

PRINCIPLES AND APPLICATIONS OF
GEOCHEMISTRY

A Comprehensive Textbook for Geology Students

Second Edition

GUNTER FAURE

THE OHIO STATE UNIVERSITY

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PLANET EARTH IN THE SOLAR SYSTEM

Future generations may remember the 20th century primarily for the advances in technology that have enabled us to begin the exploration of the solar system. Our resulting awareness of the celestial environment of the Earth has raised questions about the origin and evolution of the solar system, of the Milky Way Galaxy, and of the Universe at large. The start of an introductory geochemistry course is an appropriate time to satisfy our desire to know the origins of the world in which we live.

What Is Geochemistry?

Geology began when early man first picked up a stone, considered its qualities, and decided that it was better than the stone he already had. Good stones were useful and they were collected, mined, and traded.

HENRY FAUL AND CAROL FAUL (1983, p. 1)

Geochemistry is based on the urge to understand why some stones are “good” and how they formed. It involves applications of the principles of chemistry to the solution of geological problems and therefore could not develop until chemistry and geology had been established as scientific disciplines. These applications were practiced first during the 16th century in the mines of Europe where knowledge of minerals and their chemical compositions was used to recognize and follow veins of ore. For example, in 1574 Lazarus Ercker, the superintendent of mines for King Rudolf II of Austria, published a manual in which he described ores and outlined procedures for their analysis (Ercker, 1951). However, several centuries passed before geochemistry in the present sense of the word became established as an integral component of Earth and Planetary Science.

1.1 Early History

Two essential prerequisites for the growth of geochemistry were the discovery of the chemical elements and the development of sensitive and accurate methods for the analysis of rocks and minerals. Until the end of the 16th century matter was thought to consist of earth, water, fire, and air, whose basic qualities were described as

warm, cold, dry, and wet. The metals gold, silver, copper, iron, tin, mercury, and lead together with sulfur and carbon had been known for thousands of years but were not recognized as elements in the present sense of the word. Antimony, arsenic, bismuth, and phosphorus were studied by the alchemists during the Middle Ages.

The development of analytical chemistry during the 18th century resulted in the discovery of 46 chemical elements between 1720 and 1850. After Bunsen and Kirchhoff invented the optical emission spectrograph, 30 additional elements were added from 1850 to 1925. The transuranium elements and certain other radioactive elements were discovered later in the 20th century (Correns, 1969).

As the number of known chemical elements increased during the 19th century, chemists became aware that they could be organized into groups based on similarities of their chemical properties. These tendencies became the foundation of the periodic table of the elements proposed independently by D. I. Mendeleev in 1869 and by J. L. Meyer in 1870 (Asimov, 1965). The cause for the periodicity of the chemical properties of the elements was not known then and was recognized only after the internal structure of atoms was worked out during the first 30 years of the 20th century.

The periodic table is a manifestation of the relationship between the internal structure of atoms and the chemical and physical properties of the elements. It facilitates a rational explanation of the chemical properties of the elements and of their observed distribution in nature.

The roots of geochemistry lie mainly in the 19th century, but it acquired its present multifaceted complexity during the 20th century. The word *geochemistry* was first used in 1838 by Christian Friedrich Schönbein, who was a chemistry professor at the University of Basel in Switzerland. The term was used again in 1908, 70 years later, when Frank W. Clarke of the U.S. Geological Survey published the first edition of his book, *The Data of Geochemistry*.

Clarke was the Chief Chemist of the U.S. Geological Survey from 1884 until 1925. He started the tradition for excellence in the analysis of rocks and minerals that has helped to make the Survey one of the largest geochemical research centers in the world. The first edition of Clarke's book was amazingly modern in its approach to geochemistry. He opened with chapters on the chemical elements, the atmosphere, lakes and rivers, and the ocean followed by chapters on saline lakes and springs and on evaporite deposits. Next he took up volcanic gases, magma, rock-forming minerals, and igneous rocks and then weathering, sedimentary rocks, metamorphic rocks, and ore deposits. The book ends with chapters on fossil fuels and their origin. That is pretty much how we would present the data of geochemistry today, but Clarke did it this way in 1908! More than 15 years passed before the great Soviet geochemist V. I. Vernadsky published his geochemistry book in 1924. Clarke was the first geochemist in the modern sense of the word.

Clarke's book went through five editions, the last of which appeared in 1924. It is now being updated and expanded by the U.S. Geological Survey under the editorship of Michael Fleischer. However, the *Handbook of Geochemistry*, edited by K. H. Wedepohl from 1969 to 1978, is the most complete source of geochemical data currently available.

1.2 Geochemistry in the U.S.S.R.

Geochemistry became an important subject in the U.S.S.R. because of the need to develop the mineral resources of the country. In 1932 Soviet geologists began to analyze systematically collected soil samples using optical spectroscopy (Fersman, 1939). In subsequent years the geologists of the Central Geological and Prospecting Institute in Moscow carried out extensive "metallometric" surveys based on soil samples in search of geochemical anomalies.

Geochemistry prospered in the U.S.S.R. because of the popular support it received partly in response to the remarkable work of Alexander Fersman (1883-1945). Fersman studied mineralogy at the University of Moscow under V. I. Vernadsky, who took his students on many field trips and encouraged them to regard minerals as the products of chemical reactions. These were radical departures from conventional mineralogy practiced at the turn of the century. Fersman graduated in 1907 and was elected to a professorship in mineralogy in 1912 at the age of 27. He embarked on an extraordinary career of teaching and research in geochemistry with emphasis on applications. He traveled widely in the U.S.S.R. and explored regions rarely visited before. His sustained interest in the exploration of the Kola Peninsula in the north ultimately led to the discovery of deposits of apatite and nickel ore. As a result, a remote wilderness area was transformed into an important center of mining and industry. Fersman also explored central Asia and discovered a native sulfur deposit at Kara Kum that was actively mined for decades.

Between 1934 and 1939 Fersman published a comprehensive four-volume work entitled *Geochemistry* in which he applied the principles of physical chemistry to the distribution of the chemical elements in nature. Fersman, above all, aroused public interest in geology and geochemistry by his inspiring lectures and popular books. Alexander K. Tolstoy called him a "poet of

stones." Fersman earned this accolade by writing books intended for the layman: *Mineralogy for Everyone* (1928), *Recollections about a Stone* (1940), *My Travels, Stories about Precious Stones*, and *Geochemistry for Everyone* (1958). The last two were published posthumously. Fersman's conviction that geochemistry should serve his country is reflected in his words: "We cannot be merely idle admirers of our vast country; we must actively help reshape it and create a new life" (Shcherbakov, 1958).

The scientific legacy of Fersman's former teacher, Vladimir Ivanovich Vernadsky (1863–1945), is similarly impressive, but it has not been appreciated in the western world. Vernadsky emphasized the importance of the activities of living organisms in geological and geochemical processes. In fact, he regarded living matter as the "most powerful geological force" and wrote that the Earth's crust originated from the biosphere. These convictions about the importance of life on Earth were not widely accepted by geologists in North America, partly because Vernadsky wrote in many languages (Russian, German, French, Czech, Serbo-Croatian, and Japanese). His most important books (Vernadsky, 1924, 1929) were written in French and published in Paris. However, Vernadsky was also far ahead of his contemporaries by concluding that the biosphere may have controlled the environment on the surface of the Earth from the very beginning, long before the existence of life in Early Precambrian time was known (Lapo, 1986). Vernadsky's views on this subject are now reflected in the "Gaia Hypothesis" of Lovelock (1979), made popular on American television in the "Planet Earth" series by the Public Broadcasting System. Vernadsky also identified the biosphere as the principal transformer of solar energy into chemical energy. This idea is now widely accepted. For example, Cloud (1983) described the biosphere as "a huge metabolic device for the capture, storage and transfer of energy." Fossil fuels (coal, oil shale, petroleum, and natural gas) are now regarded as deposits of solar energy collected by the biosphere.

Vernadsky's views on the importance of the biosphere (Vernadsky, 1945) are becoming

increasingly relevant as we attempt to predict the climatic consequences of the "greenhouse effect" caused by the discharge of carbon dioxide and other gases into the atmosphere. We are carrying out an experiment on a global scale the outcome of which could be detrimental to life. The response of the biosphere to this perturbation of the environment may be crucial to the ultimate outcome of this experiment.

V. I. Vernadsky is revered in the U.S.S.R. as one of the giants of science in the 20th century. His teachings still motivate the geochemists working at the Vernadsky Institute of Geochemistry and Analytical Chemistry in Moscow, which is among the foremost geochemical research institutes in the world.

1.3 V. M. Goldschmidt

The Institute of Geochemistry at the University of Göttingen in Germany was made famous by the work of Victor M. Goldschmidt (1888–1947). Goldschmidt earned his doctorate at the University of Oslo in 1911 with a study of contact metamorphism based on the thermodynamic phase rule. In the following year Max von Laue discovered diffraction of x-rays by crystals and thereby provided a method for determining the crystal structure of a mineral and the radii of the ions of which it is composed. From 1922 to 1926 Goldschmidt and his associates at the University of Oslo used x-ray diffraction to determine the crystal structures of many minerals (Goldschmidt, 1930). In 1930 Goldschmidt moved to the University of Göttingen, where he studied the distribution of the chemical elements using an optical spectrograph. From this body of data he deduced that the chemical composition of minerals is determined by the requirements of "closest packing" of ions. Moreover, the substitution of the ions of a major element by the ions of a trace element depends on the similarity of their radii and charges. These generalizations provided a rational explanation for the observed distribution of the elements in the minerals of the crust of the Earth.

Goldschmidt returned to Oslo in 1935 but was unable to continue his work after the

German invasion of Norway in 1940. He fled to Sweden in 1942 and ultimately made his way to England, where he worked at the Macaulay Institute for Soil Research. His health had seriously deteriorated as a consequence of imprisonment in concentration camps in Norway. Goldschmidt returned to Oslo in 1946 but died there prematurely in 1947 at the age of 59. He left behind the manuscript of a partially completed book entitled *Geochemistry*, which was completed by Alex Muir and published posthumously in 1954. A special commemorative issue of *Applied Geochemistry* (1988) was devoted to Goldschmidt on the 100th anniversary of his birthday.

Goldschmidt's principal contribution to geochemistry is the rational explanation of isomorphous substitution in crystals based on the compatibility of the radii and charges of the ions. He thereby achieved one of the major goals of geochemistry. Nevertheless, the urge to know and to understand the distribution of the chemical elements has continued to motivate the work of several outstanding geochemists, notably L. H. Ahrens in South Africa, S. R. Nockolds in England, S. R. Taylor in Australia, K. Rankama in Finland, K. H. Wedepohl in Germany, A. P. Vinogradov in the U.S.S.R., D. M. Shaw in Canada, and K. K. Turekian in the United States.

1.4 Modern Geochemistry

Beginning in the 1950s, geochemists turned increasingly to the study of chemical reactions and processes. The roots of this line of research can be found in the work of A. Fersman, who used the concepts of thermodynamics to study the stability of minerals in their natural environment. In addition, J. H. van't Hoff (1852–1911) studied the crystallization of salts by evaporating seawater in Berlin and, in 1904, the Geophysical Laboratory of the Carnegie Institution of Washington was founded in the United States. The principal objective of the Geophysical Laboratory has been to study the origin of igneous rocks and ore deposits by experimental methods. The results achieved by

N. L. Bowen and his colleagues, and by their successors, at that laboratory have become the foundation of modern igneous petrology. Bowen's book, *The Evolution of the Igneous Rocks*, published in 1928, turned igneous petrology from a preoccupation with the description and classification of igneous rocks toward a concern for their origin and the geochemical differentiation of the Earth by magmatic activity.

In 1952 Brian Mason published the first edition of *Principles of Geochemistry*, which was widely used as a textbook at universities and helped to establish geochemistry as a legitimate component of Earth Science. In the next decade Robert M. Garrels and Konrad B. Krauskopf used thermodynamics and solution chemistry to determine the stability of minerals and the mobility of their ions at the surface of the Earth. They trained the modern generation of geochemists by their own research and through their popular textbooks (Garrels, 1960; Garrels and Christ, 1965; Krauskopf, 1967).

Geochemical prospecting, as we know it today, was initiated in 1947 by the U.S. Geological Survey (Hawkes and Lakin, 1949) and was based on colorimetry. The techniques developed in the United States were used in 1953 for soil surveys in the United Kingdom and in Africa (Webb, 1953). Subsequently, the Geochemical Prospecting Research Center at the Imperial College of Science and Technology in London became a center of activity in this aspect of geochemistry. Geochemical prospecting continues to be one of the most important practical applications of geochemistry and now relies on a wide range of sophisticated analytical techniques.

Environmental geochemistry has arisen recently because of the need to monitor the dispersion of metals and various organic compounds that are introduced into the environment as anthropogenic contaminants. This new application of geochemistry to the welfare of humankind is closely related to pollutant hydrogeology and medical geochemistry. Geochemical prospecting and environmental geochemistry are of paramount importance because they contribute to the continued well-being of the human species on Earth.

6 WHAT IS GEOCHEMISTRY?

Since about the middle of the 20th century geochemistry has become highly diversified into many subdivisions, among them inorganic geochemistry, organic geochemistry, isotope geochemistry, geochemical prospecting, medical geochemistry, aqueous geochemistry, trace-element geochemistry, and cosmochemistry. Each of these subdivisions has its own rapidly growing body of literature. However, the geochemists of the world have organized scientific societies that transcend the boundaries of specialization and help to unify the field. These societies also publish journals that promote the free flow of information and ideas among their members. For example, the Geochemical Society and the Meteoritical Society both sponsor *Geochimica et Cosmochimica Acta*. The European Association for Geochemistry has adopted the journal *Chemical Geology*, and the International Association of Geochemistry and Cosmochemistry sponsors *Applied Geochemistry*. Among other journals that publish papers dealing with geochemistry are

Earth and Planetary Science Letters
Contributions to Mineralogy and Petrology
Journal of Geochemical Exploration
Economic Geology
American Journal of Science
Nature
Science

Some journals are closely associated with certain regions, for example,

<i>Geokhimiya</i>	}	Russia
<i>Doklady</i> (Earth Science Section)		
<i>Lithology and Mineral Resources</i>		
<i>Geochemistry International</i>		
<i>Geochemical Journal</i>		Japan
<i>Chinese Journal of Geochemistry</i>		People's Republic of China

In fact, most Earth Science journals now publish papers in which geochemical data or principles are used to explain a geological process or to solve a particular problem. The strength of geochemistry lies in the fact that most geological processes involve chemical reactions in some significant way. Geochemistry really is for everyone, as Fersman claimed in his popular book.

What then is geochemistry? There is no easy answer to this question because geochemists concern themselves with a wide range of natural phenomena and use many different techniques to study them. According to Fersman, "Geochemistry studies the history of chemical elements in the Earth's crust and their behavior under different thermodynamic and physicochemical natural conditions." Goldschmidt's definition of geochemistry was "Geochemistry is concerned with the laws governing the distribution of the chemical elements and their isotopes throughout the Earth" (Correns, 1969). We could go on and on. Geochemistry is a highly diversified and constantly evolving subject that can be described in many different ways.

For our purposes the major goals of geochemists are

1. To know the distribution of the chemical elements in the Earth and in the solar system.
2. To discover the causes for the observed chemical composition of terrestrial and extraterrestrial materials.
3. To study chemical reactions on the surface of the Earth, in its interior, and in the solar system around us.
4. To assemble this information into geochemical cycles and to learn how these cycles have operated in the geologic past and how they may be altered in the future.

These are the lofty goals of a scientific discipline. Their intrinsic merit is apparent. However, geochemists practicing their craft today also have an obligation to humankind to assist in the devel-

opment and management of natural resources, to monitor the quality of the environment both locally and on a global scale, and to warn humanity against dangerous practices that may threaten the quality of life in the future.

With so much at stake it is not easy to express succinctly what geochemistry is all about. K. O.

Emery and J. M. Hunt (1974, p. 586) put it this way: "Studies of geochemistry ... convert idle speculation into ... understanding ...". That will be the theme of this book. We can no longer afford idle speculation in the Earth Sciences. We must have understanding. Geochemistry can show us how to achieve it.

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