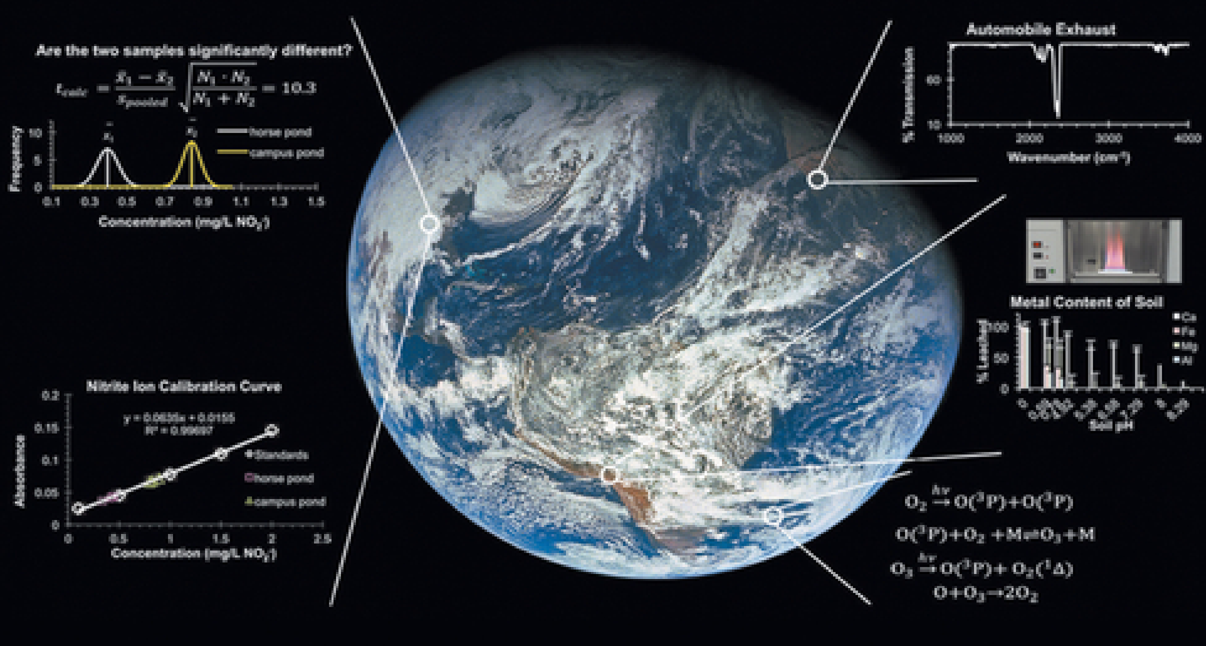
KENNETH S. OVERWAY

ENVIRONMENTAL CHEMISTRY

AN ANALYTICAL APPROACH



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10 9 8 7 6 5 4 3 2 1

Periodic Table of the Elements

1 **H** 1.00794*																1 **H** 1.00794*	2 **He** 4.002602
3 **Li** 6.941*	4 **Be** 9.012182											5 **B** 10.811*	6 **C** 12.0107*	7 **N** 14.00674*	8 **O** 15.9994*	9 **F** 18.9984032	10 **Ne** 20.1797
11 **Na** 22.98976928	12 **Mg** 24.3050											13 **Al** 26.9815386	14 **Si** 28.0855*	15 **P** 30.973762	16 **S** 32.066*	17 **Cl** 35.4527*	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.955912	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938045	26 **Fe** 55.845	27 **Co** 58.933195	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90585	40 **Zr** 91.224	41 **Nb** 92.90638	42 **Mo** 95.96	43 **Tc** (97.9072)	44 **Ru** 101.07	45 **Rh** 102.90550	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.90447	54 **Xe** 131.293
55 **Cs** 132.9054519	56 **Ba** 137.327	57 **La** 138.90547	72 **Hf** 178.49	73 **Ta** 180.94788	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.966569	80 **Hg** 200.59	81 **Tl** 204.3833*	82 **Pb** 207.2	83 **Bi** 208.98040	84 **Po** (208.9824)	85 **At** (209.9871)	86 **Rn** (222.0176)
87 **Fr** (223.0197)	88 **Ra** (226.0254)	89 **Ac** (227.0278)	104 **Rf** (265.1167)	105 **Db** (268.125)	106 **Sg** (271.133)	107 **Bh** (270)	108 **Hs** (277.150)	109 **Mt** (276.151)	110 **Ds** (281.162)	111 **Rg** (280.164)	112 **Cn** (285.174)	113 **Uut** (284.178)	114 **Fl**** (289.187)	115 **Uup** (288.192)	116 **Lv**** (293)	117 **Uus** (294)	118 **UUo** (294)

58 **Ce** 140.116	59 **Pr** 140.90765	60 **Nd** 144.242	61 **Pm** (144.9127)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.92535	66 **Dy** 162.500	67 **Ho** 164.93032	68 **Er** 167.259	69 **Tm** 168.93421	70 **Yb** 173.054	71 **Lu** 174.9668
90 **Th** 232.03806	91 **Pa** 231.03588	92 **U** 238.02891	93 **Np** (237.0482)	94 **Pu** (244.0642)	95 **Am** (243.0614)	96 **Cm** (247.0704)	97 **Bk** (247.0703)	98 **Cf** (251.0796)	99 **Es** (252.0830)	100 **Fm** (257.0951)	101 **Md** (258.0984)	102 **No** (259.1010)	103 **Lr** (262.1096)

S.E. Van Bramer 8/29/2012
* 1995 IUPAC Values from Pure Appl. Chem., Vol 68, No. 12, pp. 2339-2359, 1996. doi: 10.1351/pac199668122339, http://pac.iupac.org/publications/pac/pdf/1996/pdf/6812x2339.pdf
**Names for elements 114 and 116 are from Pure Appl. Chem., Vol. 84, No. 7, pp. 1669–1672, 2012. doi: 10.1351/PAC-REC-11-12-03
All other values from: 2009 IUPAC Values from Pure Appl. Chem., Vol. 83, No. 2, pp. 359–396, 2011. doi:10.1351/PAC-REP-10-09-14, http://pac.iupac.org/publications/pac/pdf/2011/pdf/8302x0359.pdf
-Elements with one weight have uncertainty in the last digit.
-Elements with the weight in parenthesis, weight is given for the longest lived isotope.

Electronegativity Table of the *p*-block Elements

				1 **H** 2.20	2 **He**
5 **B** 2.04	6 **C** 2.55	7 **N** 3.04	8 **O** 3.44	9 **F** 3.98	10 **Ne**
13 **Al** 1.61	14 **Si** 1.90	15 **P** 2.19	16 **S** 2.58	17 **Cl** 3.16	18 **Ar**
31 **Ga** 1.81	32 **Ge** 2.01	33 **As** 2.18	34 **Se** 2.55	35 **Br** 2.96	36 **Kr**
49 **In** 1.78	50 **Sn** 1.96	51 **Sb** 2.05	52 **Te** 2.10	53 **I** 2.66	54 **Xe** 2.60
49 **Ti** 1.8	50 **Pb** 1.8	51 **Bi** 1.9	52 **Po** 2.0	53 **At** 2.2	54 **Rn**

CONTENTS

PREFACE

Careful readers of this textbook will find it difficult to avoid the conclusion that the author is a cheerleader for collegiate General Chemistry. I have taught General Chemistry at various schools for over a decade and still enjoy the annual journey that takes me and the students through a wide array of topics that explain some of the microscopic and macroscopic observations that we all make on a daily basis. The typical topics found in an introductory sequence of chemistry courses really do provide a solid foundation for understanding most of the environmental issues facing the world's denizens. After teaching Environmental Chemistry for a few years, I felt that the textbooks available were missing some key features.

Similar to a movie about a fascinating character, an origin story is needed. In order to appreciate the condition and dynamism of our current environment, it is important to have at least a general sense of the vast history of our planet and of the dramatic changes that have occurred since its birth. The evolution of the Earth would not be complete without an understanding of the origin of the elements that compose the Earth and all of its inhabitants. To this end, I use Chapter 1 to develop an abridged, but hopefully coherent, evolution of our universe and solar system. It is pertinent that this origin story is also a convenient occasion to review some basic chemical principles that should have been learned in the previous courses and will be important for understanding the content of this book.

As a practical matter when teaching Environmental Chemistry, I was required to supplement other textbooks with a primer on measurement statistics. My students and I are making environmental measurements soon after the course begins, so knowing how to design an analysis and process the results is essential. In Chapter 2, I provide a minimal introduction to the nature of measurements and the quantitative methods and tools used in the process of testing environmental samples. This analysis relies heavily on the use of spreadsheets, a skill that is important for any quantitative scientist to master. This introduction to measurements is supplemented by an appendix that describes several of the instruments one is likely to encounter in an environmental laboratory.

Finally, the interdependence of a certain part of the environment with many others becomes obvious after even a casual study. A recursive study of environmental principles, where the complete description of an environmental system requires one to back up to study the underlying principles and the exhaustive connections between other systems followed by a restudy of the original system, is the natural way that many of us have learned about the environment. It does not, however, lend itself to the encapsulated study that a single semester represents. Therefore, I have divided the environment into the three interacting domains of The Atmosphere (Chapter 3), The Lithosphere (Chapter 4), and The Hydrosphere (Chapter 5). In each chapter, it is clear that the principles of each of these domains affect the others. Studies of the environment beyond a semester will require a great deal of recursion and following tangential topics in order to understand the whole, complicated picture. Such is the nature of most deep studies, and this textbook will hopefully provide the first steps in what may be a career-long journey.

Shall we begin?

Ken Overway
Bridgewater, Virginia
December, 2015

ABOUT THE COMPANION WEBSITE

This book is accompanied by a companion website:

www.wiley.com/go/overway/environmental_chemistry

The website includes:

- Powerpoint Slides of Figures
- PDF of Tables
- Regression Spreadsheet Template

INTRODUCTION

You are “greener” than you think you are. What I mean is that you have been twice recycled. You probably are aware that all of the molecules that make up your body have been recycled from the previous organisms, which is similar to the chemical cycles you will read about later in this book, such as the carbon cycle and the nitrogen cycle. The Earth is nearly a closed system, and it receives very little additional matter from extraterrestrial sources, except for the occasional meteor that crashes to the Earth. So, life must make use of the remains of other organism and inanimate sources in order to build organism bodies.

What you may not have been aware of is that the Earth and the entire solar system in which it resides were formed from the discarded remains of a previous solar system. This must be the case since elements beyond helium form only in the nuclear furnace of stars. Further, only in the core of a giant star do elements beyond carbon form, and only during the supernova explosion of a giant star do elements beyond iron form. Since the Earth contains all of these elements, it must be the result of at least a previous solar system. This revelation should not be entirely unexpected when you examine the vast difference between the age of the universe (13.8 billion years old) and the age of our solar system (4.6 billion years old). What happened during the 9.2 billion year gap? How did our solar system form? How did the Earth form? What are the origins of life? To answer these questions, the story of the chemical history of the universe since the Big Bang is required. Much of what you learned in General Chemistry will help you understand the origin of our home planet. It may seem like it has been 13.8 billion years since your last chemistry course, so a review is warranted. Ready?

1

ORIGINS: A CHEMICAL HISTORY OF THE EARTH FROM THE BIG BANG UNTIL NOW – 13.8 BILLION YEARS OF REVIEW

> Not only is the Universe stranger than we imagine, it is stranger than we can imagine.
>
> —Sir Arthur Eddington

> I'm astounded by people who want to 'know' the universe when it's hard enough to find your way around Chinatown.
>
> —Woody Allen

1.1 INTRODUCTION

Georges-Henri Lemaître (1894–1966), a Jesuit priest and physicist at Université Catholique de Louvain, was the first person to propose the idea of the Big Bang. This theory describes the birth of our universe as starting from a massive, single point in space at the beginning of time (literally, $t = 0$ s!), which began to expand in a manner that could loosely be called an explosion. Another famous astrophysicist and skeptic of Lemaître's hypothesis, Sir Fred Hoyle (1915–2001), jeeringly called this the "Big Bang" hypothesis. Years later, with several key experimental predictions having been observed, the Big Bang is now a theory. Lemaître developed his hypothesis from solutions to Albert Einstein's (1879–1955) theory of general relativity. Since this is not a mathematics book, and I suspect you are not interested in tackling the derivation of these equations (neither am I), so let us examine the origin of our environment and the conditions that led to the Earth that we inhabit. This chapter is not meant to be a rigorous and exhaustive explication of the Big Bang and the evidence for the evolution of the universe, which would require a deep background in atomic particle physics and cosmology. Since this is an environmental chemistry text, I will only describe items that are relevant for the environment in the context of a review of general chemistry.

1.2 THE BIG BANG

1.2.1 The Microwave Background

The first confirmation of the Big Bang comes from the prediction and measurement of what is known as the microwave background. Imagine you are in your kitchen and you turn on an electric stove. If you placed your hand over the burner element, you would feel it heat up. This feeling of heat is a combination of the convection of hot air touching your skin

Environmental Chemistry: An Analytical Approach, First Edition. Kenneth S. Overway.

Companion website: www.wiley.com/go/overway/environmental_chemistry

and infrared radiation. As the heating element warms up, you would notice the color of it changes from a dull red to a bright orange color. If it could get hotter, it would eventually look whitish because it is emitting most of the colors of the visible spectrum. What you have observed is Wien's Displacement Law, which describes blackbody radiation.

$$\lambda_{max} = \frac{2.8977685 \times 10^{-3}\,\frac{\text{m}}{\text{K}}}{T} \tag{1.1}$$

This equation shows how the temperature (T) of some black object (black so that the color of the object is not mistaken as the reflected light that gives an apple, e.g., its red or green color) affects the radiation (λ_{max}) the object emits. On a microscopic level, the emission of radiation is caused by electrons absorbing the heat of the object and converting this energy to light.

Gamma rays: Excites energy levels of the nucleus; sterilizing medical equipment **X-Rays:** Refracts from the spaces between atoms and excites core e^-; provides information on crystal structure; used in medical testing **Ultraviolet:** Excites and breaks molecular bonds; polymerizing dental fillings **Visible:** Excites atomic and molecular electronic transitions; our vision **Infrared:** Excites molecular vibrations; night vision goggles **Microwave:** Excites molecular rotations; microwave ovens **Radio waves:** Excites nuclear spins; MRI imaging and radio transmission

Table 1.1 Certain regions of the electromagnetic (EM) spectrum provide particular information about matter when absorbed or emitted.

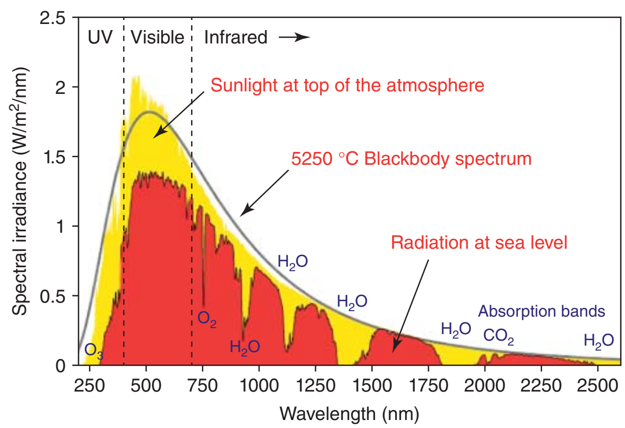

Figure 1.1 Another view of the solar radiation spectrum showing the difference between the radiation at the top of the atmosphere and at the surface. Source: Robert A. Rhode http://en.wikipedia.org/wiki/File:Solar_Spectrum.png. Used under BY-SA 3.0 //creative commons.org/licenses/by-sa/3.0/deed.en.

The λ_{max} in Wien's equation represents, roughly, the average wavelength of a spectrum, such as in Figure 1.1, which shows the emission spectrum of the Sun. Wien's Law also lets us predict the temperature of different objects, such as stars, by calculating T from λ_{max}.

Robert Dicke (1916–1977), a physicist at Princeton University, predicted that if the universe started out as a very small, very hot ball of matter (as described by the Big Bang) it would cool as it expanded. As it cooled, the radiation it would emit would change according to Wien's Law. He predicted that the temperature at which the developing universe would become transparent to light would be when the temperature dropped below 3000 K. Given that the universe has expanded a 1000 times since then, the radiation would appear red-shifted by a factor of 1000, so it should appear to be 3 K. How well does this compare to the observed temperature of the universe?

☞ For a review of the EM spectrum, see Review Example 1.1 on page 22.

When looking into the night sky, we are actually looking at the leftovers of the Big Bang, so we should be seeing the color of the universe as a result of its temperature. Since the night sky is black except for the light from stars, the background radiation from the Big Bang must not be in the visible region of the spectrum but in lower regions such as the infrared or the microwave region. When scientists at Bell Laboratories in New Jersey used a large ground-based antenna to study emission from our Milky Way galaxy in 1962, they observed a background noise that they could not eliminate no matter which direction they pointed the antenna. They also found a lot of bird poop on the equipment, but clearing that out did not eliminate the "noise." They finally determined that the noise was the background emission from the Big Bang, and it was in the microwave region of the EM spectrum (Table 1.1), just as Dicke predicted. The spectral temperature was measured to be 2.725 K. This experimental result was a major confirmation of the Big Bang Theory.

Blackbody Radiation

The electric heater element (Figure 1.2) demonstrates blackbody radiation. Any object that has a temperature above 0 K will express its temperature by emitting radiation that is proportional to its temperature. Wien's Displacement Law gives the relationship between the average wavelength of the radiation and the temperature. The Earth emits infrared radiation as a result of its temperature, and this leads to the greenhouse effect, which is discussed later. The person in the photos in Figure 1.3 also emits radiation in the infrared, allowing an image of his arm and hand to be seen despite the visible opacity of the plastic bag.

Figure 1.2 A glowing electric stove element. Courtesy K. Overway.

Figure 1.3 While visible radiation cannot penetrate the plastic bag, the infrared radiation, generated by the blackbody radiation of the man's body, can. Source: NASA.

Infrared Thermography

Infrared thermography is an application of Wien's Law and is a key component of a home energy audit. One of the most cost-effective ways to conserve energy is to improve the insulation envelope of one's house. Handheld infrared cameras, seen in Figure 1.4, allow homeowners or audit professionals to see air leaks around windows and doors. On a cold day, an uninsulated electrical outlet or poorly insulated exterior wall could be 5–8 °F colder than the surroundings. When the handheld thermal camera is pointed at a leak, the image that appears on the screen will clearly identify it by a color contrast comparison with the area around it.

Figure 1.4 A thermal camera used to find cold spots in a leaky house. Source: Passivhaus Institut "http://en.wikipedia.org/wiki/File:SONEL_KT-384.jpg." Used under BY-SA 3.0 //creativecommons.org/licenses/by-sa/3.0/deed.en.

Example 1.1: Blackbody Radiation

Wien's Displacement Law is an important tool for determining the temperature of objects based on the EM radiation that they emit and predicting the emission profile based on the temperature of an object.

1. Using Wien's Displacement Law (Eq. (1.1)), calculate the λ_{max} for a blackbody at 3000 K.
2. Using Wien's Displacement Law, calculate the λ_{max} for the Earth, which has an average surface temperature of 60 °F.
3. In which portion of the EM spectrum is the λ_{max} for the Earth?

Solution: See Section A.1 on page 231.

After the development of modern land-based and satellite telescopes, scientists observed that there were other galaxies in the universe besides our own Milky Way. Since this is true, the universe did not expand uniformly – with some clustering of matter in some places and very little matter in others. Given what we know of gravity, the clusters of matter would not expand at the same rate as matter that is more diffuse. Therefore, there must be some hot and cold spots in the universe, and the microwave background should show this. In 1989, an advanced microwave antenna was launched into space to measure this predicted heterogeneity of temperature. Further studies and better satellites produced an even finer measurement of the microwave background. The observation of the heterogeneity of the microwave background is further direct and substantial evidence of the Big Bang theory.

1.2.2 Stars and Elements

In the late 19th century, the Harvard College observatory was the center of astrophotography (see Pickering's "Harem" featurette). Astronomers from this lab were among the first to see that the colors of stars could be used to determine their temperatures and their compositions. When the EM radiation from these stars is passed through a prism, the light is dispersed into its component wavelengths, much like visible light forms a rainbow after it passes through a prism. An example of such a spectrum can be seen in Figure 1.5. Blackbody radiation (described by Wien's Law) predicts that the spectrum of the Sun should be continuous – meaning it should contain the full, unbroken spectrum – but Figure 1.5 shows that this is obviously not the case. The black lines in the spectrum indicate the presence of certain atoms and molecules in the outer atmosphere of the Sun that are absorbing some very specific wavelengths of light out of the solar spectrum. The position of the lines is a function of the energy levels of the electrons in the atoms and can be treated as an atomic fingerprint. The same sort of phenomenon happens to sunlight that reaches the surface of the Earth and is related to two very important functions of the Earth's atmosphere (see Figure 1.1), the ozone layer and the greenhouse effect, which you will learn about in Chapter 3.

Pickering's "Harem" (1913) Edward Charles Pickering, who was a director of the Harvard College Observatory in the late 19th century, had a workforce of young men acting as "computers" – doing the very tedious work of calculating and categorizing stars using the astrophotographs that the observatory produced. In 1879, Pickering hired Williamina Fleming, an immigrant who was a former teacher in Scotland but recently struck by misfortune (abandoned by her husband while pregnant) as a domestic servant. Sometime after having noticed Fleming's intelligence, Pickering was reported to have said to one of his male computers that his housekeeper could do a better job. He hired her and went on to hire many more women because they were better at computers than their male counterparts, and they were paid about half the wages of the men (meaning Pickering could hire twice as many of them!). This group came to be known as "Pickering's Harem" and produced several world-renowned female astronomers that revolutionized the way we understand stars and their composition. Source: Harvard-Smithsonian Center for Astrophysics (https://www.cfa.harvard.edu/jshaw/pick.html). See Kass-Simon and Farnes (1990, p. 92).

☞ For a review of the interactions between light and matter, see Review Example 1.2 on page 23.

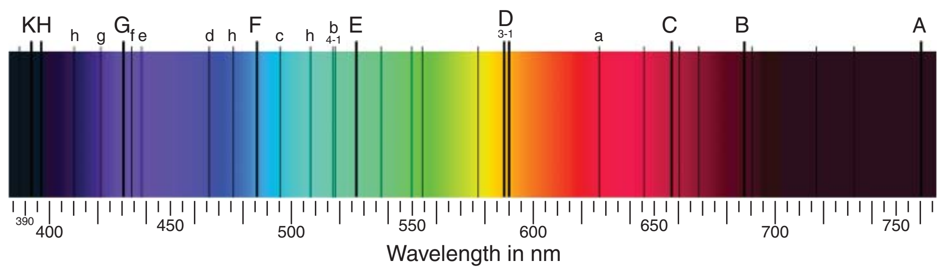

Figure 1.5 A solar spectrum showing the absorption lines from elements that compose the outer atmosphere of the Sun. Notice the sodium "D" lines, the hydrogen "C" line, and the "A" and "B" lines associated with O_2. Source: https://en.wikipedia.org/wiki/File:Fraunhofer_lines.svg.

Prefix Name	Symbol	Value
tera	T	10^{12}
giga	G	10^{9}
mega	M	10^{6}
kilo	k	10^{3}
hecto	h	10^{2}
deka	d	10^{1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}

Table 1.2 Common metric prefixes and their numerical values.

The result of all of the early astrophotography was the realization that the Sun was made mostly out of hydrogen, an unknown element, and trace amounts of other elements such as carbon and sodium. The spectroscopic fingerprint of this unknown element was so strong that scientists named it after the Greek Sun god Helios. Helium was eventually discovered on the Earth in 1895 as a by-product of radioactive decay processes in geologic formations. Early astronomers realized that the Sun and other stars contained a variety of different elements, other than hydrogen and helium, in their photospheres. Some of these elements were the result of fusion processes in the core of the stars, and other elements are the result of a star's formation from the remains of a previous generation of stars. The study of the life cycle of stars and nuclear fusion processes continued through the 20th century with the use of increasingly more powerful particle accelerators and telescopes. These studies have allowed physicists to understand the formation of the universe and the deep chasm of time between the Big Bang and the present day. In order to understand the origin of matter and the chemical principles that allow us to understand environmental chemistry, we need to take a closer look at the time line of our universe.

1.2.3 Primordial Nucleosynthesis

All of the evidence for the Big Bang may be interesting, but as an environmental chemist, you are probably wondering where all of the elements in the periodic table came from and why the Earth is the way it is (iron/nickel core, silicate crust, oceans, an atmosphere containing mostly nitrogen and oxygen). All of these elements were made in a process known as nucleosynthesis, which happened in three stages and at different points in the history of the universe.

In the initial seconds after the Big Bang, temperatures were so high that elements did not exist. As the universe cooled, the subatomic particles that chemists would recognize, protons, neutrons, and electrons, began to form. Most of the matter was in the form of hydrogen (around 75%) and helium (25%), with a little bit of lithium and other heavier elements. For a long time, temperatures were too high to allow the formation of neutral atoms, so matter existed as a plasma in much of the first half million years of the universe, with electrons separated from nuclei. Electrostatic repulsion was still present, and it prevented nucleons from combining into heavier elements. Eventually, the universe cooled enough and neutral atoms formed. The matter of the universe, at this point, was locked into mostly the elements of hydrogen and helium. It would take about 100 Myrs before heavier elements would form as a result of the birth of stars.

☞ For a review of atomic structure, see Review Example 1.4 on page 24.

☞ For a review of metric prefixes, see Review Example 1.3 on page 24.

1.2.4 Nucleosynthesis in Massive Stars

When the clouds of hydrogen and helium coalesced into the first stars, they began to heat up. The lowest energy fusion reactions are not possible until the temperature reaches about 3×10^6 Kelvin, so these protostars would only have been visible once they were hotter than about 3000 K when their blackbody radiation would have shifted into the visible spectrum. Synthesis of heavier elements, such as iron, requires temperatures around 4×10^9 Kelvin. Not all stars can reach this temperature. In fact, the surface temperature of our Sun is around 5800 K, and the core temperature is about 15×10^6 K, which is not even hot enough to produce elements such as carbon in significant amounts. Given that our Earth has a core made of mostly iron, a crust made from silicon oxides, and the asteroid belt in our solar system is composed of meteors that contain mostly iron-based rocks, our solar system must be the recycled remnants of a much larger and hotter star. High-mass stars are the element factories of the universe and develop an onion-like structure over time, where each layer has a different average temperature and is dominated by a different set of nuclear fusion reactions. As you can see from Figure 1.6, the two most abundant elements (H and He) were the result of primordial nucleosynthesis. The remaining peaks in the graph come from favored products of nuclear reactions, which occur in the various layers in a high-mass star. The layers are successively hotter than the next as a result of the increased density and pressure that occur as the star evolves. These layers develop over the life of the star as it burns through each set of nuclear fuel in an accelerating rate.

First-generation high-mass stars began their life containing the composition of the universe just after the Big Bang with about a 75:25 ratio of hydrogen and helium. Their lifetime was highly dependent on their mass, with heavier stars having shorter life cycles, thus the times provided in the following description are approximate. During the first 10 Myrs of the life of a high-mass star, it fuses hydrogen into helium. These reactions generate a lot of energy since the helium nucleus has a high binding energy. The release of energy produces the light and the heat that are necessary to keep the star from collapsing under the intense gravity (think of the Ideal Gas Law: $PV = nRT$ and the increase in volume that comes with an increase in temperature). The helium that is produced from the hydrogen fusion reactions sinks to the core since it is more dense. This generates a stratification as the core is enriched in nonreactive helium and hydrogen continues to fuse outside the core.

Once most of the hydrogen fuel is exhausted, the star starts to lose heat, and the core begins to collapse under the immense gravitational attraction of the star's mass. The helium nuclei cannot fuse until the electrostatic repulsion between the +2 nuclear charges of the

H Fusion Layer ($T \approx 3 \times 10^6$ K)
Hydrogen fusion involves several processes, the most important of which is the proton–proton chain reaction or P–P Chain. The P–P chain reactions occur in all stars, and they are the primary source of energy produced by the Sun. Hydrogen nuclei are fused together in a complicated chain process that eventually results in a stable He-4 nucleus.

$$^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{2}_{1}\mathrm{H} + {}^{0}_{+1}\beta^{+} + \nu_e \quad \text{(R1.1)}$$

$$^{2}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{0}_{0}\gamma \quad \text{(R1.2)}$$

$$^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} \rightarrow {}^{4}_{2}\mathrm{He} + 2{}^{1}_{1}\mathrm{H} \quad \text{(R1.3)}$$

For your convenience, here is a summary of nuclear particles you will see.
alpha particle (${}^{4}_{2}\alpha$ **or** ${}^{4}_{2}$He) a helium-4 nucleus
beta particle (${}^{0}_{-1}\beta$) an electron, negligible mass
positron (${}^{0}_{+1}\beta^{+}$) antimatter electron, negligible mass
gamma particle (${}^{0}_{0}\gamma$) high-energy photon
neutrino (ν_e) very rare particle, negligible mass

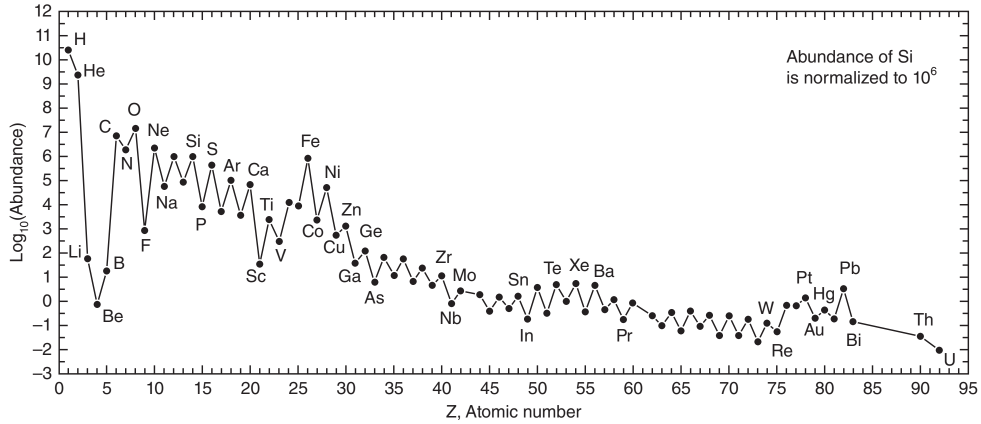

Figure 1.6 Relative abundances of the elements in the universe. Note that the *y*-axis is a logarithmic scale. Source: http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements. Used under BY-SA 3.0 //creativecommons.org/licenses/by-sa/3.0/deed.en.

☞ For a review of writing and balancing nuclear reactions, see Review Example 1.5 on page 25.

He Fusion Layer ($T \approx 1.8 \times 10^8$ K)
The fusion reaction that begins with helium is often referred to as the triple-alpha reaction, because it is a stepwise fusion of three nuclei.

$${}^{4}_{2}\text{He} + {}^{4}_{2}\text{He} \rightleftharpoons {}^{8}_{4}\text{Be} \qquad (R1.4)$$

$${}^{4}_{2}\text{He} + {}^{8}_{4}\text{Be} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{0}\gamma \qquad (R1.5)$$

To a small but significant extent, O-16 is also produced by the addition of another alpha particle.

C Fusion Layer ($T \approx 7.2 \times 10^8$ K)
Several different elements heavier than carbon are synthesized here.

$${}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \rightarrow {}^{24}_{12}\text{Mg} + {}^{0}_{0}\gamma \qquad (R1.6)$$

$${}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \rightarrow {}^{23}_{11}\text{Na} + {}^{1}_{1}\text{H} \qquad (R1.7)$$

$${}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \rightarrow {}^{20}_{10}\text{Ne} + {}^{4}_{2}\text{He} \qquad (R1.8)$$

$${}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \rightarrow {}^{16}_{8}\text{O} + 2{}^{4}_{2}\text{He} \qquad (R1.9)$$

O Fusion Layer ($T \approx 1.8 \times 10^9$ K)
Some example reactions involving oxygen fusion.

$${}^{16}_{8}\text{O} + {}^{16}_{8}\text{O} \rightarrow {}^{32}_{16}\text{S} + {}^{0}_{0}\gamma \qquad (R1.10)$$

$${}^{16}_{8}\text{O} + {}^{16}_{8}\text{O} \rightarrow {}^{31}_{15}\text{P} + {}^{1}_{1}\text{H} \qquad (R1.11)$$

$${}^{16}_{8}\text{O} + {}^{16}_{8}\text{O} \rightarrow {}^{31}_{16}\text{S} + {}^{1}_{0}\text{n} \qquad (R1.12)$$

$${}^{16}_{8}\text{O} + {}^{16}_{8}\text{O} \rightarrow {}^{30}_{14}\text{Si} + 2{}^{1}_{1}\text{H} \qquad (R1.13)$$

Ne Fusion Layer ($T \approx 1.2 \times 10^9$ K)
Some representative reactions involving neon.

$${}^{20}_{10}\text{Ne} + {}^{0}_{0}\gamma \rightarrow {}^{16}_{8}\text{O} + {}^{4}_{2}\text{He} \qquad (R1.14)$$

$${}^{20}_{10}\text{Ne} + {}^{4}_{2}\text{He} \rightarrow {}^{24}_{12}\text{Mg} + {}^{0}_{0}\gamma \qquad (R1.15)$$

nuclei is overcome, so no He fusion proceeds at the current temperature. As the pressure on the core increases, the temperature increases (think about the Ideal Gas Law again). Eventually, the core temperature increases to about 1.8×10^8 K, which is the ignition temperature of fusion reactions involving helium. As helium begins to fuse, the core stabilizes, and now the star has a helium fusion core and a layer outside of this where the remaining hydrogen fuses. The helium fusion core produces mostly carbon nuclei (along with other light nuclei), which are nonreactive at the core temperature, and thus, the carbon begins to sink to the center of the star forming a new core with a helium layer beyond the core and a hydrogen layer beyond that. The helium fusion process is much faster than hydrogen fusion, because helium fusion produces much less heat than hydrogen fusion so the star must fuse it faster in order to maintain a stable core (it would collapse if enough heat was not produced to balance gravity). Helium fusion lasts for about 1 Myrs.

The process described earlier repeats for the carbon core – collapse of the core, ignition of carbon fusion, pushing the remaining helium fusion out to a new layer, and a new-found stability. Carbon fusion produces a mixture of heavier elements such as magnesium, sodium, neon, and oxygen and lasts for about 1000 years because the binding energy difference between carbon and these other elements is even smaller, requiring a faster rate of reaction to produce the same heat as before. The new core eventually ignites neon, producing more oxygen and magnesium, pushing the remaining carbon fusion out to a new layer, and exhausting the neon supply after a few years. Next comes oxygen fusion, lasting only a year due to the diminishing heat production. The final major stage involves the ignition of silicon to form even heavier elements such as cobalt, iron, and nickel – lasting just seconds and forming the final core. At this point, the star resembles the onion-like structure seen in Figure 1.7 and has reached a catastrophic stage in its life cycle because iron and nickel are the most stable nuclei and fusing them with other nuclei consumes energy instead of generating it. The star has run out of fuel.

A dying star first cools and begins to collapse under its enormous mass. As it collapses, the pressure and temperature of the core rise, but there is no other fuel to ignite. Eventually, the temperature in the core becomes so immense that the binding energy holding protons and neutrons together in the atomic nuclei is exceeded. The result is a massive release of neutrons and neutrinos, and a supernova explosion results. Johannes Kepler (1571–1630) observed a supernova star in 1604. It was so bright that it was visible during the daytime.

The shock wave of neutrons that arises from the core moves through the other layers and causes the final stage of nucleosynthesis – neutron capture. All of the elements synthesized thus far undergo neutron capture and a subsequent beta emission reaction to produce an

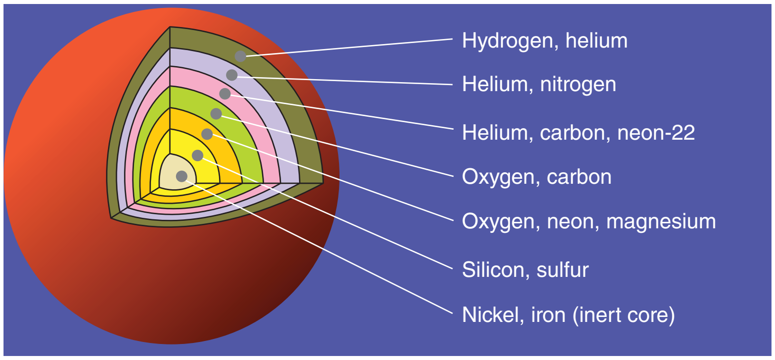

Figure 1.7 The onion-like layers of a giant star develop as it ages and approaches a supernova explosion. Source: http://commons.wikimedia.org/wiki/File:Massive_star_cutaway_pre-collapse_%28pinned%29.png. Used under CC0 1.0 //creativecommons.org/publicdomain/zero/1.0/deed.en.

element with a larger atomic number. This produces elements heavier than Fe-56.

$$^{56}_{26}\text{Fe} + {}^{1}_{0}n \rightarrow {}^{57}_{26}\text{Fe} \tag{R1.16}$$

$$^{57}_{26}\text{Fe} \rightarrow {}^{57}_{27}\text{Co} + {}^{0}_{-1}\beta \tag{R1.17}$$

The cobalt nucleus goes on to absorb another neutron and then beta-decays to form copper. This process continues until uranium is formed, which is the heaviest stable element in the periodic table. The couplet of Reactions R1.16 and R1.17 is just one example of an array of reactions where a single nucleus could absorb several neutrons (most probable since the supernova shock wave is neutron rich) and then undergoes beta decay. Eventually, the explosion blows off the outer layers of the star and forms an interstellar cloud of particles rich in elements from hydrogen to uranium. The core of the giant star either becomes a white dwarf star or, if the original star was very large, forms a black hole.

These massive stars have relatively short lives that are in the millions to hundreds of millions of years. Our Sun, which is a smaller star, will have a life span of about 10 Gyrs. The shock wave from a supernova explosion often causes the larger interstellar cloud from which the star formed to coalesce to form the next-generation star. Given the short life span of a high-mass star and given that they are the only stars massive enough to form the elements heavier than carbon, there may have been a few generations of stars that formed and exploded before our Sun formed some 9 Gyrs after the Big Bang.

Si Fusion Layer ($T \approx 3.4 \times 10^9$ K)
Silicon fusion involves a complicated series of alpha capture reactions that produce several of the elements between Si and Fe on the periodic table.

$$^{28}_{14}\text{Si} + {}^{4}_{2}\text{He} \rightarrow {}^{32}_{16}\text{S} \tag{R1.18}$$

$$^{32}_{16}\text{S} + {}^{4}_{2}\text{He} \rightarrow {}^{36}_{18}\text{Ar} \tag{R1.19}$$

$$^{36}_{18}\text{Ar} + {}^{4}_{2}\text{He} \rightarrow {}^{40}_{20}\text{Ca} \tag{R1.20}$$

This alpha capture continues until the nucleus of Ni-56 is produced, which is radioactive and has a half-life of 6 days. Ni-56 undergoes electron capture to form Co-56, which is also radioactive ($t_{1/2}$=77 days) and undergoes electron capture to form Fe-56. Thus, the final result of the very last fusion process in these giant stars is iron. This will be an important fact to remember, because it explains why iron is so abundant on the Earth and in the other terrestrial planets and asteroids.

1.2.5 Nucleosynthesis Summary

A short time after the Big Bang, the nuclei of hydrogen and helium formed, and as they cooled from a plasma to form neutral elements, the process of primordial nucleosynthesis ceased. Over a 100 million years later, the first stars began to form. The temperatures and pressures in the cores of these stars were enough to begin the process of fusion, converting hydrogen and helium into heavier nuclei. Small and medium stars, such as our Sun, usually do not produce elements heavier than carbon, whereas high-mass stars develop core temperatures high enough to synthesize elements through the first row of the transition metals (nickel and iron). Supernova explosions of high-mass stars complete the nucleosynthesis cycle by producing elements from iron to uranium through neutron capture and beta emission.

It is important to review the onion-like structure in these massive stars. As outlined earlier, there are stages where one of the products of one layer becomes the fuel for another layer. The accumulation of these elements (C, O, Si, and Fe) explains their relatively high abundance in second-, third-, and later-generation solar systems such as in the composition of the Earth.

The story of the Big Bang is a monumental achievement of brilliant scientists and powerful instrumentation that began when scientists observed differences between the spectra of stars, and now scientists use powerful telescopes and nuclear accelerators to study the processes of nucleosynthesis. It is still a field with a few mysteries left to uncover, such as the nature of Dark Matter. The most recent discovery came in July of 2012 with the announcement of the discovery of the Higgs Boson particle by the science team at the Large Hadron Collider.

Now that we know how the elements in the periodic table were produced and how the universe formed, the story of our home planet comes next. We need to zoom way in from the vastness of the universe to a single solar system in a galaxy that contains 100 billion stars. Carl Sagan summarized it best.

> We find that we live on an insignificant planet of a humdrum star lost in a galaxy tucked away in some forgotten corner of a universe in which there are far more galaxies than people.
> Sagan (1980, p. 193)

Yet this planet is very dear to us and represents the bounds of almost all we know. If humility is a virtue, then cosmology offers us plenty of that.

1.3 SOLAR NEBULAR MODEL: THE BIRTH OF OUR SOLAR SYSTEM

Pierre-Simon Laplace (1749–1827) proposed the precursor to the current solar nebular model at the end of the 18th century, describing the origin of our solar system consistent with the methodological naturalism that is a cornerstone of modern science. Legend has it (possibly apocryphal, but still instructive) that when Laplace explained his hypothesis to Napoleon Bonaparte, Napoleon asked, "How can this be! You made the system of the world, you explain the laws of all creation, but in all your book you speak not once of the existence of God!" Laplace responded with, "I did not need to make such an assumption." For Laplace, the solar system's formation could be explained by physical laws – there was no need to insert the "a miracle happened here" assumption. Scientists in pursuit of the chemical origins of life are increasingly coming to the same conclusion. Source: Pierre-Simon Laplace http://en.wikipedia.org/wiki/File:Pierre-Simon_Laplace.jpg. Used under CC0 (http://creativecommons.org/publicdomain/mark/1.0/deed.en). See Ball (1960, p. 343).

After one or more generations of high-mass stars lived their lives and ejected a soup of elements into the interstellar cloud from which they formed, the stage was set for the formation of our own solar system. The whole process probably took about 50 Myrs, but about 9 Gyrs after the Big Bang, an interstellar cloud on the outer edge of the Milky Way galaxy began to coalesce under the force of gravity. What started out as a collection of atoms, dust, rocks, and other debris began to collapse inward from all directions and adopt orbits around the center of mass. All of the orbits from all of the particles probably appeared nearly spherical from the outside, but as the cloud shrunk in size under the force of gravity, it started to flatten out. Much like an ice-skater that starts a spin with his arms out, as he pulls his arms inward, his rotational speed increases due to the conservation of angular momentum. This rotational speed increase eventually caused all of the random orbits of particles to spin around the center in the same direction and the cloud flattened into a disc.

At the center of the disc was most of the material from the cloud, but as the rotational speed increased, some of the particles of the cloud gained enough speed to establish a stable orbit around the center without continuing to collapse inward. Particles with similar stable orbits began to condense to local clusters and formed planetesimals – large chunks of material that would eventually form planets. The center of this rotating disc continued to gain mass to form a protostar – not hot enough to start fusion. As the particles and gas collided, they converted much of their momentum into heat. Within a certain radius from the center of the disc, called the frost line, temperatures were warm enough that the collapsing material remained gaseous and eventually became molten as terrestrial planets formed. These objects typically collected only the "rocky" material since the more volatile material did not condense and thus remained relatively small. Outside of the frost line, temperatures were low and gaseous, and icy planets formed. Planets beyond the frost line condensed very quickly because of the low temperatures, which caused the dust and gas to form larger and larger planetesimals, which had increasing gravitational force as the mass accumulated. This explains why the planets beyond the frost line (approximately the asteroid belt) are massive compared to the smaller, inner planets. The two largest known objects in the asteroid belt are Vesta, a rocky asteroid inside the frost line, and Ceres, a spherical icy asteroid outside of the frost line.

Eventually, the protostar at the center of this rotating disc reached 3×10^6 K and the process of hydrogen fusion began. When the Sun went nuclear, it began producing enough energy to eject charged particles, such as electrons and protons, known as the solar wind. As this wind swept through the newly formed solar system, it cleared away most of the interplanetary dust and gases that had not formed into planetesimals. What remained was the four terrestrial planets (Mercury, Venus, Earth, and Mars), still molten, and the large gaseous planets and planetoids outside of the frost line (Jupiter, Saturn, Uranus, Neptune, and the Kuiper Belt objects such as Pluto and Eris). This distinction between the inner and outer planets is a confirmation of the Solar Nebular Model, developed in the 18th century by Pierre-Simon Laplace (see featurette).

Another confirmation of the Solar Nebular Model is the orbits and orbital axes of the individual planets. All of the planets orbit the Sun in the same counterclockwise direction and in the same plane (except some objects in the Kuiper belt). The Sun and all of the planets, except two, also spin about their own axes in the counterclockwise direction – give or take a few degrees. The two exceptions are Venus, which rotates clockwise, and Uranus, which rotates on its side. While scientists are still trying to determine what happened to these two exceptions, the majority of the other planets give a cautious confirmation of the Solar Nebular Model. The Earth is a "well-behaved" planet with its counterclockwise rotation around its north pole. It is the most studied of the planets for a good reason – we live on it! Its formation is the next part of the story.

Geological Dates

Geologists and cosmologists use the unit *annum* to refer to time in the past. So, for example, 1 billion years ago would be 1 Ga (*giga annum*). In some textbooks, you might see this listed equivalently as 1 Gyrs, but the international standard method is to use annum. So, Ga, Ma, and ka in this text refer to 10^9, 10^6, and 10^3 years ago. You will see the Gyrs, Myrs, and kyrs used when a *duration* is used, which does not place the event in a geological or cosmic time line.

1.3.1 The Ages of the Earth

Over its 4.6 Gyr history,[1] the Earth has changed quite significantly. Most of this change has occurred over the first 3.8 Gyr – for nearly a billion years, the Earth has been relatively stable. In a snapshot overview, the Earth started out as molten and then cooled to form an atmosphere composed mostly of carbon dioxide and molecular nitrogen with acidic oceans rich in dissolved metals. The modern Earth has an oxidizing atmosphere with very little carbon dioxide, rich in molecular oxygen, a significant ozone layer, and basic oceans. These drastic changes have occurred over geologic eons. There is evidence to suggest that the changes described next were the result of abiotic and biotic forces. This statement bears repeating – the early forms of life on the Earth (archaebacteria, eubacteria, and others) have significantly contributed to the dramatic evolution of the entire planet.

1.3.1.1 Hadean Eon (4.6 to 4.0 Ga) During the earliest stages of development, the Earth was transformed from a molten planet to one with a solid crust in a process termed *accretion*. Earth's accretion process took about 10–100 million years, during which it was being bombarded by dust, debris, and other planetesimals in and near its orbit. One important collision between the proto-Earth and a planetesimal the size of Mars, approximately 45 Myrs after the formation of the solar system, led to the formation of the Moon and added the last

☞ *Accretion* is the process by which an object grows by acquiring additional mass. In the accretion of Earth, debris in the orbit was accumulated along with bombardment by asteroids from outside the Earth's orbit.

[1]Geologic time intervals vary from source to source, but the ranges presented in this chapter come from the 2010 designations set by the International Commission on Stratigraphy. Extensive charts can be viewed on their website (http://www.stratigraphy.org).

10% of the Earth's mass, finalized the spin velocity, and set the final tilt angle at about 23° from the vertical.

A combination of heating from radioactive decay and impact heat from collisions kept the Earth molten or caused frequent remelting throughout the early part of this eon. It is even likely that soon after some of the early oceans formed, meteor impacts caused the oceans to revaporize. Because the Earth was spinning while it was molten, its angular momentum caused the Earth to form an oblate spheroid (it is fatter around the middle than from pole to pole) and not a perfect sphere.

☞ *Differentiation* is the process by which the molten material of the early Earth separated, according to density, with the lighter material on the surface and the denser material in the core.

The various elements in the molten Earth eventually began to separate according to their density and melting point in a process called *differentiation*. If you examine Table 1.3, you will see that the densities and the melting points of the common metals and metal oxides indicate that iron and iron-based compounds have higher densities and would remain molten at lower temperatures, and they therefore sunk to the core of the planet as the less dense metals and silicates floated toward what was to become the crust. This differentiation resulted in a core that is about 85% Fe and 5% Ni and is nearly 1/3 of the Earth's total mass. The mantle and crust are dominated by silicate minerals containing a variety of alkali, alkaline earth, and transition metals.

Compounds	Melting Point (°C)	Density (g/mL)
SiO_2	1688–1700	2.65
Si	1410	2.32
CaO	2614	3.25–3.38
MgO	2852	3.58
Al_2O_3	2072	3.97
Fe_2O_3	1565	5.24
FeO	1369	5.72
Fe	1535	7.86
Ni	1455	8.9
NiO	1984	6.67

Values from CRC Handbook, 72nd ed.

Table 1.3 Melting points and densities of the major constituents of the mantle and crust.

What evidence is there for this assertion? Careful studies by seismologists and geologists have confirmed these details. Whenever there is an earthquake or nuclear weapon test, seismologists can observe seismic waves traveling through the Earth, and they observe a gradual increase in the density of the mantle until the waves reach what must be the core, where the density increases significantly. Compression waves (called *p*-waves) can travel through solids and liquids, whereas shearing waves (called *s*-waves) can only travel through solids coherently; thus, the inability of *s*-waves to travel through the core strongly suggests that it is liquid (at least the outer core). Further, the magnetic field of the Earth is consistent with convective flows of a liquid outer core. The inner core is solid, not because it is cooler than the outer core but because of the tremendous pressure the rest of the mantle and outer core exert. Temperature and pressure estimates in the core are 5400 °C and 330 GPa, which place the core in the solid region of its phase diagram.

As the surface of the Earth cooled and the higher melting point compounds rose to the surface, the crust solidified. The Earth and Venus are large enough to contain sufficient radioisotopes in the mantle and core to slow the cooling process down significantly; thus, the Earth still retains a molten outer core and a semimolten mantle. Smaller planets also delayed their complete solidification, but have long since become solid, such as Mercury, the Moon, and Mars. The Earth's surface remains active and young due to the residual trapped heat that keeps portions of the mantle in a semiliquid state. Further, the tectonic plates that form the Earth's surface are constantly shifting and recycling the crust into the molten interior. As a result, most of the lithospheric surface of the Earth is no older than 200 Ma. The oldest parts of the Earth's crust are found at the center of tectonic plates, such as in Australia and in northern Quebec near Hudson Bay, which date to 4.03 and 4.28 Ga, respectively. Rocks from the Moon and meteors have been dated to 4.5 Ga, which would corroborate the theory that the smaller bodies, such as the Moon and asteroids, would have cooled much quicker than the Earth and would have not had the tectonic activity that caused the crust of the Earth to remelt.

Isotope	Half-Life (years)
U-235	7.03×10^{8}
K-40	1.248×10^{9}
U-238	4.47×10^{9}
Th-232	1.40×10^{10}
Pt-190	4.5×10^{11}
Cd-113	8.04×10^{15}
Se-82	$> 9.5 \times 10^{19}$
Te-130	8×10^{20}
Te-128	2.2×10^{24}

Values from CRC Handbook, 93rd ed.

Table 1.4 Selected radioisotopes and their half-lives.

Table 1.4 contains a list of common radioactive isotopes and their measured half-lives. Most of these radioisotopes are heavy atoms formed during the last few seconds of the supernova explosions that formed the stellar cloud from which our solar system was born. The reliable decay of some of these isotopes can be used to date the age of the Earth. While a rock is molten, the contents are ill-defined as elements move around in the liquid. Once a rock solidifies, then its constituent elements are locked into place. If the molten rock is allowed to cool slowly, then crystals form. Crystals have very regular atomic arrangements and unusual purity since the lowest energy configuration of a crystal pushes out atomic impurities while it is forming. It is the same reason that icebergs are mostly freshwater even though they form in very salty oceans. Zircon ($ZrSiO_4$) is a silicate mineral that regularly