
ISOTOPE FRACTIONATION

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. The term 'isotope' is derived from the Greek (meaning equal place): the various isotopes of an element occupy the same position in the periodic table. Isotopes of an element can either be stable or unstable (radiogenic). Differences in chemical and physical properties arising from variations in atomic mass of an element are called '**isotope effects**'. The partitioning of isotopes between two substances or two phases of the same substance with different proportions of isotopes is called '**isotope fractionation**' (Hoefs, 1997). The isotopic composition of materials contains information that can be used, for example, to reconstruct the palaeo-environment, to understand the hydrological cycle and biochemical pathways.

History:

In 1913, isotopes were discovered by J.J. Thomson who found that the element neon has two different kinds of atoms with atomic weights 20 and 22. A few years later, 212 of the 287 naturally occurring isotopes were known. The reason for the existence of isotopes was, however, unclear until the discovery of the neutron by Chadwick in 1932. The seminal paper by Urey (1947) on the thermodynamic properties of isotopic substances provided the basis for the utilization of stable isotopes in geology, geochemistry, biogeochemistry, paleoceanography and elsewhere.

Notation, Definitions

Isotopic ratios, R , are measures of the relative abundances of isotopes of an element, E ; they are usually arranged so that the lightest stable isotope (index a) which is often also the most abundant isotope appears in the denominator: ${}^bR = {}^bE / {}^aE$ (stable boron isotopes are an exception: ${}^{11}\text{B}$ is about four times more abundant than ${}^{10}\text{B}$). The three stable oxygen isotopes ${}^{16}\text{O}$, ${}^{17}\text{O}$, and ${}^{18}\text{O}$ will be used to explain the notation and basic definitions.

The oxygen isotope with mass number 16 contains 8 protons (oxygen!) and 8 neutrons and is denoted by ${}^{16}\text{O}$. It is by far the most abundant (99.76%) of the three stable oxygen isotopes. For example, the ratio of ${}^{17}\text{O}$ to ${}^{16}\text{O}$ in water, or the ratio of ${}^{18}\text{O}$ to ${}^{16}\text{O}$ in carbon dioxide can be written as:

$${}^{17}\text{O}_{\text{H}_2\text{O}} = \frac{[\text{H}_2 \text{ } ^{17}\text{O}]}{[\text{H}_2 \text{ } ^{16}\text{O}]}, \quad {}^{18}\text{O}_{\text{CO}_2} = \frac{2[\text{C}^{18}\text{O}^{18}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]}{2[\text{C}^{16}\text{O}^{16}\text{O}] + [\text{C}^{18}\text{O}^{16}\text{O}]}$$

The **isotopic composition**, δ , of a sample, determined by mass spectrometric methods, is measured with respect to a standard (std):

$$\delta^bE_{\text{sample}} = \left(\frac{{}^bR_{\text{sample}}}{{}^bR_{\text{std}}} - 1 \right) \cdot 1000$$

where b is the atomic mass of the isotope and the factor 1000 converts the δ value to per mil. The standards (cf. Hoefs, 1997) used for stable oxygen isotopes are V-SMOW (Vienna-Standard Mean Ocean Water;

$${}^{18}R_{V\text{-SMOW}} \cdot 10^6 = 2005.20 \pm 0.43) \text{ and V-PDB (Vienna-Pee-Dee Belemnite,$$

$${}^{18}R_{V\text{-PDB}} \cdot 10^6 = 2067.1 \pm 2.1).$$

The **fractionation factor**, α , is defined as the ratio between the isotopic ratio in compound X and that in compound Y:

$${}^b\alpha_{X\text{-}Y} = \frac{{}^bR_X}{{}^bR_Y} = \frac{\delta^bE_X + 1000}{\delta^bE_Y + 1000}$$

It is a measure of the partitioning of isotopes between two or more phases in response to an isotope effect.

Whereas the δ value is the result of the whole history of the sample, the α value is characteristic for say, an equilibrium between X and Y or for a process that leads from X to Y. Since α values are usually mostly very close to 1.0, the ϵ notation is commonly used to express isotope fractionations in per mil (o/oo):

$${}^b\epsilon_{X-Y} = ({}^b\alpha_{X-Y} - 1) \cdot 1000.$$

Isotope effects

The most important isotope effects arise from differences in a) random mean velocities and b) vibrational frequencies of molecules.

a) Random mean velocity effects. In (local) thermodynamic equilibrium, the mean kinetic energy is equal for all

molecules and determined by temperature alone: $\langle E_{kin,j} \rangle = \frac{1}{2} m_j \langle v_j^2 \rangle = \frac{3}{2} k_B T = E_{thermal}$ where m_j and

$v_{rms,j} = \sqrt{\langle v_j^2 \rangle}$ are mass and random mean square (rms) velocity of molecule j , k_B is Boltzmann's constant, and T is absolute temperature. At a given temperature, the rms velocity varies with the mass of the molecule:

light molecules are faster than heavy molecules (Graham's law of diffusion: $v_{rms,1}/v_{rms,2} = \sqrt{m_2/m_1}$). As a consequence, molecules containing the light isotope diffuse faster. The ratio of the diffusion coefficients D_v for the light (mass m_a) and the heavy molecule (mass m_b) of a gas that diffuses through air (mass $m_c = 29$) is

$$\text{given by } \alpha_{a-b} = \frac{D_b}{D_a} = \sqrt{\frac{m_b + m_c}{m_b \cdot m_c} \frac{m_a \cdot m_c}{m_a + m_c}}.$$

For ${}^{13}\text{CO}_2$ and ${}^{12}\text{CO}_2$ one obtains ${}^{13}\alpha_{diff, \text{CO}_2 \text{ in air}} = \sqrt{\frac{45 + 29}{45 \cdot 29} \frac{44 \cdot 29}{44 + 29}} \approx 0.9956$. The relation does not apply,

however, for diffusion of gases through liquids where the ratio of the diffusion coefficients is closer to one (${}^{13}\alpha_{diff, \text{CO}_2 \text{ in water}} \approx 0.9993$). The variation of rms velocity with mass also leads to differences in evaporation.

b) Vibrational frequency effects. The zero-point energy of vibrations in molecules, E_0 , is mass dependent. For diatomic molecules $E_0 = h\nu/2$ where h is Planck's constant and ν is the (vibration) frequency. The ratio of frequencies, ν and ν' for two diatomic molecules of different isotopic composition is approximately given by $\nu'/\nu = \sqrt{\mu/\mu'}$ where $\mu = m_1 \cdot m_2 / (m_1 + m_2)$ is the reduced mass and m_1 and m_2 are the masses of the two atoms involved.

Example: compare the frequencies for ${}^{16}\text{O} {}^{16}\text{O}$ (ν , $\mu = 16 \cdot 16 / (16 + 16) = 8$), ${}^{17}\text{O} {}^{16}\text{O}$ (ν' , $\mu' = 17 \cdot 16 / (17 + 16) \approx 8.2424$), and ${}^{18}\text{O} {}^{16}\text{O}$ (ν'' , $\mu'' = 18 \cdot 16 / (18 + 16) \approx 8.4706$):

$\nu'/\nu \approx 0.9852$, $\nu''/\nu \approx 0.9718$, i.e. the strength of the isotope effect increases with the mass difference and thus it is not surprising that the resulting isotope fractionation is as a rule also 'mass-dependent'.

Isotope fractionation

The difference in isotopic composition between various compounds or between various phases of a single compound is called isotope fractionation. It is noted that even the largest isotope effect may not cause fractionation if the reaction goes to completion, i.e. a quantitative reaction in which the reactant is completely transformed into the product.

However, an isotopic fractionation will always be observed when a reaction has an isotope effect and the formation of the product is not quantitative.

Equilibrium isotope fractionation

Isotope fractionation can occur in equilibrium, for example, between the various isotopic forms of carbon dioxide, bicarbonate, and carbonate ions. As a rule: "The heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly." (Bigeleisen, 1965) For example, in the temperature range between 0° and 25°C the $\delta^{13}\text{C}_{\text{CO}_2}$ in seawater is 8 – 10o/oo lower ('isotopically lighter') than $\delta^{13}\text{C}_{\text{HCO}_3^-}$.

The fractionation factors for equilibrium fractionation involving three isotopes with masses $m_1 < m_2 < m_3$ usually scale such that $\alpha_{2/1} = \alpha_{3/1}^\beta$ where $\beta = (1/m_1 - 1/m_2)/(1/m_1 - 1/m_3)$ (Young et al., 2002).

For the three stable oxygen isotopes: $^{17}\alpha = (^{18}\alpha)^{0.529}$.

Nonequilibrium ('kinetic') isotope fractionation

Nonequilibrium effects are associated with incomplete or unidirectional processes such as evaporation, kinetic isotope effects in chemical reactions, diffusion, or metabolic effects. Kinetic isotope effects in chemical reactions occur when reaction rates for compounds containing light or heavy isotopes are different, which is almost always the case and thus isotope fractionation can be expected. If the reservoir of reactants is finite, the isotope effect associated with the reaction will not only yield a product of different isotopic composition but will lead to a change in the isotopic composition of the reservoir as well (**Rayleigh distillation**; Bigeleisen and Wolfsberg, 1958). Kinetic isotope effects can quantitatively be understood on the basis of the 'transition state theory' (Bigeleisen and Wolfsberg, 1958). The fractionation factors for kinetic fractionation involving three isotopes with masses $m_1 < m_2 < m_3$ often scale such that $\alpha_{2/1} = \alpha_{3/1}^\beta$ where $\beta = \ln(m_1/m_2)/\ln(m_1/m_3)$

(Young et al., 2002). For the three stable oxygen isotopes: $^{17}\alpha = (^{18}\alpha)^{0.515}$

'Mass-independent' fractionation

A fractionation of stable oxygen isotopes was reported (for the first time) in 1973 in meteorites and in 1983 in laboratory studies (Thiemens and Heidenreich, 1983). These studies show differences for certain compounds that contain ^{16}O only (substance X) and compounds that contain ^{16}O and ^{17}O (substance Y) or ^{16}O and ^{18}O (substance Z) with fractionation factors $^{17}\alpha$ (between X and Y) and $^{18}\alpha$ (between X and Z) that are almost equal, i.e. $^{17}\alpha \approx ^{18}\alpha$. These fractionation processes are called 'mass-independent'. They may occur at low pressures and, for example, play an essential role for stratospheric ozone. The resulting unusual composition of atmospheric oxygen has been used in the so-called 'triple-isotope method' to derive estimates of the biosphere productivity (Luz et al., 1999). A theoretical explanation based on an extension of the Rice, Ramsperger, Kassel, Marcus (RRKM) theory has been developed only recently (Gao and Marcus, 2001). A mass-independent isotope effect has also been observed during thermal decomposition of carbonates in vacuo (Miller et al., 2002).

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Cross-references

Carbon isotopes, stable

Oxygen isotopes
Paleotemperature, proxy reconstructions
Stable isotope analysis
Strontium isotopes
Sulfur isotopes
