Geochemical Interlude: Trace Element and Radiogenic Isotope Geochemistry

EAS 302 Lecture 8

Trace Element Geochemistry (focus on lithophile elements)

- Electronic structure of lithophile elements is such that they behave approximately as hard spheres and bonding is primarily ionic
- Geochemical behavior of lithophile trace elements is governed by how well they can substitute for other ions in crystal lattices
- This substitution depends primarily by two factors:
  - Ionic radius
  - Ionic charge
Effect of Ionic Radius and Charge

- The greater the difference in charge or radius between the ion normally in the site and the ion being substituted, the more difficult the substitution.
- Lattice sites available are principally those of Mg, Fe, and Ca, all of which have charge of 2+.
- Some rare earths can substitute for Al³⁺.

More Definitions

- Elements whose charge or size differs significantly from that of available lattice sites in mantle minerals will partition into the melt phase when melting occurs.
  - Such elements are termed *incompatible*.
  - Examples: K, Rb, Sr, Ba, rare earth elements (REE), Ta, Hf, U, Pb
- Elements readily accommodated in lattice sites of mantle minerals remain in the solid when melting occurs.
  - Such elements are termed compatible.
  - Examples: Ni, Cr, Co, Os
The (Lanthanide) Rare Earth Elements

Rare Earth behavior

• The lanthanide rare earths all have similar outer electron orbital configurations and an ionic charge of +3 (except Ce and Eu under certain conditions, which can be +4 and +2 respectively).

• Ionic radius shrinks steadily from La (the lightest rare earth) to Lu (the heaviest rare earth).

• As a consequence, behavior varies smoothly from highly incompatible (La) to slightly incompatible (Lu).
Rare Earth Element Ionic Radii

Rare Earth Abundances in Chondrites

“Sawtooth” pattern of ‘cosmic’ abundance reflects:

– (1) the way the elements were created (greater abundances of lighter elements)
– (2) greater stability of nuclei with even atomic numbers
Chondrite Normalized REE

- By “normalizing” (dividing by abundances in chondrites), the “sawtooth” pattern can be removed.

Trace Element Fractionation During Partial Melting
Differentiation of the Earth

- Melts extracted from the mantle rise to the crust, carrying with them their “enrichment” in incompatible elements.
  - Continental crust becomes “incompatible element enriched”.
  - Mantle becomes “incompatible element depleted”.

Radioactive decay and radiogenic isotopes

- “Radiogenic” isotope ratios are functions of both time and parent/daughter ratios. They can help infer the chemical evolution of the Earth.
  - Radioactive decay schemes
    - $^{87}$Rb-$^{87}$Sr (half-life 48 Ga)
    - $^{147}$Sm-$^{143}$Nd (half-life 106 Ga)
    - $^{238}$U-$^{206}$Pb (half-life 4.5 Ga)
    - $^{235}$U-$^{207}$Pb (half-life 0.7 Ga)
    - $^{232}$Th-$^{208}$Pb (half-life 14 Ga)
  - “Extinct” radionuclides
    - “Extinct” radionuclides have half-lives too short to survive 4.55 Ga, but were present in the early solar system, and earth.
Eventually, parent-daughter ratios are reflected in radiogenic isotope ratios.

**Extinct Radionuclides**

- “Extinct radionuclides” provide crucial information about the chronology of events in the early solar system.
- What are extinct radionuclides?
  - Radioactive isotopes that no longer exist in nature (at least in our solar system), but whose existence can be inferred from the presence of their decay products.
  - Have short (geologically speaking) half-lives
  - e.g.:
    - $^{129}$I decays to $^{129}$Xe half life 16 Ma
    - $^{26}$Al decays to $^{26}$Mg half life 0.7 Ma
    - $^{107}$Pd decays to $^{107}$Ag half life 9.4 Ma
    - $^{182}$Hf decay to $^{182}$W half life 9 Ma
  - As a rule of thumb, a radioactive isotope will be gone (in our terminology here we can say ‘become extinct’) after 5 to 10 half lives (depending on how much was there to start and how sensitive our detection method is).
Example: $^{107}\text{Pb} \rightarrow 107\text{Ag}$

- $^{107}\text{Pd}$ decays to $^{107}\text{Ag}$ with a half-life of 6.5 Ma
- All $^{107}\text{Pd}$ present in young solar system now long gone.
- Both Pb and Ag are siderophile – concentrated in cores (of asteroids and Earth)
  - Did these cores form before all $^{107}\text{Pd}$ had decayed away?
  - If so, $^{107}\text{Ag}$ should correlate with Pd concentration

- From the basic equation of radioactive decay, we have:
  \[ N = N_0 e^{-\lambda t} \]

- Number of daughters produced must be equal to number of parents decayed:
  \[ D = N_0 - N \]

- Combining the two equations, and taking account of the daughters initially present, we have:
  \[ D = D_0 + N_0 (1 - e^{-\lambda t}) \]

- Written as a ratio:
  \[ \frac{^{107}\text{Ag}}{^{109}\text{Ag}} = \left( \frac{^{107}\text{Ag}}{^{109}\text{Ag}} \right)_0 + \left( \frac{^{107}\text{Pd}}{^{109}\text{Ag}} \right)_0 (1 - e^{-\lambda t}) \]
Inferring the presence of extinct radionuclides: Example of $^{107}\text{Pd}$

$$\frac{^{107}\text{Ag}}{^{109}\text{Ag}} = (\frac{^{107}\text{Ag}}{^{109}\text{Ag}})_0 + (\frac{^{108}\text{Pd}}{^{109}\text{Ag}})(\frac{^{107}\text{Pd}}{^{108}\text{Pd}})_0(1 - e^{-\lambda t})$$

Early Evolution of the Earth

- Now we have the necessary tools to return to our three questions:
  - When did the Earth’s layers form?
  - What is the composition of the layers?
  - How did these layers form?
When did the Core Form?

• What do we know from differentiated meteorites:
  – Metal cores apparently segregated very early in the parent-bodies of meteorites.
  – How early?
    • Based on the abundance of $^{107}$Ag, produced by the extinct radionuclide $^{107}$Pd, cores formed in at least some meteorite parent bodies within ~10Ma of nucleosynthesis preceding collapse of the solar nebula.
• Did the Earth’s core also form this early?
  – Decay of $^{182}$Hf to $^{182}$W ($t_{1/2} = 9$ Ma) provides a test.

$^{182}$Hf-$^{182}$W test of early core formation

• Hf is a lithophile element: it should be concentrated in the Earth’s crust and mantle
• W is a siderophile element, should be concentrated in Earth’s core
• Therefore
  – Mantle & Crust: high Hf/W ratio
  – Core: low Hf/W ratio
• If the core formed early, before $^{182}$Hf had decayed away, then any W remaining in the mantle should be rich in $^{182}$W (high $^{182}$W/$^{183}$W).
• If the core formed late (after $^{182}$Hf decayed away), then $^{182}$W/$^{183}$W in mantle should be the same as in undifferentiated (i.e., chondrites) meteorites
Some Notation

\[
\frac{f_{\text{Hf/W}}}{(\text{Hf/W})_{\text{sam}}} = \frac{(\text{Hf/W})_{\text{sam}} - (\text{Hf/W})_{\text{chon}}}{(\text{Hf/W})_{\text{chon}}}
\]

\[
\varepsilon_W = \left( \frac{^{182}W/^{183}W}_{\text{sam}} - \left( \frac{^{182}W/^{183}W}_{\text{STD}} \right) \right) \times 10,000
\]

Tungsten Isotopes in the Earth and Meteorites
Core Formation must have been completed early.

- Tungsten in the silicate earth has slightly high $^{182}$W/$^{183}$W.
  - Therefore, core formation must have been complete by no more than 30 million years after beginning of formation of the solar system

Composition of the Core: Major Constituents

- From seismic and inertial properties, the core is known to have high density. Considering the chondritic abundance of suitable elements, we can estimate that the core consists of Fe-Ni alloy in roughly 16:1 proportions.
- But: the core is less dense than Fe-Ni alloy
- Therefore, a light element must also be present
  - Candidates:
    - S
    - O
    - H
    - Si
- In addition, some geophysicists have suggested the need for a radioactive element (U, Th, or K) in the core to provide the energy to drive the dynamo.
Composition of the Core: Minor Constituents

- Minor constituents can be estimated in the following way
  - Assume that the composition of the Earth is the same as CI chondrites, except for partial loss of volatile elements from the Earth.
  - Compare "Bulk Silicate Earth" (BSE) composition with the CI chondrite composition.
  - Account for loss of volatile elements.
  - The remaining difference between BSE and CI should be in the core.

Element concentrations vs. Condensation Temperature
Composition of the core

• Conclusion:
  – The Earth’s core is rich in siderophile trace elements (as we might expect).
  – S is a good candidate for the light element in the core because it more depleted in the silicate earth than expected from its volatility (but can’t rule out H or O or small amounts of Si).
  – Significant concentrations of radioactive elements (U, Th, K) in the core are unlikely.