

## Introduction

Geochemistry utilizes the principles of chemistry to explain the mechanisms regulating the workings – past and present – of the major geological systems such as the Earth’s mantle, its crust, its oceans, and its atmosphere. Geochemistry only really came of age as a science in the 1950s, when it was able to provide geologists with the means to analyze chemical elements or to determine the abundances of isotopes, and more significantly still when geologists, chemists, and physicists managed to bridge the chasms of mutual ignorance that had separated their various fields of inquiry. Geochemistry has been at the forefront of advances in a number of widely differing domains. It has made important contributions to our understanding of many terrestrial and planetary processes, such as mantle convection, the formation of planets, the origin of granite and basalt, sedimentation, changes in the Earth’s oceans and climates, and the origin of mineral deposits, to mention only a few important issues. And the way geochemists are perceived has also changed substantially over recent decades, from laboratory workers in their white coats providing age measurements for geologists or assays for mining engineers to today’s perception of them as scientists in their own right developing their own areas of investigation, testing their own models, and making daily use of the most demanding concepts of chemistry and physics. Moreover, because geochemists generate much of their raw data in the form of chemical or isotopic analyses of rocks and fluids, the development of analytical techniques has become particularly significant within this discipline.

To give the reader some idea of the complexity of the geochemist’s work and also of the methods employed, we shall begin by following three common chemical elements – sodium (Na), magnesium (Mg), and iron (Fe) – on their journey around system Earth. These three elements were created long before our Solar System formed some 4.5 billion years ago, in the cores of now extinct stars. There, the heat generated by the gravitational collapse of enormous masses of elementary particles overcame the repulsive forces between protons and triggered thermonuclear fusion. These reactions allowed particles to combine forming ever larger atomic nuclei of helium, carbon, oxygen, sodium, magnesium, and iron. This activity is still going on before our very eyes as the Sun heats and lights us with energy released by hydrogen fusion. When, after several billion years, the thermonuclear fuel runs out, the smaller stars simply cool: the larger ones, though, collapse under their own weight and explode in one of the stellar firework displays that nature occasionally stages, as with the appearance of a supernova in the Crab nebula in AD 1054. The matter scattered by such explosions drifts for a while in interstellar space as dust clouds similar to the one that can be observed in the nebula of Orion. Turbulence in the cloud and collisions between the particles make the system unstable and the particles coalesce to form small rocky bodies known as planetesimals. Chondritic meteorites give us a pretty

good idea of what these are like. Gravitational chaos amplifies very rapidly and the planetesimals collide to form larger and larger bodies surrounding a new star: a Solar System is born.

As the planet forms and evolves, our three chemical elements meet different fates. Sodium is a volatile element with a relatively low boiling point (881 °C) and large amounts of it are therefore driven off into space by the heat generated as the planet condenses. Iron, which is initially scattered within the rock mass, melts and collects at the heart of the planet to form the core, which, on Earth, generates the magnetic field. Magnesium has a boiling point of 1105 °C and behaves in an un-extraordinary way assembling with the mass of silicate material to form the mantle, the main bulk of the terrestrial planets, and residing in minerals such as olivine ( $\text{Mg}_2\text{SiO}_4$ ), the pyroxenes ( $\text{Mg}_2\text{Si}_2\text{O}_6$  and  $\text{CaMgSi}_2\text{O}_6$ ), and, if sufficient pressure builds up, garnet ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ).

The chemical histories of the planets are greatly influenced by their magmatic activity, a term that refers to all rock melting processes. On our satellite, the Moon, the formation of abundant magmas in the first tens of millions of years of its history has left its mark in the surface relief. The crust, composed of the mineral plagioclase ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), is so light that it floats on the magma from which it crystallized, forming the lunar highlands that rise above the Moon's maria. The sodium that did not vaporize migrated with the magma toward the lunar surface and combined readily in the plagioclase alongside calcium. On Earth, water is abundant because temperatures are moderate and because the planet is massive enough for gravity to have retained it. The action of water and dissolved carbonates is another significant factor in the redistribution of chemical elements. Water causes erosion and so is instrumental in the formation of soils and sedimentary rocks. The presence of chemically bound water in the continental crust promotes metamorphic change and, by melting of metamorphosed sedimentary rocks, the formation of granite that is so characteristic of the Earth's continental crust. A substantial fraction of the sodium that did manage to enter into the formation of the early crust was soon dissolved and transported to the sea, where it has resided for hundreds of millions of years. Some marine sodium entered sediment and then, in the course of magmatic processes, entered granite and therefore the continental crust.

Magnesium, by contrast, tends to remain in the dense refractory minerals. It lingers in solid residues left after melting or precipitated during crystallization of basalt at mid-oceanic ridges or at ocean island volcanoes. Where it does enter fluids, it subsequently combines with olivine and pyroxene, which precipitate out as magma cools. Magnesium is resistant to melting and is predominant in the mantle, which has ten to thirty times the magnesium content of the crust.

The Earth is a complex body whose dynamics are controlled by mechanisms that commonly work in opposing directions: differentiation mechanisms, on the one hand, maintained by fractionation of elements and isotopes between the phases arising during changes of state (melting, crystallization, evaporation, and condensation), and, on the other hand, mixing mechanisms in hybrid environments such as the ocean and detrital rocks that tend to homogenize components derived from the various geological units (rain water, granite, basalt, limestone, soil, etc.). By fractionation we mean that two elements (or two isotopes) are distributed in unequal proportions among the minerals and other chemical phases present in the same environment.

It can be seen then that the elements must be studied in terms of their properties in the context of the mineral phases and fluids accommodating them and in the context of the processes that govern changes in these phases (magmatism, erosion, and sedimentation). By mineral phase is meant all the crystals from a small neighborhood (mm to cm) that belong to the same mineral species. We will start by discussing some useful rules of inorganic and nuclear chemistry that illuminate the geochemical properties of elements. An understanding of transport mechanisms is very important in geochemistry. The term “cycle” is sometimes employed but we will see later that its meaning needs to be clarified. Conversely, the terminology used above, which emphasizes that sodium resides for a long time in the ocean or that magnesium lingers in solid residues of melting, illustrates that transfers among the different parts of the globe, such as the core, mantle, crust, and oceans, are to be considered kinetically, or, more loosely, dynamically, in terms of flows or transport rates. We will next turn our attention to the mysterious field of stable isotopes, with the idea of clarifying the principles of their fractionation in nature. Radioactive decay, which alters the atomic nucleus and therefore the nature of certain elements at rates that are unaffected by the physical, crystallographic, or chemical environment in which they occur, will allow us to include the incessant ticking of these “clocks” in our study of radioactive processes.

The book then moves on to the essential study of the dynamics and evolution of the mantle and continental crust, and the study of marine geochemistry and its implications for paleoclimatology and paleoceanography. Two new chapters on biogeochemistry and environmental geochemistry have been added to the second edition. A last chapter deals with the geochemical properties of a number of elements. Most students deplore the lack of such a systematic approach in the literature; what is supposed to be common knowledge is never taught, simply because the odds of being inaccurate, unbalanced, and superficial are too great. An appendix provides an overview of a number of methods for analyzing chemical elements and isotopes.

I have been asked so many times by genuinely motivated colleagues from other disciplines where a compact description of geochemistry could be found. I hope this short textbook will meet this demand. It will probably be found that this book relies more heavily on equations than most other geochemistry textbooks. I maintain that a proper scientific approach to our planet must use all the available tools, especially those of physics and chemistry, to supplement purely descriptive and analytical approaches. I therefore ask readers to persevere despite the superficial difficulty of some of the equations, which are, after all, nothing more than a means of encoding concepts that ordinary language is powerless to convey with adequate precision. Oscar Wilde said that “. . . nothing that is worth knowing can be taught.” A collection of observations is no more science than a dictionary is literature. Above all, I have made every attempt to avoid turning the reader of this book into a stamp collector.

But the devil is in the detail and I occasionally had to cut corners: some concepts, definitions, and proofs could have benefited from more rigor and from more detailed supporting arguments. I very much wanted to keep this book short, so I hope that my specialist colleagues will forgive the short-cuts used to this effect.

Readers may e-mail any queries, criticisms and – who knows – words of encouragement to the author ([albarede@ens-lyon.fr](mailto:albarede@ens-lyon.fr)).

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## 1

## The properties of elements



The 92 naturally occurring chemical elements (90, in fact, because promethium and technetium are no longer found in their natural state on Earth) are composed of a nucleus of subatomic nucleons orbited by negatively charged electrons. Nucleons are positively charged protons and neutral neutrons. As an atom contains equal numbers of protons and electrons with equal but opposite charges, it carries no net electrical charge. The mass of a proton is 1836 times that of an electron. The chemical properties of elements are largely, although not entirely, determined by the way their outermost shells of electrons interact with other elements. Ions are formed when atoms capture surplus electrons to give negatively charged anions or when they shed electrons to give positively charged cations. An atom may form several types of ions. Iron, for example, forms both ferric ( $\text{Fe}^{3+}$ ) ions and ferrous ( $\text{Fe}^{2+}$ ) ions, while it also occurs in the  $\text{Fe}^0$  elemental form.

A nuclide is an atomic nucleus characterized by the number  $Z$  of its protons and the number  $N$  of its neutrons regardless of its cloud of electrons. The mass number  $A$  is the sum of the nucleons  $N + Z$ . Different interactions act in the nucleus and explain its binding: the short-range (nuclear) strong force, the long-range electromagnetic force, and the mysterious intermediate weak force. Two nuclides with the same number  $Z$  of protons but different numbers  $N$  of neutrons will be accompanied by the same suite of electrons and so have very similar chemical properties; they will be isotopes of the same element. The “chart of the nuclides” (Fig. 1.1) shows that in order to be stable, nuclides must contain a specific proportion of neutrons and protons. The semi-empirical formula for the energy of a nucleus is:

$$E = aA - bA^{2/3} + c \frac{(N - Z)^2}{A} - d \frac{Z^2}{A^{1/3}} \quad (1.1)$$











