Isotope geochemistry of N, S, and other redox-active elements

Reading: S Isotopes Chapter (Canfield’s) from Valley and Cole
White’s Chapter 28 has material on N and S isotopes
For info on Se, Cr, Mo, Fe: See Reviews in Mineralogy and Geochemistry (RiMG),
volume 55, “Non-traditional Stable Isotopes”

Guide Questions:
How much do various chemical processes fractionate N isotopes?
Is the N isotope fractionation during reduction of nitrate to N₂ (denitrification) always the same
or does it vary? If so, why? Roughly how large is it?
What determines the δ¹⁵N and δ¹⁸O values of nitrate (before any denitrification)?
Are the various sources of nitrate in the environment isotopically distinct?
Are the δ¹⁵N and δ¹⁸O values of nitrate immutable or can they be altered after the nitrate is
formed?
Does the oxygen in nitrate equilibrate isotopically with the water it is dissolved in? What about
the oxygen in sulfate? Carbonate/bicarbonate?
What are the major drivers of sulfur isotope fractionation? Which reactions cause large
fractionations? Which do not? Are these kinetic or equilibrium isotope effects?
Why is sulfate in the oceans enriched in the heavy isotope relative to the bulk earth value?
What, in general, can past values of δ³⁴S tell us about the ancient oceans? What would the δ³⁴S of
the oceans be if the atmosphere were reduced (no oxygen) and sulfate were not found in the
oceans?
Are various sources of S in the atmosphere (sea sulfate aerosols vs. sulfuric acid from coal
burning, etc.) isotopically distinct?
Selenium isotope systematics are somewhat similar to those of another element? Which element
is it?
What can chromium isotopes tell us about chemical reactions affecting Cr in the environment?
If the ⁹⁸Mo/⁹⁵Mo ratio in seawater was smaller during a certain period of earth history, what does
this suggest about the oceans during that period?
Are Fe isotopes fractionated by reduction reactions? By oxidation reactions?

Nitrogen:
¹⁵N is 0.36% of the total
¹⁴N is 99.64% of the total
Isotope Ratio Standard: N₂ from the atmosphere- same value everywhere

Nitrogen critical to life processes: Amine groups in amino acids and proteins:

Nitrogen’s redox behavior:

<table>
<thead>
<tr>
<th>Form</th>
<th>Reduction/Oxidation</th>
<th>Isotopic Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate...</td>
<td>NO₃⁻</td>
<td>+5 (MOST OXIDIZED)</td>
</tr>
<tr>
<td>Nitrite...</td>
<td>NO₂⁻</td>
<td>+3</td>
</tr>
<tr>
<td>Nitrogen Gas</td>
<td>N₂</td>
<td>0</td>
</tr>
<tr>
<td>Ammonia/Ammonium</td>
<td>NH₄⁺, NH₃⁻</td>
<td>-3</td>
</tr>
<tr>
<td>Amine groups (in proteins)</td>
<td>R-NH₃</td>
<td>-3, (MOST REDUCED)</td>
</tr>
</tbody>
</table>
Fractionation mechanisms:

1. Biological:
   
   Assimilation (uptake for use in living tissue)- microbes: $\varepsilon = 1$ to 15‰
   Assimilation- higher plants: <1‰ (true for S and Se as well- different from carbon)
   Assimilation- animals: Small fractionation as plants are eaten by animals- “You are what you eat, plus or minus 1 per mil.”

   $N_2$ fixation (conversion of atmos. $N_2$ to plant nitrogen): <2‰

   Nitrification = $NH_4^+ \rightarrow NO_3^- : 25\%e \pm 10\%e$
   
   $NO_3^-$ is the form taken up by plants
   However, note that if process goes to completion, there’s no fractionation

   Denitrification = $NO_3^- \rightarrow N_2 : 5$ to 30 ‰, depends on rate, see below.

   Nitrate reduction = $NO_3^- \rightarrow NH_4^- :$ roughly the same?

   Organic matter breakdown:
   
   Light N reacts faster, leaves residual compounds heavy (small effect)
   e.g., Cultivation of soils --> heavier N
   e.g., Organic matter particles in ocean at great depth --> heavier N

   Trophic level effects:
   
   Excretion of light N as urea, etc.
   N of living tissues increasingly heavy at higher trophic levels

2. Abiotic fractionation: LARGE Equilibrium fractionation between $NH_3$ and $NH_4^+$
   $\alpha=1.034$, $1000ln\alpha = 33\%e$; $NH_3$ takes the lighter isotope preferentially

   Degassing of ammonia from, e.g., manure leaves remaining $NH_4^+$ heavy

Bacterial cells reducing nitrate, sulfate, etc.: Recall from before, that the state of the microbes’ metabolism determines the size of the isotopic fractionation...

   High nutrient conditions: Diffusion becomes somewhat rate limiting, i.e., it becomes less reversible, and mostly a one-way process. Thus, isotopic fractionation is less than when bacteria are starved.

   Low-nutrient conditions: Activated enzymes that break bonds to make the reaction happen inside the cell are not very plentiful, so this reaction step becomes rate-limiting. Diffusion between outside solution and the cell’s interior approaches equilibrium, and the overall isotopic fractionation is close to the internal enzymatic reaction. This reaction involves breaking of bonds and has a large kinetic isotope effect.

   ALSO: Different microbes may have different kinetic isotope effects, if their metabolic pathways are different.

Plot from Mariotti et al, epsilon versus rate for denitrification
N and O isotopes in nitrate

N isotope ratio inherited from N source, possibly fractionated as nitrate is formed.
O isotope ratio comes from:
   In nitrate fertilizer: All oxygens come from air, $\delta^{18}O = +22$
   In nitrified ammonia fertilizer:
      1 O from atmosphere, 2 O from water
      e.g., in Illinois: $\delta^{18}O = +10$ in water
      $[(1 \times +22\%) + (2 \times -10\%)]/3 = +1\%$
   Thus, this type of nitrate has a variable oxygen isotope ratio

IMPORTANT: O isotopes in nitrate (and sulfate) do not equilibrate with the $H_2O$ they are dissolved in. $HCO_3^-$ and other DIC species do equilibrate with the host water quickly.

Using the O and N isotopes in nitrate we can “fingerprint” various sources of nitrate in water.
Example: Sewage or manure, vs. ammonia fertilizer converted to nitrate
See Carol Kendall’s figure: $NAF = NO_3^-$ derived from nitrification of ammonia fertilizer, $NF = nitrate$ fertilizer, $SN = NO_3^-$ derived from natural soil nitrogen, $ATM = NO_3^-$ formed by lightning, power plants, and cars; $Man. = animal manure$
THIS FIGURE IS PRELIMINARY; IF YOU NEED TO USE THIS METHOD YOU SHOULD CHECK THE LATEST PLOT IN THE LITERATURE.
Effects of denitrification on $\delta^{15}$N and $\delta^{18}$O

As described above, the size of the isotopic fractionation during denitrification varies, depending on the metabolic state of the microbes. HOWEVER, it appears that the nitrogen isotope fractionation is always about twice the size of the oxygen isotope fractionation. The exact ratio was thought to be 2.1, but recently it was discovered that this value was based on faulty methods. Hopefully the correct value will be precisely determined in the next few years.

Applications

Constraining sources of nitrate. Example: Nitrate deposition from the atmosphere has negative effects on ecosystems high in the mountains. Isotopes suggest the nitrate budget of these ecosystems is dominated by anthropogenic N (I think).

Constraining denitrification. Use shifts of the isotopes to estimate amount of denitrification. Denitrification is one of the big unknowns in our understanding if N budgets for ecosystems, agricultural areas, and rivers.

Marine N cycling. In the oceans, N is often a limiting nutrient. Researchers are using the isotopes to learn about how N is fixed from atmospheric N$_2$ to form nitrate, and how it is then utilized. Also, trophic level N isotope effects might be useful in ecosystem studies.

Sulfur

Measure 34/32 ratio

Standard is a meteoritic sulfide- Canyon Diablo Troilite = CDT. Now we use VCDT.

Fractionation mechanisms

1. Bacterial sulfate reduction- all sulfate reduction is microbial at earth surface temps  
   $\epsilon = 20$ to $50 \%$, Kaplan and Rittenberg (1964)

2. Bacterial disproportionation of S$^0$ (Habicht and Canfield, 1997)  
   $4S^0 + 4H_2O \rightarrow 3H_2S + \text{SO}_4^{2-} + 2H^+$  
   The produced sulfide is $-5 \%\epsilon$ relative to the S$^0$  
   The produced sulfate is $+16 \%\epsilon$ relative to the S$^0$  
   In marine sediments, which are oxic at the top and reducing at depth, sulfur cycles as follows:  
      1. Sulfate is reduced to sulfide at depth.  
      2. Some of this sulfide escapes upward, and is oxidized to S$^0$ (no isotope shift).  
      3. This S$^0$ is consumed by disproportionating bacteria. The product sulfide is very light isotopically.

3. Abiotic equilibrium fractionation between fluids and minerals at high temperature: Use as a geothermometer.

4. Little fractionation of sulfur isotopes during:  
   • Precip. of gypsum or anhydrite
• Uptake by higher plants or algae
• Oxidation of dissolved sulfide
• Dissolution of sulfide minerals by oxidation

S isotopes in the oceans
Modern ocean is about +20‰ vs. CDT (= bulk earth)
Why is the ocean heavy compared to bulk earth?
  • Input is probably close to bulk earth
  • BUT, because of the large fract. during sulfate reduction, output of S from oceans
    (mostly pyrite) is isotopically light relative to the oceans.
IMPORTANT: Sulfate reduction is closely linked to organic carbon. Only organic-rich
sediments have much sulfate reduction. This is an important mechanism of organic carbon
oxidation.

1. Anoxic bottom water, sulfide formed at top of this: Data from modern Black Sea:
   \( \text{SO}_4^{2-} = +19.2\% \) vs. dissolved sulfide or sulfide minerals = -31.9‰ below
2. Oxic water column: Bay of Kiel, Baltic Sea, top 30 cm of seds.
   See Faure, fig. 28.1
   Sulfate diffuses downward and is reduced: isotopically heavier w/ incr. Depth
   Sulfide formed is lighter, parallels the sulfate
Now, look at data from the oceans over time (as recorded by evaporites): Fig. 28.2 from Faure

Organics in sediments: two S sources:
  Assimilated S in organics: reflects seawater value
  Sulfur added via reaction of organics with sulfide produced during sulfate reduction:
    isotopically light
  • Oil: -8 to +32
  • Coal: -30 to +32

Early earth history
Change in S isotopes at about 2.35 Ga- evidence from precambr. Shales in Africa
Shift from value ~ 0‰ ±1 to <0‰ at 2.35 Ga
Reflects evolution of \( \text{SO}_4^{2-} \) reducers: the probable sequence:
  1. methanogens
  2. photosynth. Bacteria
  3. SO4 reducers
  4. \( \text{O}_2 \) respirers

Sulfur in the atmosphere and acid rain
1. \( \text{SO}_2 \) from coal and oil burning, sulfide smelting- VARIABLE
   -must characterize on a case-by-case basis
2. \( \text{H}_2\text{S} \) from bacteria- usually light isotopically
3. Dimethyl sulfide (DMS) is a volatile sulfur compound produced by bacteria and algae- given
   off from the ocean surface, oxidizes in the atmosphere - usually light isotopically
4. Sea spray sulfate- - isotopically heavy
Selenium

Geochemistry of Se is similar to that of S. Se is directly below S in the periodic table.

Geochemistry: Several redox species

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<tr>
<td>Se(VI)</td>
<td>SeO_4^{2-}</td>
<td>selenate</td>
<td>Like sulfate; soluble, little adsorption</td>
</tr>
<tr>
<td>Se(IV)</td>
<td>SeO_3^{2-}</td>
<td>selenite</td>
<td>Soluble, stronger adsorption</td>
</tr>
<tr>
<td></td>
<td>HSeO_3^-</td>
<td>biselenite</td>
<td></td>
</tr>
<tr>
<td>Se(0)</td>
<td>Se^0</td>
<td>elemental selenium</td>
<td>Common precipitate in reducing sediments</td>
</tr>
<tr>
<td>Se(-II)</td>
<td>H_2Se, HSe^-</td>
<td>selenide</td>
<td>Precipitates (HgSe, FeSe, Cu_2Se)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Substitutes for sulfide in proteins- causes toxicity</td>
</tr>
</tbody>
</table>

Soluble and mobile as oxidized Se(VI) or Se(IV)
Insoluble and immobile if the oxidized forms are reduced to Se(0)

Isotopic fractionation (^80Se/^76Se): Like S, largest fractionation is during reduction of oxyanions:
- 3 to 10‰ for SeO_4^{2-} reduction to Se(IV)
- 6 to 10‰ for Se(IV) reduction to Se(0)
- ... other reactions less important- small fractionations

Environmental Problems:
1) agricultural wastewater in some arid regions- Se derived from organic-rich shales accumulated in soils
2) fly ash from coal-fired power plants
3) misc. industrial uses, including Electronics (diodes), dyes
4) isolated human toxicity problem in China- some coals extremely Se-rich
Also: In many places, Se deficiency is a problem. Narrow acceptable range.

Applications:
1. “Fingerprinting” Se sources
2. Detecting reduction of Se(VI) or Se(IV) (immobilization)
   - works just like nitrate; increasing reduction leads to enrichment in heavier isotopes in the remaining unreduced Se

Chromium

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<tr>
<td>Cr(VI)</td>
<td>CrO_4^{2-}, HCrO_4^{2-}</td>
<td>chromate/bichromate</td>
<td>Like sulfate; soluble, little adsorption</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Cr(OH)_2^+</td>
<td>chromium ion</td>
<td>Insoluble; adsorbs strongly</td>
</tr>
</tbody>
</table>

Isotopic fractionation (^53Cr/^52Cr): Like S and Se, largest fractionation is probably during reduction of oxyanions:
- roughly 3‰ for CrO_4^{2-} reduction to Cr(III)
- ... other reactions less important? not well studied yet

Environmental Issues: Heavily used in Industry
- Cr plating- highly concentrated Cr(VI) solutions, leakage is common
- Lumber preservatives- CCA = chromated copper arsenate (ouch!)
- Cooling waters- Cr(VI) as a preservative
- Mining/processing waste
- ALSO: Natural sources- ultramafic rocks containing chromite
  - Problem in California?

Applications:
1. “Fingerprinting” Cr sources- natural versus anthropogenic
2. Detecting reduction of Cr(VI) (immobilization) in groundwater
   - Very important; reduction is the major cause of natural attenuation and reductants can be emplaced to stop plumes from moving
   - works just like nitrate; increasing reduction leads to enrichment in heavier isotopes in the remaining unreduced Cr(VI)

Molybdenum
($^{97}\text{Mo}/^{95}\text{Mo}$ or $^{98}\text{Mo}/^{95}\text{Mo}$)
1) Paleoredox proxy for the oceans:
   - Little fractionation during scavenging and deposition of Mo in anoxic waters
   - Fractionation occurs during scavenging and deposition in oxic waters- The Mo is depleted in heavier isotopes
   - SO....the Mo isotope ratio of seawater reflects the ratio of oxic to anoxic areas.
   - Anoxic events in earth history may be recorded in Mo isotope excursions
2) Sometimes Mo is a contaminant. Possible applications like those of Se isotopes.

Iron
($^{57}\text{Fe}/^{54}\text{Fe}; ^{56}\text{Fe}/^{54}\text{Fe}$)
Fe(III) is insoluble
Fe(II) is soluble
- recent work by T.D. Bullen at USGS, Menlo Park, C. Johnson at Wisconsin, Ariel Anbar at AX State, and Alex Halliday’s group at ETH Zurich)
Importance:
1) very important redox player in groundwater, ocean sediments, early earth
2) possibly a limiting nutrient in oceans now
3) ubiquitous on earth
4) Important redox element for bacteria

Isotope systematics- currently under investigation
Oxidation of Fe(II) to Fe(III)- variable fractionation
0.5 to 2.5‰- product is isotopically HEAVY (???)
Depends on speciation of Fe(II)- complexes with $\text{HCO}_3^-$, $\text{SO}_4^{2-}$ etc.
Theoretical predictions of equilibrium fractionations between these species
Reduction of Fe(III) by microbes causes some fractionation- 1.5‰