CHAPTER 15

STRETCHING OUR HORIZONS

Cosmochemistry

OVERVIEW

In this chapter, we explore the rapidly emerging field of cosmochemistry. This subject involves the geochemical aspects of systems of planetary or solar system scale. We first consider nucleosynthesis processes in stars and use this foundation to understand the abundances of elements in the Sun and the solar system. Chondritic meteorites are discussed next, as samples of average solar system material stripped only of the lightest elements. Analyses of these meteorites provide information on the behavior of various elements in the early solar nebula; from these, we learn that elements were fractionated according to both geochemical affinity and volatility. Chondritic fractionation patterns are also important for understanding planetary compositions. We then consider evidence for proposed cosmochemical processes in the early solar nebula, such as condensation of solids from vapor and infusion of materials formed in and around other stars. The characteristics and origin of extraterrestrial organic molecules and ices are also explored; these, too, were important planetary building blocks. Finally, we consider how geochemical models for planets are formulated.

WHY STUDY COSMOCHEMISTRY?

In earlier chapters, we have sometimes used observations from extraterrestrial materials or other planetary bodies to illustrate processes or pathways in geochemistry. Perhaps these seemed exotic or even esoteric. From the geologist's uniformitarian perspective, however, the planets and other extraterrestrial bodies provide a larger laboratory in which to study geochemical behavior. Historically, the study of cosmochemistry has paralleled (and, in some cases, spurred) the development of geochemistry as a discipline, and has involved many of the same scientists. It is significant that the leading journal in geochemistry is also the premier journal in cosmochemistry and incorporates both fields in its title (*Geochimica et Cosmochimica Acta*). In this chapter, we examine several problems of huge (even astronomic) scale that attract geochemists to study the solar system and beyond, and we see how some of the answers improve our understanding of the world under our feet.

Our solar system consists of a single star surrounded by nine planets and a large retinue of smaller bodies, including their satellites, asteroids, comets, and a lot of small rocks and dust. Samples of the small rocks and dust are provided free of charge as meteorites and interplanetary dust particles, and in some cases, these can be related to the parent planets or asteroids on which they formed. Cosmochemists focus on chemical differences and similarities among these bodies. To what extent have they evolved separately, and what characteristics have they inherited from a common origin? Which processes are unique in a given body, and which processes are likely to have affected all of them? Do they contain evidence for how the solar system formed, and how has it evolved to its present state?

Most (>99%) of the mass of our solar system is concentrated in the Sun, so many questions regarding the bulk chemistry of the solar system and its early history must first address the behavior and composition of stars. Here, we rely on astrophysicists to construct models that infer the structure and evolutionary development of stars in general. These are based on observations of the Sun and distant stars and on the principles of thermodynamics and nuclear chemistry we have discussed in earlier chapters, although the language of astrophysics is different from that of geochemistry.

From the Sun, we turn to the planets, which are usually divided into two groups. Those closest to the Sun (Mercury, Venus, Earth, and Mars) are called the terrestrial planets, to distinguish them from the larger Jovian planets beyond (Jupiter, Saturn, Uranus, and Neptune). The Jovian worlds are part rock and part ice, now transformed into unusual forms by high pressures. Pluto and its satellite Charon, small icy bodies at the outer reaches of the solar system, have unusual orbits and may be related to comets. In this chapter, we focus on the terrestrial planets, as they are more likely to provide geochemical insights into the Earth. The presence and compositions of the Jovian planets, however, place important restrictions on any models for the history of the solar system as a whole.

The terrestrial bodies include not only the four inner planets, but also the moons of Earth and Mars and several thousand asteroids. Studies of these, particularly of our own Moon, have helped geochemists to determine how planetary size affects differentiation and other global-scale processes. Lunar samples brought to Earth by Apollo astronauts, by Soviet unmanned spacecraft, and as meteorites are an important resource for cosmochemists. A small group of meteorites are also thought to have come from Mars. Some of the most valuable information about terrestrial bodies, however, is based on meteorites that are fragments of asteroids. Some asteroids experienced differentiation and core formation, producing igneous rocks (achondrites) and iron meteorites, whereas others (chondrites) remained almost unchanged after their parent asteroids accreted. From meteorites, we obtain data that can be used to model the development of planetary cores, mantles, and crusts. We also use the nearly pristine nature of chondrites to deduce the chemistry of materials from which the larger terrestrial planets were assembled.

We begin a survey of cosmochemistry by considering the Sun as a star, to find chemical clues to its origin and the origin of other solar system materials. As we proceed, our focus will be drawn more to the development of planets, and finally back to the Earth itself. In this tour, you will recognize many familiar geochemical concerns and, we hope, see the place of cosmochemistry in understanding how the Earth works.

ORIGIN AND ABUNDANCE OF THE ELEMENTS

Nucleosynthesis in Stars

The universe is believed to have begun in a cataclysmic explosion—the Big Bang—and has been expanding ever since. At this beginning stage, matter existed presumably in the form of a stew of neutrons or as simple atoms (hydrogen and deuterium). The Big Bang itself may have produced some other nuclides, but only ^{4}He was formed in any abundance. In chemical terms, this was a pretty dull universe. How then did all of the other elements originate?

Local concentrations of matter periodically coalesce to form stars. In 1957, Margaret Burbidge and her husband, Geoffrey Burbidge, along with William Fowler and Fred Hoyle, teamed together to write a remarkable scientific paper that argued that other elements formed in stellar interiors by nuclear reactions with hydrogen as the sole starting material. (This paper is now rightfully considered a classic, often referred to as B^{2}FH from the initials of the authors' surnames.) When hydrogen atoms are heated to sufficiently high temperatures and held together by enormous pressures—such as occur in the deep interior of the Sun—fusion reactions occur. The proton-proton chain, the dominant energy-producing reaction in the Sun, is illustrated in figure 15.1. This fusion process, commonly called hydrogen burning, produces helium. When the hydrogen fuel in the interior begins to run low and the stellar core becomes dense enough to sustain reactions at higher pressures, another nuclear reaction may take place, in which helium atoms are fused to make carbon and oxygen. While helium burning proceeds in the core of a star, a hydrogen-burning shell works its way toward the surface; a star at this evolutionary stage expands into a red giant. This will be the fate of our Sun.

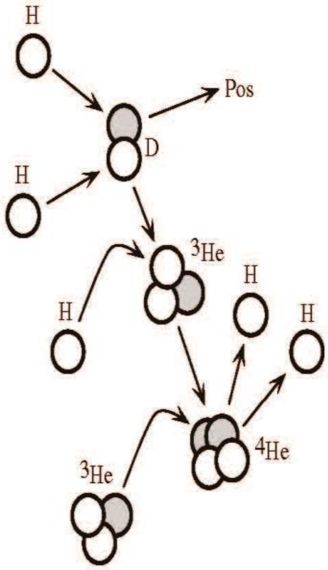

FIG. 15.1. The proton-proton chain, in which hydrogen atoms are fused into helium, is the predominant energy-producing reaction in the Sun. Open circles are protons, filled circles are neutrons, and Pos is a positron. For each gram of ^{4}He produced, 175,000 kwh of energy are released.

A star more massive than the Sun, however, can employ other fusion reactions, successively burning carbon, neon, oxygen, and silicon. The ashes from one burning stage provide the fuel for the next. The internal structure of such a massive, highly evolved star would then consist of many concentric shells, each of which produces fusion products that are then burned in the adjacent inward shell. The ultimate products of such fusion reactions are elements near iron in the periodic table (V, Cr, Mn, Fe, Co, and Ni). Fusion between nuclei cannot produce nuclides heavier than the iron group elements. For elements lighter than iron, the energy yield is higher for fusion reactions than for fission, but for elements heavier than iron, the energy yield for fission is greater. When a star reaches this evolutionary dead end, a series of both disintegrative and constructive nuclear reactions occurs among the iron group nuclei. After some time, a steady state, called *nuclear statistical equilibrium*, is reached; the relative abundances of iron group elements reflect this process.

Elements heavier than the iron group can be formed by addition of neutrons to iron group seed nuclei. We have already seen in chapter 14 that nuclei with neutron/proton ratios greater than the band of stability undergo beta decay to form more stable nuclei. Helium burning produces neutrons that are captured by iron group nuclei in a slow and rather orderly way, called the *slow* or *s process*. This process is slow enough that nuclei, if they are unstable, experience beta decay into stable nuclei before additional neutrons are added. This is illustrated in figure 15.2, in which stable and unstable nuclei are shown as white and gray boxes, respectively. A portion of the s process track is illustrated by the upper set of arrows. Neutrons are added (increasing *N*) until an unstable nuclide is produced; then beta decay occurs, resulting in a decrease of both *N* and *Z* by one. The resulting nuclide can then capture more neutrons until it beta decays again, and so forth. Notice that a helium burning star producing heavy elements by this process would have to be at least a second generation star, having somehow inherited iron group nuclei from an earlier star whose material had been recycled.

Fusion, nuclear statistical equilibrium, and s process neutron-capture reactions in massive stars thus provide mechanisms by which elements heavier than hydrogen can be produced. But how are these nuclides placed into interstellar space for later use in making planets, oceans, and people? Processed stellar matter is lost continuously from stars as fluxes of energetic ions, such as the solar wind. Other elements are liberated by supernovae—stellar explosions that scatter matter over vast distances. At the same time, supernovae generate other nuclides by a different nucleosynthetic pathway, the *rapid* or *r process*. Very rapid addition of neutrons to seed nuclei results in a chain of unstable nuclides.

One example of the r process is illustrated by the set of arrows at the bottom of figure 15.2. Reaching this part of the diagram, which is populated by unstable nuclei, happens only when neutrons are added more rapidly than the resulting nuclei can decay. The nuclides in crosshatched boxes decay much more rapidly than the seconds or minutes required for the decay of nuclides occupying gray boxes, so a nucleus shifted into a crosshatched box by r-process neutron capture immediately transforms by beta decay, as shown. When the supernova event ends, the r process nuclides transform more slowly by successive beta decays into stable nuclides. Many of these stable isotopes are the same as produced by the s process but some, such as ^{86}Kr, ^{87}Rb, and ^{96}Zr, can be reached only by the r process. In an analogous manner, such nuclides

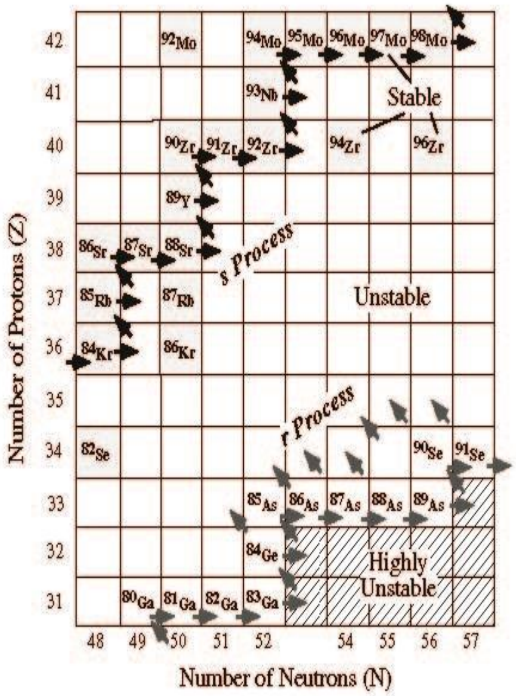

FIG. 15.2. A portion of the nuclide chart, illustrating how the s process (upper set of arrows) and the r process (lower set of arrows) produce new elements by neutron capture and subsequent decay. Shaded boxes represent stable nuclides, whereas white boxes are unstable and undergo beta decay, which shifts them up and to the left. Crosshatched boxes represent extremely unstable nuclides that transform rapidly by neutron capture.

as ^{92}Mo (fig. 15.2) on the proton-rich side of the s process band can be produced during supernovae by addition of protons to seed nuclei (the *p process*), followed by positron emission or electron capture.

Cosmic Abundance Patterns

The relative abundances of the elements in a star, then, are controlled by a combination of nucleosynthetic processes. For the moment, let's ignore how stellar or solar abundances are determined (we return to this problem shortly). Elemental abundances in the Sun, relative to 10^6 atoms of silicon, are given in table 15.1 and illustrated graphically in figure 15.3. (Normalization to silicon keeps these numbers from being astronomically large.) This abundance pattern is commonly called the *cosmic abundance of the elements*. This is a misnomer, of course; the composition of our Sun is not necessarily representative of that of the universe, but it does define the composition of our own solar system. Other stars have their own peculiar compositions because of different contributions from fusion, s and r processes, and so forth.

Let's inspect the cosmic abundance pattern in figure 15.3 to see why the Sun has this particular composition. Clearly, hydrogen and helium are the dominant elements. This is because only these two emerged from the Big Bang. Elements between helium and the iron group formed predominantly by fusion reactions. These show a rapid exponential decrease with increasing atomic number, reflecting decreasing production in the more advanced burning cycles. The Sun is presently burning only hydrogen, so these elements must have been inherited from an earlier generation of stars. Exceptions are the elements lithium, beryllium, and boron, which have abnormally low abundances. The abundances of these

TABLE 15.1. Cosmic Abundances of the Elements, Based on 10^6 Silicon Atoms

Atomic Number	Element	Symbol	Abundance	Atomic Number	Element	Symbol	Abundance
1	Hydrogen	H	2.79×10^{10}	45	Rhodium	Rh	0.344
2	Helium	He	2.72×10^{9}	46	Palladium	Pd	1.39
3	Lithium	Li	57.1	47	Silver	Ag	0.486
4	Beryllium	Be	0.73	48	Cadmium	Cd	1.61
5	Boron	B	21.2	49	Indium	In	0.184
6	Carbon	C	1.01×10^{7}	50	Tin	Sn	3.82
7	Nitrogen	N	3.13×10^{6}	51	Antimony	Sb	0.309
8	Oxygen	O	2.38×10^{7}	52	Tellurium	Te	4.81
9	Fluorine	F	843	53	Iodine	I	0.90
10	Neon	Ne	3.44×10^{6}	54	Xenon	Xe	4.7
11	Sodium	Na	5.74×10^{4}	55	Cesium	Cs	0.372
12	Magnesium	Mg	1.074×10^{6}	56	Barium	Ba	4.49
13	Aluminum	Al	8.49×10^{4}	57	Lanthanum	La	0.4460
14	Silicon	Si	1.00×10^{6}	58	Cerium	Ce	1.136
15	Phosphorus	P	1.04×10^{4}	59	Praseodymium	Pr	0.1669
16	Sulfur	S	5.15×10^{5}	60	Neodymium	Nd	0.8279
17	Chlorine	Cl	5240	61	Promethium[1]	Pm	—
18	Argon	Ar	1.01×10^{5}	62	Samarium	Sm	0.2582
19	Potassium	K	3770	63	Europium	Eu	0.0973
20	Calcium	Ca	6.11×10^{4}	64	Gadolinium	Gd	0.3300
21	Scandium	Sc	34.2	65	Terbium	Tb	0.0603
22	Titanium	Ti	2400	66	Dysprosium	Dy	0.3942
23	Vanadium	V	293	67	Holmium	Ho	0.0889
24	Chromium	Cr	1.35×10^{4}	68	Erbium	Er	0.2508
25	Manganese	Mn	9550	69	Thulium	Tm	0.0378
26	Iron	Fe	9.00×10^{5}	70	Ytterbium	Yb	0.2479
27	Cobalt	Co	2250	71	Lutetium	Lu	0.0367
28	Nickel	Ni	4.93×10^{4}	72	Hafnium	Hf	0.154
29	Copper	Cu	522	73	Tantalum	Ta	0.0207
30	Zinc	Zn	1260	74	Tungsten	W	0.133
31	Gallium	Ga	37.8	75	Rhenium	Re	0.0517
32	Germanium	Ge	119	76	Osmium	Os	0.675
33	Arsenic	As	6.56	77	Iridium	Ir	0.661
34	Selenium	Se	62.1	78	Platinum	Pt	1.34
35	Bromine	Br	11.8	79	Gold	Au	0.187
36	Krypton	Kr	45	80	Mercury	Hg	0.34
37	Rubidium	Rb	7.09	81	Thallium	Tl	0.184
38	Strontium	Sr	23.5	82	Lead	Pb	3.15
39	Yttrium	Y	4.64	83	Bismuth	Bi	0.144
40	Zirconium	Zr	11.4	90	Thorium	Th	0.0335
41	Niobium	Nb	0.698	91	Protactinium[1]	Pa	—
42	Molybdenum	Mo	2.55	92	Uranium	U	0.0090
43	Technetium[1]	Tc	—	84–89	Unstable elements[1]		—
44	Ruthenium	Ru	1.86				

Data from Anders and Grevesse (1989).

[1] Unstable element.

three elements may have been reduced in the Sun by bombardment with neutrons and protons, although the production processes just discussed tend to bypass these elements. The peak corresponding to the iron group elements represents nuclides formed by nuclear statistical equilibrium, also an addition from earlier stars. The abundances in the Sun of elements heavier than iron reflect additions of materials formed in supernovae.

Superimposed on the peaks and valleys in figure 15.3 is a peculiar sawtooth pattern, caused by higher abundances of elements with even rather than odd atomic numbers (Z). The even-numbered elements form a lopsided 98% of cosmic abundances, because nuclides with even atomic numbers are more likely to be stable, as already noted in chapter 14. This explanation, however, begs the question: Why are even-numbered atomic