# 1 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.

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 composition of the universe 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, providing 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 provide constraints on our understanding of how elements were forged inside stars before the Sun's birth. Once formed, these
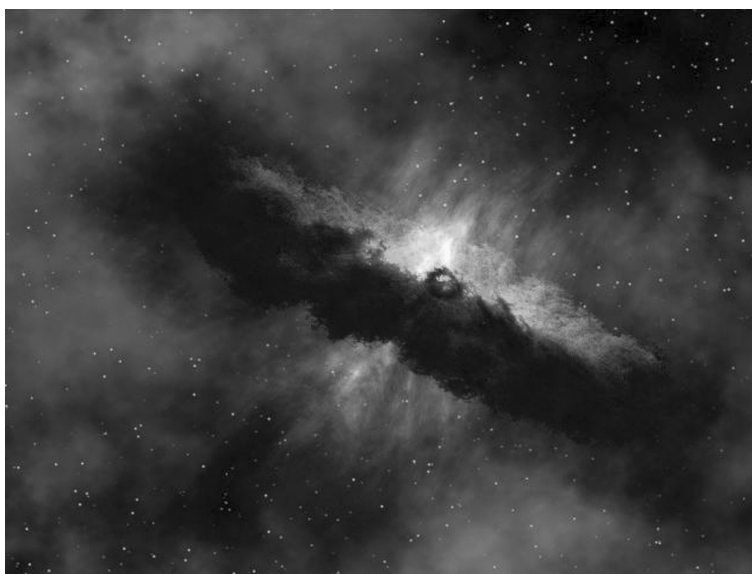
Fig. 1.1 An artist's conception of the solar nebula, surrounding the violent young Sun. Figure courtesy of NASA.

grains were released to the *interstellar medium* (ISM), the space between the stars. The ISM is filled primarily by diffuse gases, mostly hydrogen and helium, but with oxygen, carbon, and nitrogen contributing about 1% by mass and all the other elements mostly in micrometer-size dust motes. Much of the chemistry in the ISM occurs within relatively dense molecular clouds, where gas densities can reach 10^3 to 10^6 particles per cm^3, high by interstellar standards (but not by our everyday experience – Earth's atmosphere has $\sim 3 \times 10^{19}$ atoms per cm^3 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 produced 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 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 or their smaller cousins, geologically processed planetesimals, using telescopes or 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 extraterrestrial materials are fair game for cosmochemistry.

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), which allows them to combine into compounds (minerals), to be dissolved in natural fluids, or to occur in 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 exist in more than one isotopic form. Measuring isotopic abundances has great value as a geochemical tool, and the most commonly used isotope systems are illustrated by heavy boxes in Figure 1.2. Stable isotopes of some light elements provide information on sources of elements, the conditions under

Fig. 1.2   A geochemical periodic table, illustrating controls on element behavior during geologic processes.
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 non-rock (atmophile) phases
are identified. 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.

which minerals form, and the processes that separate isotopes from each other. Unstable
(radioactive) nuclides and their decay products (radiogenic nuclides) similarly constrain
element sources and geologic processes, as well as permit the ages of rocks 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 approx-
imately equivalent to the average solar system (often incorrectly called "cosmic") compo-
sition. The behavior of elements in space is governed largely by their volatility, which we
quantify by specifying the temperature interval where 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
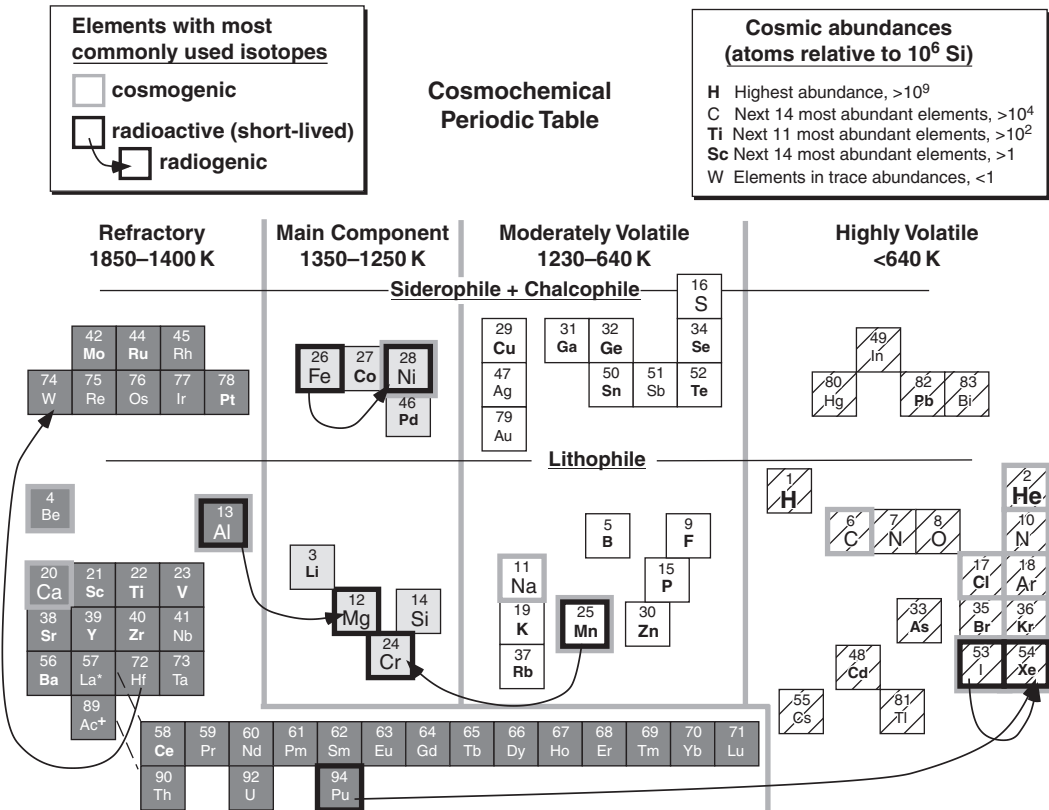
Fig. 1.3 A cosmochemical periodic table, illustrating the behavior of elements in chondritic meteorites. Cosmic abundances are indicated by symbol sizes. Volatilities of elements reflect the temperatures at which 50% of each element would condense into a solid phase from a gas of solar composition. As 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 are from tabulations by Lodders and Fegley (1998).

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

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.

Beginnings of cosmochemistry (and geochemistry)

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 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 gravitation 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.

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
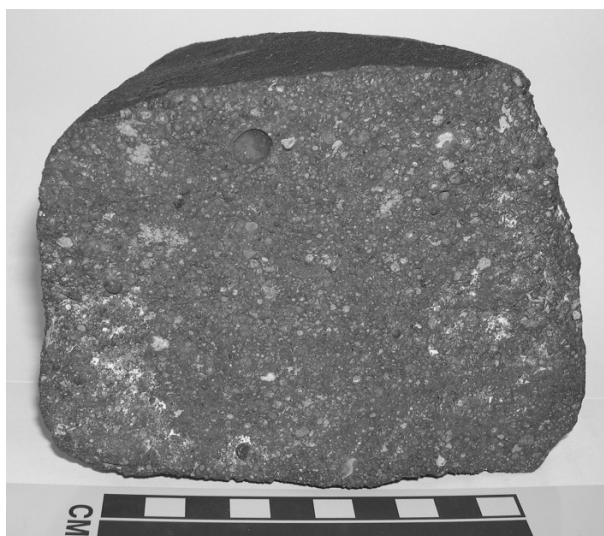
Fig. 1.4 Broken surface of the Allende meteorite, a chondrite that fell in Mexico in 1969. Note the abundant round chondrules and white calcium–aluminum inclusions.

thousands of years, the fact that meteorites actually fall was not acknowledged by the European and American scientific establishments until early in the 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 strongly held beliefs 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,"
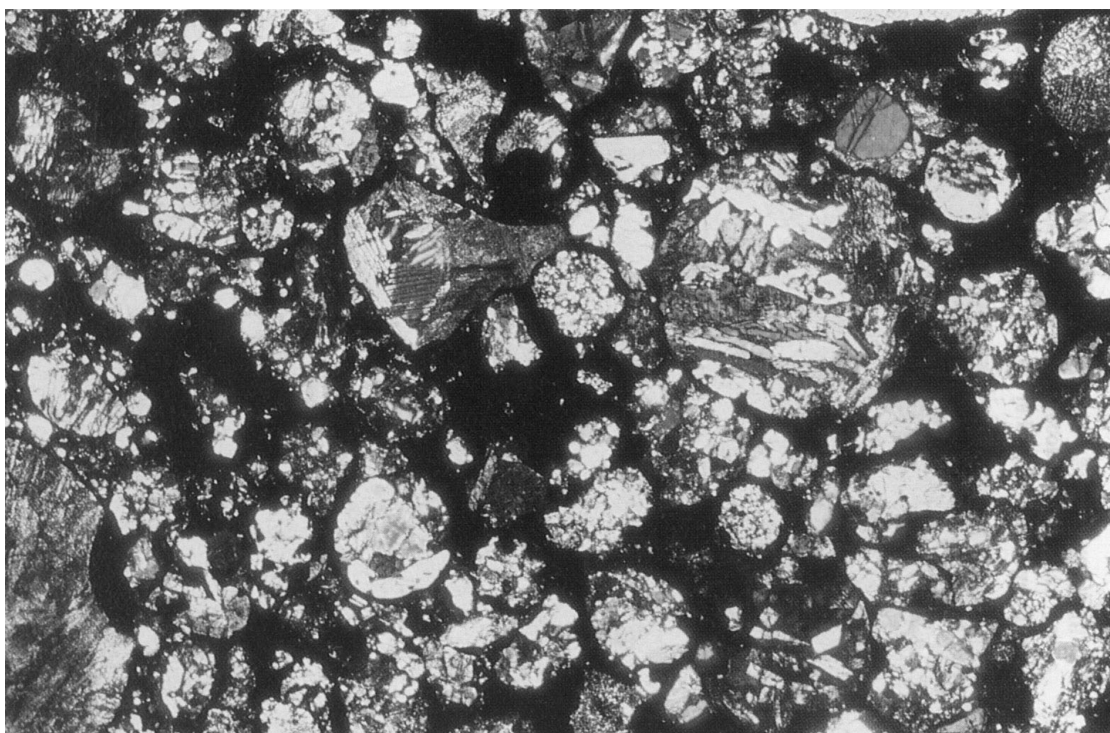
Fig. 1.5 Transmitted-light photomicrograph of the Tieschitz chondritic meteorite. Horizontal field of view is ~3.5 mm. The rounded, millimeter-size chondrules contain crystals of olivine and pyroxene, and the chondrules are set in a fine-grained, opaque matrix.

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, 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 meteorites, 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.

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 from 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.

Spectroscopy and the compositions of stars

In the early nineteenth century, determining the compositions of stars posed a fundamental hurdle for astronomy. The French philosopher Auguste Compte (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.

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 the establishment of a clear understanding of how spectra arise, permitting evaluation of the true compositions of the Sun and stars. The key to understanding stellar spectra was discovered in 1925 by Cecilia Payne (1900–79). She showed that the spectral lines arose from the excitation of the electrons surrounding the atomic nucleus and that the energy
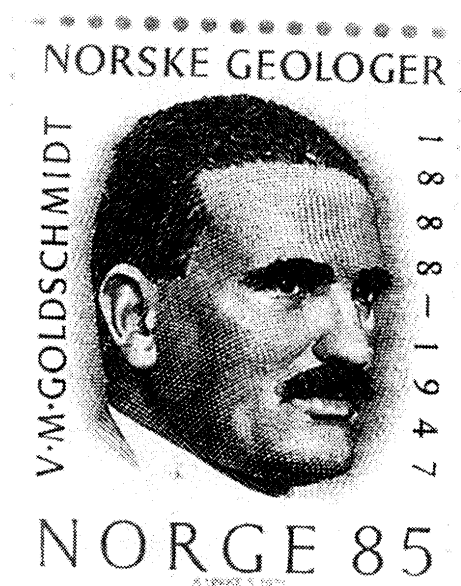
Fig. 1.6   Victor Goldschmidt, as pictured on a Norwegian postage stamp issued in 1974.

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 their 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 immediately widely accepted and was downplayed in her published thesis. But by 1930, her work had completely supplanted previous interpretations and modern spectroscopy was born.

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 1937 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 3, the term *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