

# Stable Isotope Deltas: Tiny, yet Robust Signatures in Nature

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## **Abstract**

Although most are relatively small, stable isotope deltas of naturally occurring substances are robust and enable workers in anthropology, atmospheric sciences, biology, chemistry, environmental sciences, food and drug authentication, forensic science, geochemistry, geology, oceanography, and paleoclimatology to study a variety of topics. Two fundamental processes explain the stable isotope deltas measured in most terrestrial systems: isotopic fractionation and isotope mixing. Isotopic fractionation is the result of equilibrium or kinetic physicochemical processes that fractionate isotopes because of small differences in physical or chemical properties of molecular species having different isotopes. It is shown that mixing of radioactive and stable isotope end members can be modeled to provide information on many natural processes, including carbon-14 abundances in the modern atmosphere and the stable hydrogen and oxygen isotopic compositions of the oceans during glacial and interglacial times. Calculating mixing fractions using isotope balance equations with isotope deltas can be substantially in error when substances with high concentrations of heavy isotopes (e.g., carbon-13, hydrogen-2, and oxygen-18) are mixed. In such cases, calculations using mole fractions are preferred as they produce accurate mixing fractions.

Isotope deltas are dimensionless quantities. In the International System of Units (SI) these have the unit 1 and the usual list of prefixes is not applicable. To overcome traditional limitations with expressing orders of magnitude differences in isotope deltas, we propose the term urey, after H. C. Urey (symbol Ur), for the unit 1. In such a manner, an isotope delta value expressed traditionally as  $-25$  per mil can be written  $-25$  mUr (or  $-2.5$  cUr or  $-0.25$  dUr; use of any SI prefix is possible). Likewise,

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very small isotopic differences often expressed in per meg 'units' are easily included (e.g., either +0.015 ‰ or +15 per meg can be written +15  $\mu\text{Ur}$ ).

## ***Introduction***

The investigation of stable isotope abundance variations in nature still is considered a niche discipline for well-trained specialists. In spite of its scientific role in climate research or in providing a wide variety of information about the Earth's history or the development of mankind, studies of variations of stable isotopic abundances (isotope deltas) have not caught on to a wider scientific audience, nor to the general public, perhaps because of a lack of natural science education in the general population.

An often encountered misunderstanding relates to the nature of isotopes, which are thought to be obscure or rare entities. To the contrary, all elements are made of atoms, each of which is either a stable or a radioactive isotope. For each element (defined as being comprised of atoms having the same number of protons), there can be several stable and (or) radioactive isotopes, differing in mass only because of differences in the number of neutrons in the nucleus. Isotopes were recognized at the start of the twentieth century after radioactive elements were discovered. In 1911, Fredrick Soddy demonstrated the chemical identity of meso-thorium ( $^{228}\text{Ra}$ ) and radium [1]. He concluded that these were chemical elements with different radioactive properties and with different atomic weights, but with the same chemical properties and same positions in the Periodic Table of the Elements. He advocated the word isotope (Greek: in the same place) to account for such entities [2]. Stable isotopes were first identified in 1912, when J. J. Thomson discovered by a mass-spectrometric technique that the element neon was made up of two stable isotopes, neon-20 and neon-22. [3] Neon-21 was discovered later.

## ***Stable and not-so-stable atoms***

The sum of the number of protons and neutrons is termed the isotope mass number. As an example, the element chlorine in natural terrestrial materials is comprised primarily of two stable isotopes (chlorine-35 and chlorine-37, typically written  $^{35}\text{Cl}$  and

<sup>37</sup>Cl). Terrestrial chlorine also has a minute abundance of the radioactive isotope <sup>36</sup>Cl. The abundances and atomic masses of these isotopes are shown in Table 1. Together, these isotopes combine to yield an atomic weight (relative atomic mass) for Cl of 35.453. [4] Molecular species that differ only in isotopic composition (number of isotopic substitutions) and relative molecular mass (e.g., C<sup>35</sup>Cl<sub>4</sub>, C<sup>35</sup>Cl<sub>3</sub><sup>37</sup>Cl, and C<sup>35</sup>Cl<sub>2</sub><sup>37</sup>Cl<sub>2</sub>) are termed isotopologues.

**Table 1; Abundances of the most abundant isotopes of chlorine**

Isotope	Atomic mass*	Isotopic abundance (mole fraction)
<sup>35</sup> Cl	34.968 8527 Da	75.76 %
<sup>36</sup> Cl	35.968 3070 Da	10 <sup>-14</sup> % [5]
<sup>37</sup> Cl	36.965 9026 Da	24.24 %

\* Atomic masses are expressed in unified atomic mass units, also denoted u (for unified), or in Da for dalton, which is an alternative name for u.

There are 20 chemical elements with one stable isotope, including fluorine (isotope mass number 19, written <sup>19</sup>F), sodium (<sup>23</sup>Na), phosphorous (<sup>31</sup>P), and gold (<sup>197</sup>Au). In addition, protactinium and thorium each have one long-lived radioactive isotope (<sup>231</sup>Pa and <sup>232</sup>Th), giving them a characteristic terrestrial abundance of 100 %. The standard atomic weight of elements<sup>b</sup> with only one stable isotope generally can be given to 8 significant figures because atomic masses are known to this accuracy.

Of the chemical elements, 34 have no stable isotopes. Examples of elements that have no stable isotopes are infamous and include radium, uranium, and the man-made element plutonium. Three elements having no stable isotopes (thorium, protactinium, and uranium) do have characteristic terrestrial isotopic compositions, and for each an atomic weight can be determined.

There are 61 chemical elements with 2 or more stable isotopes or 62 if one treats uranium with its 3 long-lived radioactive isotopes having characteristic terrestrial abundances. For example, hydrogen has 2 stable isotopes (isotope mass numbers 1 and 2 that are given the names protium and deuterium, respectively), carbon has 2

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<sup>b</sup> An authoritative resource for atomic weights and isotopic compositions of the elements can be found on the web site of the IUPAC Commission of Isotope Abundances and Atomic Weights (CIAAW): [www.ciaaw.org](http://www.ciaaw.org)

stable isotopes (isotope mass numbers 12 and 13), nitrogen has 2 stable isotopes (isotope mass numbers 14 and 15), and oxygen has 3 stable isotopes (isotope mass numbers 16, 17, and 18). On the high side, one finds xenon with 9 stable isotopes (ranging from  $^{124}\text{Xe}$  to  $^{136}\text{Xe}$ ) and tin with 10 stable isotopes ( $^{112}\text{Sn}$  to  $^{124}\text{Sn}$ ). [6]

In general, the various isotopes of an element have very similar chemical properties. The physical properties of isotopes also are very similar, except for those that are related to mass. The most striking differences are observed for hydrogen and deuterium, with the largest relative mass difference (see Table 2).

**Table 2; Selected physical properties of  $^2\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  °**

Property	$^2\text{H}_2\text{O}$ (Heavy water)	$\text{H}_2\text{O}$ (Light water)
Freezing point (°C)	3.82	0
Boiling point (°C)	101.4	100
Density at STP (g/mL)	1.1056	0.9982
Temp. of maximum density (°C)	11.6	4
neutral pH (at 25 °C)	7.41	7

Apart from radioactive decay, radioactive isotopes behave like their non-radioactive, stable siblings. One exceptionally useful radioactive isotope is  $^{14}\text{C}$  ('radiocarbon'), which was discovered by Ruben and Kamen in 1940 [7]. It is used in radiometric dating [8] and enables one to measure ages of ~ 60 000 years before present.  $^{14}\text{C}$  is produced continuously in the stratosphere by the interaction of cosmic rays and the stable isotope  $^{14}\text{N}$  of nitrogen molecules.  $^{14}\text{C}$  reacts with oxygen to form  $\text{CO}_2$ , which is spread throughout the atmosphere and is transferred to carbon-bearing substances, including plants, animals, the oceans, speleothems, and groundwaters. After having been captured in a solid (e.g., a tree, a carbonate, a bone, or even a molecule of DNA in a brain cell), the  $^{14}\text{C}$  decays with a half-life of 5730 years. The age of a sample can be determined by measuring the  $^{14}\text{C}$  abundance of the sample and taking into account variations in atmospheric  $^{14}\text{C}$  production over time. The natural abundance of  $^{14}\text{C}$  in modern carbon is extremely low ( $\sim 1.2 \times 10^{-12}$ ), which makes it difficult to measure, but also makes it less dangerous, considering that it is also present in our bodies at this level.

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° This information is for instance available at: [http://en.wikipedia.org/wiki/D2O#Semiheavy\\_water](http://en.wikipedia.org/wiki/D2O#Semiheavy_water)

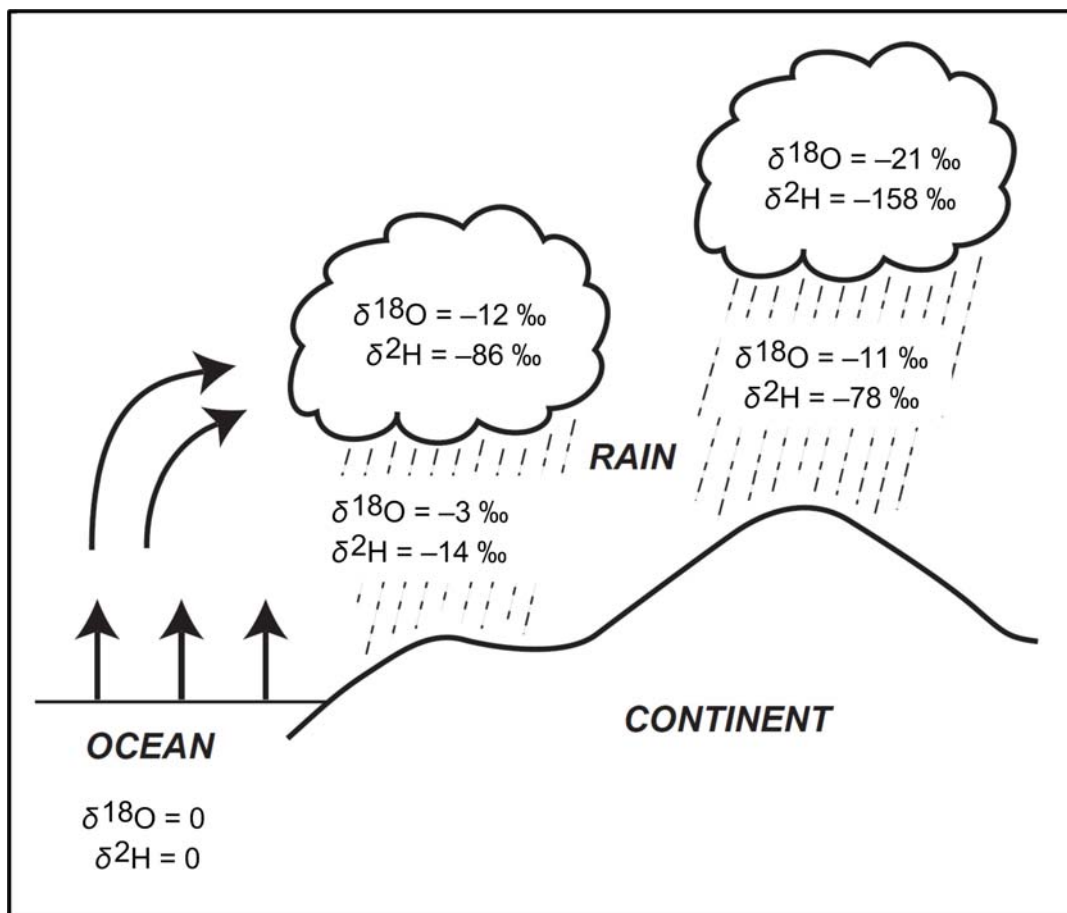
On average, the concentration of radioactive isotopes in terrestrial materials is low. Many radioactive isotopes arise from the decay of the radioactive isotopes of the three uranium-isotope decay chains ( $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ ). In addition, many radioactive isotopes have been produced by atomic bomb weapons testing between 1954 and 1964, including  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ , and  $^3\text{H}$  (the radioactive isotope of hydrogen named tritium). Radioactive isotopes generated in this manner commonly are called “bomb spike” isotopes, giving rise to bomb spike tritium, bomb spike  $^{14}\text{C}$ , and bomb spike  $^{36}\text{Cl}$ . Abundances of these radioactive isotopes above natural levels is used to distinguish modern environmental samples from pre-1950s samples, and this technique is used regularly in dating of groundwaters.

### ***Isotopic variations in nature***

Apart from radiogenic isotopes, variations in isotopic abundances are caused by kinetic or equilibrium physicochemical processes that fractionate isotopes, termed **isotopic fractionation**. For example, diffusion rates of lighter gases (gases containing the isotope of lower mass number) are higher than those of heavier gases. Chemical bonds are stronger for isotopes having the higher mass number. As a consequence of such a (kinetic) fractionation reaction, the  $\text{CO}_2$  evolved by treating calcium carbonate with acid is enriched in  $^{18}\text{O}$  relative to the original solid  $\text{CaCO}_3$ . Of the 61 chemical elements with 2 or more stable isotopes, variations in abundances of stable isotopes in naturally occurring terrestrial materials have been measured for more than 30 of these elements. For 10 of these well-studied elements (H, Li, B, C, N, O, Si, S, Cl, and Ti), lower and upper bounds of isotopic composition (and atomic weight) in naturally occurring terrestrial materials has been determined, and the Table of Standard Atomic weights of the Elements was updated accordingly in 2010. [4].

Isotopic fractionation processes commonly occur close to the reaction threshold, and although the magnitude of the isotopic fractionation may be small, the variations effected in isotopic abundance of terrestrial materials can be substantial and important for scientific studies. For example, when liquid water, consisting of  $^1\text{H}_2^{16}\text{O}$ ,

$^1\text{H}^2\text{H}^{16}\text{O}$ ,  $^1\text{H}_2^{17}\text{O}$ ,  $^1\text{H}_2^{18}\text{O}$ , and further minor mixed-isotopic species, evaporates from the oceans at ambient temperature, the water vapor is enriched in  $^1\text{H}$ ; the water vapor has an  $^2\text{H}$  abundance of 0.01435 %, while the liquid has an  $^2\text{H}$  abundance 0.01560 % (ocean water at 25 °C). Similarly, the  $^{18}\text{O}$  is depleted in the vapor phase; here the corresponding abundance values are 0.1984 % for  $^{18}\text{O}$  in the vapor and 0.2005 % for  $^{18}\text{O}$  in the liquid.



**Figure 1; Evaporation and condensation of water and associated isotopic fractionation. The  $\delta$ -notation and ‰ ‘unit’ are discussed below.**

While these differences in isotopic composition appear small, they are significant, robust, and, using the appropriate instrumentation, easy to measure. The reverse process, condensation of liquid water from vapor saturated air, e.g. from an air mass, enriches the liquid water in  $^2\text{H}$  and  $^{18}\text{O}$  by the same magnitude of isotopic fractionation (see Figure 1). As more and more water condenses from the air mass, commonly as it ascends a mountain and cools, more and more  $^2\text{H}$  and  $^{18}\text{O}$  is removed from the air mass. One consequence is that moisture precipitating from an air mass that reaches Antarctica will have only ~60 % of the  $^2\text{H}$  of moisture precipitating over a warm equatorial ocean. The  $^{18}\text{O}$  is reduced by ~5 %. This

process is called **Rayleigh fractionation** because the equations describing the process were derived by Lord Rayleigh for the case of fractional distillation of mixed liquids. Another example involves assimilation of CO<sub>2</sub> by plants during photosynthesis. During photosynthesis plants have a slight (enzymatic) preference for the lighter <sup>12</sup>C over the less abundant <sup>13</sup>C. The discrimination amounts to about 1.8 %, i.e. the CO<sub>2</sub> in air contains 1.018 times more <sup>13</sup>C than the photosynthetic product (glucose) from which all further organic material in living matter is derived<sup>d</sup>.

Not only is isotopic fractionation in nature important, but anthropogenic fractionation of isotopes has become important over time as well. One prominent example is the Manhattan project that produced the first atomic bomb during World War II<sup>e</sup>. Uranium-235 needed to be enriched over the much more abundant uranium-238. Huge industrial halls were built containing several rows ('race tracks') of 96 very large mass spectrometers ('calutrons') each. To produce the amount of <sup>235</sup>U sufficient for the atomic bomb (dropped on Hiroshima on Aug. 6, 1945, killing more than 100 000 people), the mass spectrometers were operated continuously for more than two years, eventually producing 1 kg of uranium enriched in <sup>235</sup>U per month. This example illustrates the considerable effort necessary to fractionate substantially the isotopes of heavy elements.

In addition to isotopic fractionation, the second major process to effect changes in isotopic abundances in natural and laboratory systems is **isotope mixing**, which can be utilized with both stable and radioactive isotopes. The number of processes able to fractionate isotopes substantially is small. Once isotopes are fractionated in environmental terrestrial systems, the fractionated material commonly is spread out and transported over substantial distances and is thereby mixed with other, non-fractionated or differently-fractionated materials. The above-mentioned radiocarbon 'bomb-spike' is a good example. During atomic bomb testing, atmospheric <sup>14</sup>C levels increased by more than a factor of two (from  $\sim 1.2 \times 10^{-12}$  to  $\sim 2.6 \times 10^{-12}$ ). Since the 1963 test ban, the atmospheric <sup>14</sup>CO<sub>2</sub> level has declined steadily [9]. The decline is NOT due to radioactive decay because the <sup>14</sup>C half-life of 5730 years is much too

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<sup>d</sup> This example is for C-3 plants. The other major photosynthetic cycle (C-4) has a considerably smaller preference for <sup>12</sup>C. The 3<sup>rd</sup> type of photosynthesis (CAM) is a mixture of C-3 and C-4.

<sup>e</sup> A fairly comprehensive chapter on the Manhattan Project is, for instance, available at [http://en.wikipedia.org/wiki/Manhattan\\_Project](http://en.wikipedia.org/wiki/Manhattan_Project)

long for substantial change during the last 50 years. Instead,  $^{14}\text{CO}_2$  is being removed from the atmosphere by mixing with other major carbon pools, including land plants, soils, and, last but not least, the world oceans. Within and between these compartments, additional mixing (and also additional isotopic fractionation) occurs, leaving signatures for researchers to investigate and identify processes occurring over time. By studying the kinetics of  $^{14}\text{C}$  in various compartments, a substantial amount of information about the global carbon cycle can be inferred.

### ***Investigating and expressing small isotopic variations***

To disentangle mixing processes is a difficult, often tedious task. The tools one has at hand are few, among those for instance are so called “Keeling plots” [10-13], a technique, which allows one to identify end members from measurement of concentration and isotopic signature of a given component. Measured isotopic compositions are plotted versus the reciprocal abundance. If a linear relation is observed, the mixing probably occurs from two different source / sink pools. The technique only works well with two (major) pools. It fails as soon as several compartments are acting simultaneously or when the exchange and mixing processes have several time constants [14]. Most importantly, the isotopic information is treated as an intrinsic property that is independent of the respective molar ratios. This strictly applies only when isotopic abundance variations are small. (This will be detailed further in connection with isotope balance). For more complex interactions, computer models that combine the accumulated knowledge, mathematical and physical relations, and experimental data, as one gathers them into a comprehensive scientific understanding, are indispensable. Without these and their continued development and updating, one would not be able to make the connection between experimental data and the underlying mechanisms that drive the complex systems as a whole.

Isotopic variations in nature are small, and it is not convenient to express the original differences as isotope abundances (mole fractions) typically with many leading zeros. Moreover, the absolute isotopic abundances are less important than the changes in isotopic abundances that have occurred. These changes can be treated as intrinsic



properties or labels of various substances in a study. Thus, it has been common agreement and practice for more than half a century to express deviations in isotopic compositions using a specialized notation, the isotope-delta notation. This notation is defined as the difference between the ratios of the number of heavier versus number of lighter stable isotopes in a given material versus the ratio in a reference material, normalized by the ratio of the reference material:

$$\delta^i E = (R_{sa} - R_{ref}) / R_{ref} \quad (1)$$

with  $i$  denoting the mass number of the heavy isotope of element E (the mostly more abundant lighter isotope is omitted in this short hand form of delta; for extended versions see for instance Brand et al. [15])<sup>f</sup>,  $R_{sa}$  is the respective isotope number ratio of a sample and  $R_{ref}$  is that of the reference material. For instance,  $^{13}R_{VPDB}$  is the number of  $^{13}\text{C}$  atoms divided by the number of  $^{12}\text{C}$  atoms in a sample of ‘VPDB’, which happens to be the internationally agreed-upon reference for  $\delta^{13}\text{C}$  values. Isotope-delta values are relative values, designed for comparison of known and unknown quantities (much like an ordinary weight balance). Delta values are a function of the isotopic composition of the reference (similar to % in quantity calculus). Hence, it is extremely important to always provide the correct label, in particular, the reference scale and the value(s) employed for the scale anchor(s) used in the study.

Delta is a practical way of measuring and expressing a small difference. Its major advantage is the fact that it does not require any prior knowledge of isotope relations in a reference material. This is in sharp contrast to isotopic abundances expressed as atom fractions (formerly ‘atom %’), where the quantitative relation of all isotopic constituents in the reference is needed as a-priori information when expressing deviations from this material. Relative deviations of isotope ratios can be measured with a precision that exceeds by far the uncertainty in measuring atom fractions. As an example, the “absolute”  $^{13}\text{C}$  abundance in NBS 19 (the calcite material defining the  $\delta^{13}\text{C}_{VPDB}$  scale) is known with an uncertainty of  $\pm 2.5 \text{ ‰}$  [17, 18], whereas  $\delta^{13}\text{C}$  deviations from this material can be made with a residual error of  $\pm 0.003 \text{ ‰}$  [19], three orders of magnitude better than the absolute abundance uncertainty. The scientific advantage of communicating isotope deltas rather than atomic fractions is

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<sup>f</sup> A comprehensive list of stable isotope terminology has recently been compiled by Coplen [16]

that the absolute  $^{13}\text{C}$  abundance of an established reference material might be improved by new measurements or techniques without affecting any of the isotope data published as delta values using that material as a primary reference (international measurement standard) or even secondary scale anchor.

***The urey (Ur); a proposal to replace the single-magnitude ‰ ‘unit’ with an expression fitting the international system of units (SI)***

Typically  $\delta^i\text{E}$  values are small numbers. Following tradition, they are expressed in units of part per thousand and communicated in per mil (symbol ‘‰’) ‘units’. ‘Units’ are set in quotation marks because these are not true units, as acceptable in the International System of Units, the SI [20]. The isotope delta as defined through equation (1) is a derived dimensionless quantity, a “quantity of dimension one” with unit symbol “1” in the SI. [21] The SI does not allow use of the official prefixes for units of dimension one [21], possibly because of the odd sound of a unit “micro-1”, or a “milli-1” (which would correspond to a per mil). To circumvent this oddity, we propose here to *introduce a new unit for the derived quantity isotope delta as defined through equation (1)*. As a possible implementation (subject to discussion and wider agreement), the unit could have the name ‘**urey**’ (symbol ‘Ur’), in recognition of Harold Urey [22]. The same form is used for pascal, with symbol Pa, named for Blaise Pascal. Harold C. Urey, the outstanding University of Chicago chemist first implemented routine stable isotope analytical measurements in his laboratory that enabled him to study changes in ocean temperatures in Earth’ history. In 1934, Harold C. Urey received the Nobel Prize in chemistry for his discovery of deuterium. The new unit ‘urey’ could be combined with any SI prefix used to express fractions or multiples of ten of an SI unit ( Table 3). Thus, a milliurey (Symbol ‘**mUr**’) would be equivalent to the per mil; a microurey (‘**μUr**’ etc) would denote units of  $10^{-3}$  per mil (often called ‘per meg’ or ‘ppm’) etc. One could even express a part per hundred change in the delta notation as centiurey (‘**cUr**’). Some examples include the following:

- (a) The nitrogen isotope delta value of a specimen Q relative to nitrogen in atmospheric air is  $\delta^{15}\text{N}_{\text{Q}/\text{Air-N}_2} = \delta^{15}\text{N}_{\text{Air-N}_2} = -9.5 \text{ mUr} = -9.5 \text{ ‰}$ .
- (b) The oxygen isotopic composition of Lake Howard is  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = -9.1 \text{ mUr} = -9.1 \text{ ‰}$ .

- (c) For a sample of seawater,  $\delta^{44/42}\text{Ca}_{\text{NBS915a}} = +1.2 \text{ mUr} = +1.2 \text{ ‰}$  (relative to NBS 915a calcium carbonate).
- (d) The  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  of the water in the brine pool =  $-9.1 \text{ } \mu\text{Ur} = -9.1 \text{ per meg} = -9.1 \text{ ppm}$ .

For the remainder of this article we will continue to use the urey as a realisation of the traditional SI unit 1 for the isotope delta with 1 per mil being equal to 1 mUr.

**Table 3; Examples of SI prefixes used with the urey**

Sub-multiple	SI Prefix name	SI Prefix symbol	non-SI symbols in current use (colloquial name)	non-SI symbols in current use (colloquial name)	urey
1	-	-			Ur
$10^{-1}$	deci	d			dUr
$10^{-2}$	centi	c	% (per cent, percent)	pph (part per hundred)	cUr
$10^{-3}$	milli	m	‰ (per mille, permil, per mill)	part per thousand	mUr
$10^{-6}$	micro	$\mu$	ppm (part per million)	per meg	$\mu\text{Ur}$
$10^{-9}$	nano	n	part per billion		nUr

### ***Isotope delta and mass balance***

Isotope deltas commonly are used in mass balances and amount-of-substance balances. A major complication is that the isotope delta (equation 1) is not a linear function of the isotopic abundance, which is an atom fraction or mole fraction. This is illustrated in Figure 2 in which  $\delta^{13}\text{C}$  is plotted against the  $^{13}\text{C}$  atom fraction of all stable carbon isotopes (atoms). Close to terrestrial isotopic compositions ( $^{13}\text{C}$  atom fraction  $\sim 0.011$ ,  $\delta^{13}\text{C} \sim -100$  to  $+20 \text{ mUr}$ ), the deviations from perfect linearity are small. With increasing distance from the  $\delta^{13}\text{C}$  scale origin, the non-linearity assumes significant magnitudes, eventually approaching the right hand axis (pure  $^{13}\text{C}$ ) asymptotically. Therefore, isotope delta values should not be used in mass balances or amount of substance balances if there is any possibility of excess error being introduced. A strictly linear mass balance equation is discussed within the context of ‘Keeling plots’ in the next chapter (‘phi notation’ [23]).

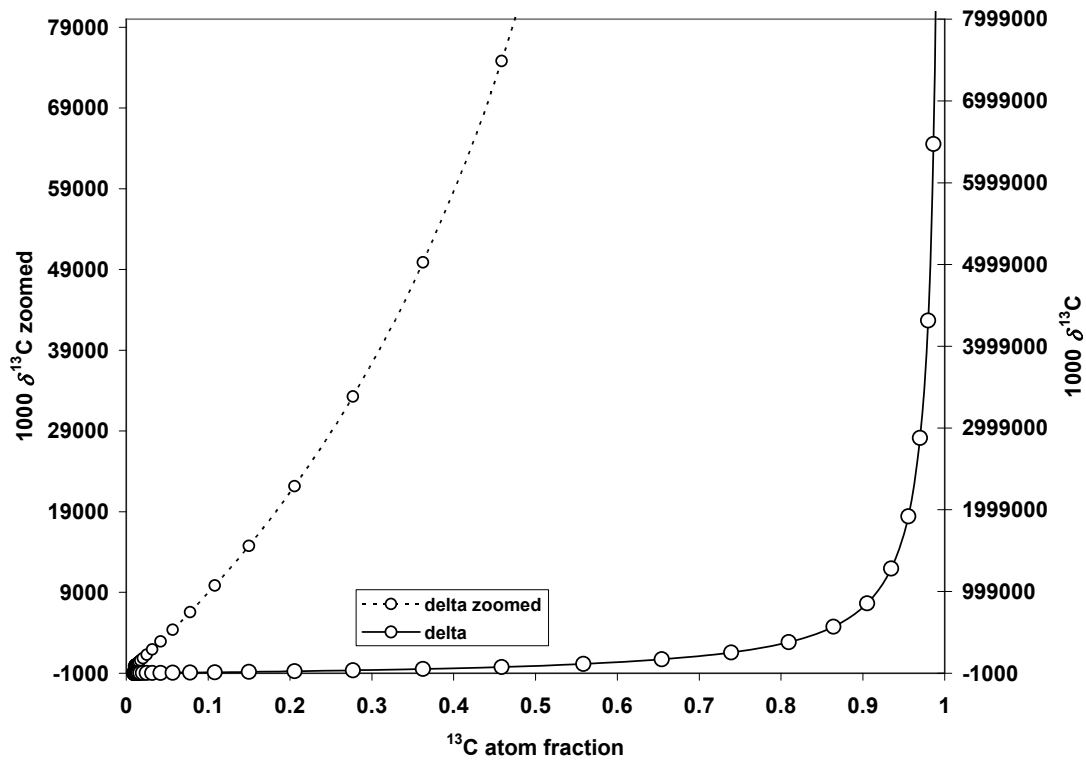


Figure 2. Isotope-delta values (here  $\delta^{13}\text{C}$ ) are not linear with atom fraction (mole fraction).

### ***Keeling plots. How accurate are mass balance calculations?***

When two water samples with different properties (e.g. salinity) are mixed stepwise, one can plot the measured salinity in the mixture versus the inverse molar ratio of one water sample to obtain the salinity values of the end members prior to mixing. The approach can be applied in hindsight. When a varying salinity is observed in a flow-through system that is dominated by two sources, the salt signatures of the sources can be inferred by plotting the observed salinity versus the reciprocal salt concentration to obtain the salinity of the end members. This 'mass' balance approach can also be applied to stable isotopes for quantifying mixing fractions. The corresponding isotope balance equation for the observed  $\delta^i E_{\text{obs}}$  after mixing of element E is

$$\delta^i E_{\text{obs}} = \delta^i E_{\text{pool1}} \times x_{\text{pool1}} + \delta^i E_{\text{pool2}} \times x_{\text{pool2}} \quad (2)$$

with  $x_{\text{pool1}}$  representing the mole fraction of element E in reservoir (1) and with  $x_{\text{pool1}} + x_{\text{pool2}} = 1$ . Eqn (2) is important in all instances where a pure isotopic signature is sought but cannot be obtained independently. In daily analytical practice, eqn (2) is indispensable, such as when raw analytical measurement results need to be corrected for sample memory effects or analytical blanks. This equation is often applied to untangle mixing processes in nature, such as when one reservoir is constant and another reservoir varies in isotopic composition over time. Using

$$x_{\text{pool}} = c_{\text{pool}} / c_{\text{obs}},$$

where  $c$  is concentration, eqn (2) can be rearranged[12] to

$$\delta^j E_{\text{obs}} = \delta^j E_{\text{pool1}} + (\delta^j E_{\text{pool2}} - \delta^j E_{\text{pool1}}) \times c_{\text{pool2}} / c_{\text{obs}} \quad (3)$$

Hence, if the concentration of E in reservoir (2),  $c_{\text{pool2}}$ , is constant (this could, for instance, represent a background concentration), a plot of the observed isotope deltas,  $\delta^j E_{\text{obs}}$ , versus the inverse of the observed concentration of E in the mixture,  $1/c_{\text{obs}}$ , yields  $\delta^j E_{\text{pool1}}$ , the delta value of reservoir (1) as the intercept. This technique is known as a “Keeling plot”. [10, 12, 13]

Keeling plots are useful when one end member can be treated as a constant (such as background air or a blank value) and the isotopic composition of the other member (e.g. soil respiration) is the target of the investigation. An illustration of the Keeling plot technique is given in Figure 3:

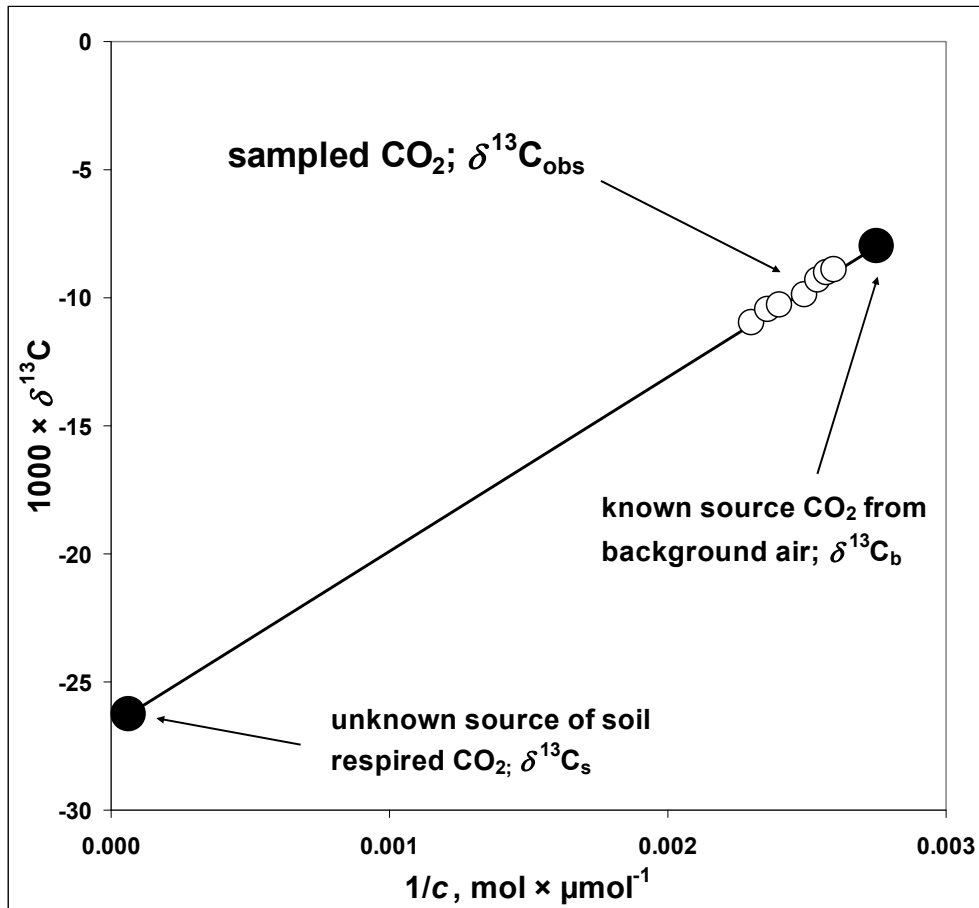


Figure 3. Keeling plot illustration. The  $\delta^{13}C_{obs}$  in this graph is represented by  $\delta^{13}C_{obs}$ ;  $\delta^{13}C_b$  refers to the background air isotopic composition at  $\sim -8$  mUr. The  $\delta^{13}C_s$  is the soil respiration carbon isotope delta value. Please note the large lever. Redrawn from Pataki et al. [12] (© American Geophysical Union).

Eqns (2) and (3) are only valid when  $\delta^i E$  values can be treated as independent properties, which is the case for mole fractions and when the isotope delta deviations are small. When using the isotope balance approach for determining delta values resulting from mixing materials with different known isotopic compositions, it is important to realize that the underlying concept of a constant molecular weight is sufficiently accurate (i.e. in natural environments). Molecular weight variations need to be taken into account, more specifically, when working with substantially altered isotopic compositions, for instance in tracer studies.

Here is an illustration of the situation:

If 1 mL of  $H_2O$  having  $\delta^{18}O = -50$  mUr is mixed with 1 mL of  $H_2O$  having  $\delta^{18}O = +50$  mUr, one might expect that the final product will be exactly 0 Ur (when the

volumes contain the same number of molecules, which is a close approximation). Hence, the isotope balance (not 'mass' balance) can be calculated as

$$\delta_{\text{final}} = -50 \text{ mUr} \times (1 \text{ mL} / 2 \text{ mL}) + 50 \text{ mUr} \times (1 \text{ mL} / 2\text{mL}) = 0 \text{ Ur} \quad (4)$$

In contrast, when mixing 1 g of (-50 mUr)-water with 1g of (+50 mUr)-water, one would obtain a marginally different value ( $\sim -20 \mu\text{Ur}$ ) because 1 g of the  $^{18}\text{O}$ -depleted water contains a slightly larger number of molecules than 1 g of  $^{18}\text{O}$ -enriched water.

While this may appear tolerable, this is not the end of the story. Suppose one mixes 1 mL of pure  $^{18}\text{O}$ -water with 1 mL of pure  $^{16}\text{O}$ -water. Neglecting the small volume effects, one will arrive at a 1:1 mixture by volume in 2 mL of water, with  $^{18}R = 1$ . The corresponding  $\delta^{18}\text{O}$  of the mixture then is

$$\delta^{18}\text{O} = {}^{18}R_{\text{sa}} / {}^{18}R_{\text{VSMOW}} - 1 = 1 / 0.002005 - 1 = 499 \text{ Ur.}$$

When attempting to obtain this value from isotope balance, as given in eqn (2), the delta values of the pure isotope end members pose a problem. Pure  $^{16}\text{O}$  water has  $^{18}R = 0$ ; hence,  $\delta^{18}\text{O} = -1000 \text{ mUr}$ . Pure  $^{18}\text{O}$ -water has no  $^{16}\text{O}$ ; hence,  $^{18}R = N(^{18}\text{O}) / N(^{16}\text{O}) = \infty$ , where  $N$  is the symbol for the SI quantity number of entities. Because  $^{18}R = \infty$ ,  $\delta^{18}\text{O}$  is not defined. Therefore, applying the isotope balance equation does not yield anywhere near 499 Ur. When mixing instead a water sample having 99 %  $^{18}\text{O}$  water by number or mole fraction with another water sample containing pure  $^{16}\text{O}$  only, the isotope balance calculated using the delta formulation is in error by two orders of magnitude (compare Figure 4).

### ***The phi notation: accurate mass balance results***

A modified isotope balance equation using isotope amount fractions  $x(^i\text{E})$ , in lieu of ratios, yields correct mixing values [23, 24]:

$$\varphi(^i\text{E}_{\text{obs}}) = \varphi(^i\text{E}_{\text{pool1}}) \times x_{\text{pool1}} + \varphi(^i\text{E}_{\text{pool2}}) \times x_{\text{pool2}} \quad (5)$$

Here,  $\varphi(^i\text{E})$  is defined in analogy to eqn (1) as

$$\varphi(^i\text{E}) = x(^i\text{E}) / x(^i\text{E})_{\text{reference}} - 1 \quad (6)$$

with  $x(^i\text{E})$  denoting the atom fraction:  $x(^i\text{E}) = N(^i\text{E}) / \sum N(^j\text{E})$ , where the summation is over all stable isotopes of element E.

As an example for these relations, oxygen-18 in water would read

$$\varphi(^{18}\text{O}) = x(^{18}\text{O}) / x(^{18}\text{O})_{\text{VSMOW}} - 1 \quad \text{and} \quad x(^{18}\text{O}) = N(^{18}\text{O}) / \sum(N(^i\text{O})) \quad (7_{a,b})$$

Numerical values of  $\delta^{18}\text{O}$  and  $\varphi(^{18}\text{O})$  are very similar, yet not identical when considering natural abundance isotopic compositions.

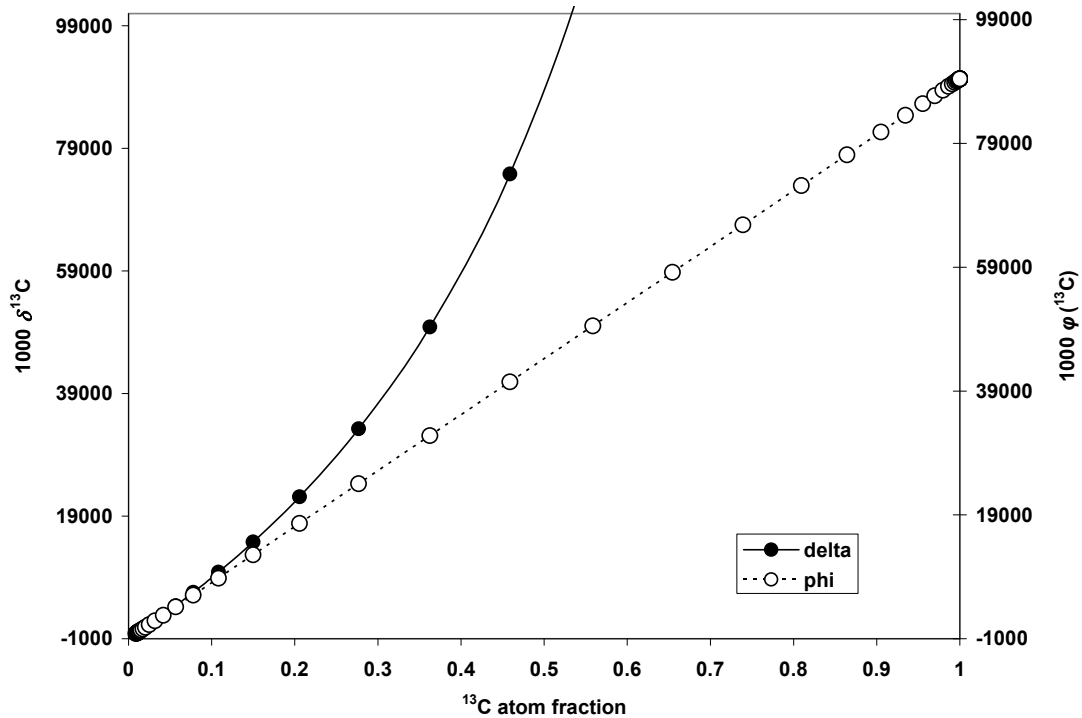


Figure 4. Delta ( $\delta$ ) versus phi ( $\varphi$ ) notation for carbon. Near natural isotopic abundance ( $^{13}\text{C}$  fraction  $\sim 0.01$ ), the two quantities are very close. For large deviations from the VPDB reference, phi is the quantity of choice for balance calculations. For pure  $^{13}\text{C}$  ( $^{13}\text{C}$  fraction = 1), phi has a value of  $\sim 89$ . Delta is not defined for this case.

Delta values can be easily converted to the phi notation using the relation

$$\varphi(^i\text{E}) = \delta^i\text{E} / ({}^iR_{\text{sa}} + 1) \quad (8)$$

with  ${}^iR_{\text{sa}} = (\delta^i\text{E} + 1) \times {}^iR_{\text{ref}}$  (by rearranging eqn 1). Hence, in contrast to the delta notation,  $\varphi$  requires that the isotope ratio  ${}^iR_{\text{ref}}$  of the reference material be known. For carbon, this for instance would be  ${}^{13}\text{R}_{\text{VPDB}} = 0.011180$  [4, 17, 18]. This also implies that the absolute error of the reference ratio enters the traceability chain and the full error budget. For values far outside the natural terrestrial abundance range, differences between the two notations become substantial, as illustrated in Figure 4 for the case of  $^{13}\text{C}$ .



## ***Reliable international standards needed***

Internationally distributed isotopic reference materials, commonly termed international measurement standards, anchor delta scales and enable comparable measurement results in stable isotope laboratories globally (Table 4).

**Table 4. Selected isotope scales and their international measurement standards**

Scale	International Measurement Standard	Medium	Value
$\delta^2\text{H}_{\text{VSMOW-SLAP}}$	VSMOW	water	0 Ur
$\delta^2\text{H}_{\text{VSMOW-SLAP}}$	SLAP	water	-428 mUr
$\delta^{13}\text{C}_{\text{VPDB-LSVEC}}$	NBS 19	calcite	+1.95 mUr
$\delta^{13}\text{C}_{\text{VPDB-LSVEC}}$	LSVEC	lithium carbonate	-46.6 mUr
$\delta^{15}\text{N}_{\text{AIR-N2}}$	AIR-N2	atmospheric nitrogen	0 Ur
$\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$	VSMOW	water	0 Ur
$\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$	SLAP	water	-55.5 mUr
$\delta^{34}\text{S}_{\text{VCDT}}$	IAEA-S-1	silver sulfide	-0.3 mUr

In addition to primary measurement standards, a wide variety of secondary isotopic reference materials are distributed internationally and most are listed at [www.ciaaw.org](http://www.ciaaw.org). To produce robust, internationally comparable isotopic results, it is important to adopt a few measurement steps, including the following:

- i. If a second international measurement standard defines the size of a delta scale, such as L-SVEC lithium carbonate for  $\delta^{13}\text{C}$  measurements [25] or SLAP water for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  measurements [26],  $\delta$  values should be normalized using both standards. And authors should state this clearly in their articles and reports.
- ii. Secondary internationally distributed isotopic reference materials that are of a nature similar to those of the unknowns being measured (sulfate, nitrate, cellulose, etc) should be analyzed. This has been called the principle of identical treatment [18] and minimizes systematic errors by subjecting sample unknowns and reference materials to exactly the same chemical and

other manipulation steps, including the transfer pathway to the mass spectrometer ion source. Authors are strongly encouraged to report the  $\delta$  values of these secondary isotopic reference materials in their reports. In this manner, measurement results can be adjusted in the future as analytical methods improve and consensus values of internationally distributed isotopic reference materials are improved and change.

The importance of reporting  $\delta$  values of secondary isotopic reference materials is shown by the measurement results in Figure 5, which displays  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  measurement results on human hair published by Ehleringer et al. [27] and by Coplen and Qi [28]. Although the  $\delta^{18}\text{O}$  results are in satisfactory agreement, the  $\delta^2\text{H}$  results differ by  $\sim 34$  mUr. Because Ehleringer et al. published no measurement results of secondary isotopic reference materials, it is difficult or impossible for readers to adjust  $\delta$  values as might be needed.

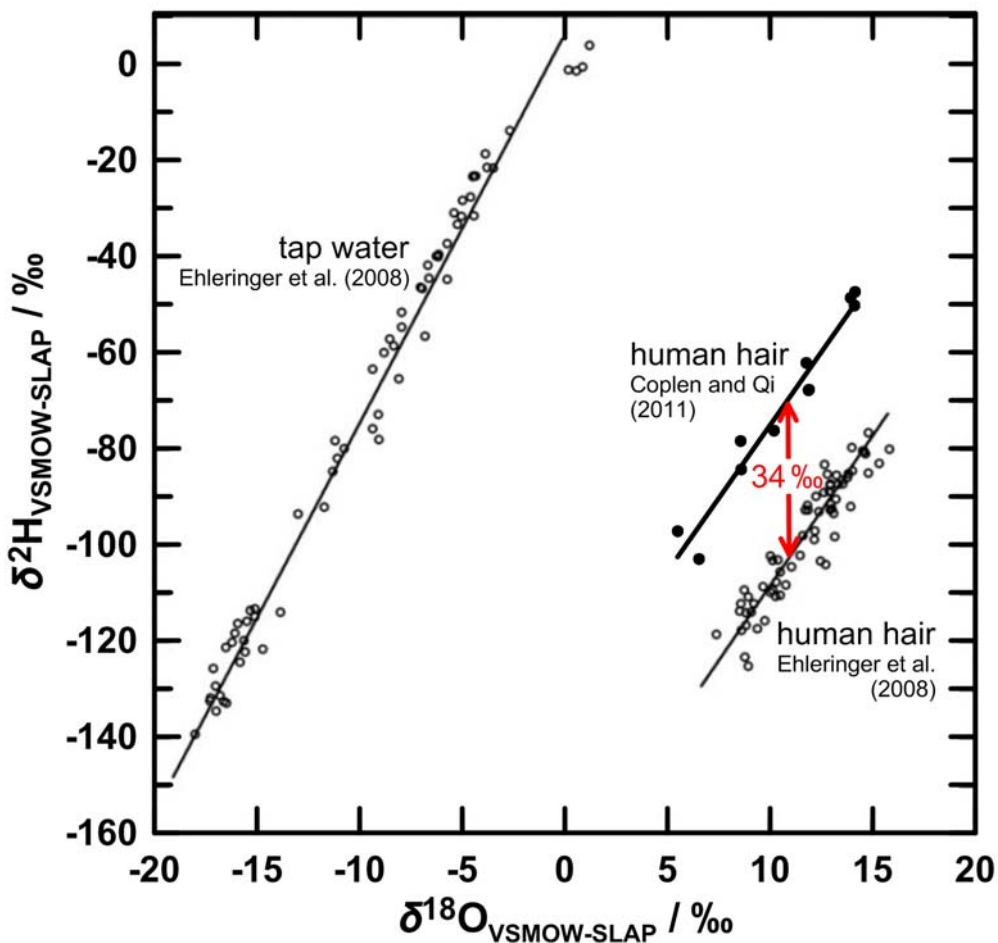


Figure 5. Hydrogen versus oxygen isotopic compositions of tap water and human scalp hair [28]. Open black circles (for human scalp hair;  $\delta^2\text{H}_{\text{VSMOW-SLAP}} = 5.73 \times \delta^{18}\text{O}_{\text{VSMOW-SLAP}} - 166$  mUr; R-square = 0.873) are from Ehleringer et al. [27], and solid black circles are from Coplen and Qi [28], ( $\delta^2\text{H}_{\text{VSMOW-SLAP}} = 6.085 \times \delta^{18}\text{O}_{\text{VSMOW-SLAP}} - 136.0$  mUr; R-square = 0.95).

## ***Examples of isotope systems***

There are numerous examples of stable isotope studies. Typically, these are studies in a particular field of science, and within the respective area, the scope of the studies usually is easily understood. However, for similar experiments, but applied in a different scientific field, a lack of understanding might arise because the context is different. When studying the fate of methane in the atmosphere, the measured stable isotope information ( $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) is normally combined with information of possible source and sink isotope signatures and with meteorological transport to arrive at the final conclusions. On the other hand, the  $\delta^{13}\text{C}$  of testosterone, its precursors in the body, and its metabolites may be studied using a combination of liquid chromatography (LC) or gas chromatography (GC) with an isotope mass spectrometer for detecting doping cases in athletics, or one may investigate  $\delta^2\text{H}$  values of lipids in lake sediments to reconstruct large scale climate change like the meandering of the monsoon system during the Holocene. In any case, these kinds of studies often are difficult to digest for scientists outside the specialized area and for workers in fields that have had little contact and experience with stable isotope subtleties.

In the following, we try to bridge such information gaps or science-language related deficiencies by discussing a few prominent examples of stable isotope systems on Earth. They are listed in no particular order. We discuss a number of very basic properties, which are often taken for granted. These include the  $\delta^{13}\text{C}$  value of atmospheric  $\text{CO}_2$  as well as the hydrogen and oxygen isotope variations in the Earth's water cycle. We maintain the urey for expressing stable isotope variations, which hopefully helps readers to become familiar with this proposed unit. Each topic is introduced as a question or statement, in textbook problem-solving style. The examples are independent of each other; thus, they may be skipped without losing reading fluency.

**- Ice sheet coverage of the polar caps and their relation to the isotopic composition of sea water: How would the isotopic composition of the world's oceans change if all polar ice were to melt?**

Physically, one is looking at a simple mixing process. The results of the mixing can be estimated using mass balance or amount-of-substance balance. The total volume of the world's oceans is  $1.47 \times 10^{18} \text{ m}^3$  (a rough estimation can be made from calculating a spherical shell with mean radius 6400 km and a thickness of 4 km; roughly 70 % of the Earth's surface is covered by oceans). The combined volume of the polar and Greenland ice sheets is  $2.52 \times 10^{16} \text{ m}^3$ . Hence, water bound in polar ice represents  $\sim 1.7$  % of the total terrestrial water mass (the combined amounts of water in rivers, lakes, and the atmosphere are comparatively small and can be neglected in this rough estimate). Assuming an average  $\delta^2\text{H}$  value of  $-250 \text{ mUr}$  for polar ice sheets, one calculates a  $\delta^2\text{H}$  decrease of about  $-4.3 \text{ mUr}$  in the world's oceans after a total melting of the polar ice caps. Similarly, one calculates a decrease of  $\sim -0.55 \text{ mUr}$  for  $\delta^{18}\text{O}$ . Assigning  $\delta^2\text{H} = 0 \text{ Ur}$  and  $\delta^{18}\text{O} = 0 \text{ Ur}$  to the present world oceans, these values represent the average whole-Earth water isotopic compositions. In comparison, the observed isotopic records in the Greenland and Antarctic ice sheets exhibit much larger  $\delta^{18}\text{O}$  variations of  $\sim 5 \text{ mUr}$  [29] and  $\delta^2\text{H}$  variations of  $30\text{--}50 \text{ mUr}$  [30] over time between ice ages and interglacial warm periods. Hence, these shifts are not accounted for by a changing ocean isotopic signature (which would have shown the opposite sign, i.e. more positive  $\delta$  values when it is cold and more negative in warmer times). Rather, they have occurred as a result of isotopic fractionation during evaporation (sea surface temperature) and partial condensation, as well as air transport. They reflect the climatic conditions, superimposed by a source having a slowly changing isotopic signature.

**- How much  $^{13}\text{C}$  corresponds to an annual atmospheric  $\text{CO}_2$  change of -0.03 mUr (back-of-the-envelope calculation) ?**

On average, Earth's carbon is  $\sim 1\%$   $^{13}\text{C}$ . A shift of 0.03 mUr then correspond to  $3 \times 10^{-7}$  of all carbon.

As an example, consider a large living room of  $100 \text{ m}^3$  (about  $40 \text{ m}^2$  with height of 2.5 m). Air typically has a  $\text{CO}_2$  molar mixing ratio of 400 ppm, corresponding to 40 L of  $\text{CO}_2$ . Of this amount, 400 mL is  $^{13}\text{CO}_2$ . A shift of 0.03 mUr then is equivalent to 12  $\mu\text{L}$  of  $^{13}\text{CO}_2$  gas. For comparison, an ordinary droplet of water from a faucet has a volume of  $\sim 100 \mu\text{L}$ .

One can extend this example to the Earth's entire atmosphere. The current total mass of carbon in the atmosphere is  $\sim 750$  Giga-tons ( $750 \times 10^{15} \text{ g}$ )<sup>g</sup>. Of this mass,  $\sim 8 \times 10^{15} \text{ g}$  is  $^{13}\text{C}$ . A shift of 0.03 mUr then amounts to  $2.4 \times 10^{11} \text{ g}$  (240 000 tons), which still appears to be a large number. After all, it reflects annually all  $^{13}\text{C}$  that mankind releases from fossil fuel to the atmosphere, land-use changes, etc. On the other hand, in a 2-L sampling flask, as is typical for air samples collected for monitoring greenhouse gas concentrations, one has  $\sim 4 \mu\text{g}$   $^{13}\text{C}$ , and a shift of 0.03 mUr corresponds to a gain or loss of 0.13 ng  $^{13}\text{C}$  (total) inside the flask. That is the mass that one needs to quantify reliably to follow the fate of carbon in the atmosphere.

However, here is a puzzle: The atmosphere has  $\sim 750 \text{ Gt}$  carbon with a  $\delta^{13}\text{C}_{\text{VPDB}} = \sim -8 \text{ mUr}$ . From inventory bookkeeping it is known that fossil fuel burning and land-use change amount to  $\sim 10 \text{ Gt}$  carbon per year. The corresponding  $\text{CO}_2$  of the latter has a carbon signature of about  $-29 \text{ mUr}$ . Hence, the total observable isotopic shift in the atmosphere per year should be  $10 \text{ Gt} / 750 \text{ Gt} \times (-29 \text{ mUr} + 8 \text{ mUr}) = -0.28 \text{ mUr}$ . The observed amount is only about one tenth of this value. Any ideas?<sup>h</sup>

□

<sup>g</sup> This can roughly be inferred from a 400 ppm  $\text{CO}_2$  concentration in the volume of a spherical shell of 6400 km mean radius and a thickness of  $\sim 7 \text{ km}$  at 1 bar pressure.

<sup>h</sup> Here is a hint: There are large carbon exchange fluxes between the atmosphere and the oceans or the land biosphere. From the  $\delta^{13}\text{C}$  change one can infer the size of the annual exchange, when one quantifies the associated carbon isotopic fractionation.

**- The atmospheric  $\delta^{13}\text{C}_{\text{VPDB}}$  value of  $\text{CO}_2$  has been surprisingly constant at  $\sim -7$  mUr over much of Earth's history. What is controlling this value?**

First, 98 % of the  $\text{CO}_2$  on Earth is dissolved in the oceans. The atmospheric  $\text{CO}_2$  content merely leaks out from this large reservoir. The annual exchange amounts to  $\sim 90$  Giga-tons carbon. There is a small isotopic fractionation of  $\sim 1$  mUr between dissolved  $\text{CO}_2$  and  $\text{CO}_2$  in the gas phase [31, 32]. In carbon isotopic equilibrium, the  $\delta^{13}\text{C}$  of sea-water  $\text{CO}_2$  therefore is similar to that of atmospheric  $\text{CO}_2^i$ ,  $\sim -8$  mUr.  $\text{CO}_2$  in ocean water is in chemical equilibrium with carbonic acid ( $\text{H}_2\text{CO}_3$ ) and its two anions, bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). During  $\text{CO}_2$  formation from this equilibrium reaction, a C–O bond must be broken, a process that favors the lighter isotopes of carbon ( $^{12}\text{C}$ ) and oxygen ( $^{16}\text{O}$ ). The lighter carbon preferentially ends up in the  $\text{CO}_2$  (i.e. the carbonates formed will be correspondingly enriched in  $^{13}\text{C}$ , i.e. with a  $\delta^{13}\text{C}$  near 0 Ur relative to VPDB) while the lighter oxygen is transferred to the outgoing water molecule (and the  $\text{CO}_2$ -oxygen will be depleted in  $^{16}\text{O}$ ). As long as the ocean temperature<sup>j</sup>, pH, and salinity remain constant, the carbon isotopic fractionation will maintain relatively constant carbon isotopic compositions, reflected in the long-term invariant atmospheric  $\delta^{13}\text{C}$  value of  $\text{CO}_2$  of  $\sim -7$  mUr.

□

<sup>i</sup> In times of global climate change, complete equilibrium is not attained. The  $\delta^{13}\text{C}_{\text{VPDB}}$  of the world ocean  $\text{CO}_2$  at present is less negative than that of atmospheric  $\text{CO}_2$ . Both have been altered by adding fossil fuel with a low  $\delta^{13}\text{C}_{\text{VPDB}}$  value.

<sup>j</sup> The  $\delta^{13}\text{C}$  temperature dependence of the  $\text{CO}_2 / \text{HCO}_3^-$  equilibrium is  $\sim -0.1$  mUr / °C.[32]

## **- O<sub>2</sub> in air and oceans: The Dole effect.**

By 1935, Malcolm Dole (and N. Morita independently) discovered a significant atomic weight difference in oxygen in atmospheric oxygen and in water [33, 34]. We now know that O<sub>2</sub> in air contains about 2 percent more <sup>18</sup>O than ocean water with the most recently accepted  $\delta^{18}\text{O}$  value of O<sub>2</sub> in air being +23.88 mUr on the VSMOW scale [35]. Why is 'heavy' oxygen preferentially entering the gas phase? This simple question turned out to require some rather sophisticated experiments and tedious investigations. Here is some of the key information:

- i. All O<sub>2</sub> has been produced solely by photosynthesis for billions of years. The history of variations of O<sub>2</sub> abundance in air displays a number of peaks and valleys, with a maximum of ~35 % approximately 300 million years ago. [36] Current atmospheric O<sub>2</sub> has a turnover time of ~1200 years.
- ii. While an equilibrium exchange of oxygen atoms between atmospheric O<sub>2</sub> and water would leave heavier isotopes (<sup>18</sup>O) preferentially enriched in atmospheric O<sub>2</sub> with an enrichment of ~6 mUr [37], equilibrium exchange does not occur in nature [38] without a suitable catalyst, which has yet to be found.
- iii. During photosynthesis, CO<sub>2</sub> and water are converted to glucose and to O<sub>2</sub>, with the O<sub>2</sub> originating solely from water. In ocean water,  $\delta^{18}\text{O}$  is ~ 0 mUr. In terrestrial plants, the source water present in plant leaves is usually considerably enriched in <sup>18</sup>O over local precipitation by evapo-transpiration [39], with a global average  $\delta^{18}\text{O}$  of ~ +6.5 mUr, albeit highly variable as a function of latitude [40]. During photosynthesis, there is no or little oxygen isotopic fractionation from water to O<sub>2</sub> [41, 42]; hence, O<sub>2</sub> released from plants is similar in oxygen isotopic composition to that of leaf water.
- iv. O<sub>2</sub> is consumed in respiration processes by plants and other living organisms, both on land and in the oceans. Respiration has several components, with different oxygen isotopic fractionation effects [43, 44], thereby altering the remaining oxygen in the atmosphere [40]. When oxygen is consumed during respiration, the lighter <sup>16</sup>O isotope is favored by 15–21 mUr, leaving atmospheric O<sub>2</sub> enriched in <sup>18</sup>O over time.

- v. The  $\delta^{18}\text{O}$  of modern atmospheric oxygen is the result of many processes and their quantitative interplay, including some occurring in the past, which have left their mark on the modern isotopic composition of atmospheric oxygen. The Dole effect, while seemingly stable today, has not been constant over time [45]. Paleo-air, as for instance entrapped in polar ice and firn, has been used to study past values of the  $\delta^{18}\text{O}$  of air, and it differs from the modern value of +23.88 mUr. On the other hand, due to the large amount of  $\text{O}_2$  in the atmosphere, a significant shift in the  $\delta^{18}\text{O}$  of atmospheric oxygen is difficult to achieve within a short time period with current processes, giving rise to the apparent stability and uniformity around the globe of the oxygen isotopic composition of atmospheric oxygen. The latter two properties have earned current atmospheric oxygen the status of an international measurement standard for oxygen stable isotope measurements [35, 46].

### **Acknowledgements**

This manuscript has benefited from a careful review by Roland A. Werner (Institute of Agricultural Sciences – ETH Zurich, Zurich, Switzerland). The support of the U.S. Geological Survey National Research Program made this report possible. Any use of trade, product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

### References

- [1] F. Soddy, "The chemistry of mesothorium," *Journal of the Chemical Society*, vol. 99, pp. 72-83, 1911.
- [2] F. Soddy, "Intra-atomic charge," *Nature*, vol. 92, 1913.
- [3] J. J. Thompson, "Further experiments on positive rays," *Philosophical Magazine*, vol. 24, pp. 209-253, 1912.
- [4] M. E. Wieser and T. B. Coplen, "Atomic weights of the elements 2009 (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 83, pp. 359-396, 2011.
- [5] F. M. Phillips, "Chlorine-36," in *Environmental tracers in subsurface hydrology*, P. Cook and A. Herczeg, Eds. Boston: Kluwer Academic Publishers, 2000, pp. 299-348.
- [6] M. Berglund and M. E. Wieser, "Isotopic compositions of the elements 2009 (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 83, pp. 397-410, 2011.
- [7] S. Ruben and M. D. Kamen, "Radioactive carbon of long half-life," *Physical Review*, vol. 57, pp. 549-549, 1940.



- [8] W. F. Libby, E. C. Anderson, and J. R. Arnold, "Age Determination by Radiocarbon Content - World-Wide Assay of Natural Radiocarbon," *Science*, vol. 109, pp. 227-228, 1949.
- [9] I. Levin, T. Naegler, B. Kromer, M. Diehl, R. J. Francey, A. J. Gomez-Pelaez, L. P. Steele, D. Wagenbach, R. Weller, and D. E. Worthy, "Observations and modelling of the global distribution and long-term trend of atmospheric  $^{14}\text{CO}_2$ ," *Tellus Series B-Chemical and Physical Meteorology*, vol. 62, pp. 26-46, 2003.
- [10] C. D. Keeling, "The Concentration and Isotopic Abundances of Atmospheric Carbon Dioxide in Rural Areas," *Geochimica Et Cosmochimica Acta*, vol. 13, pp. 322-334, 1958.
- [11] C. D. Keeling, "The Concentration and Isotopic Abundances of Carbon Dioxide in Rural and Marine Air," *Geochimica Et Cosmochimica Acta*, vol. 24, pp. 277-298, 1961.
- [12] D. E. Pataki, J. R. Ehleringer, L. B. Flanagan, D. Yakir, D. R. Bowling, C. J. Still, N. Buchmann, J. O. Kaplan, and J. A. Berry, "The application and interpretation of Keeling plots in terrestrial carbon cycle research," *Global Biogeochemical Cycles*, vol. 17, 2003.
- [13] J. B. Miller and P. P. Tans, "Calculating isotopic fractionation from atmospheric measurements at various scales," *Tellus Series B-Chemical and Physical Meteorology*, vol. 55, pp. 207-214, 2003.
- [14] N. Nickerson and D. Risk, "Keeling plots are non-linear in non-steady state diffusive environments," *Geophysical Research Letters*, vol. 36, 2009.
- [15] W. A. Brand, S. S. Assonov, and T. B. Coplen, "Correction for the O-17 interference in  $\delta^{13}\text{C}$  measurements when analyzing  $\text{CO}_2$  with stable isotope mass spectrometry (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 82, pp. 1719-1733, 2010.
- [16] T. B. Coplen, "Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results," *Rapid Communication in Mass Spectrometry*, vol. 25, pp. 2538-2560, 2011.
- [17] Q. L. Zhang, T. L. Chang, and W. J. Li, "A Calibrated Measurement of the Atomic-Weight of Carbon," *Chinese Science Bulletin*, vol. 35, pp. 290-296, 1990.
- [18] R. A. Werner and W. A. Brand, "Referencing strategies and techniques in stable isotope ratio analysis," *Rapid Communications in Mass Spectrometry*, vol. 15, pp. 501-519, 2001.
- [19] W. A. Brand, L. Huang, H. Mukai, A. Chivulescu, J. M. Richter, and M. Rothe, "How well do we know VPDB? Variability of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in  $\text{CO}_2$  generated from NBS19-calcite," *Rapid Communications in Mass Spectrometry*, vol. 23, pp. 915-926, 2009.
- [20] B. N. Taylor and A. Thompson, *BIPM; The International System of Units (SI)*. Washington: <http://pml.nist.gov/Pubs/SP330/sp330.pdf>, 2008.
- [21] R. Dybkaer, "Units for quantities of dimension one," *Metrologia*, vol. 41, pp. 69-73, 2004.
- [22] K. P. Cohen, S. K. Runcorn, H. E. Suess, and H. G. Thode, "H.C. Urey," *Bibliographica; Memoirs of Fellows of the Royal Society*, vol. 29, pp. 622-659, 1983.
- [23] J. T. Brenna, T. N. Corso, H. J. Tobias, and R. J. Caimi, "High-precision continuous-flow isotope ratio mass spectrometry," *Mass Spectrometry Reviews*, vol. 16, pp. 227-258, 1997.

- [24] T. N. Corso and J. T. Brenna, "High-precision position-specific isotope analysis," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 94, pp. 1049-1053, 1997.
- [25] T. B. Coplen, W. A. Brand, M. Gehre, M. Gröning, H. A. J. Meijer, B. Toman, and R. M. Verkouteren, "New guidelines for delta C-13 measurements," *Analytical Chemistry*, vol. 78, pp. 2439-2441, 2006.
- [26] T. B. Coplen, "Reporting of Stable Hydrogen, Carbon, and Oxygen Isotopic Abundances," *Pure and Applied Chemistry*, vol. 66, pp. 273-276, 1994.
- [27] J. R. Ehleringer, G. J. Bowen, L. A. Chesson, A. G. West, D. W. Podlesak, and T. E. Cerling, "Hydrogen and oxygen isotope ratios in human hair are related to geography," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, pp. 2788-2793, 2008.
- [28] T. B. Coplen and H. P. Qi, "USGS42 and USGS43: Human-hair stable hydrogen and oxygen isotopic reference materials and analytical methods for forensic science and implications for published measurement results," *Forensic Science International*, vol. doi:10.1016/j.forsciint.2011.07.035, 2011.
- [29] W. Dansgaard, S. J. Johnsen, H. B. Clausen, D. Dahljensen, N. S. Gundestrup, C. U. Hammer, C. S. Hvidberg, J. P. Steffensen, A. E. Sveinbjornsdottir, J. Jouzel, and G. Bond, "Evidence for General Instability of Past Climate from a 250-Kyr Ice-Core Record," *Nature*, vol. 364, pp. 218-220, 1993.
- [30] J. R. Petit, J. Jouzel, D. Raynaud, N. I. Barkov, J. M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pepin, C. Ritz, E. Saltzman, and M. Stievenard, "Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica," *Nature*, vol. 399, pp. 429-436, 1999.
- [31] J. C. Vogel, P. M. Grootes, and W. G. Mook, "Isotopic Fractionation between Gaseous and Dissolved Carbon Dioxide," *Zeitschrift Fur Physik*, vol. 230, pp. 225-&, 1970.
- [32] W. G. Mook, "C-13 in Atmospheric Co2," *Netherlands Journal of Sea Research*, vol. 20, pp. 211-223, 1986.
- [33] M. Dole, "The relative atomic vweight of oxygen in water and in air," *Journal of the American Chemical Society*, vol. 57, pp. 2731-2731, 1935.
- [34] N. Morita and T. Titani, "Difference in isotopic composition between air- and water-oxygen; electrolytic separation factor of oxygen isotopes," *Bulletin of the Chemical Society of Japan*, vol. 11, pp. 414-418, 1936.
- [35] E. Barkan and B. Luz, "High-precision measurements of O-17/O-16 and O-18/O-16 ratios in H2O," *Rapid Communications in Mass Spectrometry*, vol. 19, pp. 3737-3742, 2005.
- [36] R. A. Berner, "Atmospheric oxygen over Phanerozoic time," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 96, pp. 10955-10957, 1999.
- [37] H. C. Urey and L. J. Greiff, "Isotopic exchange equilibria," *Journal of the American Chemical Society*, vol. 57, pp. 321-327, 1935.
- [38] H. R. Krouse, W. D. Gould, R. G. L. McCready, and S. Rajan, "O-18 Incorporation into Sulfate During the Bacterial Oxidation of Sulfide Minerals and the Potential for Oxygen Isotope Exchange between O2, H2o and Oxidized Sulfur Intermediates," *Earth and Planetary Science Letters*, vol. 107, pp. 90-94, 1991.
- [39] D. Yakir and L. D. L. Sternberg, "The use of stable isotopes to study ecosystem gas exchange," *Oecologia*, vol. 123, pp. 297-311, 2000.

- [40] G. Hoffmann, M. Cuntz, C. Weber, P. Ciais, P. Friedlingstein, M. Heimann, J. Jouzel, J. Kaduk, E. Maier-Reimer, U. Seibt, and K. Six, "A model of the Earth's Dole effect," *Global Biogeochemical Cycles*, vol. 18, 2004.
- [41] R. D. Guy, M. L. Fogel, and J. A. Berry, "Photosynthetic Fractionation of the Stable Isotopes of Oxygen and Carbon," *Plant Physiology*, vol. 101, pp. 37-47, 1993.
- [42] C. L. R. Stevens, D. Schultz, C. Vanbaalen, and P. L. Parker, "Oxygen Isotope Fractionation During Photosynthesis in a Blue-Green and a Green-Alga," *Plant Physiology*, vol. 56, pp. 126-129, 1975.
- [43] B. Luz, E. Barkan, M. L. Bender, M. H. Thiemens, and K. A. Boering, "Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity," *Nature*, vol. 400, pp. 547-550, 1999.
- [44] A. Angert, E. Barkan, B. Barnett, E. Brugnoli, E. A. Davidson, J. Fessenden, S. Maneepong, N. Panapitukkul, J. T. Randerson, K. Savage, D. Yakir, and B. Luz, "Contribution of soil respiration in tropical, temperate, and boreal forests to the O-18 enrichment of atmospheric O-2," *Global Biogeochemical Cycles*, vol. 17, 2003.
- [45] M. Bender, T. Sowers, and L. Labeyrie, "The Dole Effect and Its Variations During the Last 130,000 Years as Measured in the Vostok Ice Core," *Global Biogeochemical Cycles*, vol. 8, pp. 363-376, 1994.
- [46] M. E. Wieser and M. Berglund, "Atomic weights of the elements 2007 (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 81, pp. 2131-2156, 2009.