

PRINCIPLES AND APPLICATIONS OF
GEOCHEMISTRY

A Comprehensive Textbook for Geology Students

Second Edition

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In the Beginning

The urge to trace the history of the universe back to its beginnings is irresistible.

STEVEN WEINBERG (1977, p. 1)

Certain questions about our existence on Earth are so fundamental that they have been incorporated into religious mythologies. These questions not only concern the origin of the Earth and the evolution of life but also extend to the origin of the universe and to the nature of space and time. Did the universe have a beginning and will it ever end? What existed before the universe formed? Does the universe have limits and what exists beyond those limits? It is proper to raise these questions at the beginning of a geochemistry course because they are within the scope of cosmochemistry.

2.1 The Big Bang

The universe started like a bubble in a stream. At first it was not there, and suddenly it formed and expanded rapidly as though it were exploding (Gott, 1982). Science has its share of practical jokers who immediately referred to the start of the expansion of the universe as the Big Bang (Gamow, 1952). From the very beginning the universe had all of the mass and energy it contains today. As a result, its pressure and temperature, say 10^{-32} sec after the Big Bang, were so high that matter existed in its most fundamental form as "quark soup." As the universe expanded and cooled, the quarks combined to form more familiar nuclear particles that ultimately became organized into nuclei of hydrogen and helium.

Formation of atomic nuclei began about 13.8 sec after the Big Bang when the temperature of the universe had decreased to 3×10^9 K. This process continued for about 30 min, but did not go beyond helium because the nuclear reactions could not bridge a gap in the stabilities of the nuclei of lithium, beryllium, and boron. At that time the universe was an intensely hot and rapidly expanding fireball.

Some 700,000 years later, when the temperature had decreased to about 3×10^3 K, electrons became attached to the nuclei of hydrogen and helium. Matter and radiation were thereby separated from each other, and the universe became transparent to light. Subsequently, matter began to be organized into stars, galaxies, and galactic clusters as the universe continued to expand to the present time (Weinberg, 1977).

But how do we know all this? The answer is that the expansion of the universe can be seen in the "red shift" of spectral lines of light emitted by distant galaxies, and it can be "heard" as the "cosmic microwave radiation," which is the remnant of the fireball, that still fills the universe. In addition, the properties of the universe immediately after the Big Bang were similar to those of atomic nuclei. Therefore, a very fruitful collaboration has developed among nuclear physicists and cosmologists that has enabled them to reconstruct the history of the universe back to about 10^{-32} sec after the Big Bang. These studies

have shown that the forces we recognize at low temperature are, at least in part, unified at extremely high temperatures and densities. There is hope that a Grand Unified Theory (GUT) will eventually emerge that may permit us to approach even closer to understanding the start of the universe.

What about the future? Will the universe continue to expand forever? The answer is that the future of the universe can be predicted only if we know the total amount of matter it contains. The matter that is detectable at the present time is not sufficient to permit gravity to overcome the expansion. If expansion continues, the universe will become colder and emptier with no prospect of an end. However, a large fraction of the mass of the universe is hidden from view in the form of gas and dust in interstellar and intergalactic space, and in the bodies of stars that no longer emit light. In addition, we still cannot rule out the possibility that neutrinos have mass even when they are at rest. If the mass of the universe is sufficient to slow the expansion and ultimately to reverse it, then the universe will eventually contract until it disappears again in the stream of time.

Since the universe had a beginning and is still expanding, it cannot be infinite in size. However, the edge of the universe cannot be seen with telescopes because it takes too long for the light to reach us. As the universe expands, space expands with it. In other words, it seems to be impossible to exceed the physical limits of the universe. We are trapped in our expanding bubble. If other universes exist, we cannot communicate with them.

Now that we have seen the big picture, let us review certain events in the history of the standard model of cosmology to show that progress in Science is sometimes accidental.

In 1929 the American astronomer Edwin Hubble reported that eighteen galaxies in the Virgo cluster are receding from Earth at different rates that increase with their distances from Earth. He calculated the recessional velocities of these galaxies by means of the "Doppler effect" from observed increases of the wavelengths of

characteristic spectral lines of light they emit. This "red shift" is related to the recessional velocity by an equation derived in 1842 by Johann Christian Doppler in Prague:

$$\frac{\lambda'}{\lambda} = 1 + \frac{v}{c} \quad (2.1)$$

where λ' is the wavelength of a spectral line of light emitted by a moving source, λ is the wavelength of the same line emitted by a stationary source, c is the velocity of light, and v is the recessional velocity. Hubble's estimates of the distances to the galaxies were based on the properties of the Cepheid Variables studied previously by H. S. Leavitt and H. Shapley at Harvard University. The Cepheid Variables are bright stars in the constellation Cepheus whose period of variation depends on their absolute luminosity, which is the total radiant energy emitted by an astronomical body. Hubble found such variable stars in the galaxies he was studying and determined their absolute luminosities from their periods. The intensity of light emitted by a star decreases as the square of the distance increases. Therefore, the distance to a star can be determined from a comparison of its absolute and its apparent luminosity, where the latter is defined as the radiant power received by the telescope per square centimeter. In this way, Hubble determined the recessional velocities and distances of the galaxies in the Virgo cluster and expressed their relationship as:

$$v = Hd \quad (2.2)$$

where v is the recessional velocity in km/sec, d is the distance in 10^6 light years, and H is the Hubble constant (Hubble, 1936).

The Hubble constant can be used to place a limit on the age of the universe. If two objects are moving apart with velocity v , the time (t) required for them to become separated by a distance d is:

$$t = \frac{d}{v} = \frac{1}{H} \quad (2.3)$$

The initial results indicated that the Hubble constant had a value of 170 km/sec/ 10^6 light years,

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which corresponds to an expansion time of less than 2×10^9 years. This result was very awkward because age determinations based on radioactivity had established that the Earth is older than this date. Eventually Walter Baade discovered an error in the calibration of the Cepheid Variables, and the value of the Hubble constant was revised (Baade, 1968). The presently accepted value is 15 km/sec/ 10^6 light years, which indicates an expansion time for the universe of less than 20×10^9 years. This date is compatible with independent estimates of its age based on consideration of nucleosynthesis and the evolution of stars. By combining all three methods Hainebach et al. (1978) refined the age of the universe to $(14.5 \pm 1.0) \times 10^9$ years.

The Big Bang theory of cosmology was not accepted for many years for a variety of reasons. The turning point came in 1964 when Arno A. Penzias and Robert W. Wilson discovered a microwave background radiation that corresponds to a blackbody temperature of about 3 K. The discovery of this radiation was accidental, even though its existence had been predicted twenty years earlier by George Gamow and his colleagues Ralph A. Alpher and Robert Herman. Because they were unaware of Gamow's work, Penzias and Wilson were skeptical about the phenomenon they had discovered and took great care to eliminate all extraneous sources of the background radiation. For example, they noticed that two pigeons had been nesting in the throat of the antenna they were using at Holmdel, New Jersey. The pigeons were caught and taken to a distant location, but promptly returned. Therefore, they were caught again and dealt with "by more decisive means." The pigeons had also coated the antenna with a "white dielectric material," which was carefully removed. However, the intensity of the background radiation remained constant and independent of time in the course of a year.

Word of this phenomenon reached a group of astrophysicists at nearby Princeton University who were working on models of the early history of the universe under the guidance of Robert H. Dicke. Eventually, Penzias called Dicke, and it

was agreed that they would publish two companion letters in the *Astrophysical Journal*. Penzias and Wilson announced the discovery, and Dicke and his colleagues explained the cosmological significance of the microwave background radiation (Penzias and Wilson, 1965). In 1978 Penzias and Wilson shared the Nobel Prize in physics for their discovery.

The radiation discovered by Penzias and Wilson is a remnant of the radiation that filled the universe for about 700,000 years when its temperature was greater than about 3000 K. During this early period, matter consisted of a mixture of nuclear particles and photons in thermal equilibrium with each other. Under these conditions the energy of radiation at a specific wavelength is inversely proportional to the absolute temperature. According to an equation derived by Max Planck at the start of the 20th century, the energy of blackbody radiation at a particular temperature increases rapidly with increasing wavelength to a maximum and then decreases at longer wavelengths. Radiation in thermal equilibrium with matter has the same properties as radiation inside a black box with opaque walls. Therefore, the energy distribution of radiation in the early universe is related to the wavelength and to the absolute temperature by Planck's equation. The wavelength near which most of the energy of blackbody radiation is concentrated (λ_{\max}) is approximately equal to:

$$\lambda_{\max} = \frac{0.29}{T} \quad (2.4)$$

where λ_{\max} is measured in centimeters and T is in Kelvins (Weinberg, 1977).

The original measurement of Penzias and Wilson was at a wavelength of 7.35 cm, which is much greater than the typical wavelength of radiation at 3 K. Since 1965, many additional measurements at different wavelengths have confirmed that the cosmic background radiation does fit Planck's formula for blackbody radiation. The characteristic temperature of this radiation is about 3 K, indicating that the typical wavelength of photons has increased by a factor of about 1000

because of the expansion of the universe since its temperature was 3000 K (Weinberg, 1977).

2.2 Stellar Evolution

Matter in the universe is organized into a "hierarchy of heavenly bodies" listed below in order of decreasing size.

clusters of galaxies	comets
galaxies	asteroids
stars, pulsars, and black holes	meteoroids
planets	dust particles
satellites	molecules
	atoms of H and He

On a subatomic scale, space between stars and galaxies is filled with cosmic rays (energetic nuclear particles) and photons (light).

Stars are the basic units in the hierarchy of heavenly bodies within which matter continues to evolve by nuclear reactions. Many billions of stars are grouped together to form a galaxy, and large numbers of such galaxies are associated into galactic clusters. Stars may have stellar companions or they may have orbiting planets, including ghostly comets that flare briefly when they approach the star on their eccentric orbits. The planets in our solar system have their own retinue of satellites. The space between Mars and Jupiter contains the asteroids, most of which are fragments of larger bodies that have been broken up by collisions and by the gravitational forces of Jupiter and Mars. Pieces of the asteroids have impacted as meteorites on the surfaces of the planets and their satellites and have left a record of these events in craters.

On an even smaller scale, space between stars contains clouds of gas and solid particles. The gas is composed primarily of hydrogen and of helium that were produced during the initial expansion of the universe. In addition, the interstellar medium contains elements of higher atomic number that were synthesized by nuclear reactions in the interiors of stars that have since exploded. A third component consists of compounds of hydrogen and carbon that are the precursors of life. These

clouds of gas and dust may contract to form new stars whose evolution depends on their masses and on the H/He ratio of the gas cloud from which they formed.

The evolution of stars can be described by specifying their luminosities and surface temperatures. The luminosity of a star is proportional to its mass, and its surface temperature or color is an indicator of its volume. When a cloud of interstellar gas contracts, its temperature increases, and it begins to radiate energy in the infrared and visible parts of the spectrum. As the temperature in the core of the gas cloud approaches 20×10^6 K, energy production by hydrogen fusion becomes possible, and a star is born. Most of the stars of a typical galaxy derive energy from this process and therefore plot in a band, called the *main sequence*, on the Hertzsprung–Russell diagram shown in Figure 2.1. Massive stars, called *blue giants*, have high luminosities and high surface temperatures. The Sun is a star of intermediate mass and has a surface temperature of about 5800 K. Stars that are less massive than the Sun are called *red dwarfs* and plot at the lower end of the main sequence.

As a star five times more massive than the Sun converts hydrogen to helium while on the main sequence, the density of the core increases, causing the interior of the star to contract. The core temperature therefore rises slowly during the hydrogen-burning phase. This higher temperature accelerates the fusion reaction and causes the outer envelope of the star to expand. However, when the core becomes depleted in hydrogen, the rate of energy production declines and the star contracts, raising the core temperature still further. The site of energy production now shifts from the core to the surrounding shell. The resulting changes in luminosity and surface temperature cause the star to move off the main sequence toward the realm of the *red giants* (Figure 2.1).

The helium produced by hydrogen fusion in the shell accumulates in the core, which continues to contract and therefore gets still hotter. The resulting expansion of the envelope lowers the surface temperature and causes the color to turn red. At the same time, the shell in which hydrogen

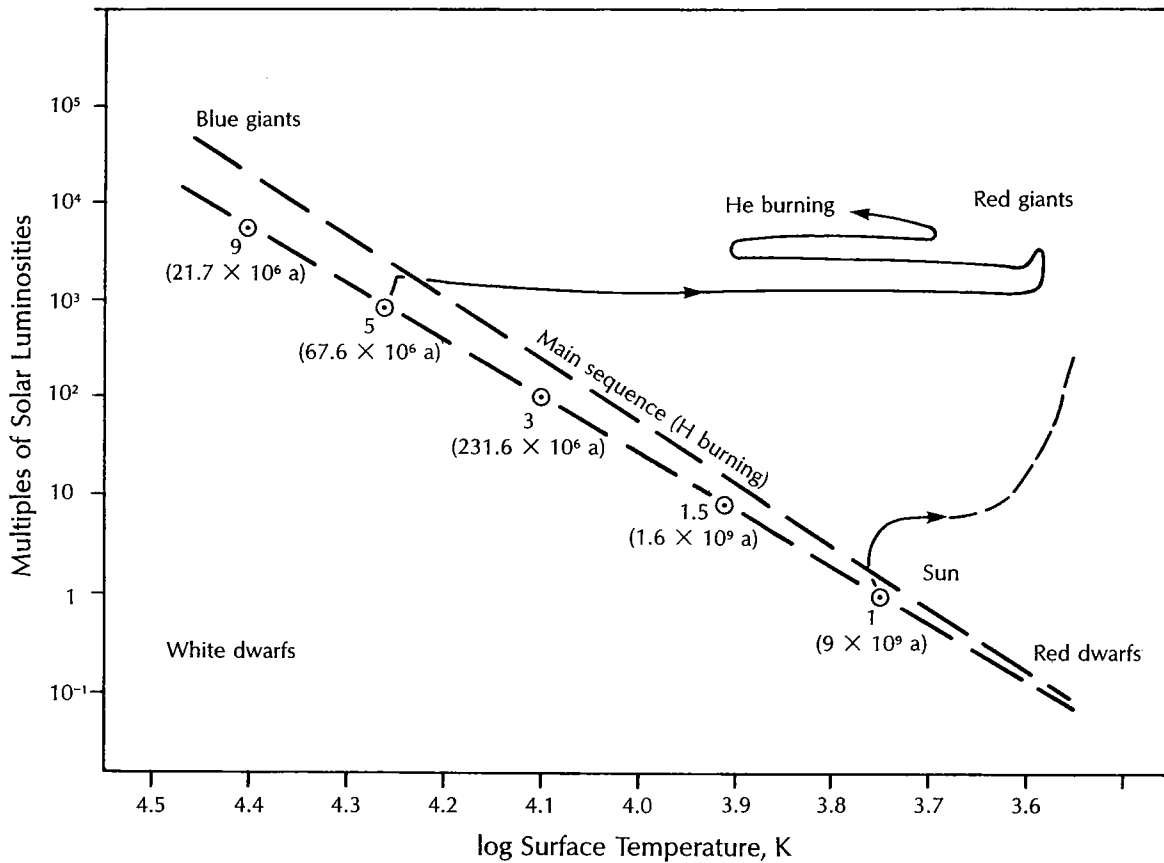


Figure 2.1 Stellar evolution on a Hertzsprung–Russell diagram for stars ranging from 1 to 9 solar masses. When a star has used up the hydrogen in its core, it contracts and then moves off the main sequence and enters the realm of the red giants, which generate energy by helium fusion. The evolutionary track and the life expectancy of stars are strongly dependent on their masses. Stars five times more massive than the sun are nearly 1000 times brighter, have surface temperatures of about 18,000 K—compared to 5800 K for the Sun—and remain on the main sequence only about 68 million years. Their evolution to the end of the major phase of helium burning takes only about 87 million years (Iben, 1967).

is reacting gradually thins as it moves toward the surface, and the luminosity of the star declines. These changes transform a main-sequence star into a bloated red giant. For example, the radius of a star five times more massive than the Sun increases about 30-fold just before helium burning in the core begins.

When the core temperature approaches 100×10^6 K, helium fusion by means of the “triple-alpha process” begins and converts three helium nuclei into the nucleus of carbon-12. At the same

time, hydrogen fusion in the shell around the core continues. The luminosities and surface temperatures (color) of red giants become increasingly variable as they evolve, reflecting changes in the rates of energy production in the core and shell. The evolutionary tracks in Figure 2.1 illustrate the importance of the mass of a star to its evolution. A star five times as massive as the Sun is 1000 times brighter while on the main sequence and has a more eventful life as a red giant than stars below about two solar masses (Iben, 1967, 1974).

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The length of time a star spends on the main sequence depends primarily on its mass and to a lesser extent on the H/He ratio of its ancestral gas cloud. In general, massive stars (blue giants) consume their fuel rapidly and may spend only 10×10^6 years on the main sequence. Small stars (red dwarfs) have much slower "metabolic" rates and remain on the main sequence for very long periods of time exceeding 10×10^9 years. The Sun, being a star of modest magnitude, has enough hydrogen in its core to last about 9×10^9 years at the present rate of consumption. Since it formed about 4.5×10^9 years ago, the Sun has achieved middle age and will provide energy to the planets of the solar system for a very long time to come. However, ultimately its luminosity will increase, and it will expand to become a red giant, as shown in Figure 2.1. The temperature on the surface of the Earth will then rise and become intolerable to life forms. The expansion of the Sun may engulf the terrestrial planets, including Earth, and vaporize them. When all of its nuclear fuel has been consumed, the Sun will assume the end stage of stellar evolution that is appropriate for a star of its mass and chemical composition.

Toward the end of the giant stage, stars become increasingly unstable. When the fuel for a particular energy-producing reaction is exhausted, the star contracts and its internal temperature rises. The increase in temperature may trigger a new set of nuclear reactions. In stars of sufficient mass, this activity culminates in a gigantic explosion (supernova) as a result of which a large fraction of the outer envelope of the star is blown away. The debris from such explosions mixes with hydrogen and helium in interstellar space to form clouds of gas and dust from which new stars may form.

As stars reach the end of their evolution they turn into white dwarfs, or neutron stars (pulsars), or black holes, depending on their masses (Wheeler, 1973). Stars whose mass is less than about 1.2 solar masses contract until their radius is only about 1×10^4 km and their density is between 10^4 and 10^8 g/cm³. Stars in this configuration have low luminosities but high surface temperatures and are therefore called white dwarfs (Figure 2.1). They gradually cool and fade from

view as their luminosities and surface temperatures diminish with time. Stars that are appreciably more massive than the Sun develop dense cores because of the synthesis of heavy chemical elements by nuclear reactions. Eventually, such stars become unstable and explode as supernovas. The core then collapses until its radius is reduced to about 10 km and its density is of the order of 10^{11} to 10^{15} g/cm³. Such stars are composed of a "neutron gas" because electrons and protons are forced to combine under the enormous pressure and the abundance of neutrons greatly increases as a result. Neutron stars have very rapid rates of rotation and emit pulsed radio waves that were first observed in 1965 by Jocelyn Bell, a graduate student working with A. Hewish at the Cavendish Laboratory of Cambridge University in England (Hewish, 1975). The Crab Nebula contains such a "pulsar," which is the remnant of a supernova observed by Chinese astronomers in 1054 A.D. (Fowler, 1967). The cores of the most massive stars collapse to form black holes in accordance with Einstein's theory of general relativity. Black holes have radii of only a few kilometers and densities in excess of 10^{16} g/cm³. Their gravitational field is so great that neither light nor matter can escape from them, hence the name "black hole." Observational evidence supporting the existence of black holes is growing and they are believed to be an important phenomenon in the evolution of galaxies.

Stars, it seems, have predictable evolutionary life cycles. They form, shine brightly for a while, and then die. Hans Bethe (1968, p. 547) put it this way:

If all this is true, stars have a life cycle much like animals. They are born, they grow, they go through a definite internal development, and finally die, to give back the material of which they are made so that new stars may live.

2.3 Nucleosynthesis

The origin of the chemical elements is intimately linked to the evolution of stars because the elements are synthesized by the nuclear reactions from which stars derive the energy they radiate into space. Only helium and deuterium, the

Table 2.1 Abundances of the Elements in the Solar System in Units of Number of Atoms per 10^6 Atoms of Silicon

Atomic no.	Element	Symbol	Abundance ^a	Atomic no.	Element	Symbol	Abundance ^a
1	hydrogen	H	2.72×10^{10}	53	iodine	I	9.0×10^{-1}
2	helium	He	2.18×10^9	54	xenon	Xe	4.35×10^0
3	lithium	Li	5.97×10^1	55	cesium	Cs	3.72×10^{-1}
4	beryllium	Be	7.8×10^{-1}	56	barium	Ba	4.36×10^0
5	boron	B	2.4×10^1	57	lanthanum	La	4.48×10^{-1}
6	carbon	C	1.21×10^7	58	cerium	Ce	1.16×10^0
7	nitrogen	N	2.48×10^6	59	praseodymium	Pr	1.74×10^{-1}
8	oxygen	O	2.01×10^7	60	neodymium	Nd	8.36×10^{-1}
9	fluorine	F	8.43×10^2	61	promethium	Pm	0
10	neon	Ne	3.76×10^6	62	samarium	Sm	2.61×10^{-1}
11	sodium	Na	5.70×10^4	63	europium	Eu	9.72×10^{-2}
12	magnesium	Mg	1.075×10^6	64	gadolinium	Gd	3.31×10^{-1}
13	aluminum	Al	8.49×10^4	65	terbium	Tb	5.89×10^{-2}
14	silicon	Si	1.00×10^6	66	dysprosium	Dy	3.98×10^{-1}
15	phosphorus	P	1.04×10^4	67	holmium	Ho	8.75×10^{-2}
16	sulfur	S	5.15×10^5	68	erbium	Er	2.53×10^{-1}
17	chlorine	Cl	5.240×10^3	69	thulium	Tm	3.86×10^{-2}
18	argon	Ar	1.04×10^5	70	ytterbium	Yb	2.43×10^{-1}
19	potassium	K	3.770×10^3	71	lutetium	Lu	3.69×10^{-2}
20	calcium	Ca	6.11×10^4	72	hafnium	Hf	1.76×10^{-1}
21	scandium	Sc	3.38×10^1	73	tantalum	Ta	2.26×10^{-2}
22	titanium	Ti	2.400×10^3	74	tungsten	W	1.37×10^{-1}
23	vanadium	V	2.95×10^2	75	rhenium	Re	5.07×10^{-2}
24	chromium	Cr	1.34×10^4	76	osmium	Os	7.17×10^{-1}
25	manganese	Mn	9.510×10^3	77	iridium	Ir	6.60×10^{-1}
26	iron	Fe	9.00×10^5	78	platinum	Pt	1.37×10^0
27	cobalt	Co	2.250×10^3	79	gold	Au	1.86×10^{-1}
28	nickel	Ni	4.93×10^4	80	mercury	Hg	5.2×10^{-1}
29	copper	Cu	5.14×10^2	81	thallium	Tl	1.84×10^{-1}
30	zinc	Zn	1.260×10^3	82	lead	Pb	3.15×10^0
31	gallium	Ga	3.78×10^2	83	bismuth	Bi	1.44×10^{-1}
32	germanium	Ge	1.18×10^2	84	polonium	Po	~0
33	arsenic	As	6.79×10^0	85	astatine	At	~0
34	selenium	Se	6.21×10^1	86	radon	Rn	~0
35	bromine	Br	1.18×10^1	87	francium	Fr	~0
36	krypton	Kr	4.53×10^1	88	radium	Ra	~0
37	rubidium	Rb	7.09×10^0	89	actinium	Ac	~0
38	strontium	Sr	2.38×10^1	90	thorium	Th	3.35×10^{-2}
39	yttrium	Y	4.64×10^0	91	protactinium	Pa	~0
40	zirconium	Zr	1.07×10^1	92	uranium	U	9.00×10^{-3}
41	niobium	Nb	7.1×10^{-1}	93	neptunium	Np	~0
42	molybdenum	Mo	2.52×10^0	94	plutonium	Pu	~0
43	technetium	Tc	0	95	americium	Am	0
44	ruthenium	Ru	1.86×10^0	96	curium	Cm	0
45	rhodium	Rh	3.44×10^{-1}	97	berkelium	Bk	0
46	palladium	Pd	1.39×10^0	98	californium	Cf	0
47	silver	Ag	5.29×10^{-1}	99	einsteinium	Es	0
48	cadmium	Cd	1.69×10^0	100	fermium	Fm	0
49	indium	In	1.84×10^{-1}	101	mendelevium	Md	0
50	tin	Sn	3.82×10^0	102	nobelium	No	0
51	antimony	Sb	3.52×10^{-1}	103	lawrencium	Lr	0
52	tellurium	Te	4.91×10^0				

^aThe terrestrial abundances of the radioactive daughters of uranium and thorium are very low and are therefore indicated as “~0.” In addition, neptunium and plutonium are produced in nuclear reactors and therefore occur on the Earth. However, the transuranium elements having atomic numbers of 95 or greater do not occur in the solar system. Their abundances are therefore stated as “0.” SOURCE: Anders and Ebihara (1982).

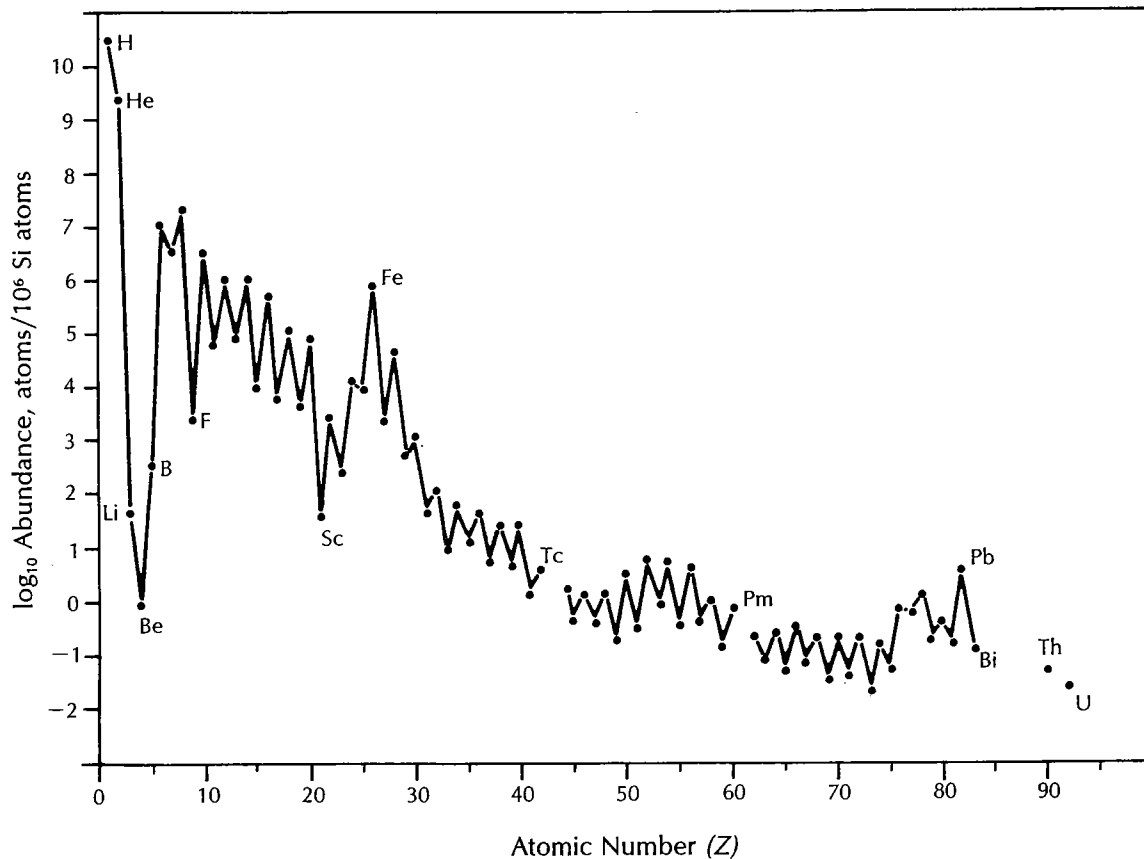


Figure 2.2 Abundances of the chemical elements in the solar system in terms of atoms per 10^6 atoms of Si. The data were derived primarily by analysis of carbonaceous chondrite meteorites and by optical spectroscopy of light from the Sun and nearby stars (Anders and Ebihara, 1982).

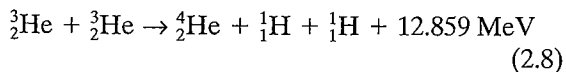
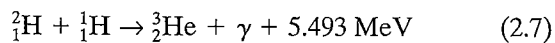
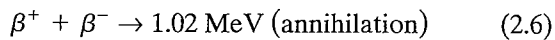
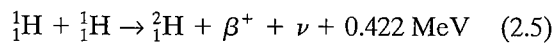
5. The abundances of lithium, beryllium, and boron are anomalously low compared to other elements of low atomic number.
6. The abundance of iron is notably higher than those of other elements with similar atomic numbers.
7. Two elements, technetium and promethium, do not occur in the solar system because all of their isotopes are unstable and decay rapidly.
8. The elements having atomic numbers greater than 83 (Bi) have no stable isotopes, but occur naturally at very low abundances because they are the daugh-

ters of long-lived radioactive isotopes of uranium and thorium.

The nucleosynthesis model of B₂FH (1957) includes eight different kinds of nuclear reactions that occur at specified temperatures in the course of the evolution of a star. Several of these reactions may take place simultaneously in the cores and outer shells of massive stars. As a result, the core of a star may have a different chemical composition than the shell surrounding it. Moreover, not all of the nuclear processes take place in all stars. Consequently, other stars in the Milky Way Galaxy do not necessarily have the same chemical composition as the Sun and her planets.

All stars on the main sequence generate energy by hydrogen fusion reactions. This process results in the synthesis of helium either by the direct proton-proton chain (equations 2.5–2.8) or by the CNO cycle (equations 2.9–2.14). The proton-proton chain works as follows. Two nuclei of hydrogen, consisting of one proton each, collide to form the nucleus of deuterium (${}^2_1\text{H}$) plus a positron (β^+) and a neutrino (ν). (The designation of atomic species is presented in Chapter 6.) Each reaction of this kind liberates 0.422 million electron volts (MeV) of energy. The positron (positively charged electron) is annihilated by interacting with a negatively charged electron giving off additional energy of 1.02 MeV. The deuterium nucleus collides with another proton to form the nucleus of helium-3 (${}^3_2\text{He}$) plus a gamma ray (γ) and 5.493 MeV of energy. Finally, two helium-3 nuclei must collide to form helium-4 (${}^4_2\text{He}$), two protons, and 12.859 MeV. The end result is that four hydrogen nuclei fuse to form one nucleus of helium-4, a gamma ray, a neutrino, and 19.794 MeV of energy.

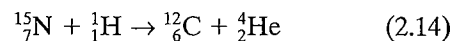
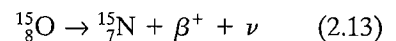
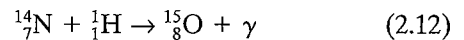
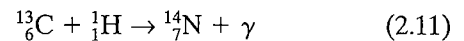
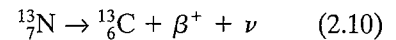
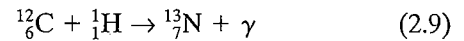
The entire process can be described by a series of equations in which the nuclei of hydrogen and helium are represented by the symbols of the appropriate isotopes (see Chapter 6), even though these isotopes do not actually exist in atomic form in stellar interiors where their electrons are removed from them because of the high temperature:



The direct proton-proton fusion to form helium-4 can only take place at a temperature of about 10×10^6 K, and even then the probability of its occurrence (or its “reaction cross section”) is very small. Nevertheless, this process was the only source of nuclear energy for first-generation stars that formed from the primordial mixture of hydrogen and helium after the Big Bang.

Once the first generation of stars had run through their evolutionary cycles and had exploded,

the interstellar gas clouds contained elements of higher atomic number. The presence of carbon-12 (${}^{12}_6\text{C}$) synthesized by the ancestral stars has made it easier for subsequent generations of stars to generate energy by hydrogen fusion. This alternative mode of hydrogen fusion was discovered by Hans Bethe and is known as the CNO cycle:



The end result is that four protons are fused to form one nucleus of ${}^4_2\text{He}$, as in the direct proton-proton chain. The nucleus of ${}^{12}_6\text{C}$ acts as a sort of catalyst and is released at the end. It can then be reused for another revolution of the CNO cycle.

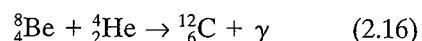
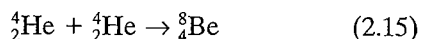
The Sun contains elements of higher atomic number than helium including ${}^{12}_6\text{C}$ and therefore carries on hydrogen fusion by the CNO cycle. In fact, most stars in our Milky Way Galaxy are second-generation stars because our Galaxy is so old that only the very smallest first-generation stars could have survived to the present time.

The low reaction cross section of the proton-proton chain by which the ancestral stars generated energy has been a source of concern to nuclear astrophysicists. When this difficulty was pointed out to Sir Arthur Eddington, who proposed hydrogen fusion in stars in 1920, he replied (Fowler, 1967):

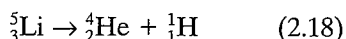
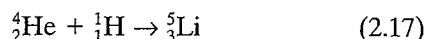
We do not argue with the critic who urges that the stars are not hot enough for this process; we tell him to go and find a hotter place.

After the hydrogen in the core has been converted to helium “ash,” hydrogen fusion ends, and the core contracts under the influence of gravity. The core temperature rises toward 100×10^6 K, and the helium “ash” becomes the fuel for the next set of energy-producing nuclear reactions. The critical reaction for helium burning is the fusion of three

alpha particles (triple-alpha process) to form a nucleus of $^{12}_6\text{C}$:

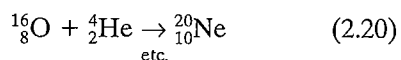
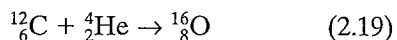


This is the critical link in the chain of nucleosynthesis because it bridges the gap in nuclear stability of the isotopes of lithium, beryllium, and boron. The crux of the problem is that the nucleus of ^8_4Be is very unstable and decays quickly with a "half-life" of about 10^{-16} sec. Therefore, ^8_4Be must absorb a third helium nucleus very soon after its formation to make it safely to stable $^{12}_6\text{C}$ (Fowler, 1967). An alternative reaction involving the addition of a proton to the nucleus of ^4_2He has an even smaller chance to succeed because the product, ^5_3Li , has a half-life of only 10^{-21} sec and decomposes to form helium and hydrogen:



The triple-alpha process is indeed the key to the synthesis of all elements beyond helium. Without it, stellar evolution would be short-circuited, and the universe would be composed only of hydrogen and helium.

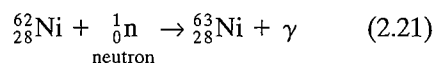
Helium burning sustains red giants only for a few tens of millions of years or less. With increasing temperature in the core, alpha particles fuse with the nuclei of $^{12}_6\text{C}$ to produce nuclei of still higher atomic number:



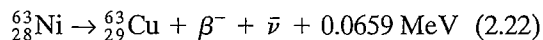
However, electrostatic repulsion between positively charged nuclei and alpha particles limits the size of the atoms that can form in this way. The heaviest atom produced by the addition of alpha particles is $^{56}_{28}\text{Ni}$, which decays to $^{56}_{27}\text{Co}$ and then to stable $^{56}_{26}\text{Fe}$. These nuclear reactions therefore cause the enhanced abundance of the elements in the iron group illustrated in Figure 2.2.

During the final stages of the evolution of red giants, several other kinds of nuclear reactions occur (B₂FH, 1957). The most important of these

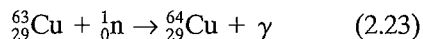
are the neutron-capture reactions, which produce a large number of the atoms having atomic numbers greater than 26 (Fe). These reactions involve the addition of a neutron to the nucleus of an atom to produce an isotope having the same atomic number but a large mass number. For example, the equation:



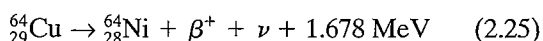
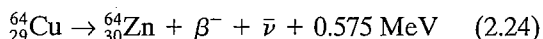
indicates that the nucleus of $^{62}_{28}\text{Ni}$ absorbs a neutron, which changes it to an excited state of $^{63}_{28}\text{Ni}$, which then deexcites by emitting a gamma ray. Nickel-63 is radioactive and decays to stable $^{63}_{29}\text{Cu}$ by emitting a β^- particle:



where $\bar{\nu}$ is an antineutrino. $^{63}_{29}\text{Cu}$ is a stable isotope of copper and can absorb another neutron to form $^{64}_{29}\text{Cu}$:

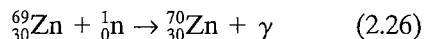


Copper-64 is radioactive and undergoes branched decay to form $^{64}_{30}\text{Zn}$ and $^{64}_{28}\text{Ni}$, both of which are stable:



This process of successive additions of neutrons is illustrated in Figure 2.3. It takes place during the red giant stage of stellar evolution when the neutron flux is low enough to permit the product nucleus to decay before the next neutron is added. This process therefore is characteristically *slow* and is therefore referred to as the *s-process*.

By examining Figure 2.3 closely we see that the track of the s-process bypasses $^{70}_{30}\text{Zn}$, which is one of the stable isotopes of zinc. In order to make this isotope by neutron capture reactions, the pace must be speeded up so that unstable $^{69}_{30}\text{Zn}$ can pick up a neutron to form $^{70}_{30}\text{Zn}$ before it decays to stable $^{70}_{31}\text{Ga}$:



An even more rapid rate of neutron capture is required to make $^{70}_{30}\text{Zn}$ from $^{65}_{29}\text{Cu}$ by addition of five neutrons in succession to form $^{70}_{29}\text{Cu}$, which then decays by β^- emission to stable $^{70}_{30}\text{Zn}$:

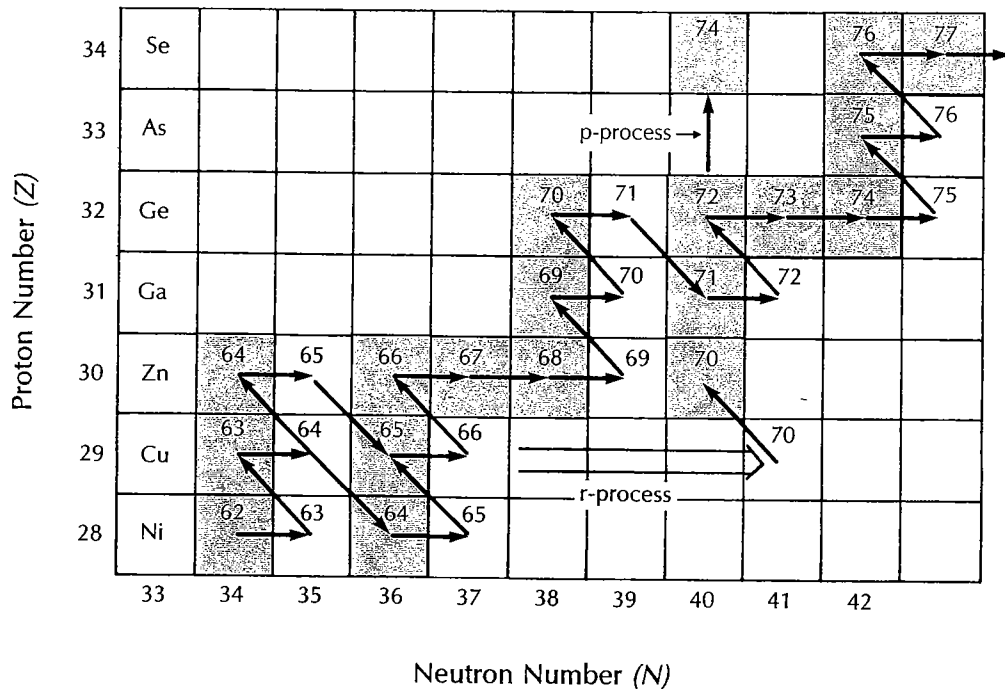
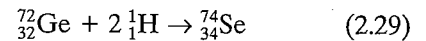
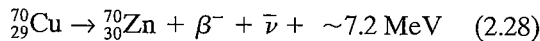
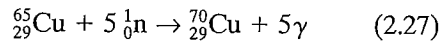


Figure 2.3 Nucleosynthesis in red giants by neutron capture on a slow time scale (s-process) followed by beta decay. The dark squares are stable isotopes, whereas the unshaded ones are radioactive. The process starts with stable $^{62}_{28}\text{Ni}$, which absorbs a neutron to form unstable $^{63}_{28}\text{Ni}$, which decays to stable $^{63}_{29}\text{Cu}$ by emitting a β^- particle. The main line of the s-process, as indicated by arrows, proceeds from $^{62}_{28}\text{Ni}$ to $^{77}_{34}\text{Se}$ and beyond but bypasses $^{70}_{30}\text{Zn}$ and $^{74}_{34}\text{Se}$. $^{70}_{30}\text{Zn}$ is produced by neutron capture on a rapid time scale (r-process) from $^{68}_{30}\text{Zn}$ via unstable $^{69}_{30}\text{Zn}$ and from $^{65}_{29}\text{Cu}$, which captures five neutrons in rapid succession to form $^{70}_{30}\text{Cu}$ followed by decay to stable $^{70}_{30}\text{Zn}$. $^{74}_{34}\text{Se}$ is a proton-rich nuclide that cannot form by either the s-process or the r-process and requires the addition of two protons (p-process) to stable $^{72}_{32}\text{Ge}$.



Capture of neutrons at such *rapid* rates is characteristic of the *r-process*, which requires a much greater neutron flux than the s-process and therefore takes place only during the last few minutes in the life of a red giant when it explodes as a supernova.

However, no neutron capture on any time scale can account for the formation of some atoms such as stable $^{74}_{34}\text{Se}$ shown also in Figure 2.3. This nuclide is synthesized by the addition of two protons to stable $^{72}_{32}\text{Ge}$ in the so-called *p-process*:

This process also takes place at the very end of the giant stage of stellar evolution.

The system of nuclear reactions originally proposed by B₂FH (1957) can account for the observed abundances of the chemical elements in the solar system and in nearby stars. Nucleosynthesis is taking place at the present time in the stars of our galaxy and in the stars of other galaxies throughout the universe. We have good evidence in the wavelength spectra of light from distant galaxies that the chemical elements we find on Earth also occur everywhere else in the universe.

However, pulsars and black holes have high internal pressures and temperatures that cause atomic nuclei to disintegrate into more primitive constituents. The relative proportions of the chemical elements in other stars are different because local conditions may affect the yields of the many nuclear reactions that contribute to their synthesis.

2.4 Summary

We live in an expanding universe whose future is uncertain. The universe started with a Big Bang about 15×10^9 years ago and has evolved since then in accordance with the laws of physics.

Stars are the basic units in the hierarchy of heavenly bodies. They form by contraction of clouds of interstellar gas and dust until their core

temperatures are sufficient to cause hydrogen fusion. Stars evolve through predictable stages depending on their masses and initial compositions. They generate energy by nuclear reactions that synthesize other elements from primordial hydrogen and helium. In the end, stars explode, and the remnants become solid objects of great density.

The abundances of the chemical elements in the solar system can be explained by the nuclear reactions that energize the stars. These reactions progress from fusion of hydrogen and helium to neutron capture and to other reactions, most of which occur only for a short time at the end of the active life of a star. The chemical elements we know on Earth occur throughout the universe, but their abundances vary because local conditions affect the yields of the nucleosynthesis processes.

Problems*

1. How has the abundance of hydrogen (H) in the universe changed since the Big Bang?
2. Why are elements with even atomic numbers more abundant than their neighbors with odd atomic numbers?
3. How do we know that the Sun is at least a "second-generation" star?
4. Why do technetium (Tc) and promethium (Pm) lack stable isotopes?
5. What other elements also lack stable isotopes?
6. Why do the elements of Problem 5 exist on the Earth, whereas Tc and Pm do not?
7. Why is lead (Pb) more abundant than we might have expected?
8. Check the abundance of argon (Ar) and determine whether it is greater than expected. If so, suggest an explanation.
9. How did lithium (Li), beryllium (Be), and boron (B) form?
10. Compare the abundances of the "rare earths" (lanthanum to lutetium) to such well-known metals as Ta, W, Pt, Au, Hg, and Pb. Are the rare earths really all that "rare"?

*Not all of these questions have unequivocal answers.

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