

Hoefs

^{34}S

^{13}C

^{11}B

^{44}Ca

^{56}Fe

^{18}O

^6Li

^{98}Mo

Stable Isotope Geochemistry

6th Edition



Springer

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Jochen Hoefs

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Preface

Stable isotope investigations in the earth sciences continue to grow, maybe faster than ever before. After publication of the 5th edition, tremendous progress has been achieved in many subfields of stable isotope geochemistry. To name a few:

- Applications of Multicollector - ICP-MS has grown rapidly and now enable investigations on natural isotope variations of a wide range of transition and heavy elements that could not previously be measured with adequate precision.
- Precise ion probe measurements on the micrometer scale allow the detection of the growth and dissolution history of minerals.
- Evidence for mass-independent fractionation in a variety of compounds and elements has increased considerably.
- High precision analysis of the multiple rare isotopes of a specific element permit the distinction of different mass-dependent fractionation mechanisms.
- Precise measurements of molecules containing more than one rare isotope indicate non-random distributions of the rare isotopes, which potentially may be utilized as one-mineral thermometers.

These recent advances made a further revision necessary. Again I have tried to provide a contemporary overview of the entire field of stable isotope geochemistry enabling a quick access to the most recent literature, although many references date back to the 1960 and 1970s when seminal papers were published. I am fully aware of omissions and shortcomings, but I hope the new edition gives a well balanced discussion of the whole field including the new isotope systems introduced mainly by MC-ICP-MS techniques.

My colleagues Michael Böttcher, Max Coleman, Alan Matthews and Harald Strauß have reviewed an early draft, which is gratefully acknowledged. Yongsheng He was of great help during the preparation of some figures. I take, however, full responsibility for any shortcomings that remain.

Contents

1	Theoretical and Experimental Principles	1
1.1	General Characteristics of Isotopes	1
1.2	Isotope Effects	4
1.3	Isotope Fractionation Processes	5
1.3.1	Isotope Exchange	6
1.3.2	Kinetic Effects	11
1.3.3	Mass Dependent and Mass Independent Isotope Effects	12
1.3.4	Multiply Substituted Isotopologues	13
1.3.5	Diffusion	15
1.3.6	Other Factors Influencing Isotopic Fractionations	17
1.3.7	Isotope Geothermometers	19
1.4	Basic Principles of Mass Spectrometry	23
1.4.1	Continuous Flow: Isotope Ratio Monitoring Mass Spectrometers	26
1.5	Standards	27
1.6	General Remarks on Sample Preparation Methods for Gases	29
1.7	Microanalytical Techniques	31
1.7.1	Laser Microprobe	31
1.7.2	Secondary Ion Mass Spectrometry	31
1.8	Stable Isotope Variations of Heavy Elements	32
2	Isotope Fractionation Processes of Selected Elements	35
2.1	Hydrogen	36
2.1.1	Preparation Techniques and Mass Spectrometric Measurements	36
2.1.2	Standards	37
2.1.3	Fractionation Processes	38

2.2	Lithium	42
2.3	Boron	45
2.4	Carbon	48
2.4.1	Preparation Techniques	48
2.4.2	Standards	49
2.4.3	Fractionation Processes	49
2.4.4	Interactions between the Carbonate-Carbon Reservoir and Organic Carbon Reservoir	53
2.5	Nitrogen	54
2.6	Oxygen	58
2.6.1	Preparation Techniques	58
2.6.2	Standards	60
2.6.3	Fractionation Processes	61
2.6.4	Fluid-Rock Interactions	66
2.7	Magnesium	68
2.8	Silicon	70
2.9	Sulfur	71
2.9.1	Preparation Techniques	72
2.9.2	Fractionation Mechanisms	73
2.10	Chlorine	78
2.10.1	Methods	79
2.10.2	Characteristic Features of Cl Isotope Geochemistry	79
2.10.3	Chlorine Isotopes in the Environment	80
2.11	Calcium	81
2.12	Chromium	83
2.13	Iron	83
2.14	Copper	86
2.15	Zinc	87
2.16	Germanium	88
2.17	Selenium	88
2.18	Molybdenum	89
2.19	Mercury	90
2.20	Thallium	92

3 Variations of Stable Isotope Ratios in Nature 93

3.1 Extraterrestrial Materials 93

 3.1.1 Chondrites 94

 3.1.2 Evolved Extraterrestrial Materials 99

3.2 The Isotopic Composition of the Earth’s Upper Mantle 103

 3.2.1 Oxygen 104

 3.2.2 Hydrogen 105

 3.2.3 Carbon 107

 3.2.4 Nitrogen 108

 3.2.5 Sulfur 109

 3.2.6 Lithium and Boron 110

3.3 Magmatic Rocks 111

 3.3.1 Fractional Crystallization 111

 3.3.2 Differences between Volcanic and Plutonic Rocks 112

 3.3.3 Low-Temperature Alteration Processes 112

 3.3.4 Assimilation of Crustal Rocks 112

 3.3.5 Basaltic Rocks from Different Tectonic Settings 113

 3.3.6 Ocean Water/Basaltic Crust Interactions 115

 3.3.7 Granitic Rocks 115

3.4 Volatiles in Magmatic Systems 117

 3.4.1 Glasses 118

 3.4.2 Volcanic Gases and Hot Springs 120

 3.4.3 Isotope Thermometers in Geothermal Systems 123

3.5 Ore Deposits and Hydrothermal Systems 123

 3.5.1 Origin of Ore Fluids 125

 3.5.2 Wall-Rock Alteration 128

 3.5.3 Fossil Hydrothermal Systems 128

 3.5.4 Hydrothermal Carbonates 129

 3.5.5 Sulfur Isotope Composition of Ore Deposits 130

 3.5.6 Metal Isotopes 136

3.6 Hydrosphere 136

 3.6.1 Meteoric Water: General Considerations 137

 3.6.2 Ice Cores 141

 3.6.3 Groundwater 142

 3.6.4 Isotope Fractionations during Evaporation 143

 3.6.5 Ocean Water 144

 3.6.6 Pore Waters 146

 3.6.7 Formation Water 147

 3.6.8 Water in Hydrated Salt Minerals 149

3.7	The Isotopic Composition of Dissolved and Particulate Compounds in Ocean and Fresh Waters	149
3.7.1	Carbon Species in Water	150
3.7.2	Nitrogen	154
3.7.3	Oxygen	155
3.7.4	Sulfate	155
3.8	Isotopic Composition of the Ocean during Geologic History	157
3.8.1	Oxygen	157
3.8.2	Carbon	159
3.8.3	Sulfur	161
3.8.4	Iron	162
3.9	Atmosphere	163
3.9.1	Atmospheric Water Vapor	164
3.9.2	Nitrogen	164
3.9.3	Oxygen	166
3.9.4	Carbon Dioxide	167
3.9.5	Carbon Monoxide	172
3.9.6	Methane	173
3.9.7	Hydrogen	174
3.9.8	Sulfur	174
3.9.9	Mass-Independent Isotope Effects in Atmospheric Compounds	175
3.10	Biosphere	177
3.10.1	Living Organic Matter	177
3.10.2	Indicators of Diet and Metabolism	182
3.10.3	Tracing Anthropogenic Organic Contaminant Sources	183
3.10.4	Fossil Organic Matter	183
3.10.5	Marine vs. Terrestrial Organic Matter	184
3.10.6	Oil	185
3.10.7	Coal	187
3.10.8	Natural Gas	187
3.11	Sedimentary Rocks	191
3.11.1	Clay Minerals	191
3.11.2	Clastic Sedimentary Rocks	193
3.11.3	Biogenic Silica and Cherts	195
3.11.4	Marine Carbonates	196
3.11.5	Diagenesis	201
3.11.6	Limestones	202
3.11.7	Dolomites	202
3.11.8	Freshwater Carbonates	203
3.11.9	Phosphates	205
3.11.10	Iron Oxides	206
3.11.11	Sedimentary Sulfur	207

- 3.12 Palaeoclimatology 208
 - 3.12.1 Continental Records 209
 - 3.12.2 Marine Records 214
- 3.13 Metamorphic Rocks 217
 - 3.13.1 Contact Metamorphism 221
 - 3.13.2 Regional Metamorphism 222
 - 3.13.3 Lower Crustal Rocks 224
 - 3.13.4 Thermometry 224
- References** 229
- Index** 281

Chapter 1

Theoretical and Experimental Principles

1.1 General Characteristics of Isotopes

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. The term *isotopes* is derived from Greek (meaning equal places) and indicates that isotopes occupy the same position in the periodic table.

It is convenient to denote isotopes in the form ${}^m_n\text{E}$, where the superscript m denotes the mass number (i.e., sum of the number of protons and neutrons in the nucleus) and the subscript n denotes the atomic number of an element, E. For example, ${}^{12}_6\text{C}$ is the isotope of carbon which has six protons and six neutrons in its nucleus. The atomic weight of each naturally occurring element is the average of the weights contributed by its various isotopes.

Isotopes can be divided into two fundamental kinds, stable and unstable (radioactive) species. The number of stable isotopes is about 300; whilst over 1,200 unstable ones have been discovered so far. The term *stable* is relative, depending on the detection limits of radioactive decay times. In the range of atomic numbers from 1 (H) to 83 (Bi), stable nuclides of all masses except 5 and 8 are known. Only 21 elements are pure elements, in the sense that they have only one stable isotope. All other elements are mixtures of at least two isotopes. The relative abundance of different isotopes of an element may vary substantially. In copper, for example, ${}^{63}\text{Cu}$ accounts for 69% and ${}^{65}\text{Cu}$ for 31% of all copper nuclei. For the light elements, however, one isotope is predominant, the others being present only in trace amounts.

The stability of nuclides is characterized by several important rules, two of which are briefly discussed here. The first is the so-called symmetry rule, which states that in a stable nuclide with low atomic number, the number of protons is approximately equal to the number of neutrons, or the neutron-to-proton ratio, N/Z , is approximately equal to unity. In stable nuclei with more than 20 protons or neutrons, the N/Z ratio is always greater than unity, with a maximum value of about 1.5 for the heaviest stable nuclei. The electrostatic Coulomb repulsion of the positively charged protons grows rapidly with increasing Z . To maintain the stability in the nuclei, more

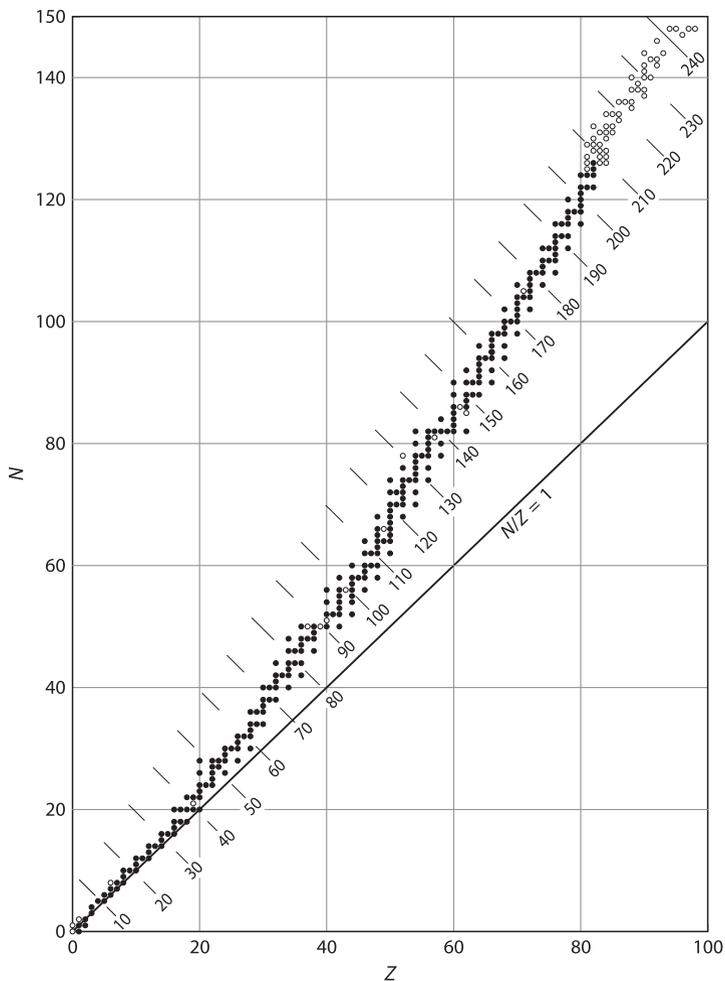


Fig. 1.1 Plot of number of protons (Z) and number of neutrons (N) in stable (filled circles) and unstable (open circles) nuclides

neutrons (which are electrically neutral) than protons are incorporated into the nucleus (see Fig. 1.1).

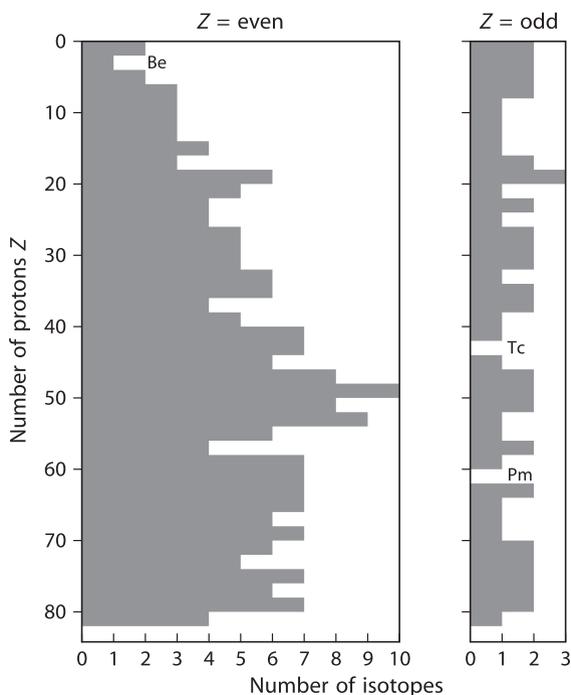
The second rule is the so-called *Oddo–Harkins* rule, which states that nuclides of even atomic numbers are more abundant than those with odd numbers. As shown in Table 1.1, the most common of the four possible combinations is even–even and the least common is odd–odd.

The same relationship is demonstrated in Fig. 1.2, which shows that there are more stable isotopes with even, than with odd, proton numbers.

Radioactive isotopes can be classified as being either artificial or natural. Only the latter are of interest in geology, because they are the basis for radiometric dating

Table 1.1 Types of atomic nuclei and their frequency of occurrence

Z-N combination	Number of stable nuclides
Even-even	160
Even-odd	56
Odd-even	50
Odd-odd	5



1.2 Isotope Effects

Differences in chemical and physical properties arising from variations in atomic mass of an element are called *isotope effects*. It is well known that the electronic structure of an element essentially determines its chemical behaviour, whereas the nucleus is more or less responsible for its physical properties. Since, all isotopes of a given element contain the same number and arrangement of electrons, a far-reaching similarity in chemical behaviour is the logical consequence. But this similarity is not unlimited; certain differences exist in physicochemical properties due to mass differences. The replacement of any atom in a molecule by one of its isotopes produces a very small change in chemical behaviour. The addition of one neutron can, for instance, considerably depress the rate of chemical reaction. Furthermore, it leads, for example, to a shift of the lines in the Raman- and IR-spectra. Such mass differences are most pronounced among the lightest elements. For example, some differences in physicochemical properties of H_2^{16}O , D_2^{16}O , H_2^{18}O are listed in Table 1.2. To summarize, the properties of molecules differing only in isotopic substitution are qualitatively the same, but quantitatively different.

Differences in the chemical properties of the isotopes of H, C, N, O, S, and other elements have been calculated by the methods of statistical mechanics and also determined experimentally. These differences in the chemical properties can lead to considerable separation of the isotopes during chemical reactions.

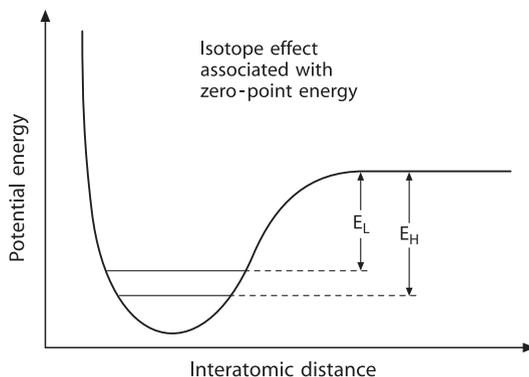
The theory of isotope effects and a related isotope fractionation mechanism will be discussed very briefly. For a more detailed introduction to the theoretical background, see Bigeleisen and Mayer (1947), Urey (1947), Melander (1960), Bigeleisen (1965), Richet et al. (1977), O'Neil (1986), Criss (1999), Chacko et al. (2001), Schauble (2004), and others.

Differences in the physicochemical properties of isotopes arise as a result of quantum mechanical effects. Figure 1.3 shows schematically the energy of a diatomic molecule, as a function of the distance between the two atoms. According to the quantum theory, the energy of a molecule is restricted to certain discrete energy levels. The lowest level is not at the minimum of the energy curve, but above it by an amount $1/2h\nu$ where h is Planck's constant and ν is the frequency with

Table 1.2 Characteristic physical properties of H_2^{16}O , D_2^{16}O , and H_2^{18}O

Property	H_2^{16}O	D_2^{16}O	H_2^{18}O
Density (20°C, in g cm^{-3})	0.997	1.1051	1.1106
Temperature of greatest density (°C)	3.98	11.24	4.30
Melting point (760 Torr, in °C)	0.00	3.81	0.28
Boiling point (760 Torr, in °C)	100.00	101.42	100.14
Vapour pressure (at 100°C, in Torr)	760.00	721.60	
Viscosity (at 20°C, in centipoise)	1.002	1.247	1.056

Fig. 1.3 Schematic potential energy curve for the interaction of two atoms in a stable molecule or between two molecules in a liquid or solid (after Bigeleisen 1965)



which the atoms in the molecule vibrate with respect to one another. Thus, even in the ground state at a temperature of absolute zero, the vibrating molecule would possess certain zero-point energy above the minimum of the potential energy curve of the molecule. It vibrates with its fundamental frequency, which depends on the mass of the isotopes. In this context, it is important to note that vibrational motions dominate chemical isotope effects; rotational and translational motions either have no effect on isotope separations or are subordinate. Therefore, molecules of the same chemical formula that have different isotopic species will have different zero-point energies: the molecule of the heavy isotope will have a lower zero-point energy than the molecule of the light isotope, as it has a lower vibrational frequency. This is shown schematically in Fig. 1.3, where the upper horizontal line (E_L) represents the dissociation energy of the light molecule and the lower line (E_H), that of the heavy one. E_L is actually not a line, but an energy interval between the zero-point energy level and the *continuous* level. This means that the bonds formed by the light isotope are weaker than bonds involving the heavy isotope. Thus, during a chemical reaction, molecules bearing the light isotope will, in general, react slightly more readily than those with the heavy isotope.

1.3 Isotope Fractionation Processes

The partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios is called *isotope fractionation*. The main phenomena producing isotope fractionations are

1. Isotope exchange reactions (equilibrium isotope distribution)
2. Kinetic processes that depend primarily on differences in reaction rates of isotopic molecules

1.3.1 Isotope Exchange

Isotope exchange includes processes with very different physicochemical mechanisms. Here, the term *isotope exchange* is used for all situations, in which there is no net reaction, but in which the isotope distribution changes between different chemical substances, between different phases, or between individual molecules.

Isotope exchange reactions are a special case of general chemical equilibrium and can be written



where the subscripts indicate that species *A* and *B* contain either the light or heavy isotope 1 or 2, respectively. For this reaction, the equilibrium constant is expressed by

$$K = \frac{\left(\frac{A_2}{A_1}\right)^a}{\left(\frac{B_2}{B_1}\right)^b}, \quad (1.2)$$

where the terms in parentheses may be, for example, the molar ratios of any species. Using the methods of statistical mechanics, the isotopic equilibrium constant may be expressed in terms of the partition functions *Q* of the various species

$$k = \frac{\left(\frac{Q_{A2}}{Q_{A1}}\right)}{\left(\frac{Q_{B2}}{Q_{B1}}\right)}. \quad (1.3)$$

Thus, the equilibrium constant then is simply the quotient of two partition function ratios, one for the two isotopic species of *A*, the other for *B*.

The partition function is defined by

$$Q = \sum_i (g_i \exp(-E_i/kT)), \quad (1.4)$$

where the summation is over all the allowed energy levels, E_i , of the molecules and g_i is the degeneracy or statistical weight of the i th level [of E_i], k is the Boltzmann constant and T is the temperature. Urey (1947) has shown that for the purpose of calculating partition function ratios of isotopic molecules, it is very convenient to introduce, for any chemical species, the ratio of its partition function to that of the corresponding isolated atom, which is called the reduced partition function. This reduced partition function ratio can be manipulated exactly in the same way as the normal partition function ratio. The partition function of a molecule can be separated into factors corresponding to each type of energy: translation, rotation, and vibration

$$Q_2/Q_1 = (Q_2/Q_1)_{\text{trans}} (Q_2/Q_1)_{\text{rot}} (Q_2/Q_1)_{\text{vib}}. \quad (1.5)$$

The difference of the translation and rotation energy is more or less the same among the compounds appearing at the left- and right-hand side of the exchange reaction equation, except for hydrogen, where rotation must be taken into account. This

leaves differences in vibrational energy as the predominant source of isotope effects. The term, vibrational energy can be separated into two components. The first is related to the zero-point energy difference and accounts for most of the variation with temperature. The second term represents the contributions of all the other bound states and is not very different from unity. The complications which may occur relative to this simple model are mainly that the oscillator is not perfectly harmonic, so an *inharmonic* correction has to be added.

For geologic purposes, the dependence of the equilibrium constant K on temperature is the most important property (4). In principle, isotope fractionation factors for isotope exchange reactions are also slightly pressure-dependent because isotopic substitution makes a minute change in the molar volume of solids and liquids. Experimental studies up to 20 kbar by Clayton et al. (1975) have shown that the pressure dependence for oxygen is, however, less than the limit of analytical detection. Thus, as far as it is known today, the pressure dependence seems with the exception of hydrogen to be of no importance for crustal and upper mantle environments (but see Polyakov and Kharlashina 1994).

Isotope fractionations tend to become zero at very high temperatures. However, they do not decrease to zero monotonically with increasing temperatures. At higher temperatures, fractionations may change sign (called crossover) and may increase in magnitude, but they must approach zero at very high temperatures. Such crossover phenomena are due to the complex manner by which thermal excitation of the vibration of atoms contributes to an isotope effect (Stern et al. 1968).

For ideal gas reactions, there are two temperature regions where the behaviour of the equilibrium constant is simple: at low temperatures (generally much below room temperature), the natural logarithm of K ($\ln K$) follows $\sim 1/T$ where T is the absolute temperature and at high temperatures, the approximation becomes $\ln K \sim 1/T^2$.

The temperature ranges in which these simple behaviours are approximated depend on the vibrational frequencies of the molecules involved in the reaction. For the calculation of a partition function ratio for a pair of isotopic molecules, the vibrational frequencies of each molecule must be known. When solid materials are considered, the evaluation of partition function ratios becomes even more complicated, because it is necessary to consider not only the independent internal vibrations of each molecule, but also the lattice vibrations.

1.3.1.1 Fractionation Factor (α)

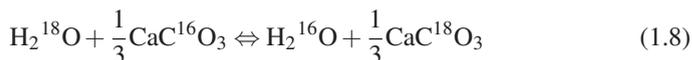
For isotope exchange reactions in geochemistry, the equilibrium constant K is often replaced by the fractionation factor $\tilde{\alpha}$. The fractionation factor is defined as the ratio of the numbers of any two isotopes in one chemical compound A divided by the corresponding ratio for another chemical compound B:

$$\alpha_{A-B} = \frac{R_A}{R_B}. \quad (1.6)$$

If the isotopes are randomly distributed over all possible positions in the compounds A and B, then α is related to the equilibrium constant K by

$$\alpha = K^{1/n} \quad (1.7)$$

where n is the number of atoms exchanged. For simplicity, isotope exchange reactions are written such that only one atom is exchanged. In these cases, the equilibrium constant is identical to the fractionation factor. For example, the fractionation factor for the exchange of ^{18}O and ^{16}O between water and CaCO_3 is expressed as follows:



with the fractionation factor $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ defined as:

$$\alpha_{\text{CaCO}_3 - \text{H}_2\text{O}} = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{CaCO}_3}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{H}_2\text{O}}} = 1.031 \text{ at } 25^\circ\text{C}. \quad (1.9a)$$

It has become common practice in recent years to replace the fractionation factor α by the ε -value (or separation factor), which is defined as

$$\varepsilon = \alpha - 1. \quad (1.9b)$$

because $\varepsilon \times 1,000$ approximates the fractionation in parts per thousand, similar to the δ value (see below).

1.3.1.2 The Delta Value (δ)

In isotope geochemistry, it is a common practice to express isotopic composition in terms of *delta*-(δ) values. For two compounds, A and B, whose isotopic compositions have been measured in the laboratory by conventional mass spectrometry:

$$\delta_A = \left(\frac{R_A}{R_{\text{st}}} - 1\right) 10^3 (\%) \quad (1.10)$$

and

$$\delta_B = \left(\frac{R_B}{R_{\text{st}}} - 1\right) 10^3 (\%), \quad (1.11)$$

where R_A and R_B are the respective isotope ratio measurements for the two compounds and R_{st} is the defined isotope ratio of a standard sample.

For the two compounds A and B, the δ -values and fractionation factor α are related by:

$$\delta_A - \delta_B = \Delta_{A-B} \approx 10^3 \ln \alpha_{A-B}. \quad (1.12)$$

Table 1.3 Comparison between δ , α , and $10^3 \ln \alpha_{A-B}$

δ_A	δ_B	Δ_{A-B}	α_{A-B}	$10^3 \ln \alpha_{A-B}$
1.00	0	1.00	1.001	1.00
5.00	0	5.00	1.005	4.99
10.00	0	10.00	1.01	9.95
15.00	0	15.00	1.015	14.98
20.00	0	20.00	1.02	19.80
10.00	5.00	5.00	1.00498	4.96
20.00	15.00	5.00	1.00493	4.91
30.00	15.00	15.00	1.01478	14.67
30.00	20.00	10.00	1.00980	9.76
30.00	10.00	20.00	1.01980	19.61

Table 1.3 illustrates the closeness of the approximation. Considering experimental uncertainties in isotope ratio determinations (typically $\geq 0.1\%$), these approximations are excellent for differences in δ -values less than about 10 and for δ -values that are relatively small in magnitude.

1.3.1.3 Evaporation–Condensation Processes

Of special interest in stable isotope geochemistry are evaporation–condensation processes, because differences in the vapour pressures of isotopic compounds lead to significant isotope fractionations. For example, from the vapour pressure data for water given in Table 1.2, it is evident that the lighter molecular species are preferentially enriched in the vapour phase, the extent depending upon the temperature. Such an isotopic separation process can be treated theoretically in terms of fractional distillation or condensation under equilibrium conditions as is expressed by the Rayleigh (1896) equation. For a condensation process, this equation is

$$\frac{R_V}{R_{V_0}} = f^{\alpha-1}, \quad (1.13)$$

where R_{V_0} is the isotope ratio of the initial bulk composition and R_V is the instantaneous ratio of the remaining vapour (v); f is the fraction of the residual vapour, and the fractionation factor α is given by R_l/R_V (l = liquid). Similarly, the instantaneous isotope ratio of the condensate (R_l) leaving the vapour is given by

$$\frac{R_l}{R_{V_0}} = \alpha f^{\alpha-1} \quad (1.14)$$

and the average isotope ratio of the separated and accumulated condensate (\bar{R}_l) at any time of condensation is expressed by

$$\frac{\bar{R}_l}{R_{V_0}} = \frac{1-f^\alpha}{1-f}. \quad (1.15)$$

For a distillation process, the instantaneous isotope ratios of the remaining liquid and the vapour leaving the liquid are given by

$$\frac{R_l}{R_{l_0}} = f^{(\frac{1}{\alpha}-1)} \quad (1.16)$$

and

$$\frac{\bar{R}_v}{R_{l_0}} = \frac{1}{\alpha} f^{(\frac{1}{\alpha}-1)}. \quad (1.17)$$

The average isotope ratio of the separated and accumulated vapour is expressed by

$$\frac{\bar{R}_v}{R_{l_0}} = \frac{1 - f^{1/\alpha}}{1 - f} \quad (f = \text{fraction of residual liquid}) \quad (1.18)$$

Any isotope fractionation occurring in such a way that the products are isolated from the reactants immediately after formation will show a characteristic trend in isotopic composition. As condensation or distillation proceeds, the residual vapour or liquid will become progressively depleted or enriched with respect to the heavy isotope. A natural example is the fractionation between oxygen isotopes in the water vapour of a cloud and the raindrops released from the cloud. The resulting decrease of the $^{18}\text{O}/^{16}\text{O}$ ratio in the residual vapour and the instantaneous isotopic composition of the raindrops released from the cloud are shown in Fig. 1.4 as a function of the fraction of vapour remaining in the cloud.

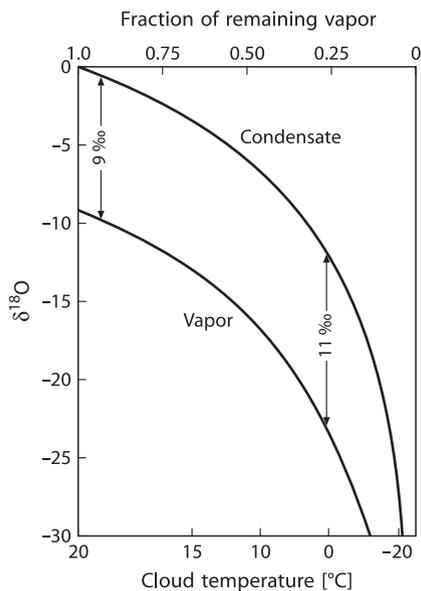


Fig. 1.4 $\delta^{18}\text{O}$ in a cloud vapour and condensate plotted as a function of a fraction of remaining vapour in a cloud for a Rayleigh process. The temperature of the cloud is shown on the lower axis. The increase in fractionation with decreasing temperature is taken into account (after Dansgaard 1964)

1.3.2 Kinetic Effects

The second main phenomena producing fractionations are kinetic isotope effects, which are associated with incomplete and unidirectional processes like evaporation, dissociation reactions, biologically mediated reactions, and diffusion. The latter process is of special significance for geological purposes, which warrants separate treatment (Sect. 1.3.3). A kinetic isotope effect also occurs, when the rate of a chemical reaction is sensitive to atomic mass at a particular position in one of the reacting species.

The theory of kinetic isotope fractionations has been discussed by Bigeleisen and Wolfsberg (1958), Melander (1960), and Melander and Saunders (1980). Knowledge of kinetic isotope effects is very important, because it can provide information about details of reaction pathways.

Quantitatively, many observed deviations from simple equilibrium processes can be interpreted as consequences of the various isotopic components having different rates of reaction. Isotope measurements taken during unidirectional chemical reactions always show a preferential enrichment of the lighter isotope in the reaction products. The isotope fractionation introduced during the course of an unidirectional reaction may be considered in terms of the ratio of rate constants for the isotopic substances. Thus, for two competing isotopic reactions



the ratio of rate constants for the reaction of light and heavy isotope species k_1/k_2 , as in the case of equilibrium constants, is expressed in terms of two partition function ratios, one for the two reactant isotopic species, and one for the two isotopic species of the activated complex or transition state, A^X :

$$\frac{k_1}{k_2} = \left[\frac{Q_{(A_2)}^*}{Q_{(A_1)}^*} / \frac{Q_{(A_2^X)}^*}{Q_{(A_1^X)}^*} \right] \frac{v_1}{v_2}. \quad (1.20)$$

The factor v_1/v_2 in the expression is a mass term ratio for the two isotopic species. The determination of the ratio of rate constants is, therefore, principally the same as the determination of an equilibrium constant, although the calculations are not so precise because of the need for detailed knowledge of the transition state. The term *transition state* refers to the molecular configuration that is most difficult to attain along the path between the reactants and the products. This theory follows the concept that a chemical reaction proceeds from some initial state to a final configuration by a continuous change, and that there is some critical intermediate configuration called the activated species or transition state. There are a small number of activated molecules in equilibrium with the reacting species and the rate of reaction is controlled by the rate of decomposition of these activated species.

1.3.3 Mass Dependent and Mass Independent Isotope Effects

1.3.3.1 Mass Dependent Effects

At thermodynamic equilibrium, isotope distributions are strictly governed by relative mass differences among different isotopes of an element. Mass dependent relationships hold for many kinetic processes as well. Thus, it has been a common belief that for most natural reactions, isotope effects arise solely because of isotopic mass differences. This means that for an element with more than two isotopes, such as oxygen or sulfur, the enrichment of ^{18}O relative to ^{16}O or ^{34}S relative to ^{32}S is expected to be approximately twice as large as the enrichment of ^{17}O relative to ^{16}O or as the enrichment of ^{33}S relative to ^{32}S . Therefore, for many years, interest in measuring more than one isotope ratio of a specific element was limited. Recent improvements of multiple-stable isotope analysis have demonstrated, however, that different mass dependent processes (e.g., diffusion, metabolism, high temperature equilibrium processes) can deviate by a few per cent and follow slightly different mass dependent fractionation laws (Young et al. 2002; Miller 2002; Farquhar et al. 2003). These very small differences are measurable and have been documented for oxygen (Luz et al. 1999), magnesium (Young et al. 2002), and sulfur (Farquhar et al. 2003).

It is a common practice to describe mass dependent isotope fractionation processes by a single linear curve on a three-isotope-plot (Matsuhisa et al. 1978). The resulting straight lines are referred to as terrestrial mass fractionation lines and deviations from it are used as indicating nonmass-dependent isotope effects. The three-isotope-plot is based on the approximation of a power law function to linear format. To describe how far a sample plots off the mass-dependent fractionation line, a new term has been introduced: $\Delta^{17}\text{O}$, $\Delta^{25}\text{Mg}$, $\Delta^{33}\text{S}$, etc. Several definitions of Δ have been introduced in the literature, which have been discussed by Assonov and Breninkmeijer (2005). The simplest definition is given by:

$$\begin{aligned}\Delta^{17}\text{O} &= \delta^{17}\text{O} - \lambda \delta^{18}\text{O} \\ \Delta^{25}\text{Mg} &= \delta^{25}\text{Mg} - \lambda \delta^{26}\text{Mg} \\ \Delta^{33}\text{S} &= \delta^{33}\text{S} - \lambda \delta^{34}\text{S},\end{aligned}$$

where λ is the main parameter that characterizes the mass dependent fractionation. The value of the coefficient λ depends on molecular mass, which for oxygen may range from 0.53 for atomic oxygen to 0.500 for species with high molecular weight. Recent progress in high precision measurement of isotope ratios allows to distinguish λ -values in the third decimal, which has obscured the difference between mass dependent and mass-independent fractionations at small Δ -values (Farquhar and Wing 2003).

1.3.3.2 Mass-Independent Effects

A few processes in nature do not follow the above mass-dependent fractionations. Deviations from mass-dependent fractionations were first observed in meteorites (Clayton et al. 1973) and in ozone (Thiemens and Heidenreich 1983). These mass-independent fractionations (MIF) describe relationships that violate the mass-dependent rules $\delta^{17}\text{O} \approx 0.5\delta^{18}\text{O}$ or $\delta^{33}\text{S} \approx 0.5\delta^{34}\text{S}$ and produce isotopic compositions with nonzero $\Delta^{17}\text{O}$ and $\Delta^{33}\text{S}$.

A number of experimental and theoretical studies have focused on the causes of mass-independent fractionation effects, but as summarized by Thiemens (1999), the mechanism for mass-independent fractionations remains uncertain. The best studied reaction is the formation of ozone in the stratosphere. Mauersberger et al. (1999) demonstrated experimentally that it is not the symmetry of a molecule that determines the magnitude of ^{17}O enrichment, but it is the difference in the geometry of the molecule. Gao and Marcus (2001) presented an advanced model, which has led to a better understanding of nonmass-dependent isotope effects.

Mass-independent isotopic fractionations are widespread in the earth's atmosphere and have been observed in O_3 , CO_2 , N_2O , and CO , which are all linked to reactions involving stratospheric ozone (Thiemens 1999). For oxygen, this is a characteristic marker in the atmosphere (see Sect. 3.9). These processes probably also play a role in the atmosphere of Mars and in the pre-solar nebula (Thiemens 1999). Oxygen isotope measurements in meteorites demonstrate that the effect is of significant importance in the formation of the solar system (Clayton et al. 1973a) (Sect. 3.1).

There are numerous terrestrial solid reservoirs, where mass-independent isotope variations have been observed. Farquhar et al. (2000c) and Bao et al. (2000) reported mass-independent oxygen isotope fractionations in terrestrial sulfates. A positive ^{17}O excess in sulfate has been found to be almost ubiquitous in desert environments (Bao et al. 2001). Significant mass-independent sulfur isotope fractionations have been reported by Farquhar et al. (2000c) in sulfides older than 2.4 Ga, whereas these fractionations do not occur in measurable amounts in sulfides younger than 2.4 Ga (see Fig. 3.29). Smaller, but clearly resolvable, MIFs have been measured in volcanic aerosol sulfates in polar ice (Baroni et al. 2007). Photolysis of SO_2 to sulfuric acid is thought to be the source reaction for these sulfur MIFs (Farquhar et al. 2001). These recent findings indicate that nonmass-dependent isotope fractionations are more abundant than originally thought and constitute a novel form of isotopic fingerprint.

1.3.4 Multiply Substituted Isotopologues

In stable isotope geochemistry, generally bulk isotopic compositions of natural samples are given (e.g., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, etc.). In the measured gases, bulk compositions depend only on abundances of molecules containing one rare isotope (e.g., $^{13}\text{C}^{16}\text{O}^{16}\text{O}$

Table 1.4 Stochastic abundances of CO₂ isotopologues (Eiler 2007)

Mass	Isotopologue	Relative abundance
44	¹² C ¹⁶ O ₂	98.40%
45	¹³ C ¹⁶ O ₂	1.11%
46	¹² C ¹⁷ O ¹⁶ O	748 ppm
	¹² C ¹⁸ O ¹⁶ O	0.40%
47	¹³ C ¹⁷ O ¹⁶ O	8.4 ppm
	¹² C ¹⁷ O ₂	0.142 ppm
	¹³ C ¹⁸ O ¹⁶ O	44.4 ppm
48	¹² C ¹⁷ O ¹⁸ O	1.50 ppm
	¹³ C ¹⁷ O ₂	1.60 ppb
49	¹² C ¹⁸ O ₂	3.96 ppm
	¹³ C ¹⁷ O ¹⁸ O	16.8 ppb
49	¹³ C ¹⁸ O ₂	44.5 ppb

or ¹²C¹⁸O¹⁶O). However, there also exist in very low concentration, molecules having more than one rare isotope such as ¹³C¹⁸O¹⁶O or ¹²C¹⁸O¹⁷O. These so-called isotopologues are molecules that differ from one another only in isotopic composition. Table 1.4 gives the stochastic abundances of isotopologues of CO₂.

Already Urey (1947) and Bigeleisen and Mayer (1947) recognized that multiply substituted isotopologues have unique thermodynamic properties different from singly substituted isotopologues of the same molecule. Natural distributions of multiply substituted isotopologues can thus provide unique constraints on geological, geochemical, and cosmochemical processes (Wang et al. 2004).

Normal gas-source mass spectrometers do not allow meaningful abundance measurements of these very rare species. However, if some demands on high abundance sensitivity, high precision, and high mass resolving power are met, John Eiler and his group (e.g., Eiler and Schauble 2004; Affek and Eiler 2006; Eiler 2007) have reported precise (<0.1‰) measurements of CO₂ with mass 47 (Δ₄₇-values) with an especially modified, but normal gas-source mass spectrometer. Δ₄₇-values are defined as ‰ difference between the measured abundance of all molecules with mass 47 relative to the abundance of 47, expected for the stochastic distribution.

This new technique is also termed *clumped isotope geochemistry* (Eiler 2007) because the respective species are produced by clumping two rare isotopes together. Deviations from stochastic distributions may result from all processes of isotope fractionation observed in nature. Thus, processes that lead to isotope fractionations of bulk compositions also lead to fractionations of multiply substituted isotopologues, implying that clumped isotope geochemistry is potentially applicable to many geochemical problems (Eiler 2007). So far, the most used application is a carbonate thermometer based on the formation of the CO₃⁻ group containing both ¹³C and ¹⁸O. Schauble et al. (2006) calculated an ~0.4‰ excess of ¹³C¹⁸O¹⁶O groups in carbonate groups at room temperature relative to what would be expected in a stochastic mixture of carbonate isotopologues with the same bulk ¹³C/¹²C,

$^{18}\text{O}/^{16}\text{O}$, and $^{17}\text{O}/^{16}\text{O}$ ratios. The excess amount of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ decreases with increasing temperature and thus may serve as a thermometer (Ghosh et al. 2006).

Potentially, the advantage of this thermometer will be that it allows the determination of temperatures of carbonate formation without knowing the isotope composition of the fluid. Came et al. (2007), for example, presented temperature estimates for early Silurian and late Carboniferous seawater, which are consistent with varying CO_2 concentrations.

1.3.5 Diffusion

Ordinary diffusion can cause significant isotope fractionations. In general, light isotopes are more mobile and hence diffusion can lead to a separation of light from heavy isotopes. For gases, the ratio of diffusion coefficients is equivalent to the inverse square root of their masses. Consider the isotopic molecules of carbon in CO_2 with masses $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ having molecular weights of 44 and 45. Solving the expression, equating the kinetic energies ($1/2 m v^2$) of both species, the ratio of velocities is equivalent to the square root of 45/44 or 1.01. That is regardless of temperature, the average velocity of $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ molecules is about 1% greater than the average velocity of $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ molecules in the same system. This isotope effect, however, is more or less limited to ideal gases, where collisions between molecules are infrequent and intermolecular forces are negligible. The carbon isotope fractionation of soil- CO_2 due to diffusional movement has been estimated to be around 4‰ for instance (Cerling 1984; Hesterberg and Siegenthaler 1991).

Distinctly different from ordinary diffusion is the process of thermal diffusion in that a temperature gradient results in a mass transport. The greater the mass difference, the greater is the tendency of the two species to separate by thermal diffusion. A natural example of thermal diffusion has been presented by Severinghaus et al. (1996), who observed a small isotope depletion of ^{15}N and ^{18}O in air from a sand dune relative to the free atmosphere. This observation is contrary to the expectation that heavier isotopes in unsaturated zones of soils would be enriched by gravitational settling. Such thermally driven diffusional isotope effects have also been described in air bubbles from ice cores (Severinghaus et al. 1998; Severinghaus and Brook 1999; Grachiev and Severinghaus 2003). Surprisingly large fractionations by thermal diffusion at very high temperatures have been reported by Richter (2007), who observed 8‰ fractionation for $^{26}\text{Mg}/^{24}\text{Mg}$ associated with a change of only 150°C across molten basalt. Earlier diffusion experiments by Richter et al. (1999, 2003) between molten basalt and rhyolite also demonstrated considerable isotope fractionations of Li, Ca, and Ge (the latter used as a Si analogue). Especially for Li, diffusion processes occurring at high temperatures seem to be of first order importance (see p. 44). Thus the notion that isotope fractionations above 1,000°C appear to be negligible has to be reconsidered.

In solutions and solids, the relationships are much more complicated than in gases. The term *solid state diffusion* generally includes volume diffusion and diffusion mechanisms where the atoms move along paths of easy diffusion such as grain boundaries and surfaces. Diffusive-penetration experiments indicate a marked enhancement of diffusion rates along grain boundaries, which are orders of magnitude faster than for volume diffusion. Thus, grain boundaries can act as pathways of rapid exchange. Volume diffusion is driven by the random temperature-dependent motion of an element or isotope within a crystal lattice and it depends on the presence of point defects, such as vacancies or interstitial atoms within the lattice.

The flux F of elements or isotopes diffusing through a medium is proportional to the concentration gradient (dc/dx) such that:

$$F = -D(dc/dx) \quad (\text{Fick's first law}), \quad (1.21)$$

where D represents the diffusion coefficient, and the minus sign denotes that the concentration gradient has a negative slope, i.e., elements or isotopes move from points of high concentration towards points of low concentration. The diffusion coefficient D varies with temperature according to the Arrhenius relation

$$D = D_0 e^{(-Ea/RT)}, \quad (1.22)$$

where D_0 is a temperature-independent factor, Ea is the activation energy, R is the gas constant and T is in Kelvin.

In recent years, there have been several attempts to determine diffusion coefficients, mostly utilizing secondary ion mass spectrometry (SIMS), where isotope compositions have been measured as a function of depth below a crystal surface after exposing the crystal to solutions or gases greatly enriched with the heavy isotopic species.

A plot of the logarithm of the diffusion coefficient versus reciprocal temperature yields a linear relationship over a significant range of temperature for most minerals. Such an Arrhenius plot for various minerals is shown in Fig. 1.5, which illustrates the variability in diffusion coefficients for different minerals. The practical application of this fact is that the different minerals in a rock will exchange oxygen at different rates and become closed systems to isotopic exchange at different temperatures. As a rock cools from the peak of a thermal event, the magnitude of isotope fractionations between exchanging minerals will increase. The rate at which the coexisting minerals can approach equilibrium at the lower temperature is limited by the volume diffusion rates of the respective minerals.

Several models for diffusive transport in and among minerals have been discussed in the literature one is the fast grain boundary (FGB) model of Eiler et al. (1992, 1993). The FGB model considers the effects of diffusion between non-adjacent grains and shows that, when mass balance terms are included, closure temperatures become a strong function of both the modal abundances of constituent minerals and the differences in diffusion coefficients among all coexisting minerals.

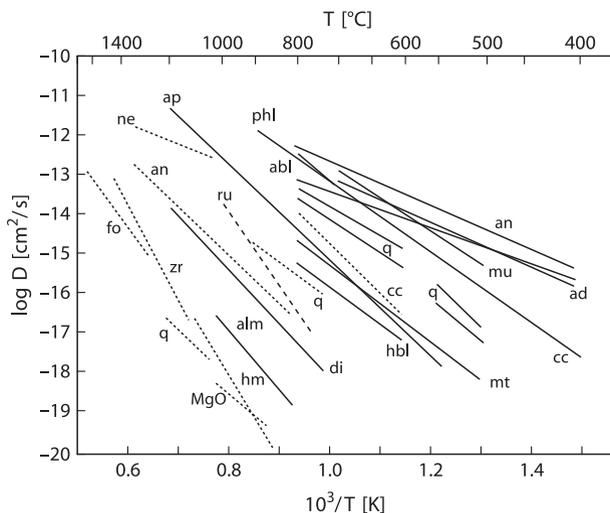


Fig. 1.5 Arrhenius plot of diffusion coefficients versus reciprocal temperatures for various minerals. Data from phases reacted under *wet* conditions are given as *solid lines*, whereas *dry* conditions are represented by *dashed lines*. Note that the rates for dry systems are generally lower and have higher activation energies (*steeper slopes*). (Modified after Cole and Chakraborty 2001)

1.3.6 Other Factors Influencing Isotopic Fractionations

1.3.6.1 Pressure

It is commonly assumed that temperature is the main variable determining the isotopic fractionation and that the effect of pressure is negligible, because molar volumes do not change with isotopic substitution. This assumption is generally fulfilled, except for hydrogen. Driesner (1997), Horita and Berndt (1999, 2002), and Polyakov et al. (2006) have shown, however, that for isotope exchange reactions involving water, changes of pressure can influence isotope fractionations. Driesner (1997) calculated hydrogen isotope fractionations between epidote and water and observed a change from -90‰ at 1 bar to -30‰ at 4,000 bars at 400°C . Horita and Berndt (1999, 2002) presented experimental evidence for a pressure effect in the system brucite $\text{Mg}(\text{OH})_2$ - water. Theoretical calculations indicate that pressure effects largely result on water rather than brucite. Thus, it is likely that D/H fractionations of any hydrous mineral are subject to similar pressure effects (Horita et al. 2002). These pressure effects have to be taken into account when calculating the hydrogen isotope composition of the fluid from the mineral composition.

1.3.6.2 Chemical Composition

Qualitatively, the isotopic composition of a mineral depends to a very high degree upon the nature of the chemical bonds within the mineral and to a smaller degree upon the atomic mass of the respective elements. In general, bonds to ions with a high ionic potential and small size are associated with high vibrational frequencies and have a tendency to incorporate preferentially the heavy isotope. This relationship can be demonstrated by considering the bonding of oxygen to the small highly charged Si^{4+} ion, compared to the relatively large Fe^{2+} ion of the common rock-forming minerals. In natural mineral assemblages, quartz is the most ^{18}O -rich mineral and magnetite is the most ^{18}O -deficient given equilibration in the system. Furthermore, carbonates are always enriched in ^{18}O relative to most other mineral groups because oxygen is bonded to the small, highly charged C^{4+} ion. The mass of the divalent cation is of secondary importance to the C–O bonding. However, the mass effects are apparent in ^{34}S distributions among sulfides, where, for example, ZnS always concentrates ^{34}S relative to coexisting PbS .

Compositional effects in silicates are complex and difficult to deduce, because of the very diverse substitution mechanisms in silicate minerals (Kohn and Valley 1998c). The largest fractionation effect is clearly related to the $\text{NaSi} = \text{CaAl}$ substitution in plagioclases, which is due to the higher Si to Al ratio of albite and the greater bond strength of the Si–O bond relative to the Al–O bond. In pyroxenes, the jadeite ($\text{NaAlSi}_2\text{O}_6$)–diopside ($\text{CaMgSi}_2\text{O}_6$) substitution also involves Al, but Al in this case replaces an octahedral rather than tetrahedral site. Chacko et al. (2001) estimate that at high temperatures the Al-substitution in pyroxenes is about 0.4‰ per mole Al-substitution in the tetrahedral site. The other very common substitutions, the Fe–Mg and the Ca–Mg substitution, do not generate any significant difference in fractionation (Chacko et al. 2001).

1.3.6.3 Crystal Structure

Structural effects are secondary in importance to those arising from the primary chemical bonding; the heavy isotope being concentrated in the more closely packed or well-ordered structures. The ^{18}O and D fractionations between ice and liquid water arise mainly from differences in the degree of hydrogen bonding (order). A relatively large isotope effect associated with structure is observed between graphite and diamond (Bottinga 1969b). With a modified increment method, Zheng (1993a) has calculated this structural effect for the SiO_2 and Al_2SiO_5 polymorphs and demonstrated that ^{18}O will be enriched in the high pressure forms. In this connection, it should be mentioned, however, that Sharp (1995) by analyzing natural Al_2SiO_5 minerals observed no differences for kyanite versus sillimanite.

1.3.7 Isotope Geothermometers

Isotope thermometry has become well established since the classic paper of Harold Urey (1947) on the thermodynamic properties of isotopic substances. The partitioning of two stable isotopes of an element between two mineral phases can be viewed as a special case of element partitioning between two minerals. The most important difference between the two exchange reactions is the pressure-insensitivity of isotope partitioning due to the negligible ΔV of reaction for isotope exchange. This represents a considerable advantage relative to the numerous types of other geothermometers, all of which exhibit a pressure dependence.

The necessary condition to apply an isotope geothermometer is isotope equilibrium. Isotope exchange equilibrium should be established during reactions whose products are in *chemical* and *mineralogical* equilibrium. Demonstration that the minerals in a rock are in oxygen isotope equilibrium is a strong evidence that the rock is in chemical equilibrium. To break Al–O and Si–O bonds and allow rearrangement towards oxygen isotope equilibrium needs sufficient energy to effect chemical equilibrium as well.

Theoretical studies show that the fractionation factor α for isotope exchange between minerals is a linear function of $1/T^2$, where T is temperature in degrees Kelvin. Bottinga and Javoy (1973) demonstrated that O-isotopic fractionation between anhydrous mineral pairs at temperatures $>500^\circ\text{C}$ can be expressed in terms of a relationship of the form:

$$1,000 \ln \alpha = A/T^2, \quad (1.23)$$

which means that the factor A has to be known in order to calculate a temperature of equilibration. By contrast, fractionations at temperatures $<500^\circ\text{C}$ can be expressed by an equation of the form

$$1,000 \ln \alpha = A/T^2 + B. \quad (1.24)$$

Although in many instances, B is approximately zero simplifying the expression.

One drawback to isotope thermometry in slowly cooled metamorphic and magmatic rocks is that, temperature estimates are often significantly lower than those from other geothermometers. This results from isotopic resetting associated with retrograde isotope exchange between coexisting phases or with transient fluids. During cooling in closed systems, volume diffusion may be the principal mechanism by which isotope exchange occurs between coexisting minerals.

Gilotti (1986) proposed a model in which experimentally-derived diffusion data can be used in conjunction with measured isotope ratios to explain disequilibrium isotope fractionations in slowly cooled, closed-system mineral assemblages. This approach describes diffusional exchange between a mineral and an infinite reservoir, whose bulk isotopic composition is constant during exchange. However, mass balance requires that loss or gain of an isotope from one mineral must be balanced by a change in the other minerals still subject to isotopic exchange. Numerical modeling

by Eiler et al. (1992) has shown that closed-system exchange depends not only on modal proportions of all of the minerals in a rock, but also on oxygen diffusivity in minerals, grain size, grain shape, and cooling rate. As shown by Kohn and Valley (1998c), there is an important water fugacity dependence as well. In the presence of fluids, further complications may arise because isotope exchange may also occur by solution-precipitation or chemical reaction rather than solely by diffusion.

Three different methods have been used to determine the equilibrium fractionations for isotope exchange reactions:

- (a) Theoretical calculations
- (b) Experimental determinations in the laboratory
- (c) Empirical or semiempirical calibrations

Method (c) is based on the idea that the calculated *formation temperature* of a rock (calculated from other geothermometers) serves as a calibration to the measured isotopic fractionations, assuming that all minerals were at equilibrium. However, because there is evidence that equilibrium is not always attained or retained in nature, such empirical calibrations should be regarded with caution.

Nevertheless, rigorous applications of equilibrium criteria to rock-type and the minerals investigated can provide important information on mineral fractionations (Kohn and Valley 1998c; Sharp 1995; Kitchen and Valley 1995).

1.3.7.1 Theoretical Calculations

Calculations of equilibrium isotope fractionation factors have been particularly successful for gases. Richet et al. (1977) calculated the partition function ratios for a large number of gaseous molecules. They demonstrated that the main source of error in the calculation is the uncertainty in the vibrational molecular constants.

The theory developed for perfect gases could be extended to solids, if the partition functions of crystals could be expressed in terms of a set of vibrational frequencies that correspond to its various fundamental modes of vibration (O'Neil 1986). By estimating thermodynamic properties from elastic, structural, and spectroscopic data, Kieffer (1982) and subsequently Clayton and Kieffer (1991) calculated oxygen isotope partition function ratios and from these calculations derived a set of fractionation factors for silicate minerals. The calculations have no inherent temperature limitations and can be applied to any phase for which adequate spectroscopic and mechanical data are available. They are, however, limited in accuracy as a consequence of the approximations needed to carry out the calculations and the limited accuracy of the spectroscopic data.

Isotope fractionations in solids depend on the nature of the bonds between atoms of an element and the nearest atoms in the crystal structure (O'Neil 1986). The correlation between bond strength and oxygen isotope fractionation was investigated by Schütze (1980), who developed an *increment* method for predicting oxygen isotope fractionations in silicate minerals. Richter and Hoernes (1988) applied this method to the calculation of oxygen isotope fractionations between silicate minerals and

water. More recently, Zheng (1991, 1993b, c) extended the increment method by using parameters of crystal chemistry with no empirical factor. The fractionation factors calculated using these methods over the temperature range 0–1,200°C are in relatively good agreement with experimental calibrations.

1.3.7.2 Experimental Calibrations

In general, experimental calibrations of isotope geothermometers have been performed between 250 and 800°C. The upper temperature limit is usually determined by the stability of the mineral being studied or by limitations of the experimental apparatus, whereas the lower temperature limit is determined by the decreasing rate of exchange.

Various experimental approaches have been used to determine fractionation factors. The three most common techniques are described below:

Two-Direction Approach

This method is analogous to reversing reactions in experimental petrology and is the only method by which the attainment of equilibrium can be convincingly demonstrated. Equilibrium fractionations are achieved by starting on opposite sides of the equilibrium distribution.

Partial-Exchange Technique

The partial-exchange technique is used when rates of isotopic exchange are relatively low and is based on the assumption that the rates of isotope exchange for companion exchange experiments are identical. Experimental runs have to be the same in every respect, except in the isotopic compositions of the starting materials. Rates of isotope exchange reactions in heterogeneous systems are relatively high at first (surface control) and then become progressively lower with time (diffusion control). Four sets of experiments are shown in Fig. 1.6 for the CO₂ – graphite system (after Scheele and Hoefs 1992). Northrop and Clayton (1966) presented a set of equations to describe the kinetics of isotope exchange reactions and developed a general equation for the partial-exchange technique. At low degrees of exchange, the fractionations determined by the partial-exchange technique are often larger than the equilibrium fractionations (O'Neil 1986).

Three-Isotope Method

This method, introduced by Matsuhisa et al. (1978) and later modified by Matthews et al. (1983a), uses the measurement of both ¹⁷O/¹⁶O and ¹⁸O/¹⁶O fractionations in a single experiment that has gone to equilibrium. The initial ¹⁸O/¹⁶O fractionation for the mineral–fluid system is selected to be close to the assumed equilibrium, while the initial ¹⁷O/¹⁶O fractionation is chosen to be very different from the

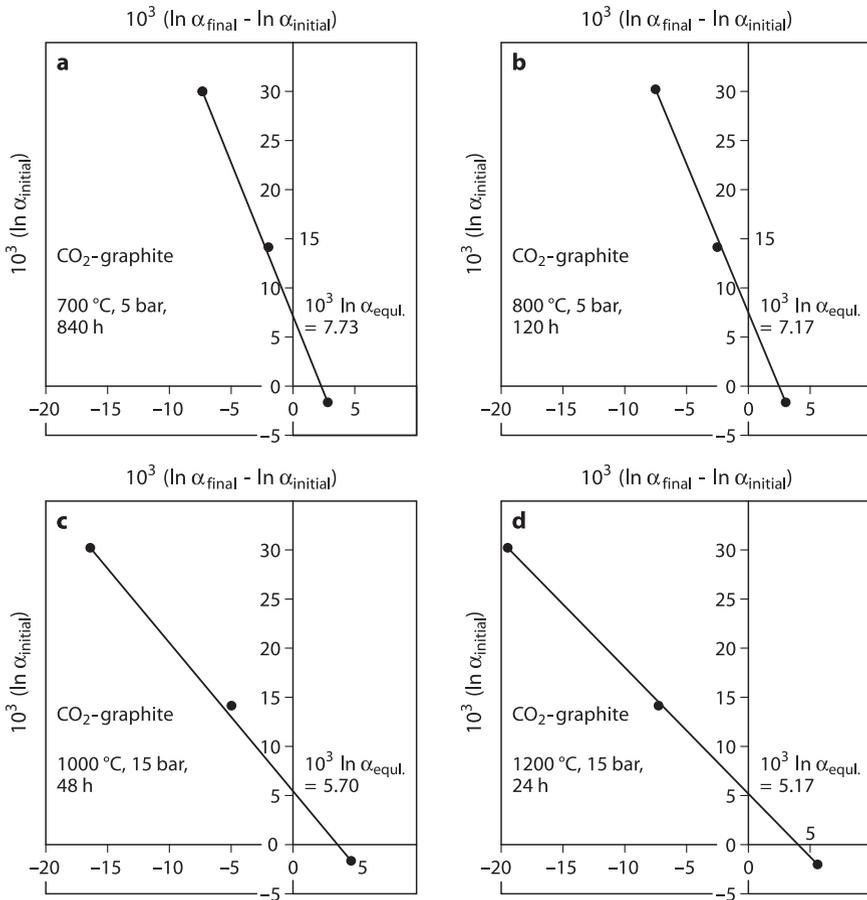


Fig. 1.6 CO₂-graphite partial-exchange experiments in a Northrop and Clayton plot at 700, 800, 1,000 and 1,200°C. The connecting line in experiment at 1,200°C has a plane slope and defines the intercept more precisely than the experiment at 700°C (after Scheele and Hoefs 1992)

equilibrium value. In this way, the change in the ¹⁷O/¹⁶O fractionations monitor the extent of isotopic exchange and the ¹⁸O/¹⁶O fractionations reflect the equilibrium value. Figure 1.7 gives a schematic diagram of the three-isotope-exchange method.

Most of the published data on mineral fractionations have been determined by exchange of single minerals with water. This approach is limited by two factors: (1) many minerals are unstable, melt, or dissolve in the presence of water and (2) the temperature dependence of the fractionation factor for aqueous systems is complicated as a consequence of the high vibrational frequencies of the water molecule. An alternative approach to the experimental determination of isotope fractionation between minerals was first employed by Clayton et al. (1989) and Chiba et al. (1989), who demonstrated that both limitations can be avoided by using CaCO₃, instead of H₂O, as the common exchange medium. These studies showed

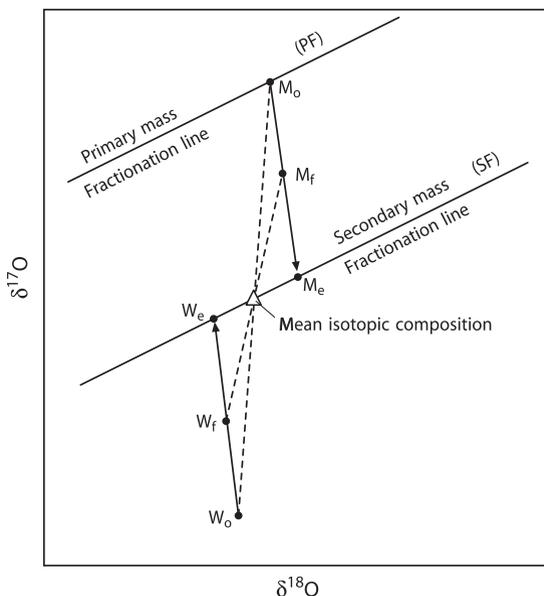


Fig. 1.7 Schematic representation of the three-isotope exchange method. Natural samples plotted on the primary mass fractionation line (PF). Initial isotopic composition are mineral (M_0) and water (W_0) which is well removed from equilibrium with M_0 in $\delta^{17}\text{O}$, but very close to equilibrium with M_0 in $\delta^{18}\text{O}$. Complete isotopic equilibrium is defined by a secondary mass fractionation line (SF) parallel to PF and passing through the bulk isotopic composition of the mineral plus water system. Isotopic compositions of partially equilibrated samples are M_f and W_f and completely equilibrated samples are M_e and W_e . Values for M_e and W_e can be determined by extrapolation from the measured values of M_0 , M_f , W_0 , and W_f (after Matthews et al. 1983a)

that most common silicates undergo rapid oxygen isotope exchange with CaCO_3 at temperatures above 600°C and pressures of 15 kbar.

Advantages of the carbonate-exchange technique are: (1) experiments up to $1,400^\circ\text{C}$, (2) no problems associated with mineral solubility and (3) ease of mineral separation (reaction of carbonate with acid). Mineral fractionations derived from hydrothermal and carbonate exchange techniques are generally in good agreement except for fractionations involving quartz and calcite. A possible explanation is a salt effect in the quartz–water system, but no salt effect has been observed in the calcite–water system (Hu and Clayton 2003).

1.4 Basic Principles of Mass Spectrometry

Mass spectrometric methods are, by far, the most effective means of measuring isotope abundances. A mass spectrometer separates charged atoms and molecules on the basis of their masses and motions in magnetic and/or electrical fields. The design

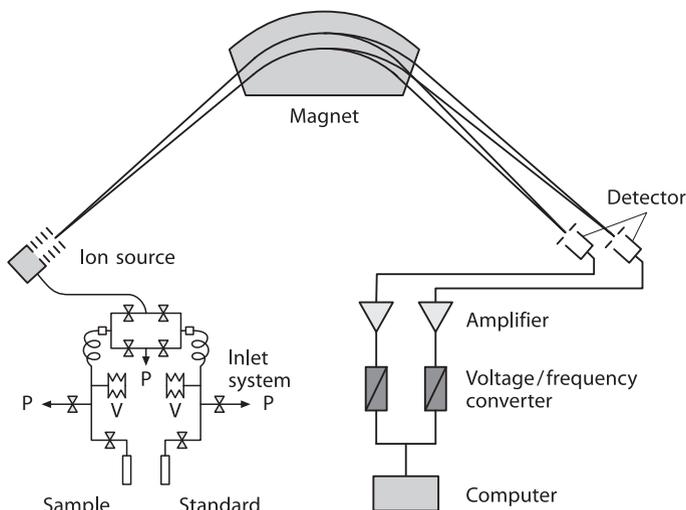


Fig. 1.8 Schematic representation of a gas-source mass spectrometer for stable isotope measurements. P denotes pumping system, V denotes a variable volume

and applications of the many types of mass spectrometers are too broad to cover here. Therefore, only the principles of mass analysis will be discussed briefly (for a more detailed review see Brand (2002)).

In principle, a mass spectrometer may be divided into four different central constituent parts: (1) the inlet system, (2) the ion source, (3) the mass analyzer, and (4) the ion detector (see Fig. 1.8).

1. Special arrangements for the *inlet system* include a changeover valve. This allows rapid, consecutive analysis between two gas samples (sample and standard gas) within a couple of seconds. The two gases are fed from reservoirs by capillaries of around 0.1 mm in diameter and about 1 m in length. While one gas flows to the ion source, the other flows to a waste pump so that flow through the capillaries remains uninterrupted. To avoid a mass discrimination, isotope abundance measurements of gaseous substances are carried out utilizing viscous gas flow. During viscous gas flow, the free path length of molecules is small, molecule collisions are frequent (causing the gas to be well mixed), and no mass separation takes place. At the end of the viscous-flow inlet system, there is a *leak*, a constriction in the flow line. The smallest amount of sample that can be analyzed with high precision using the dual inlet system is limited by the maintenance of viscous-flow conditions. This is generally in the order of 15–20 mbar (Brand 2002). When trying to reduce sample size, it is necessary to concentrate the gas into a small volume in front of the capillary.
2. The *ion source* is that part of the mass spectrometer, where ions are formed, accelerated, and focused into a narrow beam. In the ion source, the gas flow is always molecular. Ions of gaseous samples are most reliably produced by electron

bombardment. A beam of electrons is emitted by a heated filament, usually tungsten or rhenium and is accelerated by electrostatic potentials to an energy between 50 and 150 eV before entering the ionization chamber, which maximizes the efficiency of single ionization. Following ionization, any charged molecule can be further fragmented into several pieces depending on the energy the ion has acquired, producing a mass spectrum of a specific compound.

To increase the ionization probability, a homogeneous weak magnetic field is used to keep the electrons on a spiral path. At the end of the ionization chamber, electrons are collected in a positively charged trap, where the electron current is measured and kept constant by the emission regulator circuitry.

The ionized molecules are drawn out of the electron beam by action of an electric field, subsequently accelerated by up to several kV and their path shaped into a beam, which passes through an exit slit into the analyzer. Thus, the positive ions entering the magnetic field are essentially monoenergetic, i.e., they will possess the same kinetic energy, given by the equation:

$$1/2Mv^2 = eV. \quad (1.25)$$

The efficiency of the ionization process determines the sensitivity of the mass spectrometer, which generally is on the order of 1,000–2,000 molecules per ion (Brand 2002).

3. The *mass analyzer* separates the ion beams emerging from the ion source according to their m/e (mass/charge) ratios. As the ion beam passes through the magnetic field, the ions are deflected into circular paths, the radii of which are proportional to the square root of m/e . Thus, the ions are separated into beams, each characterized by a particular value of m/e .

In 1940, Nier introduced the sector magnetic analyzer. In this type of analyzer, deflection takes place in a wedge-shaped magnetic field. The ion beam enters and leaves the field at right angles to the boundary, so the deflection angle is equal to the wedge angle, for instance, 60° . The sector instrument has the advantage of its source and detector being comparatively free from the mass-discriminating influence of the analyzer field.

4. After passing through the magnetic field, the separated ions are collected in *ion detectors*, where the input is converted into an electrical impulse, which is then fed into an amplifier. The use of multiple detectors to simultaneously integrate the ion currents was introduced by Nier et al. (1947). The advantage of the simultaneous measurement with two separate amplifiers is that relative fluctuations of the ion currents as a function of time are the same for all m/e beams. Each detector channel is fitted with a high ohmic resistor appropriate for the mean natural abundance of the ion current of interest.

Modern isotope ratio mass spectrometers have at least three Faraday collectors, which are positioned along the focal plane of the mass spectrometer. Because the spacing between adjacent peaks changes with mass and because the scale is not linear, each set of isotopes often requires its own set of Faraday cups.

1.4.1 Continuous Flow: Isotope Ratio Monitoring Mass Spectrometers

Between the early 1950s, when the dual viscous-flow mass spectrometer was introduced by Nier and the mid 1980s only minor modifications have been made on the hardware of commercial mass spectrometers. Special efforts have been undertaken in the past years to reduce the sample size for isotope measurements. This has led to a modification of the classic dual inlet technique to the continuous-flow isotope ratio monitoring mass spectrometer in which the gas to be analyzed is a trace gas in a stream of carrier gas, which achieves viscous-flow conditions. Today, the majority of gas mass spectrometers are sold with the continuous flow system, instead of the dual inlet system.

The classical off-line procedures for sample preparations are time consuming and analytical precision depends on the skill of the investigator. With on-line techniques, using a combination of an elemental analyzer directly coupled to the mass spectrometer many problems of the off-line preparation can be overcome and minimized. Differences in both techniques are summarized in Table 1.5.

This new generation of mass spectrometers is often combined with chromatographic techniques. The sample size required for an isotope measurement has been drastically reduced to the nano- or even pico-molar range (Merritt and Hayes 1994). Important features of the GC-IRMS technique are (Brand 2002):

1. Ion currents are measured in the order in which molecules emerge from a GC column, without significant capability of modifying their intensity relative to the reference gas. Chromatography separates not only different chemical species, but also the different isotope species, which means that the isotope composition of a compound varies across the peak of the chemical species after elution. Therefore, each peak must be integrated over its entire width to obtain the true isotope ratio.
2. The time for measurement of the isotope signals is restricted by the width of the chromatographic peak. For sharply defined peaks, this can mean less than 5 s.

Table 1.5 Differences between the offline and online techniques

Offline method (dual inlet)	Online method (continuous flow)
Offline sample preparation	Online sample preparation
Offline purification of gases	Purification of gases by GC column
Large sample size (mg)	Small sample size (micrograms)
Direct inlet of sample gas	Sample gas inlet via carrier gas
Pressure adjust of both gases	No pressure adjust, linearity, and stability of the system are necessary conditions
Sample/standard changes (>6 times)	One peak per sample
δ -value calculated from statistical mean	δ -value calculated by peak integration and reference gas
System calibration on a monthly basis	System calibration on a daily basis and during the run
Little problems with homogeneity of sample	Problems with homogeneity of sample

3. Absolute sensitivity is much more important than with the dual inlet system. Since sample sizes required for chromatography are significantly smaller, it is often important to use a significantly large set of samples in order to obtain a statistically sound data base.

Standardization has to be accomplished through the use of an added internal standard, whose isotopic composition has been determined using conventional techniques.

The development of this technique has proceeded along several independent paths with two principal lines being elemental analyzer–IRMS and capillary gas chromatography–IRMS. In elemental analyzers, samples are combusted to CO₂, N₂, SO₂, and H₂O, which are either chemically trapped or separated on GC columns. The advantages of these techniques are an automated preparation with low costs per sample and a large sample through-put.

1.5 Standards

The accuracy with which *absolute* isotope abundances can be measured is substantially poorer than the precision with which *relative* differences in isotope abundances between two samples can be determined. Nevertheless, the determination of absolute isotope ratios is very important, because these numbers form the basis for the calculation of the relative differences, the δ -values. Table 1.6 summarizes absolute isotope ratios of primary standards used by the international stable isotope community.

To compare isotope data from different laboratories, an internationally accepted set of standards is necessary. Irregularities and problems concerning standards have been evaluated by Friedman and O'Neil (1977), Gonfiantini (1978, 1984), Coplen

Table 1.6 Absolute isotope ratios of international standards. (After Hayes 1983)

Standard	Ratio	Accepted value ($\times 10^6$) (with 95% confidence interval)	Source
SMOW	D/H	155.76 ± 0.10	Hagemann et al. (1970)
	$^{18}\text{O}/^{16}\text{O}$	$2,005.20 \pm 0.43$	Baertschi (1976)
	$^{17}\text{O}/^{16}\text{O}$	373 ± 15	Nier (1950), corrected by Hayes (1983)
PDB	$^{13}\text{C}/^{12}\text{C}$	$11,237.2 \pm 2.9$	Craig (1957)
	$^{18}\text{O}/^{16}\text{O}$	2067.1 ± 2.1	
	$^{17}\text{O}/^{16}\text{O}$	379 ± 15	
Air nitrogen	$^{15}\text{N}/^{14}\text{N}$	$3,676.5 \pm 8.1$	Junk and Svec (1958)
Canyon Diablo Troilite (CDT)	$^{34}\text{S}/^{32}\text{S}$	$45,004.5 \pm 9.3$	Jensen and Nakai (1962)

et al. (1983), Coplen (1996), and Coplen et al. (2006). The accepted unit of isotope ratio measurements is the delta value (δ given in per mill ‰). The δ value is defined as

$$\delta \text{ in } \text{‰} = \frac{R_{(\text{Sample})} - R_{(\text{Standard})}}{R_{(\text{Standard})}} 1,000, \quad (1.26)$$

where R represents the measured isotope ratio. If $\delta_A > \delta_B$, it is convenient to speak of A being enriched in the rare or *heavy* isotope, compared to B . Unfortunately, not all of the δ -values cited in the literature are given relative to a single universal standard, so that often several standards of one element are in use. To convert δ -values from one standard to another, the following equation may be used

$$\delta_{X-A} = \left[\left(\frac{\delta_{B-A}}{10^3} + 1 \right) \left(\frac{\delta_{X-B}}{10^3} + 1 \right) - 1 \right] 10^3, \quad (1.27)$$

where X represents the sample, A and B different standards.

For different elements, a convenient *working standard* is used in each laboratory. However, all values measured relative to the respective *working standard* are reported in the literature relative to a universal standard.

As an example, for the relationship between the content of an isotope in % and the δ -value in ‰, Fig. 1.9 demonstrates that large changes in the δ -value only involve very small changes in the heavy isotope content (in this case the ^{18}O content). An ideal standard used worldwide as the *zero-point* on a δ -scale should satisfy the following requirements:

1. Be homogeneous in composition
2. Be available in relatively large amounts
3. Be easy to handle for chemical preparation and isotopic measurement, and
4. Have an isotope ratio near the middle of the natural range of variation

Among the reference samples now used, relatively few meet all of these requirements. For instance, the situation for the SMOW standard is rather confusing. The

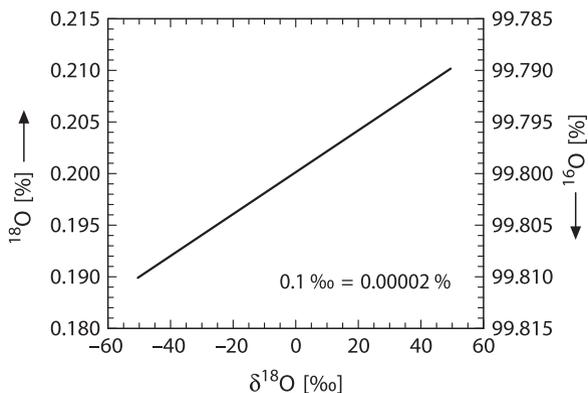


Fig. 1.9 Relationship between ^{18}O (^{16}O) content in per cent and $\delta^{18}\text{O}$ in per mill

Table 1.7 Worldwide standards in use for the isotopic composition of hydrogen, boron, carbon, nitrogen, oxygen, silicon, sulfur, and chlorine

Element	Standard	Standard
H	Standard Mean Ocean Water	V-SMOW
B	Boric acid (NBS)	SRM 951
C	Belemnite from the Cretaceous Peedee formation, South Carolina	V-PDB
N	Air nitrogen	N ₂ (atm.)
O	Standard Mean Ocean Water	V-SMOW
Si	Quartz sand	NBS-28
S	Troilite (FeS) from the Canyon Diablo iron meteorite	V-CDT
Cl	Seawater chloride	SMOC

SMOW standard was originally a hypothetical water sample with an isotopic composition very similar to average untreated ocean water (Craig 1961b), but being defined in terms of a water sample distributed by the National Bureau of Standards (NBS-1). Later, the IAEA distributed a distilled water sample named V-SMOW (Vienna-SMOW), which is very close to, but not identical in isotope composition to, the original SMOW standard. The worldwide standards now in general use are given in Table 1.7.

The problems related to standards are discussed by an IAEA advisory group, which meet from time to time. As a result of these meetings, the quality and availability of the existing standards and the need of new standards have been discussed and agreed.

A further advancement comes from inter-laboratory comparison of two standards having different isotopic composition that can be used for a normalization procedure correcting for all proportional errors due to mass spectrometry and to sample preparation. Ideally, the two standard samples should have isotope ratios as different as possible, but still within the range of natural variations. There are, however, some problems connected with data normalization, which are still under debate. For example, the CO₂ equilibration of waters and the acid extraction of CO₂ from carbonates are indirect analytical procedures, involving temperature-dependent fractionation factors (whose values are not beyond experimental uncertainties) with respect to the original samples and which might be re-evaluated on the normalized scale.

Table 1.8 summarizes gases, which are used for mass spectrometric analysis of the various elements.

1.6 General Remarks on Sample Preparation Methods for Gases

Isotopic differences between samples to be measured are often extremely small. Therefore, great care has to be taken to avoid any isotope fractionation during chemical or physical treatment of the sample. The quality of a stable isotope analysis is

Table 1.8 Gases most commonly used in isotope ratio in mass spectrometry

Element	Gas
H	H ₂
C	CO ₂ , CO
N	N ₂
O	CO ₂ , CO, O ₂
S	SO ₂ , SF ₆
Si	SiF ₄

determined by the purity of the gas prepared from the sample, quantitative yield, blank, and memory effects.

To convert geologic samples to a suitable form for analysis, many different chemical preparation techniques must be used. These diverse techniques all have one general feature in common: any preparation procedure providing a yield of less than 100% may produce a reaction product that is isotopically different from the original specimen because the different isotopic species have different reaction rates.

A quantitative yield of a pure gas is usually necessary for the mass spectrometric measurement in order to prevent not only isotope fractionation during sample preparation, but also interference in the mass spectrometer. Contamination with gases having the same molecular masses and similar physical properties may be a serious problem. This is especially critical with CO₂ and N₂O, (Craig and Keeling 1963), and N₂ and CO. When CO₂ is used, interference by hydrocarbons and a CS⁺ ion may also pose a problem.

Contamination may result from incomplete evacuation of the vacuum system and/or from degassing of the sample. The system blank should be normally less than 1% of the amount of gas prepared from a sample for analysis. For very small sample sizes, the blank may ultimately limit the analysis. Memory effects result from samples that have previously been analyzed. They will become noticeable, when samples having widely different isotopic compositions are analyzed consecutively.

How gases are transferred, distilled, or otherwise processed in vacuum lines is briefly discussed under the different elements. A more detailed description can be found in the recently published *Handbook of Stable Isotope Analytical Techniques*, edited by de Groot (2004).

All errors due to chemical preparation limit the overall precision of an isotope ratio measurement to usually 0.1–0.2‰, while modern mass spectrometer instrumentation enables a precision better than 0.02‰ for light elements other than hydrogen. Larger uncertainties are expected, when elements present in a sample at very low concentration are extracted by chemical methods (e.g., carbon and sulfur from igneous rocks).

Commercial combustion elemental analyzers perform a flash combustion, converting samples to CO₂, H₂O, N₂, and SO₂ simultaneously. These different gases are then chemically trapped, converted, or separated on GC columns and measured in a continuous flow mass spectrometer. This technique allows the determination

of several isotope ratios from the same component, increasing the possibilities of isotope fingerprinting of organic and inorganic compounds containing isotopes of more than one element of interest. Because of very high combustion temperatures, the quantitative conversion of the sample material is guaranteed.

1.7 Microanalytical Techniques

In recent years, microanalytical techniques, which permit relatively precise isotopic determinations on a variety of samples that are orders of magnitude smaller than those used in conventional techniques, have become increasingly important. Different approaches have been used in this connection, which generally reveal greater isotope heterogeneity than conventional analytical approaches. As a rule of thumb: the smaller the scale of measurement, the larger the sample heterogeneity.

1.7.1 *Laser Microprobe*

Laser assisted extraction is based on the fact that the energy of the laser beam is absorbed efficiently by a number of natural substances of interest. The absorption characteristics depend on the structure, composition, and crystallinity of the sample. High energy, finely-focussed laser beams have been used for some years for Ar isotope analysis. The first well-documented preparation techniques with CO₂ and Nd-YAG laser systems for stable isotope determinations have been described by Crowe et al. (1990), Kelley and Fallick (1990) and Sharp (1990). Their results show that sub-milligram quantities of mineral can be analyzed for oxygen, sulfur, and carbon. In order to achieve precise and accurate measurements, the samples have to be evaporated completely because steep thermal gradients during laser heating induce isotopic fractionations (Elsenheimer and Valley 1992). The thermal effects of CO₂ and Nd-YAG laser assisted preparation techniques require that sample sections be cut into small pieces before total evaporation. The spatial resolution of this technique is limited to about 500 μm.

Thermal effects can be overcome by vapourizing samples with ultraviolet (UV) KrF and ArF lasers, thus making possible in situ oxygen isotope analysis of silicates (Wiechert and Hoefs 1995; Fiebig et al. 1999; Wiechert et al. 2002).

1.7.2 *Secondary Ion Mass Spectrometry*

Two different types of SIMS are generally used: the Cameca f-series and the SHRIMP (Sensitive High mass Resolution Ion MicroProbe) series (Valley and Graham 1993; Valley et al. 1998; McKibben and Riciputi 1998). Analysis in the

ion-microprobe is accomplished by sputtering a sample surface using a finely focused primary ion beam producing secondary ions, which are extracted and analyzed in the secondary mass spectrometer. The main advantages of this technique are its high sensitivity, high spatial resolution, and its small sample size. Sputter pits for a typical 30 min SIMS analyses have a diameter of 10–30 μm and a depth of 1–6 μm , a spatial resolution that is an order of magnitude better than laser techniques. Disadvantages are that the sputtering process produces a large variety of molecular secondary ions along with atomic ions, which interfere with the atomic ions of interest and that the ionization efficiencies of different elements vary by many orders of magnitude and strongly depend on the chemical composition of the sample. This *matrix* effect is one of the major problems of quantitative analysis. The two instruments (Cameca and SHRIMP) have technical features, such as high resolving power and energy filtering, which help to overcome the problems of the presence of molecular isobaric interferences and the matrix dependence of secondary ion yields.

Fitzsimons et al. (2000) have reviewed the factors that influence the precision of SIMS stable isotope data. All sample analyses must be calibrated for instrumental mass fractionation using SIMS analyses of a standard material. Under favorable circumstances, precision can reach a few tenths of a per mill. The latest version of ion-microprobe is the Cameca-IMS-1280 type, allowing further reduction in sample and spot size and achieving precise analysis of isotope ratios at the 0.1‰ level (Page et al. 2007).

1.8 Stable Isotope Variations of Heavy Elements

Advances in TIMS-techniques and the introduction of multiple collector-ICP-MS (MC-ICP-MS) techniques have enabled the research on natural variations of a wide range of transition and heavy metal systems for the first time, which so far could not have been measured with the necessary precision. The advent of MC-ICP-MS has improved the precision on isotope measurements to about 40 ppm on elements such as Zn, Cu, Fe, Cr, Mo, and Tl. The technique combines the strength of the ICP technique (high ionization efficiency for nearly all elements) with the high precision of thermal ion source mass spectrometry equipped with an array of Faraday collectors. The uptake of elements from solution and ionization in a plasma allows correction for instrument-dependent mass fractionations by addition of external spikes or the comparison of standards with samples under identical operating conditions. All MC-ICP-MS instruments need Ar as the plasma support gas, in a similar manner to that commonly used in conventional ICP-MS. Mass interferences are thus an inherent feature of this technique, which may be circumvented by using desolvating nebulisers.

Maréchal et al. (1999) and Zhu et al. (2000a) first described techniques for the determination of Cu- and Zn-isotope ratios. Observed variations at low temperatures are on the order of several ‰, much more than originally expected on the basis

of the relatively small mass differences among isotopes of heavier elements. The magnitude of fractionations depends on several factors such as the participation of redox reactions and biologically mediated reactions. Fractionation mechanisms responsible for the observed variations are so far unknown in most cases but should be the same as for light elements. Of special importance seem speciation and absorption phenomena. Since most metals can coordinate with a number of ligands, isotope effects between dissolved aqueous species particularly at different redox states are therefore of special importance (Anbar and Rouxel 2007). Furthermore, absorption of dissolved species on particle surfaces represents another important fractionation mechanism. A small number of studies have demonstrated small fractionations $<1\text{‰}$ as metal ions are removed from solution onto oxide surfaces. Generally, the heavier isotope preferentially absorbs on metal oxide surfaces, which is consistent with shorter metal–oxygen bonds and lower coordination number for the absorbed relative to the aqueous species (Balistrieri et al. 2008). The largest fractionation (1.8‰) so far observed occurs between dissolved and absorbed Mo (Barling and Anbar 2004).

Schauble (2004) applied the theory of stable isotope fractionation to nontraditional isotope systems. He pointed out that, differences in coordination numbers among coexisting phases control isotope fractionation of cations. The lighter isotope preferentially occupies the higher coordinated site. Thus, differences in isotope composition of lithophile elements such as Mg, Ca, and Li are likely to reflect changes in coordination numbers

Although equilibrium fractionations have been documented for some transition metal (i.e., Fe), they should be small and may be overwhelmed by kinetic fractionations in low-temperature and biological systems (Schauble 2004). For any transition metal, it remains to be demonstrated that biological effects dominate the natural isotope variability.

Table 1.9 gives a summary of the respective heavy elements and the isotope variations observed so far.

Table 1.9 Natural variation ranges of heavy elements and some important geochemical properties probably causing the variations

Element	Isotopes	Variations in ‰	Geochemistry
^{24}Cr	4 isotopes (50, 52, 53, 54)	5 (?) (53/52)	Cr^{3+} , Cr^{6+} ; (contaminant)
^{26}Fe	4 isotopes (54, 56, 57, 58)	5 (56/54)	Fe^{2+} , Fe^{3+} , Fe^0 iron bacteria
^{29}Cu	^{63}Cu , ^{65}Cu	>7	Cu^+ , Cu^{2+} , Cu^0
^{30}Zn	4 isotopes (64, 66, 67, 68)	1 (66/64)	No redox reactions
^{34}Se	6 isotopes (from 74 to 82)	~ 10 (82/76)	Similarity with S
^{42}Mo	7 isotopes (from 92 to 100)	3 (97/95)	Mo^{6+} , Mo^{2+}
^{80}Hg	7 isotopes (from 196 to 204)	5	highly volatile Hg^+ , Hg^{2+} , Hg^0
^{81}Tl	^{203}Tl , ^{205}Tl	2	Tl^+ , Tl^{3+} highly volatile

Chapter 2

Isotope Fractionation Processes of Selected Elements

The foundations of stable isotope geochemistry were laid in 1947 by Urey's classic paper on the thermodynamic properties of isotopic substances and by Nier's development of the ratio mass spectrometer. Before discussing details of the naturally occurring variations in stable isotope ratios, it is useful to describe some generalities that are pertinent to the field of non-radiogenic isotope geochemistry as a whole.

1. Isotope fractionation is pronounced when the mass differences between the isotopes of a specific element are large relative to the mass of the element. Therefore, isotope fractionations are especially large for the light elements (up to a mass number of about 40). Recent developments in analytical techniques have opened the possibility to detect small variations in elements with much higher mass numbers. The heaviest element for which natural variations have been reported is thallium with isotopes of masses 203 and 205 (Rehkämper and Halliday 1999).
2. All elements that form solid, liquid, and gaseous compounds stable over a wide temperature range are likely to have variations in isotopic composition. Generally, the heavy isotope is concentrated in the solid phase in which it is more tightly bound. Heavier isotopes tend to concentrate in molecules in which they are present in the highest oxidation state.
3. Mass balance effects can cause isotope fractionations because modal proportions of substances can change during a chemical reaction. They are especially important for elements in situations where these coexist in molecules of reduced and oxidized compounds. Conservation of mass in an n component system can be described by

$$\delta_{(\text{system})} = \sum x_i \delta_i \quad (2.1)$$

where " x_i " is the mole fraction of the element in question for each of n phases within the system.

4. Isotopic variations in most biological systems are mostly caused by kinetic effects. During biological reactions (e.g. photosynthesis, bacterial processes) the lighter isotope is very often enriched in the reaction product relative to the substrate. Most of the fractionations in biological reactions generally take place

during the so-called rate determining step, which is the slowest step. It commonly involves a large reservoir, where the material actually used is small compared to the size of the reservoir.

2.1 Hydrogen

Until 1931 it was assumed that hydrogen consisted of only one isotope. Urey et al. (1932) detected the presence of a second stable isotope, which was called deuterium. (In addition to these two stable isotopes there is a third naturally occurring but radioactive isotope, ^3H , tritium, with a half-life of approximately 12.5 years). Rosman and Taylor (1998) gave the following average abundances of the stable hydrogen isotopes:

$$^1\text{H} : 99.9885\%$$

$$^2\text{D} : 0.0115\%$$

The isotope geochemistry of hydrogen is particularly interesting, for two reasons:

1. Hydrogen is omnipresent in terrestrial environments occurring in different oxidation states in the forms of H_2O , H_3O^+ , OH^- , H_2 and CH_4 , even at great depths within the Earth. Therefore, hydrogen is envisaged to play a major role, directly or indirectly, in a wide variety of naturally occurring geological processes.
2. Hydrogen has by far the largest mass difference relative to the mass of the element between its two stable isotopes. Consequently hydrogen exhibits the largest variations in stable isotope ratios of all elements.

The ranges of hydrogen isotope compositions of some geologically important reservoirs are given in Fig. 2.1. It is noteworthy that all rocks on Earth have somewhat similar hydrogen isotope compositions, which is a characteristic feature of hydrogen, but not of the other elements. The reason for this overlap in isotope composition for rocks is likely due to the enormous amounts of water that have been cycled through the outer shell of the Earth.

2.1.1 Preparation Techniques and Mass Spectrometric Measurements

Determination of the D/H ratio of water is performed on H_2 -gas. There are two different preparation techniques: (1) equilibration of milliliter-sized samples with gaseous hydrogen gas, followed by mass-spectrometric measurement and back calculation of the D/H of the equilibrated H_2 (Horita 1988). Due to the very large fractionation factor (0.2625 at 25°C) the measured H_2 is very much depleted in D, which complicates the mass-spectrometric measurement. (2) water is converted to hydrogen by passage over hot metals (uranium: Bigeleisen et al. 1952; Friedman 1953;

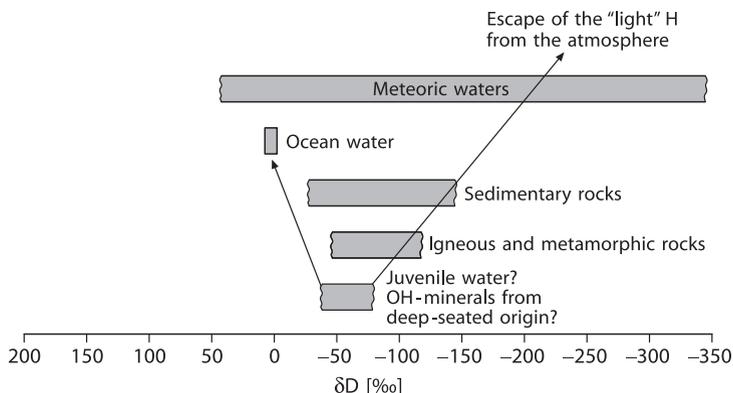


Fig. 2.1 δD ranges of some geologically important reservoirs

Godfrey 1962, zinc: Coleman et al. 1982, chromium: Gehre et al. 1996). This is still the classic method and commonly used.

A difficulty in measuring D/H isotope ratios is that, along with the H_2^+ and HD^+ formation in the ion source, H_3^+ is produced as a by-product of ion-molecule collisions. Therefore, a H_3^+ correction has to be made. The amount of H_3^+ formed is directly proportional to the number of H_2 molecules and H^+ ions. Generally the H_3^+ current measured for hydrogen from ocean water is on the order of 16% of the total mass 3. The relevant procedures for correction have been evaluated by Brand (2002).

Analytical uncertainty for hydrogen isotope measurements is usually in the range ± 0.5 to $\pm 5\%$ depending on different sample materials, preparation techniques and laboratories.

Burgoyne and Hayes (1998) and Sessions et al. (1999) introduced the continuously flow technique for the D/H measurement of individual organic compounds. The precise measurement of D/H ratios in a He carrier poses a number of analytical problems, related to the tailing from the abundant $^4He^+$ onto the minor HD^+ peak as well as on reactions occurring in the ion source that produce H_3^+ . However, these problems have been overcome and precise hydrogen isotope measurements of individual organic compounds are possible.

2.1.2 Standards

There is a range of standards for hydrogen isotopes. The primary reference standard, the zero point of the δ -scale, is V-SMOW, which is virtually identical in isotopic composition with the earlier defined SMOW, being a hypothetical water sample originally defined by Craig (1961b).

Table 2.1 Hydrogen isotope standards

Standards	Description	δ -value
V-SMOW	Vienna Standard Mean Ocean Water	0
GISP	Greenland Ice Sheet Precipitation	-189.9
V-SLAP	Vienna Standard Light Antarctic Precipitation	-428
NBS-30	Biotite	-65

V-SMOW has a D/H ratio that is higher than most natural samples on Earth, thus δ D-values in the literature are generally negative. The other standards, listed in Table 2.1, are generally used to verify the accuracy of sample preparation and mass spectrometry.

2.1.3 Fractionation Processes

The most effective processes in the generation of hydrogen isotope variations in the terrestrial environment are phase transitions of water between vapor, liquid, and ice through evaporation/precipitation and/or boiling/condensation in the atmosphere, at the Earth's surface, and in the upper part of the crust. Differences in H-isotopic composition arise due to vapor pressure differences of water and, to a smaller degree, to differences in freezing points. Because the vapor pressure of HDO is slightly lower than that of H₂O, the concentration of D is lower in the vapor than in the liquid phase. In a simple, but elegant experiment Ingraham and Criss (1998) have monitored the effect of vapor pressure on the rate of isotope exchange between water and vapor, which is shown in Fig. 2.2. Two beakers with isotopically differing waters were juxtaposed in a sealed box to monitor the exchange process at different temperatures (in this case 21 and 52°C). As shown in Fig. 2.12 in the 52°C experiment the isotopic composition of the water changes rapidly and nearly reaches equilibrium in only 27 days.

Horita and Wesolowski (1994) have summarized experimental results for the hydrogen isotope fractionation between liquid water and water vapor in the temperature range 0–350°C (see Fig. 2.3). Hydrogen isotope fractionations decrease rapidly with increasing temperatures and become zero at 220–230°C. Above the crossover temperature, water vapor is more enriched in deuterium than liquid water. Fractionations again approach zero at the critical temperature of water (Fig. 2.3).

From experiments, Lehmann and Siegenthaler (1991) determined the equilibrium H-isotope fractionation between ice and water to be +21.2‰. Under natural conditions, however, ice will not necessarily be formed in isotopic equilibrium with the bulk water, depending mainly on the freezing rate.

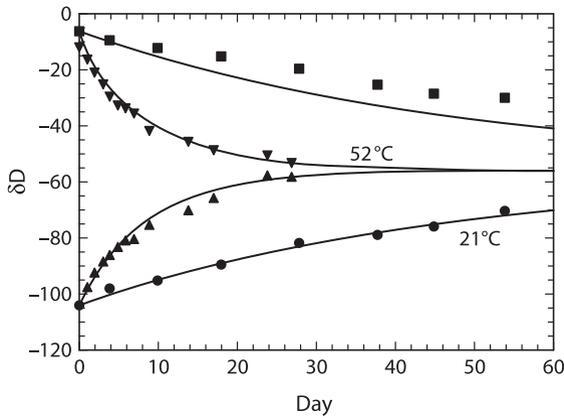


Fig. 2.2 δD values versus time for two beakers that have equal surface areas and equal volumes undergoing isotopic exchange in sealed systems. In both experiments at 21 and 52°C isotope ratios progress toward an average value of -56‰ via exchange with ambient vapour. *Solid curves* are calculated, *points* are experimental data (after Criss, 1999)

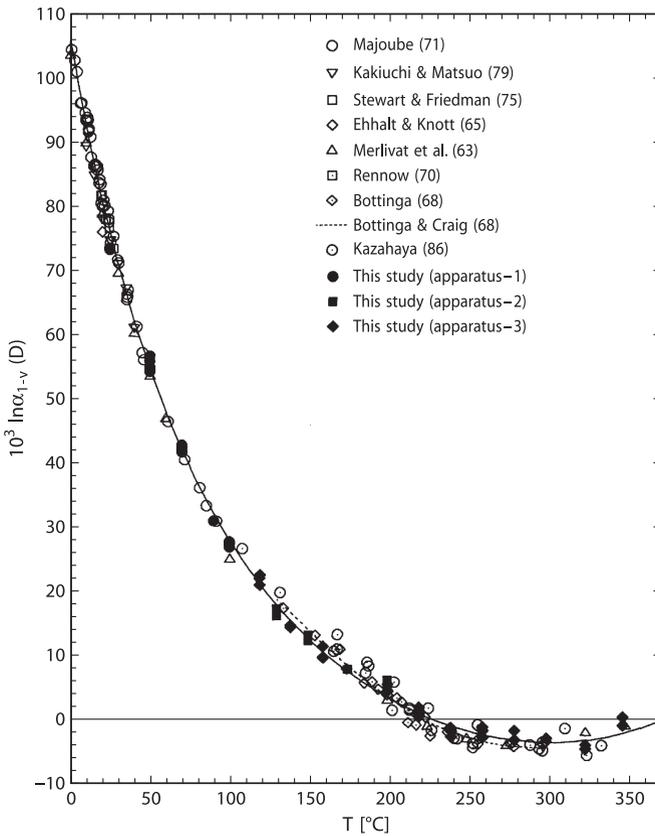


Fig. 2.3 Experimentally determined fractionation factors between liquid water and water vapour from 1 to 350°C (after Horita and Wesolowski, 1994)

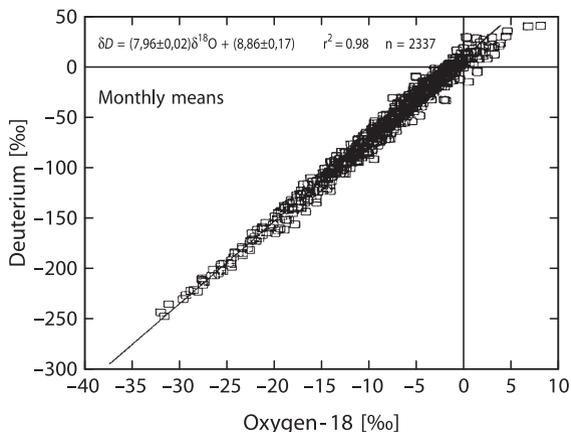


Fig. 2.4 Global relationship between monthly means of δD and $\delta^{18}O$ in precipitation, derived for all stations of the IAEA global network. *Line* indicates the global meteoric water line (MWL) (after Rozanski et al. 1993)

In all processes concerning the evaporation and condensation of water, hydrogen isotopes are fractionated in a similar fashion to those of oxygen isotopes, albeit with a different magnitude, because a corresponding difference in vapor pressures exists between H_2O and HDO in one case and $H_2^{16}O$ and $H_2^{18}O$ in the other.

Therefore, the hydrogen and oxygen isotope distributions are correlated for meteoric waters. Craig (1961a) first defined the generalized relationship:

$$\delta D = 8\delta^{18}O + 10,$$

which describes the interdependence of H- and O-isotope ratios in meteoric waters on a global scale.

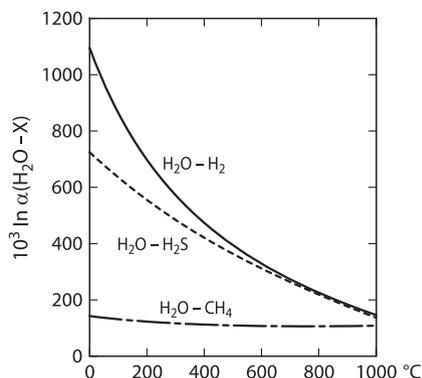
This relationship, shown in Fig. 2.4, is described in the literature as the “Global Meteoric Water Line (GMWL)”.

Neither the numerical coefficient 8 nor the constant 10, also called the deuterium excess d , are constant in nature. Both may vary depending on the conditions of evaporation, vapor transport and precipitation and, as a result, offer insight into climatic processes. The deuterium excess d is a valuable tool to derive information on relative humidities.

2.1.3.1 Equilibrium Exchange Reactions

D/H fractionations among gases are extraordinarily large, as calculated by Bottinga (1969a) and Richet et al. (1977) and plotted in Fig. 2.5. Even in magmatic systems, fractionation factors are sufficiently large to affect the δD -value of dissolved water in melts during degassing of H_2 , H_2S or CH_4 . The oxidation of H_2 or CH_4 to H_2O

Fig. 2.5 D/H fractionations between $\text{H}_2\text{O} - \text{H}_2$, $\text{H}_2\text{O} - \text{H}_2\text{S}$ and $\text{H}_2\text{O} - \text{CH}_4$ (from calculated data of Richet et al. 1977)



and CO_2 may also have an effect on the isotopic composition of water dissolved in melts due to the large fractionation factors.

With respect to mineral-water systems, different experimental studies obtained widely different results for the common hydrous minerals with respect to the absolute magnitude and the temperature dependence of D/H fractionations (Suzuoki and Epstein 1976; Graham et al. 1980; Vennemann et al. 1996). Suzuoki and Epstein (1976) first demonstrated the importance of the chemical composition of the octahedral sites in crystal lattices to the mineral H-isotope composition. Subsequently, isotope exchange experiments by Graham et al. (1980, 1984) suggested that the chemical composition of sites other than the octahedral sites can also affect hydrogen isotope compositions. These authors postulate a qualitative relationship between hydrogen-bond distances and hydrogen isotope fractionations: the shorter the hydrogen bond, the more depleted the mineral is in deuterium.

On the basis of theoretical calculations, Driesner (1997) proposed that many of the discrepancies between the experimental studies were due to pressure differences at which the experiments were carried out. Thus for hydrogen, pressure is a variable that must be taken into account in fluid-bearing systems. Later, Horita et al. (1999) presented experimental evidence for a pressure effect between brucite and water.

Chacko et al. (1999) developed an alternative method for the experimental determination of hydrogen isotope fractionation factors. Instead of using powdered minerals as starting materials these authors carried out exchange experiments with large single crystals and then analyzed the exchanged rims with the ion probe. Although the precision of the analytical data is less than that for conventional bulk techniques, the advantage of this technique is that it allows the determination of fractionation factors in experiments in which isotopic exchange occurs by a diffusional process rather than by a combination of diffusion and recrystallization.

In summary, as discussed by Vennemann and O'Neil (1996), discrepancies between published experimental calibrations in individual mineral-water systems are difficult to resolve, which limits the application of D/H fractionations in mineral-water systems to estimate δD -values of coexisting fluids.