Geochemistry 4:

Volatile

Rita Parai

Washington University in St. Louis

Sarda and Graham, 1990
What are volatiles?

(nebular classification from Sujoy’s lecture)

**volatile**
- gaseous even at low T
- $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{N}_2$, noble gases
- moderately volatile: $\text{K}$, $\text{Rb}$, $\text{Cd}$, $\text{Zn}$

**refractory**
- solid even at high T
- $\text{Ca}$, $\text{Al}$, $\text{Re}$, $\text{W}$
Why do we care about volatiles?

Earth’s volatile-rich surface environment is clement for life.

Volatile abundances affect material properties (e.g., water).

Dynamic feedbacks at play between volatile cycling and convection, plate tectonics (e.g., Crowley et al., 2011).

Noble gases are excellent tracers of major volatiles and of geodynamical processes broadly (this lecture and next week).
The mantle tetrahedron in Sr-Nd-Pb space

Hart et al. (1992)
Mixing in the mantle tetrahedron in Sr-Nd-Pb space

Hart et al. (1992)
Volatile tracers of geophysical processes

A distinct and complementary set of “clues” to help extricate information from mantle data arrays

**Philosophical point:** we use as many tools as possible

**WITH THE CAVEAT THAT:**

Different systems are sensitive to different physical processes
Some systems are affected by many physical processes

Which systems exhibit simple behavior?
Volatile abundances

== what volatiles are where and how much ==
## Terrestrial reservoir volatile abundances

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{CO}_2$</th>
<th>$\text{N}$</th>
<th>noble gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm + oceans</td>
<td>atm: variable</td>
<td>atm: 410 ppmv</td>
<td>atm: 78% by vol</td>
<td>atm: 0.93% Ar, 18 ppmv Ne, 5 ppmv He and less</td>
</tr>
<tr>
<td></td>
<td>oceans: 1.4e24 g</td>
<td>oceans: 100 ppm</td>
<td>oceans: 10-50 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>small</td>
</tr>
<tr>
<td>crust</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MORB source</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>plume source</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>outer core</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inner core</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$^{12}\text{C}$</th>
<th>$^{14}\text{N}$</th>
<th>$^{20}\text{Ne}$</th>
<th>$^{36}\text{Ar}$</th>
<th>$^{84}\text{Kr}$</th>
<th>$^{130}\text{Xe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(8.4 \pm 3.3) \times 10^3$</td>
<td>$(1.2 \pm 0.6) \times 10^1$</td>
<td>$(9.6 \pm 0.5) \times 10^{-6}$</td>
<td>$(1.0 \pm 0.6) \times 10^{-5}$</td>
<td>$(2.5 \pm 1.5) \times 10^{-7}$</td>
<td>$(3.5 \pm 0.9) \times 10^{-9}$</td>
</tr>
<tr>
<td>Earth mantle</td>
<td>Marty (2012)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(4.9 \pm 2.3) \times 10^2$</td>
<td>$(7.9 \pm 4.9) \times 10^{-1}$</td>
<td>$(5.7 \pm 3.1) \times 10^{-7}$</td>
<td>$(4.0 \pm 2.1) \times 10^{-7}$</td>
<td>$(1.4 \pm 0.8) \times 10^{-8}$</td>
<td>$(2.3 \pm 1.3) \times 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>Halliday (2013)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>hydrogen?</th>
<th>carbon?</th>
<th>nitrogen?</th>
<th>stop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>...hydrogen??</td>
<td>maybe?</td>
<td>:-(</td>
<td>go away</td>
</tr>
</tbody>
</table>

Rudnick and Gao (2003); Marty and Tolstikhin (1998); Salters and Stracke (2004); Marty (2012); Parai and Mukhopadhyay (2012); Dasgupta and Hirschmann, 2010
## Terrestrial reservoir volatile abundances

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{CO}_2$</th>
<th>$\text{N}$</th>
<th>Noble gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm + oceans</td>
<td>atm: variable</td>
<td>atm: 410 ppmv</td>
<td>atm: 78% by vol</td>
<td>atm: 0.93% Ar, 18 ppmv Ne, 5 ppmv He and less</td>
</tr>
<tr>
<td></td>
<td>oceans: 1.4e24 g</td>
<td>oceans: 10-50 ppm</td>
<td>oceans: 100 ppm</td>
<td></td>
</tr>
<tr>
<td>crust</td>
<td>0.1% by wt</td>
<td>0.7% by weight</td>
<td>83 ppm</td>
<td>small</td>
</tr>
<tr>
<td>MORB source</td>
<td>50-200 ppm</td>
<td>30-150 ppm</td>
<td>&lt;2 ppm</td>
<td>He: 4e-9 g/g</td>
</tr>
<tr>
<td>plume source</td>
<td>400-1200 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>outer core</td>
<td>hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inner core</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- $\text{H}_2\text{O}$: Atmosphere: variable, oceans: 1.4e24 g
- $\text{CO}_2$: Atmosphere: 410 ppmv, oceans: 10-50 ppm
- $\text{N}$: Atmosphere: 78% by volume, oceans: 10-50 ppm
- Noble gases: Atmosphere: 0.93% Ar, 18 ppmv Ne, 5 ppmv He and less

---

(Rudnick and Gao (2003); Marty and Tolstikhin (1998); Salters and Stracke (2004); Marty (2012); Parai and Mukhopadhyay (2012); Hirschmann, 2010;...hydrocarbons...He: 4e-9 g/g)
Challenges in constraining volatile budgets

Degassing of melts makes it difficult to constrain source abundances

What samples are representative?
Bubble accumulation?

+ For heavy noble gases, atmospheric contamination often overprints the mantle signal…
Geochemical behavior of volatile species

**Carbon dioxide (CO₂):** incompatible during partial melting, strongly degassed from erupted melts but many complicating factors (e.g., redox state, kinetics)

**H₂O:** fairly incompatible (D of ~0.01, similar to Ce partitioning), degasses at lower pressures than CO₂
As the melt rises and decompresses, CO$_2$ degassing followed by H$_2$O degassing

Métrich and Wallace (2008)
How do we measure volatile species?

**Day 857 of 90**

I thought I analyzed that rock really well.

It's okay, I'll do the next one better.
Measuring H$_2$O and CO$_2$ abundances in melt inclusions to minimize degassing

Courtesy J. Tucker

Métrich and Wallace (2008)

Jorullo volcano, Mexico
Measuring major volatiles: $\text{H}_2\text{O}$ and $\text{CO}_2$

Fourier Transform Infrared Spectroscopy (FTIR)

Secondary Ionization Mass Spectrometry (SIMS)
Mass spectrometry

Source of ions \[\rightarrow\] Separator \[\rightarrow\] Detector(s)

- Thermal ionization
- Secondary ionization
- Inductively-coupled plasma

- Magnetic sector
- Time-of-flight

- Faraday cup
- Electron multiplier

Just a really hot filament that is spewing electrons, which ionize gaseous species ("gas source")
Mass spectrometry

**Source of ions**
- Thermal ionization
- Secondary ionization
- Inductively-coupled plasma
  
  Just a really hot filament that is spewing electrons, which ionize gaseous species ("gas source")

**Separator**
- Magnetic sector
- Time-of-flight

**Detector(s)**
- Faraday cup
- Electron multiplier
Fluxes for deep Earth volatile cycling

Parai and Mukhopadhyay (2012)
What carries volatiles into subduction zones? (H₂O, CO₂, N, heavy noble gases)
Devolatilization (and thus regassing) depends on P-T path.
Geochemical behavior of volatile species

**Carbon dioxide (CO₂):** incompatible during partial melting, strongly degassed from erupted melts but many complicating factors (e.g., redox state, kinetics)

**H₂O:** fairly incompatible (D of ~0.01, similar to Ce partitioning), degasses at lower pressures than CO₂

**Noble gases:** chemically inert, incompatible, insoluble
Noble gases are atmophile

Noble gases are incompatible in the mantle and are strongly degassed from melt into the atmosphere

For a long time, it was thought that mantle processing was a one-way street for noble gases out of the mantle. Now we know that regassing of some species occurs!
Noble gases are scarce enough to be isotopically sensitive to production by decay and fission.
Noble gas primer

- $^3\text{He}, \, ^4\text{He}$
- $^{20}\text{Ne}, \, ^{21}\text{Ne}, \, ^{22}\text{Ne}$
- $^{36}\text{Ar}, \, ^{38}\text{Ar}, \, ^{40}\text{Ar}$
- $^{124,126,128}\text{Xe}, \, ^{129}\text{Xe}, \, ^{130}\text{Xe}, \, ^{131}\text{Xe}, \, ^{132}\text{Xe}, \, ^{134}\text{Xe}, \, ^{136}\text{Xe}$
Two types of noble gas isotopes

(radioactive)

radiogenic

primordial

stable, non-radiogenic
Noble gas primer

- $^3\text{He}, \ ^4\text{He}$

- $^{20}\text{Ne}, \ ^{21}\text{Ne}, \ ^{22}\text{Ne}$

- $^{36}\text{Ar}, \ ^{38}\text{Ar}, \ ^{40}\text{Ar}$

- $^{124,126,128}\text{Xe}, \ ^{129}\text{Xe}, \ ^{130}\text{Xe}, \ ^{131}\text{Xe}, \ ^{132}\text{Xe}, \ ^{134}\text{Xe}, \ ^{136}\text{Xe}$
Noble gas primer

- $^3\text{He, }^4\text{He}$ (U, Th)
- $^{20}\text{Ne, }^{21}\text{Ne, }^{22}\text{Ne}$ ($\alpha, n$) reactions
- $^{36}\text{Ar, }^{38}\text{Ar, }^{40}\text{Ar}$ ($^{40}\text{K}$)
- $^{124, 126, 128}\text{Xe, }^{129}\text{Xe, }^{130}\text{Xe, }^{131}\text{Xe, }^{132}\text{Xe, }^{134}\text{Xe, }^{136}\text{Xe}$ ($^{129}\text{I}$)
Noble gas primer

- $^3\text{He}$, $^4\text{He}$

- $^{20}\text{Ne}$, $^{21}\text{Ne}$, $^{22}\text{Ne}$

- $^{36}\text{Ar}$, $^{38}\text{Ar}$, $^{40}\text{Ar}$

- $^{124,126,128}\text{Xe}$, $^{129}\text{Xe}$, $^{130}\text{Xe}$, $^{131}\text{Xe}$, $^{132}\text{Xe}$, $^{134}\text{Xe}$, $^{136}\text{Xe}$

- $^{129}\text{I}$

- (U, Th)

- ($\alpha$,n) reactions

- ($^{40}\text{K}$)

- Pu, U fission products
Noble gas primer

- $^3\text{He}$, $^4\text{He}$
- $^{20}\text{Ne}$, $^{21}\text{Ne}$, $^{22}\text{Ne}$
- $^{36}\text{Ar}$, $^{38}\text{Ar}$, $^{40}\text{Ar}$
- $^{124,126,128}\text{Xe}$, $^{129}\text{Xe}$, $^{130}\text{Xe}$, $^{131}\text{Xe}$, $^{132}\text{Xe}$, $^{134}\text{Xe}$, $^{136}\text{Xe}$

more degassed $\rightarrow$ high radiogenic/primordial
Degassing increases the radiogenic/primordial ratio

A mantle reservoir with some $^3\text{He}$ and $^4\text{He}$
Degassing increases \(\frac{\text{radiogenic}}{\text{primordial}}\) ratio

\(^3\text{He} \quad ^4\text{He} \quad ^3\text{He} \quad ^4\text{He} \quad ^4\text{He} \quad ^4\text{He} \quad ^4\text{He} \quad ^3\text{He} \quad ^4\text{He} \quad ^3\text{He}

Loses both isotopes during degassing
Degassing increases the ratio of radiogenic primordial helium to uranium. But uranium was retained!
Degassing increases \( \frac{\text{radiogenic}}{\text{primordial}} \) ratio

Only \textit{radiogenic} isotope grows in after degassing.
Noble gas primer

- $^3\text{He}$, $^4\text{He}$
- $^{20}\text{Ne}$, $^{21}\text{Ne}$, $^{22}\text{Ne}$
- $^{36}\text{Ar}$, $^{38}\text{Ar}$, $^{40}\text{Ar}$
- $^{124,126,128}\text{Xe}$, $^{129}\text{Xe}$, $^{130}\text{Xe}$, $^{131}\text{Xe}$, $^{132}\text{Xe}$, $^{134}\text{Xe}$, $^{136}\text{Xe}$

more degassed $\rightarrow$ high radiogenic/primordial Pu, U fission products
Noble gas primer

- $^3\text{He}$, $^4\text{He}$
  - more degassed $\rightarrow$ high radiogenic/primordial
- $^{20}\text{Ne}$, $^{21}\text{Ne}$, $^{22}\text{Ne}$
- $^{36}\text{Ar}$, $^{38}\text{Ar}$, $^{40}\text{Ar}$
- $^{124,126,128}\text{Xe}$, $^{129}\text{Xe}$, $^{130}\text{Xe}$, $^{131}\text{Xe}$, $^{132}\text{Xe}$, $^{134}\text{Xe}$, $^{136}\text{Xe}$
  - $^{129}\text{I}$ $t_{1/2} = 15.7$ Myr
  - $^{244}\text{Pu}$ $t_{1/2} = 80.0$ Myr

Pu, U fission products
The right tool for every job

First 500 Myr:
accretion, origins, Moon-forming giant impact, early degassing

$I^{129} \rightarrow Xe^{129}$  Pu-fission derived Xe
$t_{1/2} = 15.7$ Myr  $t_{1/2} = 80$ Myr

long-term mantle processing (outgassing vs. regassing)
$4He, 21Ne, 40Ar, U$-fission derived Xe
Mass spectrometry

Source of ions → Separator → Detector(s)

Thermal ionization
Secondary ionization
Inductively-coupled plasma

Magnetic sector
Time-of-flight

Faraday cup
Electron multiplier

Just a really hot filament that is spewing electrons, which ionize gaseous species (“gas source”)
Mass spectrometry

Source of ions → Separator → Detector(s)

Thermal ionization
Secondary ionization
Inductively-coupled plasma

Magnetic sector
Time-of-flight

Faraday cup
Electron multiplier

Just a really hot filament that is spewing electrons, which ionize gaseous species ("gas source")
Noble gases analyzed on multi-collector Nu Noblesse
What can geochemists infer about Earth’s interior?

Mid-ocean ridge basalts (MORBs) sample a mantle source distinct from the mantle source sampled by plumes.

present-day MORB source

present-day plume source

(not to scale)
Helium isotopes in mantle rocks

Mid-ocean ridge basalts (MORBs) sample a mantle source that is on average more degassed than that sampled by plumes.

Barfod et al. (1999)
Helium isotopes co-vary with lithophile radiogenic isotopes

Farley et al. (1992)
Plume samples characterized by high $^{3}\text{He}/^{4}\text{He}$ → interpreted as sampling a less degassed (less processed by partial melting) mantle reservoir.
Helium isotopes and mantle processing history

Plume samples characterized by high $^{3}\text{He}/^{4}\text{He}$ → interpreted as sampling a less degassed (less processed by partial melting) mantle reservoir

Are heavy noble gases consistent with degassing interpretation?

Hawaii, Iceland, Galapagos

Jackson et al. (2007)
Post-eruptive atmospheric contamination

Which gases are affected?

- **He is minimally contaminated:** high concentrations in mantle rocks and low abundance in atmosphere
- Heavy noble gases (Ne, Ar, Kr, Xe) are pervasively contaminated during and after eruption

Where / when / how?

- During eruption on seafloor?
- Upon dredging, decompression and healing of microfractures?
- Adsorption?
Step-crushing of mantle-derived basalt glasses

- Multiple step-crushes per sample
- Each step-crush represents mantle gas + air mixing in varying proportions
- Step-crushes together define mixing arrays
Plume-related and mid-ocean ridge samples

Mukhopadhyay (2012); Pető et al. (2013); Tucker et al. (2012); Parai et al. (2012); Parai and Mukhopadhyay (2015).
Correcting for air contamination in Ne isotope space

Fit a line to the data and extrapolate to the mantle source $^{20}\text{Ne}/^{22}\text{Ne}$ composition
Previous determinations of mantle source compositions were limited by precision.
Goal: high-precision data in typical gas-poor mantle-derived samples

Parai et al. (2012) *EPSL*
Determining mantle source Ar compositions

A hyperbolic fit to correct for atmospheric contamination in Ar

Parai et al. (2012)
Determining mantle source Xe isotopic compositions

Parai et al. (2012) EPSL

Ar-Xe mixing hyperbolae asymptote, yielding limits on the present-day mantle source Xe isotope composition
Takeaways so far:

• Pervasive atmospheric contamination $\rightarrow$ primary systematics reflect syn- to post-eruptive mantle-air mixing

• High precision data define clear mantle-air mixing arrays, even in gas-poor samples

• Constraints on syn- to post-eruptive air contamination let us look deeper into the noble gas data
He vs. Ne systematics are coherent

Parai et al. (2012); Moreira et al. (1998); Tucker et al. (2012); Mukhopadhyay (2012)
He vs. Ne systematics are coherent

Parai et al. (2012); Moreira et al. (1998); Tucke et al. (2012); Mukhopadhyay (2012)
He vs. Ar systematics are coherent

Parai et al. (2012); Moreira et al. (1998); Tucker et al. (2012); Mukhopadhyay (2012)
He vs. Ar systematics are coherent

More degassed

Parai et al. (2012); Moreira et al. (1998); Tucker et al. (2012); Mukhopadhyay (2012); Peto et al. (2013)
He vs. Xe systematics: early degassing and atm recycling?

Parai et al. (2012); Moreira et al. (1998); Tucker et al. (2012); Mukhopadhyay (2012); Peto et al. (2013)