GEOCHEMISTRY: BRANCHES, PROCESSES, PHENOMENA

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Summary

Geochemistry is concerned with understanding the distribution and cycling of the chemical elements, and their isotopes, throughout nature. It is of fundamental importance to understanding the earth and planetary sciences on a variety of both theoretical and applied levels. Accordingly, geochemistry is a highly inter-disciplinary subject and addresses problems across a broad range of the sciences, such as geology, astronomy, planetary sciences, physics, chemistry, biology, material sciences, and others. The discipline has its origins in alchemy and early metallurgy but rapidly evolved into a modern science with the discovery of the chemical elements and their properties. Geochemistry, and the closely affiliated sub-discipline of cosmochemistry, is studied through a wide variety of theoretical, experimental, and analytical methods. The subject has evolved from a substantially descriptive to a highly quantitative and predictive discipline. For the future, geochemistry will continue to contribute to our understanding of fundamental questions regarding the origin and evolution of the earth and planets and increasingly will play an important role in many of the environmental issues facing humankind.

1. Introduction

Victor Moritz Goldschmidt (1888–1947), widely considered the father of modern geochemistry, defined this scientific discipline as the study of “the distribution and amounts of the chemical elements in minerals, ores, soils, waters, and the atmosphere, and the circulation of the elements in nature, on the basis of the properties of their atoms and ions.” As one considers the most recent advances of geochemistry in fields such as remote sensing, mineral spectroscopy, environmental geochemistry (Goldschmidt spent several of his final years in a soil science department), and biogeochemistry, it is a salutary exercise to re-examine his seminal treatise, *Geochemistry*, to appreciate the foundations that his research efforts provided for even these most ‘modern’ of branches of geochemistry.

The study of geochemistry is of central importance to the earth and planetary sciences, on both purely scientific and more immediate practical grounds, because chemical processes are fundamental to understanding how the planetary bodies formed and evolved at all scales, from subatomic to galactic. Accordingly, geochemistry plays a central role in understanding an immensely diverse set of scientific questions, such as the formation and differentiation of the earth and planets, the origin and evolution of life, the controls on global climate and climate change, and the formation and management of natural resources. Such questions include many of those that are critical for humankind to understand the context of its existence and to chart its future.

Because geochemistry is concerned with the “distribution” and “circulation” of the chemical elements throughout all of the reservoirs of the earth—geosphere (core, mantle, crust), hydrosphere (oceans, rivers, lakes, groundwater), atmosphere, biosphere –and other bodies within the Solar System, it is by nature a multidisciplinary and inter-disciplinary subject. Geochemists traditionally have interacted with, and sought their scientific questions from, the diverse fields of geology, physics, chemistry, astronomy, physical geography, anthropology, and biology. As the scientific community has come to appreciate the fragile nature of the earth’s environment, geochemists have increasingly turned their attention towards more applied problems, such as environmental geochemistry, engineering, forensics, and material science.

The field of geochemistry has grown to incorporate an enormous body of knowledge. Important geochemical processes take place across the entire range of physical conditions that are found within the solar system. Thus, mineral equilibria must be considered from pressures relevant to the accreting solar nebula (10^{-6} bar) to those within the center of planets (10^{-7} bar) and at temperatures ranging from well below 100K on the surfaces of many planets and their satellites to >5,000K in the cores of terrestrial planets. Common natural waters similarly range from cryogenic to supercritical temperatures and with ionic strengths varying over some five orders of magnitude. Planetary atmospheres are highly variable in composition and physical state, and even on earth, there is great variability in naturally formed gases from a host of atmospheric, sedimentary and igneous processes (e.g. CO_2, CH_4, H_2, H_2S, HCl, N_2O, O_3, SO_2, etc.). Accordingly, it is certainly well beyond any effort to introduce the subject of geochemistry comprehensively in such a short article as this. Indeed, it has probably grown beyond the ability of any individual to summarize the discipline. This article touches on only a few issues that hopefully provide some insight into the dynamic and growing scientific discipline of Geochemistry.

2. Historical Foundations of Geochemistry

Geochemistry has its ultimate foundations in alchemy and in the early mining and extraction of precious metals. Indeed, a sixteenth century Hungarian oath required

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analysts to "swear to the most majestic and most powerful sovereign Maximilian . . . that you will test everybody's gold and silver properly, so that the tax due to his Excellency can be honestly extracted . . . [and] to test all samples either ore or ore-stone in a similar manner." The entry of geochemistry into the modern era had to await the discovery of the elements that mostly took place over a 200-year period between about 1725 and 1925. In general, developments in basic chemistry typically are followed rapidly by their applications to geochemistry. One example of this is that the first attempts at radiometric age dating of minerals followed the discovery of radioactivity in 1896 by only about a decade.

One of the greatest controversies in the history of science, over the "age of the earth," was essentially resolved by 1907 when, on the basis of radiometric dating using uranium/lead ratios of uranium-rich minerals, Bertram Boltwood determined mineral ages of up to 2.2 billion years, thus demonstrating that the earth had been in existence for on the order of 10^9 years rather than 10^3 to 10^8 years, as previously thought. (In fact, Boltwood's ages are now known to have been too high due to his estimating a uranium decay rate that was too low and absence of knowledge of the thorium-lead decay chain.) Precise determinations of radiometric ages had to await the discovery of isotopes and development of mass spectrometers and we now know that the oldest identified objects in the solar system, inclusions within the Allende meteorite, are about 4,560±5 million years old and that the bulk of the earth had accreted within about 10 to 100 million years of that time.

Because of his seminal contributions to the development of essentially all of the basic geochemical principles, Goldschmidt is generally regarded as the father of modern geochemistry. However, at least part of this honor must be shared with others. Frank W. Clarke (1847–1931), chief Chemist of the United States Geological Survey from 1884 to 1925, wrote the first modern treatise in geochemistry, *The Data of Geochemistry*, published as a United States Geological Survey Bulletin in 1908 and continually revised by him through to 1924 (and subsequently by others). Among Clarke's most important contributions were his remarkable compilation of available geochemical data, and an overriding theme that advance in geochemical thought is predicated on obtaining high quality data. At about the same time, in Russia, Vladimir Vernadsky (1863–1945) assembled an extraordinary geochemistry group at the University of Moscow and, among other things, presaged the most modern branch of biogeochemistry.

If Goldschmidt is the father of modern geochemistry, then the American 1934 Nobel prize-winning chemist, Harold Urey (1893–1981) must be considered the father of Cosmochemistry. He built upon the explosion of knowledge about isotopes, and element distributions, and the major improvements in mass spectrometer design by Alfred Nier, that took place immediately prior to and during the Second World War. Urey was among the first to apply this knowledge systematically to understanding the origin and evolution of planets. At the University of Chicago, Urey and his colleagues, Harrison Brown, Mark Inghram, and Willard Libby (Nobel Prize, 1960), constituted one of the leading geochemistry groups in the world. The students that graduated from Chicago under the supervision of Urey and his colleagues during the 1950s, including James Arnold, Harmon Craig, Stanley Miller, Claire Patterson, Hans Suess, George

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Tilton, Gerald Wasserburg, and George Wetherill, have been dominant forces in isotope geochemistry and cosmochemistry during the second half of the twentieth century.

The historical development of geochemistry during the twentieth century followed three tightly entwined paths. The first, and most important, of these is the development of geochemical principles and theory, pioneered by the likes of Goldschmidt and Urey, and continuing through to the present. Among the recent major concepts that have been developed in geochemistry are the roles of geochemical cycles in the evolution of the earth, and the profound influence of biological activity in a wide variety of geological processes. Another area that has advanced the field of geochemical research is the careful use of equilibrium and kinetic models, based on mass balance, experiments, *ab initio* calculations, and so forth, to constrain geochemical processes.

The second path is the continuing development and improvement of analytical instruments and techniques. Early analytical methods, such as wet chemical gravimetry, were laborious and relatively insensitive. Over time these have given way to a variety of methods, the most recent being argon-plasma-source mass spectrometry, that are rapid, require vanishingly small samples, and have sensitivities that can reach the femtogram level. Among the most important benchmarks in the history of analytical geochemistry are the development of X-ray diffractometers, emission spectrographs, electron microbeam techniques (for example, electron probe, SEM, TEM), neutron activation, various spectroscopic techniques (for instance, IR, Raman, Mössbauer, EXAFS), and the invention, and continuous progress in design, of mass spectrometers.

The third path is the development of experimental methods. In addition to understanding the chemical and mineralogical composition of geological materials, it is critical to simulate the environments of geological processes under controlled conditions. Early experimental methods were pioneered by Norman L. Bowen and his colleagues at the Geophysical Laboratory of the Carnegie Institution of Washington, and they systematically investigated the phase relationships of igneous rocks at elevated temperatures and pressures. Developments in this field have focused on designing robust apparati that permit experiments at increasingly extreme conditions relevant to the earth (for instance, diamond anvils, hydrothermal bombs, chemostat), that can simulate complex, commonly non-equilibrium, geological processes, and that permit continuous interrogation of the sample throughout the experiment.

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3. Branches of Geochemistry

Unlike the field of Geophysics, that can be sub-divided with some convenience by the various geophysical phenomena and data types, subdividing the field of Geochemistry into various categories is more elusive. This can be seen simply by contrasting the chapter titles of standard introductory textbooks in Geophysics with those in Geochemistry. Geophysics textbooks routinely follow a subdivision based on analytical approach and/or geophysical phenomena, such as seismology, magnetics and paleomagnetics, gravity, heat flow, and so forth. In contrast, textbooks in Geochemistry are far less straightforward. Early textbooks were generally subdivided into three sections. One section concentrated on the distribution of elements in various rocks, minerals and geochemical reservoirs and a second described the geochemical principles that controlled the distribution of elements. Finally, such books provided a systematic description of the geochemistry of each element. Most modern texts have abandoned the systematic element-by-element description. However, it is still common to divide the field by fundamental rock type or geologic process (igneous, sedimentary, metamorphic) with varying degrees of refinement, and by geochemical reservoir (meteorites, crust, mantle, core, oceans, atmosphere). Increasingly, less effort is being given to the systematic chemical characterizations of rocks, minerals and geochemical reservoirs, and more attention is being given to understanding a wide variety of geochemical processes, using theoretical, experimental, and analytical approaches. There is a long history of emphasizing equilibrium processes in geochemistry, such as phase stability during metamorphic and igneous reactions, and accordingly thermodynamic calculations and modeling play an important role in most aspects of geochemistry, and is well entrenched in geochemical thought. However, there is also an appreciation that dynamic, non-equilibrium geological processes, such as diffusion, weathering, and fluid alteration, are equally important giving rise more recently to far greater attention being paid to the kinetics of geochemical processes.

A convenient subdivision of the major branches of modern geochemistry, relevant to the most recent research priorities and directions, is that currently used to organize published papers by the pre-eminent journal in the field, "*Geochimica et Cosmochimica Acta*":

1. Atmospheric geochemistry
2. Geochemistry of surface waters
3. Geochemistry of weathering
4. Marine geochemistry
5 Sedimentary and diagenetic geochemistry
6. Organic geochemistry
7. High-temperature aqueous geochemistry
8. Geochronometry
9. Crustal geochemistry
10. The geochemistry of the mantle and core
11. Meteorites and cosmochemistry
12. Planetary geochemistry.

The sub-discipline of biogeochemistry recently has received considerable attention but many of the fundamental principles can be traced back to the pioneering work of Vinogradov and Baas Becking.

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Biographical Sketch

Scott M. McLennan, is Professor of Geochemistry in the Department of Geosciences, State University of New York at Stony Brook. Professor McLennan obtained a Ph.D. from the Research School of Earth Sciences at the Australian National University in 1981, and remained as a Research Fellow until 1986. He joined the faculty at Stony Brook in 1987 and received a Presidential Young Investigator Award from the National Science Foundation in 1989. In 1994 he was a Visiting Scientist at the Max Planck Institut für Chemie in Mainz, Germany. His main research interests are in the area of sedimentary geochemistry, crustal geochemistry, and planetary science. He uses major element, trace element, and radiogenic isotope data from sedimentary rocks to evaluate a variety of questions related to crustal evolution, plate tectonic associations, diagenesis, and paleoclimates. Recently he has been involved with evaluating surficial processes on Mars using data returned from the Mars Pathfinder and Mars Global Surveyor missions.

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