

Chapter 1

INTRODUCTION

Contents

1.1 About this book.....	1
1.2 Historical Background	1
1.3 Scope of the Discipline	5
1.3.1 What are stable isotopes?.....	6
1.3.2 Which elements and why?	8
1.4 Abundances of the Rare Isotopes of Light Elements.....	9
1.5 Characteristics of Elements that Undergo Significant Isotopic Fractionation.....	10
1.6 Applications in the Earth Sciences	12
1.7 Isotope Effects	13
1.7.1 Kinetic isotope effects.....	13
1.7.2 Equilibrium isotope effects.....	14
References.....	16

Chapter 1

INTRODUCTION

1.1 About this book

The first edition of this book was written as a general introduction to stable isotope geochemistry. It was meant primarily as a guide and general resource for an upper division and graduate level stable isotope course. Since it was first published in 2007, the scope of stable isotopes has grown tremendously. New fields, not envisioned in the first edition, have developed and blossomed, and existing fields have grown considerably. The motivation for the original book was to provide a useful, inexpensive textbook that could also be used as foundation for new practitioners to the field. However things are changing so fast that it is impossible to keep up with new developments using the traditional publishing format. Turn-around times are too long, and the cost to the end-user are too high. This new 'live' edition is meant to overcome these problems. The book is online and freely available to all. Because it is electronic, it can be (and hopefully will be) modified easily and frequently, so that new developments can be incorporated as they become available. It is my hope that this 'live' version will remain up-to-date and be a valuable no-cost resource for stable isotope practitioners around the world.

1.2 Historical Background

The published early 'discussions' by scientists studying the structure of the atom and significance of isotopes make for remarkable reading. The early practitioners, including J.J. Thomson, E. Rutherford, F. Soddy and F.W. Aston, J. Chadwick, G. Gamow and others were generally concerned with radioactivity – the spontaneous disintegration of large atoms to smaller fragments. But in their efforts to understand the structures of atoms, they were also keenly aware of departures of elemental masses from Aston's 'whole number rule' – the idea that all elements have masses that are multiples of the mass of hydrogen. In a round-table discussion by E. Rutherford, F. W. Aston, J. Chadwick, and others, Rutherford states: "*The essential point brought out in the earlier work of Dr. Aston was that the masses of the elements are approximately expressed by whole numbers, where oxygen is taken as 16-with the exception of hydrogen itself. But the real interest, as we now see it, is not the whole number rule¹ itself, but rather the departures from it*" (Rutherford et al., 1929). Of particular interest was the element Cl, with a mass of 35.5. In an earlier 'discussion' in 1921, J.J. Thomson stated "*Mr. Aston, who has measured the atomic weight of chlorine by a different method, cannot find any chlorine – or any other substance – with an atomic weight of 35.5, but he does find substances with atomic weights of 35 and 37. Accepting the numbers on both sides, there does not seem to be any explanation other than that either chlorine is a mixture of these two substances of atomic weight 35 and 37, or else that, in the discharge tube which Mr. Aston employs to measure the atomic weight, some decomposition or integration – or both – of the chlorine atom has occurred.*" (Thomson et al., 1921). Aston had identified the two isotopes of Cl, masses 35 and 37. There was no problem with his mass

¹ The whole number rule is that the masses of the elements are multiples of the mass of hydrogen or as Rutherford states above, relative to oxygen with a mass of 16.

spectrograph! In 1931 James Chadwick published the results of his discovery of the neutron in the modestly titled paper "*Possible existence of a neutron*" (Chadwick, 1931), and the fundamental building blocks of atoms were firmly in place.

The first suggestion that physical chemical processes could cause isotopic fractionation of light elements in natural substances was made in 1925 by British scientists H. Briscoe and P. Robinson (Briscoe and Robinson, 1925). Before that time, it was generally assumed that the isotopic compositions of all substances were homogeneously distributed throughout the Earth. Briscoe and Robinson observed a variation in the atomic weight of boron in minerals from various localities. They proposed that processes like solution, crystallization, melting, and volatilization would likely cause such isotopic variations in nature. In the following year the eminent Russian scientist V. Vernadsky suggested that isotopic fractionation of the light elements should occur in living matter as well, but there were no experimental or natural data to support this hypothesis at that time. Variations in the hydrogen and oxygen isotope ratios of water in the hydrologic cycle of the Earth were recognized crudely as early as the mid-1930s on the basis of precise density measurements (Gilfillan, 1934). In that same decade, H. Urey² and his colleagues at Columbia University were conducting experiments and developing the theory for isotope exchange reactions and equilibria (Urey and Greiff, 1935), and A. Nier and his colleagues at the University of Minnesota were making significant improvements to Aston's early mass spectrometer designs, and were discovering variations in the stable isotope ratios of several light elements in natural materials (Fig. 1.1).

Probably the first *bona fide* application of light stable isotope measurements to a major geochemical problem was published by F. Wickman (1941) who calculated the total amount of bitumen and coal in the Earth on the basis of carbon isotope analyses of these materials. Titles of several articles written in the 1930s and 1940s show clearly that the power of stable isotope measurements in resolving problems in earth science was recognized long ago by outstanding scientists throughout the world (Table 1.1).

Light stable isotope geochemistry as we know it today arguably began in 1946. During that year, Harold Urey traveled to several prominent universities in Europe to deliver a lecture sponsored annually by the Royal Society of London. Urey presented results of calculations of the isotopic fractionation of stable isotope ratios of the

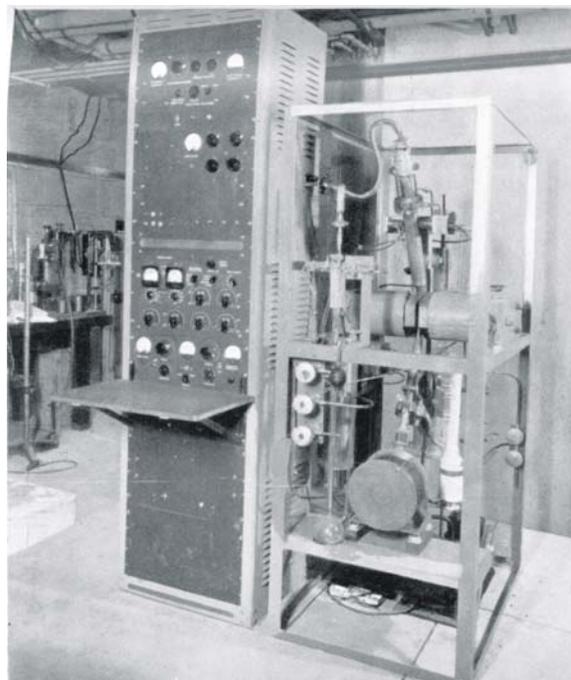


Fig. 1.1. Nier's 60° sector mass spectrometer, 1947. From Rankama (1954).

² H.C. Urey (1893-1981) won the Nobel Prize in chemistry in 1934 for his discovery of deuterium. He is considered the father of modern stable isotope geochemistry.

light elements among ideal gases and simple aqueous ions from spectroscopic data and the methods of statistical mechanics. The results of his calculations, published in the now classic paper entitled *The Thermodynamic Properties of Isotopic Substances* (Urey, 1947) remain to this day a valuable resource for isotope fractionation factors of simple compounds. At this lecture in Zurich in December of 1946, the renowned crystallographer Paul Niggli wondered if it might be possible to determine the fresh water or marine origin of ancient deposits of limestone, coral or shells from oxygen isotope analysis of the carbonate. At that time it was already known that $^{18}\text{O}/^{16}\text{O}$ ratios of marine limestones were about 3% higher than those of the ocean and that ocean water was isotopically heavier than fresh waters. Prompted by Niggli's remarks, Urey turned his attention to the temperature coefficient of the oxygen isotope fractionation between CaCO_3 and H_2O . On the basis of estimates made from his calculations, he concluded that this coefficient might be large enough to determine the temperatures of ancient oceans from oxygen isotope analyses of CaCO_3 in fossil shells. As Urey recounted the story later: "I suddenly found myself with a geological thermometer in my hands." And the games began.

Table 1.1. Selected early publications in stable isotope chemistry and geochemistry.

Year	Title	Reference
1921	Discussion on isotopes	Thomson <i>et al. Proc. Roy. Soc. Lond.</i> 99 , 87-104
1932	A hydrogen isotope of mass 2 and its concentration.	Urey, H.C., Brickwedde, F.G. and Murphy, G.M., <i>Phys. Rev.</i> 40 , 1.
1934	The natural separation of the isotopes of hydrogen.	Dole, M., <i>J. Amer. Chem. Soc.</i> 56 , 999.
1935	Isotopic exchange equilibria.	Urey, H.C. and Greiff, L.J., <i>J. Amer. Chem. Soc.</i> 57 , 321
1936	The relative atomic weight of oxygen in water and air.	Dole, M., <i>J. Chem. Phys.</i> 4 , 268-275.
1939	Isotopic composition of rain water.	Teis, R.V., <i>Compt. Rend. Acad. Sci. U.R.S.S.</i> 23 , 674.
1940	A mass spectrometer for routine isotope abundance measurements	Nier, A.O. <i>Rev. Sci. Inst.</i> 11 , 212-216
1941	Determination of the isotopic composition of [hydroxyl] waters in metamorphic rocks and minerals.	Vernadsky, W.I., Vinogradov, A.P., and Teis, R.V., <i>Compt. Rend. Acad. Sci. U.R.S.S.</i> 31 , 573.
1941	On a new possibility of calculating the total amount of coal and bitumen.	Wickman, F.E., <i>Geol. Fören. i Stockholm Förh.</i> 63 , 419.
1947	Calculation of equilibrium constants for isotopic exchange reactions.	Bigeleisen, J., Mayer, M.G. <i>J. Chem. Phys.</i> 15 , 261-267.
1947	The thermodynamic properties of isotopic substances	Urey, H.C. <i>J. Chem. Soc.</i> 562-581.
1949	Natural variations in the isotopic content of sulfur and their significance.	Thode, H.G., MacNamara, J. and Collins, C.B., <i>Can. J. Res.</i> 27B , 361.
1950	Isotopic composition of oxygen in silicate rocks.	Baertschi, P., <i>Nature</i> 166 , 112. Baertschi, P. and Silverman, S.R., <i>Geochim. Cosmochim. Acta</i> 1 , 4-6.
1951	Carbonate-water isotopic temperature scale.	Epstein, S., Buchsbaum, R., Lowenstam, H., Urey, H.C. <i>J. Geol.</i> 62 , 417-426.
1951	Relative abundance of oxygen and carbon isotopes in carbonate rocks.	Baertschi, P., <i>Nature</i> 168 , 288.
1952	Variation in the relative abundance of carbon isotopes in plants.	Wickman, F.E., <i>Geochim. Cosmochim. Acta</i> , 2 , 243.
1953	The geochemistry of the stable carbon isotopes.	Craig, H., <i>Geochim. Cosmochim. Acta</i> , 3 , 53-92.

Chapter 1. Introduction

The overall precision of the isotopic measurements required to make temperature estimates that were meaningful in paleoclimatology was not attainable in the 1940s. At that time the precision of mass spectrometric measurements of $^{18}\text{O}/^{16}\text{O}$ ratios was about a factor of ten less than required to determine temperatures to $\pm 0.5^\circ\text{C}$. In addition, there was no reproducible technique for extracting CO_2 from CaCO_3 , and there were no experimental data relating the oxygen isotope fractionation between calcium carbonate and water to temperature. Urey was not to be deterred from proceeding with this ambitious project, and he assembled an outstanding group of young scientists to work on it. This research team included postdoctoral fellow Sam Epstein, doctoral students Harmon Craig, and John McCrea, paleontologist Heinz Lowenstam and an electronics engineer Charles McKinney. By 1950, this group had successfully improved the precision of the Nier isotope ratio mass spectrometer (Nier, 1947; McKinney et al., 1950) by the necessary factor of 10, developed reproducible analytical extraction methods for biogenic carbonates and established standards and protocols that are still being followed for the most part today. The development of the oxygen isotope paleotemperature scale (Urey et al., 1948; Epstein et al., 1951; Urey et al., 1951) has been heralded as one of the outstanding scientific achievements of the twentieth century.

Concurrent with work on oxygen isotope analyses of carbonate shells, members of the Chicago group conducted survey studies of oxygen isotope variations in silicate rocks and minerals (Baertschi, 1950; Baertschi and Silverman, 1951), carbon isotope variations in nature (Craig, 1953), stable isotope ratios of natural waters (Epstein and Mayeda, 1953; Friedman, 1953) and oxygen isotope compositions of biogenic phosphates (Tudge, 1960). Important early stable isotope research was also conducted in Hamilton, Ontario on sulfur isotope ratios of rocks and minerals (Thode, 1949), in Copenhagen on oxygen isotope variations in natural waters (Dansgaard, 1954), and in Moscow on oxygen and sulfur isotope ratios of rocks and minerals (Vinogradov and Dontsova, 1947; Trofimov, 1949). Tom Hoering and his group in Arkansas investigated isotopic variations of nitrogen and chlorine in natural substances (Hoering, 1956; Hoering and Moore, 1958; Hoering and Parker, 1961). Within a few short years, it was recognized that oxygen isotope fractionations between cogenetic minerals were large enough to register temperatures of formation of high-temperature rocks (Clayton and Epstein, 1958) and that hydrogen and oxygen isotope measurements of rocks and minerals were powerful petrologic tools (Taylor and Epstein, 1962).

From these beginnings, stable isotope research has blossomed to the point where thousands of isotope ratio mass spectrometers are in operation in laboratories all over the world. Stable isotope measurements are being made to resolve problems in many diverse fields including geochemistry, climatology, hydrology, plant physiology, ecology, archaeology, meteorology, meteoritics, palaeobiology, bacteriology and the origin of life.

Almost all the early achievements in the field of isotope geology were made by gifted chemists and physicists who developed the theory and techniques, improved the mass spectrometers and extraction methods, and thought and wrote about many fundamental scientific questions of geologic interest. It is well to keep in mind that, despite developments in isotope ratio mass spectrometry, most notably very stable electronics and increased sensitivity of sources, there have been only modest improvements in the overall precision of modern stable isotope analyses over those made in the early 1950s. There are certainly exceptions to this claim. Sample sizes have come

down considerably and some of the more exotic, cutting-edge analyses could not have been made on the early machines. Most importantly however, the ease of analysis has improved dramatically. Thanks to the efforts of the mass spectrometer manufacturers to produce more user-friendly machines, many types of analyses that used to take the better part of a day can now be done in minutes. This has opened up the field of stable isotopes to a whole new class of researchers, particularly biologists, who need large numbers of analyses to see through the inherent variability of natural populations.

The new rapid techniques do not necessarily translate to better precision or accuracy. The old laborious extraction techniques for a stable isotope analysis were developed by analytical chemists who were very concerned about reproducible, quantitative chemical reactions. I have been asked by students whether the 'old' data are any good and can be used. I would say that data from much of the old literature is as good or better than data collected today. (The only question would be whether the old data are calibrated to known reference materials).

It is instructive to read the early papers. One comes to the enlightening realization that many questions being examined with the aid of stable isotope measurements today were already addressed by these early workers. Similar or identical conclusions reached from analyses of several or even only a few carefully selected materials 40-50 years ago are reappearing in recent publications that may contain hundreds of analyses, many of them superfluous. It is worthwhile, both from an historical standpoint and as proper scientific procedure to be aware of pertinent observations and conclusions published in the older literature. In this spirit, I have made an attempt to cite primary references whenever possible in this book.

1.3 Scope of the Discipline

Stable isotope measurements have an extremely wide range of applications and the principles employed are relatively easy to grasp. There are gross similarities between some of the approaches and scientific goals of stable isotope geochemistry and other geochemical systems. The basic principle of stable isotope geochemistry was first recognized by Briscoe and Robinson (1925) when they identified differences in the boron isotope ratios of natural materials. The fundamental principle is this: ***In any multiphase system, there is a preferential fractionation of isotopes, with one phase preferentially incorporating the heavy (or light) isotope relative to other coexisting phases.*** This isotope fractionation is due to subtle differences in the masses and thermodynamic properties of the different isotopes, and occurs in both equilibrium and kinetic processes. Evaporation of water into undersaturated air and incorporation of CO₂ during photosynthesis are examples of irreversible kinetic processes with large isotope fractionations. High temperature crystal growth and mineral recrystallization are processes that often approach thermodynamic equilibrium and have generally smaller isotopic fractionations. Unlike the kinetic fractionations, equilibrium fractionations follow well-understood thermodynamic rules. The traditional isotopic systems apply to the elements H, C, N, O, S. Recent analytical advances have added a whole host of additional elements to the isotope geochemists arsenal, including B, Cl, Si and the 'non-traditional' isotopes of Li, Mg, Ca, Cr, Fe, Cu, Zn, Se, and Mo (Johnson et al., 2004; Teng et al., 2017). Given that most natural materials contain one or more of these elements, the applications of stable isotopes to natural systems are extraordinarily broad

based, with new ideas being developed all the time. Figure 1.2 gives a broad-brush overview of the various fields and types of applications of stable isotopes.

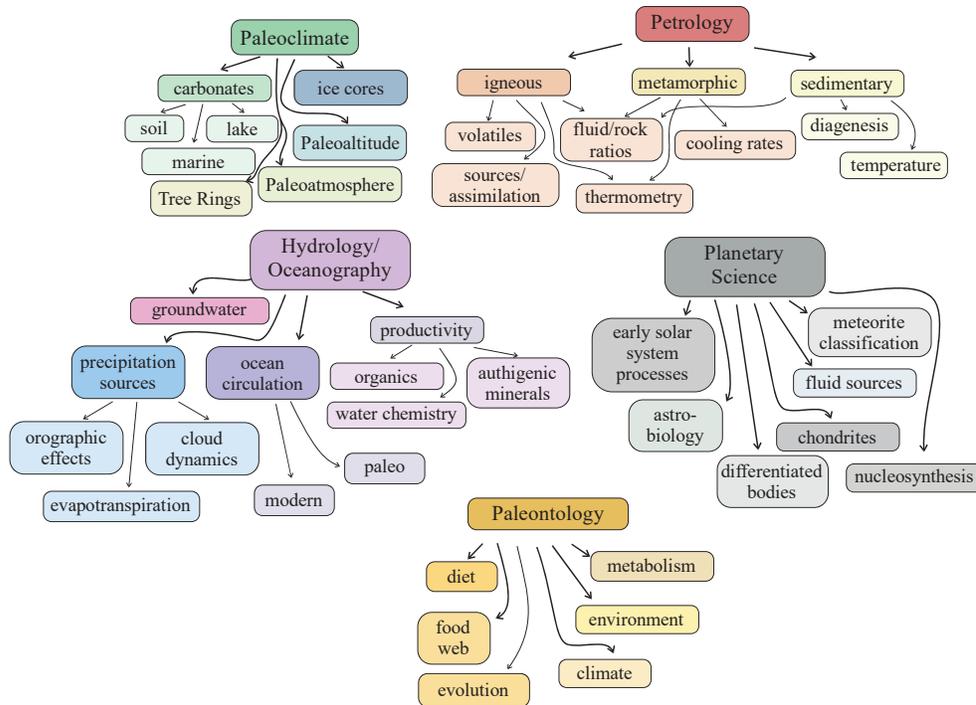


Fig. 1.2. Examples of the types of fields that are studied using stable isotopes.

1.3.1 What are stable isotopes?

In the most simple description, atoms consist of the subatomic particles **protons**, **electrons** and **neutrons**. Protons are positively charged, electrons are negatively charged and neutrons have no charge. The mass of a neutron is about equal to that of a proton and the mass of an electron is negligible relative to protons and neutrons (Table 1.2). The mass of an atom, therefore is determined by the total number of protons and neutrons.

An element is defined by the number of protons in its nucleus. In a neutral atom, the number of protons is balanced by an equal number of electrons which are present as a negatively charged cloud around the nucleus. The configuration of the electron cloud imparts to the atom its gross chemical properties. For a given element, the number of protons (**atomic number Z**) is always the same, but the number of neutrons (**neutron number N**) may vary. The **mass number A** is the sum of $Z + N$ (Table 1.3). The number of neutrons in the nucleus of an element does not affect the gross chemical properties of the element and its compounds, but mass differences due to changing N can cause subtle chemical and physical differences which results in isotopic fractionation. It is these small differences comprise the subject of this discipline.

An **isotope**³ of a given element differs from another isotope of the same element by the number of neutrons in its nucleus. Most elements in the Periodic Table have two or more naturally occurring isotopes (either stable or radioactive) but 21 elements, including fluorine and sodium, are **monoisotopic**. The nucleus of the single natural isotope of fluorine, contains 9 protons ($Z = 9$) and 10 neutrons ($A = 19$). Oxygen has three naturally occurring isotopes: ¹⁶O with 8 protons and 8 neutrons, ¹⁷O with 8 protons and 9 neutrons, and ¹⁸O with 8 protons and 10 neutrons.

Table 1.2. Charge and mass of the proton, neutron and electron.

Particle	Charge	Mass (g)	Mass (amu)
Proton	+1	$1.6726219 \times 10^{-24}$	1.0072766
Neutron	0	$1.6749275 \times 10^{-24}$	1.0086654
Electron	-1	$9.1093836 \times 10^{-28}$	0.000548597

Consider the three isotopes of hydrogen. **Protium** has one proton, one electron and a mass of 1.0078 atomic mass units, or amu. The nucleus of **deuterium**, a second isotope of hydrogen, contains one proton and one neutron. It has almost the same chemical properties as protium, but a mass of 2.0141 amu (Fig. 1.3), equal to the additional mass of a neutron less the nuclear binding energy of deuterium. **Tritium**, the third naturally occurring isotope of hydrogen, has one proton and two neutrons in its nucleus and thus has a mass of ~3 amu. Whereas both protium and deuterium are stable isotopes of hydrogen, the additional neutron in tritium imparts instability to the nucleus so that tritium is radioactive with a half life of 12.3 years. Neither protium nor deuterium will undergo spontaneous radioactive decay, although strictly speaking, any **nuclide**⁴ could undergo spontaneous decay, but the *probability* of such decay is negligible for these so-called stable isotopes. For example, ⁵⁰V, which was assumed to be stable, actually has a half-life of 1.5×10^{17} y, far longer than the age of the Universe. The three isotopes of hydrogen have very similar chemical properties but different masses, and these slight differences in mass result in slightly different strengths of bonds to other elements. These slight differences in mass and bond strengths are responsible for fractionation of the different isotopes between coexisting phases undergoing a physical or chemical reaction and provide the foundation for all of stable isotope geochemistry.

An example of important effects that can arise as a result of small differences in bond strengths is provided by the chemical and physical properties of the various **isotopologues** of water (Table 1.4), where an 'isotopologue' refers to the mass of a given compound. Although the physical and chemical properties of the isotopologues of water are clearly distinct and large, pure isotopologues are not found in nature. Rather, there exist mixtures of the end-member isotopologues which are each determined by the

³ The word *isotope* was coined in 1913 by Frederick Soddy, an English scientist who was awarded the 1921 Nobel Prize in chemistry for his investigations into the origin and nature of isotopes.

⁴ Truman Kohman of Carnegie Mellon University coined the word **nuclide** as a general term for a *specific* isotope. Including those artificially produced, there are >2500 known nuclides and most of them are radioactive. That is, stable isotopes are relatively rare in nature.

isotopes of the elements in the compound. Isotopic variations that occur in our Solar System are much smaller than the isotopic differences between artificially produced pure isotopologues.

Table 1.3 *Isotopic abundances and relative atomic masses of the pertinent elements in stable isotope geochemistry. Symbols for the main elements in the discipline are emboldened.*

Symbol	Atomic Number Z	Neutron number N	Mass Number M	Abundance (per cent)	Atomic Weight (12C = 12.)
H	1	0	1	99.985	1.007825
D	1	1	2	0.015	2.0140
Li	3	3	6	7.42	6.01512
		4	7	92.58	7.01600
B	5	5	10	19.78	10.0129
		6	11	80.22	11.00931
C	6	6	12	98.89	≅12.
		7	13	1.11	13.00335
N	7	7	14	99.63	14.00307
		8	15	0.37	15.00011
O	8	8	16	99.759	15.99491
		9	17	0.037	16.99914
		10	18	0.204	17.99916
Si	14	14	28	92.21	27.97693
		15	29	4.70	28.97649
		16	30	3.09	29.97376
S	16	16	32	95.0	31.97207
		17	33	0.76	32.97146
		18	34	4.22	33.96786
		20	36	0.014	35.96709
Cl	17	18	35	75.53	34.96885
		20	37	24.47	36.96590

1.3.2 Which elements and why?

It often comes as a surprise to learn that classical stable isotope geochemistry concerns, for the most part, variations in the stable isotope ratios of only five elements: H, C, N, O, and S (or SNOCH). Although small in number, these elements comprise the bulk of tissues in living organisms. The isotope ratios of Si and Cl in natural materials were first measured in 1954 (Allenby, 1954) and 1961 (Hoering and Parker, 1961), respectively, but only recently has interest in these systems jumped substantially. The most unexpected developments in stable isotope geochemistry is the explosive rise in the non-traditional isotopes of metals, including Li, B, Mg, Ca, Ti, V, Cr, Fe, Cu, Zn, Se, Sr, and Mo (Johnson et al., 2004). Most of these isotope ratios are measured using multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) and to a lesser

extent thermal ionization mass spectrometry (TIMS) or secondary ion mass spectrometry (SIMS). The isotopic variability in these systems is generally low (except for Li, which has enormous fractionations), but the analytical methodologies allow for differences of less than 0.1‰ to be measured with confidence.

Except for certain stable isotope relations in extraterrestrial materials and gases in the upper atmosphere of Earth, stable isotope geochemistry deals mainly with those

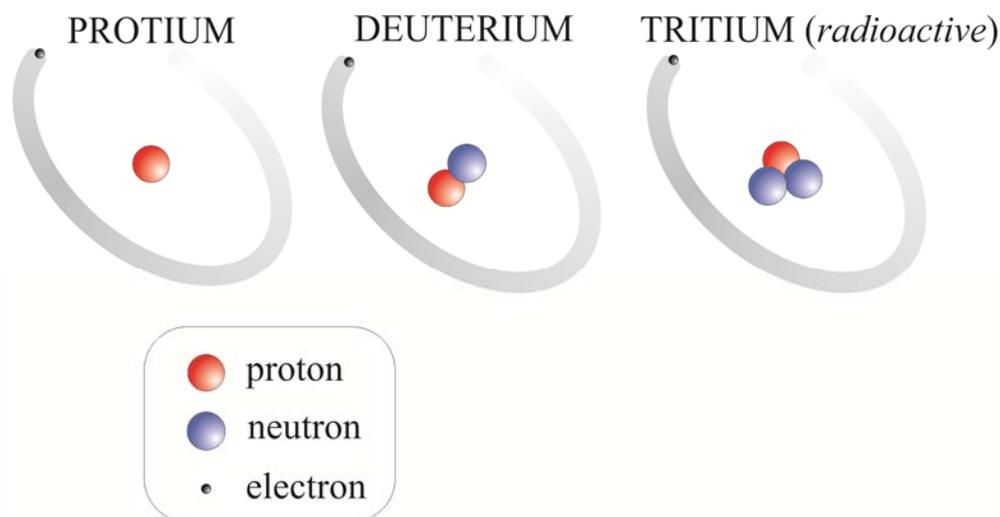


Fig. 1.3. Cartoon of the three isotopes of hydrogen. All have one proton (red sphere) and one electron but differ in the number of neutrons in the nucleus (blue sphere). The three isotopes have very similar chemical properties, but they have very different relative masses and subtly different bond strengths. This phenomenon gives rise to hydrogen isotope fractionation in physical and chemical reactions.

isotopic variations that arise either from isotopic exchange reactions or from mass-dependent fractionations that accompany biological and physical chemical processes occurring in nature or in the laboratory. While ultimately *quantum mechanical* in origin, such isotope effects are governed by kinetic theory and the laws of thermodynamics. Natural variations in the stable isotope ratios of heavy elements of geological interest like Sr, Nd, and Pb involve nuclear reactions and are governed by other factors including the ratio of radioactive parent and daughter, decay constants, and time.

1.4 Abundances of the Rare Isotopes of Light Elements

Isotopic ratios of the most of the elements of primary interest for light stable isotope geochemistry are written conventionally as the ratio of the heavy (and rare) isotope to the light (and more abundant) isotope as in $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$, *etc.* Early workers wrote these ratios in the opposite sense and reported values of absolute ratios. For example, $^{12}\text{C}/^{13}\text{C}$ or $^{32}\text{S}/^{34}\text{S}$ ratios were reported as relatively large numbers like 91.16 and 22.51, respectively. With our present knowledge of the absolute stable isotope ratios of certain international reference standards, it is now possible to compare these old analyses with modern analyses of similar materials. There is no accepted convention for writing isotopic ratios of other elements of geochemical interest. Sometimes the heavier

isotope is the more abundant isotope and is still written in the numerator, as in $^{11}\text{B}/^{10}\text{B}$. In other cases the lighter isotope is written in the numerator regardless of its relative abundance, as in $^3\text{He}/^4\text{He}$. The moderately heavy isotope systems violate the 'rare is heavy' rule. Johnson *et al.* (2004) recommend that all isotope systems should report 'heavy/light' isotope ratios to be consistent with the traditional stable isotope terminology. He isotopes will remain forever an exception. The traditional $^3\text{He}/^4\text{He}$ nomenclature, where the R value is the $^3\text{He}/^4\text{He}$ ratio of a sample relative to the $^3\text{He}/^4\text{He}$ ratio of air ($R_a = 1.4 \times 10^{-6}$) will live on.

Table 1.4 Chemical and physical properties of three of the nine isotopologues of water. (From Hutchinson, 1957 and Handbook of Chemistry and Physics)

Property	H_2^{16}O	D_2^{16}O	H_2^{18}O
Boiling Point (°C)	100.00	101.42	
Freezing Point (°C)	0.00	3.82	
Density at 0°C (gm/cm ³)	0.999841	1.10469	
Vapor Pressure at 20°C (bars × 10 ²)	2.3379	2.0265	2.3161
Temperature of Maximum Density (°C)	4.0	11.6	
Critical Temperature (°C)	374.1	371.5	
Critical Pressure (bars)	220.6	221.5	
Ionization Product, K_w at 25°C	1×10^{-14}	0.3×10^{-14}	
Dielectric Constant at 20°C	80.36	79.755	
Surface Tension at 19°C (dynes/cm)	73.66	72.83	
Viscosity at 20°C (centipoise)	1.009	1.260	
Refractive Index, n_d at 20°C	1.33300	1.32844	
Representative Solubilities at 25°C (g/g of water)			
NaCl	0.359	0.305	
BaCl ₂	0.357	0.289	

The elements under discussion in this text have one common isotope, like ^{16}O or ^{32}S , and one or more rare isotopes, like ^{17}O , ^{18}O , or ^{33}S , ^{34}S , and ^{36}S whose average abundances range from fractions of a per cent to a few per cent. The isotopic abundances and relative atomic weights of elements whose isotopic ratios vary as a result of mass-dependent processes are given in Table 1.3. Note that boron and chlorine are exceptions to the general rule given above concerning disparity in the abundances of the heavy and light isotopes of an element. In these two cases the abundances of the *rare* isotopes ^{10}B and ^{37}Cl are relatively high at 19.78 and 24.47 per cent, respectively.

1.5 Characteristics of Elements that Undergo Significant Isotopic Fractionation

The named elements share several characteristics that are not possessed by other elements whose isotopic ratios are not fractionated to any significant extent in nature or in the laboratory. These characteristics, enumerated below, are only *observed* characteristics and are not rigorously tied to theoretical principles.

1. *They have a relatively low atomic mass.* Significant mass-dependent isotopic variations in terrestrial materials have been looked for but not clearly demonstrated in heavier elements like Cu, Sn, and Ag. These heavier elements do have small fractionations that can now be measured with sufficient precision to have geological relevance, but they generally only have a total range in nature of a few per mil or less.
2. *The relative mass difference between the rare (heavy) and abundant (light) isotope is large.* Compare, for example, the values of 8.3 per cent and 12.5 per cent for the pairs ^{13}C - ^{12}C and ^{18}O - ^{16}O , respectively, with the value of only 1.2 per cent for ^{87}Sr - ^{86}Sr . The relative mass difference between D (deuterium) and H (protium) is almost 100 per cent and hydrogen isotope fractionations are accordingly about ten times larger than those of the other elements of interest. The condition of large relative mass difference is by no means sufficient to promote isotopic fractionation; the ^{48}Ca / ^{40}Ca ratio varies little in terrestrial rocks despite the large relative mass difference between the isotopes (only that of D-H is larger).
3. *They form chemical bonds that have a high degree of covalent character.* Elements like K, Ca, and Mg that occupy cation sites in minerals form ionic bonds to other elements and experience little or no site preference that could give rise to significant isotopic fractionations. Mg^{2+} , for example, is almost always surrounded by the same atomic environment in nature: an octahedron of oxygen. Nonetheless, small Ca isotope variations observed in biogenic carbonates may have an origin in mass dependent fractionation.
4. *They can exist in more than one oxidation state (C, N, S), form a wide variety of compounds (notably O), and are important constituents of naturally occurring solids and fluids.* Some of the largest fractionations in nature arise from differences in the nature of the chemical bonds to elements in different oxidation states as in the carbon isotope fractionation between CO_2 and CH_4 , and sulfur isotope fractionation between sulfide and sulfate. Silicon occurs in a number of naturally occurring compounds, but is almost always bonded to the same element (oxygen) in one oxidation state (+4). Consequently its isotopic ratios vary little in nature, outside of biological processes. Hydrogen is also bonded exclusively to oxygen in inorganic minerals as -OH groups but its isotopic composition is influenced greatly by the other ions bonded to the OH oxygen (Mg^{2+} , Al^{3+} , Fe^{2+} , etc.).
5. *The abundance of the element and rare isotope is sufficiently high (tenths to a few atom per cent) to assure the ability to make precise determinations of the isotopic ratios by mass spectrometry.* Measurements of isotopic ratios in materials at trace levels are difficult. Large amounts of material are needed and problems with blanks and contamination become quite serious. With recent advances in the sensitivity of conventional isotope ratio mass spectrometers and the introduction of continuous flow mass spectrometers, low abundance is less of an issue than it

has historically been. The abundance of the rare isotope still separates certain elements, such as He, which has a rare isotope abundance of 0.000137 %, from the elements commonly considered the 'light stable isotopes'.

1.6 Applications in the Earth Sciences

Stable isotope measurements have been applied successfully to the resolution of fundamental problems in the earth sciences, human sciences, biological sciences and several subdisciplines of chemistry. Applications in the earth sciences can be broadly classified into four main types:

1. *Thermometry* Formation temperatures of rock, mineral and gas systems are determined on the basis of temperature-dependent equilibrium fractionations of the isotopic ratios between two or more cogenetic phases. Stable isotope thermometry has played a major role in studies of paleoclimatology. Recent development of 'clumped isotopes' results in a single-mineral thermometer.
2. *Tracers* Large reservoirs like the ocean, the mantle, meteoric waters and organic matter have distinct stable isotope signatures that can be used to trace the origin of rocks, fluids, plants, contaminants, and food sources. Isotopic ratios can also be used as biomarkers.
3. *Reaction mechanisms* Distinctions can be made between diffusion and recrystallization, open and closed systems, and bacterial and thermogenic processes. Certain isotope values can be used to identify kinetic, non-equilibrium processes.
4. *Chemostratigraphy* Abrupt changes (excursions) in the stable isotope ratios of minerals and organic matter in ocean sediments and certain other terrestrial materials are used as stratigraphic markers, indicators of ocean productivity, and atmospheric chemistry.

The applications of stable isotopes are driven partly by technology and partly by the changing interests in scientific disciplines. Some applications, such as the new non-traditional isotopes, are exciting and high profile, but are also very difficult analytically and costly. An MC-ICP-MS is a very expensive instrument and clean labs are also required for many of the non-traditional measurements. This necessarily limits the number of practitioners in the field. On the other hand, the oxygen and hydrogen isotope ratio of waters can now be measured using low-cost desktop laser spectroscopy devices. As a result, far more researchers are able to measure waters than exotic non-traditional isotopes. The fields are also driven by the science, and interests wax and wane in different disciplines. Climate change concerns drive more people towards water issues and paleoclimate, so research in these fields has increased. Some fields, have 'matured' and consequently, related publications have decreased. There are also completely new techniques which have led to large number of unanticipated study fields. These include

triple isotope analyses of sulfur and oxygen and most notably, the single mineral carbonate thermometer based on 'clumped isotopes' (Eiler, 2007).

1.7 Isotope Effects

1.7.1 Kinetic isotope effects

Kinetic isotope effects are common both in nature and in the laboratory and their magnitudes are comparable to and often much larger than those of equilibrium isotope effects. Kinetic isotope effects are irreversible, and normally associated with fast, incomplete, or unidirectional processes like evaporation, diffusion, and dissociation reactions. Biological reactions such as photosynthesis are clearly irreversible, defying tradition thermodynamics which assume chemical equilibrium. Isotope effects attendant on diffusion and evaporation are explained (in part) by the different translational velocities possessed by the different isotopic forms of molecules as they move through a phase or across a phase boundary. Classical kinetic theory tells us that the average kinetic energy (K.E.) per molecule is the same for all gases at a given temperature. Consider, for example, the molecules $^{12}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ that have molecular weights of 28 and 30, respectively. Equating their kinetic energies at some T

$$\text{K.E.}(^{12}\text{C}^{16}\text{O}) = \text{K.E.}(^{12}\text{C}^{18}\text{O}) \quad (1.1)$$

and

$$\text{K.E.} = \frac{1}{2}mv^2 \quad (1.2)$$

where m is mass and v is velocity. Substituting the masses of these isotopologues of CO, the above equations reduce to

$$\frac{1}{2}(28)(v_{28})^2 = \frac{1}{2}(30)(v_{30})^2 \quad (1.3)$$

$$v_{28} = \sqrt{30/28}v_{30} = 1.035v_{30}. \quad (1.4)$$

That is, regardless of T, the average velocity of $^{12}\text{C}^{16}\text{O}$ molecules is 3.5 per cent greater than the average velocity of $^{12}\text{C}^{18}\text{O}$ molecules in the same system.

Such velocity differences can lead to isotopic fractionations in a variety of ways. For example, isotopically light molecules will preferentially diffuse out of a system and leave the reservoir enriched in the heavy isotope. On average, more $^{12}\text{CO}_2$ molecules than $^{13}\text{CO}_2$ molecules strike the surfaces of leaves and enter the stomates, an effect partially responsible for the low $^{13}\text{C}/^{12}\text{C}$ ratios of plants relative to other carbon-containing substances in nature. In the case of evaporation, the greater average translational velocities of isotopically lighter water molecules allow them to break through the liquid surface preferentially and diffuse across a boundary layer, resulting in an isotopic fractionation between vapor and liquid that is superimposed on the equilibrium isotopic fractionation between liquid and gaseous H_2O . Attesting to this phenomenon is the fact that water vapor over the oceans or over a large lake has $^{18}\text{O}/^{16}\text{O}$ and D/H ratios that are significantly lower than the ratios that would obtain at equilibrium (at 100% relative humidity). These lower ratios arise from kinetic isotope effects associated with evaporation.

While it is important to be aware of kinetic isotope effects, they are relatively rare in high-temperature processes occurring on Earth. By contrast, transient processes can occur whereby differing rates of isotopic exchange between coexisting minerals themselves, or between the minerals and an external fluid, can result in assemblages that are grossly out of isotopic equilibrium. Such examples are explained, not by kinetic isotope effects, but rather by a series of equilibrium isotope exchange reactions that have not gone to completion.

1.7.2 Equilibrium isotope effects

Equilibrium isotope effects can be considered in terms of the effect of atomic mass on bond energy. Substituting a light for heavy isotope in a molecular site does not affect the nuclear charges or electronic distribution of the molecule. It does, however, affect the bond strength. The energy required to break a bond is slightly higher for a heavy isotope than it is for a light one. This subtle difference in bond strength results in a predictable isotope fractionation between any two phases. The magnitude of this equilibrium isotopic effect is related to the bonding environment of the phases in question. Most importantly, the fractionation is dependent on temperature, so that for appropriate systems, such as calcite-water, the equilibrium oxygen isotope fractionation between the two phases is a function of temperature alone.

Equilibrium isotopic fractionations between two substances or between two phases of the same substance is the basis of stable isotope thermometry. The temperature dependence on isotope fractionation spawned the first major application of stable isotope chemistry to geological problems: the calcite oxygen isotope thermometer, first used for paleotemperature estimates over 50 years ago (Urey et al., 1948; Epstein et al., 1951; Urey et al., 1951). Figure 1.4 illustrates the equilibrium oxygen isotope fractionations between selected silicate minerals as a function of temperature. The fractionation between any two phases (roughly given by the difference in the isotopic composition of the two phases) generally follows a $1/T^2$ relationship (T in Kelvins). This means that the fractionations become smaller with increasing temperature and that the *temperature dependence* on the fractionation becomes greater at lower temperatures. The calcite-water fractionation is 28.8 ‰ at 25°C, but less than 1‰ at 600°C. The inverse temperature relationship means that a thermometer becomes more precise at lower temperature. The calcite-water thermometer has a precision of better than 1/2°C at room temperature, whereas the precision for quartz-mineral fractionations at metamorphic temperatures is an order of magnitude less precise (Fig. 1.4). (That said, being able to constrain the temperature of metamorphism to $\pm 10^\circ\text{C}$ is a remarkable achievement. Fractionations of not only oxygen isotopes, but those of hydrogen, carbon, nitrogen and sulfur have been used successfully over the years to place constraints on formation temperatures of both high and low temperature systems in nature. These concepts are discussed in more detail in later chapters of this text.

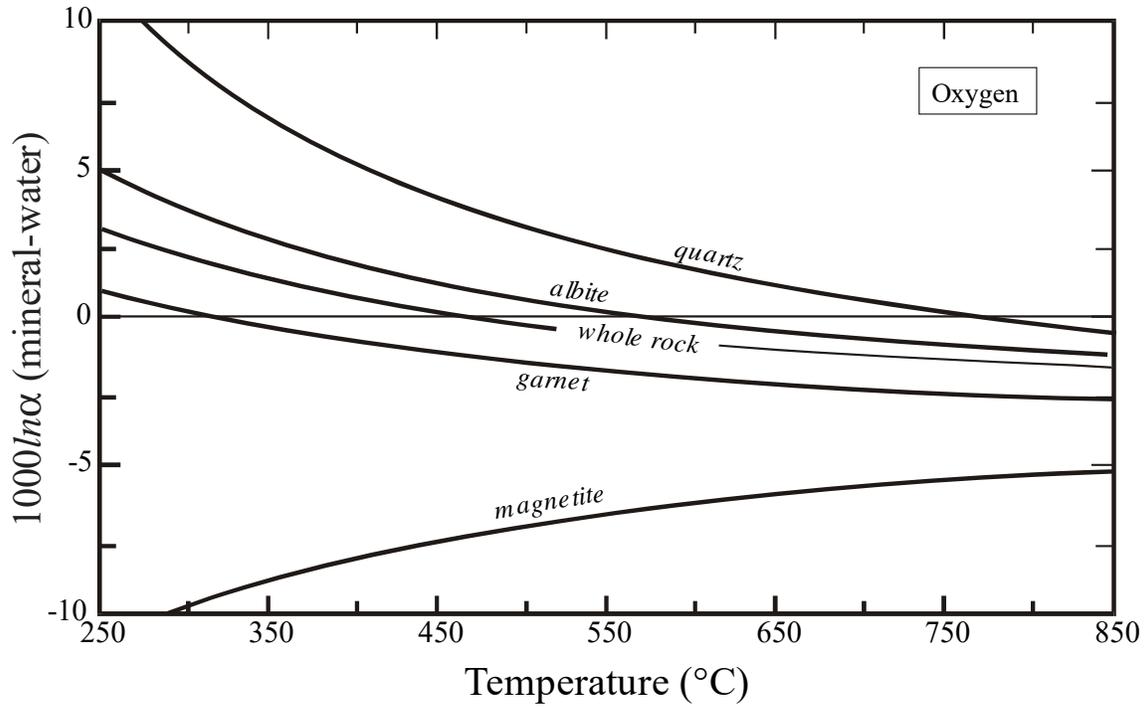


Fig. 1.4. Oxygen isotope fractionation between selected minerals as a function of temperature. In addition to oxygen, regular variations occur for most isotopic systems, including hydrogen, carbon, nitrogen and sulfur. Under certain circumstances to be discussed later, knowledge of the $\delta^{18}\text{O}$ values of two cogenetic phases allows the temperatures of formation to be determined. Note: $1000 \ln \alpha_{a-b} \approx \delta_a - \delta_b$.

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