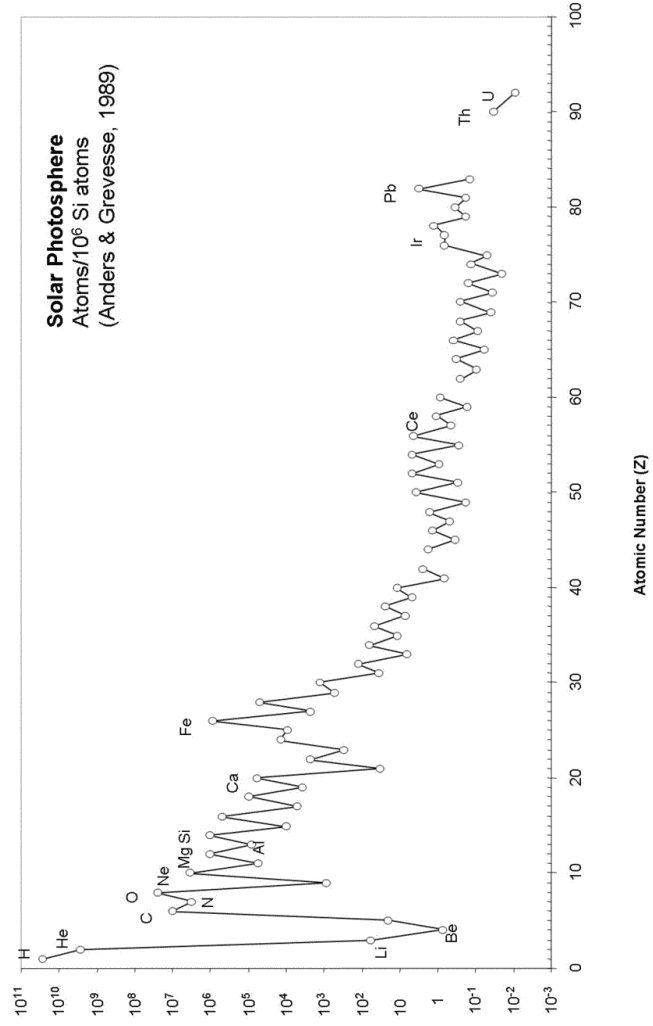


Trace-element geochemistry

Cin-Ty A. Lee

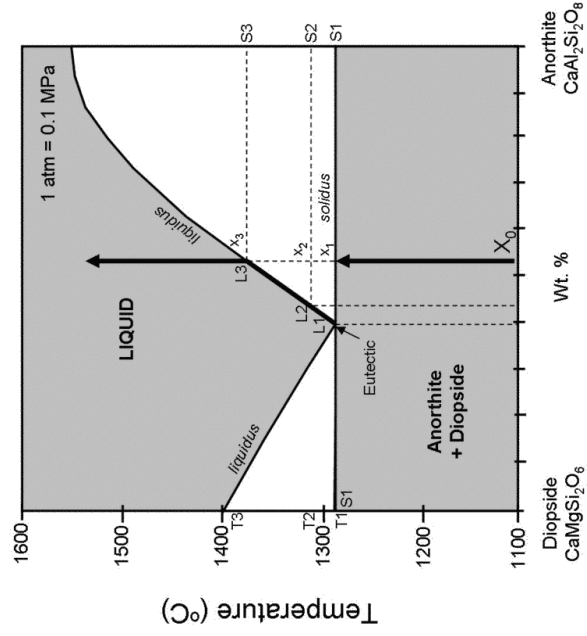
CIDER 2006 lecture series

Building blocks of our solar system



Major and minor elements dictate to first-order mineral or melt phases in the Earth:

Major elements control petrogenesis (formation of rocks)



Trace elements

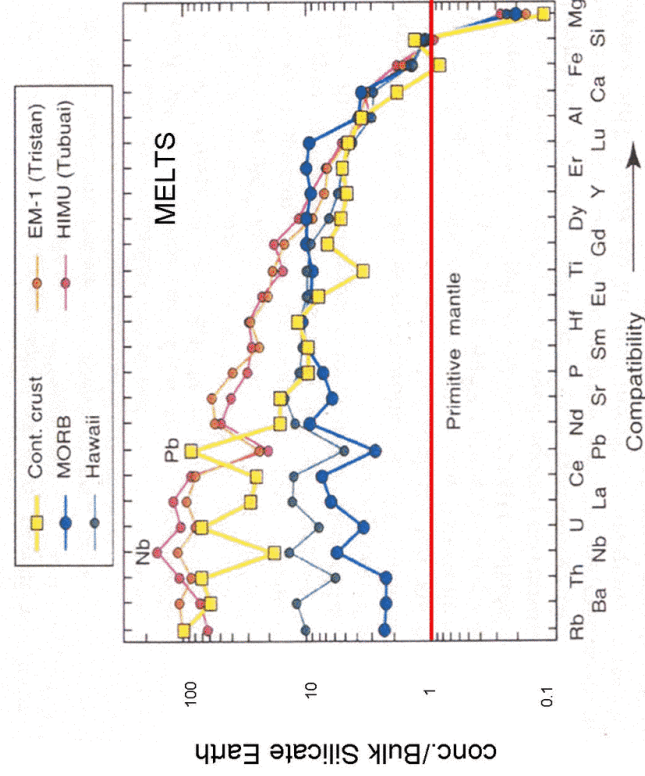
in general, they represent passive tracers of petrogenetic processes and do not control mineralogy

exceptions – H₂O, CO₂, etc. can affect phase relationships

Crash Course in trace element geochemistry

- What information can be gained from trace-elements
How do we make sense of spidergrams, etc.
- What controls the partitioning of trace-elements between different phases, namely minerals versus melts
- How can trace elements be used to study planetary differentiation processes
- Trace element geochemistry and radiogenic isotope geochemistry (next week)

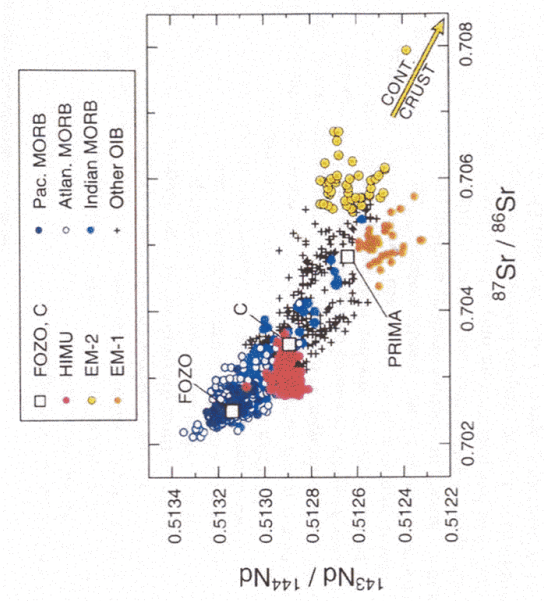
The mysterious spidergram



Hofmann, 1997
Nature 385: 219-229

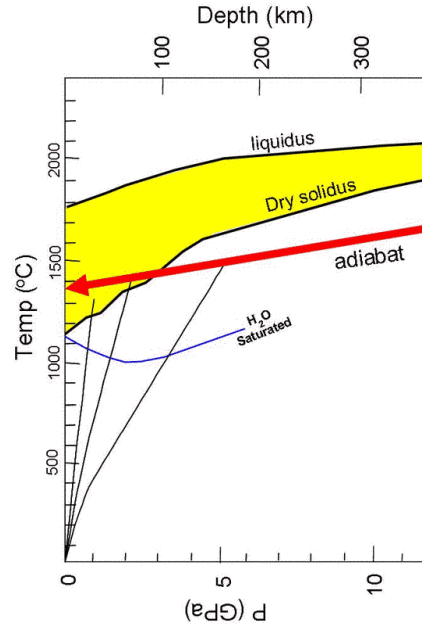
Geochemists love x-y plots, particularly of radiogenic isotopes.

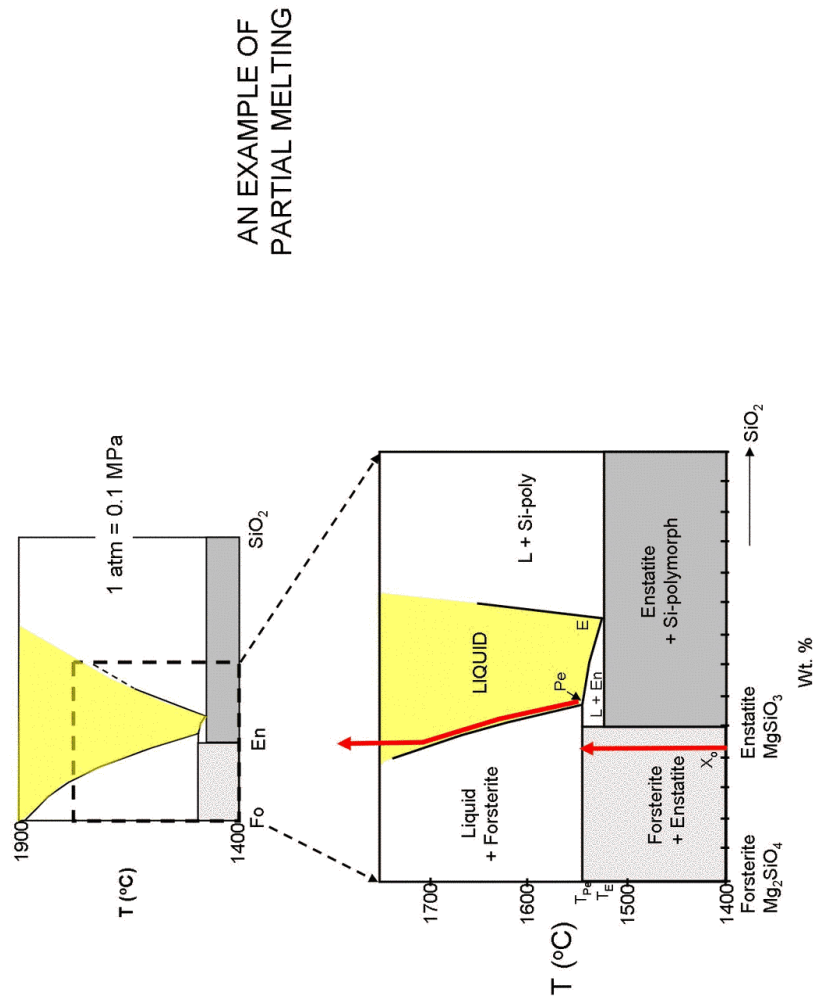
Why?



Hofmann, 1997
Nature 385: 219-229

How the mantle melts





How do trace elements get distributed

Partition coefficient

$$D = \frac{C_{\text{solid}}}{C_{\text{melt}}}$$

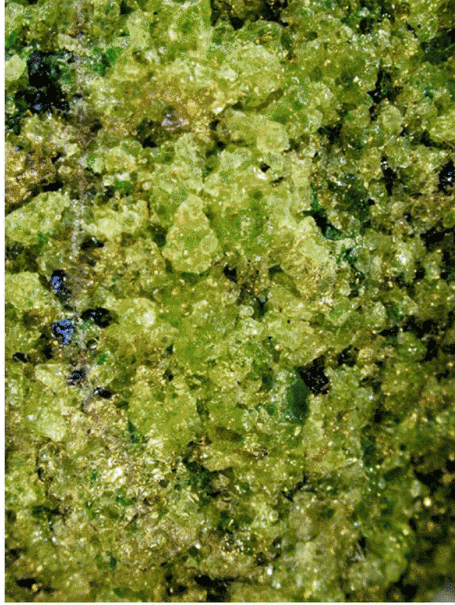
melt



Solid residue

D > 1 compatible in solid

D < 1 incompatible in solid



Phases (X_i)
 Olivine
 Orthopyroxene
 Clinopyroxene
 Garnet
 Spinel

$$D_B = \sum X_i D_i$$



$$C_{sol}^0 M_{sol}^0 = C_{sol} M_{sol} + C_{melt} M_{melt}$$

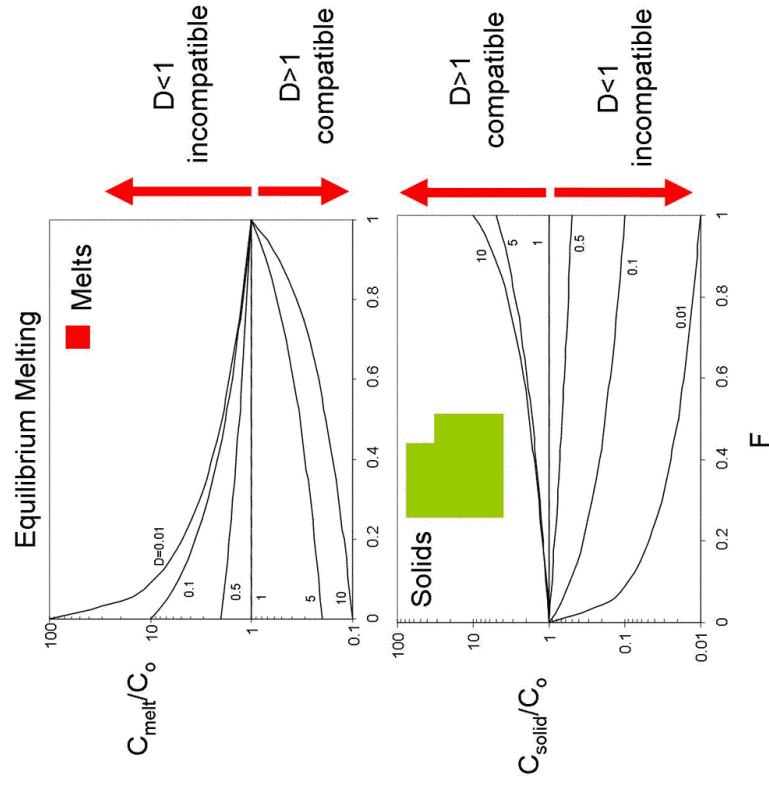
$$F = M_{melt} / M_{sol}^0$$

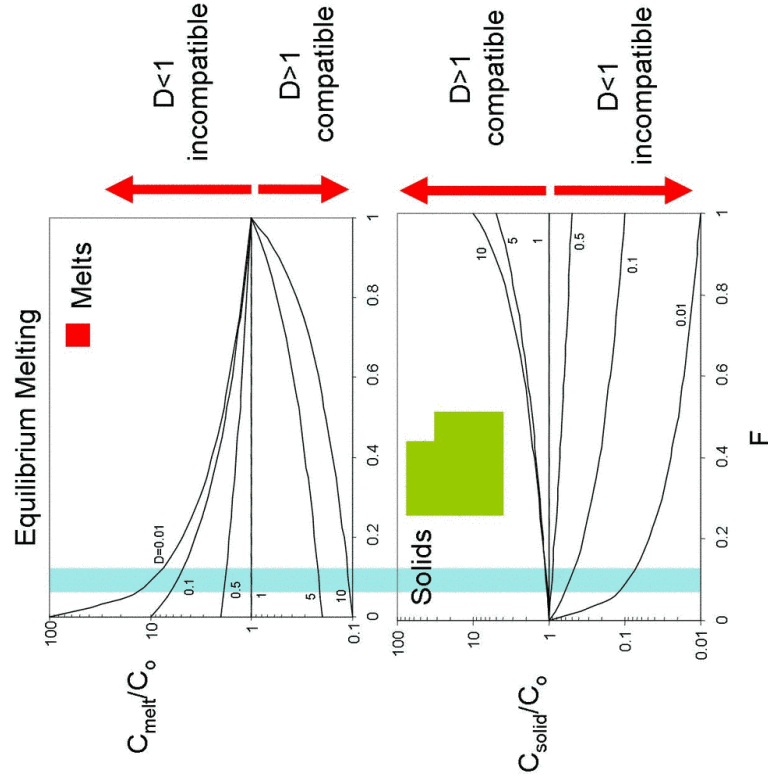
Equilibrium batch melting

$$D = \frac{C_{solid}}{C_{melt}}$$

$$\frac{C_{melt}}{C_{sol}^0} = \frac{1}{D_B + F(1 - D_B)}$$

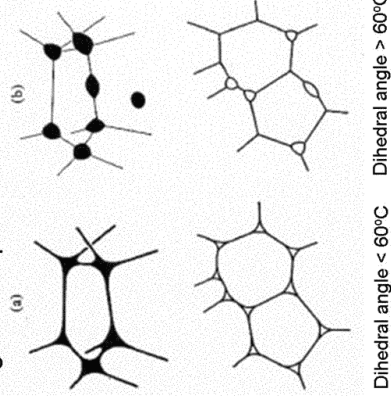
$$\frac{C_{sol}}{C_{sol}^0} = \frac{D_B}{D_B + F(1 - D_B)}$$



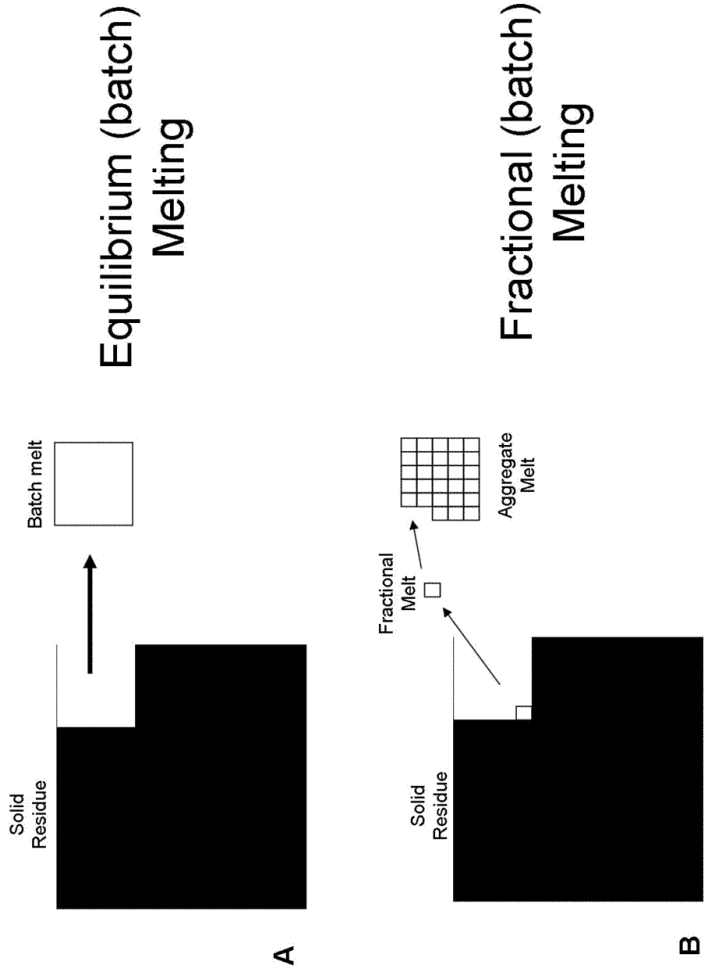


Melts can form interconnected pathways at small F , allowing for porous flow to occur if there is a buoyant force driving flow

Maximum melt retention may be small ($F \sim 0.01$), so melting might be expected to be fractional



From Brown, Hawkesworth & Wilson, 1992. Understanding the earth- a synthesis. Cambridge University Press.

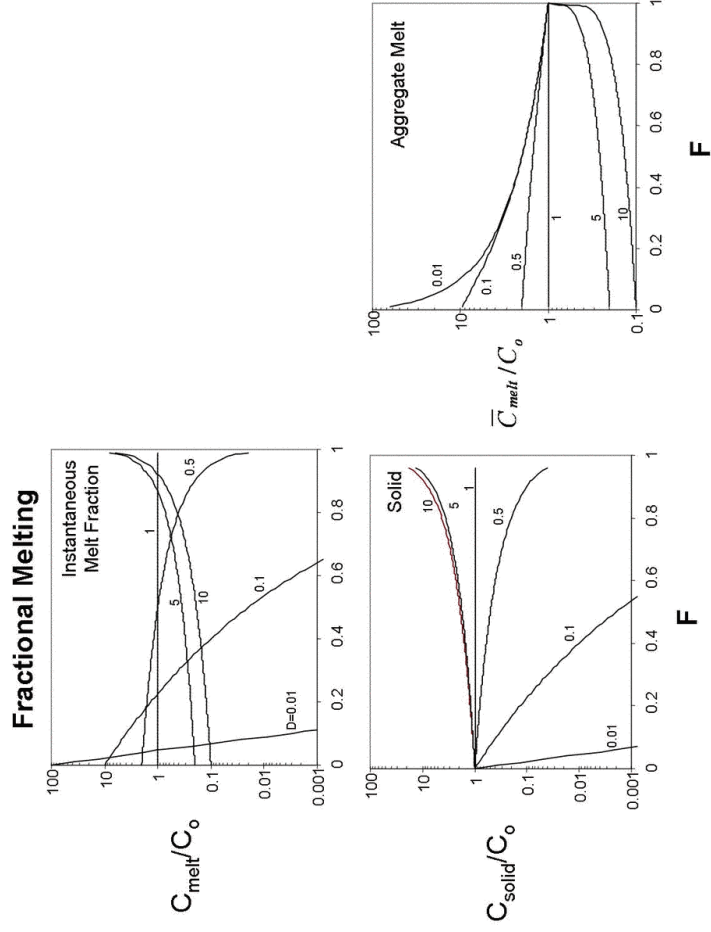


$$D_B = \frac{(m_{sol} / M_{sol})}{(dm_{melt} / dM_{melt})}$$

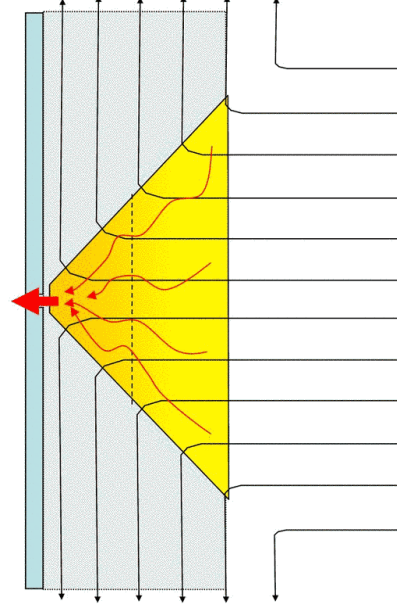
$$\frac{C_{sol}}{C_{sol}^0} = (1 - F)^{(1/D_B) - 1}$$

$$\frac{C_{melt}}{C_{sol}^0} = \frac{1}{D_B} (1 - F)^{(1/D_B) - 1}$$

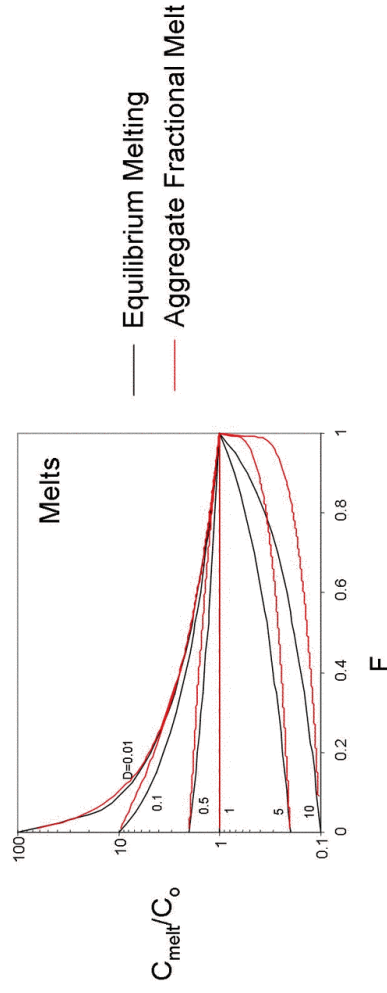
$$\bar{C}_{melt} = \frac{1 - (1 - F)^{1/D_B}}{F}$$



Mid-ocean Ridge



Fractional melts formed at a variety of depths and lateral distances from the ridge must concentrate (and pool) to a certain extent at the ridge



Aggregate fractional melt \sim Equilibrium (batch) melt
(not true for solid residues)

we can thus use the simpler batch melting equations to interpret melt compositions

one rule of thumb

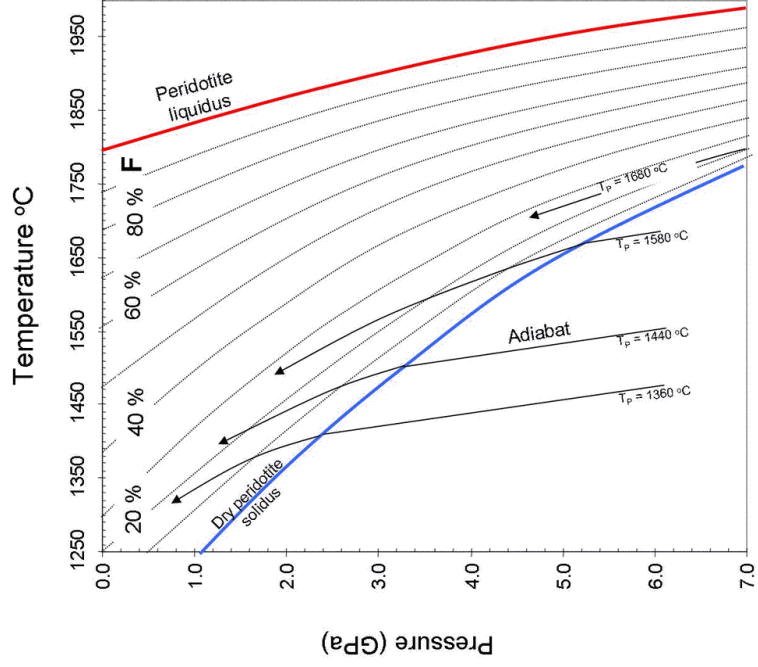
$$\frac{C_{melt}}{C_{sol}^0} = \frac{1}{D_B + F(1 - D_B)}$$

When $D = 0$ (perfectly incompatible element)
(e.g., Na, Cs, Nb, Ba)

$$\frac{C_{melt}}{C_{sol}^0} \sim \frac{1}{F}$$

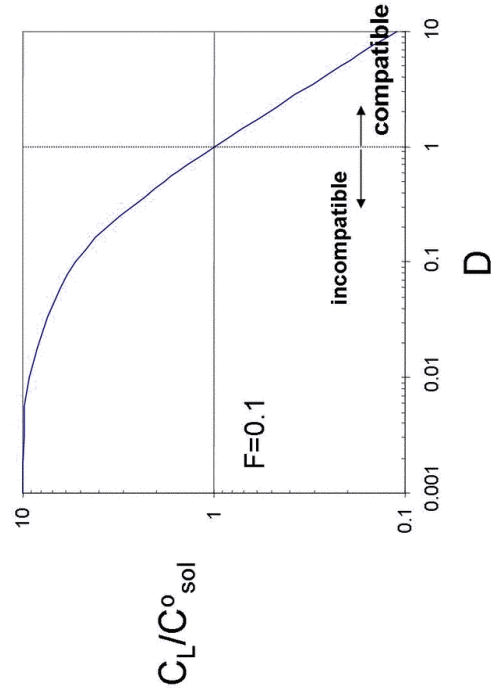
You can use the enrichment of an incompatible element to say something about melt fraction

Why is knowing F important?
 An independent way of checking for consistency in estimates of oceanic crustal thickness, mantle potential temperature, and temperature of magma source regions



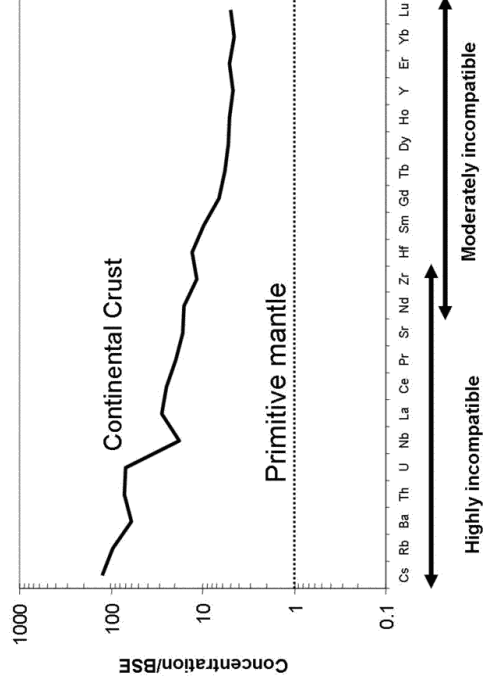
Now, let's get back to spidergrams

Composition of melt during equilibrium melting



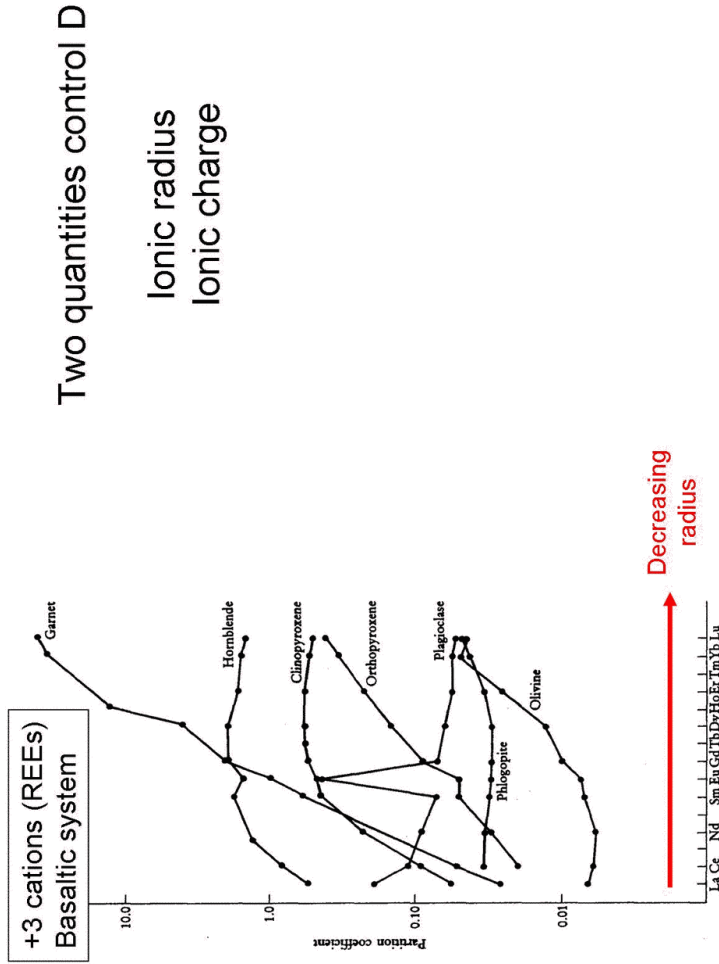
The less mysterious spidergram

Explain why there is a negative slope



- Elements have been arranged in order of decreasing incompatibility
- Relative to a primitive mantle, bulk continental crust appears to be equivalent to a 1 % melt

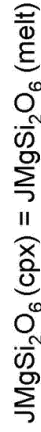
What controls trace-element partitioning between minerals and melt?



Borrowed from Rollinson

Trace-element fractionation is controlled by the ease with which the trace element can substitute for the dominant element making up the cation site of particular mineral.

Clinopyroxene $\text{CaMgSi}_2\text{O}_6$ unit cell is made up of two SiO_4^{4-} tetrahedra and two octahedral sites one centered on a Mg cation and another on a Ca cation



$$K = e^{-\Delta G^\circ / RT} = \frac{a_{\text{melt}}^{\text{JMgSi}_2\text{O}_6} \gamma_{\text{melt}}^{\text{JMgSi}_2\text{O}_6} X_{\text{melt}}^{\text{JMgSi}_2\text{O}_6}}{a_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6} \gamma_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6} X_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6}}$$

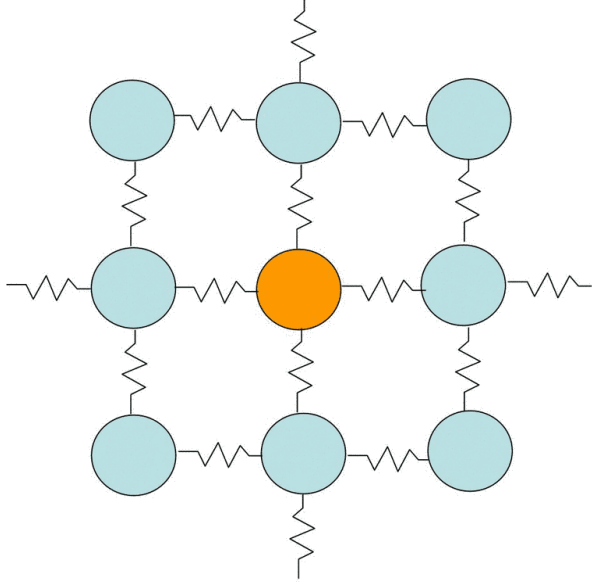
$$K = \frac{\gamma_{\text{melt}}^{\text{JMgSi}_2\text{O}_6}}{\gamma_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6}} \frac{1}{D_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6}}$$

$$D_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6} = \frac{X_{\text{Cpx}}^{\text{JMgSi}_2\text{O}_6}}{X_{\text{melt}}^{\text{JMgSi}_2\text{O}_6}}$$

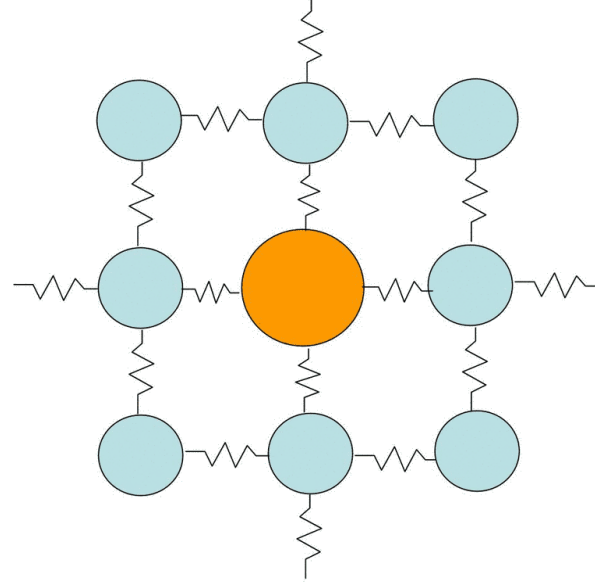
SIMPLIFIED VIEW

Imagine atoms connected by springs, which are analogs of bonds.

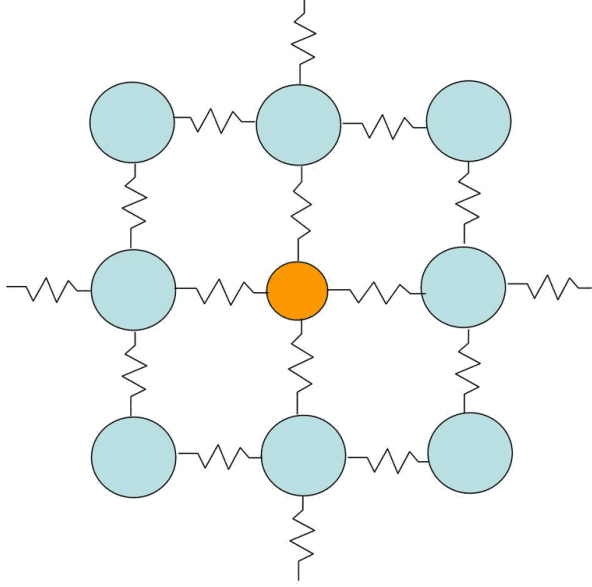
The most stable configuration is that in which the springs are stretched/compressed uniformly such that the strain energy is minimized.



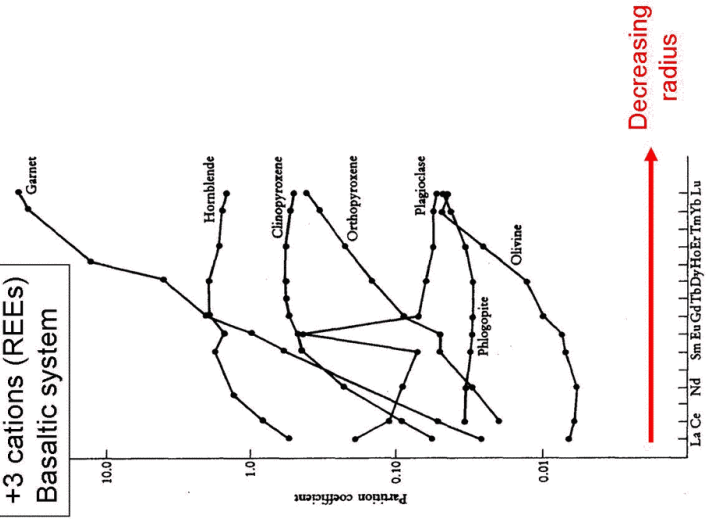
When we substitute a trace element that is too large, the bonds are compressed and strain is created. This is not a favorable configuration.



When we substitute a trace element that is too small, the bonds are extended and strain is created. This is also not a favorable configuration.



+3 cations (REEs)
Basaltic system

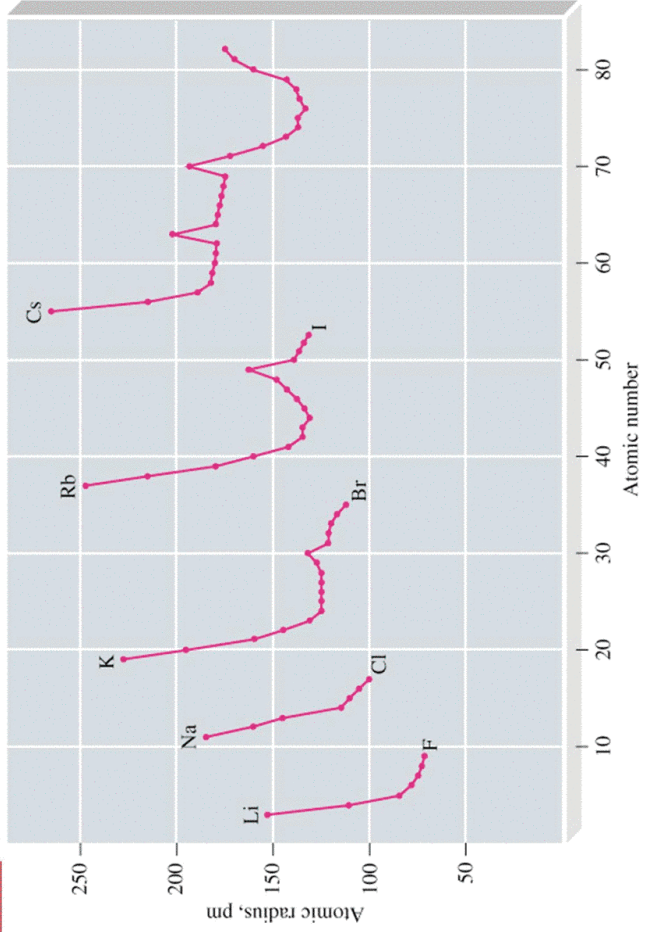


Elements with charge differing from that of the optimum site charge will be incompatible

Elements that are larger or smaller than the optimum site radius are incompatible

Borrowed from Rollinson

EFFECTIVE IONIC RADII



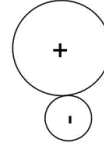
Figures from
 General Chemistry 8th Ed by Petrucci, Harwood,
 Herring (Prentice Hall)
http://cwx.prenhall.com/petrucci/media/lib/media_portfolio/index.html

CHEMICAL BONDING

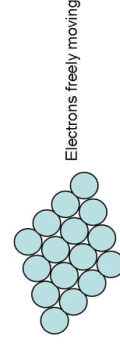
COVALENT BOND



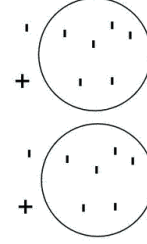
IONIC BOND



METALLIC BOND

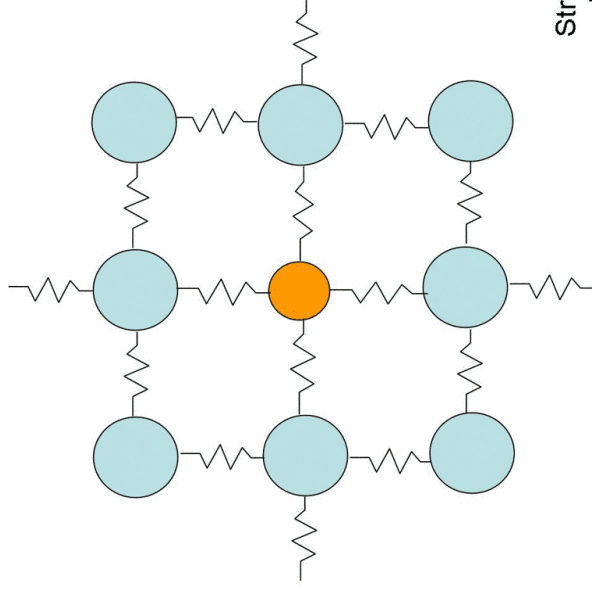


VAN DER WAAL'S BOND



The Elastic Strain Model
Blundy and Wood 1997

Strain Energy will depend on the strength or stiffness of the bond. The strength of the bond scales as a function of $Z_{\text{cation}}Z_{\text{anion}}/r_{\text{bond}}$.



$$\sigma = E \epsilon$$

Bond strength
strain (displacement)

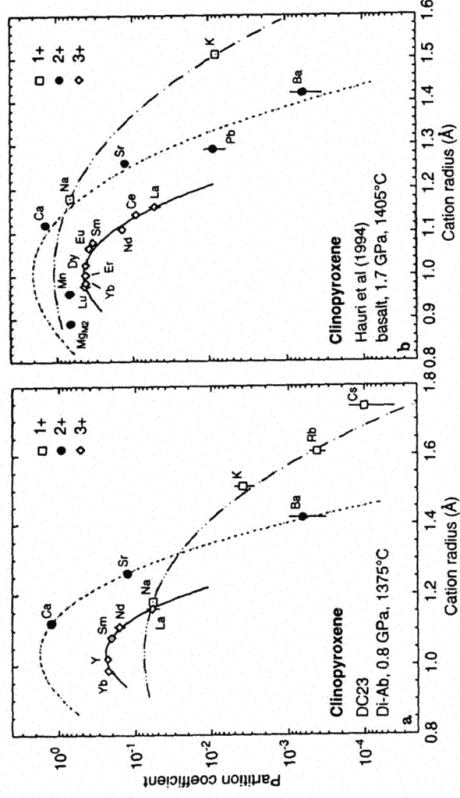
Strain energy Density $\sim \sigma \cdot \epsilon = E \epsilon \cdot \epsilon$

$$\Delta G_{\text{strain}} = 4\pi EN_A \left(\frac{r_o}{2} (r_i - r_o)^2 + \frac{1}{3} (r_i - r_o)^3 \right)$$

$$\Delta G_{\text{strain}} = 4\pi EN_A \left(\frac{r_o}{2} (r_i - r_o)^2 + \frac{1}{3} (r_i - r_o)^3 \right)$$

$$D^i = D^o \exp \left(\frac{-4\pi EN_A \left(\frac{r_o}{2} (r_i - r_o)^2 + \frac{1}{3} (r_i - r_o)^3 \right)}{RT} \right)$$

Wood and Blundy 1997



What controls the peak of the parabolas?
 What controls the width of the parabolas?

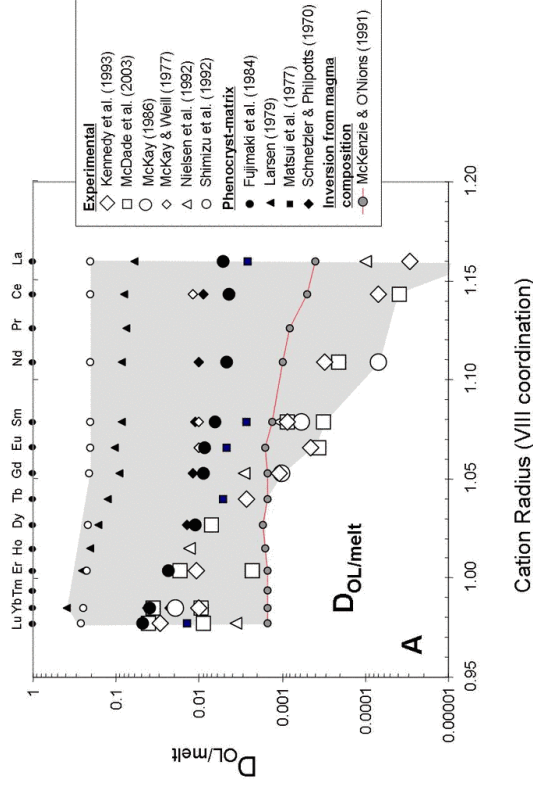
Elastic strain model is not perfectly rigorous, but it has remarkable predictive power if the partition coefficient of one element is known

$$D_i^{cpx/melt} = D_0^{cpx/melt} \exp \left(\frac{-4\pi N_A E_{cpx}}{RT} \left[\frac{r_o^{cpx}}{2} (r_o^{cpx} - r_i)^2 - \frac{1}{3} (r_o^{cpx} - r_i)^3 \right] \right)$$

$$D_i^{cpx/melt} = D_{Lu}^{cpx/melt} \exp \left(\frac{-4\pi N_A E_{cpx}}{RT} \left[\frac{r_o^{cpx}}{2} (r_{Lu}^{cpx} - r_i)^2 - \frac{1}{3} (r_{Lu}^{cpx} - r_i)^3 \right] \right)$$

How far can we push the predictive power of the elastic strain model?

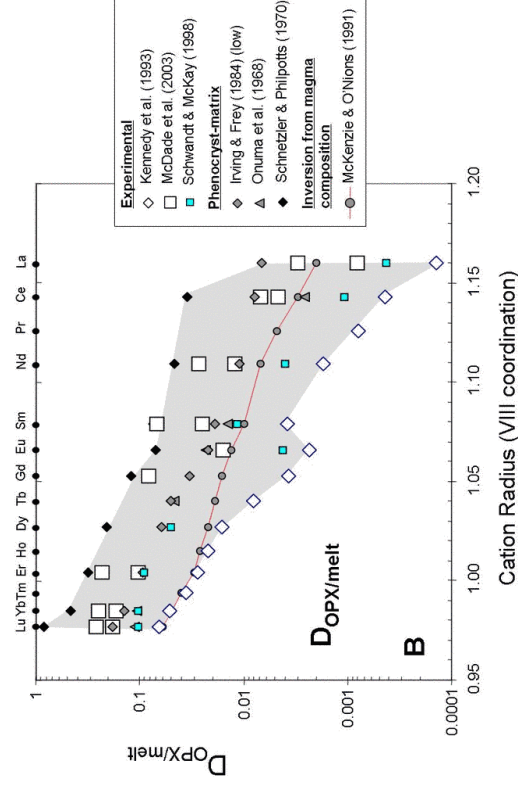
Measured REE partition coefficients of Olivine are problematic



Why is there so much scatter?

Measured REE partition coefficients for Orthopyroxene

Also scattered!



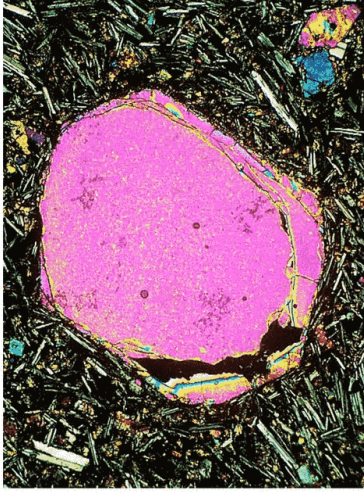
Possible reasons

Contamination in natural phenocryst-magma pairs

Concentrations near analytical detection limits

Disequilibrium in experiments

Non-Henry's law behavior in experiments



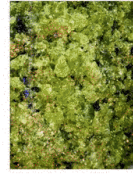
An alternative approach

$$D_{ol/melt} = C_{ol} / C_{melt}$$

$$C_{ol}/C_{Cpx} * C_{cpx}/C_{melt} = D_{ol/melt}$$

We know this pretty well
(for a given melt composition)

Let's look at peridotite xenoliths



subsolidus

>solidus

$$C_{ol}/C_{Cpx} * C_{cpx}/C_{melt} = D_{ol/melt}$$

Need to correct up to melting T

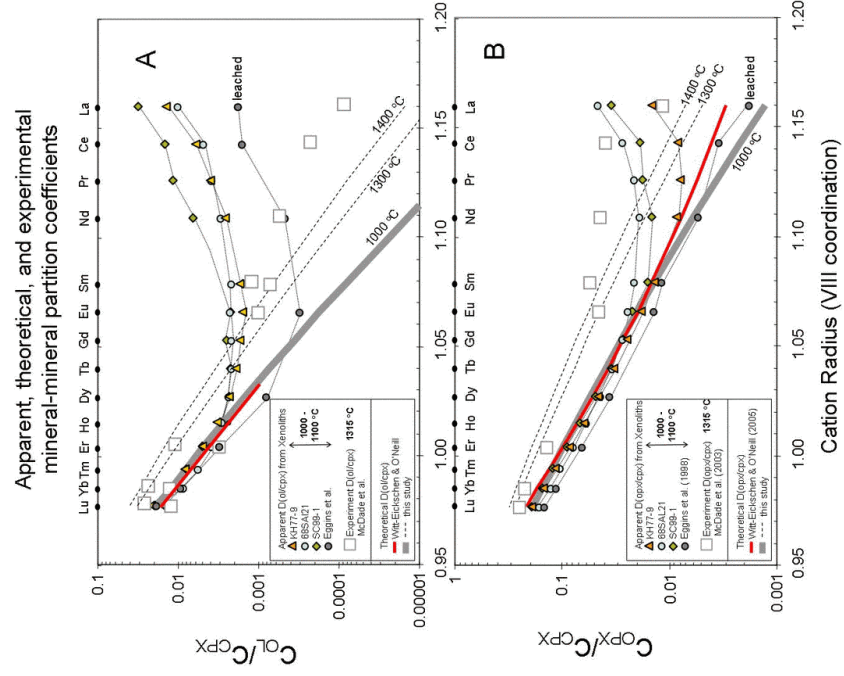
Modify Blundy and Wood (1997) model for mineral-mineral partitioning

$$K \sim D^{ol/cpx} = C_{REE}^{ol} / C_{REE}^{cpx}$$

$$D_i^{ol/cpx} = \frac{D_i^{ol/melt}}{D_i^{cpx/melt}} = D^{ol/cpx} \exp\left(\frac{-4\pi N_A}{RT} \left[\frac{1}{2}(r_{Lu}^2 - r_i^2)(E_{ol}^{ol} - E_{cpx}^{cpx}) + \frac{1}{3}(r_i^3 - r_{Lu}^3)(E_{ol} - E_{cpx}) \right]\right)$$

Pick mineral grains and analyze by solution ICP-MS for trace-elements

Lee et al. 2006 (in revision)



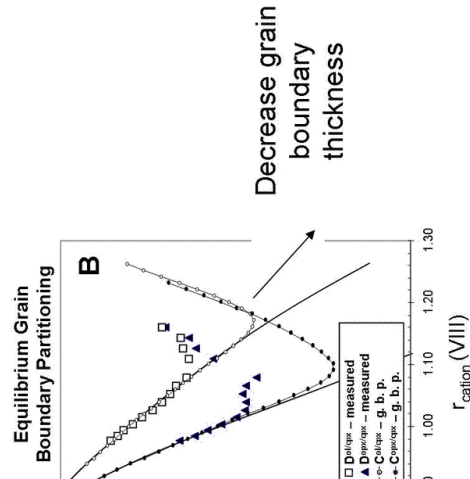
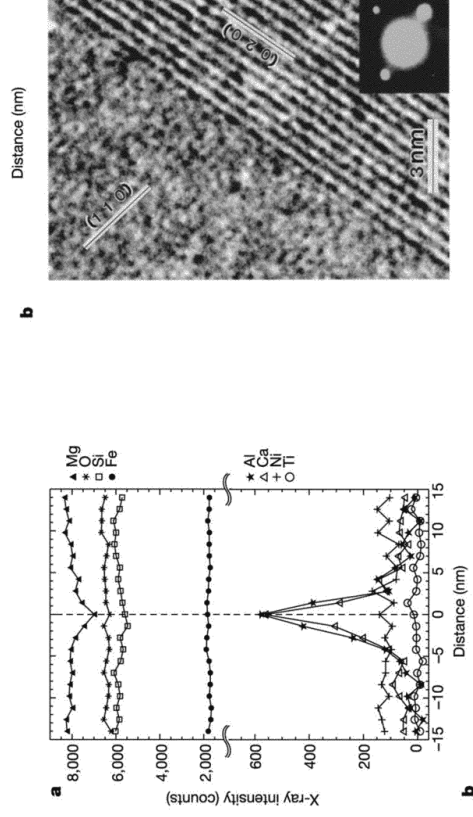
Lee et al. 2006 (in revision)

One possibility for the U-shaped patterns in previous figures....

Equilibrium grain boundary partitioning

Hiraga et al. 2004

$$\frac{X_{GB}}{X_{GB0} - X_{GB}} = \frac{X_{GM}}{1 - X_{GM}} \exp\left(\frac{\gamma}{RT}\right)$$

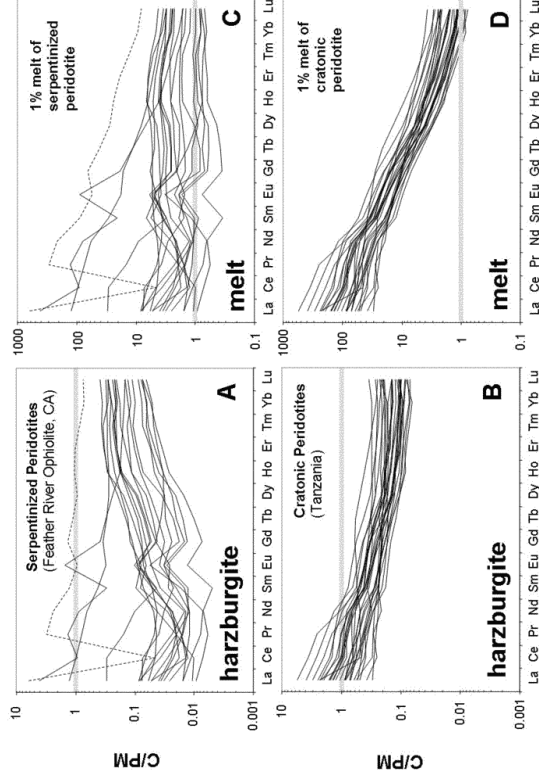


Grain boundaries are probably not significant reservoirs for LREEs (may still be significant for very incompatible trace elements)

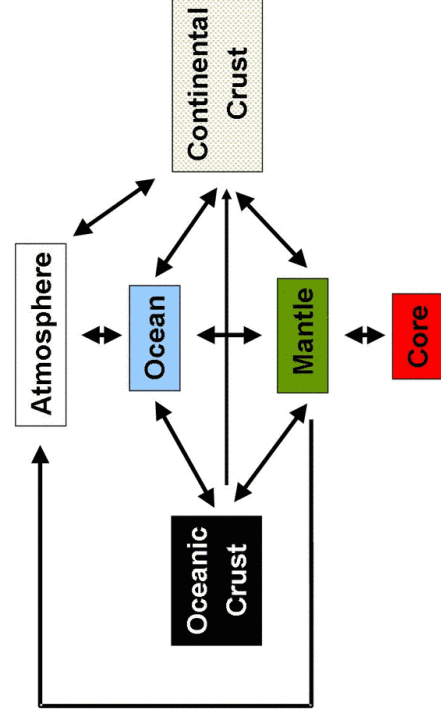
Grain boundaries are probably important as pathways for trace-element transport

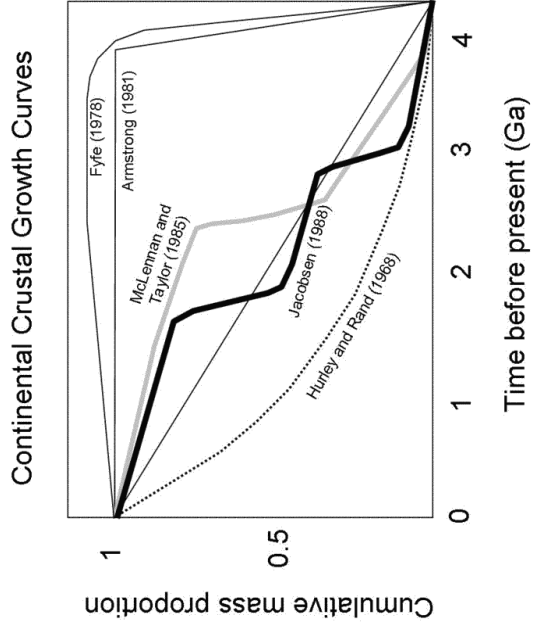
Lee et al. 2006 (in revision)

REE Partition coefficients for olivine and orthopyroxene can be useful
Under some circumstances: melting of harzburgite

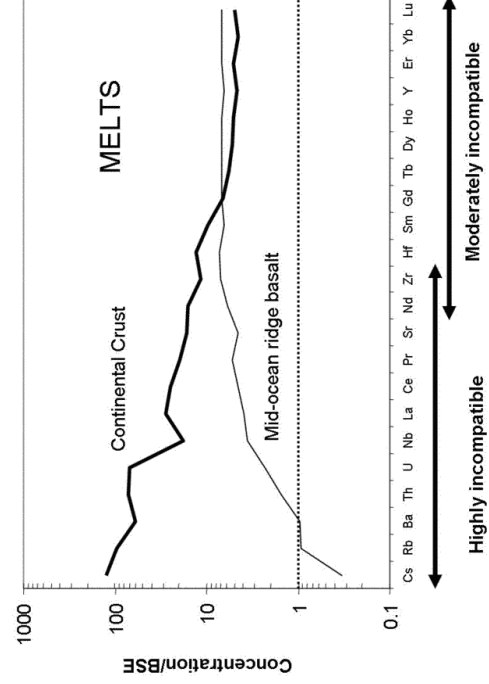


Now, let's look at how trace elements can be used to look at gross
chemical evolution of our planet

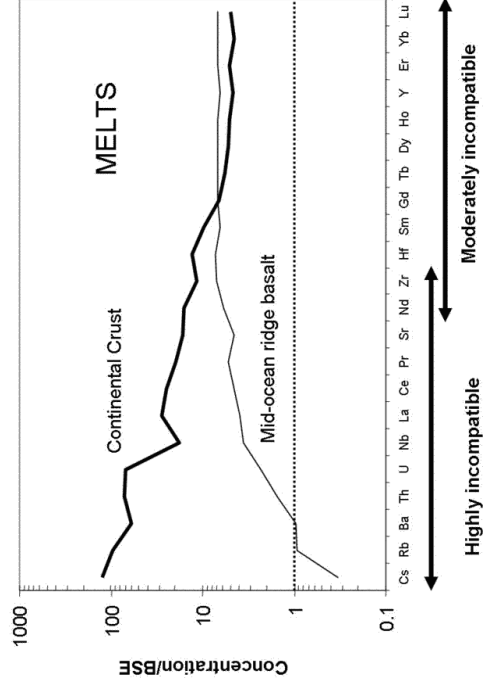




Why does the mid-ocean ridge basalt appear to have a “depleted” signature when it is a melt?

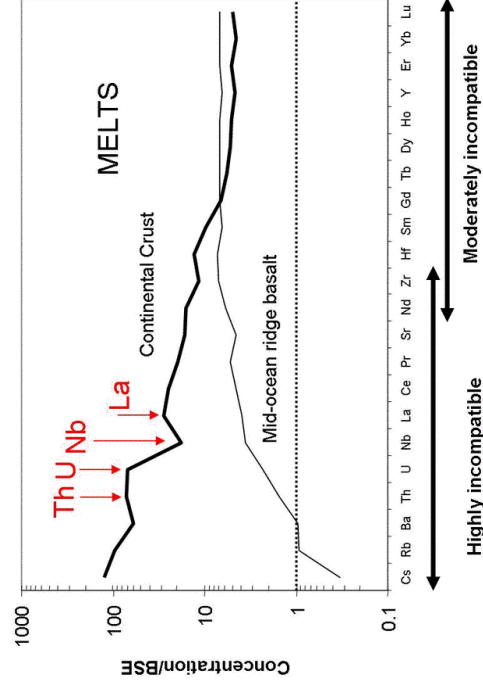


Why does the mid-ocean ridge basalt appear to have a “depleted” signature when it is a melt?



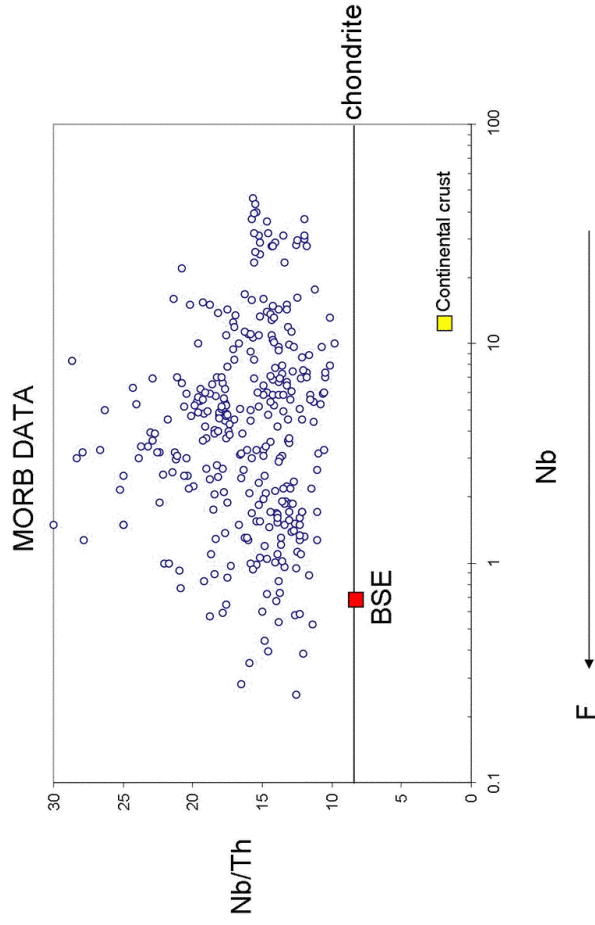
MORB taps a mantle that has already seen previous extraction of incompatible elements, most of which are stored in the continental crust

Distinct feature of continental crust is that it has a Nb depletion relative to Th, U, La



Continental crust likely to have formed in arcs, which have distinct Nb depletions due to preferential retention of Nb in arc source regions and preferential liberation of Th, U and La in subduction zone fluids

Nb/Th is relatively constant in MORB over several orders of magnitude of Nb.
 Nb/Th of MORB represents Nb/Th ratio of MORB source mantle

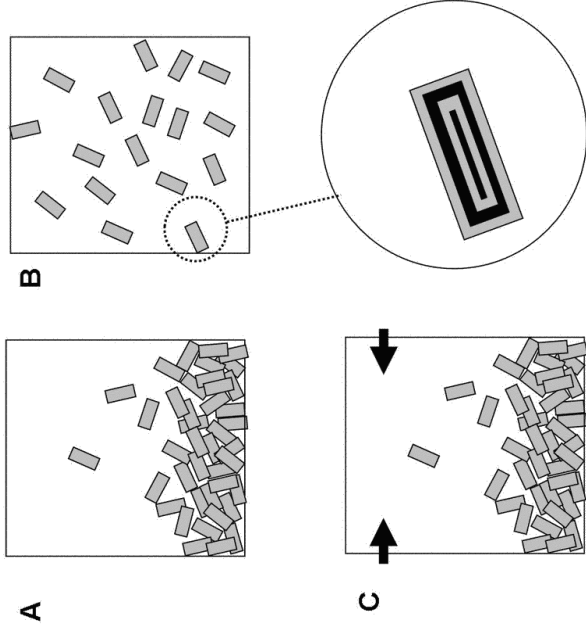


$$\frac{C_{melt}^A}{C_{melt}^B} = \frac{C_{sol}^{A0} D_B + F(1 - D_B)}{C_{sol}^{B0} D_A + F(1 - D_A)}$$

IF D_A and D_B are identical or both close to zero

then $\frac{C_{melt}^A}{C_{melt}^B}$ is constant

Fractional crystallization



$$\frac{C_{melt}^i}{C_{melt}^0} = F^{D^i-1}$$

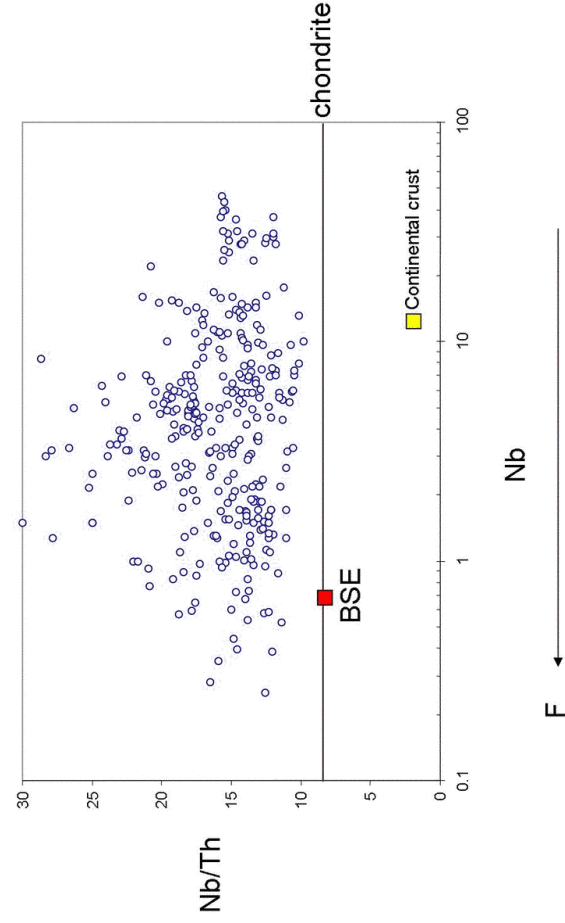
$$\left(\frac{C_{melt}^A}{C_{melt}^B} \right) = \left(\frac{C_{melt}^{oA}}{C_{melt}^{oB}} \right) F^{D^A - D^B}$$

If $D^A = D^B$ or $= 0$, then

$$\left(\frac{C_{melt}^A}{C_{melt}^B} \right) = \left(\frac{C_{melt}^{oA}}{C_{melt}^{oB}} \right)$$

Nb/Th of upper mantle is HIGH compared to Bulk Silicate Earth (BSE)

--MORB mantle is residue of extraction of continental crust (low Nb/Th)



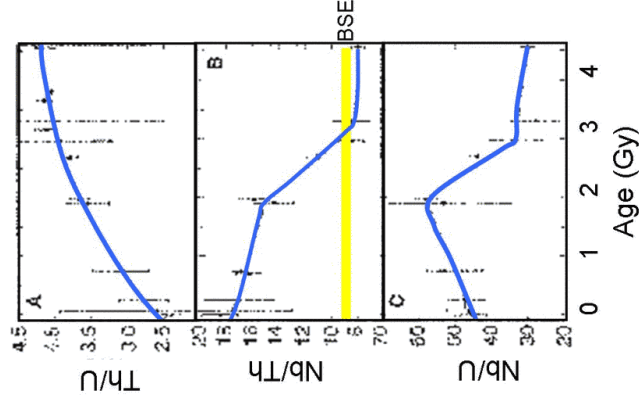
One example of how trace elements might be used to say something about planetary differentiation

Evolution of the Continents and the Atmosphere Inferred from Th-U-Nb Systematics of the Depleted Mantle

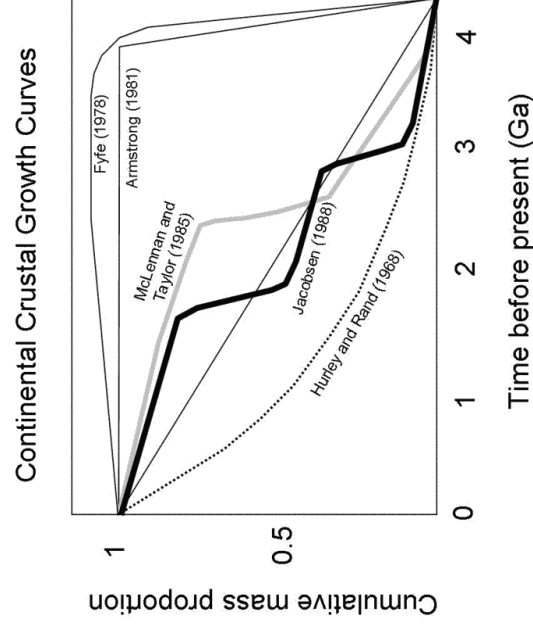
Kenneth D. Collerson* and Balz S. Kamber

Temporal evolution of depleted mantle thorium-uranium-niobium systematics constrain the amount of continental crust present through Earth's history (through the niobium/thorium ratio) and date formation of a globally oxidizing atmosphere and hydrosphere at approximately 2.0 billion years ago (through the niobium/uranium ratio). Increase in the niobium/thorium ratio shows involvement of hydrated lithosphere in differentiation of Earth since approximately 3.8 billion years ago. After approximately 2.0 billion years ago, the decreasing mantle thorium/uranium ratio portrays mainly preferential recycling of uranium in an oxidizing atmosphere and hydrosphere. Net growth rate of continental crust has varied over time, and continents are still growing today.

Science 1999



However, the debate on crustal growth will continue

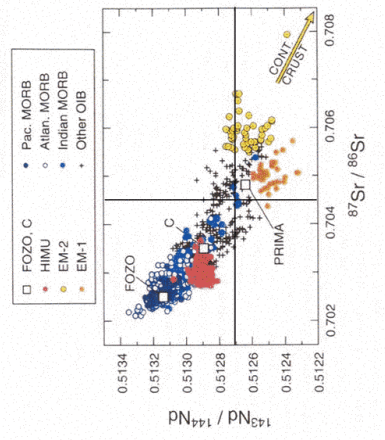


END OF CRASH COURSE IN TRACE-ELEMENT GEOCHEMISTRY

Next on the menu will be radiogenic isotope geochemistry

^{147}Sm decays to ^{143}Nd
 ^{87}Rb decays to ^{87}Sr

Parent-daughter fractionation is key



Hofmann 1997