5.1 INTRODUCTION

Meteorites are our primary source of information about the early Solar System. Chemical, isotopic, and petrological features of meteorites reflect events that occurred in the first few tens of millions of years of Solar System history. Observations on meteorites, together with astronomical observations on the birth of stars and the laws of physics, are the basis of our ideas on how the Solar System, and the Earth, formed.

Meteorites can be divided into two broad groups: primitive meteorites and differentiated meteorites. The chondrites constitute the primitive group: most of their chemical, isotopic, and petrological features resulted from processes that occurred in the cloud of gas and dust that we refer to as the solar nebula. They are far more commonly observed to fall than differentiated meteorites. All chondrites, however, have experienced at least some metamorphism on “parent bodies”, the small planets (diameters ranging from a few km to a few hundred km) from which meteorites are derived by collisions. The differentiated meteorites, which include the achondrites, stony irons, and irons, were so extensively processed in parent bodies, by melting and brecciation, that information about nebular processes has largely been lost. On the other hand, the differentiated meteorites provide insights into the early stages of planet formation. We’ll provide only a brief overview here. More details of meteoritics (the study of meteorites) can be found in McSween and Huss (2010) and White (2013).

Chondrites are so called because they contain “chondrules”, small (typically a few mm diameter) round bodies that were clearly once molten (Figure 5.1). The other main constituents of chondrites are the matrix, which is generally very fine-grained, amoeboid olivine aggregates (AOA’s), and refractory calcium-aluminum inclusions (generally called CAI’s). These last two groups formed by a variety of mechanisms, some of which appear to be complex, but we can generalize and say that all these are grains or aggregates of grains that equilibrated with nebular gas at high temperature through con-
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densation and/or evaporation. As we’ll see, the CAI’s were the first formed objects in the solar system and their ages are used to define the birth of the solar system, that is, time 0.

Most chondrites can be divided into carbonaceous (C), ordinary, and enstatite classes. The carbonaceous chondrites are, as their name implies, rich in carbon (as carbonate, graphite, organic matter, and, rarely, microdiamonds) and other volatiles and are further divided into classes CI, CV, CM, CO, CR, CH, and CB. The CI chondrites lack chondrules and are considered the compositionally the most primitive of all objects. The ordinary chondrites, so-called because the are by far the most common type, are divided into classes H, L, and LL based on iron content. Enstatite chondrites can be subdivided into EH and EL, also based on iron content. It is thought that each class of chondrites is likely derived from a single asteroidal parent body. Chondrites are further assigned a petrographic grade on the basis of the extent of metamorphism they have experienced in parent bodies. Grades 4, 5, and 6 have experienced increasing degrees of high-temperature metamorphism, while grades 1 and 2 experienced low-temperature aqueous alteration. Grade 3 is the least altered.

The various groups of differentiated meteorites can be further subdivided as well. Achondrites are in most cases igneous rocks, some roughly equivalent to terrestrial basalt, others appear to be cumulates. Other achondrites are highly brecciated mixtures. Irons, as they name implies, consist mainly of Fe-Ni metal (Ni content around 5%). Stony-irons are, as their name implies, mixtures of iron metal and silicates. Among achondrites, the Acapulcoites, Lodranites, Winonaites, and Ureilites are referred to as primitive achondrites because they retain some similarity in composition and mineralogy to chondrites. The diogenites, eucrites, and howardites, collectively called the HED meteorites, were long known to be related and thought to come from the asteroid 4 Vesta. NASA’s DAWN mission orbited Vesta from 2011 to 2012 and confirmed this inference based on spectroscopic measurements of Vesta’s surface (DAWN departed Vesta in 2012 for 1 Ceres, the largest asteroid). The diogenites are intrusive igneous rocks, the eucrites extrusive ones (lavas), while the howardites are highly brecciated mixtures of both. The angrites constitute another group of achondrites likely derived from a single parent body; they are considerably rarer than the HED group. They too include both intrusive and extrusive igneous rocks, that appear to be derived from a chondritic parent by partial melting under highly oxidizing conditions. They are highly depleted in moderately volatile elements such as Na, which has led to speculation that they might come from Mercury. Based on their reflectance spectra, the small asteroids 239 Ninetta and 3819 Robinson are also parent body candidates. The SNC meteorites, a group that includes the Shergottites, Nakhliites, and the meteorite Chassigny, derived from Mars, and a few achondrites are derived from the Moon. The irons are divided based on composition into a dozen or so groups. Most of these, referred to as the magmatic irons, represent cores of disrupted asteroids. A few, which includes the IAB, IIICD, and IIE irons are referred to as non-magmatic irons, but the term is misleading because they too solidified from liquid iron. However, rather than coming from cores, they probably formed as pools of iron liquid segregated from a silicate matrix.

In this chapter, we focus on the question of the age of meteorites and variations in their isotopic composition, and what that can tell us about the early history of our solar system and the Earth.

5.2 COSMOCHRONOLOGY

5.2.1 Conventional methods

The oft-cited value for the age of the solar system is 4.567 Ga and is based on dating of meteorites, or more precisely, their components. Before we discuss meteorite ages further, we need to consider the question of precisely what event is being dated by radiometric chronometers. Radioactive clocks record the last time the isotope ratio of the daughter element, e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, was homogenized. This is usually some thermal event. In the context of what we know of early Solar System history, the event dated might be (1) the time solid particles were removed from a homogeneous solar nebula, (2) thermal

† In the last decade or two, additional classes have been added that are defined by rarer meteorites.
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metamorphism in meteorite parent bodies, or (3) crystallization (in the case of chondrules and achondrites), or (4) impact metamorphism of meteorites or their parent bodies. In some cases, the nature of the event being dated is unclear.

The most precise ages of meteorites have been obtained using the U-Pb chronometer (Figure 5.2). Advances in analytical techniques have remarkably improved precision over the last decade or so, to the point that ages with uncertainties of only a few 100,000 years can be obtained. However, some of the issues that traditionally plague geochronology come into focus, including lack of complete initial isotopic homogeneity and deviations from closed system behavior. In addition, new issues arise, including uncertainties in half-lives of the parents and uncertainty in, as well as variation of, the $^{238}\text{U}/^{235}\text{U}$ ratio (Amelin et al., 2009). Progress is being made in resolving these issues, but further research remains necessary.

As Figure 5.2 shows, the oldest objects are CAI’s; CAI’s are good U-Pb dating targets since they are rich in refractory elements like U and depleted in volatile elements like Pb; they are largest (1 mm) and most abundant in CV chondrites, but have been found in all chondrites except the CI group. The oldest high-precision date of a CAI is 4568.67±0.17 Ma for a CAI from the CV3 meteorite NWA2364 calculated using the “canonical” $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88 (Bouvier et al., 2010). The next oldest age is a CAI from Allende, also CV3 meteorite, whose age, calculated using the canonical $^{238}\text{U}/^{235}\text{U}$ value, is 4567.59±0.11 Ma (Bouvier et al., 2007). Less precise ages ranging from 4567.4 to 4568.6 have been reported for other Allende inclusions. Amelin et al. (2009) reported a high precision Pb-Pb age of 4567.11±0.16 Ma for a CAI from the CV3 meteorite Efremovka. The accuracy of these dates has, however, been thrown into question by Bennecka et al.’s (2010) discovery of variable $^{238}\text{U}/^{235}\text{U}$ ratios in CAI’s from Allende, which range from 137.409±0.039 to 137.885±0.009, compared to the “canonical” value of 137.88. The age of the NWA2364 CAI decreases to 4,568.22±0.17 Ma if a value of 137.84 is used for that ratio and Bouvier et al. (2010) speculated that the $^{238}\text{U}/^{235}\text{U}$ of the CAI might be as low as 137.81, which would make the age 0.3 Ma younger.

Brennecka et al. (2010) concluded that the cause of the $^{235}\text{U}/^{238}\text{U}$ variability was decay of $^{247}\text{Cm}$, which decays to $^{235}\text{U}$ with a half-life of 13.6 Ma. Amelin et al. (2010) calculated an age for one Allende CAI using the $^{238}\text{U}/^{235}\text{U}$ measured in that CAI (137.876) and obtained an age of 4567.18±0.50 Ma. Using measured $^{238}\text{U}/^{235}\text{U}$ ratios in 3 CAI’s from Efremovka, which ranged from 137.27 to 137.83, Connelly et al. (2012) found that Pb ages fell within the narrow range of 4567.23±0.29 to 4567.38±0.31. Connelly et al. noted that while CAI’s have variable $^{238}\text{U}/^{235}\text{U}$, this ratio appears to be uniform in chondrules and achondrites, an observation inconsistent with $^{247}\text{Cm}$ decay. They argued that the cause was mass dependent fractionation instead.

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Figure 5.2. Summary of U-Pb ages of chondritic and achondritic meteorites.

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*NWA stands for Northwest Africa. This is one of many meteorites found in the Sahara desert over the last couple of decades.*
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Chondrules in carbonaceous chondrites have Pb-Pb ages that range from 4.562.7±0.5 Ga for a Gjuha (CB3) to 4.567.32±0.42 Ga for Allende and are thus generally slightly younger than the CAI’s. These ages assume the canonical \(^{238}\text{U}/^{235}\text{U}\) value. Amelin et al. (2010) found that the Allende whole rock and chondrules had a low \(^{238}\text{U}/^{235}\text{U}\) value, 1.37.747±0.017, which implies earlier reported ages of the chondrules were too old by about 1.4 Ma. Connelly et al. (2012) found that chondrules from Allende and NWA 5697 (an L3 ordinary chondrite) were identical within analytical error with a mean of 137.786±0.013. Using this \(^{238}\text{U}/^{235}\text{U}\) value, they found that ages of 5 chondrules from these two meteorites ranged from 4.564.71±0.30 to 4.567.32±0.42. The range in ages of 3 million years contrasts with the ages of CAI’s, which are nearly indistinguishable within analytical error.

Phosphates also have high U/Pb ratios and these were analyzed by Göpel et al. (1994) to obtain high precision ages of a variety of equilibrated (i.e., petrologic classes 4-6) ordinary chondrites, whose ages range from 4.563 to 4.502 Ga. The phosphates are thought to have formed during metamorphism, thus these ages represent the age of metamorphism of these meteorites. The oldest of these meteorites was H4 chondrite Ste. Marguerite. Bouvier et al. (2007) subsequently reported a Pb-Pb isochron age of 4.562.7 Ma, in excellent agreement with the age determined by Göpel et al. (1994). The age of CAI’s from CV3 meteorites thus seems 3 Ma older than the oldest precise ages obtained on ordinary chondrites. No attempt has been made at high precision dating of CI chondrites, as they are too fine-grained to separate phases.

Among achondrites, the chronology of the angrites is perhaps best documented. The oldest high precision Pb-Pb age is 4.564.58±0.14 Ma for the angrite SAH99555 (Connelly et al., 2008) An age nearly as old, 4.563.37±0.25 was reported for the angrite D’Orbigny (Amelin, 2008; Brenneka & Wadhwa, 2012). Angra dos Reis, the type meteorite of the class, has a Pb-Pb age of 4.557.65 ± 0.13 Ma, and Lewis Cliff 86010, a coarse grained “plutonic” angrite, has an age of 4.558.55 ± 0.15 Ma. Thus differentiation, cooling and crystallization of the angrite parent body apparently lasted some 6 million years. Wadhwa et al. (2009) reported an age of 4.566.5±0.2 Ma for unusual basaltic achondrite, Asuka 881394. Bouvier et al. (2011) determined an age of 4.562.89 ± 0.59 Ma for another unusual basaltic achondrite, NWA2976. Ibitira, a unique unbrecciated eucrite, has an age of 4.556±6 Ma. Perhaps surprisingly, these ages are similar to those of chondrites. This suggests that the parent body of these objects formed, melted, and differentiated, and the outer parts crystallized within a very short time interval. Not all achondrites are quite so old, however. A few other high precision ages (those with quoted errors of less than 10 Ma) are available and they range from this value down to 4.529±0.005 Ga for Nuevo Laredo and 4.510±0.004 Ga for Bouvante. Thus the total range of the few high precision ages in achondrites is about 50 million years. Iron

![Figure 5.3](image-url)
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Meteorites appear to be similarly old. Smoliar et al. (1996) reported a Re-Os ages of 4558±12 and 4537±8 Ma for IIIA and IIA irons, respectively; ages of other iron groups range from 4506 to 4569 Ma, but are of lower precision and are not significantly different from the IIIA and IIA ages. As can be seen in Figure 5.2, there is no obvious relationship between meteorite class and age. H chondrites do seem a bit older than other ordinary chondrites and Göpel et al. (1994) did find an inverse correlation between petrologic type and age (the least metamorphosed are oldest), but this does not appear to be true of chondrites in general. Furthermore, there appears to be little difference in age between chondrites and achondrites. The present state of conventional meteorite chronology may be summarized by saying that it appears the meteorite parent bodies formed around 4.567 ±0.001 Ga, and there is some evidence that high-temperature inclusions and chondrules in carbonaceous chondrites may have formed a few Ma earlier than other material. Sm-Nd, Lu-Hf, and Rb-Sr ages are less precise than the U-Pb ages and are often a bit younger, and perhaps date peak metamorphism of chondrite parent bodies, and melting or metamorphism on achondrite parent bodies.

In contrast to the tightly clustered ages for the chronometers discussed above, K-Ar (including 40Ar-39Ar) ages show a much wider range. As we found in Chapter 2, closure temperatures for K-Ar are generally much lower than for other chronometers, so these younger ages could reflect the time required to cool to lower closure temperature or heating events resulting from impacts. Figure 5.3 summarizes K-Ar ages of ordinary and enstatite chondrites, which range down to more than 100 Ma after formation of the solar system and the parent bodies of these meteorites. The parent bodies were initially hot due to (1) gravitation energy release during their accretion, and (2) heating by short-lived radionuclides that were present in the early solar system (and which we will discuss in the following section). Based on these ages, the size of the parent bodies can be estimated to be ~100 km. For some chondrites, notably some H-chondrites, younger ages are associated with the higher metamorphic grade, suggesting we are seeing a depth profile in the parent body, with increasing metamorphic temperatures and longer cooling times at greater depths within the parent body (Bogard, 2011). Some chondrites have 40Ar-39Ar ages of less than 1 Ga, including many L chondrite ages that cluster around 0.5 Ga. These ages reflect resetting during impact heating on the chondrite parent bodies, demonstrating that large collisions have occurred in the asteroid belt throughout solar system history.

Figure 5.4. A mosaic image of Vesta based on photographs taken by the DAWN spacecraft as it orbited Vesta from 2011 to 2012. Two very large craters in the southern hemisphere appear to be less than 2 Ga, the largest and most recent of which, the Rheasilvia Basin, may have been the impact that launched the HED meteorites into Earth-crossing orbits. NASA photo.
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Other groups of meteorites yield a variety $^{40}$Ar-$^{39}$Ar ages. Some primitive achondrites, (acapulcoites and lodranites) have ages that tightly cluster around 4.51 Ga. Silicate from IAB irons (which are among the so-called non-magmatic iron) give a continual distribution of ages between 4.53-4.32 Ga. Eucrites (from Vesta), many of which are brecciated, yield a wide range ages with peaks in the distribution occurring at 4.48 Ga, 4.0 to 3.7 Ga and 3.45-3.55 Ga, which date heating from large impacts on the surface of Vesta, and the view of Vesta from the DAWN spacecraft (Figure 5.4) certainly shows there have been many of those.

5.2.2 Extinct Radionuclides

There is evidence that certain short-lived nuclides once existed in meteorites. This evidence consists of the anomalous abundance of nuclides, $^{136}$Xe for example, known to be produced by the decay of short-lived radionuclides, such as $^{129}$I, and correlations between the abundance of the radiogenic isotope and the parent element. Consider, for example, $^{53}$Cr, which is the decay product of $^{53}$Mn. The half-life of $^{53}$Mn, only 3.7 million years, is so short that any $^{53}$Mn produced by nucleosynthesis has long since decayed. If $^{53}$Mn is no longer present, how do we know that the anomalous $^{53}$Cr is due to decay of $^{53}$Mn? We reason that the abundance of $^{53}$Mn, when and if it was present, should have correlated with the abundance of other isotopes of Mn. $^{55}$Mn is the only stable isotope of Mn. So we construct a plot similar to a conventional isochron diagram (isotope ratios vs. parent/daughter ratio), but use the stable isotope, in this case $^{55}$Mn, as a proxy for the radioactive one, $^{53}$Mn. An example is shown in Figure 5.5.

Starting from our basic equation of radioactive decay, we can derive the following equation:

$$D = D_0 + N_0(1 - e^{-\lambda t})$$  \hspace{1cm} 5.1

This is similar to the isochron equation we derived earlier, equation 2.8, but not identical. In particular, notice 5.1 contains $N_0$, the initial abundance of the parent, whereas 2.8 contains the present abundance of the parent. Notice also that the term in parenthesis on the right is different. Written for the example of the decay of $^{55}$Mn to $^{53}$Cr, we have:

$$\frac{^{53}Cr}{^{52}Cr} = \left(\frac{^{53}Cr}{^{52}Cr}\right)_0 + \left(\frac{^{53}Mn}{^{52}Cr}\right)_0(1 - e^{-\lambda t})$$  \hspace{1cm} 5.2

where as usual the subscript naught denotes the initial ratio. The problem we face is that we do not know the initial $^{53}$Mn/$^{52}$Cr ratio. We can, however, measure the $^{53}$Mn/$^{52}$Cr ratio. Assuming that initial
isotope composition of Mn was homogeneous in all the reservoirs of interest; i.e., $^{53}\text{Mn}/^{55}\text{Mn}_0$ is constant, the initial $^{53}\text{Mn}/^{52}\text{Cr}$ ratio is just:

$$\left(\frac{^{53}\text{Mn}}{^{52}\text{Cr}}\right)_0 = \left(\frac{^{55}\text{Mn}}{^{52}\text{Cr}}\right)_0 \left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}}\right)_0$$

5.3

Of course, since $^{56}\text{Mn}$ and $^{52}\text{Cr}$ are both non-radioactive and non-radiogenic, the initial ratio is equal to the present ratio (i.e., this ratio is constant through time). Substituting 5.3 into 5.2, we have:

$$\frac{^{53}\text{Cr}}{^{52}\text{Cr}} = \left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}}\right)_0 + \left(\frac{^{55}\text{Mn}}{^{52}\text{Cr}}\right)_0 \left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}}\right)_0 \left(1 - e^{-\lambda t}\right)$$

5.4

Finally, for a short-lived nuclide like $^{50}\text{Mn}$, the term $\lambda t$ is very large after 4.56 Ga, so the term $e^{-\lambda t}$ is 0 (this is equivalent to saying all the $^{53}\text{Mn}$ has decayed away). Thus we are left with:

$$\frac{^{53}\text{Cr}}{^{52}\text{Cr}} = \left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}}\right)_0 + \left(\frac{^{55}\text{Mn}}{^{52}\text{Cr}}\right)_0 \left(\frac{^{53}\text{Mn}}{^{55}\text{Mn}}\right)_0$$

5.5

On a plot of $^{55}\text{Cr}/^{52}\text{Cr}$ vs. $^{53}\text{Mn}/^{52}\text{Cr}$, the slope is proportional not to time, as in a conventional isochron diagram, but to the initial $^{53}\text{Mn}/^{53}\text{Mn}$ ratio. Thus correlations between isotope ratios such as these are evidence for the existence of extinct radionuclides.

In this way, many extinct radionuclides have been identified in meteorites from variations in the abundance of their decay products. The most important of these are listed in Table 5.1. On a cosmic scale, nucleosynthesis is a more or less continuous process – roughly once every second a supernova explodes somewhere in the universe. So we might expect that interstellar dust might contain some of the longer-lived of these nuclides at low, near-steady state concentrations. However, such events are much rarer on a local scale (fortunately for us), and the shorter-lived of these nuclides must have been synthesized nearly shortly before the solar system formed.

To understand why these short-lived radionuclides require a nucleosynthetic event, consider the example of $^{53}\text{Mn}$. Its half-life is 3.7 Ma. Hence 3.7 Ma after it was created only 50% of the original number of atoms would remain. After 2 half-lives, or 7.4 Ma, only 25% would remain, after 4 half-lives, or 14.8 Ma, only 6.125% of the original $^{53}\text{Mn}$ would remain, etc. After 10 half lives, or 37 Ma, only $1/2^{10}$ (0.1%) of the original amount would remain. The correlation between the Mn/ Cr ratio and the abundance of $^{53}\text{Cr}$ indicates some $^{53}\text{Mn}$ was present when the meteorite, or its parent body, formed. From this we can conclude that an event that synthesized $^{53}\text{Mn}$ occurred not more than roughly 30 million years before the meteorite formed. The shorter-lived nuclides provide even tighter constraints on this time scale. We’ll return to this later in the chapter.

5.2.2.1 $^{129}\text{I}$–$^{129}\text{Xe}$ and $^{244}\text{Pu}$

The first of these short-lived radionuclides discovered was $^{129}\text{I}$, which decays to $^{129}\text{Xe}$. Figure 5.6 shows the example of the analysis of the meteorite Khairpur. In this case, the analysis is done in a manner very analogous to $^{39}\text{Ar}$–$^{39}\text{Ar}$ dating; the sample is first irradiated with neutrons so that $^{129}\text{Xe}$ is produced by neutron capture by $^{127}\text{I}$ and

$$\frac{^{129}\text{Xe}^{130}\text{Xe}}{^{128}\text{Xe}^{129}\text{Xe}}$$

is plotted against temperature of the release step.
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Figure 5.7. Variation of $^{134}$Xe/$^{132}$Xe and $^{136}$Xe/$^{132}$Xe in meteorites (＊). The isotopic composition of fission products of man-made $^{244}$Pu is shown as a star (＊). After Podosek and Swindle (1989).

Figure 5.8. Summary of I-Xe ages of meteorites relative to Bjurböle. After Swindle and Podosek (1989).

ating $^{129}$I, which subsequently decays to $^{128}$Xe. The amount of $^{128}$Xe produced is proportional to the amount of $^{127}$I present (as well as the neutron flux and reaction cross section). The sample is then heated in vacuum through a series of steps and the Xe released at each step analyzed in a mass spectrometer. As was the case in Figure 5.5, the slope is proportional to the $^{129}$I/$^{127}$I ratio at the time the meteorite formed.

In addition to $^{129}$Xe produced by decay of $^{129}$I, the heavy isotopes of Xe are produced by fission of U and Pu. $^{244}$Pu is of interest because it another extinct radionuclide. Fission does not produce a single nuclide, rather a statistical distribution of many nuclides. Each fissionable isotope produces a different distribution. The distribution produced by U is similar to that produced by $^{244}$Pu, but the difference is great enough to demonstrate the existence of $^{244}$Pu in meteorites, as is shown in Figure 5.7. Fission tracks in excess of the expected number of tracks for a known uranium concentration are also indicative of the former presence of $^{244}$Pu.

These extinct radionuclides provide a means of relative dating of meteorites and other bodies. Figure 5.8 shows relative ages based on this $^{129}$I–$^{129}$Xe decay system. These ages are calculated from $^{129}$I/$^{127}$I ratios, which are in turn calculated from the ratio of excess $^{129}$Xe to $^{127}$I. Since the initial ratio of $^{129}$I/$^{127}$I is not known, the ages are relative to an arbitrary value, which is taken to be the age of the Bjurböle meteorite, a L4 chondrite.

The ages ‘date’ closure of the systems to Xe and I mobility, which is most likely during metamorphism rather than condensation from the solar nebula. The important point is that there is only slight systematic variation in age with meteorite types. Carbonaceous chondrites do seem to be older than ordinary and enstatite chondrites, while LL chondrites seem to be the youngest. Differentiated meteorites are generally younger. These are not shown, except for silicate in the El Taco iron, which is not particularly young. The bottom line here is that all
chondrites closed to 1 decay system within about 20 Ma.

5.2.2.2 $^{107}\text{Pd} - ^{107}\text{Ag}$

The existence of variations in isotopic composition of silver, and in particular variations in the abundance of $^{107}\text{Ag}$ that correlate with the $^{107}\text{Pd}/^{108}\text{Pd}$ ratio in iron meteorites indicates that $^{107}\text{Pd}$ was present when the irons formed. The half-life of $^{107}\text{Pd}$ is 9.4 million years; hence the irons must have formed within a few tens of millions of years of synthesis of the $^{107}\text{Pd}$. This in turn implies that formation of iron cores within small planetary bodies occurred within a few tens of millions of years of formation of the solar system.

Fractions of metal from the meteorite Gibeon (IVA iron) define a fossil isochron indicating an initial $^{107}\text{Pd}/^{108}\text{Pd}$ ratio of $2.5 \times 10^{-5}$ (Chen and Wasserburg, 1990). Other IVA irons generally fall along the same isochron (Figure 5.9). IIAB and IIAB irons, as well as several anomalous irons show $^{107}\text{Ag}/^{109}\text{Ag} - ^{108}\text{Pd}/^{109}\text{Ag}$ correlations that indicate $^{107}\text{Pd}/^{108}\text{Pd}$ ratios between 1.5 and $2.4 \times 10^{-5}$. Assuming these differences in initial $^{107}\text{Pd}/^{108}\text{Pd}$ are due to time and the decay of $^{107}\text{Pd}$, all of these iron meteorites would have formed no more than 10 million years after Gibeon (Chen and Wasserburg, 1996).

5.2.2.3 $^{26}\text{Al} - ^{26}\text{Mg}$

Perhaps the most significant extinct radionuclide is $^{26}\text{Al}$. Because of its short half-life (0.717 Ma), it provides much stronger constraints on the amount of time that could have passed between nucleosynthesis and processes that occurred in the early solar system. Furthermore, the abundance of $^{26}\text{Al}$ was such that its decay could have been a significant source of heat, and it was likely to have played a role in heating, melting, and metamorphism of meteorite parent bodies. $^{26}\text{Al}$ decays to $^{26}\text{Mg}$; Two examples of the correlation between $^{26}\text{Mg}/^{26}\text{Mg}$ and $^{25}\text{Al}/^{28}\text{Mg}$ is shown in Figure 5.10.

Because of the relatively short half-life of $^{26}\text{Al}$ and its potential importance as a heat source, considerable effort has been devoted to measurement of Mg isotope ratios in meteorites. Much of this work has been carried out with ion microprobes, which allow the simultaneous measurement of $^{26}\text{Mg}/^{26}\text{Mg}$ and $^{27}\text{Al}/^{24}\text{Mg}$ on spatial scales as small as 10 $\mu$. As a result, there are more than 1500 measurements more than 60 meteorites reported in the literature, mostly on CAI’s, because on CAI’s, with their high Al/Mg ratios should produce higher $^{26}\text{Mg}/^{26}\text{Mg}$ ratios, which allows for high temporal resolution.

Figure 5.11 shows that the highest inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios are found in CAI’s and that, with some exceptions, chondrules and other objects have lower inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios or lack evidence of $^{26}\text{Al}$ altogether, suggesting they formed at least several million years later, after $^{26}\text{Al}$ had largely decayed. Advances in analytical technology have allowed higher precision measurements have recently revealed that there are systematic variations in inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios even among CAI’s. MacPherson et al. (2012) found that primitive, unmelted CAI’s have initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of $5.2 \times 10^{-5}$, melted CAIs range from $5.17 \times 10^{-5}$ to $4.24 \times 10^{-5}$, and one single CAI has an range of 4.77 to $2.77 \times 10^{-5}$. The entire range is thus a factor of 2 and corresponds to time span of ~0.7 Ma, presumably the time span during which the
inner solar system was hot enough for CAI formation and reprocessing. Higher precision analyses are also revealing more details of the timing of chondrule formation. Most chondrules have inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios of less than $1 \times 10^{-5}$, but a significant fraction have values ranging as high as $2 \times 10^{-5}$, suggesting chondrule formation began as early as 1 million years after the start of CAI formation (time 0) and continued for another 2 to 3 million years after that (e.g., Villeneuve et al., 2009). These higher inferred ratios are consistent with Pb-Pb ages discussed in section 5.2.1 indicating that at least some chondrules are as old as CIA’s. Nevertheless, the majority appears to be younger.

There has been some debate as to whether differences in inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios reflected a heterogeneous distribution of recently synthesized $^{26}\text{Al}$ in the solar nebula. Under that theory, CAI’s formed in a $^{26}\text{Al}$-rich region while chondrules formed in a $^{26}\text{Al}$-poor one. Most of the presently available evidence suggests that $^{26}\text{Al}/^{27}\text{Al}$ ratios in the solar nebula were homogeneous within about 10%, implying differences in inferred initial $^{26}\text{Al}/^{27}\text{Al}$ do in fact reflect differences in formation ages (Bouvier & Wadhwa, 2010; Villeneuve, et al., 2009; Boss, 2012), although some types of CAI’s found in CM, CO, and CH chondrites may have different initial ratios (Krot et al., 2009) and the question of heterogeneous distribution of $^{26}\text{Al}$ remains debated.

Amebiolal olivine aggregates (AOA’s) found in chondrites are likely direct condensates from nebular gas. Anorthite inclusions in them have $^{26}\text{Al}/^{27}\text{Al}$ ratios up to $4 \times 10^{-5}$, suggesting they formed only slightly later than CAI’s and before most chondrules (Nagashima et al., 2013).

Extinct radionuclides alone provide only a relative chronology of early solar system events. An absolute chronology can be established by calibrating relative ages determined from extinct radionuclides with high precision Pb-Pb ages. For the earliest objects, the short-lived nuclides $^{53}\text{Mn}$ and $^{26}\text{Al}$ have proved most useful. Figure 5.12 illustrates such a time scale, anchored on objects dated by both Pb-Pb and $^{26}\text{Al}$ or $^{53}\text{Mn}$. The chronology begins with the CAI from NWA2364. Objects such as Lewis Hills 86010, St. Marguerite, and D’Orbigny provide other anchors. Objects such as Orgueil, which has not been dated by conventional radiometric methods, can be placed on the time scale based on their apparent initial $^{26}\text{Al}/^{27}\text{Al}$ or $^{53}\text{Mn}/^{55}\text{Mn}$ ratios.
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5.2.3 Extinct Radionuclides in the Earth

Several of the short-lived radionuclides listed in Table 5.1 have half-lives sufficiently long that they should have been present in the early Earth. Of greatest interest are $^{129}$I, $^{183}$Hf, and $^{146}$Sm. The decay products of these nuclides are $^{129}$Xe, $^{182}$W, and $^{142}$Nd, an atmophile, a siderophile, and a lithophile element, respectively. Their distribution can tell us about the early evolution of the Earth’s atmosphere, core, and mantle. Here we’ll consider $^{183}$Hf and $^{146}$Sm; we’ll discuss $^{129}$I in Chapter 12.

5.2.3.1 $^{182}$Hf–$^{182}$W Constraints of the Age of the Moon and the Earth’s Core

Figure 5.11. Inferred initial $^{26}$Al/$^{27}$Al for all available meteoritic data. “O&E objects” are chondrules and other constituents of ordinary and enstatite chondrites; FUN and UN refers to CAI’s with “fractionated and unknown nuclear” isotopic anomalies. After MacPherson et al. (1995).

Figure 5.12. Time scale of events in the early solar system based on calibrating $^{53}$Mn and $^{26}$Al extinct radionuclide chronology to Pb-Pb ages. Based on data in Trinquier et al. (2008), Nyquist et al. (2009), Bouvier and Wadhwa (2010), and Connelly et al (2012).
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The Hf-W pair is particularly interesting because Hf is lithophile while W is moderately siderophile. Thus the $^{182}\text{Hf}/^{183}\text{W}$ decay system should be useful in “dating” silicate-metal fractionation, including core formation in the terrestrial planets and asteroids. Both are highly refractory elements, which has the advantage that a first order assumption is that bodies such as the Earth should have a chondritic Hf/W ratio. These observations have led to a series of measurements of W isotope ratios on terrestrial materials, lunar samples, and a variety of meteorites, including those from Mars. The conclusions have evolved and new measurements have become available. Among other things, the story of Hf-W illustrates the importance of the fundamental dictum in science that results need to be independently replicated before they are accepted.

Because the variations in $^{182}\text{W}/^{183}\text{W}$ ratio are quite small, they are sometimes presented and discussed in the same $\varepsilon$ notation used for Nd and Hf isotope ratios or in $\mu$ notation, which is deviations in parts per million. There is a slight difference, however; $\varepsilon_W$ or $\mu_W$ are deviations in parts per 10,000 or 1,000,000, respectively, from a terrestrial tungsten standard, and $f_{\text{Hf}/\text{W}}$ is the fractional deviation of the Hf/W ratio from the chondritic value. Assuming that the silicate Earth has a uniform W isotope composition identical to that of the standard, then the silicate Earth has $\varepsilon_W$ of 0 by definition. The basic idea this: if the $^{182}\text{W}/^{183}\text{W}$ ratio in the silicate Earth is higher than in chondrites, it would mean that much of the Earth’s tungsten had been sequestered in the Earth’s core before $^{183}\text{Hf}$ had entirely decayed. Since the half-life of $^{183}\text{Hf}$ is 9 Ma and using our rule of thumb that a radioactive nuclide is fully decayed in 5 to 10 half-lives, this would mean the core must have formed within 45 to 90 million years of the formation of the solar system (which we take as the age of the CAI’s). If on the other hand, the $^{182}\text{W}/^{183}\text{W}$ ratio in the silicate Earth was the same as in bulk chondrites, which never underwent silicate-metal fractionation, this would mean that at least 45 to 90 million years must have elapsed (enough time for $^{183}\text{Hf}$ to fully decay) between the formation of chondrites and the formation of the Earth’s core. As we’ll see, the reality is likely more complex than either of these simple scenarios.

‘Anomalous’ W isotopic compositions were first found in the IA iron Toluca by Harper et al. (1991). They found the $^{182}\text{W}/^{183}\text{W}$ ratio in the meteorite was 2.5 epsilon units (i.e., parts in 10,000) lower than in terrestrial W. This value was revised to -3.9 epsilon units by subsequent, more precise, measurements (Jacobsen and Harper, 1996). Essentially, the low $^{182}\text{W}/^{183}\text{W}$ ratio indicates Toluca metal separated from Hf-bearing silicates before $^{183}\text{Hf}$ had entirely decayed. At this point, however, no measurements had yet been made on chondritic meteorites, so it was unclear how rapidly the Earth’s core had formed. Chondrites are undifferentiated solar system material, and therefore the reference to which other materials must be compared.

Lee and Halliday (1995) reported W isotope ratios for 2 carbonaceous chondrites (Allende and Murchison), two additional iron meteorites and a lunar basalt. They found the iron meteorites showed depletions in $^{182}\text{W}$ ($\varepsilon_W = -4.5$ and -3.7 for Arispe and Coya Norte, respectively) that were similar to that observed in Toluca by Jacobsen and Harper (1996). The chondrites, however, had $\varepsilon_W$ values that were only slightly positive, about +0.5, and were analytically indistinguishable from “terrestrial” W, as was the lunar basalt. Lee and Halliday (1995) inferred an initial $^{182}\text{Hf}/^{184}\text{Hf}$ for the solar nebula of $2.6 \times 10^{-4}$, much higher than the ratio assumed by Jacobsen and Harper (and the present best estimate listed in Table 5.1). Based on this similarity of isotopic compositions of chondritic and terrestrial W, Lee and Halliday (1995) concluded that the minimum time required for formation of the Earth’s core was 62 million years.

Subsequently, Lee and Halliday (1998) reported $\varepsilon_W$ values of +32 and +22 in the achondrites Juvinas and ALHA78132. These large differences in W isotopic composition meant that metal-silicate fractionation, i.e., core formation, occurred quite early in the parent bodies of achondritic meteorites (Juvinas and ALHA78132 are eucrites and their parent body, Vesta, is known to have an iron core based on density determined by the DAWN mission). In other words, asteroids or “planetesimals” must have differentiated to form iron cores and silicate mantles very early, virtually simultaneously with the formation of the solar system. This is consistent with other evidence discussed above for very little age difference between differentiated and undifferentiated meteorites. Lee and Halliday (1998) also reported $\varepsilon_W$ values
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in the range of +2 to +3 in 3 SNC meteorites thought to have come from Mars. These data indicated that the Martian core formed relatively early and the heterogeneity in tungsten isotopes indicates in Martian mantle was never fully homogenized. Lee et al. (1997) reported that the W isotope ratio of the Moon was about 1.2 epsilon units higher than that of terrestrial W.

At that point, the Earth appeared to be puzzlingly anomalous among differentiated planetary bodies in that silicate-metal differentiation appeared to have occurred quite late. Subsequently two groups, working independently, found that chondrites had $\varepsilon_W$ significantly lower than reported by Lee and Halliday (1995), Yin et al. (2002) reported W isotope measurements carried out in two laboratories, Harvard University and the Ecole Normale Supérieure de Lyon, which showed that the chondrites Allende and Murchison had W isotope ratios 1.9 to 2.6 epsilon units lower than the terrestrial standard (Figure 5.10). Yin et al. (2002) also analyzed separated metal and silicate fractions from two ordinary chondrites (Dhurmsala and Dalgety Downs) that allowed them to estimate the initial $^{182}$Hf/$^{180}$Hf of the solar system as $\sim 1 \times 10^{-4}$. In the same issue of the journal Nature, Kleine et al., (2002) reported similarly low $\varepsilon_W$ (i.e., -2) for the carbonaceous chondrites Allende, Orgueil, Murchison, Cold Bokkeveld, Nogoya, Murray, and Kokoonda measured in a third laboratory (University of Münster). They inferred a similar estimate of the solar system initial $^{182}$Hf/$^{180}$Hf. Furthermore, Kleine et al. (2002) analyzed a variety of terrestrial materials and found they all had identical W isotopic composition (Figure 5.10). It thus appears that the original measurements of Lee and Halliday (1995) were wrong. The measurement error most likely relates to use of what was at the time an entirely new kind of instrument, namely the multi-collector ICP-MS.

Using the revised initial $^{182}$Hf/$^{180}$Hf and previously published data on HED and SNC achondrites, Kleine et al. (2002) estimated the age of the core of Vesta as 4.2±1.3 Ma, that of Mars as 13.0±2.0 Ma and that of Earth as 33±2 Ma after the start of the solar system, and noted that the timescale for core formation increases with size of the planet. Yin et al. (2002) considered two scenarios for the formation of the core. In the first, which they call the twostage model in which the Earth first accretes (stage 1) and then undergoes core formation (stage 2), induced by the giant impact that forms the moon. In this scenario, core formation occurs 29 million years after formation of the solar system. In the second scenario, which they believed more likely, metal segregates continuously from a magma ocean. In this continuous model, the

mean age of core formation is 11 million years. In contrast, they concluded that Vesta underwent core formation within 3 million years of formation of the solar system. Klein et al. (2002) reached similar conclusions.

The next twist in the story came when it was recognized that $^{182}\text{W}$ could be produced by beta decay of $^{182}\text{Ta}$ which in turn is produced cosmodenically through the reaction $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$. Because the Earth’s surface is largely shielded from cosmic rays by the atmosphere, this reaction is entirely trivial for the Earth. However, the Moon has no atmosphere. Furthermore, the lack of lunar geologic activity means that materials are exposed at the surface for very long times (hundreds of millions of years and more) and so far we have sampled on this material at the surface. Consequently, the cosmogenic production of nuclides in lunar materials can be significant. Early studies failed to appreciate this or to fully correct for this effect. Touboul et al. (2007), working with W-rich, Ta-poor metal grains separated from lunar samples, showed that previous high $\varepsilon$W values in lunar samples were due to cosmogenic effects and when these were eliminated the Moon has an isotopically homogeneous W isotopic composition that is identical to that of the silicate Earth – about 2 epsilon units higher than chondrites.

The homogeneous isotopic composition of lunar materials Moon, including samples with highly variable Hf/W ratios such as anorthosites from the ancient lunar crust and mare basalts formed by later melting of the lunar mantle, implies that $^{182}\text{Hf}$ had effectively decayed completely before the Moon formed (or at least before its magma ocean solidified). Given the analytical precision with which W isotopes can be measured, this implies an age of the Moon of greater than 60 Ma after the beginning of the solar system (the age of Allende CAI’s). The minimum age of the Moon is constrained by Sm-Nd ages of the lunar anorthositic crust. This age is $4.456\pm0.040$ Ga, or about 100 Ma after the beginning of the solar system. Touboul et al. (2007) thus estimate an age for the Moon of $62 +90/-10$ Ma after the start of the solar system.

There is a very broad consensus among scientists that the Moon formed as a result of a collision between a nearly full-sized Earth and a second body (sometimes called Thera) about the size of Mars. This is known as the Giant Impact Hypothesis. Debris thrown into orbit about the Earth as a result of the impact subsequently coalesced to form the Moon. A collision between bodies of these sizes releases enormous amounts of energy; depending on how efficiently the gravitational-kinetic energy is converted to heat, potentially enough energy to entirely melt the Earth. At the very least, one expects significant melting would have occurred on the Earth and one of the virtues of the hypothesis is that it explains the extensive melting experienced by the Moon.  

Figure 5.14. Difference between $\varepsilon$W of Earth and Moon ($\Delta$) versus the age the giant impact (and presumably final core formation in the Earth). $f$ is the relative difference in Hf/W ratios between the silicate part of the Earth and the silicate part of the Moon (i.e., $(\text{Hf/W}_{\text{Moon}}-\text{Hf/W}_{\text{Earth}})/\text{Hf/W}_{\text{Earth}}$). The grey area shows the best value of $\Delta\varepsilon_W$ (0.09±0.10). The Hf/W ratio of the Earth’s mantle is estimated at 18 and that of the Moon is 26.5, corresponding to an $f$ of 0.47 (solid line). From Touboul et al. (2007).
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(Because it has remained geologically active, all evidence of a magma ocean on the Earth has been erased; because it quickly became geologically inactive, evidence of extensive early melting on the Moon has been preserved.) The significance of this is that such an impact would have provided a last opportunity for the metal to segregate from the mantle and sink into the core (a process that almost certainly requires the metal, if not also the silicate, to be liquid). We expect therefore, that the Moon-forming giant impact should also be the time of final separation of the core.

If, however, the core formed in a single event 60-100 Ma after the start of the solar system, we would that the silicate Earth would have a W isotopic composition very close to chondritic; instead the terrestrial value is 2 epsilon units higher than chondritic. Furthermore, if, as both tungsten and silver isotopes clearly reveal, cores of asteroids formed within 10 Ma of the start of the solar system (and likely even earlier), why was core formation on the Earth so delayed? We can reconcile these observations if we assume that core formation was a more or less continuous process that began very early and only ended with the giant impact. In essence, the scenario goes like this: Once planetesimals exceed a few 10’s of km in radius, heating, either from $^{26}$Al or release of gravitational energy in collisions, caused melting that allowed metal and silicate to separate, with the metal sinking to form cores of the planetesimals. As the bodies grew into larger ones through collision with other planetesimals, enough energy was released to allow the cores of colliding bodies to merge. This process, known as oligarchic growth, continued to build larger and larger planetary embryos. As the embryos merged through collision, fewer and fewer embryos remained and the collisions were less frequent, slowing the planetary growth process. But the collisions that did occur were far more energetic. The process, in the case of the Earth, culminates when the last two bodies in the Earth’s orbital neighborhood (or “feeding zone”) collide in the giant impact that forms the Moon. Thus metal that ultimately formed the Earth’s core actually segregated from silicate far earlier, in the much smaller planetesimals, when $^{182}$Hf was still live. The giant impact then marks only the end of the process.

The exact age deduced for this event then depends on the difference in $\epsilon_W$ and $\text{Hf/W}$ ratio between the Earth and the Moon. This is illustrated in Figure 5.14. This lead to an estimate of the age of the Moon (and completion of the Earth’s core) of 50-90 Ma.

The latest episode of this story was the recent discovery of heterogeneous $\epsilon_W$ values in Archean rocks. The interpretation is that these variations reflect inhomogeneous distribution of a ‘late accretionary veneer’ of chondritic material added to the Earth after final segregation of the core. We’ll discuss this in more detail in Chapter 7.

5.2.3.2 $^{146}$Sm-$^{142}$Nd

As we have mentioned, geochemists generally assume that rare earth and other refractory elements have the same relative concentrations in the Earth as they have in chondrites. If so, the Sm/Nd ratio of the Earth should be chondritic, and by extension the $^{142}$Sm/$^{144}$Nd ratio of the present Earth should be chondritic and the $^{146}$Sm/$^{144}$Nd of the early Earth should also have been chondritic. Thus the $^{142}$Nd/$^{144}$Nd and $^{142}$Nd/$^{144}$Nd of the bulk Earth should also be chondritic. However, recent studies of the $^{145}$Nd/$^{144}$Nd ratio in chondrites and terrestrial materials suggest that this may not be the case, at least for that part of the Earth accessible to sampling. This is surprising to say the least. These two elements are very similar to each other in chemical behavior, having identical configurations of electrons in bonding orbitals, and are both refractory lithophile elements. Indeed, Nd and Sm have 50% condensation temperatures of 1602 and 1590 K, respectively. It is difficult to see how processes operating in the solar nebula could have fractionated these elements significantly. The total range of high precision Sm/Nd ratio measurements in chondrites varies by less than 3%, which would seem to confirm that these elements were not fractionated in the solar nebula.

$^{142}$Nd is the product of $\alpha$-decay of $^{146}$Sm, a nuclide with a half-life of 68 million years. As Table 5.1 shows, the initial $^{146}$Sm/$^{144}$Sm ratio of the solar system about 0.0094, a value deduced from $^{142}$Nd/$^{144}$Nd variations in meteorites using procedures discussed above. $^{146}$Sm is the least abundant isotope of Sm, comprising only 3% of natural Sm, so even initially, $^{146}$Sm would have only constituted 0.025% of Sm. Because of this and because the range of Sm/Nd ratios in nature is small, any variations in the
$^{142}\text{Nd}/^{144}\text{Nd}$ ratio should be quite small, no more than a few 10’s of ppm. Detecting such small variations is analytically challenging, and indeed was nearly impossible before the 1990’s. Furthermore, because the half-life of $^{146}\text{Sm}$ is short, any variation in $^{142}\text{Nd}/^{144}\text{Nd}$ must be the result of fractionation occurring in at most the first few hundred million years of solar system or Earth history. However, considerable variation in the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio had been detected in SNC meteorites, which suggested early mantle differentiation on Mars. It thus seemed reasonable to look for such variations on Earth.

Geochemists focused their initial attention on early Archean rocks from the Isua area in Greenland. A study by Harper and Jacobsen (1992) reported a 33 ppm excess of $^{142}\text{Nd}$ in one 3.8 Ga old metavolcanic rock from Isua compared to laboratory standards; the latter was assumed to have the same $^{142}\text{Nd}/^{144}\text{Nd}$ ratio as chondrites. Other workers initially failed to find any excesses in other rocks from Isua, so these results were controversial. Subsequent work by Caro et al. (2003) and Boyet et al. (2003), however, eventually confirmed the original findings of Harper and Jacobsen. This means that these early parts of the crust formed from a mantle reservoir that had a high Sm/Nd ratio – and importantly, that this reservoir formed very early, most likely within the first 100 Ma. Subsequently, other $^{142}\text{Nd}/^{144}\text{Nd}$ “anomalies” were found in other early Archean rocks, including ones from Australia and Labrador (Bennett et al., 2007; O’Neil et al., 2008).

A yet more surprising result came when Boyet and Carlson (2005) analyzed the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of meteorites and found that modern terrestrial igneous rocks had $^{142}\text{Nd}/^{144}\text{Nd}$ ratios that average 20 ppm or 0.2 ε

Figure 5.15. Variation in $\varepsilon_{^{142}\text{Nd}}$ in the Earth and meteorites. Gray region is the range measurements of laboratory standards derived from terrestrial Nd. All other terrestrial materials plot within this range with the exception of some samples from Isua, Greenland. Chondrites have, on average, $\varepsilon_{^{142}\text{Nd}}$ of -0.2 relative to terrestrial standards. Data from Caro et al. (2003), Boyet and Carlson (2005), Boyet and Carlson (2006), O’Neil et al (2008), and Upadhyay et al., 2009. SNC data from the compilation of Halliday (2001).
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silon units higher than ordinary chondrites, and most eucrites as well (Figure 5.15). This implies that the modern mantle has a significantly higher Sm/Nd ratio than chondrites. How much higher depends on when the increase occurred. If the increase occurred 5 million years after the beginning of the solar system (taken as the age of CAI’s), the Sm/Nd ratio of the accessible Earth would have to be ~6% higher than chondrites; if the increase occurred at 30 million years, it would have to be ~10% higher. If the increase occurred later, the Sm/Nd ratio would have to be even higher. This increase in Sm/Nd might seem small, yet this small difference is very important in interpretation of Nd isotope systematics. For the two scenarios above, 5 Ma and 30 Ma, Boyet and Carlson (2005) calculated that the $\varepsilon_{Nd}$ of the accessible Earth would have to be ~6.9 and +11 respectively, assuming a half-life for $^{146}$Sm of 103 million years. These values fall within the range of values of mid-ocean ridge basalts. Subsequently, the half-life was found to be only 68 Ma (Kinoshita et al., 2012), which would imply slightly higher $\varepsilon_{Nd}$ for the Earth. Recalling that the Isua samples have a 30 ppm excess in $^{142}$Nd relative to a terrestrial standard, this means that the Isua samples have a 50 ppm excess in $^{142}$Nd relative to chondrites.

How might these isotopic differences come about? Three possible answers have been proposed. First, it is possible that the early solar system was isotopically heterogeneous. As we’ll see in a subsequent section, some isotopic heterogeneity existed in the early solar system. More significantly, small variations in the isotopic composition of Nd and Sm (and Ba and Sr as well) have been found in chondrites (Andreasen and Sharma, 2006; Carlson et al.; 2007; Gannoun et al., 2011; Qin et al., 2011; Boyet and Gannoun, 2013). Indeed, carbonaceous, ordinary, and enstatite chondrites each appear to have different $^{142}$Nd/$^{144}$Nd despite identical Sm/Nd (Figure 5.15). Both $^{146}$Sm and $^{144}$Sm are p-process-only nucleides produced exclusively in supernova explosions while $^{142}$Nd is primarily an s-process nuclide produced in red giants, with a small fraction (<5%) produced by the p-process (see Chapter 1 for an explanation of these processes). Incomplete mixing of material from different stellar sources thus could result in variations in $^{142}$Nd/$^{144}$Nd in the early solar system. Indeed, Qin et al. (2011) found that excesses in $^{144}$Nd, an r-process nuclide produced in supernovae, correlated with deficits of $^{142}$Nd (Figure 5.16). The correlation could be explained by incomplete mixing of material from different stellar sources. A possible origin of this is the variable production of $^{142}$Nd relative to $^{144}$Nd in supernova explosions compared to the p-process.

Figure 5.16. Variation of $^{142}$Nd/$^{144}$Nd and $^{146}$Nd/$^{144}$Nd (in epsilon units) in meteorites. The two isotope ratios are anti-correlated, suggesting incomplete mixing of s- and r-process nucleides in these materials. Also shown are the trajectories of step-wise dissolution experiment of carbonaceous chondrite Murchison (Qin et al., 2011) and enstatite chondrite ALHA77295 (Boyet and Gannoun, 2013). Modified from Qin et al. (2011) and Boyet and Gannoun (2013).

* The two standards commonly used in Nd isotope ratios measurements are the “La Jolla” standard and the “Ames” standard. Both are solutions created from industrially purified Nd.
sources. Both Qin et al. (2011) and Boyet and Gannoun (2013) also performed step-wise dissolution experiments that demonstrated internal isotopic heterogeneity in meteorites. In both cases, the most resistance fractions were enriched in s-process nuclides (and deficient in r-process nuclides). Although neither study identified the carrier phase, it is most likely silicon carbide, which, as we will see in the next section, has been identified as the carrier of s-process isotopes of noble gases and other elements. And as we’ll see in that section, there is some evidence for a late addition of supernova debris to the solar nebula – incomplete mixing of that material could explain much of the isotopic variation seen in Figure 5.16. However, as Andreasen and Sharma (2006) and Qin et al. (2011) concluded, while the observed isotopic heterogeneity could explain some or much of $^{142}$Nd/$^{144}$Nd variations observed among chondrites, it does not appear that it can entirely explain the difference between chondrites and the Earth, which plots off the correlation in Figure 5.16. Furthermore, Yokoyama et al. (2013) analyzed 2 ordinary, 1 R-type, and 1 carbonaceous chondrite using a higher temperature (240°C) dissolution technique that included sulfuric acid not used in previous studies and found that all four meteorites had homogeneous $^{142}$Nd/$^{144}$Nd that was 20±3 ppm (0.2 epsilon units) lower than the modern terrestrial value with $^{146}$Nd/$^{144}$Nd, $^{148}$Nd/$^{144}$Nd, and $^{150}$Nd/$^{144}$Nd being indistinguishable from the terrestrial ratios. As they point out, this suggests that the Nd isotopic composition of the solar nebular was homogeneous and that Nd isotopic variations in observed chondrites reflects a failure to completely digest isotopically heterogeneous presolar grains present in the meteorites. If so, then the difference between chondritic and terrestrial $^{142}$Nd/$^{144}$Nd must reflect a difference in the Sm/Nd ratio.

A second possibility was suggested by Boyet and Carlson (2005). They suggested that Earth underwent early differentiation forming an *early-enriched reservoir* (EER) such as a primordial crust that sank into the deep mantle and has not been sampled since. Alternatively, crystallization of a terrestrial magma ocean might have left a layer of residual melt, similar to the KREEP* source on the Moon. Boyet and Carlson (2005) noted that if it were rich in Fe and Ti, as is the lunar KREEP reservoir is, once crystallized, the EER could have sunk into the deep mantle, where it remains because if its high density.

A third possibility, “collisional erosion”, has been suggested by Caro et al. (2008) and O’Neill and Palme (2008). As noted earlier, planetary bodies are thought to form through the process of oligarchic growth, the later stages of which involve infrequent, energetic collisions between large bodies. Sufficient energy is released in these collisions that the growing planet extensively melts. Between collisions, one might reasonably expect a primitive basaltic crust to form through crystallization at the surface. Caro et al. (2008), O’Neill and Palme (2008), and Caro and Bourdon (2010) suggest that a substantial fraction of this crust was blasted away in these collisions, leaving the Earth depleted in elements that were concentrated in that crust, namely incompatible elements like Nd and Sm.

Common to both the latter hypotheses is the idea that planetary melting and consequent differentiation begins during, rather than after, planet accretion. Both hypotheses rely on the idea of formation, through melting and fractional crystallization, of a primitive crust enriched in incompatible elements. Such a crust would have a low Sm/Nd ratio, leaving the remainder of the planet with a higher Sm/Nd ratio than the material from which it accreted. In the Boyet and Carlson (2005) hypothesis, this early crust sinks into the deep mantle where it remains as an isolated reservoir. In collisional erosion hypothesis, this early crust is lost to space.

An additional important observation is that the Moon, and possibly Mars, also appear to have $^{142}$Nd/$^{144}$Nd ratios higher than chondritic. All lunar rocks are ancient, so not surprisingly, they have variable $^{142}$Nd/$^{144}$Nd ratios. When these ratios are plotted against $^{143}$Sm/$^{144}$Nd they display a correlation indicating the bulk Moon has $^{142}$Nd/$^{144}$Nd about 17 ppm higher than the ordinary chondrite value, identical, within uncertainty, to the modern terrestrial value (Boyet and Carlson, 2008). These lunar data are particularly significant. First, the similarity of $^{142}$Nd/$^{144}$Nd in the Earth and Moon imply that the Sm/Nd ratio of the Earth-Moon system was fixed before the giant impact that formed the Moon. One reaches the same conclusion when one considers the timing of the Moon-forming event. As we

‡ So named because magma derived from it are rich in potassium, rare earths, and phosphorus.
saw in the previous section, tungsten isotope ratios of the lunar rocks are uniform and indistinguishable from those of the Earth, indicating the Moon-forming event occurred at least 50 and as much as 150 million years after the start of the solar system. Unreasonably high Sm/Nd ratios would be required to explain the $^{142}$Nd/$^{144}$Nd of the Earth and Moon if the fractionation occurred that late. Thus the early-enriched reservoir hypothesized by Boyet and Carlson must predate the giant impact. Whether this reservoir could have survived this event without being remixed into the mantle is a matter of current debate.

$^{142}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd ratios in shergottites (meteorites from Mars) suggest the Martian $^{142}$Nd/$^{144}$Nd ratio is, like the Earth and Moon, 10 to 20 ppm higher than chondritic and Caro et al. (2008) argue that this suggests that all planetary objects in the inner solar system have Sm/Nd ratios higher than chondritic. Other Martian meteorites, the nakhlites and Chaussigny plot above this correlation. Caro et al. (2008) explain this by suggesting that the Martian mantle source of these meteorites underwent later differentiation. However, since there are multiple possible interpretations of the data, the Martian evidence must be considered equivocal at best on this point.

There are geophysical arguments both for and against the early-enriched reservoir hypothesis. If this reservoir formed by igneous processes it would have to contain at least 40% of the Earth’s inventory of highly incompatible lithophile elements to explain the 6% increase in 5m/Nd in the remaining mantle. This group of elements includes the heat-producing elements K, U, and Th. Thus the early-enriched reservoir at the base of the mantle would be responsible for some 40% of the heat production in the Earth, and 70% or more of the heat production in the mantle, leaving the remaining mantle particularly depleted in heat producing elements. That would appear to be inconsistent with fluid dynamic models of the Earth. Convecting fluids heated mainly from below are dominated by plumes that initiate as instabilities at the base of the layer (Davies, 2009). While some plumes do form at the base of the mantle and rise through it, the dominant form of convection in the Earth’s mantle is plate tectonics, which is the kind of convection expected in systems heated from within (lava lakes, for example, convect in a way similar to plate tectonics). On the other hand, seismologists have identified two large low shear wave velocities provinces (LLSVP’s) in the lower mantle, one beneath Africa, the other beneath the Pacific. The LLSVP’s cover 50% of the core–mantle boundary and rise 400-1000 km above it. The low velocities may reflect either higher temperatures or higher densities, or both; beyond that there nature is enigmatic, with several possible interpretations. One possibility is that they are dense Fe-rich regions that have existed since the Earth’s formation (Gurney and McNamara, 2008) and thus represent a plausible candidate for Boyet and Carlson’s early enriched reservoir.

Regardless of which of the latter two explanations is correct and whether an early-formed crust was eroded by collisions or sunk into the deep mantle, the implications of the non-chondritic Sm/Nd ratio of the Earth are profound. Both hypotheses imply that at least the observable Earth is depleted in the incompatible elements that would have been concentrated in that early crust. This would include the heat producing elements, K, U, and Th, so there are geodynamic implications as well.

As a final point, we note that the three hypotheses explored above are not mutually exclusive. For example, the Earth has other isotopic similarities to enstatite chondrites and the difference between the average enstatite chondrite $^{142}$Nd/$^{144}$Nd and modern terrestrial value is only 10 ppm (as opposed to the 20 ppm difference from ordinary chondrites). If we take the initial isotopic composition of the Earth to be that of enstatite chondrites, a much smaller mass fraction would have to be lost to space in the collisional erosion hypothesis or a smaller fraction hidden in the deep Earth in the ‘early-enriched reservoir’ hypothesis. Finally, as we noted, the latter two ideas both involve a primitive low Sm/Nd crust. It is possible some was lost to space and some stored in the deep mantle.

We’ll return to this topic when we explore the implications of $^{142}$Nd/$^{144}$Nd variations in early Archean rocks for the early history of the Earth in Chapter 7.

5.2.3 Origin of Short-lived Nuclides

There is some debate over exactly how the short-lived radionuclides were synthesized. As we saw earlier in this chapter, heavy element nucleosynthesis occurs mainly in red giant stars and in superno-
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vaes. Anomalous isotopic compositions of stable elements, which we discuss in the following section, provide clear evidence that meteorites contain some material synthesized in both these environments. However, they provide no constraints on when this happened. Only with the unstable nuclides can we address the question of when. On galactic scales of time and space, red giants and supernovae conti

nuously inject newly synthesized elements into the interstellar medium. Those nuclides that are unstable will steadily decay away. These two competing processes will result in steady-state abundance of these nuclides in the interstellar medium. The abundances of $^{106}$Pd, $^{129}$I, and $^{183}$Hf listed in Table 5.1 roughly match the expected steady-state galactic abundances and hence do not require a specific synthesis event. However, the abundances of shorter-lived $^{10}$Be, $^{26}$Al, $^{44}$Ca, $^{53}$Mn or $^{60}$Fe in the early Solar System requires synthesis of these nuclides at the time of, or just before, Solar System formation.

The conventional view is that these nuclides were synthesized in a nearby red giant and/or a supernova shortly before solar system formation began. Some of these elements, such as $^{26}$Al are most efficiently synthesized in red giants; others, such as $^{40}$Fe, are most efficiently synthesized in supernovae. Thus most models invoke both environments, which may or may not have been the same star at different times. From an astronomical perspective, nucleosynthesis shortly before the solar system formed is not surprising: stars usually form in clusters in large clouds of gas and dust known as nebulae. The Great Nebula in Orion is a good example. Some of the stars formed in these stellar nurseries will be quite large and have short lifetimes, ending their existence in supernova explosions. Thus stellar death, including the red giant and supernova phases, goes on simultaneously with star birth in these nebulae. Indeed, one popular hypothesis is that the formation of the solar system was actually triggered by a supernova shock wave. Boss and Vanhala (2001) provide a good discussion of this view.

Evidence of the existence of $^{10}$Be in some CAI’s has led to an alternative hypothesis, namely that many of the short-lived extinct radionuclides were produced by spallation within the solar system as it was forming. As we have seen, Be is not synthesized in stars, hence it presence in CAI’s and other primitive chondritic components is problematic for the red giant/supernova injection hypothesis. Another key observation is that young protostars emit X-rays. X-rays are produced by accelerating charged particles. Hence some have suggested that near the surface of the accreting protosun, magnetic reconnection events could produce flares that accelerate ions up to very high energies – essentially creating cosmic rays. Spallation would occur when the accelerated particles encounter dust grains – the CAI’s – that happen to be close to the forming Sun (within 0.1 AU). According to this theory, some of these irradiated CAI’s would have been carried back out to the vicinity of the asteroid belt by the energetic “X-winds” that are associated with these protostars. This theory can readily account for the abundances of $^{10}$Be, $^{26}$Al, $^{44}$Ca, and $^{53}$Mn observed. If it is correct, it provides an alternative explanation for the difference in $^{26}$Al/$^{27}$Al ratios between CAI’s and chondrules: that CAI’s formed in an $^{26}$Al rich environment near the Sun while chondrules formed further out in a region lacking spallation-produced $^{26}$Al.

Proponents of the red giant/supernova injection hypothesis point out that the spallation hypothesis cannot explain the presence of $^{60}$Fe, which cannot be produced by spallation. They concede that spallation is the only way to produce $^{10}$Be, but argue that it can be produced by collisions with particles accelerated in the enhanced solar winds of red giants and/or in the expanding envelopes of supernovae. Although some debate on this subject continues, but there is something close to a consensus that most short-lived radionuclides detected so far were mainly produced in stars and nucleosynthesis but spallation may account for some nuclei such as $^{10}$Be. They also note that chronologies deduced from short-lived radionuclides appears to agree well with high precision Pb ages (Figure 5.12), indicating homogeneous distribution of these nuclides in the solar nebula.

5.3 Stardust and Isotopic Anomalies in Meteorites

In addition to the isotopic anomalies that resulted from decay of short-lived radionuclides, there are other isotopic anomalies in meteorites that are not due to such in situ decay. Many of these anomalies, like those created by decay of extinct radionuclides, may reflect the injection of newly synthesized ma-
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ter into the cloud of dust and gas from which the solar system ultimately formed. Others, however, may reflect isotopic inhomogeneity within this cloud, and the variable abundance of exotic gas and grains of material synthesized at various times and places in the galaxy. Still other isotopic anomalies may reflect chemical fractionations within this cloud. It is these anomalies we focus on in this section.

5.3.1 Neon Alphabet Soup and ‘Pre-Solar’ Noble Gases in Meteorites

Noble gases were the first group of elements in which isotopic variations were identified, and these variations occur in virtually all of the carbonaceous chondrites that have not experienced extensive metamorphism. Much of the isotopically distinct noble gas is contained in the matrix that accreted at low temperature (below 100-200°C), specifically in highly unreactive carbon species, including organic carbon, graphite, diamond, and silicon carbide. Noble gases are present in meteorites at concentrations that are often as low as 1 part in $10^{10}$. Although they can be isolated and analyzed at these concentrations, their isotopic compositions are nonetheless partly sensitive to change due to processes such as radioactive decay (for He, Ar, and Xe), spallation and other cosmic-ray induced nuclear processes, and solar wind implantation. In addition, mass fractionation can significantly affect the isotopic compositions of the lighter noble gases (He and Ne). Up to the late 1960’s, it was thought that all isotopic variations in meteoritic noble gases were related to these processes. For example, Ne isotopic variations could be described as mixtures of three components, “Neon A” or “planetary” (similar in composition to the Earth’s atmosphere), “Neon B”, or solar, and “Neon S”, or spallogenic (cosmogenic) (Figure 5.17).

In 1969, evidence of a $^{22}$Ne-rich component, named “Neon E” was found in the high temperature (900-1100°C) release fractions of six carbonaceous chondrites. Its release at high temperature indicated it was efficiently trapped in a phase that breaks down only at high temperature.

The carrier of Neon-E proved difficult to identify. Many scientists participated in an intensive search over nearly 2 decades for the carrier phase of these components. The search quickly focused on the matrix, particularly that of CM2 chondrites. But the fine-grained nature of the matrix, together with the abundance of sticky and refractory organic compounds, made work with the groundmass difficult. In the late 1980’s, E. Anders and his colleagues at the University of Chicago (e.g., Tang and Anders, 1988) found that Neon-E is associated with fine-grained (<6 µm) graphite and SiC (silicon carbide) of the matrix. Ne-E actually consists of two isotopically distinct components: Ne-E(L), which was released at low temperature and ultimately found to reside in graphite, and Ne-E(H) which is released at high temperature resides in SiC. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of Ne-E(H) is less than 0.01, while that of Ne-E(H) is less than 0.2.

The origin of Ne-E, and Ne-E(L), which is almost pure $^{22}\text{Ne}$, posed something of a mystery. It was originally thought that it was a decay product of $^{22}\text{Na}$, which has a half-life of 2.6 years, produced in red giants. Na could readily separate from Ne and other noble gases by condensation into grains. However, this hypothesis has now largely been rejected. For one thing, Huss et al. (1997) found that SiC grains in Orgueil (CI), had far too lit-

![Figure 5.17. Neon isotopic compositions in a step-heating experiment on Orgueil CI chondrite, which produced the first evidence of ‘pre-solar’ or exotic Ne. The points connected by the line show the changing Ne isotope ratios with increasing temperature. Shaded area was the original estimate of the composition of the pure Ne-E component. Also shown are the compositions of Ne-A (‘planetary’), Ne-B (‘solar’), and Ne-E (‘spallogenic’). After Black and Pepin (1969).](image-url)
to 70% of their mass during this phase. Burning phase of their post

The other key noble gas in this context was xenon. Having 9 isotopes rather than 3 and with contributions from both $^{125}$I decay and fission of various heavy elements, isotopic variation in xenon is bound to be much more complex than those of Ne. On the other hand, its high mass minimizes mass fractionation effects, so “solar” (more properly solar wind) and “planetary” Xe are less isotopically dissimilar than Ne. The first evidence of isotopic variations in Xe came in the early 1960’s, but these variations were thought to be fissogenic (at one time it was argued they were produced by fission of short-lived superheavy elements). Subsequently, several isotopically distinct Xe components were identified. One of these is associated with Ne-E(H) in SiC and is enriched in the s-process-only isotopes of Xe ($^{128}$Xe and $^{130}$Xe) and is called, appropriately enough, Xe-S. The isotopic pattern of Xe-S is shown in Figure 5.18. This is most likely synthesized in red giants. Indeed, there is a striking similarity of the isotopic abundances to the calculated production of s-process nuclides in AGB stars. Comparison of the isotopic composition of Kr, which is also anomalous in the SiC, with theoretical calculations further narrows the site of synthesis to low-mass AGB stars, consistent with the inferences made for $^{22}$Ne synthesis. SiC grains (Figure 5.19) are thus apparently condensates from material ejected from red giant stars, which have very strong solar winds. Thus in a very real sense, these grains are truly stardust.

The Ne in the SiC is a little richer in $^{21}$Ne than the predicted products of AGB stars. This is presumably due to cosmogenic production of $^{21}$Ne. If so, some 130 Ma of cosmic ray irradiation would be required to produced the observed $^{21}$Ne, indicating the grains predate meteorite parent body formation by this amount of time (Lewis et al., 1994). If they had been degassed, however, the grains could be much older.

Another isotopically distinct component, identified in acid-dissolution residues of Allende (CV3) named Xe-HL because it is enriched in both heavy and light Xe isotopes, was released in the 700-1000°C temperature step. This particular enrichment pattern can be produced only by a combination the p- and

---

* More specifically, AGB stars are low to moderate mass stars (i.e., 0.6 to 10 solar masses) that have completed the He-burning phase of their post-main sequence evolution. They have enormously strong stellar winds, enough to lose 50 to 70% of their mass during this phase.

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Figure 5.18. Isotopic composition of Xe-S (relative to normal solar Xe with $^{130}$Xe=1). Xe-S is found in silicon carbide and associated with Ne-E(H). $^{128}$Xe and $^{130}$Xe are synthesized only in the s-process, hence the most likely site for its synthesis is red giants.

Figure 5.19. The isotopic composition of Kr and Xe of the ‘Xe-HL ’ component in the matrix of the Allende CM-2 carbonaceous chondrite. Xe-HL is characteristically enriched in both the light and heavy isotopes, while the lighter noble gases show enrichment only in the heavy isotopes.
r-processes (Figure 5.19). As we found in Chapter 1, these processes operate only in supernovae. Unlike Ne-E, Xe-HL is accompanied by the other noble gases, of which Ne, Ar, and Kr all show enrichment in their heavier isotopes. Eventually, Anders’ group identified the carrier of Xe-HL as microdiamonds. These diamonds are extraordinarily fine, averaging only 1 nm in diameter and containing typically only 10^3 or so atoms. Roughly one in every four atoms is at the surface. As a result, the properties of this material differ significantly from normal diamond, which which considerably complicated the effort to isolate it.

5.3.2. Isotopic Composition of Pre-Solar Grains

Analysis of the noble gases in the SiC, graphite and diamond by step-heating was comparatively easy, since since each of these decompose at distinct temperatures. Identifying the carriers proved more difficult. However, once the carrier grains were were identified and isolated, it became became possible to analyze the isotopic isotopic composition of other elements. The isotopic compositions of of other elements have also proved to be anomalous to varying degrees. The The noble gas, C and N isotopic compositions are summarized in Table Table 5.2. Also shown in the table is the the abundance of these phases, which is quite low.

Many of the SiC and graphite grains are large enough to image with the scanning electron microscope. The grains have several different morphologies; A cauliflower-like morphology SiC grain is shown in Figure 5.20. Other grains have onion-like layered morphologies, suggesting discontinuous, layer-by-layer growth; still others appear euhedral with distinct crystal faces. The isotopic compositions of individual grains can be analyzed by ion probe. These analyzes (e.g., Figure 5.21) reveal a diversity of isotopic compositions as well as correlations between grain size and isotopic composition. Clearly, the SiC grains do not form a single population, but represent a number of populations of grains, each produced in a different astronomical environment. The majority of grains have isotopically heavy C and light N (relative to solar), which are the compositions expected from production in the CNO cycle (Chapter 1). However, compositions produced by other mechanisms are also represented. Si isotopic compositions are also anomalous. Anomalies have
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Table 5.2. Isotopic Characteristics of Presolar Grains in CM2 Chondrites

<table>
<thead>
<tr>
<th>Phase</th>
<th>Noble Gas Component</th>
<th>Enriched in Isotopes</th>
<th>Nuclear Process</th>
<th>Grain Size, µm</th>
<th>Abundance, ppm</th>
<th>((^{13}C/^{12}C))/(^{15}N/^{14}N)</th>
<th>Stellar Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xe-HL</td>
<td>Xe-S, Ne-E(H)</td>
<td>p, r</td>
<td>0.001-0.0025</td>
<td>0.03-20</td>
<td>0.96</td>
<td>Supernova</td>
</tr>
<tr>
<td></td>
<td>124Xe, 136Xe</td>
<td>124Xe, 136Xe</td>
<td>(22)Na((\beta),(\nu))(^{22})Ne</td>
<td>0.66</td>
<td>0.015-20</td>
<td>0.012-50</td>
<td>AGB, Nova, Supernova, AGB, Supernova</td>
</tr>
<tr>
<td></td>
<td>124Xe, 136Xe</td>
<td>124Xe, 136Xe</td>
<td>(^{14})N+ (2\alpha\rightarrow^{22})Ne</td>
<td></td>
<td></td>
<td>0.55-6.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ne-E(L)</td>
<td>Ne-E(L)</td>
<td>(^{13}C/^{12}C)/(^{15}N/^{14}N)</td>
<td></td>
<td></td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12C</td>
<td>12C</td>
<td></td>
<td></td>
<td></td>
<td>0.95</td>
<td></td>
</tr>
</tbody>
</table>


also been identified in the isotopic compositions of Ti, Sr, Zr, Mo, Ba, Nd, Sm, and Dy in these grains. These have further helped to identify the stellar production environments of these grains (Figure 5.22). For example, graphite and most SiC grains display enrichment in \(^{96}\)Mo, which is an s-process isotope. This enrichment pattern is that expected for s-process nucleosynthesis in the He-burning shell of AGB stars. A subset of the SiC grains, the so-called SiC X grains, show enrichment in \(^{95}\)Mo and \(^{97}\)Mo, which are r-process isotopes, and were likely produced in the neutron burst of supernovae.

Mg isotopic compositions in both graphite and SiC are also anomalous. A fourth refractory phase identified in the groundmass (but poor in noble gases) is corundum (Al₂O₃). The graphite, SiC, and corundum have inferred initial \(^{26}\)Al/\(^{27}\)Al ratios of \(5 \times 10^{-3}\) to \(1 \times 10^{-1}\). In contrast, we found in the previous section that CAI’s had inferred initial \(^{26}\)Al/\(^{27}\)Al ratios up to \(5 \times 10^{-3}\), and that most other meteoritic materials showed no excess \(^{26}\)Mg.

Diamond, graphite, and silicon carbide were the first presolar phases to be discovered largely because of the approaches used to isolate them: acid digestion that dissolved most other phases. Furthermore, these phases are quite refractory and resist reaction with hydrous alteration that affected many primitive meteorites. The initial focus was on a few primitive CV and CM meteorites for which large amounts of material were available to researchers. Subsequent studies have identified these and other minerals in nearly all classes of unequilibrated (that is, petrologic grade less than 4) chondrites and they are

Figure 5.22. Mo isotope anomalies in SiC and graphite interstellar grains in meteorites. The “mainstream” SiC and graphite are enriched in \(^{96}\)Mo, while the SiC X grains are enriched in \(^{95}\)Mo and \(^{97}\)Mo. (The two groups of SiC grains are defined on the basis of their Si and C isotopic compositions.) From Nittler (2003).
most abundant in CI chondrites such as Orgueil. The inventory of presolar grains includes Si\textsubscript{3}N\textsubscript{4}, corundum (Al\textsubscript{2}O\textsubscript{3}), spinel (MgAl\textsubscript{2}O\textsubscript{4}), hibonite (CaAl\textsubscript{12}O\textsubscript{19}), a variety of metal carbides, Fe-Ni metal, and perhaps TiO\textsubscript{2}. Some of these occur as inclusions in other grains. Presolar grains have also been identified among interplanetary dust particles (IDP’s) collected by spacecraft and high-altitude aircraft. Up until 2004, however, all were non-silicates. This puzzled cosmochemists as spectroscopic observations of young stars reveal that silicates are abundant, meaning they should be abundant in molecular clouds like the one in which the solar system formed. In 2004, several research groups reported not only finding silicates (olivine, pyroxene, and SiO\textsubscript{2}) with highly anomalous O isotope ratios, hence indicating a presolar provenance, they reported that that presolar silicates were actually more abundant than non-silicate presolar grains. In the exceptionally primitive (i.e., unmetamorphosed) carbonaceous chondrite Acfer (CH3), Nagashima et al. (2004) and Nguyen and Zinner (2004) found presolar silicates were present in the groundmass at an abundance of about 30 to 40 parts per million, compared to 14 parts per million for presolar SiC.

### 5.3.2.1 A Late Injection of Supernova Debris?

Bizzarro et al. (2007) found a subset of early-formed differentiated meteorites, including the angrites, ureilites, and some irons and pallasites (stony-irons thought to be asteroidal core-mantle boundaries), have \textsuperscript{60}Ni deficits of around 25 ppm (0.2 epsilon units) compared to terrestrial material, enstatite and ordinary chondrites, and a Martian meteorite. Carbonaceous chondrites have \textsuperscript{60}Ni excesses of 33 ppm. \textsuperscript{60}Ni is the daughter of \textsuperscript{60}Fe, which has a half-life of 1.5 Ma. Bizzarro et al found that \textsuperscript{26}Al and \textsuperscript{60}Fe abundances are uncorrelated, which is not what one would expect if the source of the \textsuperscript{60}Fe were a Type II core collapse supernova. As we noted, \textsuperscript{26}Al is synthesized in the red giant phase of stars. But whereas red giant stars of 8-30 solar masses go on to explode as Type II supernovae, particularly massive stars throw off their \textsuperscript{26}Al-containing outer regions before exploding as Type Ib/c supernovae (in which \textsuperscript{60}Fe is synthesized). Thus in this type of stellar evolution injection of \textsuperscript{26}Al and \textsuperscript{60}Fe would be decoupled.

Brennecka et al. (2013) documented (small) isotopic variations in Sr, Mo, Ba, Nd, and Sm isotopic compositions of CAI’s that can be explained by deficits or excesses of r-process nuclides. While Sr, Mo, and Ba generally have excesses of r-process nuclides, Nd and Sm exhibit r-process deficits. They argue material from multiple supernovae are necessary to explain these observations and that an injection of supernova material occurred into a reservoir untapped by CAI’s, implying it occurred after CAI formation.

Another line of evidence of a possible supernova in the vicinity of the solar nebula arises from anomalously old Lu-Hf ages of many, but not all, meteorites and their components (discussed in Section 2.6). Albarede et al. (2006) proposed that these anomalous ages are a consequence of excitation of the \textsuperscript{176}Lu nucleus by absorption of \gamma-ray radiation into an excited state energy state, from which it decays to \textsuperscript{176}Hf with a half-life of 3.7 hours. They proposed that the \gamma-rays originated from a nearby supernova. The difficulty with this hypothesis is that gamma rays have very limited penetrating power through solids: this would affect only material on the surface of meteorite parent bodies. Alternatively, either neutrinos or cosmic rays can excite the \textsuperscript{176}Lu nucleus (Thrane et al., 2010). Supernovae do produce prodigious numbers of neutrinos, but a supernova close enough to produce the necessary neutrino flux would have completely disrupted the solar nebula, so that possibility can also be ruled out (Thrane et al., 2010). Thrane et al. (2010) and Bizzarro et al. (2012) suggested instead that \textsuperscript{176}Lu was excited by high-energy cosmic rays, which have more penetrating power than \gamma-rays and these are also produced in abundance by supernovae. However, Bouvier and Boyet (2013) obtained an age of 4560 ±190 Ma for Alende CAI’s, with an initial \textsuperscript{176}Hf/\textsuperscript{177}Hf of 0.27985 ±15, in excellent agreement with other ages of CAI’s and the initial \textsuperscript{176}Hf/\textsuperscript{177}Hf of Bouvier et al. (2008). Certainly these early-formed small objects would have been affected by any radiation penetrating the angrite parent body. As yet, no consensus has been reached on this matter.
5.3.3 Other Exotic Components in Meteorites

Besides isotopic anomalies apparently produced by decay of short-lived radionuclides such as $^{26}$Al, $^{129}$I, and $^{244}$Pu, and those associated with the interstellar grains in the matrix, other isotopic anomalies have been identified in CAI’s. Some of these have been observed only in a few CAI’s from Allende: Ca, Ba, Sm, Nd, and Sr. They have been termed FUN anomalies: fractionation and unknown nuclear. A systematic search by G. Lugmair and colleagues at the University of California at San Diego revealed that isotopic variations of the iron peak elements (elements clustered around the cosmic abundance peak at Fe), Ca through Zn, are ubiquitous in many CAI’s. Variations are up to per mil size relative to terrestrial isotope ratios, and are characterized by overabundance of the most neutron-rich nuclides ($^{48}$Ca, $^{50}$Ti, $^{54}$Cr, $^{60}$Ni, and $^{66}$Zn), often accompanied by under-abundance of the most neutron-poor isotopes. In some instances, isotopic variations within single mineral grains have been observed with the ion microprobe. In general, these isotopic variations are most readily explained if the inclusions contain an admixture of neutron-rich e-process material from a supernova.

Although recent research has turned up many examples of isotopic heterogeneity, mainly large variations on very fine scales and very small variations on larger scales, and undoubtedly will continue to do so as analytical precision improves, the overall picture of the solar nebula is of isotopic homogeneity, indicating that it was well mixed. The most notable exception is oxygen which we discuss next.

5.4 OXYGEN ISOTOPE VARIATIONS & NEBULAR PROCESSES

Another element commonly showing isotopic variations is O. Until 1973, O isotope variations in meteorites were thought to be simply the result of fractionation, as they generally are on Earth. But when R. Clayton of the Univ. of Chicago went to the trouble of measuring $^{17}$O (0.037% of O) as well as $^{18}$O and $^{16}$O, he found that these variations were not consistent with simple mass-dependent fractionation. This is illustrated in Figure 5.23, which presents $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios in delta notation, which are deviations in parts per thousand from a standard (standard mean ocean water or SMOW, in this case; see Chapter 8 for more details). In a plot of $\delta^{17}$O vs. $\delta^{18}$O, variations created by mass-dependent fractionation (we’ll explain this more fully in Chapter 8) should plot along a line with slope of $-1/2$. Terrestrial and lunar samples do indeed define such a line, but other meteorites or their components, carbonaceous chondrites and CAI’s in particular, fall along a line with slope $= 1$. One interpretation is that this reflects mixing between a more or less pure $^{16}$O component, such as might be created by helium burning, and a component of ‘normal’ isotopic composition. However, Thiemens and Heidenreich (1983) conducted experiments in which ozone produced by a high frequency electric discharge showed “mass independent fractionation”, i.e., where the ozone was equally enriched in $^{17}$O and $^{18}$O (Figure 5.24) relative to $^{16}$O. The experiment dem-
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Figure 5.24. Mass independent fractionation during the production of ozone from molecular oxygen. Squares are ozone, dots are oxygen. After Thiemens and Heidenreich (1983).

Figure 5.25. O isotope variations among minerals of various meteorite classes (Clayton et al., 1976).

Thiemens suggested that a slope of 1 on the $\delta^{17}$O — $\delta^{18}$O diagram could be produced by chemical processes. This slope is characteristic of fractionation resulting from a kinetic fractionation mechanism, which arises because non-symmetric (e.g., $^{17}$O$^{18}$O or $^{18}$O$^{16}$O) molecules have more available energy levels than symmetric (e.g., $^{16}$O$^{16}$O) molecules (as we will see in Chapter 8, symmetry enters into the partition function, which governs isotope fractionation).

Subsequent to Thiemens and Heidenreich’s work, mass-independent fractionations have been discovered in atmospheric ozone as well as in Archean sulfides. In the case of sulfur, photodissociation of atmospheric sulfur compounds appears to have been cause mass-independent fractionation. We’ll return to this in subsequent chapters.

The explanation for mass-independent O fractionation in the solar nebula may also involve photodissociation. Thiemens and Heidenreich (1983) and Clayton (2002) suggested that the anomalies arose through radiation self-shielding in the solar nebula. In this model, ultraviolet radiation from the early proto-Sun dissociated carbon monoxide, which would have been among the most abundant gases in the solar nebula. Because C$^{16}$O rather than C$^{17}$O or C$^{18}$O was the dominant oxygen-bearing species, the radiation of the wavelength necessary to dissociate C$^{16}$O would have been quickly absorbed as it traveled outward from the Sun. At greater distance from the Sun, radiation of the frequency necessary to dissociate C$^{17}$O and C$^{18}$O would still be available. Thus at these distances, C$^{17}$O and C$^{18}$O are preferentially dissociated, and equally so, making $^{17}$O and $^{18}$O preferentially available for reaction to form silicates and other meteorite components. Since the solar nebula would have been fairly opaque at this time, this isotopic fractionation would have occurred in the inner part of the nebula, near the forming star, and then expelled back out by the “X-wind”. The implication of this is that most of the solid matter that makes up the Earth and it neighbors must have cycled through this inner region at one point. Clayton’s model also predicts that the Sun itself should be poor in $^{18}$O and $^{17}$O compared to meteorites and the Earth – closer in composition to the CAIs. This prediction was confirmed, initially based on analysis of solar wind implanted in lunar soil (Hashizuma and Chaussidon (2005) and subsequently by the analysis of solar wind collected by NASA’s Genesis mission. Some mass fractionation occurs in the Genesis collectors and after correction for this, McKeegan et al. (2011) estimate the oxygen isotopic composition of the solar wind as $\delta^{16}$O = -102.3±3.3 ‰ and $\delta^{17}$O = -80.8±5‰, so that it would plot well off to the lower left of
Figure 5.22. There is reason to believe that mass fractionation occurs in generation of the solar wind, and that the Sun’s photosphere is not as depleted in light O isotopes as the solar wind. McKeegan et al. (2011) estimate the composition of the solar photosphere as δ¹⁸O = -58.5, δ¹⁷O = -59.1‰ which would place it on carbonaceous chondrite line in Figure 5.22 (but still well off the plot). The ᵈ⁰O-rich nature of the Sun compared to the Earth and nearly all planetary materials would appear to confirm Clayton’s self-shielding hypothesis, although some problems persist with the self-shielding model, as Thiemens (2006) points out.

As Figure 5.25 shows, while variations between classes are mostly mass-independent, variations within groups of meteorites fall along mass-dependent fractionation lines. This strongly suggests that, for the most part, different meteorite groups probably formed in different parts of the presolar nebula. There are a few exceptions: IIE irons fall on a mass-dependent fractionation line (MDFL) with H-chondrites, IVA irons plot on a MDFL with L and LL chondrites, basaltic and hypersthene achondrites plot on a MDFL with IAB irons and some stony-irons, and the moon and the Earth plot on a MDFL together with enstatite chondrites and achondrites. This suggests a genetic relationship between these objects, perhaps derivation from a single a single parent body in some cases.

Oxygen isotope compositions of the minerals of the FUN inclusions of Allende are erratic and do not fall on any line. These are certainly nuclear effects.

Mass-independent effects have not been found among isotopes of other elements such as Si, S and Mg in meteorites (except in some inclusions, groundmass phases, and chondrules as noted above), although large mass-dependent fractionations are ubiquitous. Thus oxygen appears unique. The reason may be related to the partition of oxygen between the gaseous and solid phases of the presolar nebula. Over a large temperature range, only about 17% of oxygen will condense, the remainder being in the gas, principally as CO and H₂O. Hydrogen and carbon have only two stable isotopes so mass-dependent and mass-independent effects cannot be distinguished.

5.5 EXPOSURE AGES OF METEORITES

Cosmogenic nuclides have been used for many years to determine cosmic-ray exposure ages of meteorites. Meteorites experience a much higher cosmic ray flux because they have no atmospheres to shield them. Unstable and stable nuclides are sometimes used together to determine such ages. The rate of change of abundance of an unstable cosmogenic nuclide is given by:

\[
\frac{dN}{dt} = P - \lambda N \tag{5.6}
\]

where \(P\) is the production rate. If we consider the case of the production of a stable nucleus, the number of stable nuclei produced at the surface of the body over some time \(t\) is simply given by:

\[
N = P \cdot t \tag{5.7}
\]

Figure 5.26. Cosmic ray exposure ages for three classes of ordinary chondrites. Filled histogram is for meteorites with regolith histories (i.e., brecciated meteorites). After Crabb and Schultz (1981).
Combining these equations, we may obtain an expression for $t$ that is independent of variations production rate:

$$N = N_s \left( \frac{P_s}{P_u} \right) \frac{t}{\lambda}$$

Cosmic ray exposure ages of meteorites have been found to be on the order of millions or tens of millions of years for stony meteorites and hundreds of millions of years for iron meteorites. Ages for the 3 classes of ordinary chondrites are shown in Figure 5.26. These ages are much less than their formation ages as determined by conventional radiometric dating. This implies that through most of their histories, meteorites must have been shielded from cosmic rays. Hence they must have come from much large bodies that were broken up by collisions. The similarity of exposure ages for all meteorites of a given class is consistent with the idea that individual meteorite classes are derived from single parent bodies.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


Bennett VC, Brandon AD, Nutman AP. 2007. Coupled $^{142}$Nd-$^{143}$Nd isotopic evidence for Hadean mantle dynamics. Science, 318: 1907-10


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cations for $^{146}$Sm-$^{142}$Nd Chronology in the Solar System. Science, 335, 1614-1617, doi: 10.1126/science.1215510.
Chapter 5: Isotope Cosmochemistry


PROBLEMS

1. One calcium-aluminum inclusion in the Allende meteorite has δ26Mg values which imply a 26Al/27Al ratio of 0.46 x 10^5 at the time of it’s formation. A second inclusion apparently formed with a 26Al/27Al ratio of 1.1 x 10^5. The half-life of 26Al is 7.2 x 10^6 years. Assuming both these inclusions formed from the sample cloud of dust and gas and that the 26Al/27Al ratio in this cloud was uniform, how much earlier did the second inclusion form than the first?

2. The calculated initial 27Al/26Al of the basaltic achondrite NWA2976 is 3.94 x 10^7. Using a half-life of 7.16 x 10^8 years and assuming an initial 5.05 x 10^5 27Al/26Al at the start of the solar system, what is the age of this meteorite?
3. Suppose you measure the $^{129}$Xe/$^{130}$Xe and I/Xe ratios in two chondritic meteorites in step-heating gas release experiments. From the first, you deduce a $^{129}$I/$^{127}$I ratio of $0.53 \times 10^{-4}$ at the time of formation. In the second, you deduce a $^{129}$I/$^{127}$I ratio of $1.47 \times 10^{-4}$ at the time of formation. How much time elapsed between formation of these meteorites, and which formed first?

4. Bouvier et al measured the following data on the H4 meteorite St. Margarite:

<table>
<thead>
<tr>
<th></th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole-rock R0</td>
<td>41.6593</td>
<td>30.4466</td>
</tr>
<tr>
<td>L0</td>
<td>24.8906</td>
<td>20.0734</td>
</tr>
<tr>
<td>Chondrule R0</td>
<td>35.8299</td>
<td>26.8506</td>
</tr>
<tr>
<td>L0</td>
<td>18.5585</td>
<td>16.0838</td>
</tr>
<tr>
<td>Px+O1 R2</td>
<td>47.2008</td>
<td>33.9302</td>
</tr>
<tr>
<td>L1</td>
<td>20.3812</td>
<td>17.2259</td>
</tr>
<tr>
<td>L2</td>
<td>21.9916</td>
<td>18.2169</td>
</tr>
</tbody>
</table>

Calculate the $^{207}$Pb/$^{204}$Pb age of this meteorite assuming a $^{238}$U/$^{235}$U ratio of 137.88. Then calculate the age assuming a $^{238}$U/$^{235}$U ratio of 138.79.

5. The initial $^{206}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb ratios of the solar system at 4.567 Ga are 9.307 and 10.294, respectively. If the value of $^{238}$U/$^{204}$Pb in the solar nebula was 0.14, calculate the evolution of $^{206}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb of the solar nebula at 100 Ma intervals from 4.567 to at 4.45 Ga. (Hint: this calculation is a little trickier than you might think).

6. In which cosmic environments could the following short-lived radionuclides be made? Justify your answer.
   a. $^{182}$Hf
   b. $^{146}$Sm
   c. $^{107}$Pd
   d. $^{129}$I
   e. $^{247}$Cm

7. Excesses of $^{135}$Ba, $^{137}$Ba, and $^{138}$Ba have been found in several chondrites. How would you explain these in terms of the different nucleosynthetic processes occurring in different stellar environments? (Hint: look at a Chart of the Nuclides and refer to Chapter 1).

5. The following data were measured on the ungrouped basaltic achondrite NWA 2976. Calculate the initial $^{26}$Al/$^{27}$Al using the isochron method (adapt equation 5.5 for the $^{26}$Al/$^{24}$Mg decay). Assuming the $^{26}$Al/$^{27}$Al abundance ratio listed in Table 5.1 was the initial ratio of the solar system, what is the age of this meteorite relative to that initial time?

<table>
<thead>
<tr>
<th></th>
<th>$^{26}$Al/$^{24}$Mg</th>
<th>$^{24}$Mg/$^{24}$Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>WR5</td>
<td>1.87</td>
<td>0.13979</td>
</tr>
<tr>
<td>PX3</td>
<td>0.67</td>
<td>0.13979</td>
</tr>
<tr>
<td>PL3</td>
<td>513.60</td>
<td>0.13999</td>
</tr>
<tr>
<td>PL4</td>
<td>143.00</td>
<td>0.13984</td>
</tr>
<tr>
<td>PL5</td>
<td>121.60</td>
<td>0.13984</td>
</tr>
<tr>
<td>PL6</td>
<td>82.27</td>
<td>0.13983</td>
</tr>
</tbody>
</table>