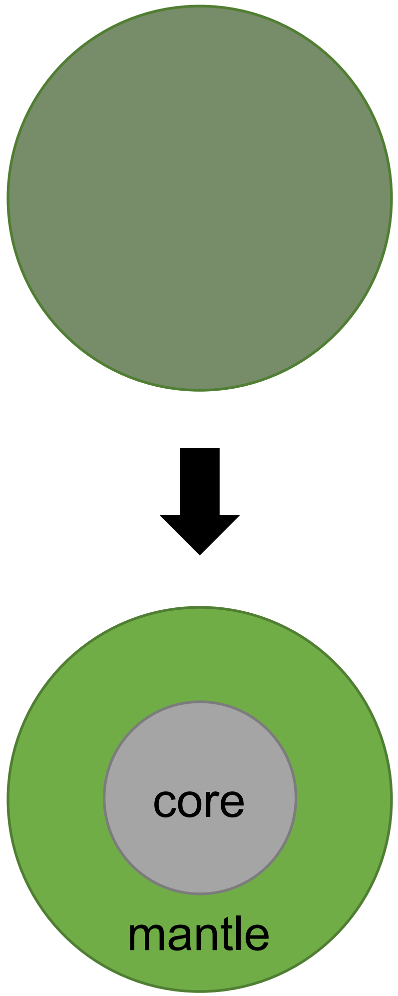
An Analytical Method for Calculating Metal–Silicate Partitioning

By M. C. Brennan

Differentiation

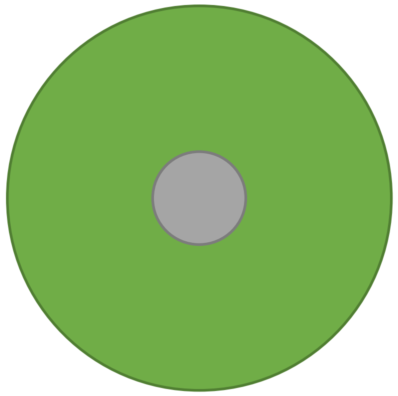
- Terrestrial bodies originated from reservoirs of homogenous material similar in composition to the Sun.
- At some point, bodies above a critical size melted and *differentiated* into a rocky mantle and a metallic core.
  - Rocks are mostly made of *silicate* minerals.
- Chemical reaction during differentiation determine the size and composition of the two parts (or *phases*).



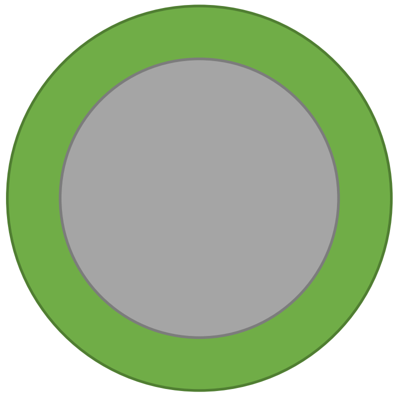
Oxygen fugacity (fO_2)

- One of the most important parameters during differentiation is the amount (or *fugacity*) of oxygen (O) atoms present.
  - Silicates are rich in O, but metals have few to no O atoms.
- An O-rich (high fO_2) planet will have a small core, with most of the iron (Fe) in the mantle.
- An O-poor (low fO_2) planet will have a large core containing most of the planet's Fe.

oxidized (O-rich)



reduced (O-poor)



Elements

- The vast majority of atoms in a planet fall into one of four categories:
  - Oxygen (O): the most abundant element, determines the relative size of the core and mantle phases
  - Iron (Fe): present in both core and mantle phases (proportions determined by fO_2)
  - Siderophile (Sp): “iron-loving” elements that always enter the core phase
  - Lithophile (Lp): “rock-loving” elements that always enter the mantle phase
- It is possible to calculate the outcome of metal–silicate partitioning using only fO_2 and the ratios between Fe, Sp, and Lp.

Element accounting

- Total number (N) of atoms in a planet equals the sum of the atoms in the core and mantle.
  - $N_{planet} = N_{core} + N_{mantle} = N_{Fe} + N_{Sp} + N_{Lp}$
- The core consists of all the siderophile elements and a portion of the Fe.
  - $N_{core} = N_{Sp} + N_{Fe}^{core}$
- The mantle consists of all the lithophile elements and the rest of the Fe.
  - $N_{mantle} = N_{Lp} + N_{Fe}^{mantle} = N_{Lp} + (N_{Fe} - N_{Fe}^{core})$
- Notice that we calculated the total atoms without O, which will be accounted for using fO_2.

Accounting for O

- In planets, *fO_2* is measured relative to a *mineral redox buffer*.
  - The iron–wüstite (IW) buffer: $2\ Fe + O_2 \rightleftharpoons 2\ FeO$
  - All elements in the mantle are attached to O atoms, so we can use wüstite (FeO) interchangeably with "mantle Fe"

- This allows us to express *fO_2* as a function of iron *activities* (*a*)
  - $a_{element} = \gamma_{element} \times X_{element}$
  - *X* is a *mole fraction*, the ratio of atoms of an element to total atoms in the phase
  - *γ* is an *activity coefficient*, a chemical parameter specific to a particular element and phase. It is usually assumed that $\gamma = 1$.

- Therefore, from the definition of the IW buffer:
  - $fO_2\ (\Delta IW) = 2\ \times\ \log_{10}\left(\frac{a_{FeO}^{mantle}}{a_{Fe}^{core}}\right) = 2\ \times\ \log_{10}\left(\frac{X_{FeO}^{mantle} \times \gamma_{FeO}^{mantle}}{X_{Fe}^{core} \times \gamma_{Fe}^{core}}\right) \approx 2\ \times\ \log_{10}\left(\frac{X_{FeO}^{mantle}}{X_{Fe}^{core}}\right)$

Partitioning

- The partitioning of a substance between two coexisting chemical phases (such as a core and a mantle) is defined by a *partition coefficient* (*D*).
  - *D* is the ratio of the molar concentrations of the substance in each phase:
    - $D_{element} = \frac{X_{element}^{phase\ A}}{X_{element}^{phase\ B}}$, where $D = \infty$ if all the atoms are in A, and $D = 0$ if all the atoms are in B
  - For Fe in a differentiated planet: $D_{Fe} = \frac{X_{Fe}^{core}}{X_{FeO}^{mantle}}$

- This can be substituted in to our *f*O_2 expression:
  - $fO_2\ (\Delta IW) \approx 2 \times \log_{10}\left(\frac{X_{FeO}^{mantle}}{X_{Fe}^{core}}\right) = 2 \times \log_{10}\left(\frac{1}{D_{Fe}}\right)$
  - $D_{Fe} \approx \frac{1}{10^{\left(fO_2/2\right)}} = 10^{\left(-fO_2/2\right)}$

- Thus, choosing the *f*O_2 of partitioning determines the planet's D_{Fe}.

Partitioning (cont.)

- Recall that *X* is the ratio of Fe atoms to total atoms in the phase:
  - $D_{Fe} = \frac{X_{Fe}^{coree}}{X_{FeO}^{mantle}} = \frac{\left(N_{Fe}^{core}/N_{core}\right)}{\left(N_{FeO}^{mantle}/N_{mantle}\right)}$
- We can now reintroduce some terms:
  - $D_{Fe} = \frac{\left(N_{Fe}^{core}/N_{core}\right)}{\left(N_{FeO}^{mantle}/N_{mantle}\right)} = \frac{\left[N_{Fe}^{core}/N_{core}\right]}{\left[(N_{Fe}-N_{Fe}^{core})/(N_{total}-N_{core})\right]} = \frac{\left[N_{Fe}^{core}/(N_{Fe}^{core}+N_{Sp})\right]}{\left[(N_{Fe}-N_{Fe}^{core})/\left(N_{planet}-(N_{Fe}^{core}+N_{Sp})\right)\right]}$
  - $D_{Fe} = \frac{N_{Fe}^{core}}{(N_{Fe}^{core}+N_{Sp})} \times \frac{\left(N_{planet}-(N_{Fe}^{core}+N_{Sp})\right)}{(N_{Fe}-N_{Fe}^{core})} = \frac{(N_{Fe}^{core}\times N_{planet})-(N_{Fe}^{core})^2-(N_{Fe}^{core}\times N_{Sp})}{(N_{Fe}^{core}\times N_{Fe})-(N_{Fe}^{core})^2+(N_{Sp}\times N_{Fe})-(N_{Fe}^{core}\times N_{Sp})}$

Partitioning (cont.)

- Simplifying further:
  - $D_{Fe} = \frac{(N_{Fe}^{core} \times N_{planet}) - (N_{Fe}^{core})^2 - (N_{Fe}^{core} \times N_{Sp})}{(N_{Fe}^{core} \times N_{Fe}) - (N_{Fe}^{core})^2 + (N_{Sp} \times N_{Fe}) - (N_{Fe}^{core} \times N_{Sp})}$
  - $D_{Fe}(N_{Fe}^{core} \times N_{Fe}) - D_{Fe}(N_{Fe}^{core})^2 + D_{Fe}(N_{Sp} \times N_{Fe}) - D_{Fe}(N_{Fe}^{core} \times N_{Sp}) = (N_{Fe}^{core} \times N_{planet}) - (N_{Fe}^{core})^2 - (N_{Fe}^{core} \times N_{Sp})$
  - $D_{Fe}(N_{Sp} \times N_{Fe}) = (N_{Fe}^{core} \times N_{planet}) - (N_{Fe}^{core})^2 + D_{Fe}(N_{Fe}^{core})^2 - (N_{Fe}^{core} \times N_{Sp}) + D_{Fe}(N_{Fe}^{core} \times N_{Sp}) - D_{Fe}(N_{Fe}^{core} \times N_{Fe})$
  - $D_{Fe}(N_{Sp} \times N_{Fe}) = (N_{Fe}^{core})^2 \times (D_{Fe} - 1) + N_{Fe}^{core}[N_{planet} - N_{Sp} + (D_{Fe} \times N_{Sp}) - (D_{Fe} \times N_{Fe})]$
  - $0 = (N_{Fe}^{core})^2(D_{Fe} - 1) + N_{Fe}^{core}[N_{planet} - N_{Sp} + (D_{Fe} \times N_{Sp}) - (D_{Fe} \times N_{Fe})] - D_{Fe}(N_{Sp} \times N_{Fe})$
  - $0 = (N_{Fe}^{core})^2(D_{Fe} - 1) + N_{Fe}^{core}[N_{planet} - N_{Sp} + D_{Fe}(N_{Sp} - N_{Fe})] - D_{Fe}(N_{Sp} \times N_{Fe})$
- This is a quadratic equation with $x = N_{Fe}^{core}$

Solving

- Quadratic equations have solutions of the form $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
    - In our case, only the positive solution is meaningful.

    - For our equation:
        - $0 = (N_{Fe}^{core})^2(D_{Fe} - 1) + N_{Fe}^{core}\left[N_{planet} - N_{Sp} + D_{Fe}\left(N_{Sp} - N_{Fe}\right)\right] - D_{Fe}\left(N_{Sp} \times N_{Fe}\right)$
        - $a = \ (D_{Fe} - 1),\ b = \ \left[N_{planet} - N_{Sp} + D_{Fe}\left(N_{Sp} - N_{Fe}\right)\right],\ c = -D_{Fe}\left(N_{Sp} \times N_{Fe}\right)$

- Thus:
    - $N_{Fe}^{core} = \frac{-N_{planet} + N_{Sp} - D_{Fe}\left(N_{Sp} - N_{Fe}\right) + \sqrt{\left[N_{planet} - N_{Sp} + D_{Fe}\left(N_{Sp} - N_{Fe}\right)\right]^2 + 4D_{Fe}(D_{Fe} - 1)\left(N_{Sp} \times N_{Fe}\right)}}{2(D_{Fe} - 1)}$

    - All variables on the right side are known bulk planetary abundances or are defined from the known fO_2.

An example

- Assume a planet with 100 total atoms (excluding O):
  - Approximate Earth proportions: $N_{Fe} = 28, N_{Sp} = 7, N_{Lp} = 65$
  - Approximate Earth differentiation fO_2: $\Delta IW - 2$

- $D_{Fe} \approx\ 10^{(2/2)} = 10$
- $a =\ (D_{Fe} - 1) = 9$
- $b =\ \left[N_{planet} - N_{Sp} + D_{Fe}\left(N_{Sp} - N_{Fe}\right)\right] = -117$
- $c = -D_{Fe}\left(N_{Sp} \times N_{Fe}\right) = -1960$

- $N_{Fe}^{core} = \frac{-b+\sqrt{b^2-4ac}}{2a} = \frac{117+\sqrt{[-117]^2+4(9)(-1960)}}{18} \approx 23$

- $\frac{23}{28} = 82\%$ of the Fe atoms are in the core, and the core contains $\frac{23+7}{100} = 30\%$ of the planet’s material.

Limitations

- Some elements other than Fe can partition between the core and mantle
  - Nickel (Ni) is the most abundant of these. In our example, $N_{Ni} \approx 2$.
  - This can be addressed by adding N_{Ni} to N_{Fe} (forcing it to partition in the same proportion as Fe) or by splitting N_{Ni} between N_{Lp} and N_{Sp}.
- N_{Fe}^{core} is very sensitive to the prescribed fO_2.
  - fO_2 may not be consistent with the amount of O needed to make silicate minerals out of N_{Lp} mantle atoms.
  - This becomes a problem in large planets like Earth, where some of the total O atoms partition into the core instead of making silicates.
  - The only self-consistent partitioning calculation is a numerical one that explicitly considers N_O.
    - For an example, see the supplement to this paper.