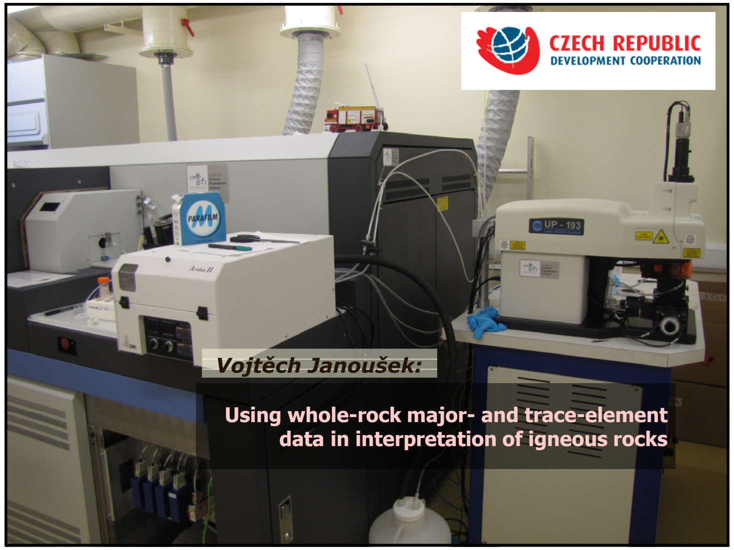



## Fractional crystallization – major elements

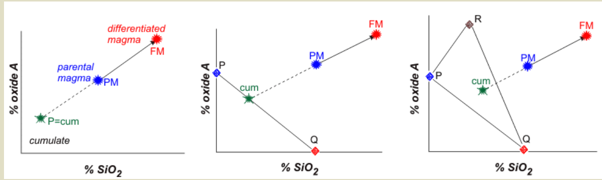
Mass balance:

$$C_{PM} = FC_{FM} + (1-F)C_{cum}$$

Lever rule:

$$f_{fc} = \frac{C^i_{PM} - C^i_{FM}}{C^i_{cum} - C^i_{FM}}$$

$C_{PM}$ = concentration in the parental melt
$C_{DM}$ = concentration in differentiated melt
$F$ = fraction of the melt remaining (1→0);
$f_{fc}$= *(1– F)* = degree of fractional crystallization

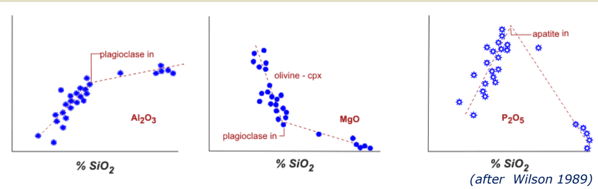



*(after Cox et al. 1979)*

*Trends produced by fractional crystallization of cumulate (cum) consisting of one (P), two (P–Q) or three (P–Q–R) minerals. PM = primary melt, FM = fractionated magma*

## Fractional crystallization – major elements

- Binary plots of major elements vs. $SiO_2$ (Harker plots) or any other index of fractionation (e.g., MgO or mg#) often show linear relationships.
- These trends on their own do not provide evidence for operation of fractional crystallization!
- Partial melting or mixing would also produce linear trends (Wall et al. 1987).
- However, the changes in fractionating assemblage result in inflections. If present, they prove operation of fractional crystallization.



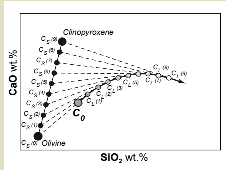

*(after Wilson 1989)*

*Harker plots for a suite of cogenetic volcanic rocks developing by fractional crystallization of olivine, clinopyroxene, plagioclase and apatite.*

## Fractional crystallization – major elements

### Continuously evolving cumulate

- Produces curved trends.



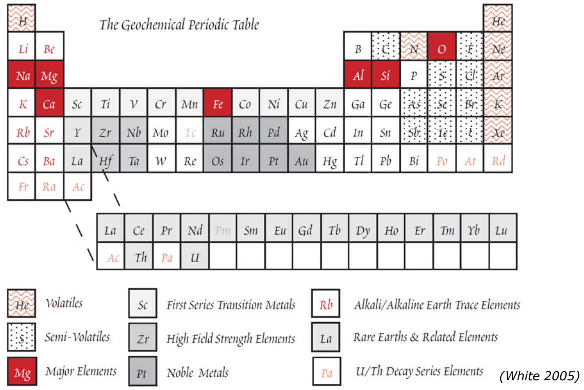

### Reverse modelling

- For reverse modelling of fractional crystallization, the composition of the primitive magma is considered to be a mixture of differentiated magma and cumulus crystals.

$$C^i_{PM} = C^i_{cum} f_{fc} + C^i_{FM}(1 - f_{fc})$$

- Numerical solution is provided, for instance, by the least-squares method (Bryan et al. 1969).

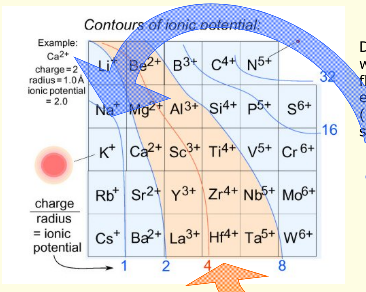
## Classification of trace elements




(White 2005)

## Classification of trace elements

**ionic potential = charge/radius**




http://www.gly.uga.edu/railsback/FundamentalsIndex.html

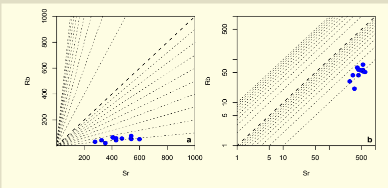
Determines, which elements will be mobile in hydrous fluids and thus strongly enriched in arc magmas (being contributed by the subducted plate)

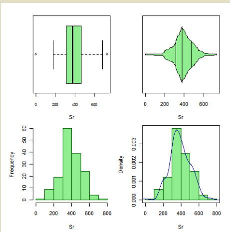
**Non-conservative elements**
Large Ion Lithophile Elements (LILE): Cs, Rb, K, Li, Ba, Sr, Pb...

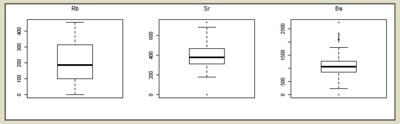
**Conservative elements**
High Field Strength Elements (HFSE): Nb, Ta, Ti, Zr, Hf...

## Presentation of trace-element data

- *Binary plots*
- *Log–log plots*
- *Histograms*
- *Boxplots* (box and whiskers plots)
- *Box and percentile plots*







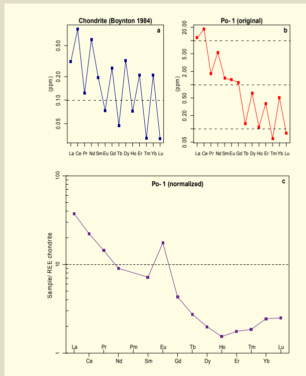
## Spiderplots

**Plotting**

- Arrange elements logically (more incompatible on the left)
- Divide each element's concentration in the sample by that in a reference material
- Plot y-axis using a log scale

**Advantages/usage**

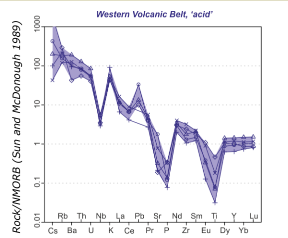
- Elimination of the Oddo-Harkins effect
  in the Solar System, the abundances of even-numbered elements are greater than those of neighbouring odd-numbered ones + abundances generally decrease with increasing atomic number.
- Spiderplots allow representing much of the sample's composition on a single graph.

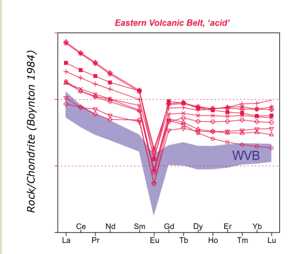


## Spiderplots

### Standards for normalization

- Chondrites ( "Bulk Silicate Earth")
- Primitive Mantle
- Mid-Ocean Ridge Basalts (NMORB)
- Ocean-Island Basalts (OIB)
- Averages of various crustal reservoirs, bulk, upper, lower…
- Ocean Ridge Granites (ORG)




*Multielement plots for metavolcanic rocks from the Devonian Vrbno Group, Silesia (Czech Republic) (Janoušek et al. 2014)*

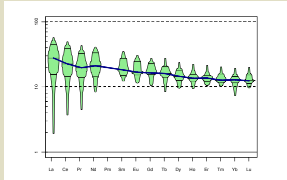
## Spiderplots – examples

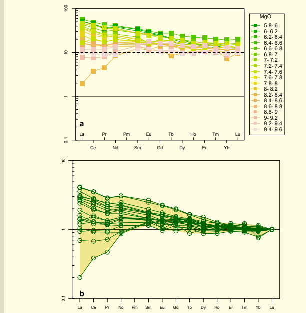
### Standards for normalization

- Most primitive/least-altered sample

### Modifications

- Fields
- Colour-coded by a certain parameter ($SiO_2$, MgO…)
- Spider box plots
- Spider box and percentile plots





*Chondrite-normalized (Boynton 1984) REE patterns for dolerites from the Devonian Vrbno Group, Silesia*

## Two types of trace elements

**"Dilute" trace elements (element partitioning)**

- Trace elements that occur in small amounts in the crystal lattice, and their activity is proportional to their concentration (Henry 1803).
- The coefficient of proportionality depends on the nature of the mineral but not on the concentration of the element.
- Modelled by element partitioning between crystals and liquid.

**Essential Structural Constituents (solubility concept)**

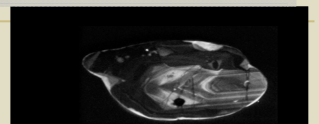
- *Essential Structural Constituents (ESC)* form a substantial part of the crystal lattice of certain accessory minerals.

  e.g., Zr in zircon, P in apatite or P, Th and LREE in monazite

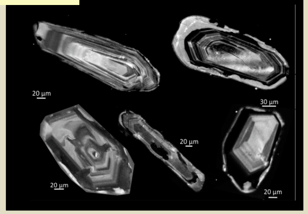
- The Henry's Law is not applicable.
- Empirical approach, using experimentally determined mineral solubility in a silicate melt.

## Behaviour of accessories – solubility concept

Example – zircon
(Watson and Harrison 1983)



$$ln\left(\frac{C_{Zrn}^{Zr}}{\left(C_L^{Zr}\right)_{sat}}\right)=\left(-3.80-\left(0.85(M-1)\right)\right)+\frac{12900}{T}$$



$T$ = temperature in K

$C_{Zrn}^{Zr}$ = 497644 ppm (49.7 wt. %) is the amount of Zr in an ideal zircon

$M$ = whole-rock chemical parameter based on cation fractions:

$$M=\frac{Na+K+2Ca}{Al\times Si}$$

## Partition coefficient

**Partition coefficient**

$$K_D^{min/L} = \frac{C_{min}}{C_L}$$

**compatible elements** $K_D \gg 1$
concentrate into the mineral rather than in the melt

**incompatible elements** $K_D \ll 1$
remain in the melt

Does not depend on:

- concentration of the given element
  concentration of any other elements in the system

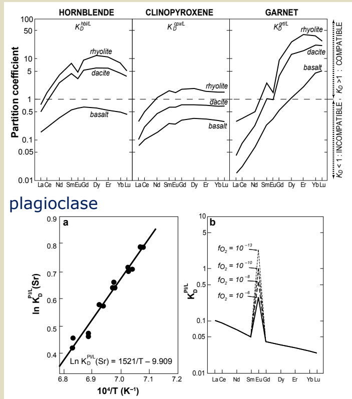
Databases of $K_D$ values:

- Rollinson (1993)
- GERM website (*http://earthref.org/KDD/*).

Measurement:

- *(Bulk analysis of mineral separates and glass* or matrix)
- *In-situ* measurement in phenocrysts and glass (ion probe, LA ICP MS,…)
- Experiments (doped material)
- Calculations (lattice strain model)

## Partition coefficient



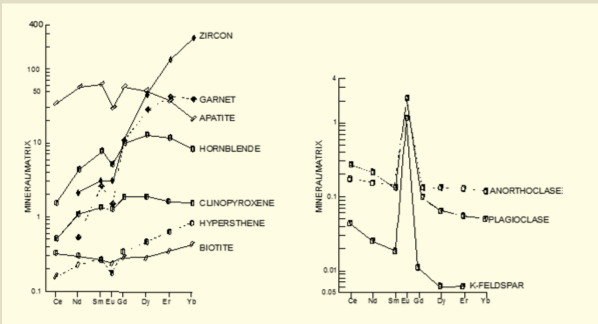

Depends on:

- *magma composition* (acid/basic, water contents…)
- *temperature*
- *pressure*
- *mineral*
- *mineral stoichiometry (composition)*
- *oxygen fugacity* (Eu in plagioclase)

Bulk distribution coefficient

$$D = \sum_i Kd_i X_i$$

## Partition coefficients



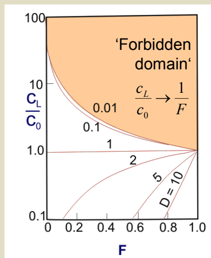

*Mineral/melt distribution coefficients for REE in dacites and rhyolites (Hanson 1978)*

## Fractional crystallization

**Rayleigh equation**

$$\frac{C_L}{C_0} = F^{(D-1)}$$

$C_0$ = concentration in the parental melt
$C_L$ = concentration in differentiated melt
$F$ = fraction of the melt remaining (1→0); *(1− F)* = degree of fc
$D$ = bulk distribution coefficient for the crystallizing phases



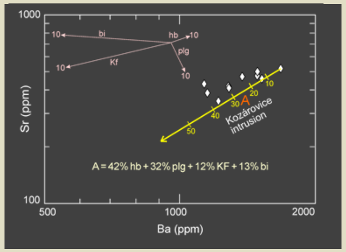

Instantaneous solid:

$$c_s^{inst} = Dc_L = Dc_0F^{(D-1)}$$

Bulk cumulate:

$$\bar{c}_s = c_0\frac{1-F^D}{1-F}$$

## Fractional crystallization




*Ba vs Sr patterns for the Kozárovice (diamonds) and Blatná (squares) intrusions of the Central Bohemian Plutonic Complex, Czech Republic (Janoušek et al. 2000)*

The identification of fractionating phases is facilitated by log–log plots of whole-rock trace-element concentrations, in which the originally exponential Rayleigh trends are converted to linear ones:

$$\log(c_L) = \log(c_0) + (D-1)\log(F)$$

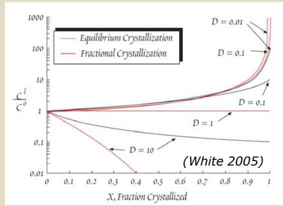
For granitoids are commonly used Rb, Sr, Ba whose distribution coefficients ($K_D$) are relatively well known (Hanson 1978).

## Equilibrium crystallization

Melt development:

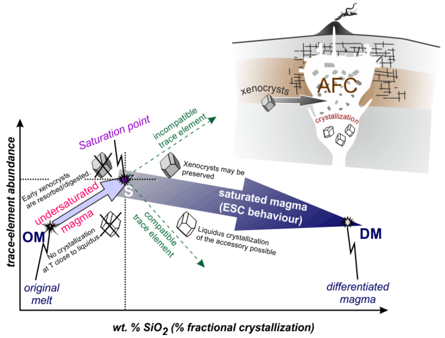
$$C_L = \frac{C_0}{D + F(1-D)}$$

$C_0$ = concentration in the parental melt
$C_L$ = concentration in differentiated melt
$F$ = fraction of the melt remaining (1→0); *(1– F)* = degree of fractional crystallization
$D$ = bulk distribution coefficient for the crystallizing phases




Regardless of its exact mechanism (fractional/equilibrium), crystallization quickly depletes compatible elements from the melt.

## Fractional crystallization – behaviour of accessories




*Watson & Harrison (1984); Hoskin et al. (2000); Janoušek (2006)*

## Fractional melting

Melt development:

$$\frac{C_S}{C_0} = (1-F)^{\left(\frac{1}{D}-1\right)}$$

$C_0$ = concentration in the (unmelted) source
$C_L$ = concentration in the melt
$F$ = degree of melting
$D$ = bulk distribution coefficient **after melting** (residue)

At any moment, the instantaneous liquid equilibrates with the solid residue. The composition of a single melt increment is:

$$\frac{C_L}{C_0} = \frac{1}{D}(1-F)^{\left(\frac{1}{D}-1\right)}$$

Average composition of the (aggregated) melt:

$$\frac{C_L}{C_0} = \frac{1}{F}\left(1-(1-F)^{\frac{1}{D}}\right)$$

## Batch melting

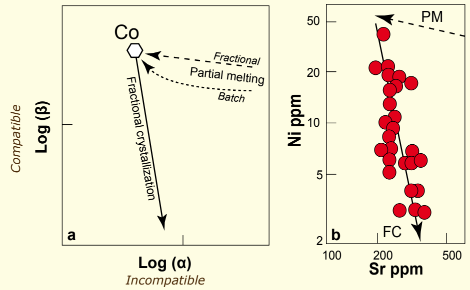
Melt development:

$$C_L = \frac{C_0}{D + F(1-D)}$$

$C_0$ = concentration in the (unmelted) source
$C_L$ = concentration in the melt
$F$ = degree of melting
$D$ = bulk distribution coefficient **after melting** (residue)

All the melt is formed, and then separated in a single batch.

## Distinguishing between fractional crystallization and partial melting




*Fractional crystallization (FC) produces an almost vertical trend whereas partial melting (PM) results in a nearly horizontal one (after Martin 1987).*

## (Binary) mixing

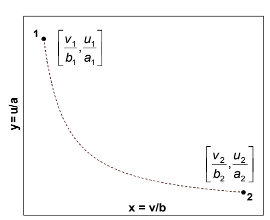
Mass-balance equation:

$$C_M = \sum_{k=1}^{m} (f_k C_k)$$

$C_M$ = concentration in the mixture
$C_k$ = concentration in the end-member $k$
$f_k$ = proportion of the given end-member $k$

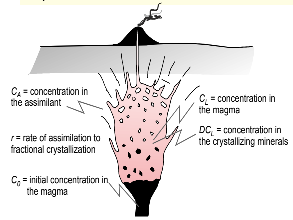
Trends in binary plots:

- *Element–element:* straight line
- *Element–ratio:* hyperbola
- *Ratio–ratio*: hyperbola [general]
- *Ratio–ratio:* straight line [common denominator]




## Combined Assimilation and fractional crystallization (AFC)

The AFC model assumes that the extra heat needed for assimilation (which is an endothermic process) is provided by the latent heat of crystallization.

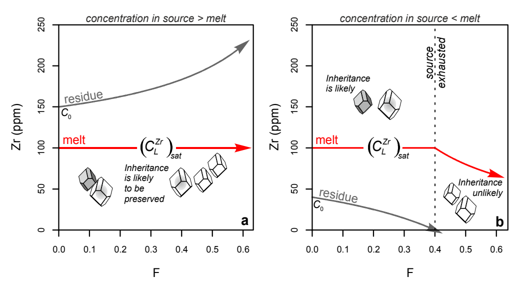



Direct AFC models can be calculated and plotted by Petrograph (Petrelli et al. 2005) or special spreadsheets (Ersoy and Helvacı 2010; Keskin 2013).

- The sophisticated AFC equations with many parameters can be easily tweaked to yield solutions nicely reproducing the observed variation but geologically unrealistic (Roberts and Clemens 1995)

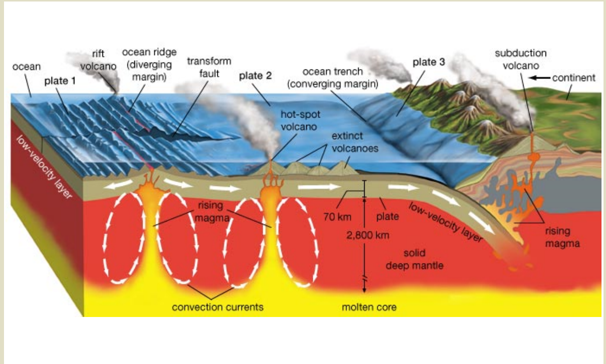
## Partial melting – behaviour of accessories

Watson and Harrison (1984); Janoušek (2006)

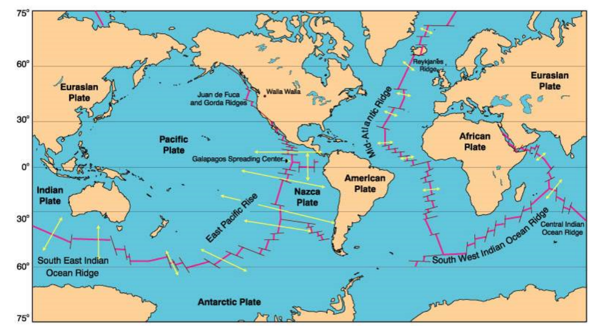



## "Igneous petrogenesis"

*Wilson (1989)*




## Mid-Ocean Rifts




*http://www.whitman.edu/geology/winter/JDW_PetClass.htm*

## Mid-Ocean Rifts

**Ophiolite complexes**

- Provide sections of the former ocean floor

| Lithology | Ocean Crustal Layers | Typical Ophiolite Thickness (km) | Normal Ocean Crust Thickness (km) ave. | Normal Ocean Crust P wave vel. (km/s) |
|---|---|---|---|---|
| Deep-Sea Sediment | 1 | ~ 0.3 | 0.5 | 1.7 -2.0 |
| Basaltic Pillow Lavas | 2A & 2B | 0.5 | 0.5 | 2.0 - 5.6 |
| Sheeted dike complex | 2C | 1.0 - 1.5 | 1.5 | 6.7 |
| Gabbro | 3A | 2 - 5 | 4.7 | 7.1 |
| Layered Gabbro | 3B | | | |
| Layered peridotite | 4 | up to 7 | | 8.1 |
| Unlayered tectonite peridotite | | | | |

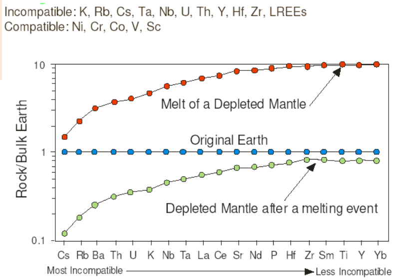
*http://www.whitman.edu/geology/winter/JDW_PetClass.htm*

## Mid-Ocean Rifts

**MORB = Mid-Ocean Ridge Basalt**
olivine tholeiite with low $K_2O$ (< 0.2 wt. %) and $TiO_2$ (< 2.0 %)

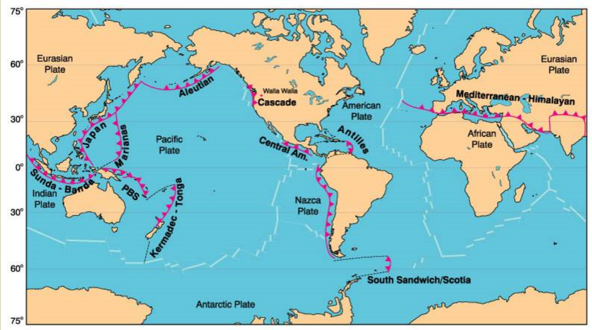
N-MORB (normal MORB)
shallow melting of a depleted mantle source:
Mg# > 65: $K_2O$ < 0.1
$TiO_2$ < 1.0

E-MORB (enriched MORB)
deeper, less depleted mantle source:
Mg# > 65: $K_2O$ > 0.1
$TiO_2$ > 1.0



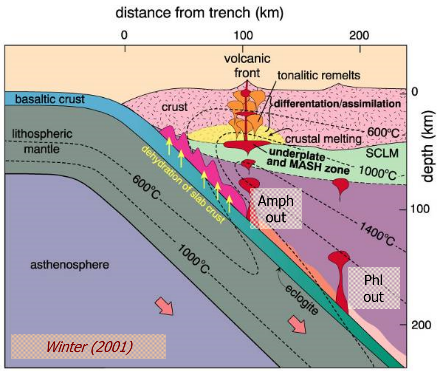

*http://homepages.uni-tuebingen.de/wolfgang.siebel/lec/man.html*

## Subduction zones (island arcs and continental arcs)

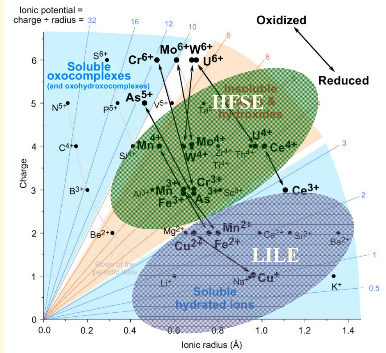



*http://www.whitman.edu/geology/winter/JDW_PetClass.htm*

## Anatomy of a subduction zone (here continental arc)




## Geochemical behaviour of trace elements in subduction zones




**Subduction signal:**
B > As, Sb, Cs > Pb > Rb > Ba, Sr, Be ~ U …

*http://www.gly.uga.edu/railsback/FundamentalsIndex.html*

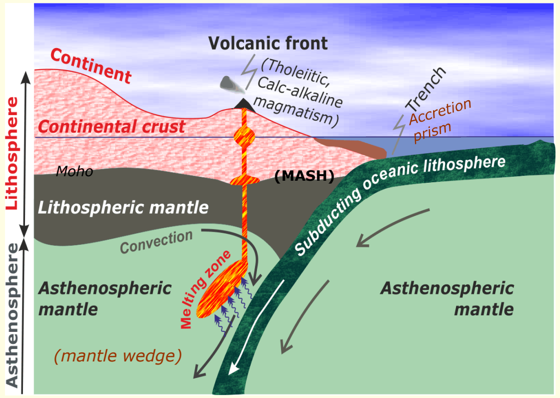
## Continental vs. island arcs

**Main differences of continental from island arcs:**

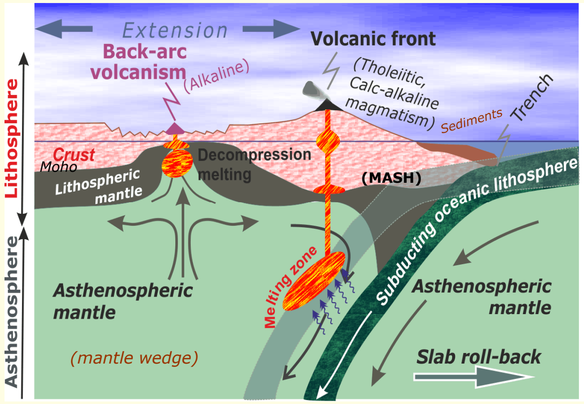
- Greater scope for **crustal contamination** while mantle-derived magmas ascend through the thick, geochemically and isotopically evolved continental crust.
- Low density of the crust acts as a "**density filter**", i.e. it decreases the ascent velocity (or even stops) the rising basic melts
- Their **stagnation leads to *fractional crystallization and assimilation*** *(MASH = Melting Assimilation Storage Homogenization; Hildreth and Moorbath 1988)* at the mantle–lower crust boundary (at about the Moho depth)


- Low solidus temperature facilitates **partial melting of the fertile continental crust**

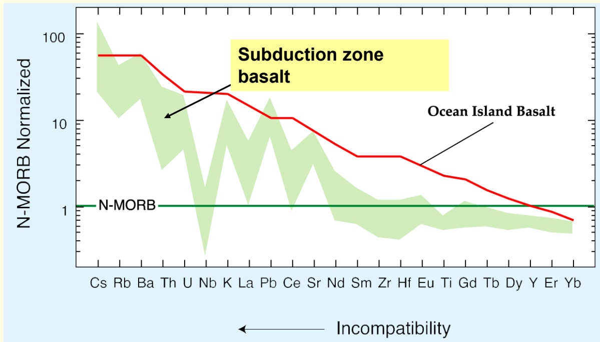
## Anatomy of a subduction zone (compression)




## Anatomy of a subduction zone (extension)




## Trace-element signature of subduction-related magmas



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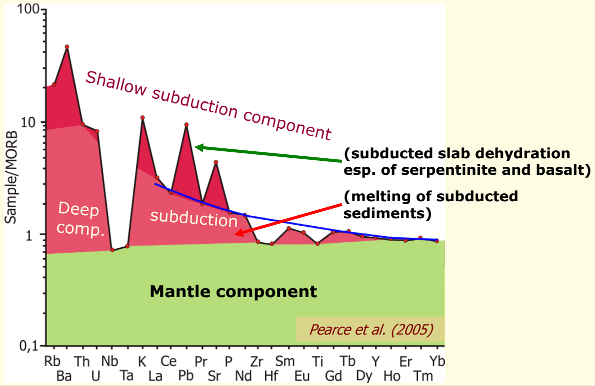
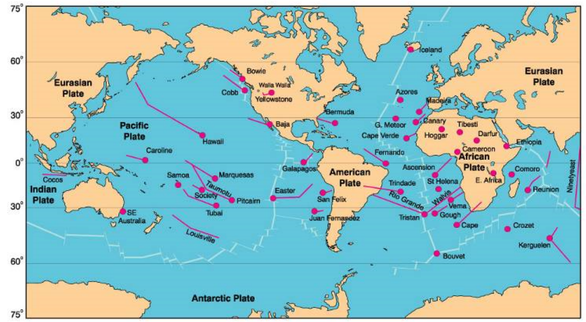


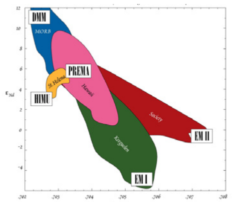

## Ocean Island Basalts

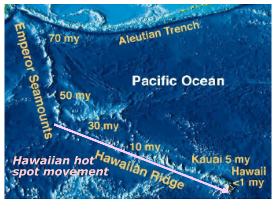


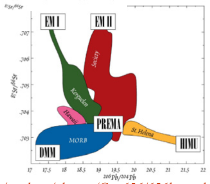

http://www.whitman.edu/geology/winter/JDW_PetClass.htm

## Ocean Island Basalts

| | |
|---|---|
| DMM | Depleted Mantle |
| HIMU | Subducted oceanic crust |
| EM I | modified subcontinental lithospheric mantle |
| EM II | subducted sediments |
| FOZO | "Focal zone" (= deep mantle?) |




http://www.geo.cornell.edu/geology/classes/Geo656/656home.html

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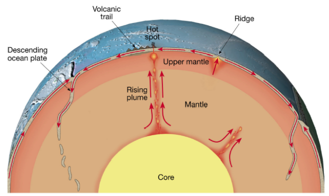
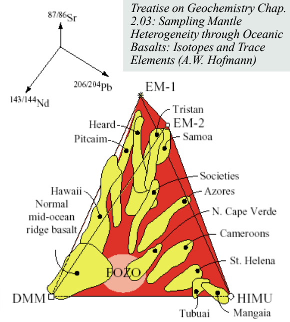
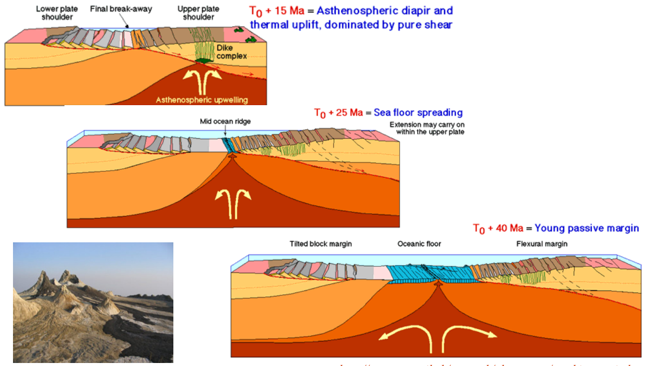
| EM II | subducted sediments |
| FOZO | "Focal zone" (= deep mantle?) |

*Treatise on Geochemistry Chap. 2.03: Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and Trace Elements (A.W. Hofmann)*



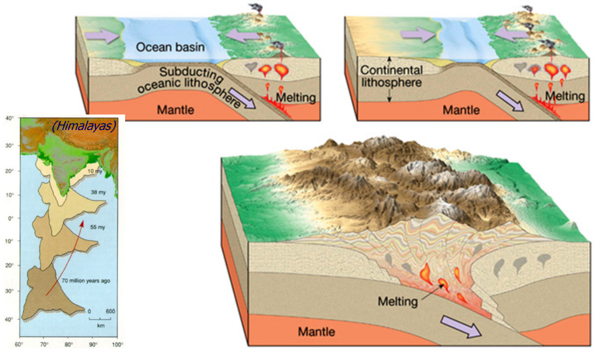



## Continental Rifts

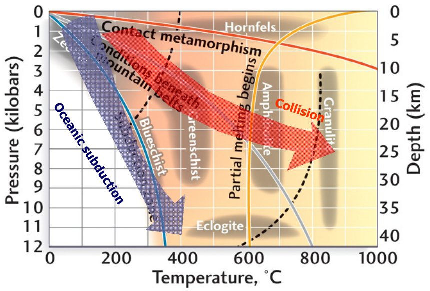



http://www-sst.unil.ch/research/plate_tecto/teaching_main.htm

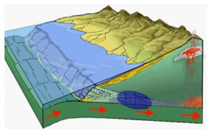
## Continental collision

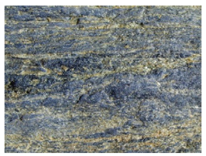



## Ocean closure



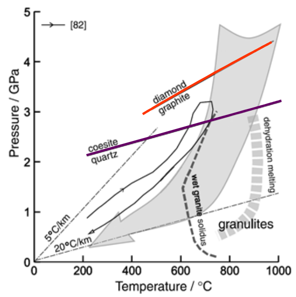

Blueschist-facies



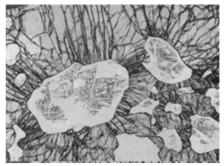


http://geology.about.com

## Continental collision




Chopin (2003)



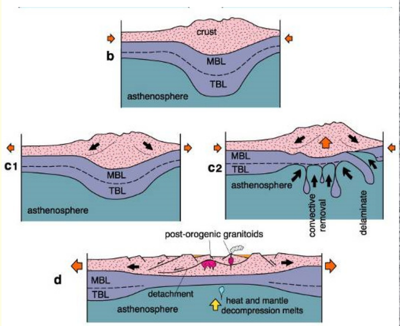
*Coesite, Dora Maira, Alps: Photo C. Chopin*

- Collision can be accompanied by deep subduction of continental crust into the upper mantle (even into stability fields of coesite and diamond)
- This may lead to a strong contamination of the lithospheric mantle by geochemically evolved upper crustal material
- Melting of such anomalous mantle domains may yield (ultra-) potassic magmas of peculiar composition

## Post-Collisional Development

**Heat for crustal anatexis**

- *Stacking/thickening*
  *in-situ* heat production by radioactive decay of K, Th, U
- *Advection of heat* by quickly exhumed hot lower crustal rocks or intruding basic magmas
- *Conduction of heat from a thermal anomaly in the mantle* (slab break-off, mantle delamination, asthenosphere upwelling, a mantle plume...),
- *Conduction of heat from anomalous mantle – in situ* radioactive decay of K, Th, U in crustally contaminated lithospheric mantle.




http://www.whitman.edu/geology/winter/JDW_PetClass.htm

## Models for petrogenesis of granitoid rocks

- **Partial melting of crustal rocks**
  - *Regional metamorphism* – deep burial (granulite-facies)
  - *Injection of basic magma, basic magma underplating*
  - *Crustal thickening or thinning*
  - *Decompression meting* during uplift of crustal rock complexes
- **Contamination of mantle-derived magmas**
  assimilation of crustal material, followed by differentiation
- **Differentiation of mantle-derived magmas**
  mainly by fractional crystallization
- **Dehydration and partial melting of hydrated oceanic crust (including sediments) in subduction zones**
  fluids and small-scale melts move upwards and trigger melting of the overlying mantle wedge
- **Partial melting of (meta-) basic rocks (amphibolites etc.)**
  previous magma pulses, relicts of the subducted oceanic crust…

## Petrogenetic classification of granitoid rocks

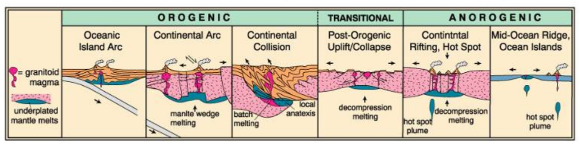
**Alumina saturation and mineralogy**

*Clarke (1992)*

| | Peraluminous | Metaluminous | Peralkaline |
|---|---|---|---|
| **Definition** | A > CNK | CNK > A > NK | A < NK |
| **Characteristic minerals** | alumosilicates, cordierite, garnet, topaz, tourmaline, spinel, corundum | Pyroxene, amphibole, epidote | Fe-rich olivine (fayalite), aegirine, arfedsonite, riebeckite |
| **Other common minerals** | biotite, muscovite | biotite, muscovite rare | rare biotite |
| **Fe–Ti oxide phase** | Ilmenite | Magnetite | Magnetite |
| **Accessories** | apatite, zircon, monazite | apatite, zircon, titanite, allanite | apatite, zircon, titanite, allanite, fluorite, cryolite, pyrochlore |
| **$(^{87}Sr/^{86}Sr)_i$** | 0.705–0.720 | 0.703–0.708 | 0.703–0.712 |
| **$\varepsilon_{Nd}$** | << 0 | ~ 0 | variable |

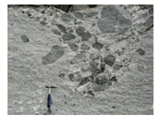
## Petrogenesis of granitic rocks

**Table 18-4.** A classification of granitoid rocks based on tectonic setting

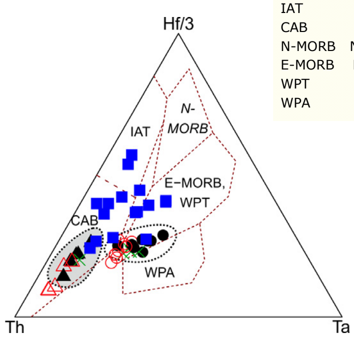



*Pitcher (1983), Barbarin (1990), Pitcher (1993)*

http://www.whitman.edu/geology/winter/JDW_PetClass.htm



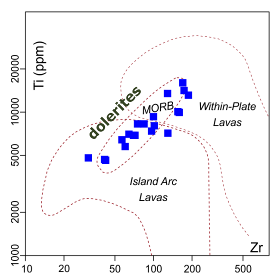
## Geotectonic diagrams (basaltoids)



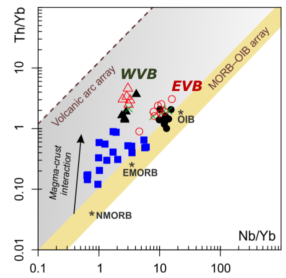

| | |
|---|---|
| IAT | Island-arc Tholeiites |
| CAB | Calc-alkaline Basalts |
| N-MORB | N-type Mid-ocean Ridge Basalts |
| E-MORB | E-type Mid-ocean Ridge Basalts |
| WPT | Within-plate Tholeiites |
| WPA | Alkaline Within-plate Basalts |

Wood (1980)

## Geotectonic diagrams (basaltoids)

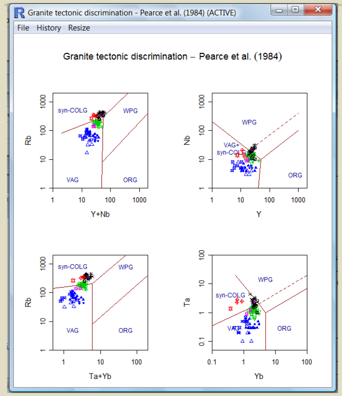



Pearce (1982)

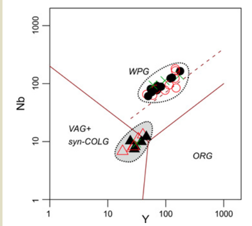



Pearce (2008)

## Geotectonic diagrams (granitoids)




| | |
|---|---|
| ORG | Ocean Ridge Granites |
| VAG | Volcanic Arc Granites |
| WPG | Within Plate Granites |
| Syn-COLG | Syn-Collision Granites |




Pearce et al. (1984)

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### Web links

- Geochemistry 455 (W.M. White, Cornell University)
  http://www.geo.cornell.edu/geology/classes/geo455/Geo455.html
- Igneous and metamorphic geology
  (J. D. Winter, Whitman University)
  http://www.whitman.edu/geology/winter/JDW_PetClass.htm
- Advanced petrology (J.-F. Moyen, University of Stellenbosch, South Africa)
  http://academic.sun.ac.za/earthSci/honours/modules/igneous_petrology.htm
- EarthRef.org. The website for Earth Science reference data and models
  http://earthref.org/


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