drop rapidly. Even at 1 AU, temperatures will be ~ 300 K after only 10^5 yr (Chiang *et al.*, 2001). Most of the dust settles to the midplane and accretes to form planetesimals over these same short timescales (Hayashi *et al.*, 1985; Lissauer, 1987; Weidenschilling, 2000); the major portion of the solid material may not be heated externally strongly after 10^5 yr.

Pre-main-sequence solar mass stars can be vastly (10^4 times) more energetic in terms of X-ray emissions from solar flare activity in their earliest stages compared with the most energetic flare activity of the present Sun (Feigelson *et al.*, 2002a). With careful sampling of large populations of young solar mass stars in the Orion nebula it appears that this is the normal behavior of stars like our Sun. This energetic solar flare activity is very important in the first million years or so, then decreases (Feigelson *et al.*, 2002a). From this it has been concluded that the early Sun had a 10^5 -fold enhancement in energetic protons which may have contributed to short-lived nuclides (Lee *et al.*, 1998; McKeegan *et al.*, 2000; Gounelle *et al.*, 2001; Feigelson *et al.*, 2002b; Leya *et al.*, 2003).

Outflows, jets, and X-winds may produce a flux of material that is scattered across the disk from the star itself or the inner regions of the disk (Shu *et al.*, 1997). The region between the outflows and jets and the disk may be subject to strong magnetic fields that focus the flow of incoming material from the disk as it is being accreted onto the star and then project it back across the disk. These “X-winds” then produce a conveyor belt that cycle material through a zone where it is vaporized before being condensed and dispersed as grains of

high-temperature condensates across the disk. If material from areas close to the Sun is scattered across the disk as proposed by [Shu *et al.* \(1997\)](#) it could provide a source for early heated and volatile depleted objects such as calcium-, aluminum-rich refractory inclusions (CAIs) and chondrules, as well as short-lived nuclides, regardless of any direct heating of the disk at 1 AU.

Therefore, from all of the recent examples of modeling and observations of circumstellar disks a number of mechanisms can be considered that might contribute to very early heating and depletion of moderately volatile elements at 1 AU. However, some of these are localized processes and the timescales for heating are expected to be short in the midplane.

It is unclear to what extent one can relate the geochemical evidence of extreme volatile depletion in the inner solar system ([Figure 2](#)) to these observations of processes active in other disks. It has been argued that the condensation of iron grains would act as a thermostat, controlling temperatures and evening out gradients within the inner regions of the solar nebula ([Wood and Morfill, 1988](#); [Boss, 1990](#); [Wood, 2000](#)). Yet the depletion in moderately volatile elements between different planetary objects is highly variable and does not even vary systematically with heliocentric distance ([Palme, 2000](#)). The most striking example of this is the Earth and Moon, which have very different budgets of moderately volatile elements. Yet they are at the same heliocentric distance and appear to have originated from an identical mix of solar system materials as judged from their oxygen isotopic composition ([Figure 3](#)) ([Clayton and Mayeda, 1975](#); [Wiechert *et al.*, 2001](#)). Oxygen isotopic compositions are highly heterogeneous among inner solar system objects

([Clayton *et al.*, 1973](#); [Clayton, 1986, 1993](#); see [Chapter 1.06](#)). Therefore, the close agreement in oxygen isotopic composition between the Earth and Moon ([Clayton and Mayeda, 1975](#)), recently demonstrated to persist to extremely high precision ([Figure 3](#)), is a striking finding that provides good evidence that the Earth and Moon were formed from material of similar origin and presumably similar composition ([Wiechert *et al.*, 2001](#)). The very fact that chondritic materials are not as heavily depleted in moderately volatile elements as the Earth and Moon provides evidence that other mechanisms of volatile loss must exist. Even the enstatite chondrites, with exactly the same oxygen isotopic composition as the Earth and Moon, are not as depleted in moderately volatile alkali elements ([Newsom, 1995](#)). The geochemical constraints on the origins of the components that formed the Earth are discussed below. But first it is necessary to review some of the history of the theories about how the Earth's chemical constituents were first incorporated into planetary building material.

1.20.2.5 The “Hot Nebula” Model

The current picture of the early solar system outlined above, with a dynamic dusty disk, enormous gradients in temperature, and a rapidly cooling midplane, is different from that prevalent in geochemistry literature 30 yr ago. The chemical condensation sequences modeled thermodynamically for a nebular gas cooling slowly and perhaps statically from 2,000 K were long considered a starting point for understanding the basic chemistry of the material accreting in the inner solar system ([Grossman and Larimer, 1974](#)). These traditional standard hot solar nebula models assumed that practically speaking *all* of the material in the terrestrial planet-forming region resulted from gradual condensation of such a nebular gas. Because so many of the concepts in the cosmochemistry literature relate to this hot nebula model, it is important to go through the implications of the newer ways of thinking about accretion of chemical components in order to better understand how the Earth was built.

Here are some of the lines of evidence previously used to support the theory of a large-scale hot nebula that now are being reconsidered.

(i) The isotopic compositions of a wide range of elements have long been known to be broadly similar in meteorites thought to come from Mars and the asteroid belt on the one hand and the Earth and Moon on the other. Given that stars produce huge degrees of isotopic heterogeneity it was assumed that the best way to achieve this homogenization was via a well-mixed gas from which all solids and liquids condensed

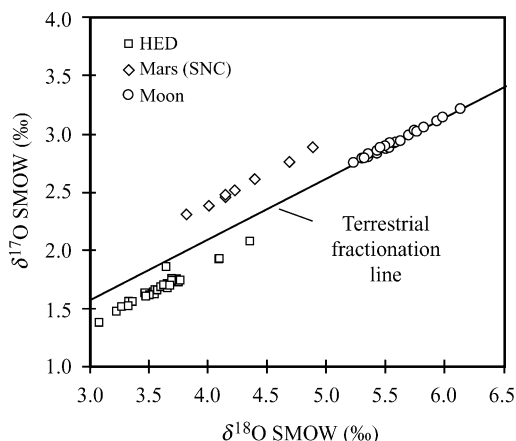


Figure 3 The oxygen isotopic compositions of the Earth and Moon are identical to extremely high precision and well resolved from the compositions of meteorites thought to come from Mars and Asteroid 4 Vesta (sources [Wiechert *et al.*, 2001, 2003](#)).

(Suess, 1965; Reynolds, 1967). However, we know now that chondrites contain presolar grains that cannot have undergone the heating experienced by some of the other components in these meteorites, namely CAIs and chondrules. Presolar grains are unstable in a silicate matrix above a few hundred degrees Celsius (e.g., Mendybaev *et al.*, 2002). The ubiquitous former presence of presolar grains (Huss, 1997; Huss and Lewis, 1995; Nittler, 2003; Nittler *et al.*, 1994) provides unequivocal evidence of dust that has been physically admixed after the formation of the other components (CAIs and chondrules). It is this well-mixed cold dust that forms the starting point for the accretion of chondrite parent bodies, and probably the planets.

(ii) The models of Cameron (1978) using a 1 solar mass disk produced extremely high temperatures ($T > 2,000$ K) throughout most of the nebular disk. Such models fueled the hot nebula model but have been abandoned in favor of minimum mass nebula models. Some such viscous accretion disk models produced very low temperatures at 1 AU because these did not include compressional heating. However, Boss (1990) provided the first comprehensive thermal model including compressional heating and grain opacity, and this model does produce temperatures in excess of 1,500 K in the terrestrial planet region.

(iii) CAIs were found to have the composition of objects that condensed at high temperatures from a gas of solar composition (Grossman, 1972; Grossman and Larimer, 1974). Their old age confirmed that they were the earliest objects to form in the solar system (Göpel *et al.*, 1991, 1994; Amelin *et al.*, 2002). Although most CAIs have bulk compositions broadly consistent with high-temperature condensation (Wänke *et al.*, 1974), nearly all of them have been melted and recrystallized, destroying any textural record of condensation. It now appears that they condensed and then were reheated and possibly partially evaporated, all within a short time. It is suspected by some that these objects condensed at very high temperatures close to the Sun and that they were scattered across the disk to be admixed with other components (Gounelle *et al.*, 2001; Shu *et al.*, 1997). This is far from certain and some “FUN” CAIs have isotopic compositions that cannot be easily reconciled with such a model (MacPherson *et al.*, 1988; see Chapter 1.06). However, the important point is that their old age and refractory nature can be explained in ways other than just with a large-scale hot solar nebula.

(iv) The overall composition of the Earth is volatile-element depleted and this depletion is broadly consistent with that predicted from condensation theory (Cassen, 1996; Humayun and Cassen, 2000; Allègre *et al.*, 2001). However, this agreement has rather little genetic significance. Why should chondrites be less depleted in

volatiles like potassium and rubidium than the terrestrial planets and asteroids (Figure 2) if this is a nebular phenomenon? One explanation is that the chondrites accreted at 2–3 AU, where Boss (1990) shows that the nebula was cooler ($< 1,000$ K). However, this provides no explanation for the extreme depletion in alkalis in eucrites and the Moon. The latter could be related to impact-induced losses (Halliday and Porcelli, 2001) but then the question arises as to whether the Earth’s depletion in alkalis also relates to this in part. There is as yet no basis for distinguishing the volatile depletion that might be produced in planetary collisions (O’Neill, 1991a,b; Halliday and Porcelli, 2001) from that predicted to occur as a result of incomplete condensation of nebular gas.

(v) Strontium isotope differences between early very rubidium-depleted objects and planetesimals such as CAIs, eucrites and angrites have long been thought to provide evidence that they must have been created within a high-Rb/Sr environment such as the solar nebula but at a temperature above the condensation of rubidium (Gray *et al.*, 1973; Wasserburg *et al.*, 1977b; Lugmair and Galer, 1992; Podosek *et al.*, 1991). The timescales over which the solar nebula has to be maintained above the condensation temperature of rubidium for this to work are a few million years. However, there is growing evidence that both cooling of the inner nebula and planetesimal growth may be very fast. Excluding the thermal effects from dense planetary atmospheres and the effects of planetary collisions, the timescale for major direct heating of the inner disk itself may be rather short (10^5 yr), but this view could change again with new observational data.

1.20.2.6 The “Hot Nebula” Model and Heterogeneous Accretion

It was at one time thought that even the terrestrial planets themselves formed directly by condensation from a hot solar nebula. This led to a class of models called heterogeneous accretion models, in which the composition of the material accreting to form the Earth changed with time as the nebula cooled. Eucken (1944) proposed such a heterogeneous accretion model in which early condensed metal formed a core to the Earth around which silicate accreted after condensation at lower temperatures. In this context the silicate-depleted, iron-enriched nature of Mercury makes sense as a body that accreted in an area of the solar nebula that was kept too hot to condense the same proportion of silicate as is found in the Earth (Lewis, 1972; Grossman and Larimer, 1974). Conversely, the lower density of Mars could partly reflect collection of an excess of silicate in cooler reaches of the inner solar nebula. So the

concept of heliocentric “feeding zones” for accretion fitted this nicely. The discovery that iron metal condenses at a lower temperature than some refractory silicates made these models harder to sustain (Levin 1972). Nevertheless, a series of models involving progressive heterogeneous accretion at successively lower condensation temperatures were developed for the Earth (e.g., Turekian and Clark, 1969; Smith, 1977, 1980).

These models “produced” a zoned Earth with an early metallic core surrounded by silicate, without the need for a separate later stage of core formation. The application of condensation theory to the striking variations in the densities and compositions of the terrestrial planets, and how metal and silicate form in distinct reservoirs has been seen as problematic for some time. Heterogeneous accretion models require fast accretion and core formation if these processes reflect condensation in the nebula and such timescales can be tested with isotopic systems. The timescales for planetary accretion now are known to be far too long for an origin by partial condensation from a hot nebular gas. Nevertheless, heterogeneous accretion models have become embedded in the textbooks in Earth sciences (e.g., Brown and Mussett, 1981) and astronomy (e.g., Seeds, 1996).

An important development stemming from heterogeneous accretion models is that they introduced the concept that the Earth was built from more than one component and that these may have been accreted in separate stages. This provided an apparent answer to the problem of how to build a planet with a reduced metallic core and an oxidized silicate mantle. However, heterogeneous accretion is hard to reconcile with modern models for the protracted dynamics of terrestrial planet accretion compared with the shortness of nebular timescales. Therefore, they have been abandoned by most scientists and are barely mentioned in modern geochemistry literature any more.

1.20.3 THE DYNAMICS OF ACCRETION OF THE EARTH

1.20.3.1 Introduction

Qualitatively speaking, all accretion involves several stages, although the relative importance must differ between planets and some mechanisms are only likely to work under certain conditions that currently are underconstrained. Although the exact mechanisms of accretion of the gas and ice giant planets are poorly understood (Boss, 2002), all such objects need to accrete very rapidly in order to trap large volumes of gas before dissipation of the solar nebula.

Probably this requires timescales of $<10^7$ yr (Podosek and Cassen, 1994). In contrast, the most widely accepted dynamic models advocated for the formation of the terrestrial planets (Wetherill, 1986), involve protracted timescales $\sim 10^7$ – 10^8 yr. Application of these same models to the outer planets would mean even longer timescales. In fact, some of the outermost planets would not have yet formed. Therefore, the bimodal distribution of planetary density and its striking spatial distribution appear to require different accretion mechanisms in these two portions of the solar system. However, one simply cannot divide the accretion dynamics into two zones. A range of rate-limiting processes probably controlled accretion of both the terrestrial and Jovian planets and the debates about which of these processes may have been common to both is far from resolved. There almost certainly was some level of commonality.

1.20.3.2 Starting Accretion: Settling and Sticking of Dust at 1 AU

In most models of accretion at 1 AU, the primary process being studied is the advanced stage of gravitationally driven accretion. However, one first has to consider how accretion got started and in many respects this is far more problematic. Having established that the disk was originally dominated by gas and dust, it must be possible to get these materials to combine and form larger objects on a scale where gravity can play a major role. The starting point is gravitational settling toward the midplane. The dust and grains literally will “rain” into the midplane. The timescales proposed for achieving an elevated concentration of dust in the midplane of the disk are rapid, $\sim 10^3$ yr (Hayashi *et al.*, 1985; Weidenschilling, 2000). Therefore, within a very short time the disk will form a concentrated midplane from which the growth of the planets ultimately must be fed.

Laboratory experiments on sticking of dust have been reviewed by Blum (2000), who concluded that sticking microscopic grains together with static and Van der Waals forces to build millimeter-sized compact objects was entirely feasible. However, building larger objects (fist- to football-pitch-sized) is vastly more problematic. Yet it is only when the objects are roughly kilometer-sized that gravity plays a major role. Benz (2000) has reviewed the dynamics of accretion of the larger of such intermediate-sized objects. The accretion of smaller objects is unresolved.

One possibility is that there was a “glue” that made objects stick together. Beyond the ice line, this may indeed have been relatively easy. But in the terrestrial planet-forming region in which

early nebular temperatures were $>1,000$ K such a cement would have been lacking in the earliest stages. Of course, it already has been pointed out that cooling probably was fast at 1 AU. However, even this may not help. The baseline temperature in the solar system was then, and is now, above 160 K (the condensation temperature of water ice), so that no matter how rapid the cooling rate, the temperature would not have fallen sufficiently. The “stickiness” required rather may have been provided by carbonaceous coatings on silicate grains which might be stable at temperatures of >500 K (Weidenschilling, 2000). Waiting for the inner solar nebula to cool before accretion proceeds may not provide an explanation, anyway, because dynamic simulations provide evidence that these processes must be completed extremely quickly. The early Sun was fed with material from the disk and Weidenschilling (1977b, 2000) has argued that unless the dust and small debris are incorporated into much larger objects very quickly (in periods of less than $\sim 10^5$ yr), they will be swept into the Sun. Using a relatively large disk, Cuzzi *et al.* (2003) propose a mechanism for keeping a small fraction of smaller CAIs and fine debris in the terrestrial planet-forming region for a few million years. Most of the dust is lost. Another way of keeping the solids dust from migrating would have been the formation of gaps in the disk, preventing transfer to the Sun. The most obvious way of making gaps in the disk is by planet formation. So there is a “chicken and egg problem.” Planets cannot form without gaps. Gaps cannot form without planets. This is a fundamental unsolved problem of terrestrial planetary accretion dynamics that probably deserves far more attention than has been given so far. Some, as yet uncertain, mechanism must exist for sticking small bodies together at 1 AU.

1.20.3.3 Starting Accretion: Migration

One mechanism to consider might be planetary migration (Lin *et al.*, 1996; Murray *et al.*, 1998). Observations of extrasolar planets provide strong evidence that planets migrate after their formation (Lin *et al.*, 1996). Resonances are observed in extrasolar planetary systems possessing multiple Jupiter-like planets. These resonances can only be explained if the planets migrated after their formation (Murray *et al.*, 1998). Two kinds of models can be considered.

(i) If accretion could not have started in the inner solar system, it might be that early icy and gas rich planets formed in the outer solar system and then migrated in toward the Sun where they opened up gaps in the disk prior to being lost into the Sun. They then left isolated zones of material

that had time to accrete into planetesimals and planets.

(ii) Another model to consider is that the terrestrial planets themselves first started forming early in the icy outer solar system and migrated in toward the Sun, where gaps opened in the disk and prevented further migration. There certainly is evidence from noble gases that Earth acquired volatile components from the solar nebula and this might be a good way to accomplish this.

Both of these models have difficulties, because of the evidence against migration in the inner solar system. First, it is hard to see why the migrating planets in model (i) would not accrete most of the material in the terrestrial planet-forming region, leaving nothing for subsequent formation of the terrestrial planets themselves. Therefore, the very existence of the terrestrial planets would imply that such migration did not happen. Furthermore, there is evidence against migration in general in the inner solar system, as follows. We know that Jupiter had to form fast (<10 Myr) in order to accrete sufficient nebular gas (see Chapter 1.04). Formation of Jupiter is thought to have had a big effect (Wetherill, 1992) causing the loss of $>99\%$ of the material from the asteroid belt (Chambers and Wetherill, 2001). Therefore, there are good reasons for believing that the relative positions of Jupiter and the asteroid belt have been maintained in some approximate sense at least since the earliest history of the solar system. Strong supporting evidence against inner solar system migration comes from the fact that the asteroid belt is zoned today (Gaffey, 1990; Taylor, 1992). ^{26}Al heating is a likely cause of this (Grimm and McSween, 1993; Ghosh and McSween, 1999). However, whatever the reason it must be an early feature, which cannot have been preserved if migration were important.

Therefore, large-scale migration from the outer solar system is not a good mechanism for initiating accretion in the terrestrial planet-forming region unless it predates formation of asteroid belt objects or the entire solar system has migrated relative to the Sun. The outer solar system provides some evidence of ejection of material and migration but the inner solar system appears to retain much of its original “structure.”

1.20.3.4 Starting Accretion: Gravitational Instabilities

Sticking together of dust and small grains might be aided by differences between gas and dust velocities in the circumstellar disk (Weidenschilling, 2000). However, the differential velocities of the grains are calculated to be huge and nobody has been able to simulate this adequately. An early solution that was proposed by Goldreich and Ward (1973) is that gravitational instabilities built up in

the disk. This means that sections of the swirling disk built up sufficient mass to establish an overall gravitational field that prevented the dust and gas in that region from moving away. With less internal differential movement there would have been more chance for clumping together and sticking. A similar kind of model has been advocated on a much larger scale for the rapid growth of Jupiter (Boss, 1997). Perhaps these earlier models need to be looked at again because they might provide the most likely explanation for the onset of terrestrial planet accretion. This mechanism has recently been reviewed by Ward (2000).

1.20.3.5 Runaway Growth

Whichever way the first stage of planetary accretion is accomplished, it should have been followed by *runaway gravitational growth* of these kilometer-scale planetesimals, leading to the formation of numerous Mercury- to Mars-sized planetary embryos. The end of this stage also should be reached very quickly according to dynamic simulations. Several important papers study this phase of planetary growth in detail (e.g., Lin and Papaloizou, 1985; Lissauer, 1987; Wetherill and Stewart, 1993; Weidenschilling, 2000; Kortenkamp *et al.*, 2000). With runaway growth, it is thought that Moon-sized “planetary-embryos” are built over timescales $\sim 10^5$ yr (Wetherill, 1986; Lissauer, 1993; Wetherill and Stewart, 1993). Exhausting the supply of material in the immediate vicinity prevents further runaway growth. However, there are trade-offs between the catastrophic and constructive effects of planetesimal collisions. Benz and Asphaug (1999) calculate a range of “weakness” of objects with the weakest in the solar system being ~ 300 km in size. Runaway growth predicts that accretion will be completed faster, closer to the Sun where the “feeding zone” of material will be more confined. On this basis material in the vicinity of the Earth would accrete into Moon-sized objects more quickly than material in the neighborhood of Mars, for example.

1.20.3.6 Larger Collisions

Additional growth to form Earth-sized planets is thought to require collisions between these “planetary embryos.” This is a stochastic process such that one cannot predict in any exact way the detailed growth histories for the terrestrial planets. However, with Monte Carlo simulations and more powerful computational codes the models have become quite sophisticated and yield similar and apparently robust results in terms of the kinds of timescales that must be

involved. The mechanisms and timescales are strongly dependent on the amount of nebular gas. The presence of nebular gas has two important effects on accretion mechanisms. First, it provides added friction and pressure that speeds up accretion dramatically. Second, it can have the effect of reducing eccentricities in the orbits of the planets. Therefore, to a first approximation one can divide the models for the overall process of accretion into three possible types that have been proposed, each with vastly differing amounts of nebular gas and therefore accretion rates:

(i) *Very rapid accretion in the presence of a huge nebula.* Cameron (1978) argued that the Earth formed with a solar mass of nebular gas in the disk. This results in very short timescales of $< 10^6$ yr for Earth’s accretion.

(ii) *Protracted accretion in the presence of a minimum mass solar nebula.* This is known as the Kyoto model and is summarized nicely in the paper by Hayashi *et al.* (1985). The timescales are 10^6 – 10^7 yr for accretion of all the terrestrial planets. The timescales increase with heliocentric distance. The Earth was calculated to form in ~ 5 Myr.

(iii) *Protracted accretion in the absence of a gaseous disk.* This model simulates the effects of accretion via planetesimal collisions assuming that all of the nebular gas has been lost. Safronov (1954) first proposed this model. He argued that the timescales for accretion of all of the terrestrial planets then would be very long, in the range of 10^7 – 10^8 yr.

Safronov’s model was confirmed with the Monte Carlo simulations of Wetherill (1980), who showed that the provenance of material would be very broad and only slightly different for each of the terrestrial planets (Wetherill, 1994). The timescales for accretion of each planet also would be very similar. By focusing on the solutions that result in terrestrial planets with the correct (broadly speaking) size and distribution and tracking the growth of these objects, Wetherill (1986) noted that the terrestrial planets would accrete at something approaching exponentially decreasing rates. The half-mass accretion time (time for half of the present mass to accumulate) was comparable (~ 5 – 7 Myr), and in reality indistinguishable, for Mercury, Venus, Earth, and Mars using such simulations. Of course these objects, being of different size, would have had different absolute growth rates.

These models did not consider the effects of the growth of gas giant planets on the terrestrial planet-forming region. However, the growth of Jupiter is unlikely to have slowed down accretion at 1 AU (Kortenkamp and Wetherill, 2000). Furthermore, if there were former gas giant planets in the terrestrial planet-forming region

they probably would have caused the terrestrial planets to be ejected from their orbits and lost.

In order to distinguish between these models one has to know the amount of nebular gas that was present at the time of accretion. For the terrestrial planets this is relatively difficult to estimate. Although the Safronov–Wetherill model, which specifically assumes no nebular gas, has become the main textbook paradigm for Earth accretion, the discovery that gas giant planets are found in the terrestrial planet-forming regions of other stars (Mayor and Queloz, 1995; Boss, 1998; Lissauer, 1999; Seager, 2003) has fueled re-examination of this issue. Furthermore, recent attempts of accretion modeling have revealed that terrestrial planets can indeed be formed in the manner predicted by Wetherill but that they have high eccentricities (Canup and Agnor, 1998). Thus, they depart strongly from circular orbits. The presence of even a small amount of nebular gas during accretion has the effect of reducing this eccentricity (Agnor and Ward, 2002). This, in turn, would have sped up accretion. As explained below, geochemical data provide strong support for a component of nebular-like gases during earth accretion.

The above models differ with respect to timing and therefore can be tested with isotopic techniques. However, not only are the models very different in terms of timescales, they also differ with respect to the environment that would be created on Earth. In the first two cases the Earth would form with a hot dense atmosphere of nebular gas that would provide a ready source of solar noble gases in the Earth. This atmosphere would have blanketed the Earth and could have caused a dramatic buildup of heat leading to magma oceans (Sasaki, 1990). Therefore, the evidence from dynamic models can also be tested with compositional data for the Earth, which provide information on the nature of early atmospheres and melting.

1.20.4 CONSTRAINTS FROM LEAD AND TUNGSTEN ISOTOPES ON THE OVERALL TIMING, RATES, AND MECHANISMS OF TERRESTRIAL ACCRETION

1.20.4.1 Introduction: Uses and Abuses of Isotopic Models

Radiogenic isotope geochemistry can help with the evaluation of the above models for accretion by determining the rates of growth of the silicate reservoirs that are residual from core formation. By far the most useful systems in this regard have been the $^{235}\text{U}/^{238}\text{U}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ and ^{182}Hf – ^{182}W systems. These are discussed in detail below.

Other long-lived systems, such as ^{87}Rb – ^{87}Sr , ^{147}Sm – ^{143}Nd , ^{176}Lu – ^{176}Hf , and ^{187}Re – ^{187}Os , have provided more limited constraints (Tilton, 1988; Carlson and Lugmair, 2000), although in a fascinating piece of work, McCulloch (1994) did attempt to place model age constraints on the age of the earth using strontium isotope data for Archean rocks (Jahn and Shih, 1974; McCulloch, 1994). The short-lived systems ^{129}I – ^{129}Xe and ^{244}Pu – ^{136}Xe have provided additional constraints (Wetherill, 1975a; Allègre *et al.*, 1995a; Ozima and Podosek, 1999; Pepin and Porcelli, 2002). Other short-lived systems that have been used to address the timescales of terrestrial accretion and differentiation are ^{53}Mn – ^{53}Cr (Birck *et al.*, 1999), ^{92}Nb – ^{92}Zr (Münker *et al.*, 2000; Jacobsen and Yin, 2001), ^{97}Tc – ^{97}Mo (Yin and Jacobsen, 1998), and ^{107}Pd – ^{107}Ag (Carlson and Hauri, 2001). None of these now appear to provide useful constraints. Either the model deployed currently is under-constrained (as with Mn–Cr) or the isotopic effects subsequently have been shown to be incorrect or better explained in other ways.

Hf–W and U–Pb methods both work well because the mechanisms and rates of accretion are intimately associated with the timing of core formation and this fractionates the parent/daughter ratio strongly. For a long while, however, it was assumed that accretion and core formation were completely distinct events. It was thought that the Earth formed as a cold object in less than a million years (e.g., Hanks and Anderson, 1969) but that it then heated up as a result of radioactive decay and later energetic impacts. On this basis, it was calculated that the Earth's core formed rather gradually after tens or even hundreds of millions of years following this buildup of heat and the onset of melting (Hsui and Toksöz, 1977; Solomon, 1979).

In a similar manner isotope geochemists have at various times treated core formation as a process that was distinctly later than accretion and erected relatively simple lead, tungsten and, most recently, zirconium isotopic model ages that “date” this event (e.g., Oversby and Ringwood, 1971; Allègre *et al.*, 1995a; Lee and Halliday, 1995; Galer and Goldstein, 1996; Harper and Jacobsen, 1996b; Jacobsen and Yin, 2001; Dauphas *et al.*, 2002; Kleine *et al.*, 2002; Schöenberg *et al.*, 2002). A more complex model was presented by Kramers (1998). Detailed discussions of U–Pb, Hf–W, and Nb–Zr systems are presented later in this chapter. However, some generalities should be mentioned first.

In looking at these models the following “rules” apply:

(i) Both U–Pb and Hf–W chronometry are unable to distinguish between early accretion with late core formation, and late accretion with concurrent late core formation because it is

dominantly core formation that fractionates the parent/daughter ratio.

(ii) If accretion or core formation or both are protracted, the isotopic model age does not define any particular event. In the case of U–Pb it could define a kind of weighted average. In the case of short-lived nuclides, such as the ^{182}Hf – ^{182}W system with a half-life of ~ 9 Myr, it cannot even provide this. Clearly, if a portion of the core formation were delayed until after ^{182}Hf had become effectively extinct, the tungsten isotopic composition of the residual silicate Earth would not be changed. Even if $>50\%$ of the mass of the core formed yesterday it would not change the tungsten isotopic composition of the silicate portion of the Earth! Therefore, the issue of how long core formation persisted is completely unconstrained by Hf–W but is constrained by U–Pb data. It also is constrained by trace element data (Newsom *et al.*, 1986).

(iii) Isotopic approaches such as those using Hf–W can only provide an indication of how quickly core formation may have started if accretion was early and very rapid. Clearly this is not a safe assumption for the Earth. If accretion were protracted, tungsten isotopes would provide only minimal constraints on when core formation started.

Tungsten and lead isotopic data can, however, be used to define the timescales for accretion, simply by assuming that core formation, the primary process that fractionates the parent/daughter ratio, started very early and that the core grew in constant proportion to the Earth (Halliday *et al.*, 1996, 2000; Harper and Jacobsen, 1996b; Jacobsen and Harper, 1996; Halliday and Lee, 1999; Halliday, 2000). There is a sound basis for the validity of this assumption, as follows.

(i) The rapid conversion of kinetic energy to heat in a planet growing by accretion of planetesimals and other planets means that it is inescapable that silicate and metal melting temperatures are achieved (Sasaki and Nakazawa, 1986; Benz and Cameron, 1990; Melosh, 1990). This energy of accretion would be sufficient to melt the entire Earth such that in all likelihood one would have magma oceans permitting rapid core formation.

(ii) There is strong observational support for this view that core formation was quasicontinuous during accretion. Iron meteorites and basaltic achondrites represent samples of small planetesimals that underwent core formation early. A strong theoretical basis for this was recently provided by Yoshino *et al.* (2003). Similarly, Mars only reached one-eighth of the mass of the Earth but clearly its size did not limit the opportunity for core formation. Also, most of the Moon is thought to come from the silicate-rich portion of a Mars-sized impacting planet, known

as “Theia” (Cameron and Benz, 1991; Canup and Asphaug, 2001; Halliday, 2000), which also was already differentiated into core and silicate. The amount of depletion in iron in eucrites, martian meteorites, and lunar samples provides support for the view that the cores of all the planetesimals and planets represented were broadly similar in their proportions to Earth’s, regardless of absolute size. The slightly more extensive depletion of iron in the silicate Earth provides evidence that core formation was more efficient or protracted, but not that it was delayed.

There is no evidence that planetary objects have to achieve an Earth-sized mass or evolve to a particular state (other than melting), before core formation will commence. It is more reasonable to assume that the core grew with the accretion of the Earth in roughly the same proportion as today. If accretion were protracted, the rate-limiting parameter affecting the isotopic composition of lead and tungsten in the silicate Earth would be the timescale for accretion. As such, the “age of the core” is an average time of formation of the Earth itself. Therefore, simple tungsten and lead isotopic model ages do not define an event as such. The isotopic data instead need to be integrated with models for the growth of the planet itself to place modeled limits for the rate of growth.

The first papers exploring this approach were by Harper and Jacobsen (1996b) and Jacobsen and Harper (1996). They pointed out that the Monte Carlo simulations produced by Wetherill (1986) showed a trend of exponentially decreasing planetary growth with time. They emulated this with a simple expression for the accretionary mean life of the Earth, where the mean life is used in the same way as in nuclear literature as the inverse of a time constant. This model is an extension of the earlier model of Jacobsen and Wasserburg (1979) evaluating the mean age of the continents using Sm–Nd. Jacobsen and Harper applied the model to the determination of the age of the Earth based on (then very limited) tungsten isotope data. Subsequent studies (Halliday *et al.*, 1996, 2000; Halliday and Lee, 1999; Halliday, 2000; Yin *et al.*, 2002), including more exhaustive tungsten as well as lead isotope modeling, are all based on this same concept. However, the data and our understanding of the critical parameters have undergone major development.

Nearly all of these models assume that:

- (i) accretion proceeded at an exponentially decreasing rate from the start of the solar system;
- (ii) core formation and its associated fractionation of radioactive parent/radiogenic daughter ratios was coeval with accretion;
- (iii) the core has always existed in its present proportion relative to the total Earth;
- (iv) the composition of the accreting material did not change with time;

(v) the accreting material equilibrated fully with the silicate portion of the Earth just prior to fractionation during core formation; and

(vi) the partitioning of the parent and daughter elements between mantle and core remained constant.

The relative importance of these assumptions and the effects of introducing changes during accretion have been partially explored in several studies (Halliday *et al.*, 1996, 2000; Halliday and Lee, 1999; Halliday, 2000). The issue of metal–silicate equilibration has been investigated recently by Yoshino *et al.* (2003). However, the data upon which many of the fundamental isotopic and chemical parameters are based are in a state of considerable uncertainty.

1.20.4.2 Lead Isotopes

Until recently, the most widely utilized approach for determining the rate of formation of the Earth was U–Pb geochronology. The beauty of using this system is that one can deploy the combined constraints from both ^{238}U – ^{206}Pb ($T_{1/2} = 4,468$ Myr) and ^{235}U – ^{207}Pb ($T_{1/2} = 704$ Myr) decay. Although the atomic abundance of both of the daughter isotopes is a function of the U/Pb ratio and age, combining the age equations allows one to cancel out the U/Pb ratio. The relative abundance of ^{207}Pb and ^{206}Pb indicates when the fractionation took place. Patterson (1956) adopted this approach in his classic experiment to determine the age of the Earth. Prior to his work, there were a number of estimates of the age of the Earth based on lead isotopic data for terrestrial galenas. However, Patterson was the first to obtain lead isotopic data for early low-U/Pb objects (iron meteorites) and this defined the initial lead isotopic composition of the solar system. From this, it was clear that the silicate Earth's lead isotopic composition required between 4.5 Gyr and 4.6 Gyr of evolution as a high-U/Pb reservoir. Measurements of the lead isotopic compositions of other high-U/Pb objects such as basaltic achondrites and lunar samples confirmed this age for the solar system.

In detail it is now clear that most U–Pb model ages of the Earth (Allègre *et al.*, 1995a) are significantly younger than the age of early solar system materials such as chondrites (Göpel *et al.*, 1991) and angrites (Wasserburg *et al.*, 1977b; Lugmair and Galer, 1992). Such a conclusion has been reached repeatedly from consideration of the lead isotope compositions of early Archean rocks (Gancarz and Wasserburg, 1977; Vervoort *et al.*, 1994), conformable ore deposits (Doe and Stacey, 1974; Manhès *et al.*, 1979; Tera, 1980; Albarède and Juteau, 1984), average bulk silicate Earth (BSE) (Galer and Goldstein, 1996) and

mid-ocean ridge basalts (MORBs) (Allègre *et al.*, 1995a), all of which usually yield model ages of <4.5 Ga. Tera (1980) obtained an age of 4.53 Ga using Pb–Pb data for old rocks but even this postdates the canonical start of the solar system by over 30 Myr.

The reason why nearly all such approaches yield similar apparent ages that postdate the start of the solar system by a few tens of millions of years is that there was a very strong U/Pb fractionation that took place during the protracted history of accretion. The U–Pb model age of the Earth can only be young if U/Pb is fractionated at a late stage. This fractionation was of far greater magnitude than that associated with any later processes. Thus it has left a clear and irreversible imprint on the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ isotope ratios of the silicate portion of the Earth. Uranium, being lithophile, is largely confined to the silicate portion of the Earth. Lead is partly siderophile and chalcophile such that >90% of it is thought to be in the core (Allègre *et al.*, 1995a). Therefore, it was long considered that the lead isotopic “age of the Earth” dates core formation (Oversby and Ringwood, 1971; Allègre *et al.*, 1982).

The exact value of this fractionation is poorly constrained, because lead also is moderately volatile, so that the U/Pb ratio of the total Earth (mantle, crust, and core combined) also is higher than chondritic. In fact, some authors even have argued that the dominant fractionation in U/Pb in the BSE was caused by volatile loss (Jacobsen and Harper, 1996b; Harper and Jacobsen, 1996b; Azbel *et al.*, 1993). This is consistent with some compilations of data for the Earth, which show that lead is barely more depleted in the bulk silicate portion of the Earth than lithophile elements of similar volatility (McDonough and Sun, 1995). It is, therefore, important to know how much of the lead depletion is caused by accretion of material that was depleted in volatile elements at an early (nebular) stage. Galer and Goldstein (1996) and Allègre *et al.* (1995a) have compellingly argued that the major late-stage U/Pb fractionation was the result of core formation. However, the uncertainty over the U/Pb of the total Earth and whether it changed with accretion time remains a primary issue limiting precise application of lead isotopes.

Using exponentially decreasing growth rates and continuous core formation one can deduce an accretionary mean life assuming a $^{238}\text{U}/^{204}\text{Pb}$ for the total Earth of 0.7 (Halliday, 2000). This value is based on the degree of depletion of moderately volatile lithophile elements, as judged from the K/U ratio of the BSE (Allègre *et al.*, 1995a). Application of this approach to the lead isotopic compositions of the Earth (Halliday, 2000) provides evidence that the Earth accreted with an accretionary mean life of between 15 Myr and

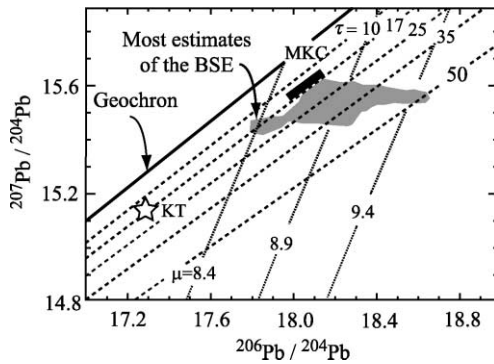


Figure 4 Lead isotopic modeling of the composition of the silicate Earth using continuous core formation. The principles behind the modeling are as in Halliday (2000). See text for explanation. The field for the BSE encompasses all of the estimates in Galer and Goldstein (1996). The values suggested by Kramers and Tolstikhin (1997) and Murphy *et al.* (2003) also are shown. The mean life (τ) is the time required to achieve 63% of the growth of the Earth with exponentially decreasing rates of accretion. The μ values are the $^{238}\text{U}/^{204}\text{Pb}$ of the BSE. It is assumed that the μ of the total Earth is 0.7 (Allègre *et al.*, 1995a). It can be seen that the lead isotopic composition of the BSE is consistent with protracted accretion over periods of 10^7 – 10^8 yr.

50 Myr, depending on which composition of the BSE is deployed (Figure 4). A similar figure to this in Halliday (2000) is slightly different (i.e., incorrect) because of a scaling error. The shaded region covers the field defined by eight estimates for the composition of the BSE as summarized by Galer and Goldstein (1996). The star shows the estimate of Kramers and Tolstikhin (1997). The thick bar shows the recent estimate provided by Murphy *et al.* (2003). Regardless of which of these 10 estimates of the lead isotopic composition is used, the mean life for accretion is at least 15 Myr. Therefore, there is no question that the lead isotopic data for the Earth provide evidence of a protracted history of accretion and concomitant core formation as envisaged by Wetherill (1986).

1.20.4.3 Tungsten Isotopes

While lead isotopes have been useful, the ^{182}Hf – ^{182}W chronometer ($T_{1/2} = 9$ Myr) has been at least as effective for defining rates of accretion (Halliday, 2000; Halliday and Lee, 1999; Harper and Jacobsen, 1996b; Jacobsen and Harper, 1996; Lee and Halliday, 1996, 1997; Yin *et al.*, 2002). Like U–Pb, the Hf–W system has been used more for defining a model age of core formation (Kramers, 1998; Horan *et al.*,

1998; Kleine *et al.*, 2002; Lee and Halliday, 1995, 1996, 1997; Quitté *et al.*, 2000; Dauphas *et al.*, 2002; Schöenberg *et al.*, 2002). As explained above this is not useful for an object like the Earth.

The half-life renders ^{182}Hf as ideal among the various short-lived chronometers for studying accretionary timescales. Moreover, there are two other major advantages of this method.

(i) Both parent and daughter elements (hafnium and tungsten) are refractory and, therefore, are in chondritic proportions in most accreting objects. Therefore, unlike U–Pb, we think we know the isotopic composition and parent/daughter ratio of the entire Earth relatively well.

(ii) Core formation, which fractionates hafnium from tungsten, is thought to be a very early process as discussed above. Therefore, the rate-limiting process is simply the accretion of the Earth.

There are several recent reviews of Hf–W (e.g., Halliday and Lee, 1999; Halliday *et al.*, 2000), to which the reader can refer for a comprehensive overview of the data and systematics. However, since these were written it has been shown that chondrites, and by inference the average solar system, have tungsten isotopic compositions that are resolvable from that of the silicate Earth (Kleine *et al.*, 2002; Lee and Halliday, 2000a; Schoenberg *et al.*, 2002; Yin *et al.*, 2002). Although the systematics, equations, and arguments have not changed greatly, this has led to considerable uncertainty over the exact initial ^{182}Hf abundance in the early solar system. Because this is of such central importance to our understanding of the timescales of accretion that follow from the data, it is discussed in detail below. Similarly, some of the tungsten isotopic effects that were once considered to reflect radioactive decay within the Moon (Lee *et al.*, 1997; Halliday and Lee, 1999) are now thought to *partly* be caused by production of cosmogenic ^{182}Ta (Leya *et al.*, 2000; Lee *et al.*, 2002).

The differences in tungsten isotopic composition are most conveniently expressed as deviations in parts per 10,000, as follows:

$$\varepsilon_{\text{W}} = \left[\frac{(^{182}\text{W}/^{184}\text{W})_{\text{sample}}}{(^{182}\text{W}/^{184}\text{W})_{\text{BSE}}} - 1 \right] \times 10^4$$

where the BSE value $(^{182}\text{W}/^{184}\text{W})_{\text{BSE}}$ is the measured value for an NIST tungsten standard. This should be representative of the BSE as found by comparison with the values for terrestrial standard rocks (Lee and Halliday, 1996; Kleine *et al.*, 2002; Schoenberg *et al.*, 2002). If ^{182}Hf was sufficiently abundant at the time of formation (i.e., at an early age), then minerals, rocks, and reservoirs with higher Hf/W ratios will produce tungsten that is significantly more radiogenic

(higher $^{182}\text{W}/^{184}\text{W}$ or ε_{W}) compared with the initial tungsten isotopic composition of the solar system. Conversely, metals with low Hf/W that segregate at an early stage from bodies with chondritic Hf/W (as expected for most early planets and planetesimals) will sample unradiogenic tungsten.

Harper *et al.* (1991a) were the first to provide a hint of a tungsten isotopic difference between the iron meteorite Toluca and the silicate Earth. It is now clear that there exists a ubiquitous clearly resolvable deficit in ^{182}W in iron meteorites and the metals of ordinary chondrites, relative to the atomic abundance found in the silicate Earth (Lee and Halliday, 1995, 1996; Harper and Jacobsen, 1996b; Jacobsen and Harper, 1996; Horan *et al.*, 1998). A summary of most of the published data for iron meteorites is given in Figure 5. It can be seen that most early segregated metals are deficient by $\sim(3-4)\varepsilon_{\text{W}}$ units (300–400 ppm) relative to the silicate Earth. Some appear to be even more negative, but the results are not well resolved. The simplest explanation for this difference is that the metals, or the silicate Earth, or both, sampled early solar system tungsten before live ^{182}Hf had decayed.

The tungsten isotopic difference between early metals and the silicate Earth reflects the time integrated Hf/W of the material that formed the

Earth and its reservoirs, during the lifetime of ^{182}Hf . The Hf/W ratio of the silicate Earth is considered to be in the range of 10–40 as a result of an intensive study by Newsom *et al.* (1996). This is an order of magnitude higher than in carbonaceous and ordinary chondrites and a consequence of terrestrial core formation. More recent estimates are provided in Walter *et al.* (2000).

If accretion and core formation were early, an excess of ^{182}W would be found in the silicate Earth, relative to average solar system (chondrites). However, the tungsten isotopic difference between early metals and the silicate Earth on its own does not provide constraints on timing. One needs to know the atomic abundance of ^{182}Hf at the start of the solar system (or the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$, the “bulk solar system initial”) and the composition of the chondritic reservoirs from which most metal and silicate reservoirs were segregated. In other words, it is essential to know to what extent the “extra” ^{182}W in the silicate Earth relative to iron meteorites accumulated in the accreted chondritic precursor materials or proto-Earth with an Hf/W ~ 1 prior to core formation, and to what extent it reflects an accelerated change in isotopic composition because of the high Hf/W (~ 15) in the silicate Earth.

For this reason some of the first attempts to use Hf–W (Harper and Jacobsen, 1996b; Jacobsen and Harper, 1996) gave interpretations that are now known to be incorrect because the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ was underconstrained. This is a central concern in Hf–W chronometry that does not apply to U–Pb; for the latter system, parent abundances can still be measured today. In order to determine the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ correctly one can use several approaches with varying degrees of reliability:

(i) The first approach is to model the expected $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ in terms of nucleosynthetic processes. Wasserburg *et al.* (1994) successfully predicted the initial abundances of many of the short-lived nuclides using a model of nucleosynthesis in AGB stars. Extrapolation of their model predicted a low $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ of $<10^{-5}$, assuming that ^{182}Hf was indeed produced in this manner. Subsequent to the discovery that the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ was $>10^{-4}$ (Lee and Halliday, 1995, 1996), a number of new models were developed based on the assumption that ^{182}Hf is produced in the same kind of r-process site as the actinides (Wasserburg *et al.*, 1996; Qian *et al.*, 1998; Qian and Wasserburg, 2000).

(ii) The second approach is to measure the tungsten isotopic composition of an early high-Hf/W phase. Ireland (1991) attempted to measure the amount of ^{182}W in zircons (with very high hafnium content) from the mesosiderite Vaca Muerta, using an ion probe, and from this deduced

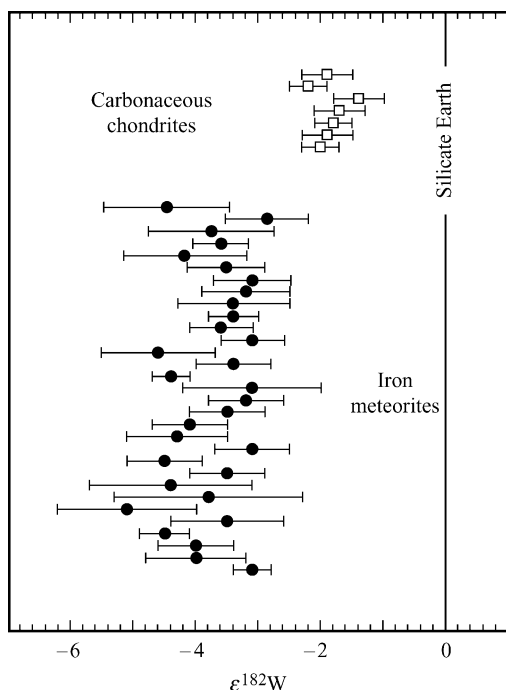


Figure 5 Well-defined deficiency in ^{182}W in early metals and carbonaceous chondrites relative to the silicate Earth (source Lee and Halliday, 1996; Horan *et al.*, 1998; Kleine *et al.*, 2002).

that the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ was $<10^{-4}$. Unfortunately, these zircons are not dated with sufficient precision (Ireland and Wlotzka, 1992) to be very certain about the time extrapolation of the exact hafnium abundances. Nevertheless, on the basis of this work and the model of Wasserburg *et al.* (1994), Jacobsen and Harper (1996) assumed that the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ was indeed low ($\sim 10^{-5}$). It was concluded that the difference in tungsten isotopic composition between the iron meteorite Toluca and the terrestrial value could only have been produced by radioactive decay within the silicate Earth with high Hf/W. Therefore, the fractionation of Hf/W produced by terrestrial core formation had to be early. They predicted that the Earth accreted very rapidly with a two-stage model age of core formation of <15 Myr after the start of the solar system.

(iii) The third approach is to simply assume that the consistent unradiogenic tungsten found in iron meteorites and metals from ordinary chondrites represents the initial tungsten isotopic composition of the solar system. This is analogous to the way in which the lead isotopic composition of iron meteorites has been used for decades. The difference between this and the present-day value of carbonaceous chondrites represents the effects of radiogenic ^{182}W growth *in situ* with chondritic Hf/W ratios. This in turn will indicate the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$. The difficulty with this approach has been to correctly determine the tungsten isotopic composition of chondrites. Using multiple collector ICPMS, Lee and Halliday (1995) were the first to publish such results and they reported that the tungsten isotopic compositions of the carbonaceous chondrites Allende and Murchison could not be resolved from that of the silicate Earth. The $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$, far from being low, appeared to be surprisingly high at $\sim 2 \times 10^{-4}$ (Lee and Halliday, 1995, 1996). Subsequently, it has been shown that these data must be incorrect (Figure 5). Three groups have independently shown (Kleine *et al.*, 2002; Schoenberg *et al.*, 2002; Yin *et al.*, 2002) that there is a small but clear deficiency in ^{182}W ($\varepsilon_{\text{W}} = -1.5$ to -2.0) in carbonaceous chondrites similar to that found in enstatite chondrites (Lee and Halliday, 2000a) relative to the BSE. Kleine *et al.* (2002), Schoenberg *et al.* (2002), and Yin *et al.* (2002) all proposed a somewhat lower $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ of $\sim 1.0 \times 10^{-4}$. However, the same authors based this result on a solar system initial tungsten isotopic composition of $\varepsilon_{\text{W}} = -3.5$, which was derived from their own, rather limited, measurements. Schoenberg *et al.* (2002) pointed out that if instead one uses the full range of tungsten isotopic composition previously reported for iron meteorites (Horan *et al.*, 1998; Jacobsen and Harper, 1996; Lee and Halliday,

Table 1 Selected W-isotope data for iron meteorites.

Iron meteorite	$\varepsilon^{182}\text{W}$	$^{182}\text{Hf}/^{180}\text{Hf}$
Bennett Co.	-4.6 ± 0.9	$(1.74 \pm 0.57) \times 10^{-4}$
Lombard	-4.3 ± 0.3	$(1.55 \pm 0.37) \times 10^{-4}$
Mt. Edith	-4.5 ± 0.6	$(1.68 \pm 0.46) \times 10^{-4}$
Duel Hill-1854	-5.1 ± 1.1	$(2.07 \pm 0.68) \times 10^{-4}$
Tlacotepec	-4.4 ± 0.4	$(1.68 \pm 0.41) \times 10^{-4}$

Source: Horan *et al.* (1998). The calculated difference between the initial and present-day W-isotopic composition of the solar system is equal to the $^{180}\text{Hf}/^{184}\text{W}$ of the solar system multiplied by the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$. The W-isotopic compositions of iron meteorites are maxima for the $(\varepsilon^{182}\text{W})_{\text{BSSI}}$, and therefore provide a limit on the minimum $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$. The $^{182}\text{Hf}/^{180}\text{Hf}$ at the time of formation of these early metals shown here is calculated from the W-isotopic composition of the metal, the W-isotopic composition of carbonaceous chondrites (Kleine *et al.*, 2002), and the average $^{180}\text{Hf}/^{184}\text{W}$ for carbonaceous chondrites of 1.34 (Newsom *et al.*, 1996).

1995, 1996) one obtains a $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ of $>1.3 \times 10^{-4}$ (Table 1).

(iv) The fourth approach is to determine an internal isochron for an early solar system object with a well-defined absolute age (Swindle, 1993). The first such isochron was for the H4 ordinary chondrite Forest Vale (Lee and Halliday, 2000a). The best-fit line regressed through these data corresponds to a slope ($=^{182}\text{Hf}/^{180}\text{Hf}$) of $(1.87 \pm 0.16) \times 10^{-4}$. The absolute age of tungsten equilibration in Forest Vale is unknown but may be 5 Myr younger than the CAI inclusions of Allende (Göpel *et al.*, 1994). Kleine *et al.* (2002) and Yin *et al.* (2002) both obtained lower initial $^{182}\text{Hf}/^{180}\text{Hf}$ values from internal isochrons, some of which are relatively precise. The two meteorites studied by Yin *et al.* (2002) are poorly characterized, thoroughly equilibrated meteorites of unknown equilibration age. The data for Ste. Marguerite obtained by Kleine *et al.* (2002) were obtained by separating a range of unknown phases with very high Hf/W. They obtained a value closer to 1.0×10^{-4} , but it is not clear whether the phases studied are the same as those analyzed from Forest Vale by Lee and Halliday (2000b) with lower Hf/W. Nevertheless, they estimated that their isochron value was closer to the true $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$.

Both, the uncertainty over $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ and the fact that the tungsten isotopic composition of the silicate Earth is now unequivocally resolvable from a now well-defined chondritic composition (Kleine *et al.*, 2002; Lee and Halliday, 2000a; Schoenberg *et al.*, 2002; Yin *et al.*, 2002), affect the calculated timescales for terrestrial accretion. It had been argued that accretion and core formation were fairly protracted and characterized by equilibration between accreting materials and the silicate Earth (Halliday, 2000; Halliday *et al.*, 1996, 2000; Halliday and Lee, 1999). In other words, the tungsten isotope data provide very strong confirmation of the models of Safronov (1954) and Wetherill (1986). This general

scenario remains the same with the new data but in detail there are changes to the exact timescales.

Previously, Halliday (2000) estimated that the mean life, the time required to accumulate 63% of the Earth's mass with exponentially decreasing accretion rates, must lie in the range of 25–40 Myr based on the combined constraints imposed by the tungsten and lead isotope data for the Earth. Yin *et al.* (2002) have argued that the mean life for Earth accretion is more like ~11 Myr based on their new data for chondrites. The lead isotope data for the Earth are hard to reconcile with such rapid accretion rates as already discussed (Figure 4). Therefore, at present there is an unresolved apparent discrepancy between the models based on tungsten and those based on lead isotope data. Resolving this discrepancy highlights the limitations in both the tungsten and the lead isotope modeling. Here are some of the most important weaknesses to be aware of:

(i) The U/Pb ratio of the total Earth is poorly known.

(ii) In all of these models it is assumed that the Earth accretes at exponentially decreasing rates. Although the exponentially decreasing rate of growth of the Earth is based on Monte Carlo simulations and makes intuitive sense given the ever decreasing probability of collisions, the reality cannot be this simple. As planets get bigger, the average size of the objects with which

they collide also must increase. As such, the later stages of planetary accretion are thought to involve major collisions. This is a stochastic process that is hard to predict and model. It means that the current modeling can only provide, at best, a rough description of the accretion history.

(iii) The Moon is thought to be the product of such a collision. The Earth's U/Pb ratio conceivably might have increased during accretion if a fraction of the moderately volatile elements were lost during very energetic events like the Moon-forming giant impact (Figure 6).

(iv) Similarly, as the objects get larger, the chances for equilibration of metal and silicate would seem to be less likely. This being the case, the tungsten and lead isotopic composition of the silicate Earth could reflect only partial equilibration with incoming material such that the tungsten and lead isotopic composition is partly inherited. This has been modeled in detail by Halliday (2000) in the context of the giant impact and more recently has been studied by Vityazev *et al.* (2003) and Yoshino *et al.* (2003) in the context of equilibration of asteroidal-sized objects. If correct, it would mean accretion was even slower than can be deduced from tungsten or lead isotopes. If lead equilibrated more readily than tungsten did, for whatever reason, it might help explain some of the discrepancy. One possible way to decouple lead from tungsten

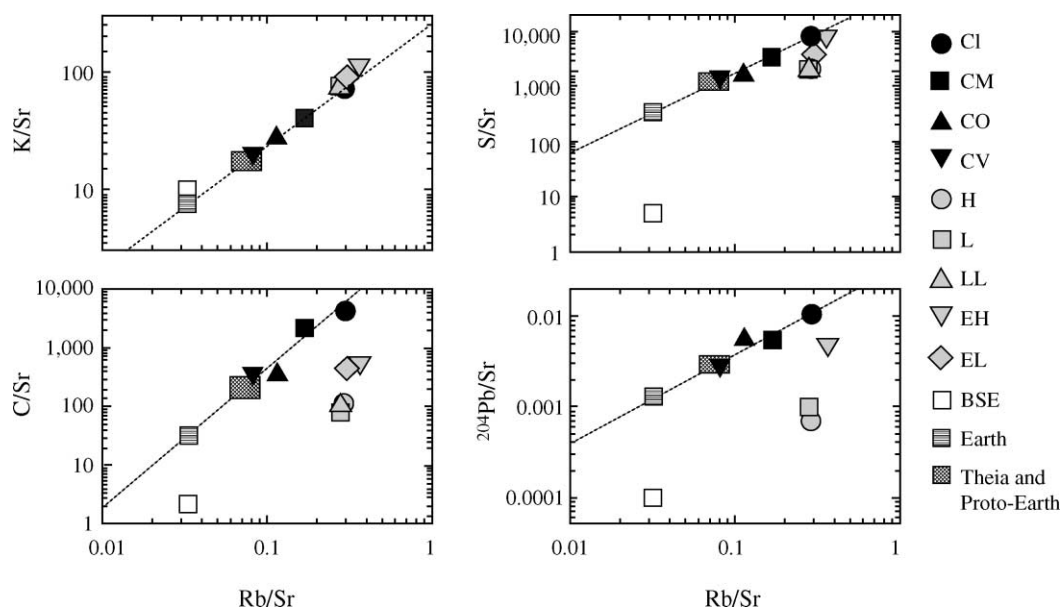


Figure 6 Volatile/refractory element ratio–ratio plots for chondrites and the silicate Earth. The correlations for carbonaceous chondrites can be used to define the composition of the Earth, the Rb/Sr ratio of which is well known, because the strontium isotopic composition of the BSE represents the time-integrated Rb/Sr. The BSE inventories of volatile siderophile elements carbon, sulfur, and lead are depleted by more than one order of magnitude because of core formation. The values for Theia are time-integrated compositions, assuming time-integrated Rb/Sr deduced from the strontium isotopic composition of the Moon (Figure 8) can be used to calculate other chemical compositions from the correlations in carbonaceous chondrites (Halliday and Porcelli, 2001). Other data are from Newsom (1995).

would be by their relative volatility. Lead could have been equilibrated by vapor-phase exchange, while tungsten would not have been able to do this and would require intimate physical mixing and reduction to achieve equilibration.

(v) ($^{182}\text{Hf}/^{180}\text{Hf}$)_{BSSI} is, at present, very poorly defined and could be significantly higher (Table 1). This would result in more protracted accretion timescales deduced from Hf–W (Table 2), which would be more consistent with the results obtained from U–Pb. An improved and more reliable Hf–W chronometry will depend on the degree to which the initial hafnium and tungsten isotopic compositions at the start of the solar system can be accurately defined (Tables 1 and 2). Techniques must be developed for studying very early objects like CAIs.

(vi) There is also a huge range of uncertainty in the Hf/W ratio of the silicate Earth (Newsom *et al.*, 1996), with values ranging between 10 and 40. The tungsten isotope age calculations presented in the literature tend to assume a value at the lower end of this range. Adoption of higher values also would result in more protracted accretion timescales based on Hf–W. The most recent independent estimates (Walter *et al.*, 2000) are significantly higher than those used by Yin *et al.* (2002) and Kleine *et al.* (2002) in support of their proposed timescales.

(vii) The lead isotopic composition of the BSE is not well defined (Figure 4). If the correct value lies closer to the Geochron than previously recognized, then the apparent accretion timescales for the Earth would be shortened.

(viii) Lastly, the decay constant for ^{182}Hf has a reported uncertainty of $\pm 22\%$ and really accurate determinations of accretion timescales require a significant reduction in this uncertainty.

Having made all of these cautionary statements, one still can state something useful about the overall accretion timescales. All recent combined accretion/continuous core formation models (Halliday, 2000; Halliday *et al.*, 2000; Yin *et al.*, 2002) are in agreement that the timescales are in the range 10^7 – 10^8 yr, as predicted by Wetherill (1986). Therefore, we can specifically evaluate the models of planetary accretion proposed earlier as follows.

If the Earth accreted very fast, in $<10^6$ yr, as proposed by Cameron (1978), the silicate Earth would have a tungsten isotopic composition that is vastly more radiogenic than that observed today (Figure 5). Such objects would have $\varepsilon_W > +10$, rather than 0 (just two ε units above average solar system). Therefore, we can say with some confidence that this model does not describe the accretion of the Earth. Protracted accretion in the absence of nebular gas, as proposed by Safronov and Wetherill, is very consistent with the close agreement between chondrites and the silicate Earth (Figure 4). To what extent the Kyoto model, which involves a significant amount of nebular gas (Hayashi *et al.*, 1985), can be confirmed or discounted is unclear at present. However, even the timescales presented by Yin *et al.* (2002) are long compared with the 5 Myr for accretion of the Earth predicted by the Kyoto model. This could change somewhat with further tungsten and lead isotope data and the definition of the critical parameters and modeling. However, the first-order conclusion is that nebular gas was at most somewhat limited during accretion and that there must have been much less gas than that implied by the minimum mass solar nebula scenario proposed in the Kyoto model.

Table 2 The apparent mean life of formation of the Earth, as well as the predicted W-isotopic compositions of the lunar mantle and silicate Earth.

$\varepsilon^{182}\text{W}_{\text{BSSI}}$	–5.0	–4.5	–4.0	–3.5
($^{182}\text{Hf}/^{180}\text{Hf}$) _{BSSI}	2.0×10^{-4}	1.7×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
Accretionary mean life of the earth (yr)	15×10^6	14×10^6	13×10^6	12×10^6
$\varepsilon^{182}\text{W}$ for: lunar initial/present-day lunar mantle/present-day silicate Earth				
Giant impact at 30×10^6 yr	+0.3/+7.1/+0.4	–0.1/+5.6/0.0	–0.4/+4.2/–0.4	–0.8/+2.8/–0.7
Giant impact at 40×10^6 yr	–0.3/+2.9/+0.8	–0.6/+2.0/+0.3	–0.8/+1.3/–0.1	–1.1/+0.6/–0.5
Giant impact at 45×10^6 yr	–0.6/+1.6/0.0	–0.8/+1.0/–0.3	–1.0/+0.5/–0.6	–1.2/–0.1/–0.9
Giant impact at 50×10^6 yr	–0.8/+0.7/–0.6	–1.0/+2.0/–0.8	–1.2/–0.2/–1.0	–1.3/–0.6/–1.2
Giant impact at 60×10^6 yr	–1.2/–0.9/–1.2	–1.3/–1.0/–1.3	–1.4/–1.0/–1.4	–1.5/–1.2/–1.6
Giant impact at 70×10^6 yr	–1.3/–1.2/–1.5	–1.4/–1.3/–1.6	–1.5/–1.4/–1.7	–1.6/–1.5/–1.7

All parameters are critically dependent on the initial W- and Hf- isotopic composition of the solar system, which at present are poorly known (see text). All calculated values assume that the W depletion in the silicate Earth and the lunar mantle are as given in Walter *et al.* (2000). The ($^{182}\text{Hf}/^{180}\text{Hf}$)_{BSSI}, model ages, and Earth and Moon compositions are all calculated using the W-isotopic composition of carbonaceous chondrites (Kleine *et al.*, 2002) and the average $^{180}\text{Hf}/^{184}\text{W}$ for carbonaceous chondrites of 1.34 (Newsom, 1990). The principles behind the modeling are as in Halliday (2000). The giant impact is assumed to have occurred when the Earth had reached 90% of its current mass, the impactor adding a further 9%. Exponentially decreasing accretion rates are assumed before and after (Halliday, 2000). The solutions in bold type provide the best match with the current data for the W-isotopic compositions of the initial Moon (~ 0), and the present-day lunar mantle (<2) and silicate Earth (0).

1.20.5 CHEMICAL AND ISOTOPIC CONSTRAINTS ON THE NATURE OF THE COMPONENTS THAT ACCRETED TO FORM THE EARTH

1.20.5.1 Chondrites and the Composition of the Disk from Which Earth Accreted

A widespread current view is that chondrites represent primitive undifferentiated material from which the Earth accreted. In reality, chondrites are anything but simple and, although they contain early and presolar objects, how primitive and how representative of the range of very early planetesimals they are is completely unclear. In all probability the Earth was built largely from more extensively differentiated materials (Taylor and Norman, 1990). Nevertheless, chondrites do represent a useful set of reference reservoirs in chemical and isotopic terms from which one can draw some conclusions about the “average stuff” from which the Earth may have been built (e.g., Ganapathy and Anders, 1974; Anders, 1977; Wolf *et al.*, 1980). Indeed, if geochemists did not have chondrite samples to provide a reference, many geochemical arguments about Earth’s origin, not to say present-day interior structure, would be far weaker.

The degree to which different kinds of chondrites reflect bulk Earth composition has been extensively debated, since none of them provide a good match. CI carbonaceous chondrites define a reference reservoir for *undepleted* solar system compositions because they are strikingly similar in composition to the Sun when normalized to an element such as silicon (Grevesse and Sauval, 1998; see Chapter 1.03). However, they are not at all similar to the Earth’s volatile-depleted composition. Nor are they much like the vast majority of other chondrites! Confirmation of the primitive nature of CIs is most readily demonstrated by comparing the relative concentrations of a well-determined moderately volatile major element to a well-determined refractory major element with the values in the Sun’s photosphere. For example, the concentrations of sodium and calcium are both known to better than a percent in the photosphere (Grevesse and Sauval, 1998) and are identical to within a percent with the values found in CIs despite a big difference in volatility between the two elements (Anders and Grevesse, 1989; Newsom, 1995). It is tempting to ascribe CIs to a complete condensation sequence. However, they also contain dispersed isotopic anomalies in Cr, for example, that indicate a lack of homogenization on a fine scale (Podosek *et al.*, 1997). This cannot be reconciled with nebular condensation from high temperatures.

Volatile-element depletion patterns in other (e.g., CV, CM, or CO) carbonaceous chondrites (Larimer and Anders, 1970; Palme *et al.*, 1988;

Takahashi *et al.*, 1978; Wolf *et al.*, 1980) and ordinary chondrites (Wasson and Chou, 1974) have long been considered to partly reflect incomplete condensation (Wasson, 1985), with the more volatile elements removed from the meteorite formation regions before cooling and the termination of condensation. However, this depletion must at least partially reflect the incorporation of volatile-depleted CAIs (Guan *et al.*, 2000) and chondrules (Grossman, 1996; Meibom *et al.*, 2000). The origins of CAIs have long been enigmatic, but recently it has been proposed that CAIs may be the product of rather localized heating close to the young Sun (Shu *et al.*, 1997) following which they were scattered across the disk. Regardless of whether this model is exactly correct, the incorporation of volatile-depleted CAIs must result in some degree of volatile-depleted composition for chondritic meteorites. Chondrules are the product of rapid melting of chondritic materials (Connolly *et al.*, 1998; Connolly and Love, 1998; Desch and Cuzzi, 2000; Jones *et al.*, 2000) and such events also may have been responsible for some degree of volatile-element depletion (Vogel *et al.*, 2002).

The discovery that pristine presolar grains are preserved in chondrites indicates that they were admixed at a (relatively) late stage. Many of the presolar grain types (Mendybaev *et al.*, 2002; Nittler, 2003) could not have survived the high temperatures associated with CAI and chondrule formation. Therefore, chondrites must include a widely dispersed presolar component (Huss, 1988, 1997; Huss and Lewis, 1995) that either settled or was swept into the chondrule-forming and/or chondrule-accumulating region and would have brought with it nebular material that was not depleted in volatiles. Therefore, volatile depletion in chondrites must reflect, to some degree at least, the mixing of more refractory material (Guan *et al.*, 2000; Kornacki and Fegley, 1986) with CI-like matrix of finer grained volatile-rich material (Grossman, 1996). CIs almost certainly represent accumulations of mixed dust inherited from the portion of the protostellar molecular cloud that collapsed to form the Sun within a region of the nebula that was never greatly heated and did not accumulate chondrules and CAIs (for whatever reason). Though undifferentiated, chondrites, with the possible exception of CIs, are not primitive and certainly do not represent the first stages of accretion of the Earth.

Perhaps the best current way to view the disk of debris from which the Earth accreted was as an environment of vigorous mixing. Volatile-depleted material that had witnessed very high temperatures at an early stage (CAIs) mixed with material that had been flash melted (chondrules) a few million years later. Then presolar grains that had escaped these processes rained into the

midplane or more likely were swept in from the outer regions of the solar system. It is within these environments that dust, chondrules and CAIs mixed and accumulated into planetesimals. There also would have been earlier formed primary planetesimals (planetary embryos) that had accreted rapidly by runaway growth but were subsequently consumed. The earliest most primitive objects probably differentiated extremely quickly aided by the heat from runaway growth and live ^{26}Al (see [Chapter 1.17](#)).

It is not clear whether we have *any* meteorites that are samples of these very earliest planetesimals. Some iron meteorites with very unradiogenic tungsten ([Horan et al., 1998](#)) might be candidates ([Table 1](#)). Nearly all silicate-rich basaltic achondrites that are precisely dated appear to have formed later (more than a million years after the start of the solar system). Some of the disk debris will have been the secondary product of collisions between these planetesimals, rather like the dust in Beta Pictoris. Some have proposed that chondrules formed in this way ([Sanders, 1996](#); [Lugmair and Shukolyukov, 2001](#)), but although the timescales appear right this is not generally accepted ([Jones et al., 2000](#)). A working model of the disk is of a conveyor belt of material rapidly accreting into early planetesimals, spiraling in toward the Sun and being fed by heated volatile-depleted material ([Krot et al., 2001](#)) scattered outwards and pristine volatile-rich material being dragged in from the far reaches of the disk ([Shu et al., 1996](#)). This mixture of materials provided the raw ingredients for early planetesimals and planets that have largely been destroyed or ejected. One of the paths of destruction was mutual collisions, and it was these events that ultimately led to the growth of terrestrial planets like the Earth.

1.20.5.2 Chondritic Component Models

Although it is now understood quite well that chondrites are complicated objects with a significant formation history, many have proposed that they should be used to define Earth's bulk composition. More detailed discussion of the Earth's composition is provided elsewhere in this treatise (e.g., see [Chapter 2.01](#)) and only the essentials for this chapter are covered here. A recent overview of some of the issues is provided by [Drake and Righter \(2002\)](#). The carbonaceous chondrites often are considered to provide the best estimates of the basic building blocks ([Agee and Walker, 1988](#); [Allègre et al., 1995a,b, 2001](#); [Anders, 1977](#); [Ganapathy and Anders, 1974](#); [Herzberg, 1984](#); [Herzberg et al., 1988](#); [Jagoutz et al., 1979](#); [Jones and Palme, 2000](#); [Kato et al., 1988a,b](#); [Newsom, 1990](#)). Because the Earth is formed from collisions between differentiated

material, it is clear that one is simply using these reference chondrites to provide little more than model estimates of the total Earth's composition. [Allègre et al. \(1995a,b, 2001\)](#), for example, have plotted the various compositions of chondrites using major and trace element ratios and have shown that the refractory lithophile elements are most closely approximated by certain specific kinds of chondrites. Relative abundances of the platinum group elements and osmium isotopic composition of the silicate Earth have been used extensively to evaluate which class of chondrites contributed the late veneer ([Newsom, 1990](#); [Rehkämper et al., 1997](#); [Meisel et al., 2001](#); [Drake and Righter, 2002](#)), a late addition of volatile rich material. [Javoy \(1998, 1999\)](#) has developed another class of models altogether based on enstatite chondrites.

If it is assumed that one can use chondrites as a reference, one can calculate the composition of the total Earth and predict the concentrations of elements that are poorly known. For example, in theory one can predict the amount of silicon in the total Earth and determine from this how much must have gone into the core. The Mainz group produced many of the classic papers pursuing this approach ([Jagoutz et al., 1979](#)). However, it was quickly realized that the Earth does not fit any class of chondrite. In particular, Jagoutz presented the idea of using element ratios to show that the Earth's upper mantle had Mg/Si that was non-chondritic. [Jagoutz et al. \(1979\)](#) used CI, ordinary and enstatite chondrites to define the bulk Earth. Anders always emphasized that all chondrites were fractionated relative to CIs in his series of papers on "Chemical fractionations in meteorites" (e.g., [Wolf et al., 1980](#)). That is, CMs and CVs, etc., are also fractionated, as are planets. [Jagoutz et al. \(1979\)](#) recognized that the fractionations of magnesium, silicon, and aluminum were found in both the Earth and in CI, O, and E chondrites, but not in C2–C3 chondrites, which exhibit a fixed Mg/Si but variable Al/Si ratio, probably because of addition of CAIs.

One also can use chondrites to determine the abundances of moderately volatile elements such as potassium. [Allègre et al. \(2001\)](#) and [Halliday and Porcelli \(2001\)](#) pursued this approach to show that the Earth's K/U is $\sim 10^4$ ([Figure 2](#)). One can calculate how much of the volatile chalcophile and siderophile elements such as sulfur, cadmium, tellurium, and lead may have gone in to the Earth's core ([Figure 6](#); [Yi et al., 2000](#); [Allègre et al., 1995b](#); [Halliday and Porcelli, 2001](#)). [Allègre et al. \(1995a\)](#) also have used this approach to estimate the total Earth's $^{238}\text{U}/^{204}\text{Pb}$.

From the budgets of potassium, silicon, carbon, and sulfur extrapolated from carbonaceous chondrite compositions, one can evaluate the amounts of various light elements possibly incorporated in

the core (Allègre *et al.*, 1995b; Halliday and Porcelli, 2001) and see if this explains the deficiency in density relative to pure iron (Ahrens and Jeanloz, 1987). Such approaches complement the results of experimental solubility measurements (e.g., Wood, 1993; Gessmann *et al.*, 2001) and more detailed comparisons with the geochemistry of meteorites (Dreibus and Palme, 1996).

It should be noted that the Jagoutz *et al.* (1979) approach and the later studies by Allègre and co-workers (Allègre *et al.*, 1995a,b, 2001) are mutually contradictory, a fact that is sometimes not recognized. Whereas Jagoutz *et al.* (1979) used CI, ordinary, and enstatite chondrites, Allègre and co-workers used CI, CM, CV, and CO chondrites (the carbonaceous chondrite mixing line) to define the bulk earth, ignoring the others.

These extrapolations and predictions are based on two assumptions that some would regard as rendering the approach flawed:

(i) The carbonaceous chondrites define very nice trends for many elements that can be used to define the Earth's composition, but the ordinary and enstatite chondrites often lie off these trends (Figure 6). There is no obvious basis for simply ignoring the chemical compositions of the ordinary and enstatite chondrites unless they have undergone some parent body process of loss or redistribution in their compositions. This is indeed likely, particularly for volatile chalcophile elements but is not well understood at present.

(ii) The Earth as well as the Moon, Mars, and basaltic achondrite parent bodies are depleted in moderately volatile elements, in particular the alkali elements potassium and rubidium, relative to most classes of chondrite (Figure 2). This needs to be explained. Humayun and Clayton (1995) performed a similar exercise, showing that since chondrites are all more volatile rich than terrestrial planets, the only way to build planets from chondrite precursors was to volatilize alkalis and other volatile elements. This was not considered feasible in view of the identical potassium isotope compositions of chondrites, the Earth and the Moon. Taylor and Norman (1990) made a similar observation that planets formed from volatile-depleted and differentiated precursors and not from chondrites. Clearly, there must have been other loss mechanisms (Halliday and Porcelli, 2001) beyond those responsible for the volatile depletion in chondrites unless the Earth, Moon, angrite parent body and Vesta simply were accreted from parts of the disk that were especially enriched in some highly refractory component, like CAIs (Longhi, 1999).

This latter point and other similar concerns represent such a major problem that some scientists abandoned the idea of just using chondrites as a starting point and instead invoked the former presence of completely hypothetical components

in the inner solar system. This hypothesis has been explored in detail as described below.

1.20.5.3 Simple Theoretical Components

In addition to making comparisons with chondrites, the bulk composition of the Earth also has been defined in terms of a "model" mixture of highly reduced, refractory material combined with a much smaller proportion of a more oxidized volatile-rich component (Wänke, 1981). These models follow on from the ideas behind earlier heterogeneous accretion models. According to these models, the Earth was formed from two components. Component A was highly reduced and free of all elements with equal or higher volatility than sodium. All other elements were in CI relative abundance. The iron and siderophile elements were in metallic form, as was part of the silicon. Component B was oxidized and contained all elements, including those more volatile than sodium in CI relative abundance. Iron and all siderophile and lithophile elements were mainly in the form of oxides.

Ringwood (1979) first proposed these models but the concept was more fully developed by Wänke (1981). In Wänke's model, the Earth accretes by heterogeneous accretion with a mixing ratio A:B ~ 85:15. Most of component B would be added after the Earth had reached about two thirds of its present mass. The oxidized volatile-rich component would be equivalent to CI carbonaceous chondrites. However, the reduced refractory rich component is hypothetical and never has been identified in terms of meteorite components.

Eventually, models that involved successive changes in accretion and core formation replaced these. How volatiles played into this was not explained except that changes in oxidation state were incorporated. An advanced example of such a model is that presented by Newsom (1990). He envisaged the history of accretion as involving stages that included concomitant core formation stages (discussed under core formation).

1.20.5.4 The Nonchondritic Mg/Si of the Earth's Primitive Upper Mantle

It has long been unclear why the primitive upper mantle of the Earth has a nonchondritic proportion of silicon to magnesium. Anderson (1979) proposed that the mantle was layered with the lower mantle having higher Si/Mg. Although a number of coeval papers presented a similar view (Herzberg, 1984; Jackson, 1983) it is thought by many geochemists these days that the major element composition of the mantle is, broadly speaking, well mixed and homogeneous as a result of 4.5 Gyr of mantle convection (e.g., Hofmann, 1988; Ringwood, 1990).

A notable exception is the enstatite chondrite model of Javoy (1999).

Wänke (1981) and Allègre *et al.* (1995b) have proposed that a significant fraction of the Earth's silicon is in the core. However, this is not well supported by experimental data. To explain the silicon deficiency this way conditions have to be so reducing that niobium would be siderophile and very little would be left in the Earth's mantle (Wade and Wood, 2001).

Ringwood (1989a) proposed that the nonchondritic Mg/Si reflected a radial zonation in the solar system caused by the *addition* of more volatile silicon to the outer portions of the solar system. That is, he viewed the Earth as possibly more representative of the solar system than chondrites.

Hewins and Herzberg (1996) proposed that the midplane of the disk from which the Earth accreted was dominated by chondrules. Chondrules have higher Mg/Si than chondrites and if the Earth accreted in a particular chondrule rich area (as it may well have done) the sorting effect could dominate planetary compositions.

1.20.5.5 Oxygen Isotopic Models and Volatile Losses

Some have proposed that one can use the oxygen isotopic composition of the Earth to identify the proportions of different kinds of chondritic components (e.g., Lodders, 2000). The isotopic composition of oxygen is variable, chiefly in a mass-dependent way, in terrestrial materials. However, meteorites show mass-independent variations as well (Clayton, 1986, 1993). Oxygen has three isotopes and a three-isotope system allows discrimination between mass-dependent planetary processes and mass-independent primordial nebular heterogeneities inherited during planet formation (Clayton and Mayeda, 1996; Franchi *et al.*, 1999; Wiechert *et al.*, 2001, 2003). Clayton pursued this approach and showed that the mix of meteorite types based on oxygen isotopes would not provide a chemical composition that was similar to that of the Earth. In particular, the alkalis would be too abundant. In fact, the implied relative proportions of volatile-rich and volatile-poor constituents are in the opposite sense of those derived in the Wänke–Ringwood mixing models mentioned above (Clayton and Mayeda, 1996). Even the differences in composition between the planets do not make sense. Earth would need to be less volatile-depleted than Mars, whereas the opposite is true (Clayton, 1993; Halliday *et al.*, 2001). The oxygen isotope compositions of Mars (based on analyses of SNC meteorites) show a *smaller* proportion of carbonaceous-chondrite-like material in Mars than in Earth (Clayton, 1993; Halliday *et al.*, 2001). It thus appears that, unless the Earth lost a

significant proportion of its moderately volatile elements after it formed, the principal carrier of moderately volatile elements involved in the formation of the terrestrial planets was not of carbonaceous chondrite composition. This, of course, leads to the viewpoint that the Earth was built from volatile-depleted material, such as differentiated planetesimals (Taylor and Norman, 1990), but it still begs the question of how volatile depletion occurred (Halliday and Porcelli, 2001).

Whether it is plausible, given the dynamics of planetary accretion discussed above, that the Earth lost a major fraction of its moderately volatile elements during its accretion history is unclear. This has been advanced as an explanation by Lodders (2000) and is supported by strontium isotope data for early solar system objects discussed below (Halliday and Porcelli, 2001). The difficulty is to come up with a mechanism that does not fractionate K isotopes (Humayun and Clayton, 1995) and permits loss of heavy volatile elements. The degree to which lack of fractionation of potassium isotopes offers a real constraint depends on the mechanisms involved (Esat, 1996; Young, 2000). There is no question that as the Earth became larger, the accretion dynamics would have become more energetic and the temperatures associated with accretion would become greater (Melosh and Sonett, 1986; Melosh and Vickery, 1989; Ahrens, 1990; Benz and Cameron, 1990; Melosh, 1990; Melosh *et al.*, 1993). However, the gravitational pull of the Earth would have become so large that it would be difficult for the Earth to lose these elements even if they were degassed into a hot protoatmosphere. This is discussed further below.

1.20.6 EARTH'S EARLIEST ATMOSPHERES AND HYDROSPHERES

1.20.6.1 Introduction

The range of possibilities to be considered for the nature of the earliest atmosphere provides such a broad spectrum of consequences for thermal and magmatic evolution that it is better to consider the atmospheres first before discussing other aspects of Earth's evolution. Therefore, in this section a brief explanation of the different kinds of early atmospheres and their likely effects on the Earth are given in cursory terms. More comprehensive information on atmospheric components is found elsewhere in Volume 4 of this treatise.

1.20.6.2 Did the Earth Have a Nebular Protoatmosphere?

Large nebular atmospheres have at various times been considered a fundamental feature of

the early Earth by geochemists (e.g., Sasaki and Nakazawa, 1988; Pepin, 2000; Porcelli *et al.*, 1998). Large amounts of nebular gases readily explain why the Earth has primordial ^3He (Clarke *et al.*, 1969; Mamyrin *et al.*, 1969; Lupton and Craig, 1975; Craig and Lupton, 1976) and why a component of solar-like neon with a solar He/Ne ratio can be found in some plume basalts (Honda *et al.*, 1991; Dixon *et al.*, 2000; Moreira *et al.*, 2001). Evidence for a solar component among the heavier noble gases has been more scant (Moreira and Allègre, 1998; Moreira *et al.*, 1998). There is a hint of a component with different $^{38}\text{Ar}/^{36}\text{Ar}$ in some basalts (Niedermann *et al.*, 1997) and this may reflect a solar argon component (Pepin and Porcelli, 2002). Also, Caffee *et al.* (1988, 1999) have made the case that a solar component of xenon can be found in well gases.

The consequences for the early behavior of the Earth are anticipated to be considerable if there was a large nebular atmosphere. Huge reducing protoatmospheres, be they nebular or impact-induced can facilitate thermal blanketing, magma oceans and core formation. For example, based on the evidence from helium and neon, Harper and Jacobsen (1996b) suggested that iron was reduced to form the core during a stage with a massive early H_2 –He atmosphere. A variety of authors had already proposed that the Earth accreted with a large solar nebular atmosphere. Harper and Jacobsen's model builds upon many earlier such ideas primarily put forward by the Kyoto school (Hayashi *et al.*, 1979, 1985; Mizuno *et al.*, 1980; Sasaki and Nakazawa, 1988; Sasaki, 1990). The thermal effects of a very large protoatmosphere have been modeled by Hayashi *et al.* (1979), who showed that surface temperatures might reach $>4,000\text{ K}$. Sasaki (1990) also showed that incredibly high temperatures might build up in the outer portions of the mantle, leading to widespread magma oceans. Dissolving volatiles like noble gases into early silicate and metal liquids may have been quite easy under these circumstances (Mizuno *et al.*, 1980; Porcelli *et al.*, 2001; Porcelli and Halliday, 2001).

Porcelli and Pepin (2000) and Porcelli *et al.* (2001) recently summarized the noble gas arguments pointing out that first-order calculations indicate that significant amounts of noble gases with a solar composition are left within the Earth's interior but orders of magnitude more have been lost, based on xenon isotopic evidence (see Chapter 4.11). Therefore, one requires a relatively large amount of nebular gas during Earth's accretion. To make the Earth this way, the timescales for accretion need to be characteristically short ($\sim 10^6$ – 10^7 yr) in order to trap such amounts of gas before the remains of the solar nebula are accreted into the Sun or other planets. Therefore, a problem may exist reconciling the apparent need to

acquire a large nebular atmosphere with the longer timescales ($\sim 10^7$ – 10^8 yr) for accretion implied by Safronov–Wetherill models and by tungsten and lead isotopic data. It is hard to get around this problem because the nebular model is predicated on the assumption that the Earth grows extremely fast such that it can retain a large atmosphere (Pepin and Porcelli, 2002).

Therefore, other models for explaining the incorporation of solar-like noble gases should be considered. The most widely voiced alternative is that of accreting material that formed earlier elsewhere that already had acquired solar-like noble gases. For example, it has been argued that the neon is acquired as “Ne–B” from accretion of chondritic material (Trieloff *et al.*, 2000). With such a component in meteorites, one apparently could readily explain the Earth's noble gas composition, which may have a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio that is lower than solar (Farley and Poreda, 1992). However, this component is no longer well defined in meteorites and the argument is less than certain because of this. In fact, Ne–B is probably just a fractionated version of solar (Ballentine *et al.*, 2001). This problem apart, the idea that the Earth acquired its solar-like noble gases from accreting earlier-formed objects is an alternative that is worth considering. Chondrites, however, mainly contain very different noble gases that are dominated by the so-called “Planetary” component (Ozima and Podosek, 2002). This component is nowadays more precisely identified as “Phase Q” (Wieler *et al.*, 1992; Busemann *et al.*, 2000). In detail, the components within chondrites show little sign of having incorporated large amounts of solar-like noble gases. Early melted objects like CAIs and chondrules are, generally speaking, strongly degassed (Vogel *et al.*, 2002, 2003).

Podosek *et al.* (2003) recently have proposed that the noble gases are incorporated into early formed planetesimals that are irradiated by intense solar-wind activity from the vigorous early Sun. With the new evidence from young solar mass stars of vastly greater flare activity (Feigelson *et al.*, 2002a,b), there is strong support for the notion that inner solar system objects would have incorporated a lot of solar-wind implanted noble gases. The beauty of this model is that small objects with larger surface-to-volume ratio trap more noble gases. Unlike the nebular model it works best if large objects take a long time to form. As such, the model is easier to reconcile with the kinds of long timescales for accretion implied by tungsten and lead isotopes. Podosek *et al.* (2003) present detailed calculations to illustrate the feasibility of such a scenario.

To summarize, although large nebular atmospheres have long been considered the most likely explanation for primordial solar-like noble gases

in the Earth, the implications of such models appear hard to reconcile with the accretionary timescales determined from tungsten and lead isotopes. Irradiating planetesimals with solar wind currently appears to be the most promising alternative. If this is correct, the Earth may still at one time have had a relatively large atmosphere, but it would have formed by degassing of the Earth's interior.

1.20.6.3 Earth's Degassed Protoatmosphere

The discovery that primordial ^3He still is being released from the Earth's interior (Clarke *et al.*, 1969; Mamyrin *et al.*, 1969; Lupton and Craig, 1975; Craig and Lupton, 1976) is one of the greatest scientific contributions made by noble gas geochemistry. Far from being totally degassed, the Earth has deep reservoirs that must supply ^3He to the upper mantle and thence to the atmosphere. However, the idea that the majority of the components in the present-day atmosphere formed by degassing of the Earth's interior is much older than this. Brown (1949) and Rubey (1951) proposed this on the basis of the similarity in chemical composition between the atmosphere and hydrosphere on the one hand and the compositions of volcanic gases on the other. In more recent years, a variety of models for the history of degassing of the Earth have been developed based on the idea that a relatively undegassed lower mantle supplied the upper mantle with volatiles, which then supplied the atmosphere (Allègre *et al.*, 1983, 1996; O'Nions and Tolstikhin, 1994; Porcelli and Wasserburg, 1995).

Some of the elements in the atmosphere provide specific "time information" on the degassing of the Earth. Of course, oxygen was added to the atmosphere gradually by photosynthesis with a major increase in the early Proterozoic (Kasting, 2001). However, the isotopic composition and concentration of argon provides powerful evidence that other gases have been added to the atmosphere from the mantle over geological time (O'Nions and Tolstikhin, 1994; Porcelli and Wasserburg, 1995). In the case of argon, a mass balance can be determined because it is dominantly (>99%) composed of ^{40}Ar , formed by radioactive decay of ^{40}K . From the Earth's potassium concentration and the atmosphere's argon concentration it can be shown that roughly half the ^{40}Ar is in the atmosphere, the remainder presumably being still stored in the Earth's mantle (Allègre *et al.*, 1996). Some have argued that this cannot be correct on geophysical grounds, leading to the proposal that the Earth's K/U ratio has been overestimated (Davies, 1999). However, the relationship with Rb/Sr (Figure 2) provides strong evidence that the Earth's K/U ratio is $\sim 10^4$

(Allègre *et al.*, 2001; Halliday and Porcelli, 2001). Furthermore, support for mantle reservoirs that are relatively undegassed can be found in both helium and neon isotopes (Allègre *et al.*, 1983, 1987; Moreira *et al.*, 1998, 2001; Moreira and Allègre, 1998; O'Nions and Tolstikhin, 1994; Niedermann *et al.*, 1997; Porcelli and Wasserburg, 1995). The average timing of this loss is poorly constrained from argon data. In principle, this amount of argon could have been supplied catastrophically in the recent past. However, it is far more reasonable to assume that because the Earth's radioactive heat production is decaying exponentially, the amount of degassing has been decreasing with time. The argon in the atmosphere is the time-integrated effect of this degassing.

Xenon isotopes provide strong evidence that the Earth's interior may have undergone an early and catastrophic degassing (Allègre *et al.*, 1983, 1987). Allègre *et al.* discovered that the MORB-source mantle had elevated ^{129}Xe relative to atmospheric xenon, indicating that the Earth and atmosphere separated from each other at an early stage. These models are hampered by a lack of constraints on the xenon budgets of the mantle and by atmospheric contamination that pervades many mantle-derived samples. Furthermore, the model assumes a closed system. If a portion of the xenon in the Earth's atmosphere was added after degassing (Javoy, 1998, 1999) by cometary or asteroidal impacts (Owen and Bar-Nun, 1995, 2000; Morbidelli *et al.*, 2000), the model becomes underconstrained. The differences that have been reported between the elemental and atomic abundances of the noble gases in the mantle relative to the atmosphere may indeed be explained by heterogeneous accretion of the atmosphere (Marty, 1989; Caffee *et al.*, 1988, 1999).

Isotopic evidence aside, many theoretical and experimental papers have focused on the production of a steam atmosphere by impact-induced degassing of the Earth's interior (Abe and Matsui, 1985, 1986, 1988; O'Keefe and Ahrens, 1977; Lange and Ahrens, 1982, 1984; Matsui and Abe, 1986a,b; Sasaki, 1990; Tyburczy *et al.*, 1986; Zahnle *et al.*, 1988). Water is highly soluble in silicate melts at high pressures (Richter and Drake, 1999; Abe *et al.*, 2000). As such, a large amount could have been stored in the Earth's mantle and then released during volcanic degassing.

Ahrens (1990) has modeled the effects of impact-induced degassing on the Earth. He considers that the Earth probably alternated between two extreme states as accretion proceeded. When the Earth was degassed it would accumulate a large reducing atmosphere. This would provide a blanket that also allowed enormous surface temperatures to be reached:

Ahrens estimates $\sim 1,500$ K. However, when an impact occurred this atmosphere would be blown off. The surface of the Earth would become cool and oxidizing again (Ahrens, 1990). There is strong isotopic evidence for such early losses of the early atmospheres as explained in the next section.

1.20.6.4 Loss of Earth's Earliest Atmosphere(s)

The xenon isotope data provide evidence that much ($>99\%$) of the Earth's early atmosphere was lost within the first 100 Myr. Several papers on this can be found in the literature and the most recent ones by Ozima and Podosek (1999) and Porcelli *et al.* (2001) are particularly useful. The basic argument for the loss is fairly simple and is not so different from the original idea of using xenon isotopes to date the Earth (Wetherill, 1975a). We have a rough idea of how much iodine exists in the Earth's mantle. The Earth's current inventory is not well constrained but we know enough (Déruelle *et al.*, 1992) to estimate the approximate level of depletion of this volatile element. It is clear from the degassing of noble gases that the present ratio of I/Xe in the Earth is orders of magnitude higher than chondritic values. We know that at the start of the solar system ^{129}I was present with an atomic abundance of $\sim 10^{-4}$ relative to stable ^{127}I (Swindle and Podosek, 1988). All of this ^{129}I formed ^{129}Xe , and should have produced xenon that was highly enriched in ^{129}Xe given the Earth's I/Xe ratio. Yet instead, the Earth has xenon that is only slightly more radiogenic than is found in meteorites rich in primordial noble gases; the ^{129}Xe excesses in the atmosphere and the mantle are both minute by comparison with that expected from the Earth's I/Xe. This provides evidence that the Earth had a low I/Xe ratio that kept its xenon isotopic compositions close to chondritic. At some point xenon was lost and by this time ^{129}I was close to being extinct such that the xenon did not become very radiogenic despite a very high I/Xe.

The xenon isotopic arguments can be extended to fissionogenic xenon. The use of the combined ^{129}I – ^{129}Xe and ^{244}Pu – $^{132,134,136}\text{Xe}$ (spontaneous fission half-life ~ 80 Myr) systems provides estimates of ~ 100 Myr for loss of xenon from the Earth (Ozima and Podosek, 1999). The fission-based models are hampered by the difficulties with resolving the heavy xenon that is formed from fission of ^{244}Pu as opposed to longer-lived uranium. The amount of ^{136}Xe that is expected to have formed from ^{244}Pu within the Earth should exceed that produced from uranium as found in well gases (Phinney *et al.*, 1978) and this has been confirmed with measurements of MORBs (Kunz *et al.*, 1998). However, the relative amount of plutonogenic Xe/uranogenic Xe will be a function

of the history of degassing of the mantle. Estimating these amounts accurately is very hard.

This problem is exacerbated by the lack of constraint that exists on the initial xenon isotopic composition of the Earth. The xenon isotopic composition of the atmosphere is strikingly different from that found in meteorites (Wieler *et al.*, 1992; Busemann *et al.*, 2000) or the solar wind (Wieler *et al.*, 1996). It is fractionated relative to solar, the light isotopes being strongly depleted (Figure 7). One can estimate the initial xenon isotopic composition of the Earth by assuming it was strongly fractionated from something more like the composition found in meteorites and the solar wind. By using meteorite data to determine a best fit to atmospheric Xe one obtains a composition called “U–Xe” (Pepin, 1997, 2000). However, this is based on finding a composition that is consistent with the present-day atmosphere. Therefore caution is needed when using the fissionogenic xenon components to estimate an accretion age for the Earth because the arguments become circular (Zhang, 1998).

The strong mass-dependent fractionation of xenon has long been thought to be caused by hydrodynamic escape (Hunten *et al.*, 1987; Walker, 1986) of the atmosphere. Xenon probably was entrained in a massive atmosphere of light gases presumably dominated by hydrogen and helium that was lost (Sasaki and Nakazawa, 1988). This is consistent with the view based on radiogenic and fissionogenic xenon that a large fraction of the Earth's atmosphere was lost during the lifetime of ^{129}I .

Support for loss of light gases from the atmosphere via hydrodynamic escape can be found in other “atmosphile” isotopic systems. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio in the mantle is elevated

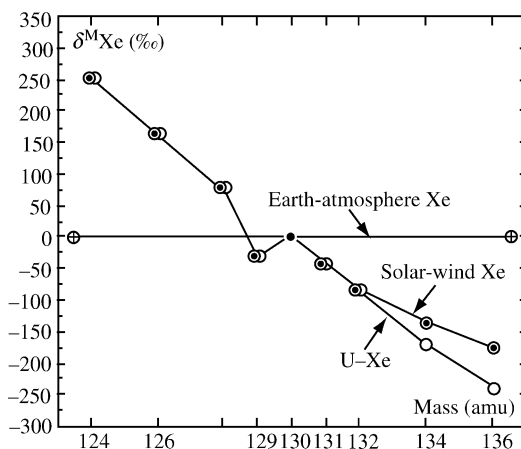


Figure 7 Mass fractionation of xenon in the atmosphere relative to the solar value (Pepin and Porcelli, 2002) (reproduced by permission of Mineralogical Society of America from *Rev. Mineral. Geochem.* 2002, 47, 191–246).

relative to the atmosphere (Tieloff *et al.*, 2000). The mantle value is close to solar (Farley and Poreda, 1992), but the atmosphere plots almost exactly according to a heavy mass-dependent fractionated composition. Similarly, the hydrosphere has a D/H ratio that is heavy relative to the mantle. However, argon and krypton isotopes provide no support for the theory (Pepin and Porcelli, 2002). Therefore, this model cannot be applied in any simple way to all of the atmophile elements.

It is possible that the atmosphere was blown off by a major impact like the Moon-forming giant impact, but this is far from clear at this stage. Another mechanism that often is considered is the effect of strong ultraviolet wavelength radiation from the early Sun (Zahnle and Walker, 1982). This might affect Xe preferentially because of the lower ionization potential. It is of course possible that the Earth simply acquired an atmosphere, with xenon, like today's (Marty, 1989; Caffee *et al.*, 1999). However, then it is not clear how to explain the strong isotopic fractionation relative to solar and meteorite compositions.

Taken together, the noble gas data provide evidence that Earth once had an atmosphere that was far more massive than today's. If true, this would have had two important geochemical consequences. First, there would have been a blanketing effect from such an atmosphere. This being the case, the temperature at the surface of the Earth would have been very high. There may well have been magma oceans, rock vapor in the atmosphere, and extreme degassing of moderately volatile as well as volatile elements. Blow-off of this atmosphere may have been related to the apparent loss of moderately volatile elements (Halliday and Porcelli, 2001). With magma oceans there would be, at best, a weak crust, mantle mixing would have been very efficient, and core formation would have proceeded quickly.

The second consequence is that it would have been relatively easy to dissolve a small amount of this "solar" gas at high pressure into the basaltic melts at the Earth's surface (Mizuno *et al.*, 1980). This "ingassing" provides a mechanism for transporting nebular gases into the Earth's interior. The ultimate source of solar helium and neon in the mantle is unknown. At one time, it was thought to be the mantle (Allègre *et al.*, 1983) and this still seems most likely (Porcelli and Ballentine, 2002) but the core also has been explored (Porcelli and Halliday, 2001) as a possible alternative.

1.20.7 MAGMA OCEANS AND CORE FORMATION

Core formation is the biggest differentiation process that has affected the planet, resulting in a large-scale change of the distribution of density

and heat production. One would think that such a basic feature would be well understood. However, the very existence of large amounts of iron metal at the center of an Earth with an oxidized mantle is problematic (Ringwood, 1977). Large reducing atmospheres and magma oceans together provide a nice explanation. For example, Ringwood (1966) considered that the iron metal in the Earth's core formed by reduction of iron in silicates and oxides and thereby suggested a huge CO atmosphere. Clearly, if the Earth's core formed by reduction of iron in a large atmosphere, the process of core formation would occur early and easily.

However, there is very little independent evidence from mantle or crustal geochemistry to substantiate the former presence of magma oceans. There has been no shortage of proposals and arguments for and against on the basis of petrological data for the Earth's upper mantle. The key problem is the uncertainty that exists regarding the relationship between the present day upper mantle and that that may have existed in the early Earth. Some have argued that the present day lower mantle is compositionally distinct in terms of major elements (e.g., Herzberg, 1984; Jackson, 1983), whereas others (e.g., Hofmann, 1988; Hofmann *et al.*, 1986; Davies, 1999) have presented strong evidence in favor of large-scale overall convective interchange. Although several papers have used the present-day major, trace, and isotopic compositions of the upper mantle to provide constraints on the earliest history of the Earth (Allègre *et al.*, 1983; Agee and Walker, 1988; Kato *et al.*, 1988a,b; McFarlane and Drake, 1990; Jones *et al.*, 1992; Drake and McFarlane, 1993; Porcelli and Wasserburg, 1995; O'Nions and Tolstikhin, 1994; Righter and Drake, 1996), it is unclear whether or not this is valid, given 4.5 Gyr of mantle convection.

For example, the trace element and hafnium isotopic compositions of the upper mantle provide no sign of perovskite fractionation in a magma ocean (Ringwood, 1990; Halliday *et al.*, 1995) and even the heavy REE pattern of the upper mantle appears to be essentially flat (e.g., Lee *et al.*, 1996). This is not to be expected if majorite garnet was a liquidus phase (Herzberg *et al.*, 1988). One explanation for the lack of such evidence is that the magma ocean was itself an efficiently mixed system with little if any crystal settling (Tonks and Melosh, 1990). Another possibility is that the entire mantle has been rehomogenized since this time. Ringwood (1990) suggested this possibility, which leaves some arguments regarding the relevance of the composition of the upper mantle in doubt. Of course, the subsequent introduction of heterogeneities by entrainment and radioactive decay and the development of an isotopically stratified mantle (Hofmann *et al.*, 1986; Moreira and Allègre, 1998) are not inconsistent with this.

Whether or not magma oceans are a necessary prerequisite for core formation is unclear. It is necessary to understand how it is possible for metallic iron to migrate through the silicate mantle (Shaw, 1978). Many have assumed that a part of the mantle at least was solid during core formation. A variety of mechanisms have been studied including grain boundary percolation (Minarik *et al.*, 1996; Rushmer *et al.*, 2000; Yoshino *et al.*, 2003) and the formation of large-scale metal structures in the upper mantle that sink like diapirs into the center of the Earth (Stevenson, 1981, 1990). Under some circumstances these may break up into small droplets of metal (Rubie *et al.*, 2003). To evaluate these models, it is essential to have some idea of the physical state of the early Earth at the time of core formation. All of these issues are addressed by modern geochemistry but are not yet well constrained. Most effort has been focused on using the composition of the silicate Earth itself to provide constraints on models of core formation.

The major problem presented by the Earth's chemical composition and core formation models is providing mechanisms that predict correctly the siderophile element abundances in the Earth's upper mantle. It long has been recognized that siderophile elements are more abundant in the mantle than expected if the silicate Earth and the core were segregated under low-pressure and moderate-temperature equilibrium conditions (Chou, 1978; Jagoutz *et al.*, 1979). Several explanations for this siderophile "excess" have been proposed, including:

- (i) partitioning into liquid metal alloy at high pressure (Ringwood, 1979);
- (ii) equilibrium partitioning between sulfur-rich liquid metal and silicate (Brett, 1984);
- (iii) inefficient core formation (Arculus and Delano, 1981; Jones and Drake, 1986);
- (iv) heterogeneous accretion and late veneers (Eucken, 1944; Turekian and Clark, 1969; Clark *et al.*, 1972; Smith, 1977, 1980; Wänke *et al.*, 1984; Newsom, 1990);
- (v) addition of material to the silicate Earth from the core of a Moon-forming impactor (Newsom and Taylor, 1986);
- (vi) very high temperature equilibration (Murthy, 1991); and
- (vii) high-temperature equilibrium partitioning in a magma ocean at the upper/lower mantle boundary (Li and Agee, 1996; Righter *et al.*, 1997).

Although the abundances and partition coefficients of some of the elements used to test these models are not well established, sufficient knowledge exists to render all of them problematic. Model (vii) appears to work well for some moderately siderophile elements. Righter and Drake (1999) make the case that the fit of the

siderophile element metal/silicate partition coefficient data is best achieved with a high water content (per cent level) in the mantle. This would have assisted the formation of a magma ocean and provided a ready source of volatiles in the Earth. Walter *et al.* (2000) reviewed the state of the art in this area. However, the number of elements with well-established high-pressure partition coefficients for testing this model is still extremely small.

To complicate chemical models further, there is some osmium isotopic evidence that a small flux of highly siderophile elements from the core could be affecting the abundances in the mantle (Walker *et al.*, 1995; Brandon *et al.*, 1998). This model has been extended to the interpretation of PGE abundances in abyssal peridotites (Snow and Schmidt, 1998). The inventories of many of these highly siderophile elements are not that well established and may be extremely variable (Rehkämper *et al.*, 1997, 1999b). In particular, the use of abyssal peridotites to assess siderophile element abundances in the upper mantle appears to be problematic (Rehkämper *et al.*, 1999a). Puchtel and Humayun (2000) argued that if PGEs are being fluxed from the core to the mantle then this is not via the Walker *et al.* (1995) mechanism of physical admixture by entrainment of outer core, but must proceed via an osmium isotopic exchange, since the excess siderophiles were not found in komatiite source regions with radiogenic ^{187}Os . Taken together, the status of core to mantle fluxes is very vague at the present time.

1.20.8 THE FORMATION OF THE MOON

The origin of the Moon has been the subject of intense scientific interest for over a century but particularly since the Apollo missions provided samples to study. The most widely accepted current theory is the giant impact theory but this idea has evolved from others and alternative hypotheses have been variously considered. Wood (1984) provides a very useful review. The main theories that have been considered are as follows:

Co-accretion. This theory proposes that the Earth and Moon simply accreted side by side. The difficulty with this model is that it does not explain the angular momentum of the Earth–Moon system, nor the difference in density, nor the difference in volatile depletion (Taylor, 1992).

Capture. This theory (Urey, 1966) proposes that the Moon was a body captured into Earth's orbit. It is dynamically difficult to do this without the Moon spiraling into the Earth and colliding. Also the Earth and Moon have indistinguishable oxygen isotope compositions (Wiechert *et al.*, 2001) in a solar system that appears to be highly heterogeneous in this respect (Clayton, 1986).

Fission. This theory proposes that the Moon split off as a blob during rapid rotation of a molten Earth. George Howard Darwin, the son of Charles Darwin originally championed this idea (Darwin, 1878, 1879). At one time (before the young age of the oceanfloor was known) it was thought by some that the Pacific Ocean might have been the residual space vacated by the loss of material. This theory is also dynamically difficult. Detailed discussions of the mechanisms can be found in Binder (1986). However, this model does have certain features that are attractive. It explains why Earth and Moon have identical oxygen isotope compositions. It explains why the Moon has a lower density because the outer part of the Earth would be deficient in iron due to core formation. It explains why so much of the angular momentum of the Earth–Moon system is in the Moon’s motion. These are key features of any successful explanation for the origin of the Moon.

Impact models. Mainly because of the difficulties with the above models, alternatives were considered following the Apollo missions. Hartmann and Davis (1975) made the proposal that the Moon formed as a result of major impacts that propelled sufficient debris into orbit to produce the Moon. However, an important new facet that came from sample return was the discovery that the Moon had an anorthositic crust implying a very hot magma ocean. Also it was necessary to link the dynamics of the Moon with that of the Earth’s spin. If an impact produced the Moon it would be easier to explain these features if it was highly energetic. This led to a series of single giant impact models in which the Moon was the product of a glancing blow collision with another differentiated planet (Cameron and Benz, 1991). A ring of debris would have been produced from the outer silicate portions of the Earth and the impactor planet (named “Theia,” the mother of “Selene,” the goddess of the Moon). Wetherill (1986) calculated that there was a realistic chance of such a collision. This model explains the angular momentum, the “fiery start,” the isotopic similarities and the density difference.

The giant-impact theory has been confirmed by a number of important observations. Perhaps most importantly, we know now that the Moon must have formed tens of millions of years after the start of the solar system (Lee *et al.*, 1997; Halliday, 2000). This is consistent with a collision between already formed planets. The masses of the Earth and the impactor at the time of the giant impact have been the subject of major uncertainty. Two main classes of models are usually considered. In the first, the Earth was largely (90%) formed at the time of the impact and the impacting planet Theia was roughly Mars-sized (Cameron and Benz, 1991). A recent class of models considers the Earth to be only half-formed at the

time of the impact, and the mass ratio Theia/ proto-Earth to be 3:7 (Cameron, 2000). The latter model is no longer considered likely; the most recent simulations have reverted to a Mars-sized impactor at the end of Earth accretion (Canup and Asphaug, 2001). The tungsten isotope data for the Earth and Moon do not provide a unique test (Halliday *et al.*, 2000).

The giant-impact model, though widely accepted, has not been without its critics. Geochemical arguments have been particularly important in this regard. The biggest concern has been the similarities between chemical and isotopic features of the Earth and Moon. Most of the dynamic simulations (Cameron and Benz, 1991; Cameron, 2000; Canup and Asphaug, 2001) predict that the material that forms the Moon is derived from Theia, rather than the Earth. Yet it became very clear at an early stage of study that samples from the Moon and Earth shared many common features that would be most readily explained if the Moon was formed from material derived from the Earth (Wänke *et al.*, 1983; Wänke and Dreibus, 1986; Ringwood, 1989b, 1992). These include the striking similarity in tungsten depletion despite a strong sensitivity to the oxidation state of the mantle (Rammensee and Wänke, 1977; Schmitt *et al.*, 1989). Other basaltic objects such as eucrites and martian meteorites exhibit very different siderophile element depletion (e.g., Treiman *et al.*, 1986, 1987; Wänke and Dreibus, 1988, 1994). Therefore, why should the Earth and Moon be identical if the Moon came from Theia (Ringwood, 1989b, 1992)? In a similar manner, the striking similarity in oxygen isotopic composition (Clayton and Mayeda, 1975), still unresolvable to extremely high precision (Wiechert *et al.*, 2001), despite enormous heterogeneity in the solar system (Clayton *et al.*, 1973; Clayton, 1986, 1993; Clayton and Mayeda, 1996), provides support for the view that the Moon was derived from the Earth (Figure 3).

One can turn these arguments around, however, and use the compositions of lunar samples to define the composition of Theia, assuming the impactor produced most of the material in the Moon (MacFarlane, 1989). Accordingly, the similarity in oxygen isotopes and trace siderophile abundances between the Earth and Moon provides evidence that Earth and Theia were neighboring planets made of an identical mix of materials with similar differentiation histories (Halliday and Porcelli, 2001). Their similarities could relate to proximity in the early solar system, increasing the probability of collision.

Certain features of the Moon may be a consequence of the giant impact itself. The volatile-depleted composition of the Moon, in particular, has been explained as a consequence of

the giant impact (O'Neill, 1991a; Jones and Palme, 2000). It has been argued (Kreutzberger *et al.*, 1986; Jones and Drake, 1993) that the Moon could not have formed as a volatile depleted residue of material from the Earth because it has Rb/Cs that is lower than that of the Earth and caesium supposedly is more volatile. However, the assumptions regarding the Earth's Rb/Cs upon which this is based are rather weak (McDonough *et al.*, 1992). Furthermore, the exact relative volatilities of the alkalis are poorly known. Using the canonical numbers, the Earth, Moon, and Mars are all more depleted in less volatile rubidium than more volatile potassium (Figure 2). From the slope of the correlation, it can be seen that the terrestrial depletion in rubidium (50% condensation temperature $\sim 1,080$ K) is $\sim 80\%$ greater than that in potassium (50% condensation temperature $\sim 1,000$ K) (Wasson, 1985). Similar problems are found if one compares sodium depletion, or alkali concentrations more generally for other early objects, including chondrites.

Attempts to date the Moon were initially focused on determining the ages of the oldest rocks and therefore providing a lower limit. These studies emphasized precise strontium, neodymium, and lead isotopic constraints (Tera *et al.*, 1973; Wasserburg *et al.*, 1977a; Hanan and Tilton, 1987; Carlson and Lugmair, 1988; Shih *et al.*, 1993; Alibert *et al.*, 1994). At the end of the Apollo era, Wasserburg *et al.* (1977a) wrote "The actual time of aggregation of the Moon is not precisely known, but the Moon existed as a planetary body at 4.45 Ga, based on mutually consistent Rb–Sr and U–Pb data. This is remarkably close to the ^{207}Pb – ^{206}Pb age of the Earth and suggests that the Moon and the Earth were formed or differentiated at the same time." Although these collective efforts made a monumental contribution, such constraints on the age of the Moon still leave considerable scope (>100 Myr) for an exact age.

Some of the most precise and reliable early ages for lunar rocks are given in Table 3. They provide considerable support for an age of >4.42 Ga. Probably the most compelling evidence comes from the early ferroan anorthosite 60025, which defines a relatively low first-stage μ (or $^{238}\text{U}/^{204}\text{Pb}$) and an age of ~ 4.5 Ga. Of course, the ages of the oldest lunar rocks only date igneous events. Carlson and Lugmair (1988) reviewed all of the most precise and concordant data and concluded that the Moon had to have formed in the time interval 4.44–4.51 Ga. This is consistent with the estimate of 4.47 ± 0.02 Ga of Tera *et al.* (1973).

Model ages can provide upper and lower limits on the age of the Moon. Halliday and Porcelli (2001) reviewed the strontium isotope data for early solar system objects and showed that

the initial strontium isotopic compositions of early lunar highlands samples (Papanastassiou and Wasserburg, 1976; Carlson and Lugmair, 1988) are all slightly higher than the best estimates of the solar system initial ratio (Figure 8). The conservative estimates of the strontium isotope data indicate that the difference between the $^{87}\text{Sr}/^{86}\text{Sr}$ of the bulk solar system initial at 4.566 Ga is 0.69891 ± 2 and the Moon at ~ 4.515 Ga is 0.69906 ± 2 is fully resolvable. An Rb–Sr model age for the Moon can be calculated by assuming that objects formed from material that separated from a solar nebula reservoir with the Moon's current Rb/Sr ratio. Because the Rb/Sr ratios of the lunar samples are extremely low, the uncertainty in formation age does not affect the calculated initial strontium isotopic composition, hence the model age, significantly. The CI chondritic Rb/Sr ratio ($^{87}\text{Rb}/^{86}\text{Sr} = 0.92$) is assumed to represent the solar nebula. This model provides an upper limit on the formation age of the object, because the solar nebula is thought to represent the most extreme Rb/Sr reservoir in which the increase in strontium isotopic composition could have been accomplished. In reality, the strontium isotopic composition probably evolved in a more complex manner over a longer time. The calculated time required to generate the difference in strontium isotopic composition in a primitive solar nebula environment is 11 ± 3 Myr. This is, therefore, the earliest point in time at which the Moon could have formed (Halliday and Porcelli, 2001).

A similar model-age approach can be used with the Hf–W system. In fact, Hf–W data provide the most powerful current constraints on the exact age of the Moon. The tungsten isotopic compositions of bulk rock lunar samples range from $\varepsilon_{\text{W}} \sim 0$ like the silicate Earth to $\varepsilon_{\text{W}} > 10$ (Lee *et al.*, 1997, 2002). This was originally interpreted as the result of radioactive decay of formerly live ^{182}Hf within the Moon, which has a variable but generally high Hf/W ratio in its mantle (Lee *et al.*, 1997). Now we know that a major portion of the ^{182}W excess in lunar samples is cosmogenic and the result of the reaction $^{181}\text{Ta}(n, \gamma)^{182}\text{Ta}(\beta^-)^{182}\text{W}$ while these rocks were exposed on the surface of the Moon (Leya *et al.*, 2000; Lee *et al.*, 2002). This can be corrected using (i) estimates of the cosmic ray flux from samarium and gadolinium compositions, (ii) the exposure age and Ta/W ratio, or (iii) internal isochrons of tungsten isotopic composition against Ta/W (Lee *et al.*, 2002). The best current estimates for the corrected compositions are shown in Figure 9. The spread in the data is reduced and the stated uncertainties are greater relative to the raw tungsten isotopic compositions (Lee *et al.*, 1997). Most data are within error of the Earth. A small excess ^{182}W is still resolvable for

Table 3 Recent estimates of the ages of early solar system objects and the age of the Moon.

<i>Object</i>	<i>Sample(s)</i>	<i>Method</i>	<i>References</i>	<i>Age (Ga)</i>
Earliest solar system	Allende CAIs	U–Pb	Göpel <i>et al.</i> (1991)	4.566 ± 0.002
Earliest solar system	Efremovka CAIs	U–Pb	Amelin <i>et al.</i> (2002)	4.5672 ± 0.0006
Chondrule formation	Acfer chondrules	U–Pb	Amelin <i>et al.</i> (2002)	4.5647 ± 0.0006
Angrites	Angra dos Reis and LEW 86010	U–Pb	Lugmair and Galer (1992)	4.5578 ± 0.0005
Early eucrites	Chervony Kut	Mn–Cr	Lugmair and Shukolyukov (1998)	4.563 ± 0.001
Earth accretion	Mean age	U–Pb	Halliday (2000)	≤ 4.55
Earth accretion	Mean age	U–Pb	Halliday (2000)	≥ 4.49
Earth accretion	Mean age	Hf–W	Yin <i>et al.</i> (2002)	≥ 4.55
Lunar highlands	Ferroan anorthosite 60025	U–Pb	Hanan and Tilton (1987)	4.50 ± 0.01
Lunar highlands	Ferroan anorthosite 60025	Sm–Nd	Carlson and Lugmair (1988)	4.44 ± 0.02
Lunar highlands	Norite from breccia 15445	Sm–Nd	Shih <i>et al.</i> (1993)	4.46 ± 0.07
Lunar highlands	Ferroan noritic anorthosite in breccia 67016	Sm–Nd	Alibert <i>et al.</i> (1994)	4.56 ± 0.07
Moon	Best estimate of age	U–Pb	Tera <i>et al.</i> (1973)	4.47 ± 0.02
Moon	Best estimate of age	U–Pb, Sm–Nd	Carlson and Lugmair (1988)	$4.44\text{--}4.51$
Moon	Best estimate of age	Hf–W	Halliday <i>et al.</i> (1996)	4.47 ± 0.04
Moon	Best estimate of age	Hf–W	Lee <i>et al.</i> (1997)	4.51 ± 0.01
Moon	Maximum age	Hf–W	Halliday (2000)	≤ 4.52
Moon	Maximum age	Rb–Sr	Halliday and Porcelli (2001)	≤ 4.55
Moon	Best estimate of age	Hf–W	Lee <i>et al.</i> (2002)	4.51 ± 0.01
Moon	Best estimate of age	Hf–W	Kleine <i>et al.</i> (2002)	4.54 ± 0.01

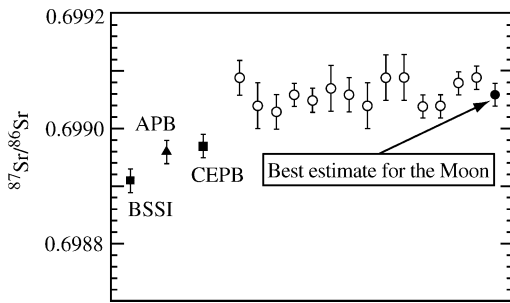


Figure 8 Initial strontium isotope composition of early lunar highland rocks relative to other early solar system objects. APB: Angrite Parent Body; CEPB: Cumulate Eucrite Parent Body; BSSI: Bulk Solar System Initial (source [Halliday and Porcelli, 2001](#)).

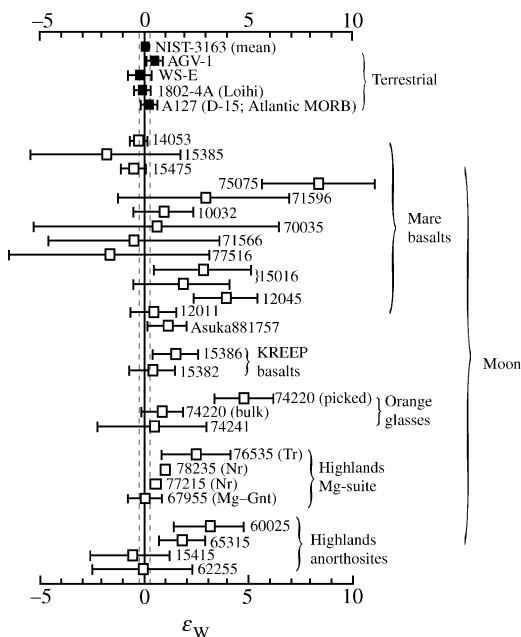


Figure 9 The tungsten isotopic compositions of lunar samples after calculated corrections for cosmogenic contributions (source [Leya et al., 2000](#)).

some samples, but these should be treated with caution.

The most obvious and clear implication of these data is that the Moon, a high-Hf/W object, must have formed late ([Lee et al., 1997](#)). [Halliday \(2000\)](#) argued that the tungsten isotopic composition was hard to explain if the Moon formed before ~50 Myr after the start of the solar system. The revised parameters for the average solar system ([Kleine et al., 2002](#)) mean that the Moon, like the Earth, has a well-defined excess of ^{182}W . This may have been inherited from the protolith silicate reservoirs from which the Moon formed. Alternatively, a portion might reflect ^{182}Hf decay within the Moon itself. Assuming that the Moon started as an isotopically homogeneous reservoir

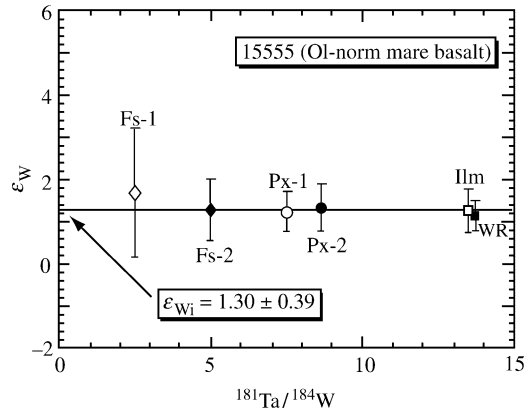


Figure 10 The tungsten isotopic composition of Apollo 15 basalt 15555 shows no internal variation as a function of Ta/W, consistent with its low exposure age (source [Lee et al., 2002](#)).

the most likely explanation for the small but well-defined excess ^{182}W found in Apollo basalts such as 15555 ([Figure 10](#)) relative to some of the other lunar rocks is that the Moon formed at a time when there was still a small amount of live ^{182}Hf in the lunar interior. This means that the Moon had to have formed within the first 60 Myr of the solar system ([Halliday, 2000](#); [Lee et al., 2002](#)). The Moon must also have formed by the time defined by the earliest lunar rocks. The earliest most precisely determined crystallization age of a lunar rock is that of 60025 which has a Pb–Pb age of close to 4.50 Ga ([Hanan and Tilton, 1987](#)). Therefore, the Moon appears to have formed before ~4.50 Ga.

Defining the age more precisely is proving difficult at this stage. First, more precise estimates of the Hf–W systematics of lunar rocks are needed. The amount of data for which the cosmogenically produced ^{182}W effects are well resolved is very limited ([Lee et al., 2002](#)) and analysis is time consuming and difficult. Second, the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ is poorly defined, as described above. If one uses a value of 1.0×10^{-4} ([Kleine et al., 2002](#); [Schöenberg et al., 2002](#); [Yin et al., 2002](#)), the small tungsten isotopic effects of the Moon probably were produced ≥ 30 Myr after the start of the solar system ([Kleine et al., 2002](#)). If, however, the $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{BSSI}}$ is slightly higher, as discussed above, the model age would be closer to 40–45 Myr ([Table 3](#)). The uncertainty in the ^{182}Hf decay constant ($\sim \pm 22\%$) also limits more precise constraints.

Either way, these Hf–W data provide very strong support for the giant-impact theory of lunar origin ([Cameron and Benz, 1991](#)). It is hard to explain how the Moon could have formed at such a late stage unless it was the result of a planetary

collision. The giant-impact theory predicts that the age of the Moon should postdate the origin of the solar system by some considerable amount of time, probably tens of millions of years if Wetherill's predictions are correct. This is consistent with the evidence from tungsten isotopes.

The giant impact can also be integrated into modeling of the lead isotopic composition of the Earth (Halliday, 2000). Doing so, one can constrain the timing. Assuming a Mars-sized impactor was added to the Earth in the final stages of accretion (Canup and Asphaug, 2001) and that, prior to this, Earth's accretion could be approximated by exponentially decreasing rates (Halliday, 2000), one can calibrate the predicted lead isotopic composition of the Earth in terms of the time of the giant impact (Figure 11). It can be seen that all of the many estimates for the lead isotopic composition of the BSE compiled by Galer and Goldstein (1996) plus the more recent estimates of Kramers and Tolstikhin (1997) and Murphy *et al.* (2003) appear inconsistent with a giant impact that is earlier than ~ 45 Myr after the start of the solar system.

Xenon isotope data have also been used to argue specifically that the Earth lost its inventory of noble gases as a consequence of the giant impact (Pepin, 1997; Porcelli and Pepin, 2000). The timing of the "xenon loss event" looks more

like 50–80 Myr on the basis of the most recent estimates of fissionogenic components (Porcelli and Pepin, 2000) (Figure 12). This agrees nicely with some estimates for the timing of the giant impact (Tables 2 and 3, and Figure 11) based on tungsten and lead isotopes. If the value of ~ 30 Myr is correct (Kleine *et al.*, 2002), there appears to be a problem linking the xenon loss event with the Moon forming giant impact, yet it is hard to decouple these. If the tungsten chronometry recently proposed by Yin *et al.* (2002) and Kleine *et al.* (2002) is correct it would seem that the giant impact cannot have been the last big event that blew off a substantial fraction of the Earth's atmosphere. On the basis of dynamic simulations, however, it is thought that subsequent events cannot have been anything like as severe as the giant impact (Canup and Agnor, 2000; Canup and Asphaug, 2001). It is, of course, conceivable that the protoatmosphere was lost by a different mechanism such as strong UV radiation (Zahnle and Walker, 1982). However, this begs the question of how the (earlier) giant impact could have still resulted in retention of noble gases. It certainly is hard to imagine the giant impact without loss of the Earth's primordial atmosphere (Melosh and Vickery, 1989; Ahrens, 1990; Benz and Cameron, 1990; Zahnle, 1993).

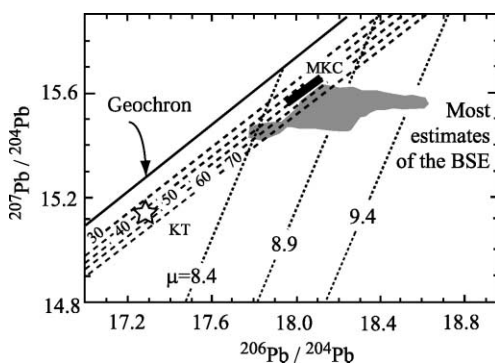


Figure 11 Lead isotopic modeling of the composition of the silicate Earth using continuous core formation and a sudden giant impact when the Earth is 90% formed. The impactor adds a further 9% to the mass of the Earth. The principles behind the modeling are as in Halliday (2000). See text for explanation. The field for the BSE encompasses all of the estimates in Galer and Goldstein (1996). The values suggested by Kramers and Tolstikhin (1997) and Murphy *et al.* (2002) are also shown. The figure is calibrated with the time of the giant impact (Myr). The μ values are the $^{238}\text{U}/^{204}\text{Pb}$ of the BSE. It is assumed that the μ of the total Earth is 0.7 (Allègre *et al.*, 1995a). It can be seen that the lead isotopic composition of the BSE is hard to reconcile with formation of the Moon before ~ 45 Myr after the start of the solar system.

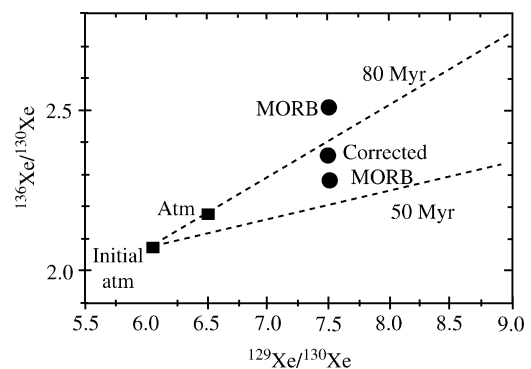


Figure 12 The relationship between the amounts of radiogenic ^{129}Xe inferred to come from ^{129}I decay within the Earth and fissionogenic ^{136}Xe thought to be dominated by decay of ^{244}Pu within the Earth. The differences in composition between the atmosphere and upper mantle relate to the timing of atmosphere formation. The compositions of both reservoirs are not very different from solar or initial U–Xe. This provides evidence that the strong depletion of xenon, leading to very high I/Xe, for example, was late. The data are shown modeled as a major loss event 50–80 Myr after the start of the solar system (Porcelli and Ballentine, 2002). The exact correction for uranium-derived fission ^{136}Xe in the MORB-mantle is unclear. Two values are shown from Phinney *et al.* (1978) and Kunz *et al.* (1998).

1.20.9 MASS LOSS AND COMPOSITIONAL CHANGES DURING ACCRETION

Collisions like the giant impact may well represent an important growth mechanism for terrestrial planets in general (Cameron and Benz, 1991; Canup and Agnor, 2000). These collisions are extraordinarily energetic and the question arises as to whether it is to be expected that accretion itself will lead to losses (“erosion”) of material from the combined planetary masses. If this is the case it is only to be expected that the composition of the Earth does not add up to what one might expect from “chondrite building blocks” and, for example, the oxygen isotope composition (Clayton and Mayeda, 1996). There are several indications that the Earth may have lost a significant fraction of some elements during accretion and earliest development; all are circumstantial lines of evidence:

(i) As discussed above it has been argued that impact processes in particular are responsible for eroding protoatmospheres (Melosh and Vickery, 1989; Ahrens, 1990; Benz and Cameron, 1990; Zahnle, 1993). If these atmospheres were very dense and hot they may have contained a significant fraction of Earth’s moderately volatile elements.

(ii) “Glancing blow” collisions between already differentiated planets, as during the giant impact, might be expected to preferentially remove major portions of the outer silicate portions of the planet as it grows. The Fe/Mg ratio of a planet is the simplest chemical parameter relating to planetary density and indicates the approximate size of the core relative to the silicate mantle. Mercury, with its high density, is a prime candidate for a body that lost a great deal of its outer silicate material by giant impacts (Benz *et al.*, 1987). Therefore, by analogy the proportional size of the Earth’s core may have increased as a consequence of such impact erosion. Conversely, Mars (Halliday *et al.*, 2001) with a density lower than that of the Earth, may actually be a closer approximation of the material from which Earth accreted than Earth itself is (Halliday *et al.*, 2001; Halliday and Porcelli, 2001).

(iii) Such late collisional loss of Earth’s silicate is clearly evident from the low density of the Moon. The disk of material from which the Moon accreted during the giant impact was silicate-rich. Most simulations predict that Theia provided the major source of lunar material. The density difference between silicate and metal leads to a loss of silicate from the combined Theia–proto-Earth system, even when the loss primarily is from the impactor. Note, however, that the giant-impact simulations retain most of the mass overall (Benz and Cameron, 1990). Very little is lost to space from a body as large as the Earth.

(iv) If there was early basaltic crust on the Earth (Chase and Patchett, 1988; Galer and Goldstein, 1991) or Theia or other impacting planets, repeated impact erosion could have had an effect on the Si/Mg ratio of the primitive mantle. However, the maximum effect will be very small because silicon is a major element in the mantle. Earth’s Si/Mg ratio is indeed low, as discussed above, but this may instead represent other loss processes. Nevertheless, the erosion effects could have been accentuated by the fact that silicon is relatively volatile and there probably was a magma ocean. With extremely high temperatures and a heavy protoatmosphere (Ahrens, 1990; Sasaki, 1990; Abe *et al.*, 2000), it seems possible that one could form a “rock atmosphere” by boiling the surface of the magma ocean. This atmosphere would in turn be very vulnerable to impact-induced blow-off.

(v) The budgets of other elements that are more heavily concentrated in the outer portions of the Earth, such as the highly incompatible lithophile elements caesium, barium, rubidium, thorium, uranium, niobium, and potassium and the light rare earths, were possibly also depleted by impact erosion. Indeed some people have argued that the primitive mantle is slightly higher than chondritic in Sm/Nd (Nägler and Kramers, 1998). However, it is worth noting that there is no evidence for europium anomalies in the BSE as might be expected from impact loss of feldspathic flotation cumulates. These issues are further complicated by the fact that the early Earth (or impacting planets) may have had magma oceans with liquidus phases such as majorite or calcium- or magnesium-perovskite (Kato *et al.*, 1988a,b). This in turn could have led to a very variable element distribution in a stratified magma ocean. There is no compelling evidence in hafnium isotopes, yet, for loss of a portion of the partially molten mantle fractionated in the presence of perovskite (Ringwood, 1990).

(vi) The oxygen isotopic compositions of lunar samples have been measured repeatedly to extremely high precision (Wiechert *et al.*, 2001) using new laser fluorination techniques. The $\Delta^{17}\text{O}$ of the Moon relative to the terrestrial fractionation line can be shown to be zero (Figure 3). Based on a 99.7% confidence interval (triple standard error of the mean) the lunar fractionation line is, within $\pm 0.005\text{‰}$, identical to that of the Earth. There now is no doubt that the mix of material that accreted to form the Earth and the Moon was effectively identical in its provenance. Yet there is a big difference in the budgets of moderately volatile elements (e.g., K/U or Rb/Sr). One explanation is that there were major losses of moderately volatile elements during the giant impact (O’Neill, 1991a,b; Halliday and Porcelli, 2001).

(vii) The strontium isotopic compositions of early lunar highland rocks provide powerful support for late losses of alkalis (Figure 8). Theia had a time integrated Rb/Sr that was more than an order of magnitude higher than the actual Rb/Sr of the Moon, providing evidence that the processes of accretion resulted in substantial loss of alkalis (Halliday and Porcelli, 2001). Some of the calculated time-integrated compositions of the precursors to the present Earth and Moon are shown in Figure 6.

(viii) The abundances of volatile highly siderophile elements in the Earth are slightly depleted relative to refractory highly siderophile elements (Yi *et al.*, 2000). This appears to reflect the composition of a late veneer. If this is representative of the composition of material that accreted to form the Earth as a whole it implies that there were substantial losses of volatile elements from the protoplanets that built the Earth (Yi *et al.*, 2000).

Therefore, there exist several of lines of evidence to support the view that impact erosion may have had a significant effect on Earth's composition. However, in most cases the evidence is suggestive rather than strongly compelling. Furthermore, we have a very poor idea of how this is possible without fractionating potassium isotopes (Humayun and Clayton, 1995), unless the entire inventory of potassium is vaporized (O'Neill, 1991a,b; Halliday *et al.*, 1996; Halliday and Porcelli, 2001). We also do not understand how to lose heavy elements except via hydrodynamic escape of a large protoatmosphere (Hunten *et al.*, 1987; Walker, 1986). Some of the loss may have been from the proto-planets that built the Earth.

1.20.10 EVIDENCE FOR LATE ACCRETION, CORE FORMATION, AND CHANGES IN VOLATILES AFTER THE GIANT IMPACT

There are a number of lines of evidence that the Earth may have been affected by additions of further material subsequent to the giant impact. Similarly, there is limited evidence that there was additional core formation. Alternatively, there also are geochemical and dynamic constraints that strongly limit the amount of core formation and accretion since the giant impact. This is a very interesting area of research that is ripe for further development. Here are some of the key observations:

(i) It has long been recognized that there is an apparent excess of highly siderophile elements in the silicate Earth (Chou, 1978; Jagoutz *et al.*, 1979). These excess siderophiles already have been discussed above in the context of core formation. However, until Murthy's (1991) paper, the most widely accepted explanation was that there was a "late veneer" of material accreted after

core formation and corresponding to the final one percent or less of the Earth's mass. Nowadays the effects of high temperatures and pressures on partitioning can be investigated and it seems clear that some of the excess siderophile signature reflects silicate-metal equilibration at depth. The volatile highly siderophile elements carbon, sulfur, selenium, and tellurium are more depleted in the silicate Earth than the refractory siderophiles (Figure 1; Yi *et al.*, 2000). Therefore, if there was a late veneer it probably was material that was on average depleted in volatiles, but not as depleted as would be deduced from the lithophile volatile elements (Yi *et al.*, 2000).

(ii) The light xenon isotopic compositions of well gases may be slightly different from those of the atmosphere in a manner that cannot be easily related to mass-dependent fractionation (Caffee *et al.*, 1988). These isotopes are not affected by radiogenic or fissionogenic additions. The effect is small and currently is one of the most important measurements that need to be made at higher precision. Any resolvable differences need to then be found in other reservoirs (e.g., MORBs) in order to establish that this is a fundamental difference indicating that a fraction of atmospheric xenon is not acquired by outgassing from the interior of the Earth. It could be that the Earth's atmospheric xenon was simply added later and that the isotopic compositions have no genetic link with those found in the Earth's interior.

(iii) Support for this possibility has come from the commonly held view that the Earth's water was added after the giant impact. Having lost so much of its volatiles by early degassing, hydrodynamic escape and impacts the Earth still has a substantial amount of water. Some have proposed that comets may have added a component of water to the Earth, but the D/H ratio would appear to be incorrect for this unless the component represented a minor fraction (Owen and Bar-Nun, 1995, 2000). An alternative set of proposals has been built around volatile-rich chondritic planetary embryos (Morbidelli *et al.*, 2000).

(iv) Further support for this latter "asteroidal" solution comes from the conclusion that the asteroid belt was at one time relatively massive. More than 99% of the mass of the asteroid belt has been ejected or added to other objects (Chambers and Wetherill, 2001). The Earth, being *en route* as some of the material preferentially travels toward the Sun may well have picked up a fraction of its volatiles in this way.

(v) The Moon itself provides a useful monitor of the amount of late material that could have been added to the Earth (Ryder *et al.*, 2000). The Moon provides an impact history (Hartmann *et al.*, 2000) that can be scaled to the Earth (Ryder *et al.*, 2000). In particular, there is evidence of widespread and intense bombardment of the Moon during the

Hadean and this can be scaled up, largely in terms of relative cross-sectional area, to yield an impact curve for the Earth (Sleep *et al.*, 1989).

(vi) However, the Moon also is highly depleted in volatiles and its surface is very depleted in highly siderophile elements. Therefore, the Moon also provides a limit on how much can be added to the Earth. This is one reason why the more recent models of Cameron (2000) involving a giant impact that left an additional third are hard to accommodate. However, the database for this currently is poor (Richter *et al.*, 2000).

(vii) It has been argued that the greater depletion in iron and in tellurium in the silicate Earth relative to the Moon reflects an additional small amount of terrestrial core formation following the giant impact (Halliday *et al.*, 1996; Yi *et al.*, 2000). It could also simply reflect differences between Theia and the Earth. If there was further post-giant-impact core formation on Earth, it must have occurred prior to the addition of the late veneer.

1.20.11 THE HADEAN

1.20.11.1 Early Mantle Depletion

1.20.11.1.1 Introduction

Just as the I–Pu–Xe system is useful for studying the rate of formation of the atmosphere and U–Pb and Hf–W are ideal for studying the rates of accretion and core formation, lithophile element isotopic systems are useful for studying the history of melting of the silicate Earth. Two in particular, ^{92}Nb ($T_{1/2} = 36$ Myr) and ^{146}Sm ($T_{1/2} = 106$ Myr), have sufficiently long half-lives to be viable but have been explored with only limited success. Another chronometer of use is the long-lived chronometer ^{176}Lu ($T_{1/2} = 34\text{--}38$ Gyr).

1.20.11.1.2 $^{92}\text{Nb}\text{--}^{92}\text{Zr}$

^{92}Nb decays by electron capture to ^{92}Zr with a half-life of 36 ± 3 Myr. At one time it was thought to offer the potential to obtain an age for the Moon by dating early lunar ilmenites and the formation of ilmenite-rich layers in the lunar mantle. Others proposed that it provided constraints on the time-scales for the earliest formation of continents on Earth (Münker *et al.*, 2000). In addition, it was argued that it would date terrestrial core formation (Jacobsen and Yin, 2001). There have been many attempts to utilize this isotopic system over the past few years. To do so, it is necessary to first determine the initial ^{92}Nb abundance in early solar system objects accurately and various authors have made claims that differ by two orders of magnitude.

Harper *et al.* (1991b) analyzed a single niobium-rutile found in the Toluca iron meteorite and

presented the first evidence for the former existence of ^{92}Nb from which an initial $^{92}\text{Nb}/^{93}\text{Nb}$ of $(1.6 \pm 0.3) \times 10^{-5}$ was inferred. However, the blank correction was very large. Subsequently, three studies using multiple collector inductively coupled plasma mass spectrometry proposed that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ ratio of the solar system was more than two orders of magnitude higher (Münker *et al.*, 2000; Sanloup *et al.*, 2000; Yin *et al.*, 2000). Early processes that should fractionate Nb/Zr include silicate partial melting because niobium is more incompatible than zirconium (Hofmann *et al.*, 1986). Other processes relate to formation of titanium-rich (hence niobium-rich) and zirconium-rich minerals, the production of continental crust, terrestrial core formation (Wade and Wood, 2001) and the differentiation of the Moon. Therefore, on the basis of the very high ^{92}Nb abundance proposed, it was argued that, because there was no difference between the zirconium isotopic compositions of early terrestrial zircons and chondrites, the Earth's crust must have formed relatively late (Münker *et al.*, 2000). Similarly, because it is likely that a considerable amount of the Earth's niobium went into the core it was argued that core formation must have been protracted or delayed (Jacobsen and Yin, 2001). We now know that these arguments are incorrect. Precise internal isochrons have provided evidence that the initial abundance of ^{92}Nb in the early solar system is indeed low and close to 10^{-5} (Schönbächler *et al.*, 2002).

Therefore, rather than proving useful, the $^{92}\text{Nb}\text{--}^{92}\text{Zr}$ has no prospect of being able to provide constraints on these issues because the initial ^{92}Nb abundance is too low.

1.20.11.1.3 $^{146}\text{Sm}\text{--}^{142}\text{Nd}$

High-quality terrestrial data now have been generated for the $^{146}\text{Sm}\text{--}^{142}\text{Nd}$ (half-life = 106 Myr) chronometer (Goldstein and Galer, 1992; Harper and Jacobsen, 1992; McCulloch and Bennett, 1993; Sharma *et al.*, 1996). Differences in $^{142}\text{Nd}/^{144}\text{Nd}$ in early Archean rocks would indicate that the development of a crust on Earth was an early process and that subsequent recycling had failed to eradicate these effects. For many years, only one sample provided a hint of such an effect (Harper and Jacobsen, 1992) although these data have been questioned (Sharma *et al.*, 1996). Recently very high precision measurements of Isua sediments have resolved a 15 ± 4 ppm effect (Caro *et al.*, 2003).

Any such anomalies are clearly small and far less than might be expected from extensive, repeated depletion of the mantle by partial melting in the Hadean. It seems inescapable that there was melting on the early Earth. Therefore, the interesting and important result of these studies

is that such isotopic effects must largely have been eliminated. The most likely mechanism is very efficient mantle convection. In the earliest Earth convection may have been much more vigorous (Chase and Patchett, 1988; Galer and Goldstein, 1991) because of the large amount of heat left from the secular cooling and the greater radioactive heat production.

1.20.11.1.4 ^{176}Lu – ^{176}Hf

A similar view is obtained from hafnium isotopic analyses of very early zircons. The ^{176}Lu – ^{176}Hf isotopic system ($T_{1/2} = 34$ – 38 Gyr) is ideally suited for studying early crustal evolution, because hafnium behaves in an almost identical fashion to zirconium. As a result, the highly resistant and easily dated mineral zircon typically contains ~ 1 wt% Hf, sufficient to render hafnium isotopic analyses of single zircons feasible using modern methods (Amelin *et al.*, 1999). The concentration of lutetium in zircon is almost negligible by comparison. As a result, the initial hafnium isotopic composition is relatively insensitive to the exact age of the grain and there is no error magnification involved in extrapolating back to the early Archean. Furthermore, one can determine the age of the single zircon grain very precisely using modern U–Pb methods. One can obtain an extremely precise initial hafnium isotopic composition for a particular point in time on a single grain, thereby avoiding the problems of mixed populations. The U–Pb age and hafnium isotopic compositions of zircons also are extremely resistant to resetting and define a reliable composition at a well-defined time in the early Earth. The hafnium isotopic composition that zircon had when it grew depends on whether the magma formed from a reservoir with a time-integrated history of melt depletion or enrichment. Therefore, one can use these early zircons to search for traces of early mantle depletion.

Note that this is similar to the approach adopted earlier with ^{147}Sm – ^{143}Nd upon which many ideas of Hadean mantle depletion, melting processes and early crust were based (Chase and Patchett, 1988; Galer and Goldstein, 1991). However, the difficulty with insuring closed-system behavior with bulk rock Sm–Nd in metamorphic rocks and achieving a robust age correction of long-lived ^{147}Sm over four billion years has meant that this approach is now viewed as suspect (Nägler and Kramers, 1998). The ^{176}Lu – ^{176}Hf isotopic system and use of low-Lu/Hf zircons is far more reliable in this respect (Amelin *et al.*, 1999, 2000). In practice, however, the interpretation is not that simple, for two reasons:

(i) The hafnium isotopic composition and Lu/Hf ratio of the Earth's primitive mantle is poorly known. It is assumed that it is broadly

chondritic (Blichert-Toft and Albarède, 1997), but which exact kind of chondrite class best defines the isotopic composition of the primitive mantle is unclear. Without this information, one cannot extrapolate back in time to the early Earth and state with certainty what the composition of the primitive mantle reservoir was. Therefore, one cannot be sure what a certain isotopic composition means in terms of the level of time-integrated depletion.

(ii) The half-life of ^{176}Lu is *not* well established and is the subject of current debate and research (Scherer *et al.*, 2001). Although the determination of the initial hafnium isotopic composition of zircon is not greatly affected by this, because the Lu/Hf ratio is so low that the age correction is tiny, the correction to the value for the primitive mantle is very sensitive to this uncertainty.

With these caveats, one can deduce the following. Early single grains appear to have recorded hafnium isotopic compositions that provide evidence for chondritic or enriched reservoirs. There is no evidence of depleted reservoirs in the earliest (Hadean) zircons dated thus far (Amelin *et al.*, 1999). Use of alternative values for the decay constants or values for the primitive mantle parameters increases the proportion of hafnium with an enriched signature (Amelin *et al.*, 2000), but does not provide evidence for early mantle depletion events. Therefore, there is little doubt that the Hadean mantle was extremely well mixed. Why this should be is unclear, but it probably relates in some way to the lack of preserved continental material from prior to 4.0 Ga.

1.20.11.2 Hadean Continents

Except for the small amount of evidence for early mantle melting we are in the dark about how and when Earth's continents first formed (Figure 13). We already have pointed out that in its early stages Earth may have had a magma ocean, sustained by heat from accretion and the blanketing effects of a dense early atmosphere. With the loss of the early atmosphere during planetary collisions, the Earth would have cooled quickly, the outer portions would have solidified and it would thereby have developed its first primitive crust.

We have little evidence of what such a crust might have looked like. Unlike on the Moon and Mars, Earth appears to have no rock preserved that is more than 4.0 Gyr old. There was intense bombardment of the Moon until ~ 3.9 Gyr ago (Wetherill, 1975b; Hartmann *et al.*, 2000; Ryder *et al.*, 2000). Earth's earlier crust may therefore have been decimated by concomitant impacts.

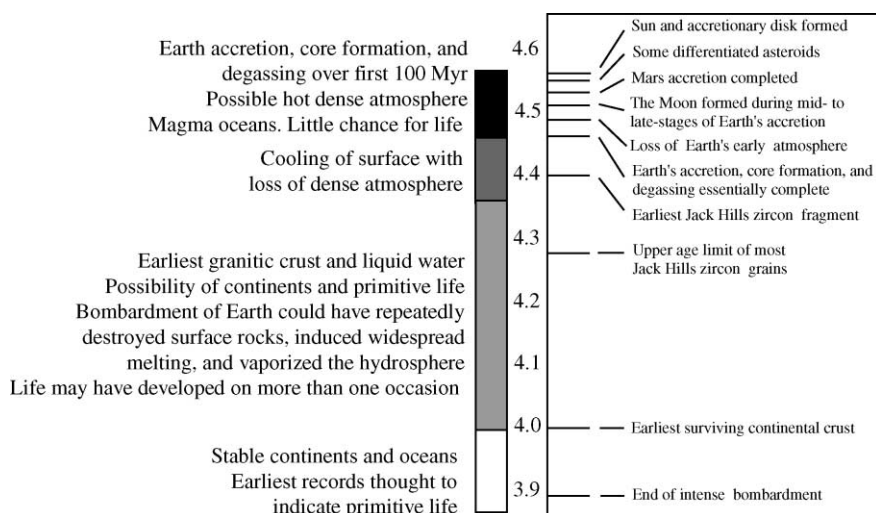


Figure 13 Schematic showing the timescales for various events through the “Dark Ages” of the Hadean.

It may also be that a hotter Earth had a surface that was inherently unstable. Some argued that the earliest crust was like the lunar highlands—made from a welded mush of crystals that had previously floated on the magma ocean. Others have suggested that it was made of denser rocks more like those of the Earth’s present oceanfloor (Galer and Goldstein, 1991). But firm evidence has so far been sparse.

Froude *et al.* (1983) reported the exciting discovery of pre-4.0 Ga zircon grains formed on Earth. The host rock from which these grains were recovered is not so old. The pre-4.0 Gyr rocks were largely destroyed but the zircons survived by becoming incorporated in sands that formed a sedimentary rock that now is exposed in Australia as the Jack Hills Metaconglomerate. By measuring uranium-lead ages a sizeable population of grains between 4.1 Gyr and 4.2 Gyr was discovered (Froude *et al.*, 1983). Subsequently, Wilde *et al.* (2001) and Mojzsis *et al.* (2001) reported uranium-lead ages and oxygen isotopic compositions of further old zircon grains. A portion of one grain appears to have formed 4.40 Gyr ago and this is the oldest terrestrial solid yet identified. More recent work has been published by Peck *et al.* (2001) and Valley *et al.* (2002).

These zircons provide powerful evidence for the former existence of some unknown amount of continental crust in the Hadean. Nearly all zircons grew from granite magmas, not similar at all to those forming the oceanfloor or the lunar highlands. Granite magmas usually form at $>700^{\circ}\text{C}$ and >20 km depth, mainly by melting preexisting crust above subduction zones. Being buoyant they are typical of continental mountain regions such as the Andes—sites of very active erosion. The existence of such zircons would be consistent with continental crust as far back as 4.40 Gyr— ~ 100

Myr after the formation of the Moon and the earliest atmosphere. It would be nice to have more data and one is extrapolating through many orders of magnitude in mass when inferring extensive continents from single zircons. Large ocean islands like Iceland have small volumes of granitic magma and so one can conceive of protocontinents that started from the accumulation of such basaltic nuclei, the overall mass of silicic crustal material increasing gradually.

Oxygen isotopic measurements can be used to infer the presence of liquid water on the Earth’s early surface. The oxygen isotopic composition reflects that of the magma from which the zircon crystallized, which in turn reflects that of the rocks that were melted to form the magma. Heavy oxygen (with a high proportion of ^{18}O) is produced by low-temperature interactions between a rock and liquid water such as those that form clay by weathering. The somewhat heavy oxygen of these zircons provides evidence that the rocks that were melted to form the magma included components that had earlier been at the surface in the presence of liquid water. Early on, when Earth was hotter, they might also have formed by melting of wet oceanfloor basalt that was taken back into the mantle by a process potentially comparable to modern subduction. Either way, the data indicate that surface rocks affected by low-temperature fluids were probably being transported to significant depths and melted, as occurs today.

These grains represent a unique archive for information on the early Earth. The potential is considerable. For example, Wilde *et al.* (2001) and Peck *et al.* (2001) also used trace elements and tiny inclusions to reconstruct the composition of the parent magma. In all of this work there is a need to be very aware that the grains may have

been disturbed after they formed. Wet diffusion of oxygen could lead to an ^{18}O -rich composition that was acquired during subsequent metamorphic or magmatic histories. Thus, ancillary information on diffusivities and the degree to which compositions might have been perturbed by later metamorphism must be acquired. Most importantly, however, there exists an urgent need of many more grains.

1.20.11.3 The Hadean Atmosphere, Hydrosphere, and Biosphere

The nature of the Earth's atmosphere and hydrosphere after the Earth had cooled, following the cessation of the main stages of accretion, has been the subject of a fair amount of research (Wiechert, 2002), particularly given the *lack* of data upon which to base firm conclusions. An interesting and important question is to what extent it may have been possible for life to develop during this period (Mojzsis *et al.*, 1996; Sleep *et al.*, 2001; Zahnle and Sleep, 1996). A great deal has been written on this and because it is covered elsewhere in this treatise only cursory background is provided here.

The first-order constraints that exist on the nature of Earth's early exosphere (Sleep *et al.*, 1989; Sleep and Zahnle, 2001) are as follows:

(i) The Sun was fainter and cooler than today because of the natural start-up of fusion reactions that set it on the Main Sequence (Kasting and Grinspoon, 1991; Sagan and Chyba, 1997; Pavlov *et al.*, 2000). Therefore, the level of radiation will have been less.

(ii) Earth's interior was a few 100 K hotter because of secular cooling from accretion and far greater radiogenic heat production. The Earth's heat flow was 2–3 times higher. Therefore, one can assume that more heat was escaping via mantle melting and production of oceanic crust.

(iii) This, in turn, means more mantle-derived volatiles such as CO_2 were being released.

(iv) It also means that there was more hydrothermal alteration of the oceanfloor. Therefore, CO_2 was converted to carbonate in altered basalt and returned to the mantle at subduction zones (if those really existed already).

(v) There may have been far less marine carbonate. We can infer this from the geological record for the Archean. Therefore, it appears that atmospheric CO_2 levels were low—most of the CO_2 was being recycled to the mantle.

(vi) Because atmospheric CO_2 exerts a profound effect on temperature as a greenhouse gas, low concentrations of CO_2 imply that atmospheric temperatures were cold, unless another greenhouse gas such as methane (CH_4) was very abundant (Pavlov *et al.*, 2000). However, clear

geochemical evidence for a strong role of methane in the Archean currently is lacking.

(vii) Impacts, depending on their number and magnitude (Hartmann *et al.*, 2000; Ryder *et al.*, 2000), may have had a devastating effect on the early biosphere. Impact ejecta will react with atmospheric and oceanic CO_2 and thereby lower atmospheric CO_2 levels reducing atmospheric temperatures still further.

The Hadean is fast becoming one of the most interesting areas of geochemical research. With so little hard evidence (Figure 13), much of the progress probably will come from theoretical modeling and comparative planetology.

1.20.12 CONCLUDING REMARKS—THE PROGNOSIS

Since the early 1990s, there has been great progress in understanding the origins and early development of the Earth. In some cases, this has been a function of improved modeling. This is particularly true for noble gases. However, in most cases it has been the acquisition of new kinds of data that has proven invaluable. The most obvious examples are in isotope geochemistry and cosmochemistry.

It is perhaps worth finishing by pointing out the kinds of developments that can be expected to have an impact on our understanding of the early Earth. One can ask a question like “what if we could measure...?” Here are some things that would be very interesting and useful to explore:

(i) If planets such as the Earth formed by very energetic collisions that were sufficient to cause vaporization of elements and compounds that normally are solid, it may be possible to find evidence for the kinetic effects of boiling in isotopic fractionations. Humayun and Clayton (1995) explored potassium at per mil levels of precision and found no significant evidence of fractionation. Poitrasson *et al.* (2003) have found evidence that the iron on the Moon may be very slightly heavy relative to other planetary objects. Note that this has nothing to do with the fractionations produced in the lunar surface during irradiation and implantation (Wiesli *et al.*, 2003). Perhaps boiling during the giant impact caused this. This is just a preliminary inference at this stage. But if so, small fractionations also should be found in other elements of similar volatility such as lithium, magnesium, silicon, and nickel. There is much to be done to explore these effects at very high precision.

(ii) A vast amount of work still is needed on core formation, understanding the depletion of siderophile elements in the Earth's mantle (Walter *et al.*, 2000), and determining the abundances of light elements in the core (Gessmann *et al.*, 2001). Much of this depends on using proxy elements

that are very sensitive to pressure, temperature, water content or f_{O_2} (e.g., Wade and Wood, 2001). A problem at present is that too many of the elements of interest are sensitive to more than one parameter and, therefore, the solutions are under constrained. Also, new experiments are needed at very high pressures—close to those of the core–mantle boundary.

(iii) The origins of Earth's water and volatiles more generally are the subject of considerable debate (e.g., Anders and Owen, 1977; Carr and Wänke, 1992; Owen and Bar-Nun, 1995, 2000; Javoy, 1998; Caffee *et al.*, 1999; Righter and Drake, 1999; Abe *et al.*, 2000; Morbidelli *et al.*, 2000). A great deal probably will be learned from further modeling. For example, it is very important to understand what kinds of processes in the early Earth could have caused loss of early atmospheres. We do not understand how volatiles are retained during a Moon-forming giant impact (Melosh and Sonett, 1986; Melosh, 1990; Melosh *et al.*, 1993) or what the early Sun might have done to the atmosphere. We need to acquire more reliable data on the isotopic compositions of volatiles in the deep Earth. We might be able to learn much more about Earth's volatile history from more precise measurements of the volatile components in other planets. In this respect more detailed studies of Mars and how closely it resembles the Earth (Carr and Wänke, 1992) could prove critical.

(iv) Mojzsis *et al.* (2001) and Wilde *et al.* (2001) have made major advances in studying the Hadean using single zircons. Apart from needing many more such samples, one has to ask what other kinds of information might be extractable from such zircons. The oxygen isotopic composition provides evidence for early low-temperature water. Exploring the melt inclusions and the trace-element concentrations also has been shown to have potential (Peck *et al.*, 2001). Zircons are also iron-rich and conceivably could eventually be used to provide evidence for biological processes in the Hadean. However, the sensitivities of the techniques need to be improved vastly for this to be achieved with single grains. Furthermore, the current status of the rapidly expanding field of iron isotope geochemistry provides no clear basis for assuming a distinctive signal of biotic effects will be realizable. Also, the really interesting zircons are so precious that one should use minimally destructive techniques like SIMS on single grains. However, the required precision for measuring isotopic ratios in a useful manner is not available for trace elements in minerals using this method at present. Similarly, hafnium isotopes on single zircon grains provide the most reliable and powerful constraints on the extent of mantle depletion (Amelin *et al.*, 1999) but require destruction of a part of the grain. Developing

improved methods that achieve far higher overall sensitivity is critical.

(v) Determining the rates of accretion of the Earth and Moon more reliably will be critically dependent on the correct and precise determination of the initial tungsten and hafnium isotopic compositions of the solar system, and the ^{182}Hf decay constant. The initial isotopic compositions really require the more widespread application of negative ion thermal ionization mass spectrometry (N-TIMS) (Quitté *et al.*, 2000). The decay constant work is going to require the acquisition of ^{182}Hf , probably from neutron-irradiated ^{180}Hf .

(vi) Similarly, progress in using hafnium isotopes to study the degree of early mantle depletion is being thwarted by the uncertainties associated with the ^{176}Lu decay constant (Scherer *et al.*, 2001), and some new experimental work is needed in this area.

(vii) A major need is for a closer integration of the modeling of different isotopic systems. As of early 2000s, this has really only been attempted for tungsten and lead (Halliday, 2000). In the future it will be essential to integrate xenon isotopes in with these and other accretion models.

(viii) Finally, another major area of modeling has to occur in the area of “early Earth system science.” There needs to be integrated modeling of the evolution of the atmosphere, oceans, surface temperature, mantle convection, and magma oceans. This is now being attempted. For example, the studies by Sleep and Zahnle (2001) and Sleep *et al.* (1989, 2001) are paving the way for more comprehensive models that might involve the fluid dynamics of mantle convection.

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