IGNEOUS ROCKS, METEORITES, & FLUID-ROCK INTERACTIONS
Oxygen & Hydrogen Isotopes in Igneous Rocks

Main problem of Igneous Petrology:
   Explain diversity of igneous rocks

Main problem of Stable Isotope Studies of Igneous Rocks
   Explain diversity of $\delta^{18}$O and $\delta$D values in Igneous Rocks
   Most Rocks: ~44 wt % oxygen

Observe Magmas:

\[
\delta^{18}\text{O} = -2^* \text{ to } +16 \quad \text{but mostly } +5.5 \text{ to } +11.0
\]

\[
\delta\text{D} = -200 \text{ to } +30 \quad \text{but mostly } -50 \text{ to } -85
\]

* Rx to -10.5
Primordial $^{18}\text{O}$ Values:

Lunar materials remarkably uniform at $+5.4$ to $+6.8$ inc. Mare basalts, breccias, highland crystalline rocks

Lunar igneous rocks: $+5.7 \pm 0.2$

MORB basalts
Most abundant igneous rx on Earth; $\sim 12 \text{ km}^3 / \text{y}$
$^{18}\text{O} = 5.7 \pm 0.5$

Mafic lavas & most other mantle materials: $^{18}\text{O} = +5.0$ to $+8.0$
Exceptions: Ophiolites & Eclogites
**Primordial $\delta^{18}O$ Values:**

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- **MORB basalts**
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- **Mafic lavas** & most other mantle materials: $\delta^{18}O = +5.0$ to $+8.0$
  - Exceptions: Ophiolites & Eclogites

**Conclusion:**

- $\delta^{18}O \sim 6.0$ for Earth-Moon system
- No apparent secular trend over geologic time
δ^{18}O

Age, Ga

Gorgona
Bushveld
Stillwater
Belingwe
Barberton

Komatiites
Mafic Intrusions

after Kyser 1986
**Primordial \( \delta D \) Values:** Hard to tell. Huge variations

Meteorites: -500 to +9000

Moon: lost volatiles, (also, solar wind bombardment)

Earth: High bulk \( \delta D \sim -15 \text{ to } -20 \) \( (^1\text{H} \text{ loss to space ?}) \)
   - Hydrosphere \( \delta D \sim -10 \) (inc. icecaps, GW, etc)
   - Most Rocks: \( \delta D \sim -40 \text{ to } -95 \)

Similarity of magmatic and deep-seated waters to most rocks, sediments, ophiolites, greywackes, shales, clays, etc.

**Magmatic water is derived from dehydration of surface material that has been subducted!**

Steady state
**Terrestrial igneous rocks:** large isotopic variations

To study, must first distinguish magmatic and subsolidus processes.

**Important Criterion:**
Fractionation pattern of igneous minerals:
Tendency to approach isotopic equilibrium @ hi T

Qtz > KF, alb > plag > musc > px ≈ amph > bio > ol > ilm > mgt

Note: some compositional dependences

**Other criteria:**
Geologic studies
Spatial variations
Correlations of $\delta^{18}O$ with chemistry, physical character, petrography
Open vs. Closed Systems
Bowen's Series

Olivines -3.29 Fo

Mg Pyroxenes

Mg-Ca Pyroxenes -2.37 Di

Amphiboles

Biotites

Potash Feldspar

Muscovite

Quartz

Spinels -5.91 Mgt

Calcic Plagioclases -1.68 An

Calci-alkalic Plagioclases -1.26

Alkali-calcic Plagioclases -0.91

Alkaline Plagioclase -0.56 Ab

\[ 1000 \ln \alpha_{\text{mineral-calcite}} = \frac{c \times 10^6}{T^2} \]
\[ 1000 \ln \alpha = C_3 / T^2 \]

DENSITY, g/cm$^3$
How are variations produced? Fractional crystallization (F.C.)?
F.C. potentially can cause large enrichments, esp. @ late stages.

Rayleigh equn: \( \frac{R}{R_0} = \frac{1000 + \delta_{\text{melt}}}{1000 + \delta^0_{\text{melt}}} = f^{\alpha^{-1}} \)

\[ \alpha = \frac{R_{\text{ol}}}{R_{\text{melt}}} < 1.002 \] for important rock forming minerals (qtz, feld, px, ol, bio, hbl, leucite)

\[ \alpha = \frac{R_{\text{plag}}}{R_{\text{melt}}} < 1.0006 \] Strange, “backwards” fractionation behavior:
Negative (to -0.5) in rhyolites
Positive (to +0.6) in basalts (but more calcic!)
=> Properties of melt must change!

Crystallization of ol, mgt, px, ilm, hbl, bio increases \( \delta^{18}\text{O} \) value of melt
Crystallization of qtz will decrease \( \delta^{18}\text{O} \) value of melt
Feldspar crystallization: small changes (\( \alpha \) small. changes sign)

F.C. can’t cause observed variations in nature: \( \alpha \)'s too small!

Observation: only a slight (< 1.5 ‰) \( \delta^{18}\text{O} \) enrichment during simple fractional crystallization.
\[ \delta^{18}_O \]

Fig. 5.3

- **Simple Mixing**
  - \( r = 0 \)

- **Catazonal**
  - \( r = 0.5 \)

- **Zone Refining**
  - \( r = 1 \)

- **Mesozonal**
  - \( r = 1.5 \)

- **Epizonal**
  - \( r = 5 \)

- **Fractional Crystallization**
  - \( r \to \infty \)

\[ \alpha = 0.999 \]

\[ \alpha = 1.001 \]
Counter-example: Degassing of magmas
Significant D/H effect

\[ \alpha = \frac{R_{\text{vap}}}{R_{\text{melt}}} \approx 1.035 \]
\[ \delta_i = -50 \% \]
Initial Water content: 1.8 wt % H₂O

<table>
<thead>
<tr>
<th>f</th>
<th>( \delta D_{\text{melt}} )</th>
<th>Wt. % H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-50.0</td>
<td>1.8</td>
</tr>
<tr>
<td>0.9</td>
<td>-53.5</td>
<td>1.6</td>
</tr>
<tr>
<td>0.75</td>
<td>-59.5</td>
<td>1.35</td>
</tr>
<tr>
<td>0.5</td>
<td>-72.8</td>
<td>0.90</td>
</tr>
<tr>
<td>0.25</td>
<td>-95.0</td>
<td>0.45</td>
</tr>
<tr>
<td>0.1</td>
<td>-123.6</td>
<td>0.18</td>
</tr>
</tbody>
</table>

B.E.Taylor, MSA 16, ch. 7, Figs. 8, 18
Fig. 5.1

- MARINE LIMESTONES
- CLASTIC SEDIMENTS
- METAMORPHIC ROCKS
- ALTERED IGNEOUS ROCKS
- GRANITIC ROCKS
- RHYOLITES & TUFFS
- OPHIOLITES
- ANDESITES
- ELOGITES
- MANTLE NODULES
- BASIC LAVAS
- MOR BASALTS
- LUNAR ROCKS

$\delta^{18}O$ vs $\delta^{18}O$

- Shales
- SST

Range: to -10.5
Most surface rocks have high $\delta^{18}$O values

**Chemical Sediments:** precipitates in ocean
- Recent limestones $\sim +30$
- Cherts to +36
- Ancient limestones $> +18$

**Clastic Sediments:**
- Beach sands: +9 to +12.5
- Sandstones +13 ± 2.5
- Greywackes: +13 ± 1.5
- Shales: +14 to +19

**Metamorphic Rocks:**
- $\delta^{18}$O values are mostly between those of igneous and sedimentary rocks.
- Commonly inherit the $\delta^{18}$O values of the protolith,
- Can become reduced with increasing grade.
Most surface rocks have high $\delta^{18}$O values

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**Metamorphic Rocks:**
$\delta^{18}$O values are mostly between those of igneous and sedimentary rocks.
Commonly inherit the $\delta^{18}$O values of the protolith,
Can become reduced with increasing grade.

Where is $\alpha$ large? @ Low T $\Rightarrow$ near surface of Earth
Earth vs. Moon: Water!
H.P. Taylor's "Central Dogma"
of oxygen isotope geochemistry of igneous rocks:

All relatively $^{18}$O rich or $^{18}$O depleted silicate melts on Earth must have in part been derived from, or have exchanged with, a precursor material that once resided on or near the Earth's surface.

Specifically, magmas w/ $\delta^{18}$O < +4.5 or $\delta^{18}$O > +7.0
after Criss 2008
Last Lec.

Earth & Moon have similar bulk $\delta^{18}O$ values, but terrestrial magmas span much greater range in $^{18}O$ and D.

Main Reasons:

1) **Lithosphere-Hydrosphere Interactions**
   - Earth is active planet- subduction
   - Creation of isotopically diverse suites at low T
   - Assimilation of this diverse material into magmas

2) **Subsolidus Processes**

Key to understanding lies in $\delta$-values of coexisting minerals.
Need theoretical tools
PRIMARY CRYSTALLIZATION, AFC, and SLOW COOLING

F.C. Inadequate to produce observed $^{18}$O variations
Need interactions of magmas with crustal reservoirs

AFC Assimilation-Fractional Crystallization

Bowen (1928): *Assimilation is not a simple, 2-component process*

Need 3-end members: **Magma, Country Rocks, and Cumulates**

Assimilation promotes the crystallization of cumulates already forming, releasing the latent heat needed to melt and dissolve stoped blocks.

**AFC does not** radically change the major-element chemistry

**AFC does** enhance the proportions of the late differentiates drastically alter the trace element concentrations drastically alter isotope ratios.
MAGMA

\[ M_m \quad \text{Mass} \]
\[ C_m \quad \text{Concentration} \]
\[ R_m \quad \text{Isotope Ratio} \]

ASSIMILATE

\[ A \quad \text{Rate In} \]
\[ C_a \quad \text{Concentration} \]
\[ R_a \quad \text{Isotope Ratio} \]

CUMULATES

\[ r \, A \quad \text{Rate Produced} \]
\[ C_c = D \, C_m \quad \text{Concentration} \]
\[ R_c = \alpha \, R_m \quad \text{Isotope Ratio} \]

Note: \( R = \text{Mass Isotope/Total Mass Element} \)
NOTE: \[ D = \frac{C_{\text{xls}}}{C_{\text{melt}}} = \beta_{\text{HPT}} \] \[ r_{\text{here}} = \text{mass cumulates/mass assimilated} = \frac{1}{r_{\text{DePaolo}}} \]

<table>
<thead>
<tr>
<th>ASSIMILATE</th>
<th>MAGMA</th>
<th>CUMULATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>RATE IN = A</td>
<td>Mass ( M_m )</td>
<td>Rate Produced = r A</td>
</tr>
<tr>
<td>Concentration = ( C_a )</td>
<td>Concentration = ( C_m )</td>
<td>Concentration = ( D C_m )</td>
</tr>
<tr>
<td>Isotope Ratio = ( R_a )</td>
<td>Isotope Ratio = ( R_m )</td>
<td>Isotope Ratio = ( R_c = \alpha R_m )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mass</th>
<th>Rate of Change (in - out)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of Magma ( M_m )</td>
<td>( \frac{dM_m}{dt} = A - A r )</td>
</tr>
<tr>
<td>Mass of Element ( \mu = M_m C_m )</td>
<td>( \frac{d\mu}{dt} = A C_a - A r D C_m )</td>
</tr>
<tr>
<td>Mass of Isotope ( \Phi = M_m C_m R_m )</td>
<td>( \frac{d\Phi}{dt} = A C_a R_a - A r D C_m \alpha R_m )</td>
</tr>
</tbody>
</table>
AFC PROCESSES for Oxygen Isotopes:
Capable of producing large $^{18}$O enrichments or depletions in magmas
Low $^{18}$O Magmas; e.g. Yellowstone

Simplification: $D=1$ so $C_a = C_{xl}$

\[
\frac{\delta_m - \delta^i_m}{\delta^f_m - \delta^i_m} = 1 - f^{b/(r-1)}
\]

where

\[
f = \frac{M_m}{M^i_m}
\]

\[
b = 1 - r + \alpha r
\]

\[
b = \frac{1000 + \delta_a}{1000 + \delta^f_m}
\]

Criss 1999
\( \delta^{18}O \) vs. \( f \) diagram with different processes:

- **Initial Magma**
- **Simple Mixing**
- **Catazonal**
- **Zone Refining**
- **Mesozonal**
- **Epizonal**

Parameters:

- **Simple Mixing** \( r = 0 \)
- **Catazonal** \( r = 0.5 \)
- **Zone Refining** \( r \to \infty \)
- **Mesozonal** \( r = 1.5 \)
- **Epizonal** \( r = 5 \)

Equations:

- \( \alpha = 0.999 \)
- \( \alpha = 1.001 \)
- \( CR = +20 \% \)
<table>
<thead>
<tr>
<th>PROCESS</th>
<th>Country Rock Temperature</th>
<th>$r$</th>
<th>$D_{Sr}$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F. C.</td>
<td>Cold</td>
<td>$\infty$</td>
<td>$&gt; 1$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>Epizonal AFC</td>
<td>Cold</td>
<td>$&gt; 3.5$</td>
<td>$&gt; 1$</td>
<td>$\sim 5$</td>
</tr>
<tr>
<td>Mesozonal AFC</td>
<td>Hot</td>
<td>1.0 - 3.25</td>
<td>$&gt; 1$</td>
<td>$\geq 1$</td>
</tr>
<tr>
<td>Catazonal AFC</td>
<td>Very Hot-Melting Zone</td>
<td>0 - 1</td>
<td>$&gt; 1$</td>
<td>$\sim 1$</td>
</tr>
<tr>
<td>Upper Mantle AFC</td>
<td>Very Hot-Plag Unstable</td>
<td>0 - 1</td>
<td>$&lt; 1$</td>
<td>$\sim 1$</td>
</tr>
</tbody>
</table>

$$\lambda = 1 + r(D - 1)$$
AFC PROCESS  for Oxygen Isotopes:
Capable of producing large $^{18}$O enrichments or depletions in magmas
Low $^{18}$O Magmas; e.g. Yellowstone

Simplification:  \( D=1 \)  so  \( C_a = C_{xl} \)

\[
\frac{\delta_m - \delta^i_m}{\delta_f^m - \delta^i_m} = 1 - \frac{b}{(r-1)}
\]

where

\[
f = \frac{M^m}{M^i_m}
\]

\[
b = 1 - r + \alpha r
\]

\[
b = \frac{1000 + \delta_a}{1000 + \delta_f^m}
\]

Criss 1999
AFC PROCESS: Isotope Isotope Equation:

\[
\left\{ \left( \frac{1}{G} - 1 \right) \frac{\lambda C^i_m}{C_a} + 1 \right\}^{1/\lambda}_{element \ A} = \left\{ \left( \frac{1}{G} - 1 \right) \frac{\lambda C^i_m}{C_a} + 1 \right\}^{1/\lambda}_{element \ B}
\]

where

\[
G = \frac{R_m - R_a}{R^i_m - R_a}
\]

\[
\lambda = 1 + r(D - 1)
\]

Criss 1999
Adamello
after Taylor (1980)

35-40 Ma
Basalt + 5.7  0.7039  900 ppm Sr
C.Rk +14.0  0.736   150 ppm S

\[ \lambda = 3.0 \]

\[ \delta^{18}O \]

\[ \frac{^{87}Sr}{^{86}Sr} \]

Fig. 5.5
AFC PROCESS: Isotope vs Concentration Equation

Simplification: $\alpha = 1$

$$\frac{R_m - R^i_m}{R_a - R^i_m} = \frac{\frac{1}{C_m} - \frac{1}{C^i_m}}{\frac{\lambda}{C_m} - \frac{1}{C^i_m}}$$

where

$$\lambda = 1 + r(D - 1)$$

Plot $R$ vs $1/C$

Line segments originate at magmatic endmember, project to the point $(R_a, \lambda/C_a)$

Fleck & Criss (1985)
AFC PROCESS: Sr Isotope vs Concentration Equation

$$\left( \frac{^{87}Sr}{^{86}Sr} \right)_m - \left( \frac{^{87}Sr}{^{86}Sr} \right)_i \equiv \frac{1}{Sr_m} - \frac{1}{Sr_i}$$

$$\left( \frac{^{87}Sr}{^{86}Sr} \right)_a - \left( \frac{^{87}Sr}{^{86}Sr} \right)_i$$

where

$$\lambda = 1 + r(D - 1)$$

Plot $R$ vs $1/C$

Line segments originate at magmatic endmember, project to the point $(R_a, \lambda/C_a)$

Fleck & Criss (1985)
AFC PROCESSES: Rb/Sr Pseudoisochron

\[
\frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_m - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_i}{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_a - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_i} \Rightarrow \frac{\left(\frac{\text{Rb}}{\text{Sr}}\right)_m - \left(\frac{\text{Rb}}{\text{Sr}}\right)_i}{\left(\frac{\text{Rb}}{\text{Sr}}\right)_a - \left(\frac{\text{Rb}}{\text{Sr}}\right)_i}
\]

for

\[r = 0 \quad or \quad D_{\text{Sr}} = D_{\text{Rb}}\]

Simple Mixing process

For any AFC process

Fleck & Criss (1985)
Approximate limit of known Belt outcrop

Criss & Fleck 1990
δ¹⁸O Values

Criss & Fleck 1987
$(^{87}\text{Sr}/^{86}\text{Sr})_{80}$ vs $1000/\text{Sr}$

- **SFCR Plutons**
- **PreC**
- **WSD**

**Precambrian**

**Accreted Terranes**

Fleck & Criss 1985
ARC-CONTINENT SUTURE ZONE

λ = 0

PM

λ = 0.5

λ = 1
Simple Mixing

λ = 2

λ = 5

λ = ∞
Fractional Crystallization

Average PreC

1000/Sr

87Sr/86Sr
$^{87}\text{Sr}/^{86}\text{Sr}_i = 0.70364 + 0.061931x$

$R = 0.86606$

$1640\text{ Ma} + 80\text{ Ma}$

Fleck & Criss 1985
Fleck & Criss 1985
end