A Primer on the Concepts and Uses of Stable Isotope Geochemistry

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For the Summer, 2022 COESSING School
August 2, 2022
“I have lived much of my life among molecules. They are good company.”
— George Wald

Chemists, physicists and most other scientists and engineers approach molecules, minerals and other materials like small machines, asking questions about their structure, dynamics, behaviors and uses.

Protein enlarged by a factor of \(~10^9\) and slowed by a factor of \(~10^{12}\)

The ~52 million known compounds

~1.7 M Inorganic

~50 M Organic

~4000 minerals
Geoscientists and other natural scientists ask other sorts of questions, motivated by a need to know the unique history of each sample:

- From *what* was it made?
  - *How* was it made?
    - *When* was it made?
    - *Where* have it’s travels brought it?
  - *What conditions* has it experienced? (T, P, pH, etc.)
  - *What processes* has it experienced after formation?
  - *To whom* does it belong?
DNA is a familiar case where chemical structure alone answers many of these sorts of questions

- Tremendous structural complexity and diversity
- Individualized through mutation and inheritance
- Analyzable through gene sequencing

Forensics
Diagnosis
Treatment
Engineering
But most of the rest of the chemical world seems anonymous by comparison.

- Also serve essential functions
- But most are structurally simple
- More importantly, they are uniform. Everyone’s sugar molecules seem the same

Or are they...
Atoms

“Look closely. The beautiful may be small.”
Immanuel Kant

Proton – positive charge, heavy
Neutron – uncharged, heavy
Electron – negative charge, light
Electron orbital ‘path’

Number of Protons ➔ electronic structure ➔ chemical properties
Isotopes: ‘At the same place’

i.e., two (or more) nuclear species that occupy the same space on the periodic table of elements

**Hydrogen**
- 99.99% of natural hydrogen

**Deuterium**
- 0.01% of natural hydrogen
  - Stable

**Tritium**
- 1 part in $10^{18}$ of natural hydrogen
  - Radioactive
Isotopes turn molecules into nearly infinitely complex records of process, history and forensic identity.

*Consider Sucrose (table sugar)*

- **Single substitutions**: $D \text{ or } ^{18}O \text{ or } ^{13}C$
- **Position-specific differences**: $^{13}C$
- **Non-adjacent multiple substitution**: $D \text{ and } D$
- **Adjacent multiple substitution**: $^{18}O \text{ and } D$

$\sim 3 \times 10^{15}$ different versions

The human genome has $\sim 25,000$ genes

Our galaxy contains $\sim 3 \times 10^{11}$ stars
Radioactive decay is one source of isotopic ‘signals’

*Dating the Chernobyl reactor disaster using radioactive iodine*


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**Production ratio**

$^{133}_{\text{I}}/^{131}_{\text{I}}$

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![Image of a graph showing the production ratio of $^{133}_{\text{I}}/^{131}_{\text{I}}$ over April 1986.]
We date the DNA in your cells using radioactive $^{14}$C from cold-war era atom bombs.
Chemical physics, especially quantum mechanics, leads to more subtle, but complex and ubiquitous natural isotopic variations

“Because atomic behavior is so unlike ordinary experience, it is difficult to get used to, and it appears peculiar and mysterious to everyone – both to the novice and to the experienced physicist.”

Richard Feynman (1963)
Diffusion of gas through pores or tubes can separate isotopes

Kinetic energy ($E$) is proportional to temperature

\[
\text{Velocity} = \left(\frac{2x E}{\text{Mass}}\right)^{1/2}
\]

Stomata of a Box Elder leaf; photo by Andrew Syred
Gravitational ‘settling’

- Heavy isotope
- Light isotope

Acceleration

‘Top heavy’ = unstable

‘Bottom heavy’ = stable

Glacial firn, Weissmiesgletscher Switzerland
Photo by J. Alean
Chemical bonds are (sort of) like springs
Higher mass = lower frequency

Energy ∝ frequency, thus...

Higher mass = lower frequency = lower energy = more stable

Chemical isotope effects
Absorption spectra of molecules changes with isotopic substitution

Infrared light transmitted through CO$_2$ gas;
Absorption features are where light couples with molecular vibrations

"isotope effect"
The effect of isotopic mass on bond vibrations can change how something smells (at least, to a fly)

It is widely believed that our sense of smell depends on molecular shape matching a sensor site – like a key to a lock

But flies exposed to an odorant they normally love (e.g., Acetophenone) will avoid it if its molecular vibration frequencies are changed through isotopic substitution

Franco et al., 2011
Chemical isotope effects

‘Heavy’ water boils at 101.4 °C, not 100 °C (and it is poisonous!)
A schematic view of earth’s water cycle
Tracking the locations of migratory graduate students

Ehleringer et al., 2008
Isotope effect on a heterogeneous reaction

Energy

Carbonate

Water

Carbon

Oxygen

Hydrogen
Isotope effect on a heterogeneous reaction

Energy

Carbonate

Water

Better
So, some types of chemical bonds ‘steal’ rare, heavy isotopes from other types of bonds.
Another simple but important term

The entropy (or ‘randomness’) of isotopic distribution

- Very few ways atoms can be arranged that ‘look’ different
- A low entropy state

- Very many ways atoms can be arranged that ‘look’ different
- A high entropy state
Temperature dependence of isotope exchange reactions

Easiest to understand through classical thermodynamics

\[ \Delta G = \Delta H - T\Delta S \]

Total energy change of reaction (negative is better)

- Enthalpy of reaction; like frequency effect on vibration energy
- Entropy of reaction; random states have high entropy

Enthalpy ‘wins’:
\(^{18}\text{O} \) concentrated into carbonate, out of water

Entropy ‘wins’:
\(^{18}\text{O} \) randomly shared between carbonate and water
The ‘Zachos curve’ — A record of Cenozoic ocean temperature*

(* Assuming you know how much $^{18}$O is in sea water!)

Benthic Foraminifera

Zachos, 2001
The broadest overview of organismal-scale biosynthetic isotopic fractionation

**Autotrophy**

\[
\text{CO}_2 \xrightarrow{\text{Fixation}} \text{Photosynthesize (C}_3\text{-C}_6 \text{ carbohydrates)} \xrightarrow{\text{Biosynthesis}} \begin{array}{c}
\text{Proteins} \\
\text{Carbohydrates} \\
\text{Lipids} \\
\text{Nucleic Acids}
\end{array}
\]

**Heterotrophy**

Organic material, "food" \xrightarrow{\text{Assimilation}} \text{Metabolic Intermediates (C}_2\text{-C}_6 \text{ acids and carbohydrates)} \xrightarrow{\text{Biosynthesis}} \begin{array}{c}
\text{Proteins} \\
\text{Carbohydrates} \\
\text{Lipids} \\
\text{Nucleic Acids}
\end{array}

These sorts of reactions involve reduction of inorganic carbon (or analogous changes in oxidation state and bonding environment of H, N, S, etc.) and are generally very effective at separating isotopes.

“You are what you eat” principle: Bulk living biomass of heterotrophs is similar in $^{13}$C content to their food; i.e., if you ‘shuffle’ reduced carbon instead of reducing oxidized carbon, there is little overall isotopic discrimination (though possibly molecule- and site-specific effects).
Biological isotope effects associated with carbon fixation

\[ \text{Light} + \text{RuBisCO} \]
\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Sugar} + \text{O}_2 \]

Abundance of $^{13}\text{C}$

- CO$_2$ in air
- C4 plants
- C3 plants
- Microbial methane
Carbon isotope ecology based on differences in $^{13}$C content between C3 and C4 plants

*Tracking the diets of migratory elephants*

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Cerling et al., 2006
Criminal forensics of plant products

- Isotopic signatures of plants depend on growth conditions (humidity, soil type, etc.)
- This imparts a poorly understood but observable ‘provinciality’
- Used for many purposes, including rolling up drug trafficking organizations
Experimental evidence that you are what you eat

Isotopic composition of natural human hormones

*C4 plants (e.g., corn)*

*Background values*

*Forced increase in C4-based foods*

*All drift toward food source*

*C3 plants (e.g., soy bean)*
Synthetic testosterone is usually made from phytosterol precursors, typically from soy. Isotopic composition of Floyd Landis’ hormones:

- **C4 plants (e.g., corn)**
- **C3 plants (e.g., soy bean)**

Isotopic proof that Floyd Landis is both a cheat and not very smart.
The preceding well-known applications are great, but what about all the other details molecular isotopic structure could record?

Consider Sucrose (table sugar)

- Single substitutions: $D$ or $^{18}O$ or $^{13}C$
- Position-specific differences
- Non-adjacent multiple substitution: $D$ and $D$
- Adjacent multiple substitution: $^{18}O$ and $D$

$\sim 3 \times 10^{15}$ different versions
New technology is what turns ideas into action

*We must measure what is measurable and make measurable what cannot be measured.*

—Galileo Galilei c. 1610

**Nuclear magnetic resonance spectroscopy**

**High resolution sector mass spectrometry**

**Cavity ring down spectroscopy**

**Fourier transform mass spectrometry**

**Ultra-high resolution sector MS**
Multiple rare-isotope substitutions (isotope ‘clumping’) is a special, energetically favorable state of intramolecular rare-isotope ordering.

\[ \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \]

\( \mu = 1/2, \nu = 4395 \text{ cm}^{-1} \)

\[ \nu' = \frac{1}{2\pi}\left(\frac{k}{\mu'}\right)^{1/2} \]

\( \mu' = 2/3, \nu' = 3806 \text{ cm}^{-1} \quad \Delta\nu = 589 \text{ cm}^{-1} \)

\[ \nu'' = \frac{1}{2\pi}\left(\frac{k}{\mu''}\right)^{1/2} \]

\( \mu'' = 1, \nu'' = 3108 \text{ cm}^{-1} \quad \Delta\nu = 1287 \text{ cm}^{-1} \)

\[ 1287 > 2 \times 589 \]
Isotopic ‘clumping’ reactions

‘Scrambled’; favored at high temperatures

A very slow vibrating, very stable ‘clump’

‘Clumped’; favored at low temperatures
Just as for heteroegeneous reactions, the enthalpy and entropy terms compete, creating a temperature dependence.
Determining the temperature of origin of anthropogenic \( CO_2 \)

\[
\Delta_{47} (\%o) = \frac{^{13}C^{16}O_2 + ^{12}C^{18}O^{16}O}{^{12}C^{16}O_2 + ^{13}C^{18}O^{16}O}
\]

Affek and Eiler, 2006
Let’s try to solve something really tricky — the body temperatures of dinosaurs

*Did Dinosaurs more closely resemble modern lizards or modern birds?*
Predicting body temperatures for various hypotheses regarding Dinosaur metabolism

- Mammals and birds
  - Gigantothermy
  - The familiar form of endothermy

- Modern reptiles
  - The familiar form of ectothermy

- And, ectotherms will vary with environment as well as size.
- Heterotherms might vary with ontogenetic age.
‘Clumping’ in the carbonate minerals

\[ \text{Ca}^{13}\text{C}^{16}\text{O}_3 + \text{Ca}^{12}\text{C}^{18}\text{O}^{16}\text{O}_2 \leftrightarrow \text{Ca}^{12}\text{C}^{16}\text{O}_3 + \text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2 \]

*Disordered*  
Favored at high temperature

*Ordered*  
Favored at low temperature
Isotopic ‘clumping’ in teeth and egg shells

Cross-section of a modern Crocodile tooth

Close-up of a Cretaceous mammal tooth

\[ ^{13}\text{C}^{16}\text{O}_3 + ^{12}\text{C}^{18}\text{O}^{16}\text{O}_2 = ^{12}\text{C}^{16}\text{O}_3 + ^{13}\text{C}^{18}\text{O}^{16}\text{O}_2 \]
Taking our method for a spin with a variety of ‘known’ living and extinct animals

Body mass (kg; logarithmic)

Body T (°C)

Line of death

Cold environments (deep sea)

Endotherms

Ectotherms
An overview of all data for dinosaurs

- Some are ‘warm blooded’ in a simple sense
- But overall too variable, and often too cold, to closely resemble birds and mammals
- ‘Gigantothermy’ is a plausible model for the animals studied to-date
This sort of measurement has opened new fronts on many challenging problems in earth history.

**Paleoclimate reconstructions**

Pre-industrial
(280 ppm CO₂)

Last glacial
Maximum
(180 ppm CO₂)

∆T = 4 ˚C

Work of Aradhna Tripati
A brand-new paper uses this method to re-examine the Cenozoic history of ocean temperatures.
Some take-aways

• The naturally-occurring, ‘stable’ isotopes are all around us, making up ~1%, on average, of all the atoms you encounter

• They combine in a dizzyingly complex variety of ways to create vast families of isotopically unique molecules

• The presence of isotopes changes properties, stabilities and rates of reaction for molecules, minerals and other materials

• Separation of isotopes through various physical and chemical processes imparts distinctive signatures that serve as records of natural conditions and processes

• Three iconic uses in the earth sciences are hydrology, ‘geothermometry’ and forensic fingerprinting of metabolisms in natural ecosystems

• Advances in analytical technology are making it possible to use molecular isotope structures as new, highly flexible tools for study of natural processes