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. 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.

Chondrites are so called because they contain “chondrules”, small (typically a few mm diameter) round bodies that were clearly once molten (Figure 5.01). 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 which are also grain that equilibrated with nebular gas at high temperature through condensation and/or evaporation. 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 con-

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1 In the last decade or two, additional classes have been added that are defined by rarer meteorites.
Conventional methods

Meteorite ages are generally taken to be the age of Solar System. The oft-cited value for this age is 4.567 Ga. Before we discuss meteorite ages in detail, 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 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 oldest reliable high precision age is from CAI inclusions of Efremovka, a CV3 meteorite, with an age of 4567.2±0.6 Ma (Amelin et al., 2002). This is more precise, but not significantly different in age from the previous “oldest age”, which was CAI inclusions from Allende, also CV3 meteorite, with a Pb isotope age of 4566±3 Ma. Amelin and Krot (2007) 4566.6 ± 1.0 Ma for chondrules from Allende and Bouvier et al. (2008) reported and age of 4567.59 ± 0.10 Ma for a single large Allende chondrule. These oldest ages are taken as the age of the solar system, and time 0 for the relative ages determined from the extinct radionuclides discussed in the following section. The matrix of Allende may be somewhat younger, although this is uncertain. Precise Pb-Pb ages of 4.552 Ga have been reported by several laboratories for the St. Severin LL chondrite. The same age (4.552±0.003 Ga) has been reported for 2 L5 chondrites. U-Pb ages determined on phosphates in equilibrated (i.e., petrologic classes 4-6) ordinary chondrites range from 4.563 to 4.502 Ga. As these phosphates are thought to be secondary and to have formed during metamorphism, these ages apparently represent the age of metamorphism of these meteorites. Combined whole rock Rb-Sr ages for H, E, and LL chondrites are 4.498±0.015 Ga. However, within the uncertainty of the value of the $^{87}\text{Rb}$ decay constant, this age could be 4.555 Ga (uncertainties normally reported on ages are based only on the scatter about the isochron and the uncertainty associated with the analysis, they do not include uncertainty associated with the decay constant). No attempt has been made at high-precision dating of CI chondrites as they are too fine-grained to separate phases.

Pb isotope ages of the unusual achondrite Angra dos Reis, type meteorite of a rare class of Ca-rich achondrites called ‘angrites’, give a very precise age of 4557.8±0.0004 Ma. A slightly older Pb-Pb age of 45662±0.0001 Ma has been reported for the angrite SAH99555 (Baker et al., 2005), but subsequent re-analysis yielded slightly younger ages of 4564.48±14 and 4564.86±38 Ma. Ibitira, a unique unbrecciated eucrite (achondrite), has an age of 4.556±0.006 Ga. Perhaps surprisingly, these ages are the same as those of chondrites. This suggests that the parent body of these objects formed, melted, and crystallized within a very short time interval. Not all achondrites are quite so old. 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 Nueve Laredo. Thus the total range of the few high precision ages in achondrites is about 30 million years.

K-Ar ages are often much younger. This probably reflects Ar outgassing as a result of collisions. These K-Ar ages therefore probably date impact metamorphic events rather than formation ages.

The present state of conventional meteorite chronology may be summarized by saying that it appears the meteorite parent bodies formed around 4.566±0.005 Ga, and there is some evidence that high-temperature inclusions (CAI's: calcium-aluminum inclusions) and chondrules in carbonaceous chondrites may have formed a few Ma earlier than other material. Resolving events on a finer time-scale than this has proved difficult using conventional techniques. There are, however, other techniques that help to resolve events in early solar system history, and we now turn to these.

Initial Ratios

Attempts have been made to use initial isotope ratios to deduce a more detailed chronology, but these have been only moderately successful. Figure 5.02 shows initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of meteorites and lunar rocks and a time scale showing how $^{87}\text{Sr}/^{86}\text{Sr}$ should evolve in either a chondritic or solar reservoir. The reference ‘initial’ $^{87}\text{Sr}/^{86}\text{Sr}$ of the solar system is taken as 0.69897±3, based on the work of Panastassiou and Wasserburg (1969) on basaltic achondrites (this value is known as BABI: basaltic achondrite best initial). Basaltic achondrites were chosen since they have low Rb/Sr and hence the initial ratio (but not the age) is well constrained in an isochron. Subsequent high precision analyses of individual achondrites yield identical results, except for Angra Dos Reis and Kao beta, which have slightly lower ratios: 0.69885. This suggests their parent body(ies) were isolated from the solar system somewhat earlier. CAI’s and Rb-poor chondrules from Allende have an even lower initial ratio: 0.69877±3. Allende chondrules appear to be among the earliest formed objects. The parent body of the basaltic achondrites appears to have formed 10 to 20 Ma later. Note there is no distinction in the apparent age of the oldest lunar rocks and the basaltic achondrites: from this we may conclude there was little or no difference in time of formation of the moon, and presumably the Earth, and the basaltic achondrite parent body.

![Figure 5.02. Initial Sr isotope ratios plotted against a time scale for $^{87}\text{Sr}/^{86}\text{Sr}$ assuming a chondritic Rb/Sr ratio. After Kirsten (1978).](image-url)
Chapter 5

Extinct Radionuclides

The initial $^{148}$Nd/$^{144}$Nd ratio of the solar system was calculated to be 0.506686±70 (normalized to $^{148}$Nd/$^{144}$Nd = 0.72190) based on the work on chondrites by Bouvier et al. (2008); the earlier value of Jacobsen and Wasserburg was slightly lower at 0.506609±8. Achondrites seem to have slightly higher initial ratios, suggesting they formed a bit later.

The initial isotopic composition of Pb is taken from the work of Tatsumoto et al. (1973) on troilite from the Canyon Diablo iron meteorite as $^{206}$Pb/$^{204}$Pb: 9.307, $^{207}$Pb/$^{204}$Pb: 10.294, $^{208}$Pb/$^{204}$Pb: 29.476. These values are in agreement with the best initial values determined from chondrites, including Allende chondrules. More recent work by Chen and Wasserburg (1983) confirms these results, i.e.: 9.3066, 10.293, and 29.475 respectively.

Extinct Radionuclides

There is evidence that certain short-lived nuclides once existed in meteorites. This evidence consists of the anomalous abundance of nuclides, for example, $^{129}$Xe, known to be produced by the decay of short-lived radionuclides, e.g., $^{129}$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 $^{53}$Mn. An example is shown in Figure 5.03.

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

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

This is similar to the isochron equation we derived earlier, equation 2.08, but not identical. In particular, notice 5.01 contains $N_0$, the initial abundance of the parent, whereas 2.08 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 $^{53}$Mn to $^{53}$Cr, we have:

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

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

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

Of course, since $^{55}$Mn and $^{52}$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 5.03 into 5.02, we have:
We’ll relax the constraints on this time scale.

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

Finally, for a short-lived nuclide like \(^{53}\text{Mn}\), the term \(\lambda t\) is very large after 4.55 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:

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

On a plot of \(^{53}\text{Cr}/^{52}\text{Cr}\) vs. \(^{55}\text{Mn}/^{52}\text{Cr}\), the slope is proportional not to time, as in a conventional isochron diagram, but to the initial \(^{55}\text{Mn}/^{52}\text{Cr}\) ratio. Thus correlations between isotope ratios such as these is 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 5.01. On a cosmic scale, nucleosynthesis is a more or less continuous process – roughly once every second, a supernova explodes somewhere in the universe. The longer-lived of these nuclides at low 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 nearby 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.

\(^{129}\text{I} - ^{129}\text{Xe} and ^{244}\text{Pu}\)

Among the most useful of these short-lived radionuclides, and the first to be discovered, has been \(^{129}\text{I}\), which decays to \(^{129}\text{Xe} \) and \(^{244}\text{Pu}\).
129\(^{\text{Xe}}\). Figure 5.04 shows the example of the analysis of the meteorite Khairpur. In this case, the analysis is done in a manner very analogous to \(^{40}\text{Ar} - ^{39}\text{Ar}\) dating: the sample is first irradiated with neutrons so that \(^{129}\text{Xe}\) is produced by neutron capture and subsequent decay of \(^{127}\text{I}\). The amount of \(^{129}\text{Xe}\) produced is proportional to the amount of \(^{127}\text{I}\) 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 5.03, the slope is proportional to the \(^{129}\text{I}/^{127}\text{I}\) ratio at the time the meteorite formed.

In addition to \(^{129}\text{Xe}\) produced by decay of \(^{129}\text{I}\), the heavy isotopes of Xe are produced by fission of U and Pu. \(^{244}\text{Pu}\) is of interest because it is 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 \(^{244}\text{Pu}\), but the difference is great enough to demonstrate the existence of \(^{244}\text{Pu}\) in meteorites, as is shown in Figure 5.05. Fission tracks in excess of the expected number of tracks for a known uranium concentration are also indicative of the former presence of \(^{244}\text{Pu}\).

These extinct radionuclides provide a means of relative dating of meteorites and other bodies. Of the various systems, the \(^{129}\text{I} - ^{129}\text{Xe}\) decay is perhaps most useful. Figure 5.06 shows relative ages based on this decay system. These ages are calculated from \(^{129}\text{I}/^{127}\text{I}\) ratios, which are in turn calculated from the ratio of excess \(^{129}\text{Xe}\) to \(^{127}\text{I}\). Since the initial ratio of \(^{129}\text{I}/^{127}\text{I}\) 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, but it is not clear if this occurred at condensation or during metamorphism. Perhaps both are involved. 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 the I-Xe decay system within about 20 Ma.

An interesting aspect of Figure 5.06 is that the achondrites, which are igneous in nature, and the irons are at most only slightly younger on average than the chondrites. Irons and achondrites are both products of melting on meteorite parent bodies. That they appear to be little younger than chondrites indicates that and melting and differentiation of those planetismals must have occurred very shortly after the solar system itself formed and within tens of millions of years of the synthesis of \(^{129}\)I.

The existence of variations in isotopic composition of silver, and in particular variations in the abundance of \(^{107}\)Ag that correlate with the Pd/Ag ratio in iron meteorites indicates that \(^{107}\)Pd was present when the irons formed. The half-life of \(^{107}\)Pd is 9.4 million years; hence the irons must have formed within a few tens of millions of years of synthesis of the \(^{107}\)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 \(^{107}\)Pd/\(^{108}\)Pd ratio of \(2.5 \times 10^{-5}\) (Chen and Wasserburg, 1990). Other IVA irons generally fall along the same isochron (Figure 5.07). IIAB and IIAB irons, as well as several anomalous
Isotope Geochemistry

Chapter 5

Extinct Radionuclides in the Earth

Chapter 5

Evolution of the Earth

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Extinct Radionuclides in the Earth

Several of the short-lived radionuclides listed in Table 5.01 have half-lives sufficiently long that they should have been present in the early Earth. Of greatest interest are 129I, 182Hf, and 146Sm. The decay products of these nuclides are 129Xe, 182W, and 142Nd, 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 182Hf and 142Sm. We'll discuss 129I in the lecture on the origin and evolution of the atmosphere.

182Hf–182W Constraints of the Age of the Moon and the Earth's Core

The Hf-W pair is particularly interesting because Hf is lithophile while W is moderately siderophile. Thus the 182Hf-182W decay system should be useful in “dating” silicate-metal fractionation, including

26Al–26Mg

Another key extinct radionuclide has been 26Al. Because of its short half-life (0.72 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 26Al was such that its decay could have been a significant source of heat. 26Al decays to 26Mg; an example of the correlation between 26Mg/24Mg and 27Al/24Mg is shown in Figure 5.08.

Because of the relatively short half-life of 26 Al and its potential importance as a heat source, considerable effort has been devoted to measurement of Mg isotope ratios in meteorites. Most of this work has been carried out with ion microprobes, which allow the simultaneous measurement of 26Mg/24Mg and 27Al/24Mg on spatial scales as small as 10 µ. As a result, there are some 1500 measurements on 60 meteorites reported in the literature, mostly on CAI's. The reason for the focus on CAI's is, of course, because their high Al/Mg ratios should produce higher 26Mg/24Mg ratios.

Figure 5.09 summarizes these data. These measurements show a maximum in the 26Al/27Al ratio of around 4.5 × 10^-5. Significant 26Mg anomalies, which in turn provide evidence of 26Al, are mainly confined to CAI's. This may in part reflect the easy with the anomalies are detected in this material and the focus of research efforts, but it almost certainly also reflects real differences in the 26Al/27Al ratios between these objects and other materials in meteorites. The usual interpretation is that this difference reflects a difference in the timing of the formation of the CAI's and other materials, most notably chondrules. In this interpretation, CAI's would be 2 to 3 million years older than chondrules. Based on the U-Pb dating of Allende mentioned earlier, however, chondrules appear to be just as old as CAI's. This observation may favor an alternative hypothesis is which the chondrules and CAI's form at the same time in different environments, with the 26Al by produced by spallation. We'll discuss these alternative interpretations later in the Chapter.

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182Hf–182W Constraints of the Age of the Moon and the Earth’s Core

The Hf-W pair is particularly interesting because Hf is lithophile while W is moderately siderophile. Thus the 182Hf-182W decay system should be useful in “dating” silicate-metal fractionation, including
core formation in the terrestrial planets and asteroids. Both are highly refractory elements, while has the advantage the one can reasonably assume that bodies such as the Earth should have a chondritic Hf/W ratio, but the disadvantage that both elements are difficult to analyze by conventional thermal ionization. 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 be accepted.

Because the variations in $^{182}\text{W}/^{183}\text{W}$ ratio are quite small, they are generally presented and discussed in the same $\epsilon$ notation used for Nd and Hf isotope ratios. There is a slight difference, however; $\epsilon_{\text{W}}$ is the deviation in parts per 10,000 from a terrestrial tungsten standard, and $f_{\text{Hf/W}}$ 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 (a reasonable assumption, but which has not yet been proven), then the silicate Earth has $\epsilon_{\text{W}}$ of 0 by definition. The basic question can posed this way: 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 $^{182}\text{Hf}$ had entirely decayed. Since the half-life of $^{182}\text{Hf}$ 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 time chondritic meteorites formed (i.e., of the formation of the solar system). If on the other hand, the $^{182}\text{W}/^{183}\text{W}$ ratio in the silicate Earth was the same as in chondrites, which never underwent silicate-metal fractionation, this would mean that at least 45 to 90 million years must have elapsed (enough time for $^{182}\text{Hf}$ to fully decay) between the formation of chondrites and the formation of the Earth’s core.

‘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 $^{182}\text{Hf}$ 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 (Arispe, IA, and Coya Norte, IIA) and a lunar basalt. They found the iron meteorites showed depletions in $^{182}\text{W}$ ($\epsilon_{\text{W}} = -4.5$ and -3.7 for Arispe and Coya Norte respectively) that were similar to that observed in Toluca reported by Jacobsen and Harper (1996). The chondrites, however, had $\epsilon_{\text{W}}$ 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 $^{182}\text{Hf}/^{180}\text{Hf}$ for the solar nebula of $2.6 \times 10^4$, much higher than assumed by Jacobsen and Harper. 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 $\epsilon_{\text{W}}$ 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; in other words, asteroids or “planetismals” must have differentiated to form iron cores and silicate mantles very early, virtually simultaneous 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 $\epsilon_{\text{W}}$ values 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. 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, 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 $1 \times 10^{-4}$. In the same issue of the journal Nature, Kleine et al. (2002) reported similarly low $\epsilon_W$ (i.e., -2) for the carbonaceous chondrites Allende, Orgueil, Murchison, Cold Bokkeveld, Nogoya, Murray, and Kokoonda measured in a third laboratory (University of Münster). 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 what was at the time an entirely new kind of instrument, namely the multi-collector ICP-MS.

Yin et al. (2002) considered two scenarios for the formation of the core. In the first, which they call the two-stage 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 that 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 the parent body of the eucrite class of achondrites (suspected to be the large asteroid Vesta) underwent core formation within 3 million years of formation of the solar system. Klein et al. (2002) reached similar conclusions. Yin et al. (2002) restrial, lunar, and chondritic W isotopic compositions. That isochron has an age corresponding to 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 the parent body of the eucrite class of achondrites (suspected to be the large asteroid Vesta) underwent core formation within 3 million years of

Figure 5.10. W isotope ratios measured in chondrites, the iron meteorite Toluca, and terrestrial materials. Data from Kleine et al. (2002), Yin et al (2002), Touboul et al (2007, 2009).
formation of the solar system. Klein et al. (2002) reached a similar conclusion that the Moon and the Earth’s core formed early.

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 cosmonogically through the reaction $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}$. Because the Earth’s surface is somewhat protected from cosmic rays by the atmosphere, this reaction is entirely trivial at the surface of 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). Consequently, the cosmonic production of nuclides in lunar materials can be significant. Early studies failed to appreciate this or failed 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 cosmonic effects and when these were eliminated the Moon has and 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±0.040 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 (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. (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 a magma ocean 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 silver isotopes clearly reveal, cores of asteroids formed within 10 Ma of the start of the solar system, 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 $^{26}\text{Al}$ or release of gravitational energy in collisions, caused melting that allowed and 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, when they 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
Geochemists focused their initial attention on early crustal rocks from the Isua area in Greenland. Some rocks from this area are as old as 3.8 Ga and have initial $^{143}$Nd/$^{144}$Nd ratios several epsilon units above the chondritic value, suggested there were derived from an incompatible element-depleted man-
tle with high Sm/Nd. A study by Harper and Jacobsen (1992) reported a 33 ppm excess of $^{142}$Nd in one 3.8 Ga old metavolcanic rock from Isua. This excess was based on a comparison between the rock and laboratory standards; the latter was assumed to have the same $^{142}$Nd/$^{144}$Nd ratio as chondrites. Other workers failed to find any excesses in other rocks from Isua, so these results were controversial. More recent work using advanced mass spectrometers by Caro et al. (2003) and Boyet et al. (2003), however, has confirmed the original findings of Harper and Jacobsen. This means that these early parts of the crust formed from a mantle reservoir that had Sm/Nd ratios higher than the chondritic one – and importantly, that this reservoir formed very early, most likely within the first 100 Ma. Subsequently, other $^{142}$Nd/$^{144}$Nd “anomalies” were found in other Archean rocks, including ones from Australia and Labrador (Bennett et al., 2007; O’Neil et al., 2009).

A yet more surprising result came when Boyet and Carlson (2005) analyzed the $^{142}$Nd/$^{144}$Nd ratios of meteorites and found that terrestrial rocks had $^{142}$Nd/$^{144}$Nd ratios that average 20 ppm or 0.2 epsilon units higher than chondrites, and most eucrites as well (Figure 5.12). This implies that the accessible Earth 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 8% higher than chondrites; if the increase occurred at 30 million years,

Figure 5.12. Variation in $\varepsilon^{142}$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, $\varepsilon^{142}$Nd of -0.2 relative to the terrestrial standards. Data from Caro et al. (2003), Boyet and Carlson (2005), Boyet and Carlson (2006) and O’Neil et al (2008). SNC data from the compilation of Halliday (2001).
Chapter 5

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; after all, we have already stated that the assumption that the Earth has chondritic abundances of refractory elements is probably only valid to 10%. Yet this small difference is very important in interpretation of Nd isotope systematics. For the two scenarios above, 5 Ma and 30 Ma, the εNd of the accessible Earth would be +6.9 and +11 respectively. These values fall within the range of values of mid-ocean ridge basalts. Recalling that the Isua samples have a 30 ppm excess in 142Nd relative to a terrestrial standard, this means that the Isua samples have a 50 ppm excess in 142Nd relative to chondrites.

How might the increase in Sm/Nd come about? First, we need to recall that meteorites come from the asteroid belt and their compositions might not be representative of the composition of the inner solar nebula from which the Earth and the other terrestrial planets formed. Its possible the inner solar nebula had a higher Sm/Nd ratio. That said, it is very difficult to see why this should be so. The observable fractionation in primitive meteorites relates to volatility and lithophile/siderophile tendency. As we have seen, Sm and Nd have quite high and very similar condensation temperatures and neither shows a significant siderophile tendency. Although the possibility cannot be excluded, there is simply no good reason to believe that the Sm/Nd ratio of the material from which the Earth should be different from chondrites. It is also possible that the early solar system was isotopically heterogeneous and that the material from which the Earth formed was richer in either 146Sm or 142Nd than the material that formed chondrite parent bodies. Andreasen and Sharma (2006) and Carlson et al. (2007) found that carbonaceous chondrites have a roughly 100 ppm deficit of 146Sm. This is significant because while 146Nd is primarily a s-process element produced in red giants, both 146Sm and 142Sm are p-process-only isotopes produced in supernova explosions. Incomplete mixing of material from different stars thus could result in variations in 146Nd/144Nd in the early solar system. However, Andreasen and Sharma (2006) concluded that while the observed isotopic heterogeneity in 146Sm implied enough variation in 146Sm to explain 142Nd/144Nd variations observed among chondrites, it could not explain the difference between the Earth and chondrites.

At present, there are two principal theories to explain the difference between terrestrial and chondritic 142Nd/144Nd. The first postulates that the bulk Earth does have a chondritic Sm/Nd ratio (and chondritic 142Nd/144Nd), but that low Sm/Nd and 142Nd/144Nd material is sequestered in a hidden reservoir deep in the mantle and that consequently the observable Earth has high Sm/Nd and high 142Nd/144Nd. The second postulates that the Earth has high, non-chondritic Sm/Nd and 142Nd/144Nd as a consequence of loss of low Sm/Nd material during its accretion as a consequence of collisional erosion. Let’s now explore these two possibilities.

The first possibility was suggested by Boyet and Carlson (2005). They suggested that Earth underwent early differentiation forming an early enriched reservoir, such as a primordial crust that sank into the deep mantle and has not been sampled since. This differentiation might have occurred as a consequence of crystallization of a terrestrial magma ocean analogous to the lunar magma ocean. Alternatively, crystallization of the 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, once crystallized, the EER could have sunk into the deep mantle, where it remains because if its high density. As Boyet and Carlson (2005) point out, this early enriched reservoir must have formed in the upper mantle. Below the 660 km discontinuity, Mg- and Ca-perovskite would crystallize and fractionate incompatible elements in a manner much different than observed.

The second possibility, “collisional erosion”, has been suggested by Caro et al. (2008), O’Neill and Palme (2008), and Caro and Bourdon (2010). As discussed earlier, planetary bodies are thought to form through the process of “oligarchic growth”. The initial stages of this process involve aggregations of dust-sized particles to form sand, which in turn aggregate to form pebble-sized particles, etc. The final

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* 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.
stages of this process involve infrequent, very 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. Boyet 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: incompatible elements. The existence of meteorites from the Moon and Mars demonstrates that collisions can indeed accelerate fragments of a planet’s surface to escape velocity. Additional evidence of the erosive capacity of these collisions is the large crater in the southern hemisphere of the large asteroid Vesta discovered by the Hubble Space Telescope. The volume excavated by this crater is roughly 1% of the total mass of Vesta, most of which appears to have been lost from the asteroid. Another observation that supports this idea is the density of the planet Mercury, which is 5427 kg/m$^3$, implying it has a much larger iron core than the other terrestrial planets, occupying 75% of its diameter (in contrast to a little of half for the Earth). An alternative way of looking at this is Mercury’s mantle is anomalously small. It has been proposed that Mercury lost much of its silicate mantle through as a consequence of a giant collision (Benz et al., 1988).

Common to both 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 from the Earth. Several observations suggest the latter hypothesis is preferable.

The first of these observations is that both the Moon and 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 $^{142}$Sm/$^{142}$Nd they display a correlation indicating the bulk Moon has $^{142}$Nd/$^{144}$Nd about 17 ppm higher than the chondritic 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 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. It is very unlikely this reservoir could have survived this event without being remixed into the mantle (Caro and Bourdon, 2010).

$^{142}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd ratios in shergottites (meteorites from Mars) suggest the Martian $^{142}$Nd/$^{144}$Nd ratio, 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. However, the other Martian meteorites, the naklites 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.

Geophysical considerations also cast doubt on the existence of a highly incompatible element-enriched reservoir in the deep mantle. In order to explain the 6% increase in Sm/Nd ratio in the remaining mantle, this reservoir would have to contain at least 40% of the Earth’s inventory of highly incompatible lithophile elements. 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. If this were the case, the mantle should be heated mainly from below. As Davies (2009) points out, this would pro-
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 supernovae. Anomalous isotopic compositions of stable elements, which we discuss below, provides 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 continually 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 $^{10}$Be, $^{26}$Al, $^{41}$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 red giant and/or a supernova in the region where the solar system formed just shortly before its formation. Some of these elements, such as $^{26}$Al are most efficiently synthesized in red giants; others, such as $^{60}$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 not in isolation, but 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 radionuclides were produced by spallation within the solar system as it was forming. As we have seen, $^{10}$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, $^{41}$Ca, and $^{53}$Mn observed. If it is correct, it solves the problem of the age gap between CAI’s and chondrules. Based on their apparent $^{26}$Al/$^{27}$Al ratios, CAI’s appear to be several...
Isotope Geochemistry

Chapter 5

Spring 2010

million years older than chondrules. Yet the time required for these particles to drift through the solar nebula is only about 10,000 years. The spallation hypothesis means that initial isotope ratios are not simple functions of time, but might also vary in space, particularly radial distance from the protosun, because of variations in radiation flux. Russell et al. (2001) provide a concise summary of this hypothesis.

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. Thus debate continues on this subject. We point out only that the two sets of ideas are not mutually exclusive, and it is very possible that both spallation and stellar/explosive nucleosynthesis were involved.

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 \textit{in situ} decay. Many of these anomalies, like those created by decay of extinct radionuclides, may reflect the injection of newly synthesized material 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.

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 they occur in virtually all of the carbonaceous chondrites that have not experienced extensive metamorphism. In contrast to the isotopic anomalies of metals mentioned above, most 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),

![Figure 5.13. 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 (‘solar’), Ne-B (‘planetary’), and Ne-E (‘spallogenic’). After Black and Pepin (1969).](image-url)
Isotope Geochemistry

Chapter 5  Spring 2010

“Neon B”, or solar, and “Neon S”, or spallogenic (cosmogenic) (Figure 5.13). In 1969, evidence of a $^{22}\text{Ne}$-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 meteorites. 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. Neon-E actually consists of two isotopically distinct components: Neon-E(L), which was found to reside in graphite, and Neon-E(H) which resides in SiC. The $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of Neon-E(H) is less than 0.01, while that of Neon-E(H) is less than 0.2.

The origin of Neon-E, and Neon-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 little Na to account for the observed amount of $^{22}\text{Ne}$. More detailed analytical work (Lewis et al., 1990) found that the Neon isotopic abundances actually match rather well that expected for nucleosynthesis in the He-burning shells of low mass, carbon-rich, thermally pulsing red giants called Asymptotic Giant Branch (AGB) stars. $^{22}\text{Ne}$ is synthesized from $^{16}\text{N}$, which is synthesized from C, N, and O nuclei during the previous hydrogen burning phase, through the sequence $^{14}\text{N}(\alpha,\gamma)^{17}\text{F}(\beta,\gamma)^{18}\text{O}(\alpha,\gamma)^{22}\text{Ne}$ (Gallino et al., 1990).

The other key noble gas in this context is xenon. Having 9 isotopes rather than 3 and with contributions from both $^{129}\text{I}$ decay and fission of various heavy elements, isotopic variation in xenon are bound to be much more complex than those of Neon. On the other hand, its high mass minimizes mass fractionation effects, so “solar” (more properly solar wind) and “planetary” Xe are isotopically similar. The first evidence of other 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 Neon-E(H) in SiC and is enriched in the s-process-only isotopes of Xe ($^{128}\text{Xe}$ and $^{130}\text{Xe}$) and is called, appropriately enough, Xe-S. The isotopic pattern of Xe-S is shown in Figure 5.14. 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 (1-2 solar masses) AGB stars, consistent with the inferences made for $^{22}\text{Ne}$ synthesis. SiC grains (Figure 5.15) are thus apparently condensates from material ejected from

* More specifically, AGB stars are low to modern 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.

Figure 5.14. Isotopic composition of Xe-S (relative to normal solar Xe with $^{130}\text{Xe}$=1). Xe-S is found in silicon carbide and associated with Neon-E(H). $^{128}\text{Xe}$ and $^{130}\text{Xe}$ are synthesized only in the s-process, hence the most likely site for its synthesis is red giants.
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 $^{22}\text{Ne}$ than the predicted products of AGB stars. This is presumably due to cosmogenic production of $^{22}\text{Ne}$. If so, some 130 Ma of cosmic ray irradiation would be required to produce the observed $^{22}\text{Ne}$, 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 apparently be produced only by a combination of the p- and r-processes (Figure 12.4). These processes, of course, 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 considerably complicated the effort to isolate it.

Analysis of the noble gases in the SiC, graphite and diamond by step-heating was comparatively easy, since each of these decompose at distinct temperatures. Identifying the carriers proved more difficult. However, once the carrier grains were identified and isolated, it became possible to analyze the isotopic composition of other elements. The isotopic compositions of other elements have also proved to be anomalous to varying degrees. The noble gas, C and N isotopic compositions are summarized in Table 5.02. Also shown in the table is the abundance of these phases, which is quite low.

Many of the SiC and graphite grains are large enough so the isotopic compositions of the major elements in individual grains can be analyzed by ion probe. These analyzes (e.g., Figure 5.17) reveal a diversity of isotopic compositions as well as correlations between grain size and isotopic composition.

Table 5.02. Isotopic Characteristics of Interstellar Grains

<table>
<thead>
<tr>
<th>Phase</th>
<th>Diamond</th>
<th>SiC</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopic Component</td>
<td>Xe-HL</td>
<td>Xe-S, Ne-E(H)</td>
<td>Ne-E(L)</td>
</tr>
<tr>
<td>Enriched in Isotopes</td>
<td>$^{124}\text{Xe}, ^{136}\text{Xe}$</td>
<td>$^{128}\text{Xe}, ^{130}\text{Xe}, ^{22}\text{Ne}$</td>
<td>$^{22}\text{Ne}$</td>
</tr>
<tr>
<td>Nuclear Process</td>
<td>p, r</td>
<td>s, $^{22}\text{Na}(\beta, \nu)^{22}\text{Ne}$</td>
<td>$^{14}\text{N}+2\alpha\rightarrow^{22}\text{Ne}$</td>
</tr>
<tr>
<td>Grain Size, $\mu$</td>
<td>0.001</td>
<td>0.03-10</td>
<td>0.8-7</td>
</tr>
<tr>
<td>Abundance in C2 chondrites, ppm</td>
<td>400</td>
<td>7</td>
<td>&lt;2</td>
</tr>
<tr>
<td>($^{15}\text{C}/^{12}\text{C})/(^{15}\text{C}/^{12}\text{C})_o$</td>
<td>0.96</td>
<td>0.03 – 50</td>
<td>0.012 – 50</td>
</tr>
<tr>
<td>($^{15}\text{N}/^{14}\text{N})/(^{15}\text{N}/^{14}\text{N})_0$</td>
<td>0.66</td>
<td>0.015 – 20</td>
<td>0.55 – 6.7</td>
</tr>
</tbody>
</table>

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 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 5.18). 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 ($\text{Al}_2\text{O}_3$). The graphite, SiC, and corundum have inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios of $5 \times 10^{-5}$ to $1 \times 10^{-1}$. In contrast, we found in the previous lecture that CAI’s had inferred initial $^{26}\text{Al}/^{27}\text{Al}$ ratios up to $5 \times 10^{-5}$, and that most other meteoritic materials showed no excess $^{26}\text{Mg}$. More recently, presolar grains have been shown to include Si$_3$N$_4$, spinel, hibonite, a variety of metal carbides, and perhaps TiO$_2$ and Fe-Ni metal.

Up until 2004, all the presolar grains identified in meteorites and in interstellar dust particles (IDP’s) collected by spacecraft and high-altitude aircraft 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) 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 carbonaceous chondrite Acfer, 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.
This late discovery most likely reflects the approaches used to isolate the presolar grains. The high-temperature of release of the anomalous noble gases suggested the carrier grains were quite refractory. Anders and coworkers attacked the problem with a brut-force method: dissolving away whatever could be dissolved, then studying the residue. This led to acid-resistance phases such as SiC, graphite, and diamond. The most recent approaches use ion microprobes to produce isotopic ratio maps of thin sections of meteorites. Once an isotopic anomalous grain is identified, its composition is readily determined in situ with an electron microprobe.

A Late Injection of Supernova Debris?

Bizzaro 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 $^{60}$Ni deficits of around 25 ppm (0.2 epsilon units) compared to terrestrial material, an enstatite, ordinary and carbonaceous chondrites, and a Martian meteorite. $^{60}$Ni is the daughter of $^{60}$Fe, which as a half-life of 1.5 Ma. They suggested that a type Ib supernova injected $^{60}$Fe into the solar nebula after the parent bodies of the early-formed objects had accreted, but before the terrestrial planets and the parent bodies of the terrestrial planets had accreted. Type Ib and Ic supernovae result from core collapse of massive stars that have thrown off their outer layers during earlier red giant phases. Such a supernova would not have injected $^{26}$Al produced during the red giant phase (unlike a type II supernova).

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 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, Ca, Ba, Sm, Nd, and Sr. They have been termed termed FUN anomalies: fractionation and unknown nuclear. Other variations are widespread, but appear to be due to fractionation, e.g., Si and Mg. A systematic search by G. Lugmair and colleagues at the University of California at San Diego has revealed that isotopic variations of the iron peak elements (elements clustered around the cosmic abundance peak at Fe), Ca through Zn, 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, $^{61}$Ni, and $^{66}$Zn), often accompanied by under-abundance of the most neutron-poor isotopes. In some instances, instances, isotopic variations within single mineral grains have been observed with the ion

Figure 5.18. 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 $^{96}$Mo and $^{97}$Mo. From Nittler (2003).
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.

With the exception of these dramatic isotopic variations on very fine scales and of oxygen, discussed below, decades of research has shown that the isotopic composition of the solar system is strikingly uniform on larger scales. The conclusion has been that the solar nebula was very well mixed. But as precision in isotopic measurement improves, this picture may be breaking down. Based in part on variations in 142Nd/144Nd, Andreasen and Sharma (2006) have suggested that carbonaceous chondrites have a roughly 100 ppm deficit of the p-process isotopes 146Sm and 144Sm relative to ordinary chondrites. Ranen and Jacobsen (2006) found that chondrites have small excesses in 137Ba and 138Ba, which are r-process isotopes, relative to the Earth. Thus small amplitude isotopic heterogeneities might have existed in the solar nebula as the Earth and meteorite parent bodies were forming.

Ubiquitous Oxygen Isotope Variations

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 17O (0.037% of O) as well as 18O and 16O, he found that these variations were not consistent with simple mass-dependent fractionation. This is illustrated in Figure 5.19. On a plot of 17O/16O vs. 18O/16O, variations created by fractionation 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 fall along a line with slope = 1. One interpretation is that this reflects mixing between a more or less pure 16O 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 17O and 18O (Figure 5.20) relative to 16O. The experiment demonstrates that a slope of 1 on the δ17O — δ18O diagram could be produced by chemical processes. Thiemens suggested this kind of fractionation results from a kinetic fractionation mechanism, which arises because non-symmetric (e.g., 16O17O or 16O18O) molecules have more

Figure 5.19. Variation of O isotope ratios in meteorites and terrestrial and lunar samples. Most of the data from Allende inclusions is off the plot to the left. From the work of R. N. Clayton.
available energy levels than symmetric (e.g., $^{16}$O$^{16}$O) molecules (as we will see later in the course, symmetry enters into the partition function, which governs isotope fractionation). Subsequent studies have suggested it results from asymmetric molecules having a greater number of quantum states than symmetric ones. Others have suggested it results from the collision process itself.

Subsequent to Thiemens and Heidenreich’s work, mass-independent fractionations have been discovered in O and S isotopes of terrestrial materials; we’ll consider the details latter in the course. Mass-independent fractionation in oxygen has been found in atmospheric ozone. In the case of sulfur, photodissociation of atmospheric sulfur compounds appears to cause mass-independent fractionation.

The explanation for mass-independent O fractionation in the solar nebula may also involve photodissociation. Clayton (2002) suggested that the anomalies arose through radiation self-shielding in the solar nebula. In his 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$^{16}$O would have been absent, while that needed 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 $^{16}$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 $^{16}$O and $^{17}$O compared to meteorites and the Earth – closer in composition to the CAI’s. This prediction appears to have recently been confirmed based on analysis of solar wind implanted in lunar soil. Hashizuma and Chaussidon (2005) found that surfaces of lunar soil particles have oxygen isotope compositions up to 20‰ enriched in $^{16}$O. This solar wind-implanted oxygen presumably represents the O isotopic composition of the Sun, which has most of the mass, and most of the O in the solar system. It would thus seem that it is meteorites and planets that are anoma-

Figure 5.20. Mass independent fractionation during the production of ozone from molecular oxygen. Squares are ozone, dots are oxygen. After Thiemen and Heidenreich (1983).

Figure 5.21. O isotope variations among minerals of various meteorite classes (Clayton et al., 1976).
Isotope Geochemistry

Chapter 5

Spring 2010

Isotopically and variably depleted in $^{16}$O, just as Clayton’s theory predicts.

As Figure 5.21 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), though 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 H$_2$O. Hydrogen and carbon have only two stable isotopes so mass-dependent and mass-independent effects cannot be distinguished.

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:

$$\frac{dN}{dt} = P - \lambda N \quad 5.06$$

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:

$$N = Pt \quad 5.07$$

Combining these equations, we may obtain an expression for $t$ that is independent of variations production rate:

$$N = \frac{N_u}{N_u} \left( \frac{P}{P_u} \right) \frac{t}{\lambda} \quad 5.08$$

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 5.22. These ages are much less than

Figure 5.22. 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).
Isotope Geochemistry

Chapter 5

Spring 2010

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 implies individual meteorite classes are derived from single parent bodies.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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Isotope Geochemistry

Chapter 5


