STABLE ISOTOPE GEOCHEMISTRY

Ian D. Clark
University of Ottawa, Ottawa, Canada

Keywords: oxygen-18, carbon-13, sulphur-34, deuterium, nitrogen-15, chlorine, lithium-6, boron, carbon cycle, hydrologic cycle, isotope fractionation

Contents

Summary

The mid-twentieth-century discovery that nuclides occurred of differing mass yet of the same element gave Earth scientists an exciting new tool to trace the origin and natural cycling of compounds in the geosphere, hydrosphere, and biosphere. The pioneers of stable isotope geochemistry began systematically measuring the abundance of the isotopes of water–deuterium and ^{18}O, and found that their partitioning through the water cycle held valuable climate information. From isotopes archived in marine sediments and ice sheets, we have reconstructed the variations of past climates and are learning why they change. With ^{13}C, these isotopes now provide insights into carbon cycling, greenhouse gases, and modern meteorological processes. Stable isotopes in crustal materials, including ^{34}S, support studies on the genesis of ore deposits and tectonic processes. Environmental research employs stable isotopes to trace food webs, and contaminant pathways in ecosystems and fresh water resources. As the mechanisms of isotope fractionation and partitioning become more widely understood, stable isotopes are increasingly employed as natural tracers in the sciences. With recent analytical innovations that now provide large volumes of inexpensive and precise data, isotopes have become an indispensable component of geochemical and biological studies.

1. Background

Early in the twentieth century, Ernest Rutherford, firing alpha particles at gold foil,

found that the mass of the atom was not distributed throughout, but concentrated in a very small "nucleus," a discovery that gave Niels Bohr the basis to develop the model of electron orbits and quantum mechanics. However, the fractional masses of the elements remained an enigma until Francis Aston developed the positive-ray experiments of J.J. Thompson into a mass spectrograph. By focusing a stream of positively charged gas ions through a magnetic field onto a photographic plate, he produced separate points of exposure. The mass spectrograph showed that elements with fractional atomic weights, such as chlorine at mass 35.45, were comprised of atoms with different, near-integer masses. Occupying the same position on the periodic table, these isotopes (from Greek *isos* = equal, *topos* = place) of a given element had the same chemical characteristics, but differed in mass. In 1932, the discovery of the neutron, whose role is to neutralize the electrostatic repulsive forces between protons in the atomic nucleus, showed that isotopes of an element differed in the number of this uncharged particle. Since that time, roughly 2000 isotopes of the 92 naturally occurring elements have been identified.

2. Elements, Nuclides, and Stable Isotopes

The nuclear structure of a nuclide or isotope-specific atom is defined by its atomic number (Z), which represents its number of protons and specifies the element, and by the number of neutrons (N) in the nucleus, which defines the isotope of that element. For a given nuclide, the sum of protons and neutrons defines the atomic mass number (A), expressed by the notation, $_Z^A Nu_N$. For example, most oxygen has 8 protons and 8 neutrons, giving an atomic weight of 16 ($_8^{16}O_8$) while about 0.2% of oxygen has 10 neutrons ($_8^{18}O_{10}$). In reality, the actual mass of a nuclide is slightly less than the combined sum of its neutrons and protons. The "missing" mass is converted to the nuclear binding energy through Einstein's relationship $E=mc^2$. Conventional notation for a nuclide uses only the elemental symbol and atomic weight (e.g. ^{18}O or ^{34}S).

The number of neutrons in the nucleus can vary, but the range is limited by the instability created when the nuclide has too many or too few neutrons. This makes the nuclide radioactive with a characteristic probability of decay or half-life. Stable isotopes on the other hand, do not spontaneously disintegrate by any known mode of decay. To date, some 270 stable nuclides and over 1700 radionuclides have been identified. In the light elements (Z up to 20) the greatest stability occurs with a Z:N ratio close to 1, and increases towards 1.5 for heavy elements. In a chart arranged according to Z and N the stable isotopes of the elements form a stable valley from hydrogen to uranium. Departures from this stable valley produce radionuclides of decreasing stability (shorter half-lives). Oxygen, for example, has eleven isotopes (^{12}O to ^{22}O) although only the median isotopes, ^{16}O, ^{17}O and ^{18}O, are stable. The others are radioactive with half-lives varying from 122 seconds to less than a femto-second.

Most of the stable isotopes that exist today originated through nucleosynthesis during the formation of our early solar system. Others are the stable products of ongoing radioactive decay, such as ^{206}Pb from ^{238}U or ^{87}Sr from ^{87}Rb. Still others are created by ongoing nuclear reactions, for example ^3He from decay of ^3H, which is created by solar radiation on ^{14}N, or ^{36}Ar, a decay product of ^{36}Cl produced by solar or subsurface radiation of ^{35}Cl, ^{39}K or ^{40}Ca. As radioactive decay is a function of time, radiogenic

isotopes are most useful for dating geological and biological materials and processes, and are not the subject of this section. By contrast, the pool of stable isotopes most useful in stable isotope geochemistry (Table 1), remain essentially unchanged over geological time, and so are useful to trace the geological, hydrological, and biological cycling of elements.
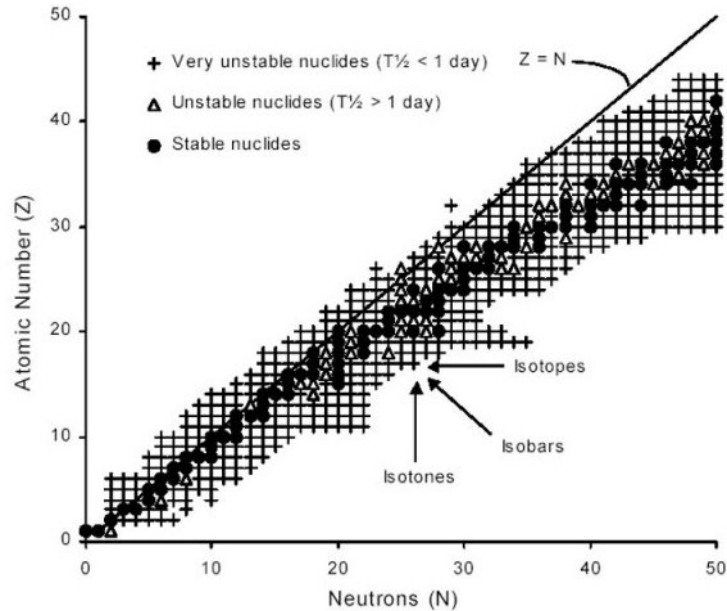

Figure 1. Chart of the stable and radioactive isotopes up to atomic number 50

3. The Mass Spectrometer and Isotope Ratio Measurement

In 1936, Alfred Nier built a mass spectrometer and produced the first precise measurements of isotopic ratios. His design remains the basis of modern instruments. Samples are mounted as solids in a high vacuum chamber (the source), or bled into the source as a gas. An ionizing filament pulls an electron off the molecule, creating a positively charged ion that is accelerated across a voltage gradient. The stream of ions exiting the source is focused along a flight tube that curves through an external magnet. Like light in a prism, the magnetic field splits the ionized gas stream into discrete beams according to mass. The various isotopes separate into a spectrum of masses, which are measured with single or multiple ion collectors mounted at the end of the flight tube. The ratio of the current strengths for each mass is proportional to the mass ratio in the sample. Recent developments in the measurement of isotope ratios include the continuous-flow gas source mass spectrometer, which allows measurement of nano-mole sized samples by injecting a pulse of the sample gas to a stream of helium passing through the source.

Isotope ratios are expressed as parts per thousand or permil (‰) differences from the ratios in known reference materials. This is due to the uncertainty inherent in gas source mass spectrometers. As only a fraction of the inlet gas is ionized and measured by the collectors, transient and instrument factors will affect the measurement. By alternately measuring the mass ratio in a sample and known reference gas, these factors cancel out,

allowing a high degree of precision. The delta permil (δ-‰) notation is used to express isotope ratios relative to a reference such as Vienna Standard Mean Ocean Water (VSMOW) for ^{18}O:

$$\delta^{18}O_{sample} = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{VSMOW}} - 1 \right] \cdot 1000‰ \text{ VSMOW} \qquad (1)$$

For example, the measurement: $\delta^{18}O = -10‰$ VSMOW would have 10 permil or 1 percent less ^{18}O than the reference VSMOW.

Stable isotope laboratories calibrate their working reference gases to internationally recognized reference materials, provided by the International Atomic Energy Agency (IAEA) in Vienna (<www.iaea.org>) and the National Institute of Standards and Technology in Gaithersburg, MD, USA (<www.nist.gov>). Accordingly, data produced by different laboratories are referenced to the same standards and so are directly comparable.

Although most elements present in geological and biological systems have various isotopes, only a few are of practical importance in stable isotope geochemistry: those with abundance and relative mass differences sufficiently large to measurably affect their physical and chemical properties. Table 1 lists the stable isotopes most relevant to geological studies, along with their abundance, international reference, and the most commonly analyzed compounds.

Isotope & Ratio	Abundance (%)	Reference (ratio)	Commonly measured phases
^{2}H $\frac{^{2}H}{^{1}H}$	0.015	VSMOW ($1.5576 \cdot 10^{-4}$)	H_2O, clays, cellulose, CH_4, H_2
^{3}He $\frac{^{3}He}{^{4}He}$	0.000138	Atmospheric He ($1.384 \cdot 10^{-6}$)	He gas in groundwaters, rocks, seawater, air
^{6}Li $\frac{^{6}Li}{^{7}Li}$	7.5	LSVEC ($8.3062 \cdot 10^{-2}$)	Seawater, hydrothermal water, whole rock Li
^{11}B $\frac{^{11}B}{^{10}B}$	80.1	NBS 951 (4.04362)	Seawater, clays, borate salts, basalts
^{13}C $\frac{^{13}C}{^{12}C}$	1.11	VPDB ($1.1237 \cdot 10^{-2}$)	CO_2, minerals, DIC, hydrocarbon, organics
^{15}N $\frac{^{15}N}{^{14}N}$	0.366	AIR ($3.677 \cdot 10^{-3}$)	N_2, NH_4^+, NO_3^-, N-organics
^{18}O $\frac{^{18}O}{^{16}O}$	0.204	VSMOW ($2.0052 \cdot 10^{-3}$)	H_2O, minerals, organics, CO_2, O_2, SO_4^{2-} NO_3^-
^{34}S $\frac{^{34}S}{^{32}S}$	4.21	CDT ($4.5005 \cdot 10^{-2}$)	Minerals, SO_4^{2-}, H_2S, H_2S, S-organics

^{37}Cl	$\dfrac{^{37}Cl}{^{35}Cl}$	24.23	SMOC (0.324)	Seawater, brines, salts, Cl-organics
^{81}Br	$\dfrac{^{81}Br}{^{79}Br}$	49.31	SMOB	Seawater, brines, salts
^{87}Sr	$\dfrac{^{87}Sr}{^{86}Sr}$	7.0 and 9.8		Seawater, carbonates, sulphates, feldspars

Table 1. Principal stable isotopes of geological interest

-
-
-

TO ACCESS ALL THE **18 PAGES** OF THIS CHAPTER,
Visit: http://www.eolss.net/Eolss-sampleAllChapter.aspx

Bibliography

Clark, I.D. and Fritz, P. (1997). *Environmental Isotopes in Hydrogeology*, 328 pp. Boca Raton, FL CRC Lewis. [This upper-undergraduate text book covers the theory and application of stable and radioisotopes in groundwater resource and quality studies. It provides solved problems and compiles temperature equations for most isotopes exchange reactions of geochemical interest.]

Claypool G.E., Holser W.T., Kaplan I.R., Sakai H., and Zak, I. (1980). The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* **28**, 199–260. [This publication compiles $\delta^{34}S$ and $\delta^{18}O$ data for marine sulfate from phanerizoic sites world wide, and discusses the observed trends in terms of tectonism, weathering and marine evolution.]

Cook P. and Herczeg A.L. (eds.) (2000). *Environmental Tracers in Subsurface Hydrology*, 529 pp. Kluwer Academic, Boston, 529 pp. [This resource book includes contributions by 33 experts on the range of isotopes and other geochemical tools to trace groundwater origin, movement, age, and geochemical history.]

Fritz P. and Fontes J.-Ch. (eds.) (1980). *Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment A.,* 545 pp. Amsterdam, the Netherlands: Elsevier. [This and the second volume (below) present the state of knowledge of previously disseminated literature on stable and radio-isotope geochemistry in the hydrosphere and geosphere.]

Fritz P. and Fontes J.-Ch. (eds.) (1986). *Handbook of Environmental Isotope Geochemistry, Vol. 2, The Terrestrial Environment, B.* 557 pp. Amsterdam, the Netherlands: Elsevier. [The second volume presenting the state of knowledge of previously disseminated literature on the of stable and radio-isotope geochemistry in the hydrosphere and geosphere.]

Kendall C. and McDonnell J.J. (eds.) (1998). *Isotope tracers in Catchment Hydrology*, 839 pp. Amsterdam, the Netherlands: Elsevier Science. [A very comprehensive resource text that presents the application of isotope geochemistry from the perspective of the basic hydrographic unit: the catchment. The book integrates surface waters and groundwaters as well as geological and biological processes.]

Rozanski K., Araguás-Araguás L., and Gonfiantini R. (1993). Isotopic patterns in modern global precipitation. *Continental Isotope Indicators of Climate*, AGU Monograph, 78, 1–36. [This paper reviews the extensive archives of isotope data for precipitation from over 150 sites worldwide. They provide global and regional interpretations of isotope hydrology]

Biographical Sketch

Professor Ian D. Clark, holds a B.Sc. Co-op degree in Earth Sciences and an M.Sc. in Hydrogeology from the University of Waterloo, and received his doctorate degree from the Université de Paris-Sud, Orsay. His interest in isotope hydrogeology began with his M.Sc. research on a geothermal prospect in western Canada. He completed his doctoral program in Orsay, France, studying groundwater and paleoclimates in the Sultanate of Oman, working with Dr. Jean Charles Fontes and Dr. Peter Fritz. In 1988, Ian joined the Department of Earth Sciences at the University of Ottawa, and now supervises research in isotope hydrogeology and paleoclimatology in the Canadian Arctic. Other current research activities include studies of hydrogeological analogues for nuclear waste repositories and contaminant geochemistry.