TRACE-ELEMENT & ISOTOPE GEOCHEMISTRY

Major Element   this is petrology

    > 1 wt %

    majors have concentrations high enough to saturate phases

minor element

    $0.1 - 1$ wt %

trace element

    < 0.1 wt.%

    concentrations too low to dictate phase saturation

    - trace elements passively substitute into phases

1 wt % = 1g / 100g of rock

1 ppm = $1/10^6$ g

1 ppb = $1/10^9$ g

1 ppt = $1/10^{12}$ g   (be careful, sometimes ppt = parts per thousand)

    1 wt % = 10^4 ppm

Elements defined by proton number Z

    Atom has a nucleus and an electron shell

        Z protons   (Z electrons)

        N neutrons

        $A = Z + N$ = atomic number
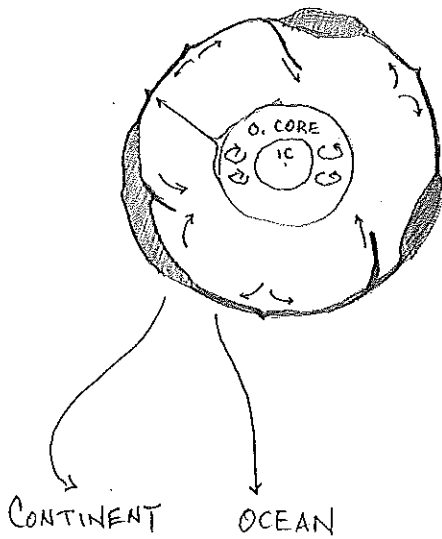
Atoms can have variable N, nuclides

$$^A_N Z \qquad e.g. \qquad ^{16}_8 O \quad ^{17}_8 O \quad ^{18}_8 O$$
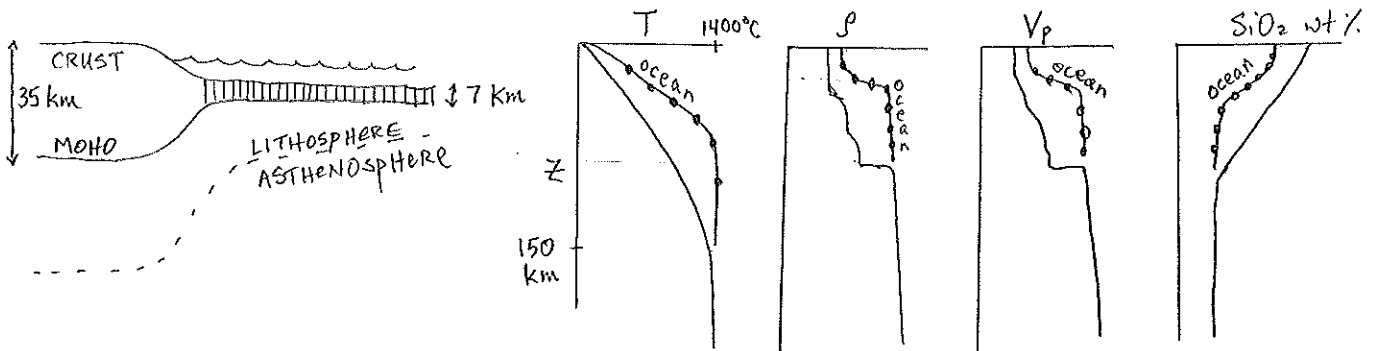
INTRODUCTION

BULK EARTH = total Earth

BULK SILICATE EARTH = BULK EARTH - CORE

CORE

ATMOSPHERE

OCEANS

CONTINENT   OCEAN

CONTINENTAL CRUST ~ 0.3% OF B.S.E.

ELEMENTAL COMPOSITION

	BULK EARTH	BULK SILICATE EARTH	CONT. CRUST	OCEANIC CRUST
O wt%	32	44	44	44
Na	0.25	0.29	2.4	2.1
Mg	14.9	22	2.2	4.6
Al	1.43	2.2	7.96	8.5
Si	14.6	22	28.8	23.1
Ca	1.66	2.5	3.9	8.08
K	~.02	~.02	2.14	0.13
Fe	32	6.3	4.3	8.2
Ni	1.7	0.2	0.0056	0.0135
U	$\sim 1\times10^{-7}$	$\sim 2\times10^{-7}$	2×10^{-4}	1×10^{-5}

WHERE IS MOST OF THE EARTH'S OXYGEN, IRON ?
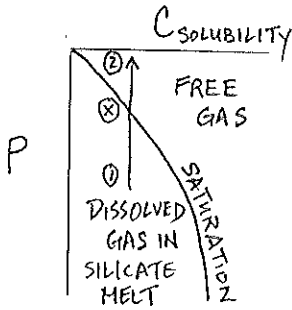
WHY ARE SOME ELEMENTS ENRICHED IN CONTINENTAL CRUST?

DIFFERENTIATION

PHYSICAL SEGREGATION OF DIFFERENT PHASES
- REQUIRES GRAVITY
- USUALLY INVOLVES SEPARATION OF SOLID, LIQUID, GAS
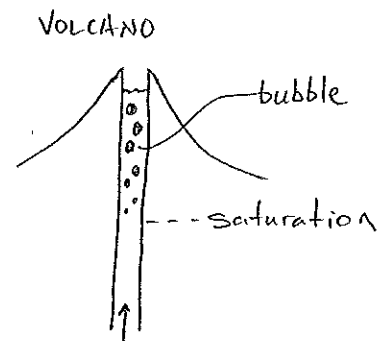 (although solid state segregation is also possible on smaller lengthscales)
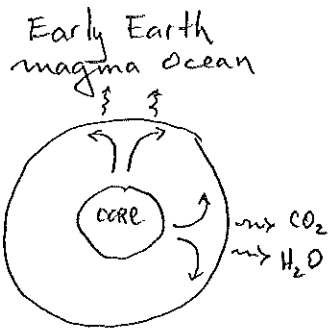
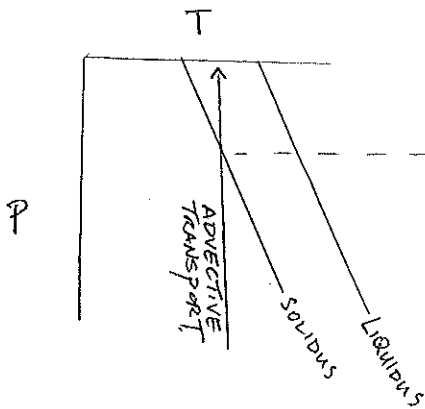EXAMPLES
- GAS-LIQUID SEPARATION: FORMATION OF ATMOSPHERE

magma at ① decompresses and crosses saturation curve to ②
at ⓧ gas bubbles exsolve.

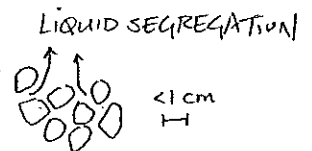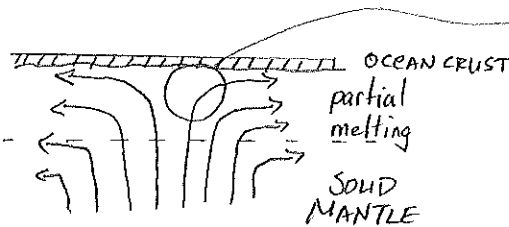Since $\rho_{gas} \ll \rho_{melt}$, bubbles rise to surface and escape

Early Earth
magma ocean
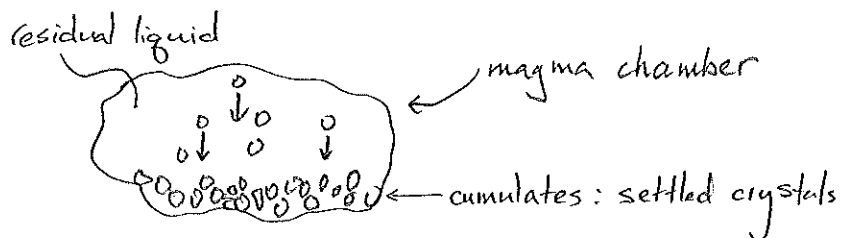
VOLCANO

- SOLID LIQUID SEPERATION

$$\rho_S > \rho_L$$

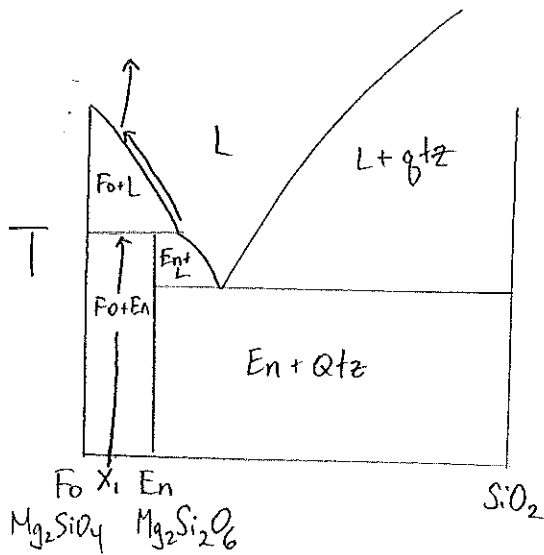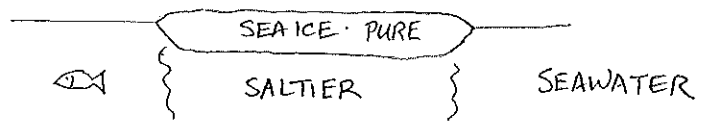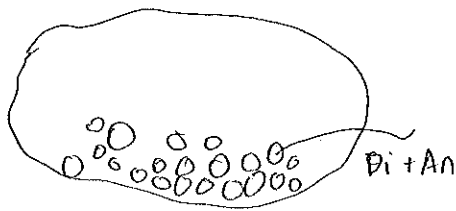- PARTIAL MELTING

LIQUID SEGREGATION
<1 cm

OCEAN CRUST
partial melting
SOLID MANTLE

- CRYSTAL SEGREGATION OF MAGMA

residual liquid

magma chamber

cumulates: settled crystals

SOLIDS AND LIQUIDS GENERALLY DON'T HAVE SAME COMPOSITION
SO PHYSICAL SEGREGATION LEADS TO CHEMICAL DIFFERENTIATION

T — L

An+L   Di + L

An + Di

An χ Di
$CaAl_2Si_2O_6$ $CaMgSi_2O_6$

$L + H_2O_{ice}$ 0°C   L

T

-4°C

$L + NaCl$

$H_2O_{ice} + NaCl$

H_2O X   NaCl

$P = 1\ atm$

Di + An

SEA ICE · PURE

SALTIER   SEAWATER

T — L

Fo + L

$L + qtz$

$En + L$

Fo + En

En + Qtz

Fo X_1 En SiO_2
Mg_2SiO_4 $Mg_2Si_2O_6$

Partial melting of mantle
yields melts richer in Si
than source.

Composition of Bulk Earth

General trends
- Low mass elements most abundant with exception of volatiles
- Local maximum at Fe
- Zigzaw pattern
  even AN common
  odd AN rare

The zigzaw pattern is inherited from the sun and
  is a result of nucleosynthesis. All rocks inherit this relative pattern.
We thus normalize all data to another Rock reference.

- cont. crust is enriched in REEs relative to mantle
- MORB is also enriched, but LREE is depleted

How do we enrich or depleted elements?

Partitioning of trace-elements   TRACE $< 1000 \, ppm$

OLIVINE-MELT equilibria
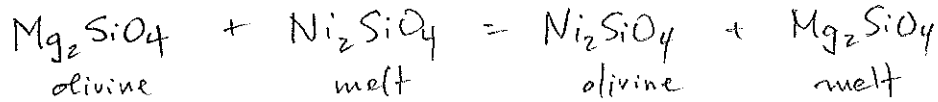 let's consider Ni exchange

$$Mg_2SiO_4 \; + \; Ni_2SiO_4 \; = \; Ni_2SiO_4 \; + \; Mg_2SiO_4$$
$\quad$ olivine $\qquad$ melt $\qquad\quad$ olivine $\qquad$ melt

$$K_i = \frac{a^{OL}_{Ni_2SiO_4} \; a^{melt}_{FO}}{a^{OL}_{FO} \; a^{melt}_{Ni_2SiO_4}}$$

a = activity
equilibrium constant depends on T, P

$$\Delta G_{rxn} = -RT \ln K_i$$

$$K = \frac{X^2_{Ni \, in \, OL} \; X^2_{Mg \, in \, melt}}{X^2_{Mg \, in \, OL} \; X^2_{Ni \, in \, melt}} = \left(\frac{X_{Ni \, OL}}{X_{Ni \, melt}} \right)^2 \left(\frac{X_{Mg \, in \, melt}}{X^2_{Mg \, in \, OL}} \right)^2$$

X = mole fraction of cation in a site

here, Ni we assume as trace, but Mg as a major element.
— Thus if we assume $X_{Mg \, melt} / X_{Mg \, OL}$ are constant
— we can focus our attention on $X_{Ni \, OL} / X_{Ni \, melt}$

Partition Coefficient

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

where C is weight concentration

$$D \sim \frac{X_{i \, solid}}{X_{i \, melt}}$$

BUT may depend on bulk composition
$T, + P.$

$D \geqslant 1 \quad$ compatible

$D = 0.5 - 1 \quad$ moderately incompatible

$D < 0.1 \quad$ incompatible (highly)

PARTITIONING

BULK PARTITION COEFFICIENT

$$\underline{D}_B = \sum D_i X_i$$

where D_i are mineral/melt partition coefficients

ROCK CONTAINS more than one PHASE

X_i are the volume fraction of mineral i

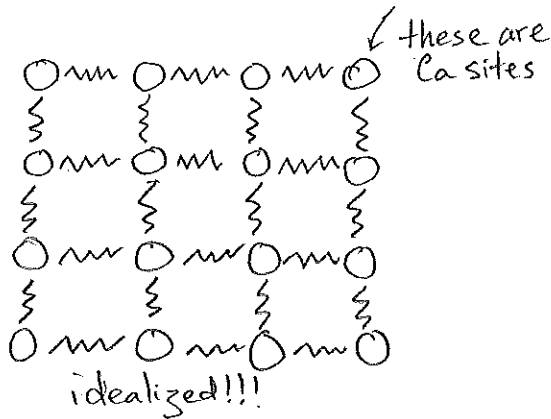$$\sum X_i = 1$$

WHAT CONTROLS D_i FOR A GIVEN MINERAL?

GOLDSCHMIDT RULES (observational)

- ions of similar radii and charge partition into mineral in similar proportions
- ion of smaller radius for a given charge partitions into mineral preferentially, i.e. higher field strength $z/r \rightarrow$ compatible
- ion of greater charge for a given radius partitions into mineral preferentially, i.e. again higher z/r for given r is more compatible
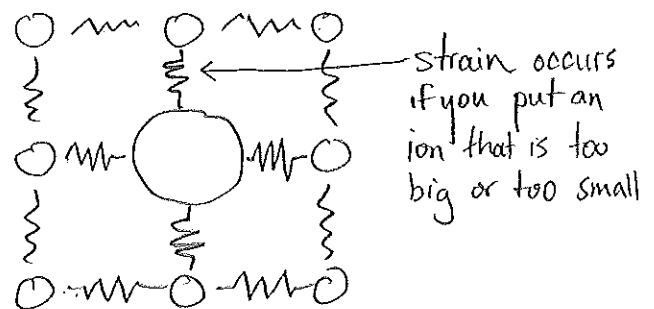
* a more quantitative view

Wood + Blundy 1997

Consider a lattice site, e.g. M2 site in pyroxene $CaMgSi_2O_6$
$$M2\ M1\ T_2\ O_6$$

these are Ca sites

idealized!!!

Substituting ions of different charge or radius than Ca

strain occurs if you put an ion that is too big or too small

Free energy generated by substituting an ion into site is

$$\Delta G_{strain} = 4\pi E N_A \left(\frac{r_0}{2}(r_i-r_0)^2 + \frac{1}{3}(r_i-r_0)^3 \right)$$
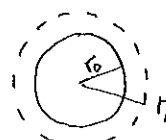
$r_i - r_0 = $ strain

$E = $ Young's Modulus in GPa (units of stress or $\frac{force}{area}$)
measure of the stiffness of a bond

we can arrive at the above as follows

stress imparted to lattice site by substitution is

$$\sigma = E \epsilon$$

stress Pa Pa strain

$r_i - r_0 = $ displacement

$\frac{r_i - r_0}{r_0} = \epsilon$

total energy needed to substitute ion is = to work needed

$$W = F \cdot d$$

force   displacement

$$W = \sigma \cdot A \cdot d$$

stress   surface area   displacement

$$W = E \epsilon A d$$

$$\sim E \left(\frac{r_i-r_0}{r_0}\right)(4\pi r_0^2)(r_i-r_0)$$

$$\sim 4\pi E \, r_0 \, (r_i-r_0)^2$$

– this is the first term in above eqn of ΔG_{strain}
– 2nd term $(r_i-r_0)^3$ is an empirical correction for asymmetry.

→ if $r_i = r_0$ $\Delta G_{strain} = 0$
   and element is compatible, $D \geq 1$

→ if $r_i \gg r_0$ } $\Delta G_{strain} > 0$, $D < 1$
   or $r_i \ll r_0$ }

recognizing that we are interested in partitioning b/wn solid + melt, we need to estimate ΔG_{strain} for melt and solid

- we assume that ΔG_{strain} for melt is small so the total strain energy of substitution lies in the mineral

recall $\Delta G = -RT \ln K$

↖ exchange equilibrium constant

$\Delta G \sim -RT \ln D$ (if melt + min major element composition are constant)

↑
ΔG_{strain}

$$D = D_0 \exp\left\{ \frac{-4\pi E N_A \left(\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3 \right)}{RT} \right\}$$

$E = \dfrac{3K}{1 - 2\sigma}$
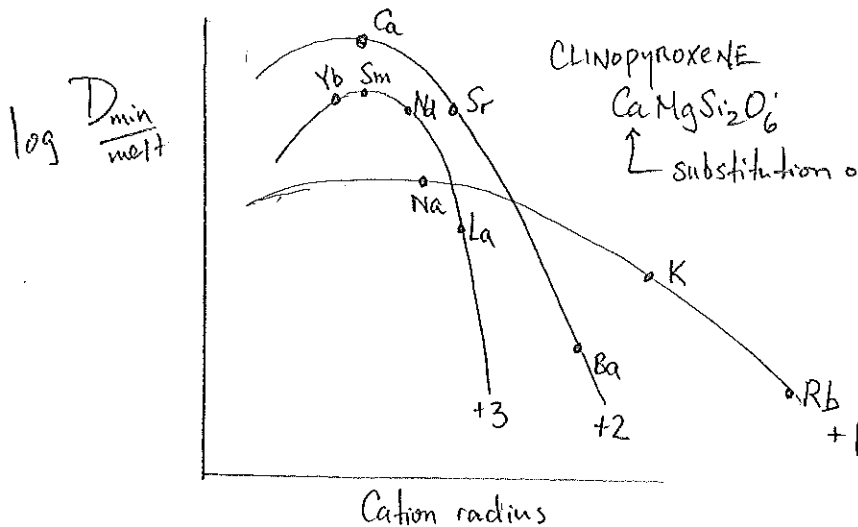
← BULK MODULUS

↑
Young's modulus

↳ POISSON'S RATIO

$K \sim \dfrac{Z_a Z_c e^2 (n-1)}{d_0 V_0}$

charge anion / charge cation / e^-
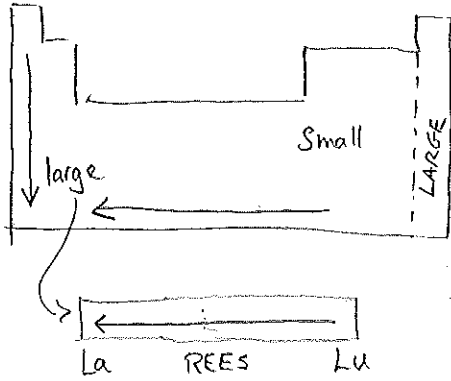
interatomic separation / molecular volume

} K, E depend on charge of cation higher the charge higher E

$\log \dfrac{D_{min}}{melt}$

Cation radius

CLINOPYROXENE
$CaMgSi_2O_6$
↑ substitution of trace elements into Ca site

Q: why is $D_{Sr} < D_{Ca}$?

Q: why are parabolas wider for +1 charges? Narrow for +3 charges? What about +4?

ATOMIC RADIUS

Small

LARGE

large

La   REES   Lu

Lanthanide contraction

- radius of atom depends on electron shell
- the larger the # of shells, the larger the atom
- within an energy level as Z increases atoms contract because total charge is increasing but average r of highest shell doesn't change too much

IONIC RADIUS

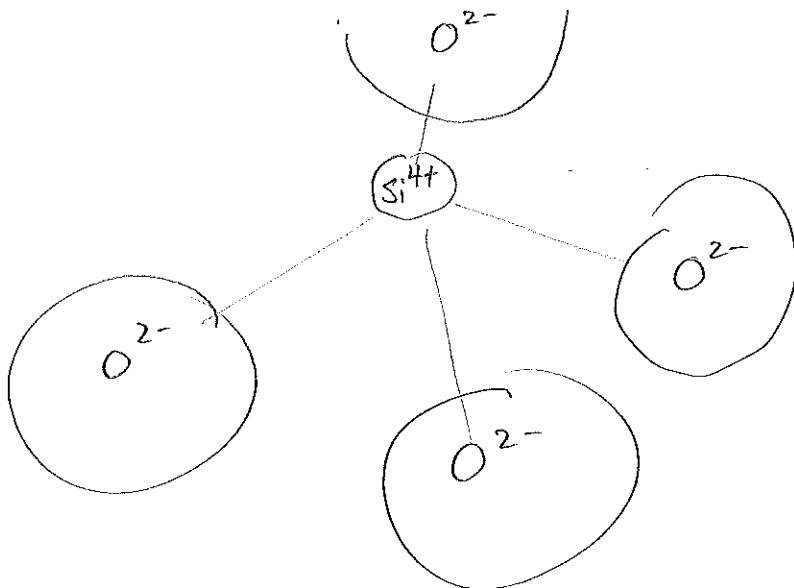follows similar trends as atomic radius

$$r_{Cation} < r_{atom}$$

electron removed, which reduces repulsion within the shell.

$$r_{anion} > r_{atom}$$

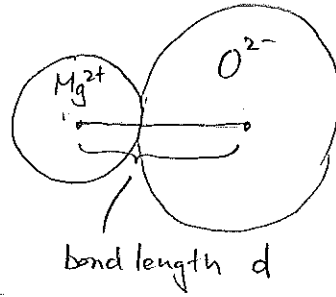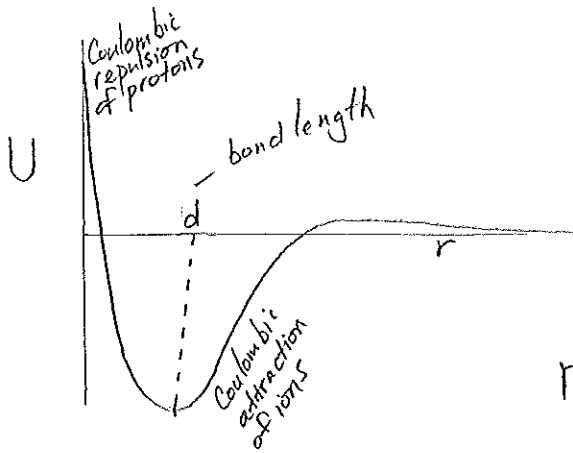e^- added increases e^- repulsion in outer shell, causing e^- to spread out

$$r_{cation} < r_{anion}$$

O^{2-} are very large compared to cations

Silica Tetrahedra

ionic radii

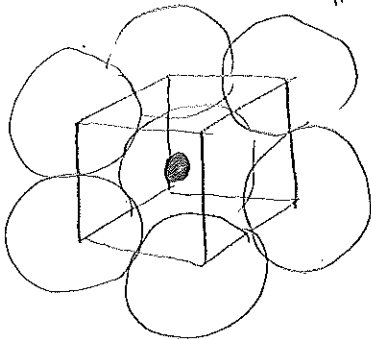U — potential energy curve with axes U and r, labeled *Coulombic repulsion of protons*, *bond length d*, and *Coulombic attraction of ions*

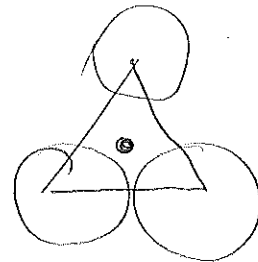Mg^{2+} and O^{2-} diagram, bond length d

$$r_{Mg^{2+}} = d - r_{O^{2-}}$$

— assume O^{2-} radius is 1.40 A°, and cation radii are determined by measuring bond length of oxide compounds

in detail cation radii depends a little on coordination number CN
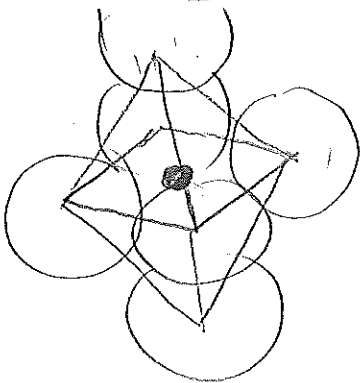
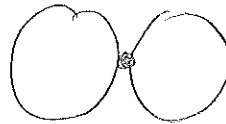CN is # of ligands to anions

CN=8 cubic
$R_C/R_A > 0.732$
  ↑   ↑
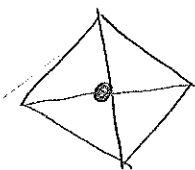cation   anion

TRIANGULAR
CN=3
$R_C/R_A = 0.225 - 0.155$
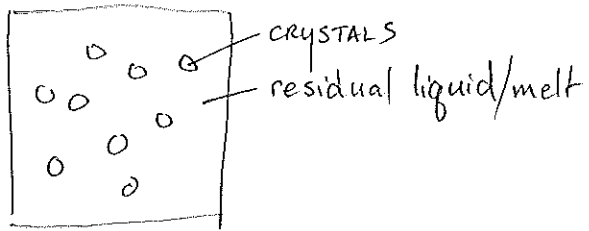

CN=6 octahedral
$R_C/R_A = 0.732 - 0.414$

LINEAR
CN=2
$R_C/R_A < 0.155$

CN=4 tetrahedral
$R_C/R_A = 0.414 - 0.225$

mass balance for a closed system   BATCH EQUILIBRATION

crystals and solids always
equilibrated

M_0 = mass of system

M_S = mass of solids

M_L = mass of liquids

$C_{0,L}$ = Concentration of element
when system is 100% liquid

C_L = conc. in liquid

C_S = conc in solid

$M_0 = M_S + M_L$ ← mass balance
over liquid + crystals

$C_{0L} M_0 = C_L M_L + C_S M_S$ ← mass balance
over element

$$D = \frac{C_S}{C_L}$$

$$C_0 M_0 = C_L M_L + D C_L M_S$$
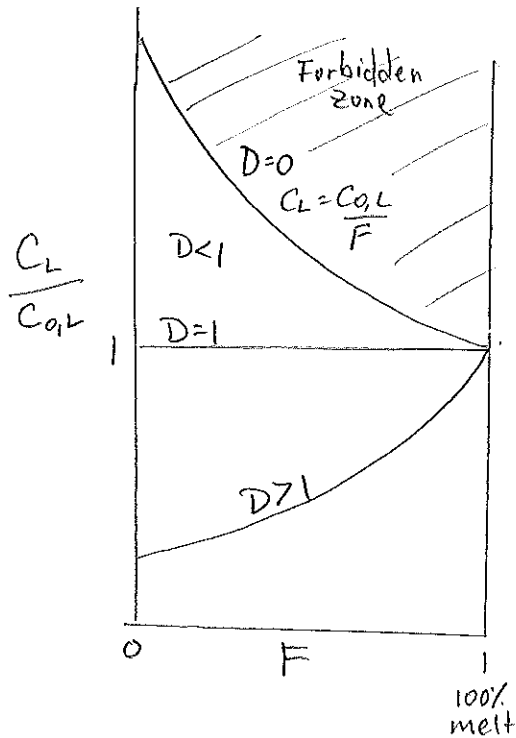
define F = melt fraction = $\dfrac{M_L}{M_0}$

$$(1-F) = \frac{M_S}{M_0}$$

$$C_0 = C_L F + D C_L (1-F)$$

Rearrange

$$\frac{C_L}{C_{0,L}} = \frac{1}{F + D(1-F)}$$

$$\frac{C_S}{C_{0,L}} = \frac{D}{F + D(1-F)}$$

BATCH EQUILIBRATION CONTINUED

BATCH CRYSTALLIZATION + BATCH MELTING EQUAL

To enrich a melt in incompatible element, crystallize.

• what is the maximum an incompatible element can be enriched?
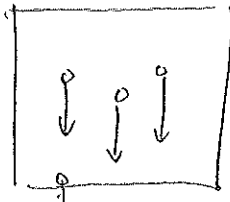
set $D = 0$ in

$$\frac{C_L}{C_{0,L}} = \frac{1}{F + D(1-F)}$$

$$\rightarrow \frac{C_L}{C_{0,L}} = \frac{1}{F} \qquad \text{max. enrichment}$$

or when $F \rightarrow 0$, an incompatible element can also be enriched

In the figure:

- Forbidden Zone
- $D = 0$
- $C_L = \frac{C_{0,L}}{F}$
- $D < 1$
- $D = 1$
- $D > 1$
- y-axis: $\frac{C_L}{C_{0,L}}$, value 1 marked
- x-axis: F, from 0 to 1 (100% melt)

FRACTIONAL CRYSTALLIZATION (RAYLEIGH FRACTIONATION)

CRYSTALS ARE TAKEN OUT OF SYSTEM (DISEQUILIBRIUM) and cannot communicate with melt

M_m = mass of melt

change in mass of melt = rate of crystal segregation

$$\frac{dM_m}{dt} = -\frac{dM_s}{dt} \qquad\qquad F = \frac{M_m}{M_{m,0}}$$

change in mass of element in melt = rate of element loss via crystal segregation

$$d(C_m M_m)/dt = -C_s \frac{dM_s}{dt}$$

$$C_m dM_m + M_m dC_m = -D C_m dM_s$$

$$C_m dM_m + M_m dC_m = D C_m dM_m$$
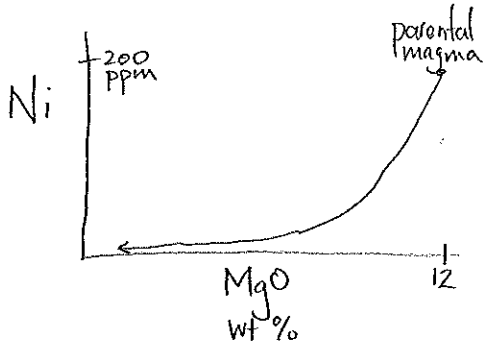
$$M_m dC_m = (D-1) C_m dM_m$$

SOLVE MISSING STEP $\longrightarrow$

$$\boxed{\frac{C_m}{C_{m,0}} = \left(\frac{M_m}{M_0}\right)^{D-1} \qquad \text{or} \qquad \frac{C_m}{C_{m,0}} = F^{D-1}}$$
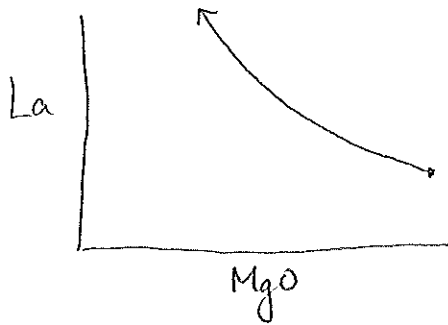
$$\text{and} \qquad \frac{C_s}{C_{m,0}} = D F^{D-1}$$

Example
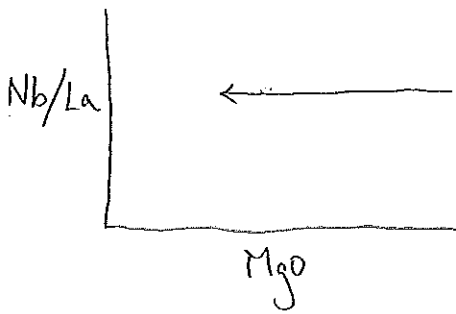
Fractional Crystallization of basalt
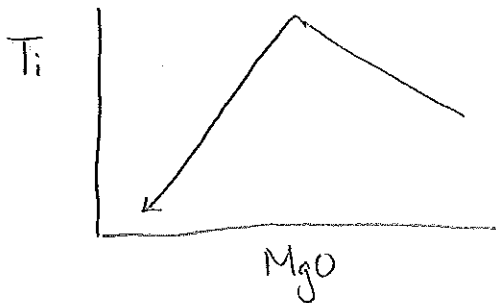 olivine is first to precipitate, followed by cpx + plagioclase

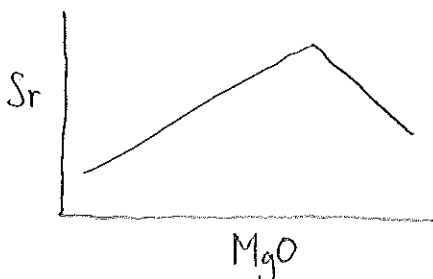Ni is compatible in olivine
MgO is compatible also

La is incompatible

what does this mean for Nb?

Ti is initially incompatible
 but then becomes compatible w/ the
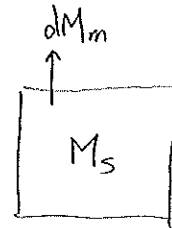 appearance of magnetite

Sr compatible in plagioclase

FRACTIONAL MELTING

Consider case in which each melt increment escapes towards surface
- melt is extracted instantaneously
  - once extracted, no longer in communication

example = mantle melting.

mass balance

$$-dM_m = dM_s$$

change in mass of element = rate of change
    in solid   of element loss by melt

$$d(C_s M_s) = -C_m dM_m$$

$$C_s dM_s + M_s dC_s = C_m dM_s = \frac{C_s}{D} dM_s$$

fill in steps!

$$\frac{C_s}{C_{s,o}} = (1-F)^{\frac{1}{D}-1}$$

$$\frac{C_m}{C_{s,o}} = \frac{1}{D}(1-F)^{\frac{1}{D}-1} \left. \right\} \text{instantaneous melt}$$

IF we pool the melts and determine average

$$\overline{\frac{C_m}{C_{s,o}}} = \frac{1}{F}\int_0^F \frac{C_m}{C_{s,o}} dF = \frac{1}{F}\int_{F=0}^F \frac{1}{D}(1-F)^{\frac{1}{D}-1} dF$$

this equation can be solved easily if you
substitute $dF = -d(1-F)$

$$\frac{\overline{C_m}}{C_{s,o}} = \frac{1-(1-F)^{\frac{1}{D}}}{F}$$

$M_{s,o}$ = initial mass of solid

M_s = mass of solid

dM_m = melt increment

$M_m = \int dM_m$ total melt

$(1-F) = \frac{M_s}{M_{s,o}}$

C_s = conc. in solid

C_m = conc in melt

$C_{s,o}$ = initial conc. in solid

$\uparrow dM_m$

$\boxed{M_s}$

BASIC BOX MODELING

① CONSTANT INPUT, CONSTANT RESERVOIR MASS, LINEAR SYSTEM

river in → ocean → sed out

M = mass of reservoir

m_{oc} = mass of element in reservoir

$\dfrac{dM}{dt} = 0$ Let's assume reservoir mass constant

that is $\dfrac{dM}{dt} = \underbrace{\dfrac{dM_{in}}{dt}}_{rivers} + \underbrace{\dfrac{dM_{out}}{dt}}_{evaporation} = 0$

$\dfrac{dm_{oc}}{dt} = J_{in} + J_{out}$

$\nearrow$ input rate $\uparrow$ output rate

Let's assume J_{in} is riverine input   moles/yr

J_{out} : lets assume it must scale with concentration in ocean

$\qquad J_{out} = -k_{oc\text{-}sed} \, m_{oc}$

$\qquad\qquad$ where $k_{oc\text{-}sed} \sim 1/time$ and negative sign is to indicate direction

$\qquad$ we could also say

$\qquad\qquad J_{out} = C_{sed} \cdot \dfrac{dM_{sed}}{dt}$

$\qquad$ assume $D = C_{sed}/C_{oc}$

$\qquad\qquad J_{out} = D \, C_{oc} \dfrac{dM_{sed}}{dt} = D \dfrac{dM_{sed}}{dt} \cdot \dfrac{m_{oc}}{M_{oc}}$

$\qquad$ if M_{oc} and $\dfrac{dM_{sed}}{dt}$ are constant

$\qquad\qquad k \sim D \dfrac{dM_{sed}}{dt}$ so k is a measure of partition coefficient (sort of)

$\dfrac{dm_{oc}}{dt} = C_{oc}\dfrac{dM_{oc}}{dt} + M_{oc}\dfrac{dC_{oc}}{dt} = J_{in} - k_{oc\text{-}sed}\, C_{oc}\, M_{oc}$

$$\boxed{\dfrac{dm_{oc}}{dt} = J_{in} - k_{oc\text{-}sed}\, m_{oc}}$$

steady state $t \to \infty$

$$\frac{dm_{oc}}{dt} = 0 \quad \Rightarrow \quad J_{in} = K_{oc-sed} M_{oc}$$

$$M_{oc} = C_{oc} M_{oc} = \frac{J_{in}}{K_{oc-sed}}$$

$$C_{oc}^{\infty} = \frac{1}{K_{oc-sed}} \cdot \frac{C_{riv}}{M_{oc}} \frac{dM_{riv}}{dt}$$

full solution after integrating is
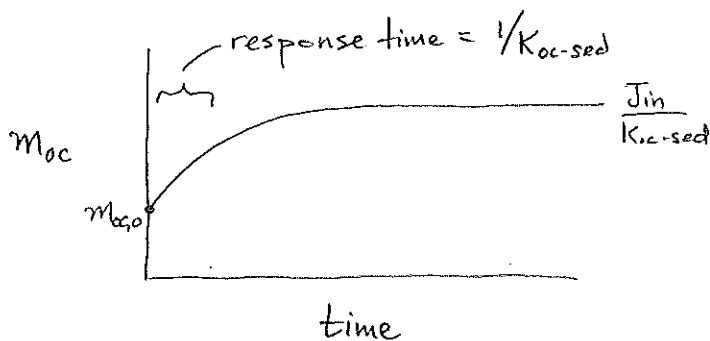
$$m_{oc} = \frac{J_{in}}{K_{oc-sed}} - \left(\frac{J_{in} - k M_{oc,0}}{k} \right) e^{-K_{oc-sed} t}$$

check when $t \to \infty$

$$m_{oc}(\infty) = \frac{J_{in}}{K_{oc-sed}}$$
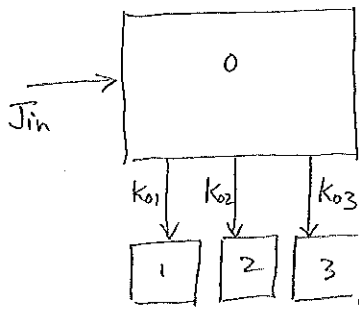
when $t = 0$

$$m_{oc}(0) = m_{oc,0}$$

K_{oc-sed} is a rate constant

$1/K_{oc-sed}$ is the response time

average residence time at steady state of element in ocean reservoir

is $\boxed{\dfrac{m_{oc}}{J_{in}} = \tau_{residence} = \dfrac{1}{K_{oc-sed}} = \tau_{response}}$
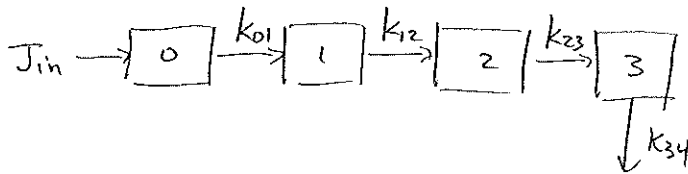
① PARALLEL SINKS

$$J_{in} = k_{o1} M_o + k_{o2} M_o + k_{o3} M_o$$

$$\tau_{res} = \frac{m_o}{J_{in}} = \frac{1}{\sum k_i}$$

largest (fastest k) dictates residence time

$$M_o^{\infty} = \frac{J_{in}}{\sum k_i}$$

② SERIES

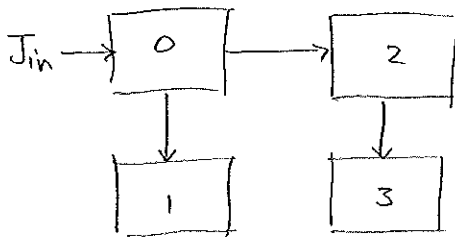$$J_{in} = k_{o1} M_o = k_{12} M_1 = k_{23} M_2 = k_{34} M_3$$

residence time of each reservoir is

$$\tau_i = \frac{1}{k_{ij}}$$

$$M_o^{\infty} = \frac{J_{in}}{k_{o1}}$$

$$M_i^{\infty} = \frac{J_{in}}{k_{i,i+1}}$$

③ SERIES + PARALLEL

consider $0 =$ estuary $1 =$ est. sediments

  $2 =$ ocean $3 =$ marine sediments

oceanic (2) residence time

$$\tau_2 = \frac{1}{k_{23}} = \frac{m_2}{k_{o2} M_o}$$

apparent oceanic residence if you don't know reservoir 0 exists

$$\tau_{2app} = \frac{m_2}{J_{in}}$$

may be important for
Re, Os, Fe, Mn

But we know $\dfrac{m_o}{J_{in}} = \dfrac{1}{k_{o1} + k_{o2}}$

so $\tau_2 = \dfrac{m_2 (k_{o1} + k_{o2})}{k_{o2} \, J_{in}} = \dfrac{k_{o1} + k_{o2}}{k_{o2}} \, \tau_{app} = \left(\dfrac{k_{o1}}{k_{o2}} + 1 \right) \tau_{app}$

if $k_{o1} > 0$ then one underestimates
residence time in ocean(2)

fraction lost to estuarine
sediments.