

I Introduction to Cosmochemistry

Overview

Cosmochemistry is defined, and its relationship to geochemistry is explained. We describe the historical beginnings of cosmochemistry, and the lines of research that coalesced into the field of cosmochemistry are discussed. We then briefly introduce the tools of cosmochemistry and the datasets that have been produced by these tools. The relationships between cosmochemistry and geochemistry on the one hand and astronomy, astrophysics, and geology on the other are considered.

1.1 What Is Cosmochemistry?

A significant portion of the universe is comprised of elements, ions, and the compounds formed by their combinations – in effect, chemistry on the grandest scale possible. These chemical components can occur as gases or superheated plasmas, less commonly as solids, and very rarely as liquids.

Cosmochemistry is the study of the chemical compositions of the universe and its constituents, and the processes that produced those compositions. This is a tall order, to be sure. Understandably, cosmochemistry focuses primarily on the objects in our own solar system, because that is where we have direct access to the most chemical information. That part of cosmochemistry encompasses the compositions of the Sun, its retinue of planets and their satellites, the almost innumerable asteroids and comets, and the smaller samples (meteorites, interplanetary dust particles or “IDPs,” returned lunar samples) derived from them. From their chemistry, determined by laboratory measurements of samples or by various remote-sensing techniques, cosmochemists try to unravel the processes that formed or affected them and to fix the chronology of these events. Meteorites offer a unique window on the *solar nebula* – the disk-shaped

cocoon of gas and dust that enveloped the early Sun some ~4.57 billion years ago, and from which planetesimals and planets accreted (Fig. 1.1).

Within some meteorites are also found minuscule *presolar grains*, which provide us with an opportunity to analyze directly the chemistry of interstellar matter. Some of these tiny grains are pure samples of the matter ejected from dying stars, and they provide constraints on our understanding of how elements were forged inside stars before the Sun’s birth. Once formed, these grains were released into the *interstellar medium* (ISM), the space between the stars. The ISM is filled primarily with diffuse gases, mostly hydrogen and helium, but with oxygen, carbon, and nitrogen contributing about 1% by mass and all the other elements existing mostly as micrometer-sized dust motes. Much of the chemistry in the ISM occurs within relatively dense *molecular clouds*, where gas densities can reach 10^3 – 10^6 particles/cm³, high by interstellar standards (but not by our everyday experience: Earth’s atmosphere has $\sim 3 \times 10^{19}$ atoms/cm³ at sea level). These clouds are very cold, with temperatures ranging from 10 to 100 K, so interstellar grains become coated with ices. Reactions between ice mantles and gas molecules produce organic compounds that can be extracted from meteorites and identified by their bizarre isotopic compositions. Many dust grains were undoubtedly destroyed in the ISM, but some hardy survivors were incorporated into the nebula when the molecular cloud collapsed, and thence were accreted into meteorites.

Processes that occur inside stars, in interstellar space, and within the solar nebula have no counterparts in our terrestrial experience. They can be studied or inferred from astronomical observations and astrophysical theory, but cosmochemical analyses of materials actually formed or affected by these processes provide constraints and insights that remote sensing and theory cannot. Our

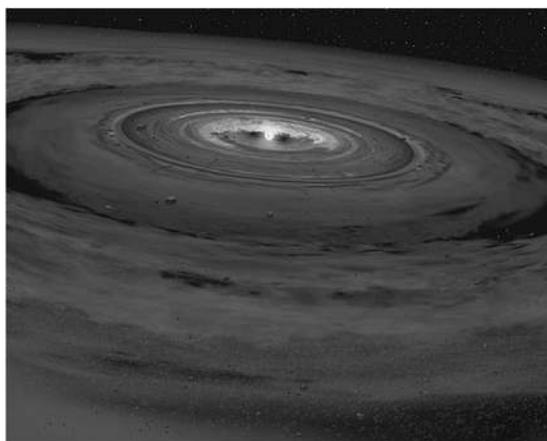


Figure 1.1 An artist's conception of the solar nebula, surrounding the violent young Sun. Figure courtesy of NASA.

terrestrial experience places us on firmer ground in deciphering the geologic processes occurring on the Earth's Moon. In studying lunar rocks and soils, we can use familiar geochemical tools developed for understanding the Earth. We have also measured the chemical compositions of some other planetary bodies and their smaller cousins, geologically processed planetesimals, using telescopes and instruments on spacecraft. In some cases, we even have meteorites ejected during impacts onto these bodies. Chemical measurements (whether from laboratory analyses of samples or *in situ* analyses of rocks and soils by orbiting or landed spacecraft) add quantitative dimensions to our understanding of planetary science. All extra-terrestrial materials are fair game for cosmochemistry.

1.2 Geochemistry versus Cosmochemistry

Traditionally, cosmochemistry has been treated as a branch of *geochemistry* – usually defined as the study of the chemical composition of the Earth. Geochemistry focuses on the chemical analysis of terrestrial materials, as implied by the prefix “geo,” and geochemistry textbooks commonly devote only a single chapter to cosmochemistry, if the subject is introduced at all. However, the line between geochemistry and cosmochemistry has always been somewhat fuzzy. The most prominent technical journal in this discipline, *Geochimica et Cosmochimica Acta*, has carried both names since its inception in 1950. The burgeoning field of planetary geochemistry appropriates the “geo” prefix, even though its subject is not Earth. A broader and more appropriate definition of geochemistry might be the study of element

and isotope behavior during geologic processes, such as occur on and within the Earth and other planets, moons, and planetesimals. Using this definition, we will include *planetary geochemistry* as an essential part of our treatment of cosmochemistry.

It is worth noting, though, that the geochemical and cosmochemical behaviors of elements do show some significant differences. A geochemical perspective of the Periodic Table is illustrated in Figure 1.2 (adapted from Railsback, 2003). As depicted, this diagram is decidedly Earth-centric, but the controls on element behavior during geologic processes apply to other bodies as well. Determining relative elemental abundances is an important part of geochemistry, and the relative abundances of elements in the Earth's crust vary over many orders of magnitude. Crustal abundances are illustrated in Figure 1.2, because most geochemical data are based on readily accessible samples of the crust. Geochemistry is also concerned with determining the composition of the Earth's interior – its mantle and core – and a more comprehensive figure would include those abundances as well. Very few native elements (pure elements not chemically bound to any others) occur naturally in the Earth, so Figure 1.2 distinguishes elements that occur commonly as cations or anions (positively and negatively charged particles, respectively). The electrical properties of elements control how they combine into compounds (minerals), dissolve in natural fluids, or are concentrated into melts (magmas) at high temperatures. The elements in Figure 1.2 are also grouped by their so-called geochemical affinities: *lithophile* (rock-loving) elements tend to form silicates or oxides (the constituents of most rocks), *siderophile* (iron-loving) elements combine with iron into metal alloys, *chalcophile* (sulfur-loving) elements react with sulfur to form sulfides, and *atmophile* elements tend to form gases and reside in the atmosphere. Many elements exhibit several affinities, depending on conditions, so the assignments illustrated in Figure 1.2 offer only a rough approximation of the complexity of element geochemical behavior. Finally, an important part of geochemistry takes advantage of the fact that most elements have more than one *isotope*. Measuring isotopic abundances has great value as a geochemical tool, and the most commonly used isotope systems are illustrated by boxes with heavy lines in Figure 1.2. Stable isotopes of some light elements provide information on sources of elements, the conditions under which minerals form, and the processes that separate isotopes from each other. Unstable (*radioactive*) *nuclides* and their decay products (*radio-genic* nuclides) similarly constrain element sources and geologic processes, as well as permit the ages of rocks

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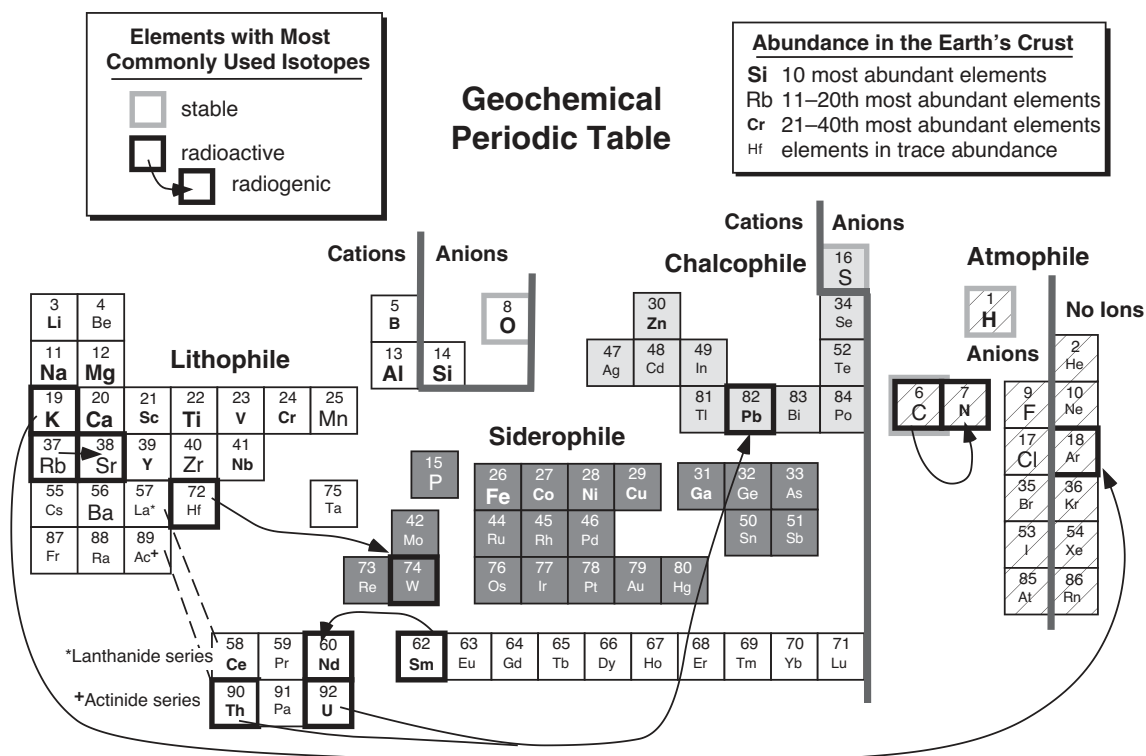


Figure 1.2 A geochemical Periodic Table, illustrating controls on element behavior during geologic processes. Relative abundances of elements in the Earth's crust are indicated by symbol sizes. Cations and anions are usually combined into minerals. Elements having affinities for silicate or oxide minerals (lithophile), metal (siderophile), sulfide minerals (chalcophile), and gas (atmosphile) phases are distinguished. Elements having stable isotopes that are commonly used in geochemistry are shown as boxes with bold gray outlines. Radioactive and radiogenic isotopes used for chronology are shown by boxes with bold black outlines and arrows showing decay relationships.

and events to be determined. The isotopic compositions of many other elements in terrestrial materials are now being analyzed, and a future Figure 1.2 will certainly expand the list of commonly used isotopic systems.

By way of contrast, Figure 1.3 illustrates a cosmochemical perspective of the Periodic Table. The element abundances shown in this figure are atomic concentrations in the Sun (relative to the abundance of silicon), as best we can determine them. The Sun comprises >99.8% of the mass of solar system matter, so solar composition is approximately equivalent to the average solar system (often incorrectly called *cosmic*) composition. The behavior of elements in space is governed largely by their *volatility*, which we quantify by specifying the temperature interval at which elements change state from a gas to a solid on cooling. (The liquid state is not generally encountered at the very low pressures of space; liquids tend to be more common in geochemistry than cosmochemistry.) All elements occur as gases at high enough

temperatures, and they either condense at lower temperatures to form solid minerals or ices, or react with already condensed phases to form other solid phases. Some elements condense at such low temperatures that they effectively remain as gases. Thermodynamic data can be used to predict the temperatures at which solid phases become more stable than their components in a gas of solar composition. Assignment of elements to the various *refractory* and *volatile* groups in Figure 1.3 is based on the temperature at which 50% of each element has condensed into solid phases. It is convenient in cosmochemistry to identify elements according to the kinds of minerals into which they condense – lithophile, siderophile, and chalcophile. Some volatile elements only condense at very low temperatures to form ices, or do not condense at all. Also illustrated in Figure 1.3 are the most commonly used isotope systems in cosmochemistry; the complete list is considerably longer than for geochemistry, and would include stable isotopes measured in

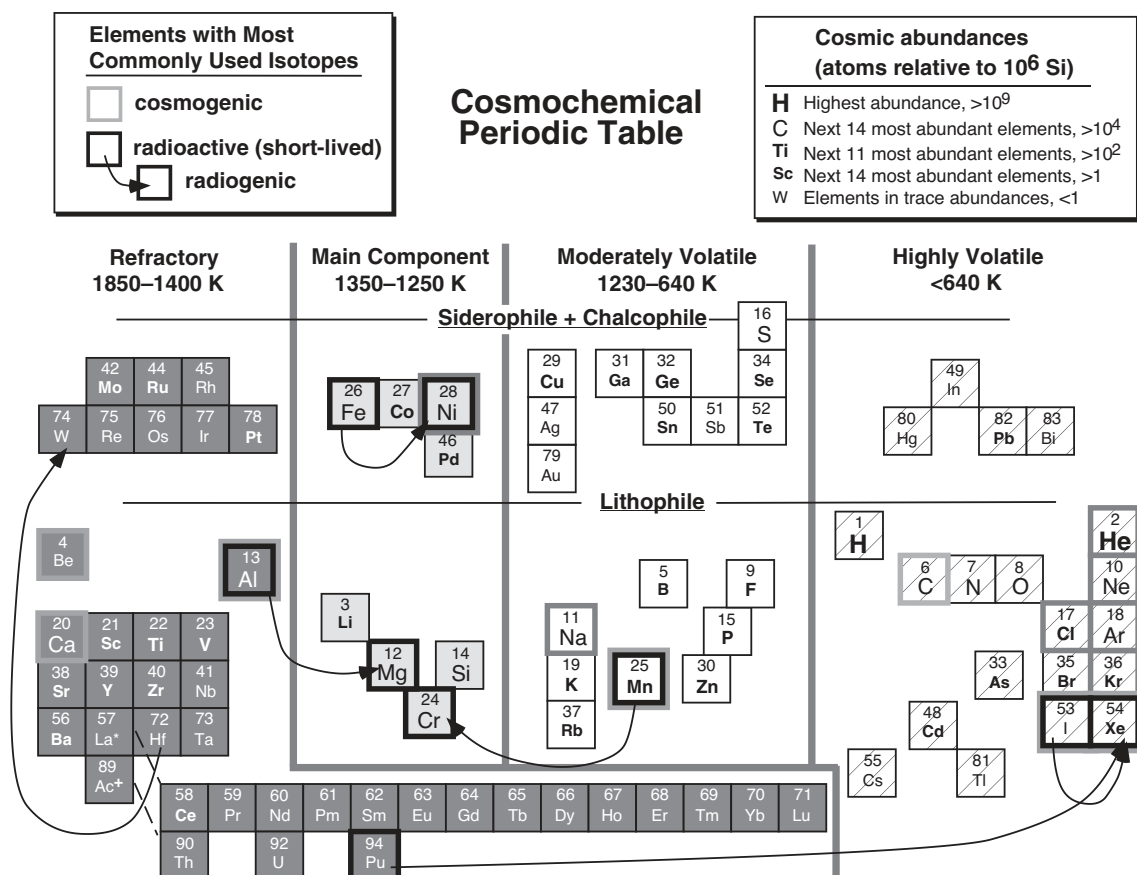


Figure 1.3 A cosmochemical Periodic Table, illustrating the behavior of elements in chondritic meteorites. Relative solar system abundances are indicated by symbol sizes. Volatilities of elements reflect the temperatures at which 50% of each element would condense into a solid phase from a gas of solar composition. As in Figure 1.2, the chemical affinities of each element – lithophile for silicates and oxides, siderophile for metals, and chalcophile for sulfides – are indicated. Some of the most highly volatile phases may have remained uncondensed in the nebula. Stable, radioactive, and radiogenic isotopes used in cosmochemistry are indicated by bold outlines, as in Figure 1.2. Abundances and 50% condensation temperatures come from tabulations by Lodders and Fegley (1998).

presolar grains in meteorites, cosmogenic nuclides formed by interaction with cosmic rays in space, and now-extinct radioactive isotopes that existed in the early solar system.

Comparison of Figures 1.2 and 1.3 reveals that the chemical behavior of an element may differ depending on whether it is in a geochemical or cosmochemical environment. This book's topics will refer to both figures in understanding the compositions of extraterrestrial materials. In cosmochemistry we are concerned with the origin and behavior of elements in space, whereas in planetary geochemistry we focus on their behavior once they are accreted into bodies that undergo geologic (usually thermal) processing. Planetary geochemistry follows more or less the same rules as on the Earth, although these rules must be modified

to accommodate different geologic conditions or starting compositions. And the geochemical consequences of biology, so important on Earth, do not apply on other worlds, so far as we can determine presently.

1.3 Beginnings of Cosmochemistry (and Geochemistry)

1.3.1 Philosophical Foundations

The philosophical foundations of cosmochemistry date to the last half of the eighteenth century when Immanuel Kant (1724–1804) and Pierre-Simon Marquis de Laplace (1749–1827) put forward comprehensive models for the origin of the solar system. Kant's model, published in 1755, started with the Sun at the center of a gaseous

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nebula. In order for this cocoon of gas and dust to be stable in the gravitational field of the Sun, the nebula had to rotate about the Sun. Kant suggested that the matter in the disk would segregate into large bodies that would become the planets. This segregation would take place slowly, with each body developing into a miniature version of the solar system. Kant showed that the rotation of the planets and their satellites would be in the same sense as their revolution around the Sun. In 1796, Laplace published a model that started with the primordial Sun occupying the entire volume now occupied by the planetary orbits. This hot, luminous “solar nebula” rotated as a rigid body so that linear velocity was greatest at the outer edge. As the nebula cooled and contracted, it rotated faster to preserve angular momentum. When centrifugal force exceeded gravitational attraction, a ring was left behind. This process was repeated many times and the rings contracted to form planets. During the nineteenth century, these two models became intertwined into a “nebular hypothesis” that was generally accepted in some form until the beginning of the twentieth century. Ideas based on these models, such as a hot solar nebula, have remained part of mainstream cosmochemical thought until very recently.

1.3.2 Meteorites and Microscopy

Meteorites (Fig. 1.4) are central to cosmochemistry, because they are our most accessible source of extraterrestrial samples. Though people have seen stones falling from the sky for thousands of years, the fact that meteorites actually fall was not acknowledged by the European and American scientific establishments until early in the



Figure 1.4 Broken surface of the Allende chondritic meteorite. Note the abundant round or broken chondrules and irregular white calcium-aluminum inclusions. Centimeter scale at the bottom.

nineteenth century. Credit for putting meteorites on the scientific map generally goes to Ernst Chladni (1756–1827). In a 63-page book with the long title (translated from German) *On the Origin of the Mass of Iron Found by Pallas and of Other Similar Iron Masses, and on a Few Natural Phenomena Connected Therewith*, published in 1794, Chladni laid out a case based on historical records of observed falls that stone and iron masses enter the Earth’s atmosphere from space and form fireballs as they plunge through the atmosphere. These ideas contradicted two beliefs that were strongly held by his scientific contemporaries: rocks and masses of metal do not fall from the sky, and no small bodies exist in space beyond the Moon. However, during the next five years, four falls of stony meteorites were witnessed and widely reported in Europe. Chemist Edward Howard (1774–1816) and mineralogist Jacques-Louis de Bournon (1751–1825) carried out a series of chemical and mineralogical analyses of stones said to have fallen from the sky and found that they were similar in texture and composition, and significantly different from terrestrial rocks. The publication of these findings in early 1802 was followed by the fall in 1803 of nearly 3000 stones at L’Aigle in Normandy, France. These events provided evidence to support Chladni’s claims, and meteorites entered the realm of scientific study.

A major step in understanding meteorites came with Henry Clifton Sorby’s (1826–1908) development of the petrographic microscope in the mid-1800s. Using this instrument, thin sections (paper-thin slices of rock, mounted on glass slides) are observed by passing polarized light through them from below, providing a means of identifying minerals and observing the textures of rocks. Sorby soon turned his attention to a type of meteorite called *chondrites*, describing the round droplets of solidified melt in them (called *chondrules*, after the Greek “chondros” for “grains” or “seeds”) as drops of a fiery rain (Fig. 1.5). Chondrites will be described in detail in Chapter 6.

A significant part of meteoritics literature focuses on petrographic description and classification. This does not usually make for exciting reading, but an orderly classification is essential for interpreting the chemical compositions of meteorites and recognizing relationships among them. Beginning in the 1860s, Gustav Rose (1798–1873) at the University Museum of Berlin and Nevil Story-Maskelyne (1823–1911) at the British Museum developed meteorite taxonomies based on microscope observations. Gustav Tschermak (1836–1927) later refined Rose’s classification, and Aristides Brezina (1848–1909) refined the Rose–Tschermak classification,

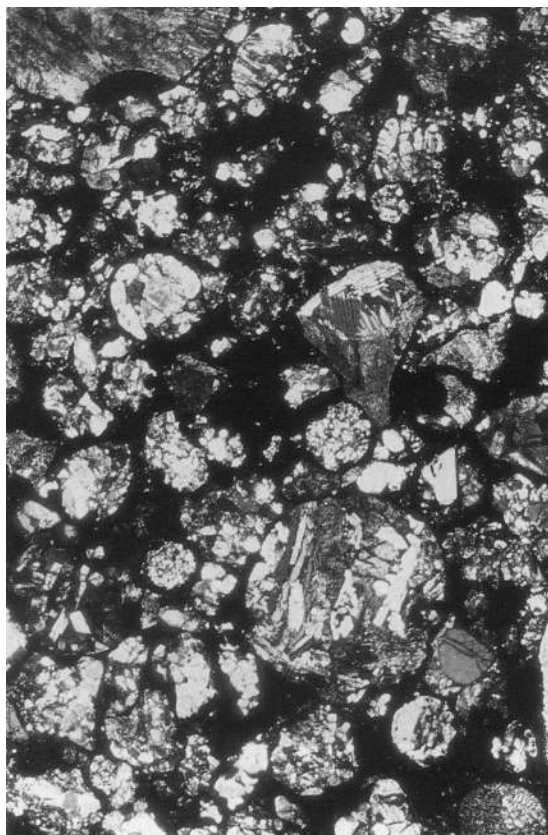


Figure 1.5 Transmitted-light photomicrograph of the Tieschitz chondritic meteorite. The rounded, millimeter-sized chondrules contain crystals of olivine and pyroxene, and the chondrules are set in a fine-grained, opaque matrix. Horizontal field of view is ~2.3 mm.

which reached its final form in 1904. This classification was based on mineralogy, because at the time there were few chemical analyses of meteorites, and those that existed were of uneven quality. George Prior (1862–1936) devised a simpler mineralogical classification for chondrites in 1920. Prior’s major mineralogical subdivisions for meteorites are still used today, but his system has been supplanted by one devised by Randall Van Schmus and John Wood (1967) that separates primary characteristics of chondrites, such as bulk composition, from secondary characteristics, such as degree of metamorphic or aqueous alteration. We will discuss meteorite classification in detail in Chapter 6.

1.3.3 Spectroscopy and the Compositions of Stars

In the early nineteenth century, determining the compositions of the Sun and other stars posed a fundamental hurdle for astronomy. The French philosopher Auguste Comte (1798–1857) confidently asserted that never, by any means, would we be able to study the chemical compositions of celestial bodies. But *spectroscopy* soon proved him wrong. Spectroscopes attached to telescopes were used to spread out starlight into its component wavelengths. The spectra of stars and of the Sun showed numerous narrow, dark gaps where particular wavelengths were missing. These gaps (absorption lines) are due to the various chemical elements in a star’s outer layers absorbing light emanating from the hotter interior. Each element absorbs (or emits) light at specific wavelengths characteristic of its electronic structure.

Box 1.1 Lockyer and the Discovery of Helium in the Sun

Joseph Lockyer (1836–1920) was one of the pioneers of solar spectroscopy. In examining the spectra of solar prominences in 1869, Lockyer noticed an absorption line that he could not identify. Reasoning that it represented an element not present on Earth, he proposed a new element – helium, from the Greek word “helios” for “Sun.” This idea failed to achieve acceptance by Lockyer’s scientific colleagues, until a gas having the same mysterious spectral line was found 25 years later in rocks. The helium in terrestrial uranium ore formed as a decay product of radioactive uranium. Thus, this abundant element was first discovered in the Sun rather than in the laboratory. Lockyer’s cosmochemical discovery was recognized by the British government, which created a solar physics laboratory for him. Lockyer also founded the scientific journal *Nature*, which he edited for 50 years.

In the late 1800s, after decades of work on the spectroscopy of stars, Lockyer developed his “meteoritic hypothesis.” According to this idea, meteorites were the primary dust of the universe. Nebulae observed by astronomers were interpreted as swarms of meteorites bound together through gravitation and interacting much like atoms in a gas. Lockyer postulated that the solar system and other objects had formed from these meteorite swarms (Lockyer, 1890). Although the original hypothesis was soon abandoned, the idea that meteorites might be chemically primitive materials that sample the cosmos was not far off the mark.

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Identifying the elements present in the Sun and stars from their spectra was one thing, but determining their relative abundances was quite another. The solar absorption lines for iron are particularly prominent, leading astronomers to believe that iron was the most abundant element in the Sun, as it is in the Earth and in many meteorites. Princeton astronomer Henry Russell (1877–1957) even conjectured that if the Earth's crust were heated to the temperature of the Sun, its spectrum would resemble the solar spectrum. It took until the 1920s before a clear understanding of how spectra arise was established, permitting evaluation of the true compositions of the Sun and stars. The key to understanding stellar spectra was discovered in 1925 by Cecilia Payne (1900–1979). She showed that the spectral lines arose from the excitation of the electrons surrounding the atomic nucleus and that the energy levels of the electrons were a function of stellar temperature. When temperature was taken into account, the abundances of elements in stars were shown to be nearly the same in a variety of stars, in spite of them having different spectra. Her work also showed that hydrogen and helium are the most abundant elements in the Sun and other stars. This last result was not widely immediately accepted and was downplayed in her published thesis. But by 1930, her work had completely supplanted previous interpretations and modern spectroscopy was born.

1.3.4 Solar System Element Abundances

The term “cosmochemistry” apparently derives from the work of Victor Goldschmidt (Fig. 1.6), who is often described as the father of geochemistry. This is yet another crossover and, in truth, Goldschmidt also established cosmochemistry as a discipline. In 1938, he published a cosmic abundance table based on the proportions of elements in meteorites. He used the term “cosmic” because, like his contemporaries, he believed that meteorites were interstellar matter. Chemist William Harkins (1873–1951) had formulated an earlier (1917) table of elemental abundances – arguably the first cosmochemistry paper, although he did not use that term. As explained in Chapter 4, *solar system abundance* is now preferred over *cosmic abundance*, although the terms are often used interchangeably.

Goldschmidt and his colleagues in Germany, and later in Norway (where he escaped the grasp of the Nazis in World War II), analyzed and compiled a wealth of chemical data on terrestrial rocks and meteorites. The compositions of terrestrial rocks have been modified by partial melting (leaving some components behind as residues) and by fractional crystallization (where crystals are segregated from the melt, causing the liquid's

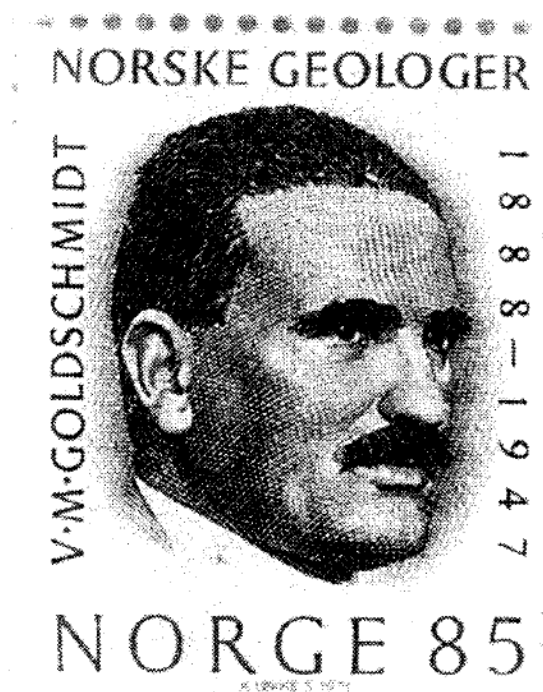


Figure 1.6 Victor Goldschmidt, as pictured on a Norwegian postage stamp issued in 1974.

composition to change). However, Goldschmidt recognized that chondrites have not experienced wholesale melting and have thereby escaped geologic processing. They are basically cosmic sediments – physical mixtures of nebular matter whose chemical abundances have remained unchanged since they formed. To obtain accurate compositions using the then-new analytical technique of emission spectroscopy, Goldschmidt separated chondrites into their more readily measurable silicate, metal, and sulfide components and analyzed each in turn. Consequently, he was able to determine how various elements were partitioned among these coexisting phases (thereby inventing the terms “lithophile,” “siderophile,” and “chalcophile” to describe their geochemical affinities). He then calculated what he called the “cosmic abundances” of 66 elements by using the weighted means of element concentrations in meteorite silicate (10 parts), metal (2 parts), and sulfide (1 part). At about the same time, astronomers began using the Sun's spectra to estimate elemental abundances. It soon became apparent that solar elemental abundances were similar to Goldschmidt's cosmic (chondritic) abundances, except that the meteorites were depleted in the most volatile elements like hydrogen and helium. Cosmic abundances (more appropriately called solar

system abundances) are a cornerstone of cosmochemistry because they represent the raw material from which the solar system formed.

1.3.5 Isotopes and Nuclear Physics

Isotopes were recognized at the beginning of the twentieth century as a result of studies of radioactivity. Careful studies found three naturally occurring radioactive decay series – the thorium, uranium, and actinium series – all of which ended with stable lead. The existence of isotopes was confirmed in 1911 when Fredrick Soddy (1877–1956) measured the atomic masses of lead obtained from uranium-rich and thorium-rich ores and showed that they were different. During this same period, J. J. Thompson (1856–1940) discovered that ions accelerated through an electric field would adopt different parabolic trajectories depending upon their masses. Thompson's student, Francis Aston (1877–1945), used this principle to design several different mass spectrographs, which separated particles by mass/charge ratio and recorded the output on photographic plates. By 1920, Aston was reporting the presence and relative abundances of isotopes of numerous elements, including oxygen, neon, argon, krypton, xenon, and mercury (Aston, 1920). In 1922, he received the Nobel Prize in Chemistry for his work on isotopes using a mass spectrograph. However, an understanding of the structure of the atom had to await the discovery of the neutron in 1930.

During the 1930s, further technological advances permitted detailed studies of the masses and relative abundances of isotopes. Modern mass spectrometers designed by Alfred Nier (1911–1994) at the University of Minnesota had greater mass-resolving power and were more sensitive than any built previously. Nier made accurate measurements of the isotopic abundances of argon, potassium, zinc, rubidium, and cadmium and, in the process, discovered ^{40}K , which would later become an important isotope for dating rocks. He also pioneered the development of uranium–lead and thorium–lead dating.

In 1940, Nier successfully separated ^{235}U from ^{238}U using a mass spectrometer, providing an enabling technology for the Manhattan Project. During World War II, many of the top nuclear physicists worked on the development of the atomic bomb. The fascinating story of these years and their effect upon the participants is beyond the scope of this book. But as the war ended, many of them turned their attention away from the tools of war toward understanding our planet and universe, and their knowledge became available to cosmochemistry.

The leading figure in cosmochemistry during the 1950s and 1960s was Harold Urey (1893–1981). Urey



Figure 1.7 Harold Urey, one of the fathers of cosmochemistry. NASA image.

(Fig. 1.7) was one of the first practitioners of cosmochemistry as we understand it today. He was awarded the Nobel Prize in Chemistry in 1934 for his work on deuterium and heavy water. During the war, he and his colleagues developed the gaseous diffusion method for separating ^{235}U from ^{238}U . After the war, he became a professor at the University of Chicago, where he did pioneering work using the $^{18}\text{O}/^{16}\text{O}$ ratio in paleoclimate research, developed theories about the origin of the elements and their abundances in stars, pointed out the importance of short-lived radionuclides such as ^{26}Al , investigated the origins of life on Earth, and made many other contributions. He was a leader in developing the scientific rationale for returning samples from the Moon.

During World War II, Hans Suess (1909–1993) was part of a team of German scientists working on heavy water. In 1950, he emigrated to the United States. His work with Urey on *nucleosynthesis* and the abundances of the elements is a cornerstone of cosmochemistry. In 1965, along with Heinrich Wänke (1928–2015), he proposed that the extremely high noble gas contents in some chondritic meteorites were due to the implantation of solar wind. He also worked on climate research and ^{14}C dating. Together, Suess and Urey (1956) published

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the first table of cosmic abundances to include the abundances of the isotopes.

The new knowledge of nuclear physics affected cosmochemistry in another way. A classic paper by astrophysicists Margaret and Geoffrey Burbidge (husband and wife), William Fowler, and Fred Hoyle (this paper was so influential that it has come to be known by scientists simply as “B²FH”), and a similar contribution by Alastair Cameron, both published in 1957, provided the theoretical basis for understanding how elements are produced in stars, as described in Chapter 3.

Radiometric dating using long-lived radionuclides came into its own in the 1940s and 1950s with the advent of better mass spectrometers. The uranium-isotope decay scheme was first shown to be useful as a geochronometer by Fritz Houtermans and Arthur Holmes in 1946. The first accurate determination of the age of the Earth was made in 1956 by Clair Patterson, who used the uranium–lead method to date meteorites. The ⁴⁰K–⁴⁰Ar decay scheme was shown to be a useful chronometer for meteorites by Gerald Wasserburg in his doctoral thesis, completed in 1954. The first age determination by the ⁸⁷Rb–⁸⁷Sr method was published by Hahn et al. (1943), and the method came into wide use in the 1950s. Its application to meteorites peaked in the late 1960s and 1970s, in conjunction with work on the lunar samples.

The first *short-lived radionuclide* (one whose primordial abundance has decayed away) was shown to have been present in meteorites by John Reynolds in 1960. Reynolds found large excesses of ¹²⁹Xe, the decay product of short-lived ¹²⁹I, in chondritic meteorites. This discovery showed that elements had been synthesized in stars shortly before the formation of the solar system. A more important short-lived radionuclide, ²⁶Al, was demonstrated to have been present in meteorites by Typhoon Lee et al. in 1977. This isotope is particularly significant, as it is thought to have been a potent source of heating for asteroids and planets early in solar system history. A variety of other short-lived isotopes have now been confirmed in meteorites and are the basis for high-resolution chronometry of the early solar system.

Nuclides formed by nuclear reactions induced by high-energy cosmic rays are called *cosmogenic*. Cosmogenic isotopes are more common in meteorites than on the Earth, because our planet’s atmosphere screens out most cosmic rays. However, meteorites traveling in space are heavily irradiated by cosmic rays, and the production of cosmogenic isotopes can be used to estimate the times since the meteorites were liberated

from their parent asteroids (these times are called *cosmic-ray exposure ages*). The first cosmic-ray exposure ages were measured in the late 1950s. Since then, thousands of cosmic-ray exposure ages have been estimated using a variety of cosmogenic nuclides, and new modeling techniques have allowed the interpretation of complex irradiation histories.

In 1956, John Reynolds pioneered a new and highly sensitive method for measuring noble gases, which effectively created the field of noble gas geochemistry and cosmochemistry. Noble gases have many isotopes and, because they do not bond with rock-forming elements, they have very low abundances in most materials. Thus, additions from the decay of radioactive nuclides or cosmic-ray interactions are easy to detect. Noble gases also exhibit different elemental and isotopic ratios in meteorites, reflecting different processes operating in the early solar system. In addition, isotopic anomalies that could not be explained by any processes known to be operating in the solar system were found in xenon (discovered by John Reynolds and Grenville Turner in 1964) and neon (discovered by David Black and Robert Pepin in 1969) extracted from meteorites. These noble gases provided the first hints that presolar grains might have survived in the nebula, although they were not widely recognized at the time.

The pursuit of the carriers of exotic noble gas components by Edward Anders and colleagues at the University of Chicago and in other laboratories eventually led to the isolation of presolar grains from meteorites. The approach used by Anders involved laborious tracking of exotic noble gas carriers through steps of increasingly harsh chemical dissolutions and physical separations. He was rewarded with the discovery of presolar diamond (the first isolated presolar grain), silicon carbide, and graphite, the carriers of the three main exotic noble gas components. These three materials are all carbon rich, but subsequent work has identified presolar oxides, nitrides, and silicates, as discussed in Chapter 5.

1.3.6 Spacecraft, Returned Samples, and Remote Chemical Analyses

The launch of Sputnik by the Soviet Union in 1957 changed the world forever. The immediate impact was to change the nature of the Cold War by demonstrating the feasibility of intercontinental ballistic missiles. But Sputnik also raised the curtain on the scientific exploration of space and on visiting and obtaining samples from other solar system bodies. The first target was the Moon. Close-up images of the Moon were provided by the United States’ Ranger missions, which

Table 1.1 Samples returned by spacecraft missions

Sample source	Mass	Date Returned to Earth	Mission
Moon: Mare Tranquilitatis	21.55 kg	Jul 24, 1969	Apollo 11 (NASA)
Moon: Oceanus Procellarum	34.30 kg	Nov 24, 1969	Apollo 12 (NASA)
Moon: Mare Fecunditatis	101 g	Sep 24, 1970	Luna 16 (USSR)
Moon: Fra Mauro Highlands	42.80 kg	Feb 9, 1971	Apollo 14 (NASA)
Moon: Hadley–Apennine	76.70 kg	Aug 7, 1971	Apollo 15 (NASA)
Moon: Apollonius Highlands	55 g	Feb 25, 1972	Luna 20 (USSR)
Moon: Descartes Highlands	95.20 kg	Apr 27, 1972	Apollo 16 (NASA)
Moon: Taurus–Littrow	110.40 kg	Dec 19, 1972	Apollo 17 (NASA)
Moon: Mare Crisium	170.1 g	Aug 22, 1976	Luna 24 (USSR)
Earth–Sun Lagrange 1	Solar wind atoms	Sep 8, 2004	Genesis (NASA)
Comet Wild 2	1000s of dust particles	Jan 15, 2006	Stardust (NASA)
Asteroid 25143 Itokawa	1000s of particles	Jun 13, 2010	Hayabusa (JAXA)
Asteroid 162173 Ryugu	~5.4 g	Dec 5, 2020	Hayabusa2 (JAXA)
Moon: South Pole–Aitken	~2 kg	Dec 2020	Chang'e 5 (CNSA)
Asteroid 101955 Bennu	~250 g?	Sep 2023 (planned)	OSIRIS-REx (NASA)

**Figure 1.8** Apollo astronaut on the Moon. NASA image.

impacted the Moon in 1964 and 1965. The first lunar chemical data were provided by the Soviet Luna and American Surveyor spacecraft in 1966. The first manned landing on the Moon was the Apollo 11 mission in 1969. Five more successful Apollo missions followed, before the program was abruptly terminated.

The return of 381 kg of lunar rocks and soils from six sites on the Moon's nearside by Apollo astronauts (Fig. 1.8) and 326 g from three sites by Soviet Luna robotic landers in the 1970s (Table 1.1) provided a bonanza of new extraterrestrial materials for cosmochemistry. The intense interest in these samples encouraged a considerable expansion of laboratory techniques

and capabilities. Fortunately, two large meteorites (the Allende and Murchison chondrites) fell to Earth in 1969, just as the new laboratories were gearing up for lunar sample return. The new analytical techniques were applied to these meteorites, initially as a means of demonstrating capability, but the two chondrites turned out to be incredibly interesting in their own right and provided a new impetus for the study of all types of extraterrestrial materials. Because lunar samples were so precious, many groups simultaneously analyzed the same rocks, and competition forced the quality of the analyses to new heights. Lunar rocks were especially useful because mapping of the Moon by telescopes and orbiting spacecraft provided the geologic context for these samples. Lunar soils allowed for wider sampling of rock types, because the soils consist of rock particles thrown tremendous distances by impacts. In addition, lunar soils contain implanted solar wind particles, providing a window onto solar element abundances. A decade after the Apollo program ended, the first lunar meteorites were recognized in Antarctica. Their discovery, made possible by comparing them with Apollo samples, proved that rocks could be ejected from one body and travel to another. For the first time, rocks delivered by natural processes from another planet were available for direct geochemical analysis. While the Apollo and Luna samples were collected from a geographically restricted area (<5% of the surface area) of the Moon, the nearly 150 distinct lunar meteorites (as of time of writing) are thought to provide a more