Isotope Geochemistry
Isotopes

- Isotopes have different number of neutrons, and thus a different mass
- Affect on reactions in small, but real, and provides another measurement of reactions – affected by similar physicochemical parameters!
- Also a critical tracer – the isotopes can be used to track molecules in a reaction!
<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Atomic Weight (amu)</th>
<th>Abundance (atom %)</th>
</tr>
</thead>
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<tr>
<td><strong>Hydrogen (Z = 1)</strong></td>
<td>$^1$H (Protium)</td>
<td>1.007825</td>
<td>99.985</td>
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<tr>
<td></td>
<td>$^2$H (D or Deuterium)</td>
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<td><strong>Carbon (Z = 6)</strong></td>
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<tr>
<td></td>
<td>$^{13}$C</td>
<td>13.00335</td>
<td>1.10</td>
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<tr>
<td><strong>Nitrogen (Z = 7)</strong></td>
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<td>14.003074</td>
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<td><strong>Oxygen (Z = 8)</strong></td>
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<tr>
<td></td>
<td>$^{18}$O</td>
<td>17.999160</td>
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</table>

Fractionation

- A reaction or process which selects for one of the stable isotopes of a particular element
- If the process selects for the heavier isotope, the reaction product is ‘heavy’, the

![Diagram showing isotope fractionation](image-url)

An Isotope Effect causes Fractionation
Fractionation Factor, $\alpha$

- $R$ is the ratio of heavy to light isotopes
- $\alpha$, or fractionation factor, is the ratio between reactant and product

\[
\alpha = \frac{R_{\text{reactants}}}{R_{\text{products}}}
\]

\[
\alpha^{18}\text{O}_{\text{water-vapor}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{water}}}{(^{18}\text{O}/^{16}\text{O})_{\text{vapor}}}
\]
Why a ratio???

- Differences between 2 isotopes of one element is VERY small – to measure them individually with enough precision is difficult to impossible for most isotope systems
- By comparing a sample ratio to a standard ratio, the difference between these two can be determined much more precisely!!
Isotope Standards

• VSMOW – Vienna Standard Mean Ocean Water – bunch of ocean water kept in Austria – O and H standard

• PDB – Pee Dee Belemnite – fossil of a belemnite from the Pee Dee formation in Canada – C and O

• CDT – Canyon Diablo Troilite – meteorite fragment from meteor crater in Arizona, contains FeS mineral Troilite – S

• AIR – Atmospheric air - N
Measuring Isotopes

• While different, isotopes of the same element exist in certain fractions corresponding to their natural abundance (adjusted by fractionation)

\[ \alpha_b^a = \frac{R_a}{R_b} \]

Where \( R_a \) is the ratio of heavy/light isotope and \( \alpha \) is the fractionation factor

• We measure isotopes as a ratio of the isotope vs. a standard material (per mille \( \%o \))

\[ \delta^{18}O = \left( \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 10^3 \%
\]

\[ 10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a \]
δ is “delta”, and is the isotope ratio of a particular thing (molecule, mineral, gas) relative to a standard times 1000. sometimes called ‘del’

\[ \delta^{18}O = \left( \frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 10^3 \]

Δ is “delta” and is the difference between two different isotope ratios in a reaction:

\[ \Delta_{A-B} = \delta_A - \delta_B \]

Many isotopers are very sensitive about misuses of isotope terminology. Harmon Craig’s immortal limerick says it all:

There was was a young man from Cornell
Who pronounced every "delta" as "del"
But the spirit of Urey
Returned in a fury
And transferred that fellow to hell
Equilibrium vs. Kinetic fractionation

- Fractionation is a reaction, but one in which the free energy differences are on the order of 1000x smaller than other types of chemical reactions.
- Just like other chemical reactions, we can describe the proportion of reactants and products as an equilibrium or as a kinetic function.
Because the kinetic energy for heavy and light isotopes is the same, we can write:

\[
\frac{v_L}{v_H} = \sqrt{\frac{m_H}{m_L}}
\]

In the case of \(^{12}\text{C}^{16}\text{O}\) and \(^{13}\text{C}^{16}\text{O}\) we have:

\[
\frac{v_L}{v_H} = \sqrt{\frac{28.99827}{27.994915}} = 1.0177
\]

Regardless of the temperature, the velocity of \(^{12}\text{C}^{16}\text{O}\) is 1.0177 times that of \(^{13}\text{C}^{16}\text{O}\), so the lighter molecule will diffuse faster and evaporate faster.
Equilibrium Fractionation

• For an exchange reaction:
  $$\frac{1}{2} \text{C}^{16}\text{O}_2 + \text{H}_2^{18}\text{O} \leftrightarrow \frac{1}{2} \text{C}^{18}\text{O}_2 + \text{H}_2^{16}\text{O}$$

• Write the equilibrium:
  $$K = \frac{(\text{C}^{18}\text{O}_2)^{\frac{1}{2}} (\text{H}^{16}\text{O}_2)^{\frac{1}{2}}}{(\text{C}^{16}\text{O}_2)^{\frac{1}{2}} (\text{H}^{18}\text{O}_2)^{\frac{1}{2}}}$$

• Where activity coefficients effectively cancel out

• For isotope reactions, $K$ is always small, usually 1.0xx (this $K$ is 1.047 for example)
WHY IS K DIFFERENT FROM 1.0?

Because $^{18}\text{O}$ forms a stronger covalent bond with C than does $^{16}\text{O}$.

The vibrational energy of a molecule is given by the equations:

\[ E_{\text{vibrational}} = \frac{1}{2} h \nu \]

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]

\[ F = -kx \]

Thus, the frequency of vibration depends on the mass of the atoms, so the energy of a molecule depends on its mass.
• The heavy isotope forms a lower energy bond; it does not vibrate as violently. Therefore, it forms a stronger bond in the compound.

• The Rule of Bigeleisen (1965) - The heavy isotope goes preferentially into the compound with the strongest bonds.
Temperature effects on fractionation

• The fractionation factors, $\alpha$, are affected by $T$ (recall that this affects $E_A$) and defined empirically:

$$10^3 \ln \alpha_b^a = \frac{A \times 10^6}{T^2} + B$$

Where $A$ and $B$ are constants determined for particular reactions and $T$ is temp. in Kelvins

• Then,

$$10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a$$

• As $T$ increases, $\Delta$ decreases – at high $T$ $\Delta$ goes to zero
FRACTIONATION DURING PHYSICAL PROCESSES

• Mass differences also give rise to fractionation during physical processes (diffusion, evaporation, freezing, etc.).

• Fractionation during physical process is a result of differences in the velocities of isotopic molecules of the same compound.

• Consider molecules in a gas. All molecules have the same average kinetic energy, which is a function of temperature.

\[ E_{kinetic} = \frac{1}{2} m v^2 \]
Using isotopes to get information on physical and chemical processes

- Fractionation is due to some reaction, different isotopes can have different fractionation for the same reaction, and different reactions have different fractionations, as well as being different at different temperatures and pressures.

- Use this to understand physical-chemical processes, mass transfer, temperature changes, and other things...
Figure 2. Typical oxygen isotopic composition of selected natural materials. Dashed line represents the earth’s mantle. Modified from Hoefs (1997) and Best (2003). Igneous rock values exclude hydrothermally altered rocks.
**Figure 3.** Typical carbon isotopic composition of selected natural materials. Dashed line represents the earth's mantle. Modified from Hoefs (1997). Terrestrial plants include ranges for C3 and C4 plants that use different photosynthetic pathways.
Equilibrium Fractionation II

- For a mass-dependent reaction:
  - $\text{Ca}^{2+} + \text{C}^{18}\text{O}_3^{2-} \rightarrow \text{CaC}^{18}\text{O}_3$
  - $\text{Ca}^{2+} + \text{C}^{16}\text{O}_3^{2-} \rightarrow \text{CaC}^{16}\text{O}_3$
- Measure $\delta^{18}\text{O}$ in calcite ($\delta^{18}\text{O}_{cc}$) and water ($\delta^{18}\text{O}_{sw}$)
- Assumes $^{18}\text{O}/^{16}\text{O}$ between $\text{H}_2\text{O}$ and $\text{CO}_3^{2-}$ at some equilibrium

$$T \, ^\circ\text{C} = 16.998 - 4.52 \left( \delta^{18}\text{O}_{cc} - \delta^{18}\text{O}_{sw} \right) + 0.028 \left( \delta^{18}\text{O}_{cc} - \delta^{18}\text{O}_{sw} \right)^2$$
Empirical Relationship between Temp. & Oxygen Isotope Ratios in Carbonates

At lower temperatures, calcite crystallization tends to incorporate a relatively larger proportion of $^{18}$O because the energy level (vibration) of ions containing this heavier isotope decreases by a greater amount than ions containing $^{16}$O.

As temperatures drop, the energy level of $^{18}$O declines progressively by an amount that is disproportionately greater than that of the lighter $^{16}$O.
Distillation

- 2 varieties, Batch and Rayleigh distillation dependent on if the products stay in contact and re-equilibrate with the reactants.

- Batch Distillation:

  \[ \delta_f = \delta_i - (1 - F) \times 10^3 \ln \alpha_{CO2-Rock} \]

  where the isotope of the rock (\( \delta_i \)) depends on its initial value (\( \delta_f \)) and the fractionation factor.

- Rayleigh Distillation

  \[ \delta_f - \delta_i = 10^3(F^{(\alpha - 1)} - 1) \]
RAYLEIGH DISTILLATION

Isotopic fractionation that occurs during condensation in a moist air mass can be described by Rayleigh Distillation. The equation governing this process is:

\[ R_v = R_v^o f^{a - 1} \]

where \( R_v \) = isotope ratio of remaining vapor, \( R_v^o \) = isotope ratio in initial vapor, \( f \) = the fraction of vapor remaining and \( a \) = the isotopic fractionation factor.
Effect of Rayleigh distillation on the $\delta^{18}\text{O}$ value of water vapor remaining in the air mass and of meteoric precipitation falling from it at a constant temperature of 25°C. Complications:
1) Re-evaporation
2) Temperature dependency of $\alpha$
Evaporation of surface water in equatorial regions causes formation of air masses with H$_2$O vapor depleted in $^{18}$O and D compared to seawater. This moist air is forced into more northerly, cooler air in the northern hemisphere, where water condenses, and this condensate is enriched in $^{18}$O and D compared to the remaining vapor. The relationship between the isotopic composition of liquid and vapor is:

$$\delta^{18}O_l = \alpha^l_v (\delta^{18}O_v + 10^3) - 10^3$$
Assuming that $\delta^{18}O_v = -13.1\%$ and $\alpha_v \text{l}(O) = 1.0092$ at 25°C, then

$$\delta^{18}O_l = 1.0092(-13.1 + 10^3) - 10^3 = -4.0\%$$

and assuming $\delta D_v = -94.8\%$ and $\alpha_v \text{l}(H) = 1.074$ at 25°C, then

$$\delta D_l = 1.074(-94.8 + 10^3) - 10^3 = -27.8\%$$

These equations give the isotopic composition of the first bit of precipitation. As $^{18}O$ and D are removed from the vapor, the remaining vapor becomes more and more depleted. Thus, $\delta^{18}O$ and $\delta D$ values become increasingly negative with increasing geographic latitude (and altitude.
Because both H and O occur together in water, $\delta^{18}O$ and $\delta D$ are highly correlated, yielding the meteoric water line (MWL):

$$\delta D \approx 8\delta^{18}O + 10$$
Majzlan et al., unpublished data
Deviation from MWL

• Any additional fractionation process which affects O and D differently, or one to the exclusion of the other will skew a water away from the MWL plot

• These effects include:
  – Elevation effects - (δD -8‰/1000m, -4‰/°C)
  – Temperature (α different!)
  – Evapotranspiration and steam loss
  – Water/rock interaction (little H in most rocks)
Iron Isotopes

Earth’s Oceans 3 Ga had no oxygen and lots of Fe$^{2+}$, cyanobacteria evolved, produced O$_2$ which oxidized the iron to form BIFs – in time the Fe$^{2+}$ was more depleted and the oceans were stratified, then later become oxic as they are today.

This interpretation is largely based on iron isotopes in iron oxides and sulfide minerals deposited at those times (Rouxel et al., 2005).
Experiments

- \( \text{Fe}^{2+} \) and \( \text{FeS}_{\text{mackinawite}} \) at equilibrium, separate physically (filter) and measure each component:

From Butler et al., 2005 EPSL 236 430-442
Fe –isotope exchange with a particle

- Particles coarsen via Ostwald ripening or topotactic alignment – how fast can isotopes exchange with Fe in a crystal actively getting bigger?
- At certain size internal Fe\(^{2+}\) does not exchange...
What can we get from using multiple isotopes?

• Many isotope systems have more than 2 stable isotopes – $^{56}\text{Fe}$, $^{57}\text{Fe}$, $^{58}\text{Fe}$; $^{32}\text{S}$, $^{33}\text{S}$, $^{34}\text{S}$, $^{36}\text{S}$

• Looking at multiple isotopes can provide new insight on multiple processes, especially useful for complicated reaction pathways, also helps get at equilibrium v. kinetic processes, and mass-dependent v. independent processes…
• Tracing S-isotopic fractionation from different communities of organisms (Sulfate-reducers, sulfur disproportionation, phototrophic S oxid.)

From Zerckle et al., 2009 GCA 73, 291-306
S isotopes and microbes

- The fractionation of H\textsubscript{2}S formed from bacterial sulfate reduction (BSR) is affected by several processes:
  - Recycling and physical differentiation yields excessively depleted H\textsubscript{2}S
  - Open systems – H\textsubscript{2}S loss removes \(^{34}\text{S}\)
  - Limited sulfate – governed by Rayleigh process, enriching \(^{34}\text{S}\)
  - Different organisms and different organic substrates yield very different experimental \(\delta^{34}\text{S}\)
- Ends up as a poor indicator of BSR vs. TSR
Mass-independent fractionation

- Mass effects for 3 stable isotopes (such as $^{18}\text{O}$, $^{17}\text{O}$, and $^{16}\text{O}$) should have a mass-dependent relationship between each for any process.
- Deviation from this is mass-independent and thought to be indicative of a nuclear process (radiogenic, nucleosynthetic, spallation) as opposed to a physicochemical process.
- Found mainly associated with atmospheric chemistry, effect can be preserved as many geochemical reactions in water and rock are mass-dependent.
Volatilization

- calcite + quartz = wollastonite + carbon dioxide
  \[ \text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2 \]
- As the CO\(_2\) is produced, it is likely to be expelled

**Figure 4.** \(\delta^{18}\text{O}\) versus \(\delta^{13}\text{C}\) for volatilization (CO\(_2\)-loss) of a rock with initial \(\delta^{18}\text{O} = 22\%\) and \(\delta^{13}\text{C} = 0\%\). Two values of \(\alpha\) for oxygen (CO\(_2\)-rock) are shown for both Rayleigh (solid lines) and batch (dashed lines) processes, \(\alpha_{\text{carbon}} = 1.0022\). F values shown are for carbon. The F values for oxygen are related by \(F_{\text{oxygen}} = 0.4F_{\text{carbon}} + 0.6\), which is the calc-silicate limit discussed in the text. (modified from Valley, 1986)
• Other volatilization reaction examples...

1. \(3 \text{Do} + 4 \text{Qz} + \text{H}_2\text{O} = \text{Tc} + 3 \text{Cc} + 3 \text{CO}_2\)
2. \(6 \text{Cc} + 4 \text{Qz} + 5 \text{Tc} = 3 \text{Tr} + 2 \text{H}_2\text{O} + 6 \text{CO}_2\)
3. \(3 \text{Cc} + 2 \text{Tc} = \text{Tr} + \text{Do} + \text{H}_2\text{O} + \text{CO}_2\)
4. \(5 \text{Do} + 8 \text{Qz} + \text{H}_2\text{O} = \text{Tr} + 3 \text{Cc} + 7 \text{CO}_2\)
5. \(\text{Do} + 2 \text{Qz} = \text{Di} + 2 \text{CO}_2\)
6. \(\text{Tr} + 2 \text{Qz} + 3 \text{Cc} = 5 \text{Di} + 3 \text{CO}_2 + \text{H}_2\text{O}\)
7. \(\text{Tr} + 3 \text{Cc} = \text{Do} + 4 \text{Di} + \text{H}_2\text{O} + \text{CO}_2\)
8. \(5 \text{Do} + 4 \text{Tr} = 6 \text{Fo} + 13 \text{Di} + 4 \text{H}_2\text{O} + 10 \text{CO}_2\)
9. \(11 \text{Do} + \text{Tr} = 8 \text{Fo} + 13 \text{Cc} + \text{H}_2\text{O} + 9 \text{CO}_2\)
10. \(3 \text{Do} + \text{Di} = 4 \text{Cc} + 2 \text{Fo} + 2 \text{CO}_2\)
11. \(5 \text{Cc} + 3 \text{Tr} = 2 \text{Fo} + 11 \text{Di} + 3 \text{H}_2\text{O} + 5 \text{CO}_2\)
12. \(\text{Do} = \text{Pe} + \text{Cc} + \text{CO}_2\)

Cc = calcite, \(\text{CaCO}_3\)
Do = dolomite, \(\text{CaMg} (\text{CO}_3)_2\)
Di = diopside, \(\text{CaMgSi}_2\text{O}_6\)
Fo = forsterite, \(\text{Mg}_2\text{SiO}_4\)
Pe = periclase, \(\text{MgO}\)
Qz = quartz, \(\text{SiO}_2\)
Tc = talc, \(\text{Mg}_3\text{Si}_4\text{O}_{10} (\text{OH})_2\)
Tr = tremolite, \(\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22} (\text{OH})_2\)
Figure 5. Fractionation of oxygen isotopes between selected minerals (and volatiles) and calcite. $10^3\ln\alpha$ between solids is normally assumed to be linear with $1/T^2$ as shown. Dashed lines are projected outside their experimental temperature range. Fractionation factors used are from various studies summarized in Chacko et al., 2001. H$_2$O-calcite is from O’Neil et al. (1969), updated by Friedman and O’Neil (1977), dolomite-calcite is from Sheppard & Schwarz (1970).
Figure 1. Fractionation of oxygen isotopes between calcite and water as a function of temperature (0-500°C). From O’Neil et al. (1969), updated by Friedman and O’Neil (1977), $10^3 \ln \alpha_{\text{Cc-H}_2\text{O}} = 2.78(10^6 T^{-2}) - 2.89$, $T$ in Kelvin in this equation.
Figure 1. Periodic table with selected elemental properties relevant for stable isotope research. Indicated are the number of stable isotopes of an element (upper right corner), the mass of the isotope commonly used in the delta value or alternatively the most abundant isotope (upper left corner), and the potential influence of radiogenic (RAD) and cosmogenic processes (COS) as well as mass-independent fractionation (MIF) on the stable isotope system (below the element symbol). In most cases, MIF due to nuclear volume \(^{11}\) or magnetic isotope effects \(^{23}\) (see section “Mass-Independent Fractionation (MIF)”) has only been observed in laboratory scale studies and has not yet been detected in natural samples (except for O, S, and Hg, marked in bold). The “traditional” stable isotope systems are marked with a red border. Elements for which high-precision stable isotope methods have been developed are marked with a bold symbol. The actinides possessing no stable isotopes are not included (except for U with two long-lived radionuclides exhibiting stable isotope fractionation). Please see SI Table S1 for details on individual elements.
Figure 2. Schematic illustration of metal stable isotope fractionation during mineral dissolution and delta values of the involved nuclides from Wiederhold (2015). In the presented example, a small fraction (2%) of an iron mineral with 1 million Fe atoms is dissolved (at conditions: 95% \(^{56}\)Fe + 5% \(^{54}\)Fe; the surface layer corresponds to 4% of the total mineral). Without isotope fractionation, the dissolved \(^{56}\)Fe atoms contain 1000 \(^{56}\)Fe atoms. However, metal isotope fractionation manifests itself by the preferential release of one light \(^{54}\)Fe atom with a value of −1‰ in solution. The influence on the isotopic signature of the bulk mineral is negligible (+0.02 ‰) due to its low concentration. However, a relative enrichment of heavy isotopes is created at the mineral surface. The general magnitude of metal stable isotope fractionation illustrated in this example is similar to the extent of fractionation observed in nature. However, in order to compare the dimension in mind that one gram of soil usually contains about 10^9 Fe atoms.

Figure 3. Schematic illustration of kinetic (a) and equilibrium (b) stable isotope fractionation. Natural samples can be affected by both types of fractionation and it is often challenging to elucidate their relative controls on the observed metal stable isotope signatures. Please note that the equations in panel a explaining the “driving force” of kinetic isotope fractionation can usually not be applied directly using \(m_1\) and \(m_2\) as the masses of the studied metal isotopes, because metals are in most cases part of a larger complex or molecule which is reacting in the kinetic process. Furthermore, the indicated trends for equilibrium fractionation in panel b should only be regarded as qualitative rules of thumb (see text for details).

Figure 4. Rayleigh fractionation describing the evolution of isotope ratios in different pools of a unidirectional process, displayed here for the example of Cr isotope ratios ($\delta^{33}\text{Cr}$) during the reduction of aqueous Cr(VI) to Cr(III) precipitates, with a starting composition of 0% and an enrichment factor $e$ of -13%. The largest fractionations are found in the reactant (dotted line) at advanced stages of the reaction (low fraction remaining). The difference between the reactant and the instantaneous product (dashed line) corresponds to the enrichment factor $e$ at all stages of the reaction. In contrast, the difference between the reactant and the cumulative product (solid line) is increasing with progressing reaction and the $\delta$ value of the cumulative product of a completed reaction (fraction remaining equals zero) is identical to the starting composition of the reactant. Please see section “Process Tracing” for equations used for calculations of lines.

Figure 5. Schematic illustration of fractionation mechanisms for the Hg isotope system (adapted from Wiederhold et al.37). The arrows indicate qualitatively the influence of the mass difference effect (MDE), the nuclear volume effect (NVE), and the magnetic isotope effect (MIE) on the seven stable Hg isotopes. Mass-independent fractionation (MIF), which is defined as a measured anomaly compared with the trend of the MDE, is observed mainly for the two odd-mass isotopes $^{199}$Hg and $^{201}$Hg and can be caused either by the NVE due to their nonlinear increase in nuclear charge radii or the MIE due to their nuclear spin and magnetic moment. The relative extent of the nuclear charge radius anomalies ($x/y = 1.6$) causes the characteristic slope in a $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ plot for the NVE in comparison to slopes observed for Hg(II) photoreduction (1.2) and methyl Hg photodemethylation (1.36) due to the MIE.56 The magnitude of MIF due to the NVE is generally much smaller than MIF by the MIE. The MIE occurs only during kinetically controlled processes (in natural systems probably always related to photosynthetic reactions) whereas the NVE and the MDE occur during both kinetic and equilibrium processes. The relative importance of MDE and NVE on the overall fractionation can vary depending on the reacting species.37

Figure 7. Schematic illustration of the principles of mixing models for source tracing with metal stable isotope signatures. Panel a depicts the mass balance between two metal pools of opposite isotope signatures and equal size. The effect of different pool sizes (pool A = 4 pool B) is shown in panel b, and the combined effect of different pool sizes and isotope signatures is illustrated in panel c. Panel d illustrates a schematic example of a natural river system for which the relative fractions of natural and anthropogenic metal sources can be identified by metal isotope signatures.
Fig. 4. A plot of experimentally measured copper isotope fractionations between solution Cu(II) and copper species or minerals in abiogenic conditions. The significant fractionation differences between Cu(II) and Cu(I) species are clearly revealed. Data sources: CuS and Cu(OH)$_2$—this study; other fractionation factors are taken from the data given in Table 1.

Fig. 3. $\delta^{65}\text{Cu}$ values for all analyzed samples from the Schwarzwald mining district.

Fig. 4. Copper isotope compositions of various copper minerals from selected localities in the Schwarzwald mining district. Note the large spread in $\delta^{65}\text{Cu}$ at each locality. The vertical dashed lines indicate the range of copper isotope compositions of fresh, unoxidized primary ores from the localities and show the difference between the two sample groups discussed in the text.
Fig. 5. (a) $\delta^{65}$Cu of minerals from the same hand specimen. The diagram is divided into three parts: the uppermost part shows secondary Cu(II) minerals in contact with relics of primary Cu(I) minerals from the two "anomalous" localities, where the fresh, primary Cu(I) minerals appear to have $\delta^{65}$Cu values significantly different from 0; the middle part shows secondary Cu(II) minerals in contact with relics of primary Cu(I) minerals from localities where the fresh, primary Cu(I) minerals have $\delta^{65}$Cu values around 0; the lowermost part shows secondary Cu(II) minerals in contact with relics of secondary Cu(I) minerals (cuprite). The grey symbols indicate the $\delta^{65}$Cu values of fresh, primary Cu(I) minerals from the respective locality. Note, that no fresh sample could be measured from Neubulach. (b) $\delta^{65}$Cu values of Cu(I) ore minerals (chalcopyrite, fahlore and emplectite). Completely fresh samples cluster in a narrow range around 0‰ (note, however, that the fresh emplectite from Königswart is significantly lighter), whereas partly oxidized samples exhibit a range of $\delta^{65}$Cu values down to −3‰. (c) Photograph of sample M2-2 from the Friedrich-Christian mine in Wildschapbach. The particles analyzed (Tables 1 and 2) were taken from about the areas, where the "malachite" and the "chalcopyrite" arrows point. Abbreviations: fahl, fahlore; cup, cuprite; mal, malachite; chry, chrysocolla; ol, olivenite; ccp, chalcopyrite.
Fig. 6. The results of Rayleigh-type mass balance calculations using an initial fluid with a δ⁶⁴Cu of zero. (a) A Cu(I)-bearing fluid is oxidized and Cu(II) is precipitated quantitatively e.g. as malachite; Cu(I)/Cu(II) fractionation in the fluid is governed by a fractionation factor of 1.004 as experimentally determined by Zhu et al. (2002). (b) A Cu(II)-bearing fluid precipitates a Cu(II) mineral; fractionation here is governed by the fluid solid fractionation factor of 1.0002 as determined by Marechal and Sheppard (2002). \( F \) is the fraction of original species consumed.
Majzlan et al., unpublished data
Experimental investigations
Precipitation (Cu(II)_{aq} - Cu(II)_s)
- Ehrlich et al., 2004
- Maréchal and Sheppard, 2002
Reduction (Cu(II)_{aq} - Cu(I)_s)-precipitation
- Zhu et al., 2002
- Ehrlich et al., 2004
- Pękal et al., 2011
Reduction (Cu(0)_s - Cu(II)_{aq})-Electrodeposition
  - This study
  - Black et al., 2011

Theoretical predictions
Fujii et al., 2013
1. $\Delta^6 \text{Cu}[\text{Cu}(\text{H}_2\text{O})_6^{2+} - \text{CuSO}_{4(\text{aq})}]_{\text{eq}}$
2. $\Delta^6 \text{Cu}[\text{Cu}(\text{H}_2\text{O})_5^{2+} - \text{CuSO}_{4(\text{aq})}]_{\text{eq}}$
3. $\Delta^6 \text{Cu}[\text{Cu}(\text{H}_2\text{O})_5^{-} - \text{Cu}(\text{H}_2\text{O})_6^{2+}]_{\text{eq}}$
4. $\Delta^6 \text{Cu}[\text{Cu}(\text{H}_2\text{O})_5^{-} - \text{Cu}(\text{H}_2\text{O})_6^{2+}]_{\text{eq}}$

Sherman, 2013
5. $\Delta^6 \text{Cu}[\text{Cu}_2\text{O} - \text{Cu}(\text{H}_2\text{O})_3^{2+}]_{\text{eq}}$
6. $\Delta^6 \text{Cu}[\text{CuFeS}_2 - \text{Cu}(\text{H}_2\text{O})_5^{2+}]_{\text{eq}}$

Black et al., 2011
7. $\Delta^6 \text{Cu}[\text{Cu}^3 - \text{Cu}(\text{H}_2\text{O})_6^{2+}]_{\text{eq}}$
Fig. 16. a) Cu isotopic composition of the primary tetrahedrite, trombolite, and various supergene copper minerals (as marked in the figure) at the site Piesky; b) relationship between δ^{65}Cu and δ^{13}C in malachite (white circles) and azurite (grey circles) samples. Measured values are listed in Tables 4 and 5. The error bars are one standard deviation, calculated from the scatter of the analytical data for each sample.
Fig. 17. Rayleigh fractionation model for a reactant (aqueous solution with initial $\delta^{65}\text{Cu} = -2.45\%_o$, the isotopic composition of the primary tetrahedrite), and a product (covellite).
Figure 1
Overview of the general patterns in isotope fractionation that have been observed experimentally ($\Delta^{199}$Hg versus $\delta^{202}$Hg). For comparison, the scale is the same as in Figure 2. For each process, the direction of the arrow indicates the isotopic evolution of either the reactant or product as indicated by colored labels. Reactions are as follows: The light blue arrow indicates fractionation during equilibrium evaporation (MIF due to the nuclear volume effect) (Estrade et al. 2009, Ghosh et al. 2013); the dark blue arrow indicates fractionation during microbial reduction of Hg(II) and demethylation of MeHg (Kritee et al. 2007, 2009); the light green arrow indicates fractionation during Hg binding to thiol ligands and Hg sorption to iron oxides (Jiskra et al. 2012, Wiederhold et al. 2010); the dark green arrow indicates fractionation during methylation of Hg(II) by sulfate-reducing bacteria (Rodriguez-Gonzalez et al. 2009); the red arrow indicates fractionation during photochemical demethylation of MeHg from aqueous solutions (MIF due to the magnetic isotope effect) (Bergquist & Blum 2007); the orange arrow indicates fractionation during photochemical reduction of Hg(II) from aqueous solutions (MIF due to the magnetic isotope effect) (Bergquist & Blum 2007, Zheng & Hintelmann 2010); the magenta arrow indicates fractionation during photochemical reduction of Hg(II) from snow crystals (MIF due to the magnetic isotope effect) (Sherman et al. 2010); and the purple arrow indicates fractionation due to artificial light-induced Hg(II) reduction via thiol ligands (MIF due to the magnetic isotope effect) (Zheng & Hintelmann 2010). Abreviations: MIF, mass-independent fractionation; NIST SRM 3133, National Institute of Standards and Technology Standard Reference Material 3133.