4

Solar System Raw Materials

We explain nucleosynthesis in evolving stars and use this foundation to understand the chemical composition of our own star and of the Solar System. Element abundances are determined from the Sun's spectrum, and from laboratory measurements of the solar wind and chondritic meteorites. The metal-rich Solar System composition reflects the recycling of elements formed in earlier generations of stars. Condensation models of a cooling nebular gas having this composition produced the minerals found in refractory inclusions in chondrites. The deuterium enrichment in organic matter in chondrites suggests that hydrocarbons formed at low temperatures in molecular clouds and were subsequently processed into complex molecules in the solar nebula and in parent bodies. Ices condensed far from the Sun and were incorporated into the giant planets and comets. Element fractionations in the nebula were largely controlled by element volatility or by the physical sorting of solid grains. Separation of isotopes by mass was common in the nebula, although oxygen shows mass-independent fractionation.

4.1 Adding Cosmo to Chemistry

Cosmochemistry is the name given to the study of the chemical composition of the Universe and the processes that produced that composition. In this chapter, we use the methods of cosmochemistry to describe the raw materials – the elements and the compounds formed from their combinations – from which the Sun and its retinue of planets and satellites were fashioned.

The Sun comprises 99.8 percent of the mass of the Solar System, so to a first approximation the solar composition is that of the Solar System. What are the relative abundances of elements in the Sun, and how did that mixture come to be? Surrounding the infant Sun was a **solar nebula**, a swirling cocoon of gas and dust that eventually became our planetary system. How was the nebula processed to form the minerals that are found in surviving nebular samples from that early period? The initial chemistry of the nebula must have been the same as the solar composition, but the differing compositions of planets indicate chemical fractionation processes that we also need to understand.

To address these problems, cosmochemistry utilizes laboratory analyses of extraterrestrial samples, supplemented by remote sensing (spectroscopic) measurements. The types of materials in hand (meteorites, interplanetary dust particles, samples returned by spacecraft missions, presolar grains) and the principles of spectroscopy were previously described in Chapters 2 and 3. Chemical and mineralogical analyses can be used to decipher the composition of the Solar System and to reveal the processes that produced its raw materials.

4.2 Origin of the Elements

Elements are synthesized primarily in stars, so the raw materials for the formation of planets and the origin of life are stardust. Let's see how elements are made.

4.2.1 Stellar (and Solar) Formation and Evolution

Some astronomical perspective is useful in understanding the composition of our neighboring star. Clusters of stars form together in giant **molecular clouds**, concentrations of gas and dust in interstellar space. An example is shown in Figure 4.1. The molecular clouds are mostly hydrogen (which occurs as H_2 molecules, hence the name) and some helium, with oxygen, carbon, and nitrogen contributing about 1 percent by mass and all the other elements occurring mostly as tiny dust motes. In astronomical jargon, everything but hydrogen and helium are "metals." The newly formed stars inherit the elemental composition of their parent molecular cloud.

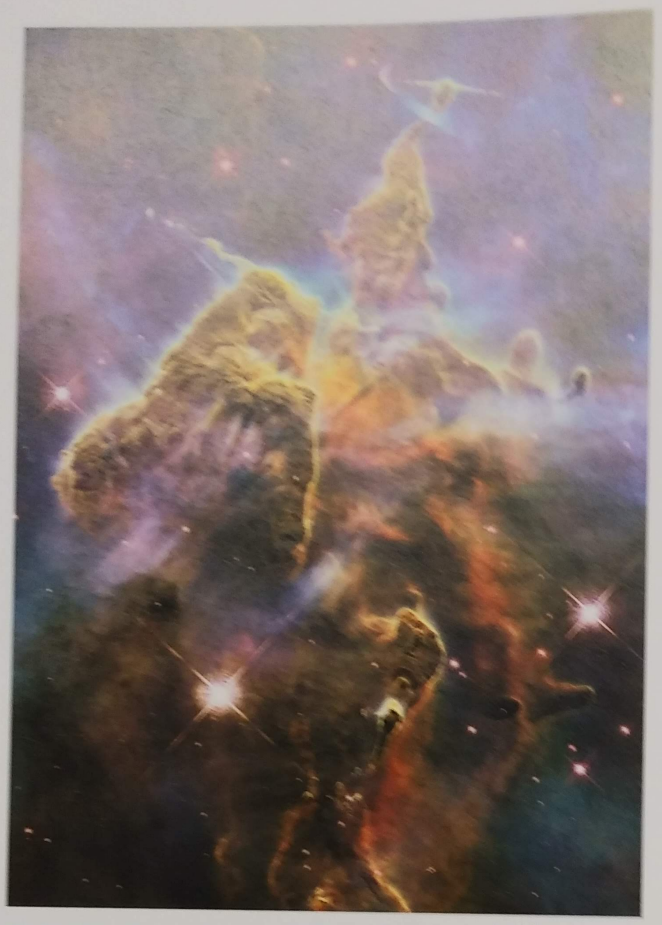

Figure 4.1 Hubble Space Telescope image of a star-forming region in the Carina Nebula. Concentrations of gas and dust in this molecular cloud are collapsing to form new stars. Stellar winds compress the cloud into pillars. One new star at the tip of the longest pillar has bipolar outflows. NASA image.

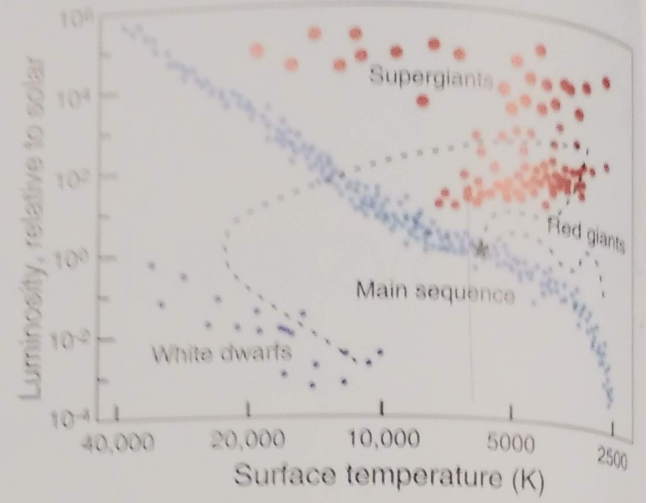

Figure 4.2 Herzsprung–Russell (H-R) diagram showing the distribution of stars in terms of luminosity and temperature. The black star is our Sun. Also shown by dashed lines are the Sun's evolutionary path to the main sequence, and thence to the red giant stage and finally to the white dwarf stage.

Figure 4.3 The Crab Nebula, the remnant of a supernova that exploded a thousand years ago. X-ray, visible, and infrared images from the Chandra, Hubble, and Spitzer Space Telescopes were combined to produce this composite. Combined NASA and ESA images.

Stars can be classified using the **Herzsprung–Russell (H-R) diagram**, plotting stellar luminosity (brightness is a proxy for mass) versus surface temperature (Figure 4.2). The most massive stars are situated at the top of the diagram, and the hottest stars plot on the left. The main sequence, a band stretching diagonally from upper left to lower right, contains about 90 percent of all stars. Our Sun lies on the main sequence; its position is marked with a black star. A new star appears on the main sequence when its temperature increases to the point where fusion of hydrogen, its main constituent, is triggered. Massive, hot stars near the top of the main sequence evolve at a furious rate and have lifetimes of only a few million years, whereas cooler, dimmer stars last for billions of years. Once the hydrogen fuel in the core of a massive star is exhausted, it expands and cools to form a red giant or a supergiant. Fusion of heavier elements continues within the interiors of red giants, as described in Section 4.2.2. Stars with masses greater than ten times that of the Sun are the progenitors of supergiants, which end their lives in gigantic explosions called **supernovae** (Figure 4.3). These explosions can leave behind stellar corpses highly compressed by gravity – black holes or neutron stars. Smaller stars like the Sun form red giants that increase in temperature, and eventually slough off their outer layers and migrate across the H-R diagram to form white dwarfs (the Sun's path in Figure 4.2). White dwarfs, too,

can undergo supernovae, if they merge with matter from a neighboring star.

4.2.2 Nucleosynthesis, Slow and Fast

The transmutation of hydrogen into helium occurs by fusion in the cores of main sequence stars. (Although we talk about elements in stars, a more appropriate term is "nuclides" because multiple isotopes of the elements are formed.) Hydrogen fusion is often called hydrogen "burning." Although the hydrogen is fuel, fusion in stars is a nuclear rather than chemical reaction, and no combination with oxygen occurs as in conventional burning. Once hydrogen in the core is exhausted, temperatures and pressures increase enough to initiate helium burning. At this point, the star migrates off the main sequence and swells to become a red giant. Hydrogen burning continues in a shell surrounding the helium-burning core, as illustrated in Figure 4.4. Subsequently, the core burns carbon, neon, oxygen, and silicon, as the ashes of one stage become the fuel for the next. Silicon burning finally produces a core of iron nuclei. The fusion of lighter elements into heavier ones results in the conversion of a small amount of mass (M) into energy (E), as described by Einstein's famous $E = MC^2$, where C is the speed of light; this sustains the star's luminosity and explains how the Sun shines.

The production of elements heavier than iron requires more energy than is released by adding particles to the nuclei. No more energy can be gained by fusing iron into heavier nuclei, so the star begins to collapse due to its own gravity. The intense pressures cause the iron core to be converted into a dense mass of neutrons, and a strong neutron flux develops above this interior stellar core. Nuclides beyond iron are mostly formed by capture of these neutrons, with each captured neutron increasing the mass of the nucleus by one unit. If the resulting nuclide is stable, it remains an isotope of the original element. If not, the atom undergoes β-decay, in which a neutron emits an electron to become a proton, thereby changing into an isotope of the next heavier element. Two neutron-capture processes are illustrated in Figure 4.5. The zigzag line of yellow boxes represents stable nuclides, the horizontal arrows illustrate neutron capture, and the diagonal arrows are β-decay. In the slow – or "s" – process, neutrons are captured at a rate that is slow compared to the rate of β-decay. This occurs in the pulsing outer shells of red giants and accounts for about half the elements heavier than iron. The rapid – or "r" – process is neutron capture on such a rapid timescale that multiple neutrons are captured before β-decay occurs. Some stable nuclides, such as ^{87}Rb or ^{94}Zr, can only be reached by the r-process (Figure 4.5). Nucleosynthesis by the r-process occurs when the collapsing mass of the star bounces off the dense neutron core, producing a supernova explosion. The merger of neutron stars, first observed in 2017, also results in r-process nucleosynthesis, although the relative role of this source versus supernovae in producing heavy elements is unclear.

A supernova event, occurring when the collapsing stellar core implodes, ejects the newly synthesized elements back into interstellar space. These elements can be incorporated subsequently into new stars, so that the "metal" content increases with each new generation of stars. First-generation stars contain only hydrogen and helium. The heavy element content of the Sun requires that it formed in a later generation from elements produced in earlier stars. Since planets are formed from heavy elements, they are only associated with stars that are metal-rich.

In addition to **stellar nucleosynthesis**, there are two other ways to form new elements. Many of the nuclides formed during a supernova are unstable and undergo radioactive decay to form stable "radiogenic" nuclides over timescales of millions to billions of years. Of course, the s- and r-processes produce new nuclides from unstable nuclides as well, but on an extremely short timescale, so we distinguish that from radioactive decay that occurs outside stars. Other so-called "cosmogenic" nuclides are produced through irradiation by high-energy cosmic rays. Both of these processes are important in accounting for the chemical composition of the solar nebula and of the planets that formed within it.

4.3 Composition of the Solar System

High-resolution measurements of the spectrum of light emitted from the Sun reveal thousands of absorption lines (Fraunhofer lines, as described in Section 2.4) caused by the various elements absorbing light at specific wavelengths. The widths of these lines are proportional to the element abundances. Combined with a model of the solar atmosphere and an understanding of how the lines are formed and interact, the **solar spectrum** can be used to determine the chemical composition of the Sun.

An independent measure of the chemistry of the Sun can be gained from analysis of the solar wind – charged particles emitted from the solar atmosphere. The *Genesis* spacecraft collected solar wind during its 2.5 years in orbit outside the Earth's magnetic field (which repels charged solar particles). The solar wind sample (10^{20} atoms = 0.4 mg) was returned to Earth in 2004. A parachute unfortunately failed to open and the spacecraft crashed in the Utah desert, shattering many of the

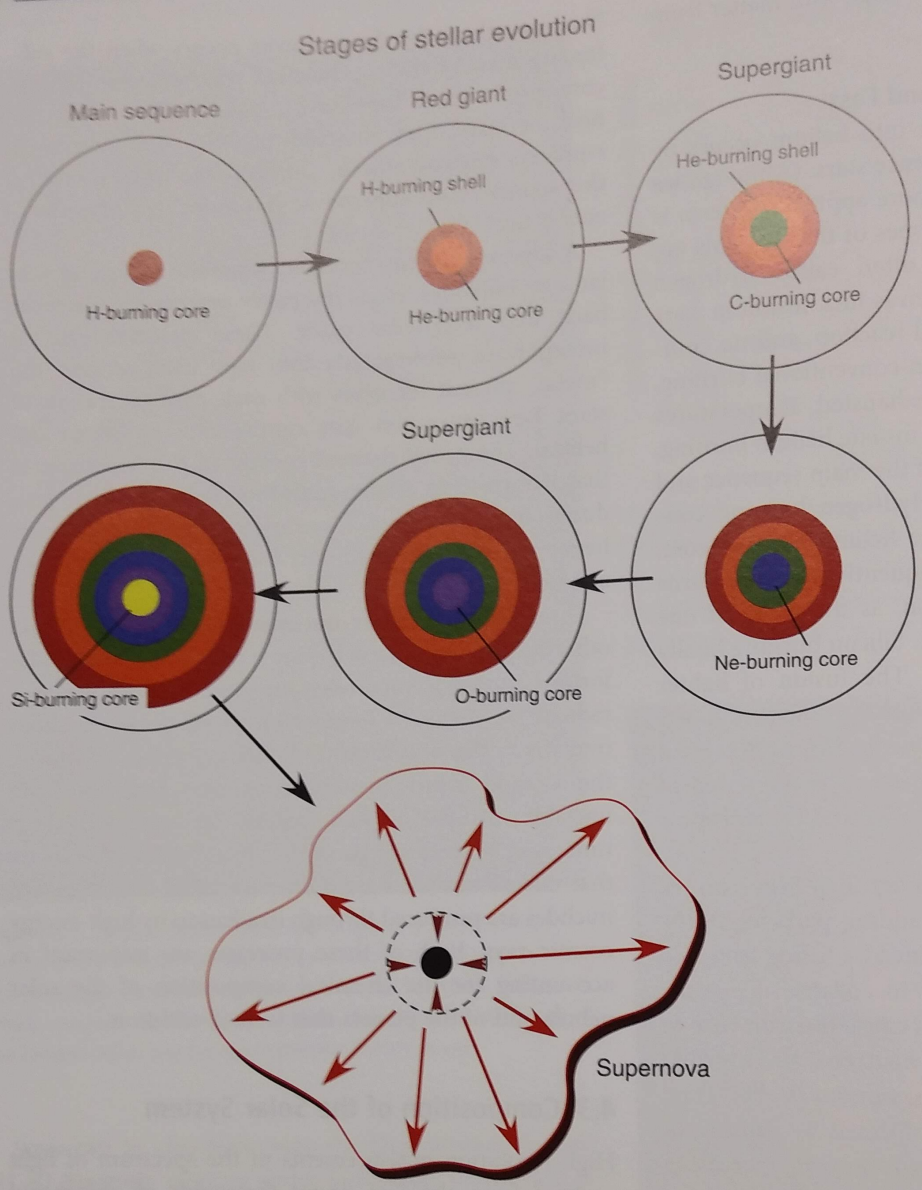

Figure 4.4 Schematic evolution of stars of greater than ten solar masses. Stars on the main sequence fuse hydrogen in their cores, giving way to helium burning as they become red giants. Cores become burning shells, as carbon, neon, oxygen, and silicon successively fuse. Once iron forms in the core, fusion ends and the star explodes as a supernova. Modified from McSween and Huss (2010).

solar wind collector plates. However, by careful cleaning and analysis, scientists have been able to salvage measurements of the solar wind composition. Corrections must be applied to the measured values, because the elements were fractionated on expulsion from the Sun, which preferentially ejects elements that are easier to ionize. This solar wind sample has been especially important in providing data on the isotopic composition of the Sun.

The solar composition is no longer the same as it was when first formed. Nuclear burning has transformed some hydrogen into helium, and in the process has modified the isotopic compositions of hydrogen, helium, carbon, oxygen, and nitrogen. Also, lithium has become severely depleted in the Sun due to nuclear reactions.

For many years, it has been recognized that certain meteorites (chondrites; see Box 4.1) have chemical compositions that mimic that of the Sun. We can think of chondrites as a sort of solar sludge; if you could cool and condense a gas of solar composition into solid, rocky matter, you would make a chondrite. Not all chondrites

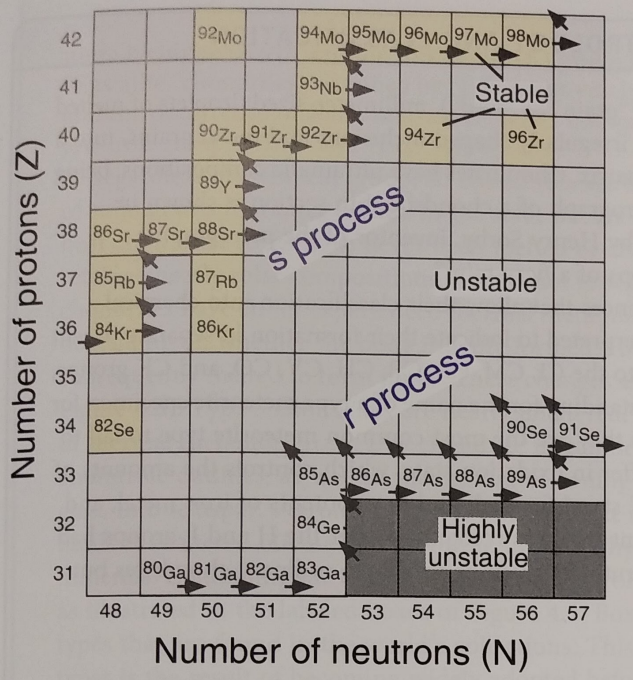

Figure 4.5 A portion of the chart of the nuclides, illustrating how the s-process (upper arrows) and r-process (lower arrows) produce new elements by neutron capture. Yellow boxes are stable nuclides, and light gray boxes are unstable nuclides that undergo β-decay that shifts them up and to the left, as shown by diagonal arrows. Neutrons are captured much faster in the r-process, until a nuclide finally reaches a highly unstable (dark gray) box and undergoes a series of β-decays until a stable nuclide is reached. Modified from McSween et al. (2003).

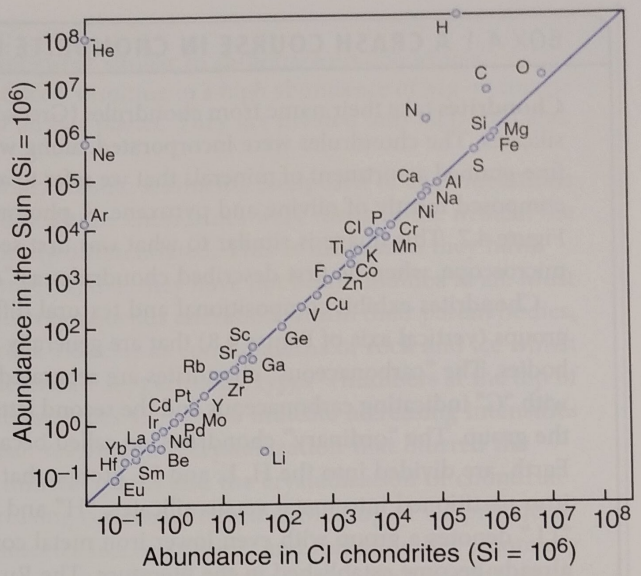

Figure 4.6 Comparison of element abundances in the Sun with those in CI carbonaceous chondrites. The only elements that deviate are gaseous elements that are hardest to condense into solids, and lithium which has been destroyed in stellar nucleosynthesis. After McSween et al. (2003).

are the same, and one kind in particular – CI carbonaceous chondrites – provides the best match. Figure 4.6 compares element abundances in the Sun and in CI chondrites, both normalized to the same number of silicon atoms. The main deviations are hydrogen, helium, nitrogen, carbon, and oxygen, which exist largely in the gas phase even at room temperature and thus are hard to condense, explaining their lower abundances in chondrites. Lithium has been depleted in the Sun during the time since the chondrites formed, so for this element the chondrites record the composition of the nebula better than does the present-day Sun. Because meteorites can be analyzed in the laboratory, this incredible agreement provides a way to estimate relative solar abundances for elements that have low solar abundances or do not have prominent absorption lines.

The abundances of elements in the Solar System, relative to a million silicon atoms, are illustrated in Figure 4.9. To define the abundances of some elements the solar value is used, whereas for others CI chondrite analyses provide the best determination. The Solar System element abundances are often called **cosmic abundances**, a term coined by geochemist Victor Goldschmidt in 1937. However, stellar spectroscopy indicates that our Solar System does not have exactly the same composition as most of the galaxy, which we might call the cosmos. Relative to nearby solar-sized stars of comparable age, the Sun has a higher proportion of "metals," reflected in its 50 percent higher Fe/H ratio. Because this book is about planetary geoscience, we will focus on Solar System abundances.

Let's take a more careful look at Figure 4.9. First, note that the abundances are plotted on a logarithmic scale, to allow for the fact that they vary over many orders of magnitude. Hydrogen and helium, originally produced in the so-called Big Bang that formed the Universe, make up more than 98 percent of the mass of the Solar System. Moving to the right in the diagram, we see that lithium, beryllium, and boron have very low abundances. For the most part, these elements are not made in stars and were formed in only small amounts during the Big Bang or through irradiation by cosmic rays. Carbon, oxygen, neon, and silicon are relatively abundant, reflecting their roles as products of fusion in massive stars (Figure 4.4). The peak in the abundance of iron occurs because it is a very stable nuclide and represents the end point of normal fusion reactions. For the elements heavier than iron that are formed during supernovae, abundances decrease with increasing mass because progressively more

BOX 4.1 A CRASH COURSE IN CHONDRITE PETROLOGY AND CLASSIFICATION

Chondrites take their name from chondrules (Greek for "grain" or "seed"), millimeter-sized droplets of melted silicates. The chondrules were incorporated, along with irregularly shaped inclusions and metal grains, into a fine-grained assortment of minerals that we refer to as matrix. Chondrites have ultramafic compositions, being composed mostly of olivine and pyroxene. A photomicrograph of a chondrite thin section is shown in Figure 4.7. This image is similar to what was first seen by Henry Sorby, inventor of the petrographic microscope, when he first described chondrules as "drops of a fiery rain."

Chondrites exhibit compositional and textural differences that allow their classification into chemical groups (vertical axis of Figure 4.8) that are generally interpreted to indicate their formation in separate parent bodies. The "carbonaceous" chondrites are separated into the CI, CM, CR, CB, CH, CV, CO, and CK groups, with "C" indicating carbonaceous and the second letter standing for the name of a type meteorite specimen for the group. The "ordinary" chondrites, so called because they are the most common meteorite type to fall to Earth, are divided into the H, L, and LL groups that differ in oxidation state, which controls the amounts of iron partitioned into metal versus silicates; "H" and "L" stand for high and low contents of iron metal, and "LL" denotes a group with even lower iron metal content that was recognized after the H and L groups had already become established in the literature. The Rumaruti (R) group is similar to ordinary chondrites but

Figure 4.7 Thin-section photomicrograph of the Tiechitz H3 chondrite that fell in what is now the Czech Republic in 1878. Numerous millimeter-sized chondrules composed of olivine, pyroxene, and glass are contained in a fine-grained matrix.

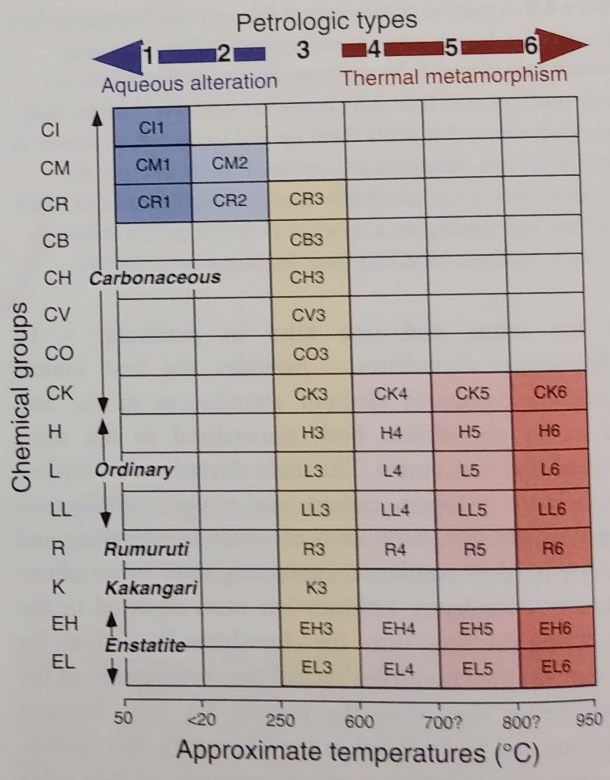

Figure 4.8 The classification scheme for chondritic meteorites. Chondrites are divided into chemical groups (shown on the vertical axis) and characterized by petrologic type, reflecting the degree of thermal metamorphism or aqueous alteration (top of the figure). Only the filled boxes (for example, CM2 or L5) are known chondrite types. Modified from McSween and Huss (2010).

more highly oxidized, and the Kakangari (K) group is somewhat similar to carbonaceous chondrites. "Enstatite" chondrites, identified by "E," are extremely reduced, resulting in a high abundance of Mg–pyroxene and the occurrence of some unusual minerals not found on our planet. They are divided into high-iron and low-iron groups ("EH" and "EL," respectively).

Regardless of chemical group, all chondrites are basically cosmic sediments composed of agglomerations of solid grains that once existed in the solar nebula. Although the chondrules were melts in the nebula, the host chondritic rocks have never been melted or chemically differentiated. This is the reason they have retained nearly solar compositions. That is not to say, however, that they have not been modified at all. Most chondrites have either experienced thermal metamorphism or aqueous alteration within their parent bodies, depending on whether the body initially formed from rock alone or as combinations of rock and ice which subsequently melted to form fluids. These changes are described as "petrologic types" (numbers at the top of Figure 4.8). Type 3 chondrites are nearly unaltered, whereas types 4, 5, and 6 indicate increasing intensities of thermal metamorphism. Dry chondrite metamorphism resulted in recrystallization that blurred the chondrule outlines, as well as the erasure of zoning in mineral grains and the crystallization of chondrule glass into feldspar. Petrologic types 2 and 1 reflect increasing aqueous alteration. Melting of ice produced fluids that altered olivine and pyroxene to form phyllosilicates like serpentine, and formed other secondary minerals. Combining the chemical group and petrologic type, a chondrite might be classified as CM2 or L5, as illustrated in the labeled boxes of Figure 4.8. Boxes with interior labels in this figure indicate chondrite types that are found in the world's collections. This quirky but serviceable taxonomic system of petrologic types is the result of becoming widely adopted before it was recognized that two different processes were involved.

Even after a century of study, the chondrites remain enigmatic objects. We still do not know exactly how chondrules formed, although ideas abound. Most enigmatic are the CI chondrites which, unlike all the other groups, contain no chondrules at all. They are essentially all matrix material that has been heavily altered by fluids to form serpentine, magnetite, carbonates, and other secondary minerals. How what might be considered a congealed mud puddle has so faithfully retained its solar composition is a mystery.

energy is required to force more neutrons into the nuclei of heavier atoms. Finally, the peculiar sawtooth pattern in Figure 4.9 results from the higher abundances of elements with even rather than odd atomic numbers. The even-numbered elements are more stable because their nuclei are bound together more strongly. To remove the sawtooth structure from diagrams that plot element abundance versus atomic number, such as rare earth element diagrams, geochemists typically normalize the abundances to chondrites.

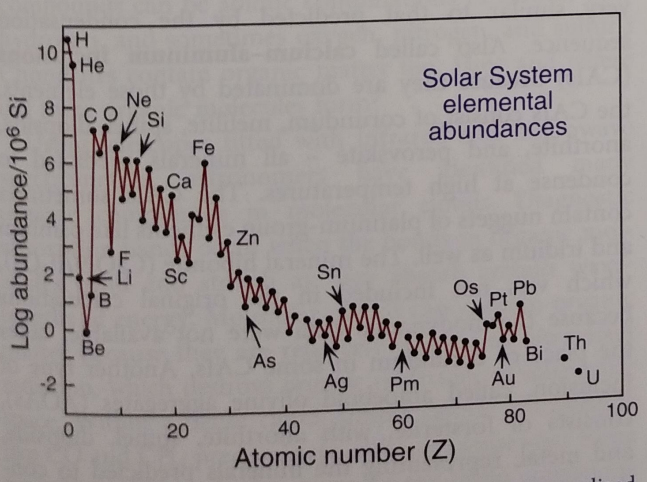

Figure 4.9 Solar System abundance of the elements, normalized to a million silicon atoms.

The chemical composition of the Solar System can thus be understood as a mixture of primordial hydrogen and helium with "metals" that are the products of nucleosynthesis in earlier generations of stars whose matter has been recycled. These earlier stars provided not only the heavy elements needed for the formation of rocky planets like the Earth, but also the biogenic elements used by our planet's life forms. As Carl Sagan noted, "we are all made from star stuff."

4.4 Minerals, Ices, and Organic Matter

4.4.1 Condensation of Minerals

Models of the physical and dynamic conditions in the solar nebula suggest that the interior near the early Sun became very hot, with temperature decreasing outward. The solid dust grains in the interior would have been vaporized and then recondensed as the nebula cooled.

Nebular pressures (estimated at only 10^{-3} to 10^{-5} atm) were too low to allow liquids to be stable, so nebular vapor would have condensed directly into solid minerals.

The **condensation** temperature of an element is the temperature at which the most refractory solid phase containing that element first becomes stable in a cooling gas of solar composition. Equilibrium condensation can be modeled using thermodynamic data for all potential gas and mineral species containing each element in the nebula. At any temperature, the gas or mineral species that has the lowest Gibbs free energy is the stable phase. Condensation calculations were done long before digital computers arrived, but modern calculations using computers allow more complex computations involving 23 elements with the highest Solar System abundances.

So what does the condensation sequence look like? The curves labeled with element symbols in Figure 4.10 show the fraction of each element condensed from the nebular gas as temperature decreases. However, most elements condense as minerals rather than in native form. The condensation temperatures of various solid phases are illustrated by the positions of italicized mineral names in this diagram. Not every mineral in the sequence actually condenses directly from the vapor; instead, some early-condensed minerals react with the cooling gas to produce new minerals or to modify the compositions of solid solution minerals. This situation is analogous to Bowen's reaction series, which describes the discontinuous crystallization or continuous reactions of minerals in a cooling magma.

Corundum (Al_2O_3) is the first condensate that contains a major element, although rare elements like osmium and zirconium may condense as nuggets at even higher temperatures. The next mineral to condense is perovskite ($CaTiO_3$). Corundum then reacts with the vapor to form spinel ($MgAl_2O_4$) and melilite ($Ca_2[MgSi, Al_2]SiO_7$), and the latter reacts in turn to form diopside ($CaMgSi_2O_6$) at lower temperature. This is followed by the condensation of iron–nickel metal, anorthite ($CaAl_2Si_2O_8$), and forsterite (Mg_2SiO_4); the latter subsequently reacts with the gas to form enstatite ($Mg_2Si_2O_6$). All of these minerals appear above 1250 K.

Below this temperature, solid solutions come into play. Anorthite begins to incorporate sodium and potassium to form other feldspars, and olivine and pyroxene become increasingly iron-rich. Metallic iron reacts with sulfur in the vapor to produce troilite (FeS), and then oxidizes to form magnetite (Fe_3O_4). Finally, hydrated silicates like serpentine can form by reaction of previously condensed silicates with water vapor.

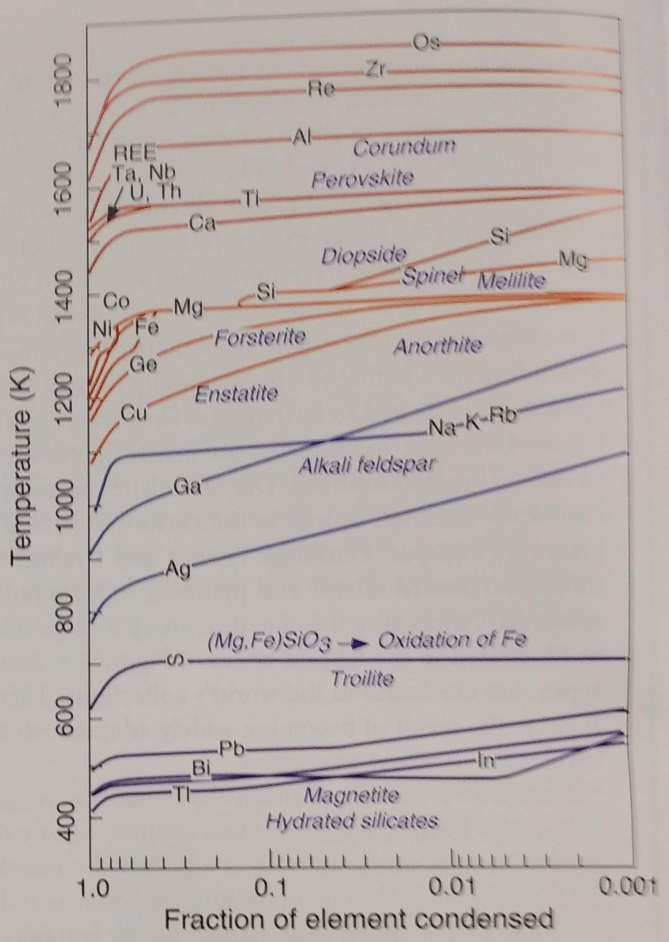

Figure 4.10 The calculated condensation sequence for a cooling gas of solar composition at 10^{-4} atm pressure. Condensation points for minerals are shown in italics, and curves show the fraction of each element condensed as a function of temperature. Modified from Grossman and Larimer (1974).

The chondrites contain direct evidence of nebular condensation. The mineral assemblage of some bizarre refractory inclusions (Figure 4.11) found in chondrites is very similar to that predicted by the condensation sequence. Also called **calcium–aluminum inclusions** (CAIs) because they are dominated by those elements, the CAIs consist of corundum, melilite, spinel, diopside, anorthite, and perovskite – all minerals predicted to condense at high temperatures. The CAIs sometimes contain nuggets of platinum-group elements like osmium and iridium as well. The mineral hibonite ($CaO{\cdot}9Al_2O_3$), which was not included in the original calculations because thermodynamic data were not available, takes the place of corundum in some CAIs. Another type of inclusion, called amoeboid olivine aggregates (AOAs), consists of forsterite, with anorthite, spinel, diopside, and metal, representing the minerals predicted to condense at somewhat lower temperatures.

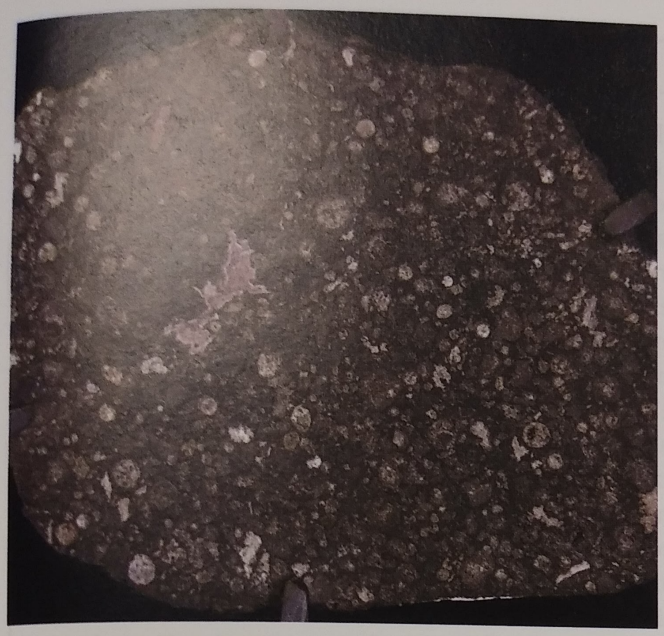

Figure 4.11 Cut slab of the Allende (Mexico) carbonaceous chondrite, showing a large white calcium–aluminum inclusion and numerous chondrules.

We should also note that evaporation is the opposite of condensation, and an alternative explanation for these inclusions could be that they are residues remaining after partial evaporation. In either case it is clear that the solar nebula experienced temperatures high enough to vaporize (or distill) nebular solids, before cooling to low temperatures.

4.4.2 Making Organic Molecules

Although the carbon atoms in our bodies were originally produced by nucleosynthesis in stars, these atoms now occur as parts of complex **organic molecules**. (Note: Although the term "organic" resembles "organism," it does not necessarily connote a connection to life; organic compounds can be abiotic combinations of carbon with hydrogen, and sometimes oxygen, nitrogen, and sulfur.) Chondrites contain organic matter too. How and where did these organic molecules form?

Using telescopes fitted with infrared and microwave spectrometers, astronomers have identified many organic compounds in molecular clouds. Diagnostic absorption bands occur when the bonds in organic molecules bend and stretch as they absorb certain wavelengths of energy. Molecular clouds can contain organic matter because they are relatively opaque to ultraviolet radiation, which destroys organic molecules in interstellar space. Within a dense cloud, simple carbon compounds like CO and CH_4 predominate, although somewhat more complex compounds also occur. In the frigid conditions within molecular clouds, deuterium (^2H) is utilized preferentially over hydrogen in chemical reactions, so the organic hydrocarbons formed there are distinctly deuterium-rich.

When the solar nebula formed, organic compounds inherited from the parent molecular cloud were further heated to form even more complex molecules that were stable at higher temperatures. Such molecules are composed of carbon chains (aliphatic compounds) and rings (aromatic compounds) with side branches containing other elements. The nebular-processed organic matter was then incorporated into planetesimals, the parent bodies of chondrites, where further reactions occurred.

Carbonaceous chondrites and the comet grains returned by the *Stardust* spacecraft provide direct sampling of extraterrestrial organic compounds for analysis using the panoply of methods available in the laboratory. Some molecules are easy to characterize, because they are soluble in various solvents and can be easily extracted from the meteorites. These include amino acids, the building blocks of life, as well as other compounds built of hydrocarbon chains or connected multiple rings with as many as 30 carbon atoms. Most organic matter in chondrites, however, consists of large, insoluble molecules (kerogen) that can only be separated by dissolving away the minerals of the host rock. Characterizing this gooey material poses a daunting challenge, and requires harsh degradation techniques that break the macromolecules into smaller fragments. The average composition of this material, expressed relative to 100 carbon atoms, is $C_{100}H_{70}N_3O_{12}S_2$ in one well-studied carbonaceous chondrite. The insoluble material is intimately mixed with flakes, tubes, and spheres of graphite.

The deuterium enrichment in extraterrestrial organic matter indicates a connection with molecular clouds. However, most of that material was likely processed in the nebula by heating and cosmic-ray irradiation or within meteorite parent bodies during aqueous alteration. The organic matter in comets appears to be more primitive and may be related more closely to molecules inherited from interstellar space.

4.4.3 Condensation of Ices: The Only Stuff Left

We now turn to the simple gaseous molecules, H_2O, CH_4, and NH_3, that were abundant in the nebula but not used completely in the formation of complex organic molecules. What happened to these gases? In the condensation sequence (Figure 4.10), we saw that some water can be incorporated in hydrous silicates at very low

BOX 4.2 STARDUST IN CHONDRITES

Vaporization of all the solid dust would have formed a homogeneous gas, thereby erasing any isotopic heterogeneity in the solar nebula. However, some variations in the amounts of s- and r-process isotopes are found in chondrites, indicating that not everything in the solar nebula was vaporized. Can the solid carriers of these isotopes be separated from normal Solar System material comprising the bulk of the chondrites? Presolar grains formed around other stars or expelled from supernova explosions should be recognizable by their exotic isotopic compositions. Surviving presolar grains are referred to more prosaically as stardust.

In 1987, cosmochemist Edward Anders and his coworkers first isolated stardust grains from a chondrite. Their method employed stepwise dissolution of a carbonaceous chondrite using harsh acid, while monitoring the presence of exotic nuclides (in this case, some s- and r-process isotopes of neon and xenon) in the residue at each step. After numerous steps, less than one-thousandth of the original mass remained, and the purified residue suddenly turned from black to white. Anders' prize was a tiny amount of carbon dust that proved to be miniature (nanophase) diamonds (Figure 4.12). These grains likely condensed from vapor as a carbon-rich red giant sloughed off its exterior gas; the grains were subsequently tagged with distinctive neon and xenon isotopes from the star's interior when it exploded and propelled the newly synthesized nuclides outward.

Buoyed by this success, the team soon discovered grains of another stardust mineral, moissanite (SiC). Measurement of the isotopic compositions of silicon and carbon identified this phase as presolar. Since then, other kinds of stardust, including graphite as well as unusual oxides and nitrides that occur as minute inclusions inside graphite and moissanite, have been recognized. Even though presolar silicate grains are more abundant than the carbon-rich stardust, they were not recognized until later because they are destroyed by the harsh chemical treatments used to isolate the carbon-rich grains. The identification of presolar olivine and pyroxene had to wait until they could be picked out in isotopic maps of chondrite thin sections made using the ion microprobe.

The s- and r-process isotopes used to identify presolar grains provide ground truth for the theoretical astrophysical models of nucleosynthesis in stars, as well as identify new nucleosynthesis pathways not yet considered. Who could have dreamed that the inner workings of stars could be better understood from tiny motes of dust in meteorites?

Figure 4.12 Tiny (nanophase) presolar diamonds, greatly magnified under an electron microscope. The yellow color results from trapped nitrogen and other gases. Image courtesy of E. Anders.

temperatures, but there is no obvious place to put methane or ammonia. At temperatures below about 200 K these gases would condense as **ices**.

Our understanding of ices in the Solar System is rudimentary, because they have been studied only by remote sensing. Ices that condensed at very low temperatures may have originally been amorphous, but they would crystallize when warmed. Ices were important in the formation of the giant planets and their satellites, which consist of rocky cores with mantles of ice or their high-pressure equivalents. At even greater distances from the Sun – in the Kuiper belt and Oort cloud – condensed ices occur as major constituents of comets. The preponderance of ice at greater heliocentric distance has led to the concept of a nebular "snow line" beyond which water ice was stable. The snow line must have been located within the present asteroid belt, since the most distant asteroids originally contained

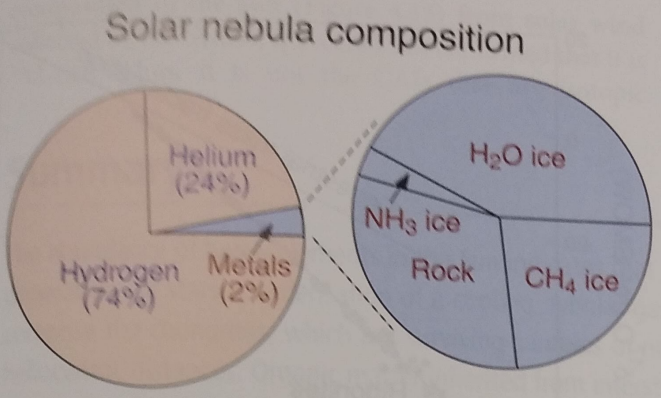

Figure 4.13 Abundance (in wt%) of the major components of the solar nebula. The diagram on the right expands the "metals" field (astronomical jargon) into condensed ices and rock.

ice that melted to cause the aqueous alteration observed in some chondrites.

The proportion of ices to rock by mass in the solar nebula was appreciable. Figure 4.13 illustrates the nebular composition in terms of hydrogen, helium, and metals. The right-hand diagram expands the metal portion into condensed H_2O, CH_4, and NH_3 ices and rock. Jupiter and Saturn formed mostly from nebular hydrogen and helium, Uranus and Neptune primarily from ices, and the terrestrial planets from rock.

4.5 Chemical Fractionations in the Solar Nebula

Condensation, described in the previous section, offers opportunities to separate elements and isotopes. These fractionations can have profound effects on the compositions of planets.

4.5.1 Element Fractionations

The geochemical behavior of elements can be distinguished as follows: **lithophile** (rock-loving) elements tend to occur as silicates or oxides; **siderophile** (iron-loving) elements combine with iron into metal alloys; **chalcophile** (sulfur-loving) elements react with sulfur to form sulfides; and **atmophile** elements tend to form gases and reside in the atmosphere. These geochemical affinities are not absolute, as many elements can exhibit multiple preferences. Elements in planets are partitioned into core, mantle/crust, and atmosphere depending on these geochemical affinities. Even within the crust, elements can be concentrated into ore deposits based on their geochemical preferences.

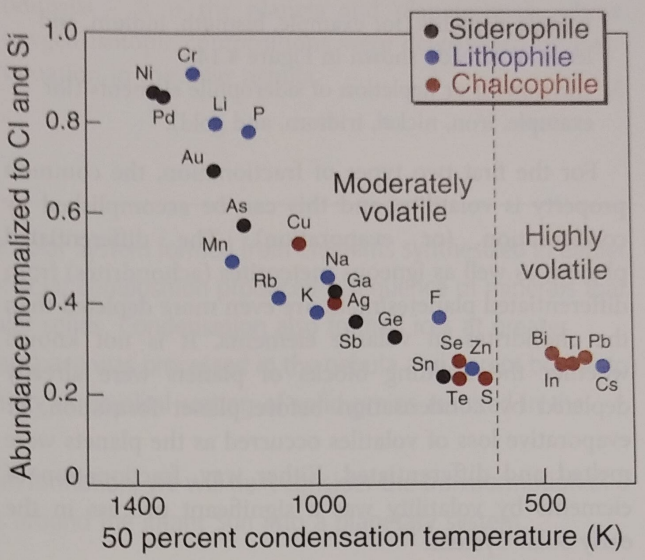

Figure 4.14 Element abundances in CV carbonaceous chondrites as a function of volatility, expressed as the temperature at which half of the element has condensed from vapor to solid. In the nebula, volatility ruled, regardless of the element's geochemical affinity. After Palme and Boynton (1993).

In the solar nebula, though, element distributions were mostly governed by volatility. Elements that condense from the nebular vapor at high temperatures are said to be **refractory**, and those that condense at low temperatures are **volatile**. The importance of volatility (easier to say that refractorility) is illustrated in Figure 4.14, a plot of the abundance of elements in carbonaceous chondrites, normalized to CI chondrite (i.e., solar values), versus the temperature at which 50 percent of the element has condensed (this is a commonly used measuring stick for element volatility in the nebula). The element abundances decrease systematically with volatility, regardless of whether they are lithophile, siderophile, or chalcophile. This diagram shows that moderately and highly volatile elements did not fully condense in most chondrites (CI chondrites are the exception).

Documenting the separation, or fractionation, of elements in the nebula is important for understanding the compositional differences among planets. The various groups of chondrites, which are surviving nebular samples, show at least three types of chemical fractionations, relative to the Solar System composition:

1. enrichment or depletion of refractory elements (for example, calcium, aluminum, and titanium);
2. depletion of moderately volatile elements (for example, manganese, potassium, and germanium) and highly

volatile elements (for example, bismuth, indium, and lead), as already shown in Figure 4.14;
3. enrichment or depletion of siderophile elements (for example, iron, nickel, iridium, and gold).

For the first two types of fractionation, the common property is volatility, and this can be accomplished by condensation (or evaporation). The differentiated planets, as well as igneous meteorites (achondrites) from differentiated planetesimals, are even more depleted than the chondrites in volatile elements. It is not known whether the building blocks of planets were already depleted by condensation before planet formation, or evaporative loss of volatiles occurred as the planets were melted and differentiated. Either way, fractionation of elements by volatility was a significant process in the early Solar System.

Physical sorting of solid grains is another process that leads to chemical fractionation. Concentration or depletion of siderophile elements resulted when metal grains were separated from silicate material. The high density of metal relative to silicate could have promoted size sorting or preferential settling of metal grains toward the nebula midplane. Similarly, CAIs (and the refractory elements they contain) are much more abundant in carbonaceous chondrites than in other chondrite classes, suggesting that some process concentrated these inclusions in the nebula region where carbonaceous chondrites formed.

4.5.2 Isotope Fractionations

During nebular processes such as condensation or evaporation, isotopes can also be fractionated by different amounts, depending on temperature. Isotope fractionations can also occur during geologic processes like melting and crystallization.

To illustrate how isotopes are fractionated, let's consider oxygen, which has three stable isotopes: ^{16}O, ^{17}O, and ^{18}O. Oxygen isotopes in terrestrial rocks have been fractionated according to their masses, as illustrated in Figure 4.15. In this diagram, $\delta^{17}O$ and $\delta^{18}O$ refer to the ratios of those isotopes to ^{16}O, relative to a standard. The difference between ^{18}O and ^{16}O is two mass units, twice the difference between ^{17}O and ^{16}O. Thus, any mass-dependent process that can modify $^{17}O/^{16}O$ will be twice as effective in modifying $^{18}O/^{16}O$. As a consequence, geologic processes spread out the oxygen isotopic compositions of terrestrial rocks along a mass-fractionation line with slope = ½ in Figure 4.15. Various classes of meteorites each define their own mass-fractionation lines, parallel to the terrestrial line, above or below it depending on their starting

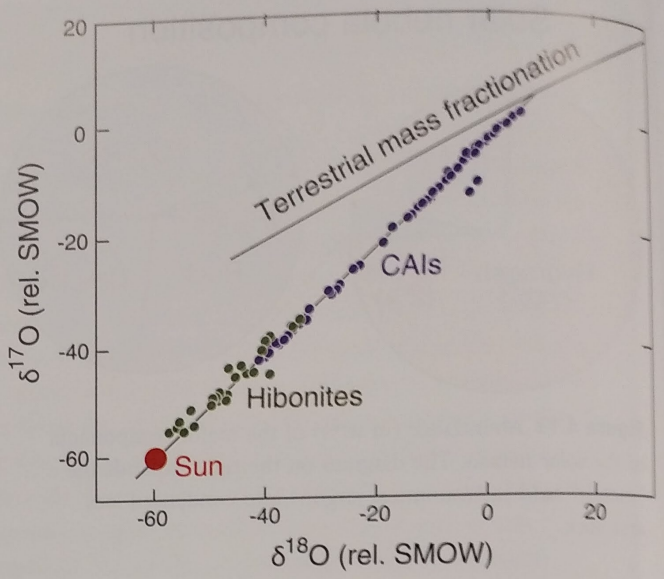

Figure 4.15 Oxygen isotopic compositions of refractory inclusions (CAIs) and individual hibonite grains from CAIs in chondrites. The δ notation refers to the ratio of the oxygen isotope to ^{16}O (per mil), relative to standard mean ocean water (SMOW). The composition of the Sun, as measured from solar wind, lies on an extension of the CAI–hibonite line. Modified from McKeegan et al. (2011).

compositions. Most isotopic fractionations in planets and planetesimals were mass-dependent.

The CAIs in chondrites, however, define a line with slope = 1 in Figure 4.15. Hibonites, the earliest condensing phase in CAIs, show even more extreme oxygen isotopic compositions. When oxygen isotopes in CAIs were first measured in 1973, Robert Clayton and his coworkers interpreted this steeper line to reflect mixing of two end members: nebular gas plotting on or above the terrestrial mass-fractionation line, and presolar grains containing pure ^{16}O (plotting on an extension of the CAI line). Subsequently, this trend has been explained as resulting from mass-independent fractionation in the solar nebula. Carbon has a high Solar System abundance, so much of the nebular oxygen was originally tied up in carbon monoxide (rather than carbon dioxide) gas. Because ^{16}O is much more abundant than the other oxygen isotopes, there were large differences in the amounts of $C^{16}O$, on the one hand, and $C^{17}O$ and $C^{18}O$ on the other. One idea is that this difference caused the less abundant $C^{17}O$ and $C^{18}O$ molecules to be preferentially dissociated into elements by irradiation. Another idea is that the oxygen isotopes became fractionated as vapor condensed into solids. In either case, the heavy oxygen isotopes then reacted with nebular hydrogen to form water vapor, which in turn reacted with condensates to form the compositions of the Earth and other bodies. Measurement of the oxygen isotopic

composition of the Sun (Figure 4.15) from solar wind collected by the *Genesis* spacecraft has confirmed that it is ^{16}O-rich. Thus, it is not the CAIs that are isotopic oddballs – it is the planets and planetesimals whose oxygen isotopic compositions were determined by fractionation in the solar nebula.

Summary

The abundance of heavy elements in the Sun indicates that the Solar System formed from elements synthesized in earlier generations of stars. Condensation of a cooling nebular gas of solar composition produced a sequence of minerals that comprise the chondrites, which are surviving samples of nebular solids. Condensation also formed ices at greater heliocentric distances. Organic matter inherited from interstellar space was processed in the nebula and parent bodies to form more complex molecules. Fractionation by element volatility or physical sorting of solid grains resulted in the compositional variations now seen in Solar System bodies.

Having examined the raw materials available for Solar System formation, we will next consider the transformation of a swarm of gas molecules, mineral dust, and organic molecules around the infant Sun into a planetary system.

Review Questions

1. Why does the Sun shine?
2. How do stars evolve on the H-R diagram? What nucleosynthesis processes occur at different stages? How do elements get recycled?
3. What do we mean by Solar System element abundances, and how are they determined?
4. What are chondrites, and why are they important?
5. What is the condensation sequence?
6. How do the geochemical and cosmochemical behaviors of elements differ?

SUGGESTIONS FOR FURTHER READING

Ebel, D. S. (2006) Condensation of rocky material in astrophysical environments. In *Meteorites and the Early Solar System II*, eds. Lauretta, D. S., and McSween, H. Y. Tucson, AZ: University of Arizona Press, pp. 253–277. An excellent summary of modern condensation calculations.

Lodders, K. (2003) Solar System abundances and condensation temperatures of the elements. *Astrophysical Journal*, **591**, 1220–1247. A comprehensive discussion of solar system abundances of the elements from the perspective of a cosmochemist.

McSween, H. Y., and Huss, G. R. (2010) *Cosmochemistry*. Cambridge: Cambridge University Press. A more thorough discussion of the origin of the elements, their Solar System abundances, and fractionations.

Tolstikhin, I., and Kramers, J. (2008) *The Evolution of Matter*. Cambridge: Cambridge University Press. A more comprehensive treatment of Solar System abundances, stellar evolution, and nucleosynthesis than in this book.

REFERENCES

Grossman, L., and Larimer, J. W. (1974) Early chemical history of the solar system. *Review of Geophysics and Space Physics*, **12**, 71–101.

McKeegan, K. D., Kallio, A. P. A., Heber, V. S., et al. (2011) The oxygen isotopic composition of the Sun inferred from captured solar wind. *Science*, **332**, 1528–1532.

McSween, H. Y., and Huss, G. R. (2010) *Cosmochemistry*. Cambridge: Cambridge University Press.

McSween, H. Y., Richardson, S. M., and Uhle, M. E. (2003) *Geochemistry: Pathways and Processes*. 2nd edition. New York: Columbia University Press.

Palme, H., and Boynton, W. V. (1993) Meteoritic constraints on conditions in the solar nebula. In *Protostars and Planets III*, eds. Levy, E. H., and Lunine, J. I. Tucson, TX: University of Arizona Press, pp. 979–1004.